Best Available Techniques (BAT) Reference Document for the Production of Large Volume Organic Chemicals

Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control)

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Title Best Available Techniques (BAT) Reference Document for the Production of Large Volume Organic Chemicals

Abstract
The Best Available Techniques (BAT) Reference Document (BREF) for the Production of Large Volume Organic Chemicals is part of a series of documents presenting the results of an exchange of information between EU Member States, the industries concerned, non-governmental organisations promoting environmental protection, and the Commission, to draw up, review and – where necessary – update BAT reference documents as required by Article 13(1) of Directive 2010/78/EU on Industrial Emissions (the Directive). This document is published by the European Commission pursuant to Article 13(6) of the Directive.

The BREF for the production of Large Volume Organic Chemicals covers the production of the following organic chemicals, as specified in Section 4.1 of Annex I to Directive 2010/75/EU:

a. simple hydrocarbons (linear or cyclic, saturated or unsaturated, aliphatic or aromatic);
b. oxygen-containing hydrocarbons such as alcohols, aldehydes, ketones, carboxylic acids, esters and mixtures of esters, acetates, ethers, peroxides and epoxy resins;
c. sulphurous hydrocarbons;
d. nitrogenous hydrocarbons such as amines, amides, nitrous compounds, nitro compounds or nitrate compounds, nitriles, cyanates, isocyanates;
e. phosphorus-containing hydrocarbons;
f. halogenic hydrocarbons;
g. organometallic compounds;
k. surface-active agents and surfactants.

This document also covers the production of hydrogen peroxide as specified in Section 4.2 (e) of Annex I to Directive 2010/75/EU; and the combustion of fuels in process furnaces/heaters, where this is part of the abovementioned activities. The production of the aforementioned chemicals is covered by this document when it is done in continuous processes where the total production capacity of those chemicals exceeds 20 kt/yr.
Important issues for the implementation of Directive 2010/75/EU in the production of large volume organic chemicals are the reduction of emissions to air and water from chemical processes, efficient usage of energy and water, resource efficiency, minimisation, recovery and recycling of process residues; as well as an effective implementation of environmental and energy management systems.This BREF contains fourteen Chapters. Chapters 1 and 2 provide general information on the Large Volume Organics industrial sector and on generic industrial production processes used in this sector. Chapters 3 to 12 provide general information, applied processes and techniques, current emission and consumption levels, techniques to consider in determination of BAT and emerging techniques for various illustrative processes: lower olefins, aromatics, ethylbenzene and styrene, formaldehyde, ethylene oxide and ethylene glycols, phenol, ethanolamines, toluene diisocyanate and methylene diphenyl diisocyanate, ethylene dichloride and vinyl chloride monomer and hydrogen peroxide. Chapter 13 presents BAT conclusions as defined in Article 3(12) of the Directive. Concluding remarks and recommendations for future work are presented in Chapter 14.

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This report was produced by the European Integrated Pollution Prevention and Control Bureau (EIPPCB) at the European Commission's Joint Research Centre – Directorate B: Growth and Innovation under the supervision of Serge Roudier (Head of the EIPPCB) and Luis Delgado Sancho (Head of the Circular Economy and Industrial Leadership Unit).

The authors of this BREF were Mr Heino Falcke, Mr Simon Holbrook, Mr Iain Clenahan, Mr Alfredo Lopez Carretero, Mr Teoman Sanalan, Mr Joze Roth, Mr Benoit Zerger and Mr Thomas Brinkmann.

This report was drawn up in the framework of the implementation of the Industrial Emissions Directive (2010/75/EU) and is the result of the exchange of information provided for in Article 13 of the Directive.

Most of the information (data and technical comments) was provided by industry, via CEFIC (European Chemical Industry Council) and its affiliated associations and sector groups (like the Aromatics Sector Group, ECVM - The European Council of Vinyl Manufacturers, EEPC - European Ethylene Producers Committee, the Ethanolamines Sector Group, the Ethylene Oxide Sector Group, Formacare, the Hydrogen Peroxide Sector Group, Isopa - European Diisocyanate & Polyol Producers Association, the Lower Olefins Sector Group, Petrochemicals Europe, the Phenol Sector Group). Many EU Member States provided important pieces of information via an additional data collection: Austria, the Czech Republic, Italy, the Netherlands, Portugal, Spain, Sweden, and the United Kingdom. The initiative of the EEB (European Environmental Bureau), and some Member States, and the cooperation of CEFIC were helpful to provide the inclusion of example plant names for the candidate techniques.

The whole EIPPCB team provided contributions and peer reviewing.

This document is one from the series of foreseen documents listed below (at the time of writing not all of the documents have been drafted):

Best Available Techniques Reference Document	**Code**
Ceramic Manufacturing Industry	CER
Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector	CWW
Common Waste Gas Treatment in the Chemical Sector	WGC
Emissions from Storage	EFS
Energy Efficiency	ENE
Ferrous Metals Processing Industry	FMP
Food, Drink and Milk Industries	FDM
Industrial Cooling Systems	ICS
Intensive Rearing of Poultry and Pigs	IRPP
Iron and Steel Production	IS
Large Combustion Plants	LCP
Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers	LVIC-AAF
Large Volume Inorganic Chemicals – Solids and Others Industry	LVIC-S
Large Volume Organic Chemicals	*LVOC*
Management of Tailings and Waste-rock in Mining Activities	MTWR
Manufacture of Glass	GLS
Manufacture of Organic Fine Chemicals	OFC
Non-ferrous Metals Industries	NFM
Production of Cement, Lime and Magnesium Oxide	CLM
Production of Chlor-alkali	CAK
Production of Polymers	POL
Production of Pulp, Paper and Board	PP
Production of Speciality Inorganic Chemicals	SIC
Production of Wood-based Panels	WBP
Refining of Mineral Oil and Gas	REF
Slaughterhouses and Animals By-products Industries	SA
Smitheries and Foundries Industry	SF
Surface Treatment of Metals and Plastics	STM
Surface Treatment Using Organic Solvents including Wood Preservation using Chemicals	STS
Tanning of Hides and Skins	TAN
Textiles Industry	TXT
Waste Incineration	WI
Waste Treatment	WT
Reference Document	
Economics and Cross-media Effects	ECM
Monitoring of Emissions to Air and Water from IED installations	ROM

Electronic versions of draft and finalised documents are publicly available and can be downloaded from http://eippcb.jrc.ec.europa.eu.

PREFACE

1. Status of this document

Unless otherwise stated, references to ‘the Directive’ in this document refer to Directive 2010/75/EU of the European Parliament and the Council on industrial emissions (integrated pollution prevention and control) (Recast).

The original best available techniques (BAT) reference document (BREF) on Large Volume Organic Chemical Industry was adopted by the European Commission in 2003. This document is the result of a review of that BREF. The review commenced in January 2010.

This BAT reference document for the Production of Large Volume Organic Chemicals forms part of a series presenting the results of an exchange of information between EU Member States, the industries concerned, non-governmental organisations promoting environmental protection and the Commission, to draw up, review, and where necessary, update BAT reference documents as required by Article 13(1) of the Directive. This document is published by the European Commission pursuant to Article 13(6) of the Directive.

As set out in Article 13(5) of the Directive, the Commission Implementing Decision (EU) 2017/2017 on the BAT conclusions contained in Chapter 13 was adopted on 21 November 2017 and published on 7 December 2017[1].

2. Participants in the information exchange

As required in Article 13(3) of the Directive, the Commission has established a forum to promote the exchange of information, which is composed of representatives from Member States, the industries concerned and non-governmental organisations promoting environmental protection (Commission Decision of 16 May 2011 establishing a forum for the exchange of information pursuant to Article 13 of the Directive 2010/75/EU on industrial emissions (2011/C 146/03), OJ C 146, 17.05.2011, p. 3).

Forum members have nominated technical experts constituting the technical working group (TWG) that was the main source of information for drafting this document. The work of the TWG was led by the European IPPC Bureau (of the Commission's Joint Research Centre).

3. Structure and contents of this document

Chapters 1 and 2 provide general information on the Large Volume Organic Chemicals sector as a whole. Chapter 1 describes the role of the LVOC sector within the chemical industry and economic trends.

Chapter 2 provides information on technical and environmental issues:

- Section 2.1 is made up of short thumbnail descriptions of the production of a range of LVOC products.
- Section 2.2 describes unit processes (chemical reactions) which are used to produce LVOC.
- Section 2.3 deals on a generic level with the consumption of raw materials and energy within the LVOC sector and the emissions generated by LVOC processes.

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[1] OJ L 323 07.12.2017, p.1.

- Section 2.4 describes in more detail the techniques to prevent or, where this is not practicable, to reduce the environmental impact of installations in the sector that were considered in determining the BAT. This information includes, where relevant and available, the environmental performance levels (e.g. emission and consumption levels) which can be achieved by using the techniques, the associated monitoring and the costs and the cross-media issues associated with the techniques.
- Section 2.5 of Chapter 2 presents information on 'emerging techniques' as defined in Article 3(14) of the Directive.

Chapters 3 to 12 describe processes which are illustrative of the Large Volume Organic Chemicals Sector. Each chapter follows the structure below:

- Sections 1 and 2 of Chapters 3 to 12 provide general information on the industrial process or processes and on the techniques used within this part of the sector.
- Section 3 of Chapters 3 to 12 provides data and information concerning the environmental performance of installations within this part of the sector, and in operation at the time of writing, in terms of current emissions, consumption and nature of raw materials, water consumption, use of energy and the generation of waste.
- Section 4 of Chapters 3 to 12 describes in more detail the techniques to prevent or, where this is not practicable, to reduce the environmental impact of installations in this part of the sector that were considered in determining the BAT. This information includes, where relevant and available, the environmental performance levels (e.g. emission and consumption levels) which can be achieved by using the techniques, the associated monitoring and the costs and the cross-media issues associated with the techniques.
- Section 5 of Chapters 3 to 12 presents information on 'emerging techniques' as defined in Article 3(14) of the Directive for this part of the sector.

Chapter 13 presents the BAT conclusions as defined in Article 3(12) of the Directive.

Concluding remarks and recommendations for future work are presented in Chapter 14.

4. Information sources and the derivation of BAT

This document is based on information collected from a number of sources, in particular through the TWG that was established specifically for the exchange of information under Article 13 of the Directive.

The information provided by the TWG mainly consists of:

- data from plant operators provided in the data collection via questionnaires;
- comments from TWG members on drafts and working documents;
- emission surveys or aggregated data from industry.

The information has been collated and assessed by the European IPPC Bureau (of the Commission's Joint Research Centre) who led the work on determining BAT, guided by the principles of technical expertise, transparency and neutrality. The work of the TWG and all other contributors is gratefully acknowledged.

The BAT conclusions have been established through an iterative process involving the following steps:

- identification of the key environmental issues for the sector;

- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these environmental performance levels were achieved, such as costs, cross-media effects, and the main driving forces involved in the implementation of the techniques;
- selection of the best available techniques (BAT), their associated emission levels (and other environmental performance levels) and the associated monitoring for this sector according to Article 3(10) of, and Annex III to, the Directive.

Expert judgement by the European IPPC Bureau and the TWG has played a key role in each of these steps and the way in which the information is presented here.

Hardly any economic data were available for the techniques presented in Chapter 2 and Chapters 3 to 12. In the absence of data concerning costs, conclusions on the economic viability of techniques are drawn from observations on existing installations.

5. Review of BAT reference documents (BREFs)

BAT is a dynamic concept and so the review of BREFs is a continuing process. For example, new measures and techniques may emerge, science and technologies are continuously developing and new or emerging processes are being successfully introduced into the industries. In order to reflect such changes and their consequences for BAT, this document will be periodically reviewed and, if necessary, updated accordingly.

6. Contact information

All comments and suggestions should be made to the European IPPC Bureau at the Joint Research Centre (JRC) at the following address:

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Best Available Techniques Reference Document in the Large Volume Organic Chemical Industry

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SCOPE

This BREF for the production of Large Volume Organic Chemicals concerns the production of the following organic chemicals, as specified in Section 4.1 of Annex I to Directive 2010/75/EU:

a. simple hydrocarbons (linear or cyclic, saturated or unsaturated, aliphatic or aromatic);
b. oxygen-containing hydrocarbons such as alcohols, aldehydes, ketones, carboxylic acids, esters and mixtures of esters, acetates, ethers, peroxides and epoxy resins;
c. sulphurous hydrocarbons;
d. nitrogenous hydrocarbons such as amines, amides, nitrous compounds, nitro compounds or nitrate compounds, nitriles, cyanates, isocyanates;
e. phosphorus-containing hydrocarbons;
f. halogenic hydrocarbons;
g. organometallic compounds;
k. surface-active agents and surfactants.

This BREF also covers the production of hydrogen peroxide as specified in Section 4.2 (e) of Annex I to Directive 2010/75/EU.

This BREF covers combustion of fuels in process furnaces/heaters, where this is part of the abovementioned activities.

This BREF covers the production of the aforementioned chemicals in continuous processes where the total production capacity of those chemicals exceeds 20 kt/year.

This BREF does not address the following:

- combustion of fuels other than in a process furnace/heater or a thermal/catalytic oxidiser; this may be covered by the BREF for Large Combustion Plants (LCP);
- incineration of waste; this may be covered by the BREF for Waste Incineration (WI);
- ethanol production taking place in an installation covered by the activity description in Section 6.4 (b) (ii) of Annex I to Directive 2010/75/EU or as a directly associated activity to such an installation; this may be covered by the BREF for Food, Drink and Milk Industries (FDM).

The scope of this document does not include matters that concern only safety in the workplace or the safety of products because these matters are not covered by the Directive. They are discussed only where they affect matters within the scope of the Directive.

The scope of this document is very broad in terms of number and differences of individual production processes; therefore this BREF contains a mixture of generic and detailed information that is presented on three main levels:

- General principles of management systems, unit processes, unit operations and infrastructure that are valid for all LVOC production processes.
- Generic product groups that are linked by common chemistry or production techniques. For each of these groups, there is a description of the key processes, their environmental issues and appropriate techniques for pollution prevention/control.
- Specific information on a number of selected ‘illustrative processes’. These illustrative processes have been chosen according to two main criteria. Firstly, that the process is of major industrial importance within the LVOC sector in terms of number of plants, distribution between Member States and total production capacity in Europe. Secondly, that the process was expected to have the potential for environmental issues, and the

information exchange was expected to be particularly valuable for operators and regulators.

Other BREFs which are complementary for the activities covered by this BREF include:

- Common Waste Water/Waste Gas Treatment/Management Systems in the Chemical Sector (CWW);
- Common Waste Gas Treatment in the Chemical Sector (WGC) [not drawn up yet].

Other reference documents which are relevant for the sector covered in this document are the following:

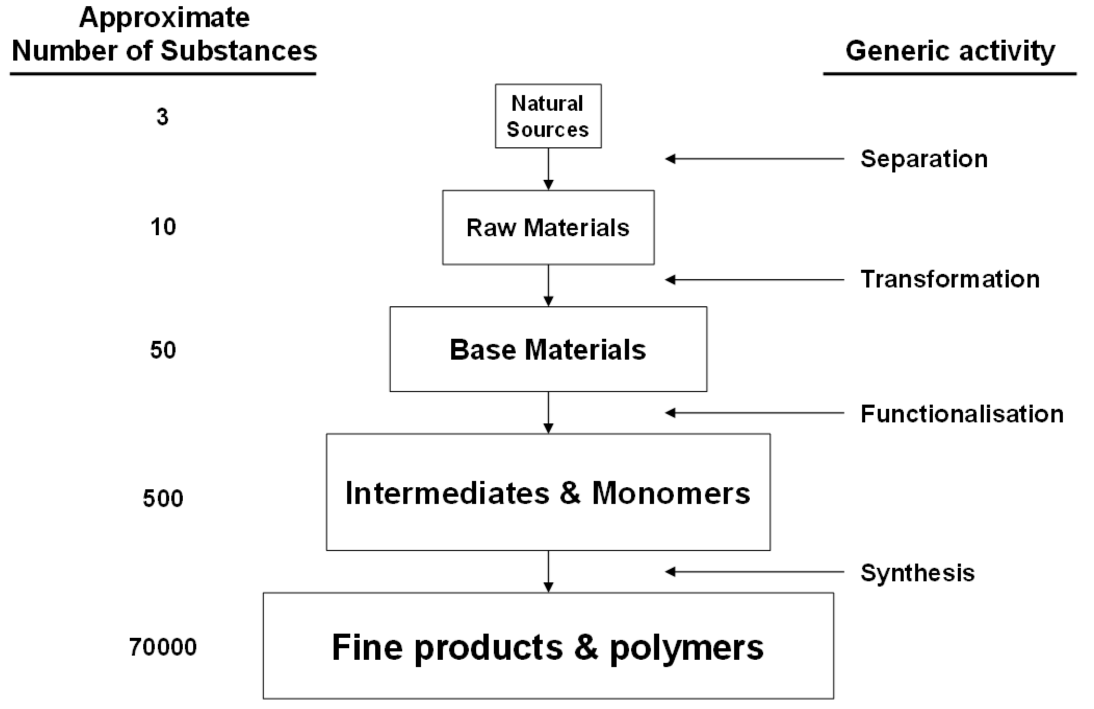
- Economics and Cross-media Effects (ECM);
- Emissions from Storage (EFS);
- Energy Efficiency (ENE);
- Industrial Cooling Systems (ICS);
- Large Combustion Plants (LCP);
- Refining of Mineral Oil and Gas (REF);
- Monitoring of Emissions to Air and Water from IED installations (ROM);
- Waste Incineration (WI);
- Waste Treatment (WT).

1 BACKGROUND INFORMATION

1.1 LVOC as part of the chemical industry

This chapter provides general information about the LVOC industry in terms of its integration with the upstream and downstream chemical processes, macroeconomics and some of the main factors that affect the sector.

Industrial organic chemistry is characterised by the production of a huge variety of compounds in a step-wise manner from a few natural sources of carbon. This production pyramid is shown schematically in Figure 1.1 using typical chemical industry nomenclature.



Source: [179, CITEPA 1997]

Figure 1.1: Structure of industrial organic chemistry

The initial separation steps are carried out in refineries where a few **natural sources** of carbon (crude oil, natural gas and coal) are used to produce a limited number of high volume **raw materials** for the chemical industry (e.g. naphtha). Today, some 95 % of organic products are obtained from oil and gas. The remainder comes either from coal, which is a declining source, or renewable biomass, which is an increasing source.

Refineries export these raw materials to petrochemical plants where they are transformed by a complex combination of physical and chemical operations into a variety of **base materials** (e.g. ethylene, C_3-C_4 olefins, BTX aromatics, synthesis gas and acetylene).

The base materials are subjected to further processing sequences, which introduce functional groups to produce an even greater number of **intermediates and monomers** (e.g. alcohols, aldehydes, ketones, acids, nitriles, amines, chlorinated organic compounds).

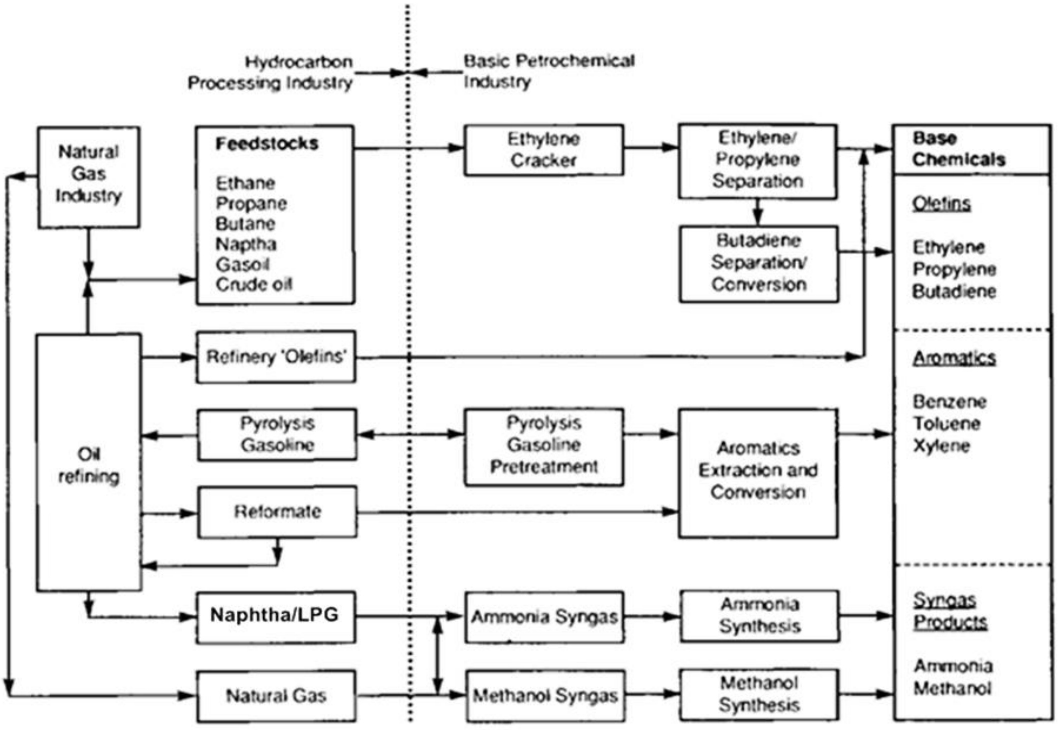
The intermediates and monomers are converted into a large variety of **fine products and polymers** with high levels of functionality and high commercial value (e.g. solvents, detergents, plastics, dyestuffs and pharmaceuticals).

The LVOC BREF can generally be considered as covering the middle three process tiers of the pyramid in Figure 1.1, i.e. taking raw materials to produce base materials, intermediates and monomers. These are also known as ‘commodity’ or ‘bulk’ chemicals.

LVOC plants have the following general characteristics:

- they often operate on large sites, where synergies between different processes allow the integration of utilities, storage and/or abatement systems;
- they produce a limited range of products in large quantities;
- they normally operate with infrequent shutdowns and start-ups;
- they are normally highly automated, requiring only limited manual intervention;
- due to their large throughput and continuous operation, they are not readily adaptable to process or product changes

In practice, defining the scope of LVOC is often more complex than Figure 1.1 suggests. The upstream interface with refining is blurred as both sectors often occupy the same site and have some common products (e.g. olefins and aromatics). However, the general distinction is that refineries produce fractions (made up of groups of hydrocarbons) that are primarily used as fuels (or fuel modifiers) whilst the petrochemical industry produces specific hydrocarbons for use as basic building blocks in the wider chemical industry. The refinery separation processes are covered by the REF BREF. This interface is represented schematically in Figure 1.2.



Source: [180, EC DGXI 1993]

Figure 1.2: Interface between petrochemical and hydrocarbon industries

Downstream from the production of LVOC, there is an integral association with the rest of the chemical industry and again it is difficult to establish definitive boundaries. The IED information exchange for the review of the LVOC BREF focused on a relatively small number of chemicals, with the remainder to be included in the WGC BREF, or separate BREFs produced over the next few years as part of the Chemical BREFs strategy.

Figure 1.3 illustrates the complexity of the industry by showing the range of products that result from the basic hydrocarbon raw materials. Many of the products are intermediates for the rest of the chemical industry and have limited use in their own right.

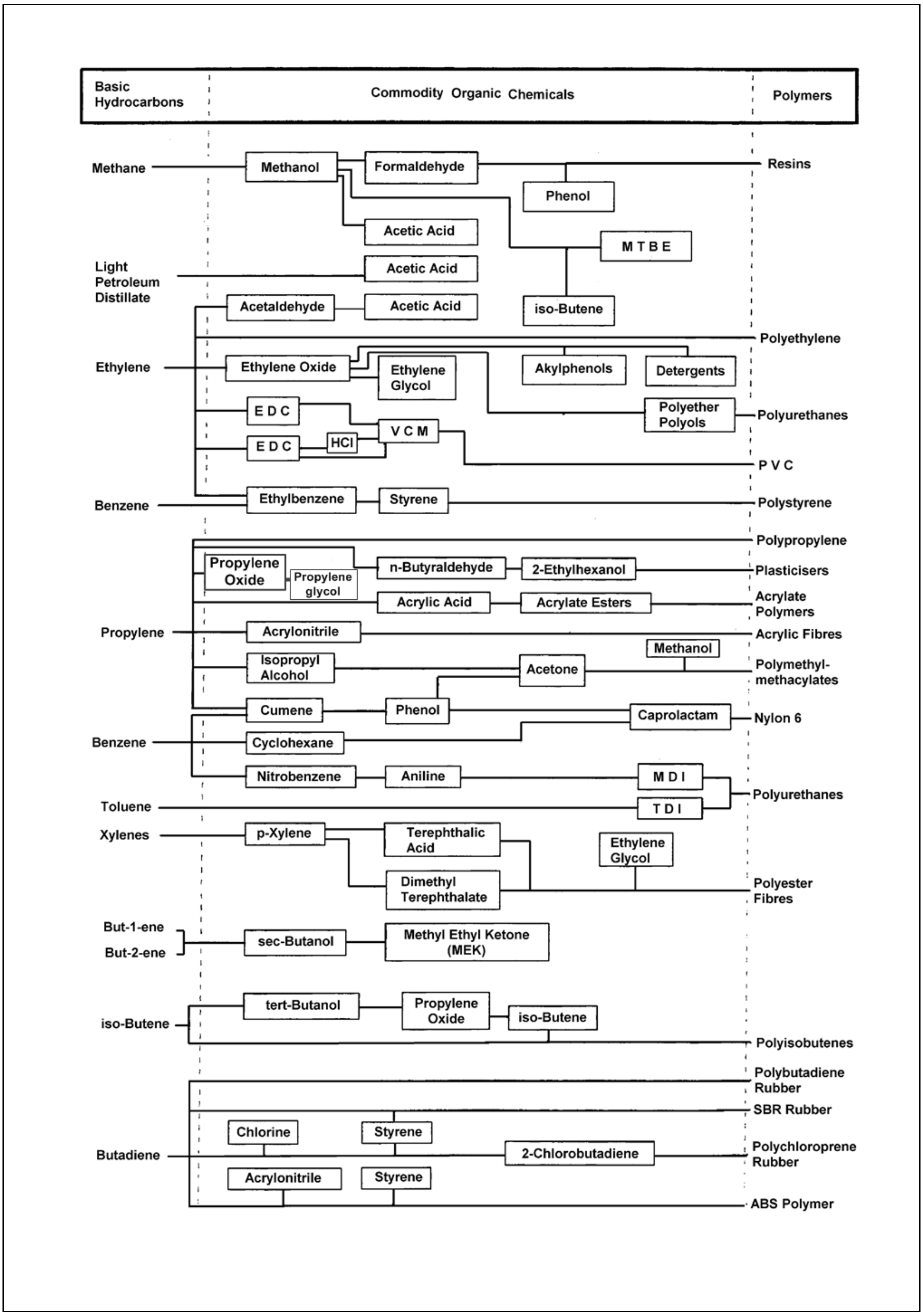


Figure 1.3: Pathways in the organic chemistry industry

Production of LVOC is usually carried out on large, highly integrated chemical sites. The integration of production units can confer significant economic and environmental benefits, e.g.:

- a high degree of process flexibility that allows operating regimes to be fine-tuned to produce chemicals in the most efficient manner;
- energy use can be optimised by balancing energy sources and sinks;
- by-products may be used as feedstock in other plants (e.g. crackers, furnaces, reactors), thus negating the need for disposal, or may be used as fuel;
- there are economies of scale in the treatment of waste streams;
- the loss of intermediates during transportation is reduced.

However, depending on the issue, at integrated production sites it can be more difficult to assess and compare some aspects of the environmental performance of individual LVOC plants.

1.2 Economic trends in LVOC

Sector economics

The production of LVOC has significant economic importance in Europe. Although there are a large number of chemicals produced in Europe, the production figures are dominated by a relatively small number of chemicals manufactured by large companies. Germany is Europe's largest producer, but there are also well-established LVOC industries in the Netherlands, France, the UK, Italy, Spain and Belgium. Production in the other Member States is significantly lower.

It is difficult to provide specific economic data for the LVOC industry as a whole because there is no absolute definition of the sector and there is considerable variation in the business background to different production processes.

Global position

In overall terms, the European Union is the world's third largest producer of chemical products and accounted for nearly one sixth of estimated world production in 2015. In financial terms, the European chemical industry in 2015 had a turnover of EUR 615 billion, of which EUR 519 billion came from EU countries. This exceeds the turnover of equivalent industries in the NAFTA zone (EUR 583 billion) and Japan (EUR 136 billion) but continues to lag behind China (EUR 1 409 billion). The EU chemicals market share has halved in 20 years, from 32 % in 1995 to 15 % in 2015. The EU chemicals market is dominated by the production of organic base chemicals and their turnover is some four times the turnover generated by the production of inorganic base chemicals. Apart from China (with which it is in balance) and Japan (with which it has a slight deficit), the EU has a surplus with each main trading region – NAFTA, Asia, Latin America, Africa, Rest of Europe and Africa. The EU chemicals trade surplus in 2015 reached nearly EUR 44.8 billion with speciality and consumer chemicals accounting for 92 % of that surplus [178, CEFIC 2016].

Competition

Basic petrochemical products are usually sold on chemical specifications, rather than on brand name or performance in use. Within any region, different producers have different costs of production due to variations in scale, process plant, feedstock source and type and energy costs. There are few possibilities for product differentiation and so economies of scale are particularly important. Like other commodities, the basic petrochemical business is therefore characterised by competition on price, with the cost of production playing a very large part. The market for bulk chemicals is very competitive and market share is often considered in global terms.

Integration

Process integration is a significant factor in the economics of the primary chemical industry. The integration is both upstream (many processes are linked to refining) or downstream (many LVOC products are intermediates for associated production processes). This integration can improve the competitive position of companies, but it complicates any cost comparisons between installations. The price of LVOC is strongly determined by the economic status of downstream users and their demand, and it is generally difficult to pass price increases on to purchasers.

Profitability

The profitability of the European LVOC industry is traditionally very cyclical. To some extent, this cyclical nature reflects the normal cycles of commercial demand. However, the cycle is accentuated by the high capital investment costs of installing new technology and operators only tend to invest in additional capacity when their cash flow is good. Projects to increase capacity have long lead times and when they come online they can produce over-capacity that temporarily depresses margins. As a result, reductions in manufacturing costs tend to be incremental and many installations are relatively old.

The LVOC industry is also highly energy-intensive and profitability is therefore strongly linked to oil prices. The further downstream a process is from the basic hydrocarbons, then the more attenuated the effects of oil price volatility become.

Trends

In the 10-year period from 2005 to 2015, the chemicals industry had an average growth rate of 0.3 %, a rate slightly lower than the 0.4 % average growth rate for all of the manufacturing industry. These low growth rates were mainly impacted by the dramatic declines in chemical production levels during the 2009 economic downturn following the global financial crisis of 2008. The EU chemicals industry was profoundly affected by the spillover effects of the economic and financial crisis but has been following the recovery trend that has occurred since 2010. The EU chemicals sector enjoyed a strong 2010, posting a 10.2 % growth rate compared with 2009. However, there has been no overall growth during 2011–2015 [178, CEFIC 2016].

Employment in the EU chemicals industry fell steadily from 1.29 million in 2005 to 1.17 million in 2010. Since 2010 employment has remained stable and stands at 1.16 million in 2015 [178, CEFIC 2016].

Bio-based LVOC process routes

Bio-based organic chemicals are increasingly being produced on an industrial scale. Bio-based feedstock represents 5 % of the EU chemical industry. Industrial policy and import duties have a big impact on bio-based feedstock prices. Some of them are either heavily dependent on internal subsidies or are affected by competitors that are receiving high subsidies from other countries outside the EU. As with bio-based fuels, some plants have closed in the EU due to market instability. The environmental benefits of these unit processes often include lower CO_2 emissions when the photosynthesis of crop-based raw materials is taken into account.

Table 1.1: Global market projection for platforms and fine chemicals (1) by bio-based process routes

Product category	Products	Market volume 'Bio' 2010 (2)	Projected market volume 'Bio' 2020 (2)
Succinic acid	Polymers, sweetener	2 500	>> 1 000 000
1,4 Butanediol	Polyesters, polyurethanes	< 100	> 200 000
1,3 Propanediol	Polyesters	45 000 (3)	1 400 000
Epichlorhydrin	Epoxy resins	10 000	300 000
Acrylic acid	Polyacrylates	Pilot quantities	450 000
Isoprene	Elastomers	Pilot quantities	50 000
Ethanol	Chemicals	n.a.	430 000
Lactic acid	Monomeric acid	280 000	500 000
	Polylactic acid (PLA)	140 000	1 200 000
Sorbitol	Surfactants, polyethers, isosorbide	140 000 (3)	300 000
	Others	1 100 000	1 340 000

(1) Figures from Novamont Spa, Valbiom NNFCC, Roquette Frères S.A.
(2) In tonnes.
(3) Mostly outside Europe.
Source: Busch & Wittmeyer, Current market situation 2010 and market forecast 2020 as cited in: [209, Nita et al. 2013]

2 GENERIC LVOC PRODUCTION PROCESSES

The core activity of a chemical production process is the conversion of raw materials into the desired **chemical products** using the necessary chemical reactions **(unit processes)** and physical changes **(unit operations).** This typically involves the five steps described below:

1. Raw material supply and preparation. The receipt and storage of raw materials and ancillary reagents, and their charging into reactors.
2. Synthesis. The core of every process where raw materials are transformed into crude product by means of a chemical reaction (‘unit processes’), often with the aid of a catalyst.
3. Product separation and refinement. Using ‘unit operations’, the product is separated from other reaction components (e.g. unreacted feed, by-products, solvents and catalysts) and purified of contaminants to the necessary specification.
4. Product handling and storage. The storage, packaging and export of the product.
5. Emission abatement. The collection, reuse, treatment and disposal of unwanted liquids, gases and solids for those pollutants that have not been addressed by process-integrated measures.

Operators aim to achieve the process steps effectively and efficiently so that profits are maximised and yet without detriment to the environment or to employee health and safety.

These aims are achieved by the use of many complementary facilities and activities, namely:

- a comprehensive infrastructure that interconnects the units (e.g. refrigeration, vacuum, safety facilities);
- an energy system that produces steam or electrical energy for use in the process, and cooling facilities (where needed);
- a management system that ensures the operation of the process under all scenarios.

Since this BREF does not provide a comprehensive description of all LVOC processes, it is important to understand the generic principles of unit processes, unit operations, site infrastructure, energy management and management systems. This ‘toolkit’ of fundamentals then enables a basic understanding of any LVOC production process, its potential environmental impacts, and suitable techniques for preventing and controlling emissions. The following sections therefore describe, in a generic manner, the main features of these fundamentals as applied to the production of LVOC.

2.1 Chemical products in LVOC production

A large variety of chemical products are encompassed by the term LVOC. The detailed information exchange exercise has been restricted to those chemicals produced by the illustrative processes described in Chapters 3 to 12. For the remaining chemical products, a number of very brief (‘thumbnail’) descriptions of the most significant within each branch of the LVOC sector are provided in this chapter. Most of these thumbnail descriptions have been copied from the previous version of the LVOC BREF, which was published in 2003, without being revised and updated. New thumbnails have been written for acrylonitrile (based on the illustrative chapter in the 2003 LVOC BREF), bioethanol, hydrogen cyanide and propylene oxide.

These descriptions have been prepared where the process used to produce the chemical is commercially or environmentally significant, and where information was readily available. Most of the processes described have European production capacities in excess of 20 kt/yr, but the inclusion (or exclusion) of a particular process description should not be seen as representing a legal interpretation of the term LVOC.

The descriptions have been restricted to a brief outline of the chemical products, any significant emissions from their production process, and particular techniques for pollution prevention or control. Since the descriptions aim to give an initial overview of the products and processes, they do not necessarily describe all production routes. The descriptions are, therefore, a starting point in the determination of BAT and additional information will be needed, in accordance with Articles 14(5) and 14(6) of the IED.

The chemical products described in the next section are grouped according to the categories in Section 4.1 of Annex I to the Industrial Emissions Directive (IED) in the order 4.1(a) to 4.1(g). Products that belong to more than one category are listed under the highest category. Therefore, a product listed in a later section may also belong to former sections; e.g. halogenic compounds listed in Section 2.1.6 may also contain nitrogen or oxygen, but products listed in Section 2.1.2 (oxygen-containing hydrocarbons) will not contain any other elements (than C, H and O). This does not mean that the process to produce a product under Section 2.1.2 may not involve another type of compound (e.g. nitrogenous or halogenic hydrocarbons).

2.1.1 Simple hydrocarbons

The Industrial Emissions Directive (IED) (Section 4.1(a) of Annex I) defines this subgroup as simple hydrocarbons (linear or cyclic, saturated or unsaturated, aliphatic or aromatic). Processes for the production of the following hydrocarbons are described in the subsequent illustrative chapters of this document.

2.1.1.1 Lower olefins

This group comprises a range of unsaturated hydrocarbons, primarily ethylene, propylene, butylenes and butadienes. They are important building blocks for the production of a range of products that are based on organic chemistry, including plastics, polymers and man-made fibres. Steam cracking is currently the most commonly applied technology for the production of lower olefins which is described in Chapter 3 of this document.

2.1.1.2 Aromatics

Aromatic plants produce a number of intermediate chemicals such as benzene, toluene, xylenes and cyclohexane. These manufacturing plants are often situated in aromatic complexes and can have a number of different configurations. They operate downstream of refineries and upstream of other LVOC plants such as phenol, styrene or PTA plants. Production of aromatics is described in Chapter 4 of this document.

2.1.1.3 Ethylbenzene

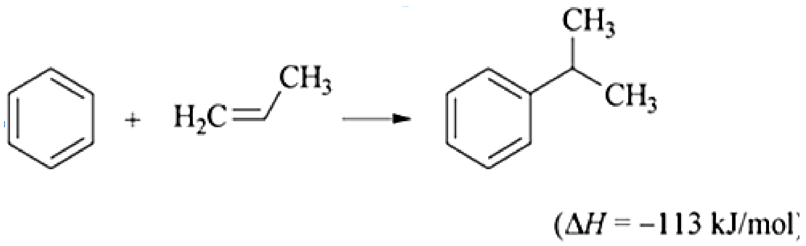
Ethylbenzene is used almost exclusively as an intermediate for the manufacture of styrene monomer, which is one of the most important large volume commodity chemicals. Commercially, almost all ethylbenzene is produced by alkylating benzene with ethylene. This process is described in Chapter 5 of this document.

2.1.1.4 Styrene monomer

Two processes are described for the production of styrene monomer, which is an important petrochemical used in the production of polystyrene and other styrenic resins such as acrylonitrile butadiene styrene and styrene acrylonitrile. Chapter 5 describes its production through the dehydrogenation of ethylbenzene.

2.1.1.5 Isopropylbenzene (cumene)

The production of cumene is not described as an illustrative process and so is described here in outline only. Other alkylbenzene compounds are produced by a similar process (see Chapter 5 for ethylbenzene).

Cumene production	
Uses	Converted to cumene hydroperoxide, an intermediate in the synthesis of other industrial chemicals, primarily phenol and acetone
Benzene alkylation with propylene	
Prevalence	Accounts for approximately 80–90 % of production within the EU
Summary	Alkylation of benzene with propene and distillation to purify cumene  **Figure 2.1: Alkylation of benzene with propene**
Process options	The alkylation route accounts for the majority of large cumene plants: - Catalyst selection: zeolites were introduced in the late 1980s with better selectivity and simpler catalyst management. SPA (supported phosphoric acid), $AlCl_3$ or HF. - Vapour phase reaction (zeolites fixed bed) vs liquid phase (220 °C, SPA or new zeolites). - Feedstock: normal vs diluted to reduce reaction temperature and impurities.
Yield	- 95 % with SPA (oligomerisation of propene); 98 % with $AlCl_3$. - 99 % with zeolites (after transalkylation of di-isopropylbenzene (DIPB) to cumene).
Proprietary processes	UOP (Lummus), Exxon (Mobil/Raytheon), CR&L, Mobil Badger, Enichem, Monsanto, BASF, Dow, Kellog, Hulls, CDTech
Co-products	- Propane is obtained when propylene feedstock is consumed at lower purities. - DIPB could be isolated for sale (instead of transalkylation) as hydroquinone feedstock.
By-products	- Heavy aromatic compounds (tars) can be consumed as fuel. - Polyalkylated (polymers) are avoided with excess benzene feed. - Butylbenzene is avoided by feed purity (butylene and toluene). - Di-isopropylbenzene that is transalkylated to cumene. - Diphenylethane. - Xylene.
Raw materials	- Benzene: needs to be dried out before reaction. - Propylene: propane is removed prior to or post alkylation reaction.
Energy	- Energy is recovered from exothermic alkylation reaction for distillation usage. - Large duty required to purify DIPB from heavy tars.
Air	- Distillation vacuum system will have light vents that need to be channelled (to flare or thermal oxidiser). - Catalyst management (especially SPA) involves frequent filter maintenance operations in reaction downstream section with benzene present.
Water	- Cooling water consumption (bleeds) can be reduced by the use of air condensers. - Water is removed from feedstock (benzene and C_3) by distillation.
Waste	- Spent catalyst is key waste: zeolites generate significantly less volume. - Acid catalyst can be treated in a kiln.
Odour	- Thermal oxidiser commonly required. - High-boiling organics can be odorous.
Other	Exposure to benzene: fugitive emissions.

2.1.2 Oxygen-containing hydrocarbons

The Industrial Emissions Directive (IED) (Section 4.1(b) of Annex I) defines this subgroup as ‘oxygen-containing hydrocarbons such as alcohols, aldehydes, ketones, carboxylic acids, esters and mixtures of esters, acetates, ethers, peroxides and epoxy resins’.

Processes for the production of the following oxygen-containing hydrocarbons are described in the subsequent illustrative chapters of this document:

- **Ethylene oxide and ethylene glycols**: (see Chapter 7).
- **Formaldehyde:** (see Chapter 6).
- **Phenol:** (see Chapter 8).
- **Propylene oxide:** The co-production of propylene oxide with styrene monomer is described in Chapter 5. Production of propylene oxide by other process routes is included as a thumbnail description (see Section 2.1.2.8 below).
- **Hydrogen peroxide** (see Chapter 12). (Although hydrogen peroxide is not an organic chemical, it is included in this document because it is produced using organic chemicals and the chemical processes used are similar to those used for other LVOC.)

The following chemical products are not described as an illustrative process and so are described here in outline only.

2.1.2.1 Alcohols

2.1.2.1.1 Ethylhexanol

2-Ethylhexanol is mainly used as the alcohol component in the manufacture of ester plasticisers (especially di-2-ethylhexyl phthalate – DOP) for soft polyvinyl chloride. The second largest application is the production of 2-ethylhexyl acrylate which is used to manufacture coating materials (especially emulsion paints), adhesives, printing inks, impregnating agents and reactive diluent/cross-linking agents. In addition, 2-ethylhexyl nitrate is a cetane number improver and 2-ethylhexyl phosphates are used as lubricating oil additives. It is also used to make surfactants (anti-foaming agents, dispersants, flotation agents) and as a solvent (for polymerisation catalysts and in extracting agents).

Butyraldehyde (butanal) is the main feedstock for the 2-ethylhexanol process and is normally produced in the same installation. The manufacture of butyraldehyde is by the oxo synthesis route (hydroformylation of propylene and CO/H_2 synthesis gas). This is an exothermic gas/organic liquid phase reaction using a homogeneous cobalt catalyst at 130–150 °C and 100–300 bar. The high demands on the purity of 2-ethylhexanol products place similar purity demands on the butyraldehyde raw material. Isobutyraldehyde is formed to a greater extent (with cobalt catalysts) or a lesser extent (with rhodium catalysts) during hydroformylation and must be separated to prevent mixed aldolisation. The subsequent production of 2-ethylhexanol from butyraldehyde involves four main stages:

1. **Aldolisation and dehydration:** The aldol condensation of butyraldehyde raw material to 2-ethylhexenal proceeds rapidly in the presence of an aqueous sodium hydroxide catalyst. The ensuing dehydration of the hydroxyaldehyde is conducted promptly because the aldol is unstable and can impair the product quality and yield. Local overheating in the reaction mixture must be avoided, as this may cause secondary reactions that decrease yields, and thorough mixing is required. The ratio of aldehyde to aqueous sodium hydroxide solution is in the range of 1:10 to 1:20. The aqueous/organic liquid phase reaction may take place in a mixing pump, a packed column or a stirring vessel. The various processes operate at a temperature of 80–150 °C and pressures

below 0.5 MPa to give conversion rates of > 98 %. The heat of the aldolisation reaction may be used for steam generation (e.g. 120 kg steam/t butyraldehyde) although this is only possible when the process is run close to 150 °C (and this is not common).

2. **Phase separation and purification:** The reaction mixture is separated into an upper organic phase (the intermediate product 2-ethylhexenal) and a lower aqueous phase (containing the aldolisation solution). The 2-ethylhexenal is washed with process water to remove sodium hydroxide (giving a waste water stream) and then purified by distillation. The water content of the product is decreased by fractional condensation to decrease the energy demand at the following vaporisation. Most of the aqueous aldolisation solution can be recycled but the rest must be removed from the system via a side-stream because the aldolisation solution becomes diluted by water produced in the reaction. This bleed also removes the aldolisation by-products. The bleed has such a high COD value that pretreatment is required when the efficiency of the biological treatment is low (COD removal < 90 %). Suitable pretreatment methods are oxidation, acid treatment/filtration, and extraction (which allow partial recycling of valuable products).

3. **Hydrogenation:** The unsaturated organic product (2-ethylhexenal) from the phase separator can either be hydrogenated in a single stage (e.g. fixed nickel or copper catalyst) or in several stages (a combination of gas–liquid phases, or liquid–liquid phases in a sump phase or trickle-bed reactor). The hydrogenation stage achieves a conversion of 100 % and a selectivity of > 99 %. The heat of reaction for the hydrogenation of the C=C double bond and the aldehyde group is relatively high (178 kJ/Mol) and enables energy recovery through steam generation. The temperature must be controlled to prevent any local overheating that would decrease yields. With single-step hydrogenation, remixing with the hydrogenation product has been proposed to dissipate heat (150–200 °C) and, in contrast to other processes, medium pressure is initially necessary to ensure adequate conversion. Modern plants normally utilise two stages to remove residual amounts of carbonyl compounds and to ensure that high-grade 2-ethylhexanol is obtained. An initial gas phase reaction is followed by a liquid phase reaction. Nickel, copper or mixed systems are preferred as heterogeneous hydrogenation catalysts. Optimisation of the catalyst increases efficiency by high selectivity, easier separation of by-products (giving energy savings) and extending catalyst life (> 2 500 t product/t catalyst) which reduces waste. The reaction takes place with a hydrogen excess and this is recycled. A higher purity of hydrogen (99.9 vol-% instead of 97.5 vol-%) may reduce waste gas volumes from about 1.3 m^3/t to about 0.05 m^3/t ethylhexenol.

4. **Distillation:** Fractional distillation of the hydrogenation product normally takes place in three stages. In the first stage, the light ends are separated at the head and can be employed for the manufacture of 1-butanol. In the second stage, pure 2-ethylhexanol is collected at the head. In the third stage, the recyclable intermediate fractions are separated from the heavy oil (which may be used for heating purposes).

Process variants: The Aldox process is a process variant where the aldolisation and oxo reactions have been combined into a single step. This is used by Shell in the US and Exxon in the US and Japan. Adding co-catalysts, such as compounds of Zn, Sn, Ti, Al, or Cu or potassium hydroxide (KOH), to the original oxo catalyst allows the three reaction steps (i.e. propene hydroformylation, aldol condensation and hydrogenation) to take place simultaneously. In addition to the KOH co-catalyst, Shell also uses a ligand-modified hydroformylation catalyst in their Aldox process.

Consumption*:* The raw materials required to make one tonne of 2-ethylhexanol are: 1 145 kg of 100 % butyraldehyde, 360 m^3 hydrogen and 1 kg nickel or copper catalyst. The yield is ≥ 98 %.

Environmental issues

Air: Waste air from hydrogenation and the storage of intermediate products can be incinerated or combusted in the site power plant. The waste gas stream from the storage of the final product (filling process) may be emitted to atmosphere without treatment. The estimated maximum loss is 4 g total C per tonne of product.

Water: Waste water is mainly reaction water from the aqueous aldolisation step and process water from washing the intermediate product 2-ethylhexenal. The typical rate of effluent production is 0.15–0.2 m^3/t of product. C_4 compounds (mainly n-butyraldehyde and sodium butyrate) constitute roughly 50 % of the effluent organics and the remainder is C_8 compounds (or $C > 8$). These give an effluent with acute toxicity to fish (LID = 32–45) and COD of < 50 g/l (10 kg COD/t of product). Waste water shows moderate biodegradability in municipal waste water treatment plants, which can reduce the COD of process water by 60 % and the reaction water COD by > 90 %. This is sufficient to eliminate toxicity to fish. To improve the elimination of COD, the waste water may be pretreated using neutralisation with sulphuric acid and phase separation (to give a 40 % COD reduction), and extraction with 2-ethylhexanol combined with distillation to recover the 2-ethylhexanol (giving a 75 % COD reduction for the total pretreatment). The organic load is reduced to 0.4 kg COD/t of product after pretreatment and biological treatment (total elimination 95 %). A similar performance can be obtained by minimising the waste water stream by optimising the washing step and treatment in an adapted waste water plant. Energy may be gained by incineration of the extract. In a Swedish plant, the waste water treatment involves decantation, stripping, biological treatment in biorotors, sedimentation and sand filtration; reducing the organic load by more than 99 %.

Wastes: Generally there are few or no wastes for disposal. Wastes from the last fractionation step amount to < 50 kg/t of product and are combusted to recover their energy value. Copper and nickel from used hydrogenation catalyst amount to < 0.4 kg/t of product and are recovered.

2.1.2.1.2 Bisphenol acetone (BPA)

Also known as bisphenol A or 4,4-isopropyllidenediphenol, BPA is a raw material for the production of polycarbonate and epoxy resins. BPA is produced by the condensation reaction of phenol and acetone by two process variants:

BPA Route 1: The catalysed reaction of acetone and phenol is carried out with an excess of phenol to maximise acetone consumption. The reaction product consists of BPA, BPA isomers, BPA oligomers, phenol, hydrogen chloride and water. The hydrogen chloride catalyst is recovered by distillation, and this also creates a waste water stream. Further distillation recovers phenol. BPA, BPA isomers and BPA oligomers are then removed with hot toluene solvent to leave a by-product of heavy tar. Cooling of the remaining liquid causes BPA to crystallise out and enables separation from the liquid in a centrifuge. Wet powder from the centrifuge is melted and vacuum-stripped of toluene. Toluene from the centrifuge and stripper is recovered as a light tar by-product (BPA-C). The melt is prilled to give a final product of BPA pellets.

BPA Route 2: In this route, BPA is also produced by the catalytic reaction of acetone with excess phenol, but is crystallised and further processed without the hot toluene purification step. Acetone conversion is nearly 100 % and avoids the formation of by-products in the subsequent column. The reaction product consists of BPA, BPA isomers, phenol and water. BPA is crystallised out of the mix by cooling, and is then separated by filtration. BPA from the filter is flash-stripped of residual phenol. The molten BPA is prilled to give the final product. Liquid from the filter (consisting of phenol, BPA, BPA isomers and heavy ends) is sent to a recovery unit where BPA isomers are isomerised into BPA and recycled to the main crystallisation unit. A purge stream in this section removes the heavy ends (tars) for incineration. In some cases, when the BPA is being used to make epoxy resins, the purification of the final BPA by crystallisation and filtration is not required.

Environmental issues for route 1

Air: HCl from the acid gas scrubbing system; phenol from the phenol vent gas scrubber; toluene from the toluene vent gas scrubber and prill tower; toluene-containing gas from the transportation and storage of BPA pellets; and flue-gas emissions from the hot oil furnace.

Water: The water reaction product is separated by distillation, neutralised with caustic and treated centrally.

Wastes: No specific wastes as tar streams are reused by customers.

Energy: The reaction is exothermic.

Environmental issues for route 2

Air: Light ends arise from the phenol vent gas scrubber are incinerated. When methyl mercaptan is used as a catalyst, the off-gas is flared. Waste gas from the prill tower contains small amounts of solid BPA that require filtration. Phenol-containing gas from the transportation and storage of BPA flakes is also an issue.

Water: The water reaction product is washed in a special unit (distillation towers and strippers) to recover dissolved phenol and acetone, and is then treated biologically.

Wastes: Heavy ends are burnt in an incinerator.

Energy: The reaction is exothermic.

2.1.2.1.3 Ethanol

Ethanol produced by chemical synthesis

Nowadays, most industrial ethanol is manufactured by fermentation (see bioethanol below). However, industrial ethanol for special purposes (e.g. pharmaceutical, synthetical or analytical purposes with specific demands on the composition of the ethanol batch) is manufactured by the vapour phase hydration of ethylene over a solid phosphoric acid catalyst supported on porous clay beds at around 240 °C and 68 barg:

$$C_2H_4 + H_2O \rightarrow CH_3CH_2OH$$

The reactor product is scrubbed with water to separate the ethanol. Unreacted ethylene is recycled. Ethanol is obtained from its aqueous solution by a series of distillations, followed by azeotropic distillation with benzene. Alternative ethanol production routes are the indirect hydration of ethylene with H_2SO_4, and alcoholic fermentation (see bioethanol below).

Environmental issues

Air: Hydrocarbons from process vents.

Water: Caustic effluent from washing of the aqueous product prior to distillation and phosphates from the distillation process. The reactors are copper-lined and at each reactor catalyst regeneration there is a surge of copper in the aqueous effluent.

Wastes: Organic solvents, phosphoric acid and phosphates from spent catalyst.

Ethanol produced by fermentation (bioethanol)

Bioethanol	
Uses	Ethanol is used in food and beverages (~ 15%), as fuel and for other industrial uses (~85%), e.g. motor fuel, additive for gasoline or solvent. The production of ethanol for alcoholic beverages and other foodstuffs is included in the FDM BREF.
Sugars (alcoholic) fermentation	
Prevalence	Accounts for the vast majority of ethanol production within the EU. Large-scale ethanol production in Europe is predominantly based on grain (e.g. wheat, barley, triticale, rye and corn) and intermediate, co- and by-products from the production of sugar from sugar beets (e.g. diffusion juice, clarified juice, concentrated juice and molasses) as well as from the production of starch (e.g. B-, C-starch). Further details on the bioethanol production process can be found in the FDM BREF.
Summary	Bioprocess: microbial (yeast) fermentation of sugars, $C_6H_{12}O_6$ + yeast → $2C_2H_5OH + 2CO_2$+ heat followed by distillation, dehydration, and denaturing (optional).
Process options	• Sugar to ethanol is the common and simplest route. • Starch crops require hydrolysis of carbohydrates to obtain glucose. Enzymes are used to convert starch into sugar: $(C_{12}H_{22}O_{11} + H_2O + enzyme \rightarrow 2\ C_6H_{12}O_6)$ • Ligno-cellulosic feedstock requires biochemical conversion of hemicellulose into sugars (saccharification of cellulose at demo stage).
Yield	• Each gram of glucose can produce 0.51 g of ethanol and 0.49 g of CO_2. • Around 390 litres of ethanol are produced from 1 t of cereals. • 9–15 vol-% alcohol solution is obtained in fermentation reactors.
Proprietary processes	• Cargill, Abengoa, CropEnergies, Tereos, Ineos, Novozymes, Genecor, Diversa.
Co-products and by-products	• CO_2. • Ethanol from cereals: o Stillage in various forms: i) distillers grains with solubles (DGS); ii) condensed distillers solubles (CDS); or iii) dried distillers grains with solubles (DDGS): fibre and protein that can be used as feed for livestock. 320 kg DDGS per t of maize. Used as animal feed. o Gluten and bran (if separated before fementation, see dry fractionation below). • Ethanol from sugar beet: vinasse, sugar beet pulp, dried slop, fusel oils (used as animal feed or fuel). • Ethanol yield can be lowered by formation of small amounts of by-products such as glycerol, succinate, higher organic alcohols (such as propanediol, fusel oils). • Wet milling of corn generates germ (50 % oil).
Raw materials	The dominant current process is the production of ethanol through the fermentation of sugar- and/or starch-containing raw materials (e.g. grain, clarified and concentrated juice or molasses). Currently expansion of the raw materials used involves the use of (ligno-)cellulose. For this purpose, the first pilot and/or demonstration plants already exist.
Energy	• 10–20 MJ/litre (low values are modern dry mill technology). • Purification of ethanol via distillation is energy-intensive. • Also energy-intensive are: milling, jet cookers, dryers and pelletiser of DDGS. • Starch-based route consumes more energy. • Recovery: co-generation of heat and power (CHP) opportunities since process heat is required at low temperature; biogas from digester in WWT. • New high-pressure distillation systems have reduced steam consumption by 40 % (3.0–4.2 kg steam for every litre of 96 vol-% ethanol). Energy costs can be reduced by up to 80 % in low-pressure distillation columns by using a vapour recompression system.

Bioethanol	
	- Use of thermo-tolerant yeast and cellulolytic enzymes in a combined saccharification fermentation process is an advantage because the optimum temperature for the hydrolysis of cellulose is 45–50 °C, and cooling problems can be simplified during large-scale fermentation.
Air	VOC emissions are generated during fermentation, distillation and drying. Thermal or catalytic oxidisers, adsorption or (biological) absorption (bioscrubber) can be used for their abatement. - CO_2 is generated in fermentation, and the dryer stack also generates CO_2. - Dust (PM_{10}) is formed during the raw material delivery, handling, milling (of cereals) or drying of co- or by-products. - Combustion from boilers in the plant generates CO, NO_X, SO_X. - If co-product drying is in place, carbon monoxide may also be a result. - Other from auxiliary systems: hydrogen sulphide and VOCs released from the WWT, PM_{10} from the cooling towers, fugitive PM_{10} and VOC emissions from haulage road traffic and equipment leaks. Potential VOC evaporative loss from wet distillers grains storage pile. - (Dry fractionation:) Most fractionation systems separate the corn kernel into three main components: starch (endosperm), germ and bran. By removing non-fermentable material from the fermentable starch in the kernel before the corn enters the ethanol process, the plant can improve throughput while reducing the use of organics in fermentation, thus generating less VOC emissions (about 10 % less).
Water	- Most consumption (70 %) related to energy production: the boiler system that drives the plant and cooling of process water and equipment. The rest (30 %) is related to the fermentation process, feed treatment and cooling. - ~ 4 kg water withdrawn/kg ethanol produced. - Anaerobic digesters are preferred for waste water treatment since the load is primarily organic with high COD and BOD.
Waste	- Spent molecular sieves, spent membranes, WWT sludge. - Co-products and by-products (if not utilised).
Odour	Thermal oxidisers or bioscrubbers are commonly used for treatment of fermentation gases or gases from DDGS drying.

2.1.2.1.4 Isopropyl alcohol (isopropanol)

Isopropyl alcohol is produced by indirect or direct hydration.

The **indirect hydration** of propylene using sulphuric acid as a homogeneous catalyst produces isopropyl alcohol and four other solvents (di-isopropyl ether, dimethyl ketone, secondary butyl alcohol, and methyl ethyl ketone). Propylene and butylenes in mixed C_3 streams and mixed C_4 streams are reacted with 70–75 % sulphuric acid to form the corresponding alkyl sulphates, which are subsequently hydrolysed to the corresponding alcohols. The related ethers are formed as by-products. The crude alcohols are purified by distillation to give an isopropyl alcohol azeotrope with water and a relatively pure secondary butyl alcohol. These may be sold or converted to the related ketones by dehydrogenation over a brass catalyst.

The **direct hydration** of propylene uses a heterogeneous catalyst either in the vapour phase, the liquid phase or a vapour liquid mixture. The propylene feed is purified first by distillation to remove propane. Propylene is then hydrated in the vapour phase. The major by-product is di-isopropyl ether, but other by-products include n-propanol, acetone, hexanol and low-molecular-weight polymer. The reaction takes place at approximately 180 °C and 34 barg over a catalyst of 42–46 % phosphoric acid on porous clay beds. The product is water-scrubbed to separate the isopropyl alcohol. Unreacted propylene is recycled, a purge being taken to prevent propane build-up. Finally, isopropyl alcohol is purified azeotropically by distillation using cyclohexane as an entrainer.

Environmental issues for indirect hydration

Air: Oxides of carbon, oxides of nitrogen and oxides of sulphur from the incineration of waste process gases; hydrocarbons from tank vents, strippers, condensers and reaction time tanks; isopropyl alcohol from the cooling tower; chromium from the incineration of solvent slops; nickel from the incineration of caustic sludge.

Water: Alcohols, ketones, furfural, copper and zinc from aqueous interceptor discharges, spent sulphuric acid and caustic soda.

Wastes: Spent brass catalyst if not regenerated; ash from the incinerator.

Environmental issues for direct hydration

Air: Hydrocarbons from tank and process vents; fugitive releases of hydrocarbons.

Water: Propanols, organic phosphates and inorganic phosphates from the water wash.

Wastes: Phosphoric acid and phosphates as spent catalyst.

2.1.2.1.5 Methanol

Methanol is used as a solvent and as a feedstock for the production of formaldehyde, acetic acid, and MTBE. Methanol is formed by the catalytic conversion of synthesis gas (carbon monoxide, carbon dioxide and hydrogen) which is generated by the catalytic cracking of natural gas (steam reforming). High- and low-pressure versions of the process exist.

Environmental issues

Air: The main emissions are carbon dioxide and nitrogen oxides. NO_X emissions can be reduced by cutting steam production.

Water: Biological treatment.

Wastes: Wastes are recycled or incinerated.

Energy: Self-supporting process (energy neutral).

2.1.2.1.6 Oxo alcohols

The oxo alcohols range from C_4 butanols to C_{20} alcohols, and they are produced by hydroformylation or carbonylation/hydrogenation. For example, olefins and synthesis gas are catalytically reacted to form aldehydes, which are then hydrogenated to oxo alcohols. The by-products are a light oxo alcohol fraction (used as fuel) and a high oxo alcohol fraction (that is cracked to recover oxo alcohols).

- In the manufacture of normal butyl alcohol by **hydroformylation**, synthesis gas and propylene are reacted over a catalyst at 170 °C and 70 barg. Unreacted propylene and synthesis gas are removed and the resultant mixture of catalyst in alcohol is distilled to separate the normal butyl alcohol from isobutyl alcohol.
- The C_7-C_{15} alcohols are produced by reacting the respective olefins and synthesis gas over a catalyst at 180–200 °C and 50 barg. After the depressuring and recycling of evolved gas, the crude product is distilled under vacuum. The crude alcohol is treated with caustic soda to saponify formate by-products, water-washed and then distilled to remove unreacted olefins, by-product paraffin hydrocarbons and heavy fractions. The

alcohols are hydrogenated at an elevated temperature and pressure over a nickel catalyst to remove the traces of aldehydes.

In the **carbonylation/hydrogenation** route, the liquid olefins are reacted with carbon monoxide and hydrogen at 145 °C and 260–270 barg to give liquid aldehydes and by-products including heavy ends. The aldehydes are separated from the carbon monoxide and hydrogen, vaporised with hydrogen and then hydrogenated to give the corresponding alcohol. The alcohol is cooled, separated from the hydrogen and purified by distillation to remove unreacted olefins, methanol, water and heavy ends.

Environmental issues for the hydroformulation route

Air: Oxides of carbon, oxides of nitrogen and oxides of sulphur from the incineration of process waste gases and plant ejector vents. n-Butanol and mixed hydrocarbons from plant ejector vents and sludge incineration.

Water: Suspended solids, butanols, aldehydes and butyl formate from contaminated process aqueous effluent.

Wastes: Zinc oxide, cobalt, molybdenum, chromium oxide, iron oxide, copper oxide and activated carbon from the desulphurisation and converter catalysts and activated carbon absorbers.

Environmental issues for the carbonnylation/hydrogenation route

Air: Oxides of carbon from the catalyst let-down vessels and reactor blowdown. Alcohols from hydrorefiner vents.

Water: Hydrocarbons in ejector condensate. Methanol in wash waters.

Wastes: Spent catalyst.

2.1.2.1.7 Propylene glycol

Propylene glycol is used as a solvent and in organic synthesis. It is produced by the hydration of propylene oxide (PO) with water to form monopropylene glycol and dipropylene glycol (MPG and DPG). Before the reaction, the PO is purified (washed) with caustic soda. The by-products are tripropylene glycol and higher compounds. Through distillation, the different products are separated (MPG and DPG are side-streams of the column). The top and bottom stream of the distillation column are externally reprocessed to products.

Environmental issues

Air: The main emission is carbon dioxide.

Water: A caustic soda solution arises and is directed to the waste water treatment plant or is externally incinerated.

Wastes: Acids and bases treated in a biological waste water treatment plant.

Energy: Exothermic process with energy recovery.

2.1.2.1.8 Tertiary butyl alcohol (TBA)

TBA is a raw material for the production of MTBE. TBA can be produced by the direct hydration of isobutene ($C_4H_8 + H_2O$); the indirect hydration of isobutene ($C_4H_8 + H_2SO_4$); or as a by-product during the production of propylene oxide (Oxirane process) ($C_3H_6 + C_4H_{10} + O_2$). TBA is also formed by the air oxidation of isobutane, with the tertiary butyl hydroperoxide (TBHP) by-product being further reacted with propylene to produce TBA and propylene oxide.

Environmental issues

Water: No significant emissions identified. Waste water is biologically treated.

Energy: Endothermic process.

2.1.2.2 Aldehydes and ketones

In addition to the description of the formaldehyde process in Chapter 6, other aldehydes and ketones include the following.

2.1.2.2.1 Acetaldehyde

Acetaldehyde is produced by the oxidation of ethylene or C_3/C_4 alkanes, or by the oxidative dehydrogenation of ethanol. The oxidation of ethylene is performed in aqueous solution with homogeneous catalysis with Cu or Pd chlorides. The one-step process leads to chlorinated by-products (chloroacetaldehyde) which are easily degraded/hydrolysed by biological treatment. The two-step process leads to considerable concentrations of non-degradable chlorinated substances, which can be effectively pretreated by hydrolysis.

2.1.2.2.2 Acetone

Acetone can be produced by the oxidation of propylene ($C_3H_6 + ½ O_2$); the dehydrogenation or oxidation of isopropanol (C_3H_7OH); or as a co-product in the cumene process for phenol production (see Chapter 8).

2.1.2.2.3 Cyclohexanone/ol

Cyclohexanone/ol is produced catalytically by the oxidation of cyclohexane. By-products are adipic, glutaric and succinic acid (C_1-C_5 acids). The intermediate reaction product (cyclohexylester) is decomposed with water. The aqueous phase from this hydrolysis contains water-soluble organic acids and the catalyst (‘acid waste water stream’). The organic phase is washed with NaOH to decompose esters and peroxides, giving an ‘alkali waste water’. The reaction mixture is further purified by distillation. In new installations, cyclohexanone/ol is produced by the hydrogenation of phenol.

Environmental issues

Water: The catalyst is recycled from the acid waste water stream by crystallisation and can be improved by pretreatment with wet oxidation or extraction (to reduce the high organic load). Another option is the recovery of by-product organic acids and incineration of the remaining aqueous residue. The alkali waste water is treated (optional recovery of organic acids), giving a residue which is incinerated. The remaining waste water is treated biologically with high efficiency (> 90 % COD elimination).

2.1.2.2.4 Methyl ethyl ketone (MEK)

MEK is produced by the catalytic dehydrogenation of 2-butanol (C_4H_9OH).

2.1.2.2.5 Methyl isobutyl ketone

Methyl isobutyl ketone, or hexone, is produced by the self-condensation of acetone followed by hydrogenation on a palladium catalyst in the presence of an ion exchange resin.

2.1.2.3 Carboxylic acids

2.1.2.3.1 Acetic acid

Acetic acid can be produced by three routes:

a. Acetaldehyde oxidation occurs catalytically in air in the presence of manganese acetate at 50–80 °C and 10 barg. The oxidation reaction product is distilled to remove gases, including unreacted acetaldehyde, methyl acetate, acetone, carbon monoxide, carbon dioxide and nitrogen. Crude glacial acetic acid is obtained, with impurities of formaldehyde and formic acid. Final purification of the acid involves distillation in the presence of potassium permanganate, sodium dichlorate or other oxidants.

b. The liquid phase catalytic oxidation of light hydrocarbons occurs in air at 150–200 °C and 40–50 barg. The aqueous reaction product is purified in a series of distillation columns producing acetic, formic and propionic acids and acetone. Lean off-gas from the reactor is dried and recovered in activated carbon beds. The remaining gas is combusted.

c. Methanol carbonylation can use vessels constructed in Hastelloy C and at pressures of 700 barg with copper/cobalt catalyst systems in the presence of iodine. The alternative is to use rhodium/phosphine complexes as the catalyst system and hydrogen/methyl iodide as the promoter at pressures of 33–36 barg and temperatures of 150–200 °C. Purification involves multiple distillations to remove the catalyst mixture, water, mixed acids and other impurities.

<u>Environmental issues for routes A and B</u>

Air: Light hydrocarbon off-gas from the activated carbon beds/thermal destruction system. Acetic acid, acetaldehyde, acetone, carbon monoxide and other organics from vacuum pump discharges. Scrubbed vent gases from the acetone recovery unit containing acetone, methyl acetate, benzene, acetic acid, methyl ethyl ketone, esters, methanol and some high-boiling components. Special control techniques may include thermal oxidation of the reactor off-gas, including recovery of heat and power by use of off-gas expanders and waste heat recovery.

Water: Acetic acid, ketones, methanol and acetaldehyde from vacuum systems. Final residues of butyric and succinic acids and aqueous streams from the distillation unit. Water from the acetone recovery unit containing methanol, ethanol and traces of acetone and sodium salts. Discharge from hydro-extractive distillation of propionic acid contains propionic acid, acetylacetone and 2,4-hexadiene.

Wastes: Waste from dryers, activated carbon beds and catalyst systems. Corrosion products containing a glass lead mixture contaminated with nickel oxalate and oxides of chromium and iron.

Environmental issues for route C

Air: High-pressure off-gas from the reactor, which is absorbed and scrubbed in a light ends recovery system, before venting to a thermal destruction unit, and which contains small quantities of hydrogen iodide. Flared light ends from the first two distillation columns that pass via a low-pressure absorber system containing chilled acetic acid before being vented to a thermal destruction unit, again containing small quantities of hydrogen iodide. Special control techniques may include off-gas scrubbers, using methanol or acid that is recycled back to the process.

Water: Liquor from the iodine scrubber during catalyst addition. Liquor from the final column light end scrubbers contaminated with acetic acid.

Wastes: Heavy fractions from the heavy acids column (comprising propionic and acetic acids together with potassium salts and catalyst).

2.1.2.3.2 Acrylic acid

Acrylic acid (prop-2-enoic acid)	
Uses	Intermediate in the production of acrylates.
Oxidation of propene	
Prevalence	Accounts for 100 % of production within the EU in 2014.
Summary	Heterogeneous catalytic oxidation of propene in the vapour phase ($2CH_2CHCH_3$ + $3O_2$ -> CH_2CHOOH + H_2O) with air and steam.
Process options	• The oxidation can be conducted in a single stage, or in two stages via acrolein. • Acryclic acid can be absorbed into either water or a high-boiling (> 160 °C) organic solvent such as biphenyl or diphenyl ether. • Acrylic acid that is absorbed in water is subsequently extracted into an organic solvent that either has a lower boiling point than acrylic acid (light solvent) or one that has a higher boiling point than acrylic acid (heavy solvent).
Yield	• The single stage route gives a maximum yield of 60 %. • The use of two-stage oxidation allows the operating conditions for each stage to be optimised for selectivity and yield, thereby giving better yields. The process proceeds via an acrolein intermediate, which is toxic. A first stage yield of > 85 % (for both acrolein and acrylic acid), and a second stage yield of > 99 % (acrolein conversion) can be achieved. • The use of a high-boiling organic solvent to absorb acrylic acid can result in lower yields due to higher losses of acrylic acid in vent gases. • The use of a heavy extraction solvent after water absorption can result in poor product quality.
Proprietary processes	• The individual processes are proprietary, either to the process owner or via the process licensor.
Co-products	None.
By-products	Acetic acid.
Raw materials	• Organic solvents are required for the absorption of acrylic acid in the reactor gas. • As acrylic acid is readily polymerised, inhibitors (such as hydroquinone) are often used, and distillation columns are normally operated at reduced pressure (in order to reduce columns' temperature profiles).
Energy	• The reaction is exothermic, and heat can therefore be recovered from the reaction gases (e.g. to generate steam). • It might be possible to substitute reactor vent gas for fresh steam. • Absorption of acrylic acid into a high-boiling organic solvent results in lower energy consumption, as the energy demand of waste water stripping and solvent drying is avoided. • The use of a heavy extraction solvent uses less energy as it does not need to be distilled.

Acrylic acid (prop-2-enoic acid)	
Air	• The reactor gas that remains after the absorption of acrylic acid needs to be vented, as it may contain acrolein (which is toxic). • The use of a high-boiling organic solvent for acrylic acid absorption will give a waste reactor gas stream that contains higher levels of acrylic acid, and which is also likely to contain some of the absorption solvent.
Water	• High-boiling organic solvents such as biphenyl and diphenyl ether are both dangerous for the environment. • The use of water to absorb the acrylic acid will result in an aqueous waste stream. This should be stripped of solvents, and then subjected to biological treatment.
Waste	• The catalysts used for single-stage oxidation have a relatively limited life expectancy and therefore need to be replaced frequently. • Catalysts employed for converting propene to acrolein have long lifetimes, perhaps only requiring replacement after 10 years of use. • The final isolation of acrylic acid by distillation produces a heavy fraction that can be used as a fuel. The quantity can be minimised (and the yield maximised) by converting acrylic acid dimer to monomer, which can be returned to the process.
Odour	• Acrolein has a powerful odour. • High-boiling organic solvents can be odorous. • Some light organic solvents for acrylic acid extraction (e.g. butyl acetate, 2-butanone) have characteristic odours.

2.1.2.3.3 Adipic acid

The commercial manufacture of adipic acid is achieved in two stages. In the first stage, the oxidation of cyclohexane, or the hydrogenation of phenol, gives a cyclohexanone/cyclohexanol mixture (known as ketone alcohol). In the second stage, ketone alcohol is catalytically (copper, vanadium salts) oxidised with nitric acid. By-products are glutaric and Bernstein acids and nitrous oxides, especially N_2O. NO_X is stripped with air, giving a waste gas stream. Water is removed from the reaction mixture by distillation, giving a waste water stream. Adipic acid is isolated and purified by two-stage crystallisation/centrifugation and washing with water.

Environmental issues

Air: The process releases substantial quantities of nitrous oxide (N_2O) from the stripping columns and crystallisers. This N_2O-rich off-gas can be reused in two ways:

- by burning at high temperatures in the presence of steam to manufacture nitric acid (this utilises the N_2O off-gas and also avoids the N_2O generated in nitric acid production); or
- by using N_2O to selectively oxidise benzene to phenol.

If N_2O is not reused, the two most widely used end-of-pipe techniques are catalytic decomposition and thermal destruction:

a) Catalytic decomposition uses metal oxide catalysts (e.g. MgO) to decompose the N_2O into N_2 and O_2. Heat from the strongly exothermic reaction may be used to produce steam. The catalyst typically needs to be replaced twice a year.
b) Thermal destruction involves combustion of a mixture of the off-gases and methane. The N_2O acts as an oxygen source and is reduced to nitrogen, giving emissions of NO and some residual N_2O. The combustion process can be used to raise steam. The heat of N_2O decomposition, combined with fuel energy, helps provide low-cost steam.

Reducing furnace technology was developed by Bayer and operation started in 1994. The other German manufacturer, BASF, installed a catalytic system at their Ludwigshafen plant in 1997. In June 1998, the French company Alsachimie, a subsidiary of Rhodia, brought a system on-stream to convert N_2O to nitric acid at their Chalampe site.

The costs of catalytic decomposition and thermal destruction are broadly similar.
Other emissions: Adipic acid particulates from drying and handling. Other organics from feedstock, absorbers and purification columns in the ketone alcohol section. Caproic, adipic, valeric, butyric, propionic and acetic acids (all of which have pungent odours) from acid handling and storage.

Water: Cyclohexanone/ol stage: Catalyst and organics from ketone alcohol purification. Oily water. Low-pH waste streams containing adipic, boric, glutaric and succinic acids with copper, vanadium and sulphuric acid. Special control techniques are ion exchange systems to remove inorganic salts, such as copper or vanadium salts from catalysts; evaporation and crystallisation to recover boric acid and other by-products. The remaining organic waste water components are biologically treated. Organic loads can be reduced by optimised phase separation and extraction with incineration of the organic phase.

Adipic acid stage: The mother liquor from the first centrifugation (of crude adipic acid) is partly recycled to the oxidation reactor and a bleed is treated to recover HNO_3, catalyst and organic acids. Mother liquor and wash water from the second centrifugation are reused in the first centrifugation stage. The waste water stream from distillation is treated biologically with high efficiency (> 90 % COD elimination). By consequently separating uncontaminated cooling water streams, recycling of aqueous waste streams, recovery of HNO_3 and changing from discontinuous to continuous operation, in an existing plant the waste water flow could be reduced by 98 % and the COD load by 86 % (Bayer). Emission after biological treatment is < 3 kg TOC/t of product.

Wastes: Ketone alcohol catalyst from plant cleaning. Non-volatile organic residues and organic recovery tails from ketone alcohol production. Wastes arising at shutdown, i.e. tar-contaminated sand, oxidiser residues, ketone alcohol sump dredgings. Boric acid sweepings. Caustic wash residues.

2.1.2.3.4 Carboxylic acid

Carboxylic acid is used for the production of vanillin, ethyl vanillin, allantoin, ion exchange resins and as a raw material in the pharmaceutical industry. A few different processes for the production of glyoxylic acid exist:

- **Oxidation of glyoxal:** a solution of glyoxal in water is oxidised with nitric acid or with nitrogen oxides. In the first separation step, oxalic acid is crystallised at temperatures of approximately 20 °C. With further cooling to temperatures between –10 °C and 0 °C, glyoxylic acid crystallises.
- **Oxidation of acetaldehyde:** during the oxidation of acetaldehyde for glyoxal production, 10 % glyoxylic acid is produced. An increase in temperature and higher concentrations of nitric acid will provide higher amounts of glyoxylic acid.
- **Oxidation of ethylene:** ethylene is oxidised with nitric acid to glyoxylic acid in the presence of palladium salt.
- **Ozonolysis of maleic anhydride:** the raw material for the production of glyoxylic acid with ozonolysis is maleic anhydride. The process uses temperatures between –15 °C and –25 °C. By-products are formic acid and carbonic acid. The advantage is that nitric acid is replaced by ozone for the oxidation and, thus, lower emissions can be expected. The disadvantage of this process is the high amount of electric energy necessary for the production of ozone. The exhaust gas from the ozonolysis plants is incinerated. Liquid by-products, contaminated solvents, and distillation residues from the ozonolysis plants may be incinerated.

2.1.2.3.5 Formic acid

Formic acid can be produced as a by-product of acetic acid manufacture (a liquid phase catalytic oxidation), or from routes based on methyl formate, methyl formate via formamide, or sodium formate.

2.1.2.3.6 Methacrylic acid

Methacrylic acid is manufactured by the acetone cyanohydrin process, or the vapour phase catalytic oxidation of isobutylene or tertiary butanol. The acetone cyanohydrin process comprises five stages, starting with the conversion of the cyanohydrin to an amide in a stirred reaction vessel. The amide is then hydrolysed to methacrylic acid. The methacrylic acid is recovered in a phase separator and purified by distillation. Organic material is recovered for recycling and spent acid can be recovered.

Environmental issues

Air: Vent gases from the by-product acid separator. Vent gases from the reactor and hydrolyser containing carbon monoxide, sulphur dioxide, and organic compounds, including methacrylic acid. Control techniques include destruction of the fuel-rich vent in a gas burner.

Water: Waste streams from vacuum systems containing organics. Waste water from the organics recovery unit. Special control techniques include the recovery of organics from purge water.

2.1.2.3.7 Propionic acid

Propionic acid is either manufactured as a by-product of acetic acid production, or by the oxo process.

2.1.2.3.8 Terephthalic acid

Terephthalic acid is manufactured by first oxidising para-xylene in an acetic acid carrier liquid to produce a crude terephthalic acid, followed by selective catalytic hydrogenation of the crude product to allow the recovery of pure terephthalic acid. Both the oxidation and the purification steps employ crystallisation of the reaction products, followed by solid-liquid separation (using a centrifuge or filter) and solids drying to recover pure terephthalic acid from the process solvents/by-products. Special control techniques include: the recovery of by-product organic acid and catalyst traces as a solid residue; the optimisation of the reactor conditions to minimise by-product production; lagoons to cope with peak BOD loads (from equipment washing or process blockages), and incineration of off-gases.

Environmental issues

Air: Off-gases from the oxidation stage containing carbon monoxide, acetic acid, methyl acetate, para-xylene and methyl bromide. Solvent recovery column vent (containing carbon monoxide, methyl acetate, para-xylene and acetic acid). Atmospheric absorber vent (containing acetic acid and methyl acetate). Waste gases from purification plant scrubber containing terephthalic and acetic acids. Off-gas dryer vents (containing methyl acetate, acetic acid and para-xylene).

Water: Aqueous condensate from solvent recovery and acetic acid dehydration columns containing acetic acid, formaldehyde, methyl acetate, para-xylene and methanol. Waste water from purification of the crude terephthalic acid contains para-toluic acid, terephthalic acid,

benzoic acid and other organic acids, together with manganese and cobalt salts. Aqueous condensate from the residue treatment crystalliser steam eductors. Recovery of by-product. Biological treatment because of the high BOD loads.
Wastes: Filter cake from the residue recovery area.

2.1.2.4 Esters

2.1.2.4.1 Acrylate

Acrylate is produced by the esterification of acrylic acid with different alcohols (e.g. CH_3OH or C_2H_5OH). The highly odorous emissions are minimised by incinerating both waste water and waste gas.

2.1.2.4.2 Dimethyl terephthalate (DMT)

DMT is used to produce polyester resins for fibres and photographic film. DMT is produced by the oxidation of para-xylene and methanol with concurrent esterification. In the first oxidation step, p-xylene is catalytically oxidised with air to p-toluylic acid (PTS) and water. The first esterification step converts PTS and methanol to PTE (para-toluylacetic methylester) and water. PTE is then oxidised to MMT (monomethyl terephthalate) and water. In the second esterification step, DMT and water are formed from MMT and methanol. Raw DMT is purified by distillation. Methanol used in the DMT production can be recycled from the polymerisation step (PET production). The waste water stream may be incinerated but also treated in a waste water treatment plant. Even if the reaction is exothermic, a large amount of energy is required to keep the process at the right temperature (above the melting point of products). DMT can also be produced by the esterification of terephthalic acid and methanol.

Environmental issues

Air: The high concentrations of organic dust in the oxidation reactor off-gas are reduced by cooling (with heat recovery), washing (to remove polar compounds), and activated carbon filtration. Organic residues are incinerated and off-gases are filtered (to remove cobalt and manganese). The vent gases are washed in a scrubber and the residual gas is incinerated.

Water: The waste water stream is incinerated.

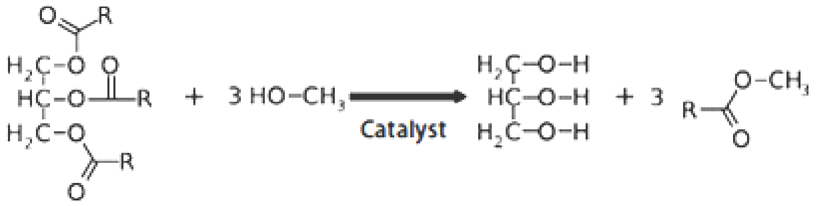
Wastes: Hazardous wastes are incinerated.

Energy: Exothermic process with energy recovery.

2.1.2.4.3 Ethyl acetate

Ethyl acetate is produced by the esterification of acetic acid and methanol (CH_3COOH + C_2H_5OH), or from acetaldehyde using the Tishchenko reaction.

2.1.2.5 Fatty acid methyl esters for use as biodiesel

Biodiesel (FAME)	
Uses	Biodiesel from renewable resources including recyclates from such sources; used neat or blended with mineral fuels for transportation and power generation, as lubricant and as intermediate for production of other organic substances.
Transesterification of fatty acids from vegetable oils or animal fats	
Prevalence	Accounts for approximately 90 % of biodiesel production within the EU.
Summary	Triglycerides are transesterified into monoalkyl esters of long-chain fatty acids by reaction with simple alcohols, mainly methanol. Co-product is glycerol.  **Figure 2.2: Transesterification of triglycerides to FAME** In some plants, the free fatty acids are esterified within the same or in separate reaction steps. The biodiesel and glycerol phases must then be separated and purified. Process steps may include gravity settling, centrifuging, distillation and filtration.
Process options	• Reactant: Although transesterification/esterification can be executed with several alcohols, methanol has some advantages: - It requires the lowest possible methanol/raw material mass ratio. - Separation between water and methanol can be done by simple distillation (internal recycling) compared to ethanol. - Fuel specification for biodiesel is based mainly on methyl esters. • Operating conditions: low-temperature (below the boiling point of the reaction mixture) and low-pressure process (typically atmospheric conditions) and excess alcohol. • Catalyst: homogeneous (alkaline or acid), heterogeneous, enzymes. • Single or multiple feedstocks: vegetable oils, animal fats or waste cooking oils. Some technologies are additionally capable of processing feedstock with higher amounts of free fatty acids by utilising either acid-catalysed pre-esterification of the free fatty acids followed by transesterification or by direct conversion of all fatty material to biodiesel in a single step by high-temperature acid esterification.
Yield	Depends on process options and feedstock: 80–99+ %.
Proprietary processes	Agrartechnik Schlaitdorf, Axens, BDI, CD-Technology, GEA Westfalia, CPM Sket, CMB, DeSmet Ballestra, Energea Lurgi, STH Engineering.
Co-products	Glycerol (approximately 10 % of overall plant production).
By-products	Oilseed processing is not part of the biodiesel process but can also generate wastes or co-products.
Raw materials and catalysts	• 'First Generation': C_{18}-dominated edible oils like rapeseed oil, soybean oil, palm oil, sunflower oil, canola oil, additionally animal fat and spent oils (also C_{18}-dominated). • 'Second Generation': used cooking oil; fuels under R&D (jathropa oil, algae oil, oil from other microorganisms) or esters that are not C_{18}. • Sodium methylate or potassium ethylate (alcohol and catalysts utilised in the mixture). • Alcohol: (primarily methanol but ethanol/butanol possible). • Sodium or potassium hydroxide. Hydrochloric acid and sulphuric acid (to neutralise the alkalis after the reaction stage).
Energy	Electricity for pumps, control systems, etc., specific energy consumption: 50–160 kWh/t biodiesel. Steam and other thermal energy for heating reactants, distillations etc., specific energy consumption: 300–480 kWh/t biodiesel.
Air	VOCs. Some hazardous primarily methanol.
Water	• Waste water: boiler, water softener and cooling tower blowdown.

Biodiesel (FAME)	
	• Washing the biodiesel product to remove impurities. The wash water contains glycerol, methanol, unreacted feed oils, and some biodiesel. Some small biodiesel operators may use resins or organic absorbents to remove impurities rather than distillation of the whole crude FAME. • The methanol is removed from this water by distillation and reused for the process. • Biodiesel wash water and crude glycerine (with or without methanol recovery) have a very high BOD (10 000–15 000 mg/l); however, glycerol and methanol are highly biodegradable and, if loaded to a waste water treatment plant having sufficient capacity, can be biodegraded completely. • Most of the methanol left over from the biodiesel process is in the crude glycerol, but is generally recovered. • The unused catalyst and soaps from the glycerol by-product are neutralised and removed. Salts may also form during this phase and may be recovered as another by-product to be used as fertiliser. • Most of the water used is recycled internally.
Waste	• To remove the impurities, the biodiesel may be filtered to remove any residual catalyst monoglycerides etc. The resulting filter cake is waste. • Spent filter media such as diatomaceous earth, filter aid, resins and socks (bags) saturated with biodiesel can spontaneously combust. • Wastes containing methanol, such as crude glycerol, will have a low flashpoint and are likely to be classified as hazardous waste. • Wastes containing spent catalyst that have not been neutralised are potentially corrosive and are likely to be classified as hazardous waste.
Odour	The process has the potential to emit odour and odour control measures are required.

2.1.2.6 Acetates

2.1.2.6.1 Vinyl acetate

Vinyl acetate can be produced by the oxidation of ethylene (C_2H_4 + ½ O_2 + CH_3COOH) or the catalytic addition of acetylene to acetic acid (C_2H_2 + CH_3COOH). Ethylene, acetic acid and oxygen undergo a vapour phase reaction at 160 °C and 8 barg over a noble metal catalyst of palladium and gold and potassium acetate supported on silica beds. The product is quenched, carbon dioxide is removed using hot potassium carbonate, and unconverted oxygen and ethylene are recycled. Acetaldehyde, ethyl acetate and higher esters are formed as by-products. A purge stream prevents inert build-up. Unconverted acetic acid is separated from the crude product by distillation and recycled. The vinyl acetate is purified in a series of distillation columns. Vinyl acetate can also be produced from acetylene and acetic acid.

Environmental issues

Air: Hydrocarbons from the reactor loop purge. Carbon dioxide from the absorption/desorption system.

Water: Sodium acetate in the neutralised aqueous effluent from water stripping.

Wastes: High boilers, light ends, etc. are used as fuel.

2.1.2.7 Ethers

2.1.2.7.1 Glycol ethers

Mono, di and higher glycol ethers are produced catalytically from an alkene oxide (ethylene or propylene oxide) and an alcohol (methanol or n-butanol). The products are purified through distillation, and residual streams (containing catalysts) are incinerated.

Environmental issues

Air: VOCs, ethylene oxide and propylene oxide (mainly from fugitive sources).

Water: Biological treatment.

Wastes: No significant wastes.

Energy: Exothermic process.

2.1.2.7.2 Methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE)

MTBE is an important additive for petrol and more information can be found in the REF BREF. Minor production occurs from the dehydrogenation of isobutane and the oxidation of isobutane. However, the majority of MTBE is produced by the addition of methanol to isobutene, in the presence of an acid catalyst (CH_3OH + C_4H_8). The crude product is purified by distillation. When production is integrated in a refinery, a mixture containing different butanes, butenes and isobutene is used as feedstock and, after the isobutene has been reacted, the other compounds are returned to the refinery. Methanol is recovered. The by-products of tertiary butyl alcohol, dimethyl ether and di-isobutene can be used as fuel.

ETBE is produced by a similar process to MTBE but using ethanol, rather than methanol. ETBE production is described in the REF BREF.

Environmental issues

Air: End-of-pipe technology: use of a flare. VOC losses predominantly from fugitive sources.

Water: Waste water is treated physically (sand/oil removal by filtration and gravity separation) and biologically.

Wastes: Significant process waste not identified. Used catalyst treated externally. Remaining liquids are recycled or also treated externally.

Energy: Exothermic process.

2.1.2.8 Epoxides

Ethylene oxide is considered in detail in Chapter 7.

The production of propylene oxide is included in this document in outline only.

Propylene oxide (production processes excluding co-production with styrene)	
Uses	Propylene oxide (PO) is a major industrial product with a production of more than 7 million tonnes per year worldwide. Approximately 70 % of it is used to produce polyether polyols, which is a raw material for polyurethane production. The remainder is used to produce propylene glycol, which is a raw material for unsaturated polyesters, and an additive in food products and cosmetics.
Process options	The available production routes are: • **Co-production with styrene.** This is described in Chapter 5 on styrene production. • **The chlorohydrin process**. This has a large environmental footprint because of the high electricity usage to generate chloride feedstock and the production of approximately 40 tonnes of waste water and 2 tonnes of chloride salts per tonne of PO. It was the main process for producing both ethylene oxide and PO but has been in decline since the 1940s, following the development of a more efficient direct epoxidation process using a silver catalyst. The chlorohydrin process is present in only one Member State in the EU and is not considered further in this document. • **Epoxidation of propylene with hydrogen peroxide**. The first reaction stage achieves 90 % hydroperoxide (HP) conversion operating at 30 bar and below 90 °C in the liquid phase using methanol as the solvent. The PO produced is removed from the reaction mixture by distillation. More olefin is added and the second reaction stage achieves an HP conversion above 99 %. The PO produced is again removed from the reaction mixture by distillation. The optimised process, using TS-1 catalyst, can achieve a total PO selectivity exceeding 94 %. The unreacted propylene off-gas stream is recycled to the main reactor after removal of oxygen traces for safety reasons. Hydrogen peroxide is converted completely and the propylene conversion in the process is nearly quantitative. The methanol solvent is recycled and the final water stream is tested for traces of glycols and methoxypropanols prior to being discharged to the waste water treatment unit. The environmental benefits include: reducing waste water by 70–80 % and energy usage by 35 %, compared with existing PO technologies; reducing infrastructure and physical footprint with simpler raw material integration and avoidance of co-products. However, there is extra energy lost in these processes, in the form of hydrogen being converted to water. This route leads to the smallest environmental footprint. However, as there is only one production plant in Europe the information available is limited. It is therefore not considered further in this document. • **Epoxidation of propylene with organic peroxides**. A Japanese chemical company has developed a PO-only production method using cumene hydroperoxide (CMHP). Cumene is oxidised in air to obtain cumene hydroperoxide. Cumylalcohol (CMA) and PO are obtained from CMHP and propylene in the presence of a high-activity titanium epoxidation catalyst. CMA is hydrogenated to obtain cumene, which is recycled in the process. This process is not considered further in this document. • **Epoxidation using molten salts.** A process for the epoxidation of propylene using molten alkali-nitrate salts was developed by a company in the US. In this process, a PO selectivity of 65 % at 15 % propylene conversion is reported when a propylene-air mixture flows through a molten alkali-nitrate salt mixture. Nitrous oxide (N_2O) has been investigated extensively as an alternative oxidising agent for the epoxidation of propylene, especially after the discovery of Fe-ZSM-5 zeolite, in which selective oxidations could be up to 80 %. This technique is not commonly applied, so it is not considered further in this document.

2.1.2.9 Anhydrides

2.1.2.9.1 Acetic anhydride

The main production routes are the acetic acid/ketene route and carbonylation of methyl acetate:

- In the acetic acid/ketene route, acetic acid is catalytically decomposed (cracked) to give ketene and water at 700 °C and reduced pressure. Alternatively, positive pressure may be used. Product vapours from the process comprise ketene, some unreacted acetic acid and by-products. The ketene is added to acetic acid under reduced pressure to give acetic anhydride that is recovered by distillation.
- In the carbonylation route, methanol is first esterified with acetic acid (possibly from a recycled source) or a portion of the product acetic anhydride, to produce methyl acetate. Carbonylation of methyl acetate yields acetic anhydride. This route is associated with the carbonylation of methanol to acetic acid.

2.1.2.9.2 Maleic anhydride

Maleic anhydride is used for the production of unsaturated polyesters, the production of fumaric and maleic acid, as an intermediate for the production of pesticides, fungicides, insecticides and herbicides and as an additive for lubricating oil. In 1991, 36 % of maleic acid production capacity was still based on benzene oxidation and the rest was from the oxidation of C_4 compounds, especially butane and butene. A small amount of maleic anhydride by-product results from the production of phthalic anhydride.

Oxidation of benzene: Most of the reactors use a fixed bed of catalysts for the reaction, but fluidised-bed reactors are also used. All of the different processes for benzene oxidation use similar catalysts based on V_2O_5 (may be modified with MoO_3). Due to the highly exothermic reaction, normally tube bundle reactors with up to 13 000 externally cooled tubes are used. Fused salts are used as circulating heat exchange liquid to remove the reaction heat and to produce steam (approximately 80 % of heat can be used for steam production). The oxidation of the benzene/air mixture takes place at 350–450 °C and 1.5–2.5 bar with residence times over the catalysts of about 0.1 s and an air excess. For separation of maleic anhydride from the reaction gas mixture, the reaction gas is cooled in several heat exchangers. In the last cooler the temperature is below the condensation temperature of the anhydride and 50 % to 60 % of the anhydride is obtained directly from the reaction gas mixture. The remainder is washed out with water in the product recovery absorber in the form of maleic acid. The 40 % maleic acid is converted to maleic anhydride, usually by azeotropic distillation with xylene. Some processes may use a double effect vacuum evaporator at this point.

Environmental issues

Air: The product recovery absorber vent contains CO, CO_2, benzene, formaldehyde maleic acid and formic acid; the benzene is recovered by adsorption (e.g. on activated carbon) and reused in the production process. Fugitive emissions of benzene, maleic acid and maleic anhydride also arise from the storage and the handling of these substances. Emissions of xylene from the vacuum pumps and the xylene-stripping column.

Water: The xylene content of the effluent is extracted in a xylene-stripping column. Waste water is treated in central biological facilities.

Energy: Highly exothermic reaction.

Oxidation of butene: The principle of butene oxidation is very similar to the oxidation of benzene. Again, fixed-bed tube reactors with a catalyst based on V_2O_5 are used. The reaction takes place at 350–450 °C and 2–3 bar. Important by-products of this reaction are CO_2, CO, formaldehyde, and acetic, acrylic, fumaric, crotonic and glyoxylic acids. A process variant uses a V_2O_5-H_3PO_4 catalyst in a fluidised bed and has the advantage of easier heat removal at constant reaction temperatures. In contrast to benzene oxidation in the work-up, no partial condensation of maleic anhydride takes place. The reaction gas is washed with dilute aqueous maleic acid solution. The dilute maleic acid solution is concentrated under vacuum or with the help of water-entraining agents. The exhaust gas contains 10 % to 20 % of the initial hydrocarbons that could be removed by incineration. The emission from the dehydration units has to be taken into account.

Oxidation of butane: N-butane is the most economic raw material for maleic anhydride production. The process conditions are similar to those for benzene oxidation. Again, the catalysts are based on vanadium oxides, but they differ in the promoters such as phosphorus and the oxides of Fe, Cr, Ti, Co, Ni, Mo. Fixed-bed, as well as fluidised-bed, processes (e.g. ALMA process) are used. Exothermic reaction heat is removed from the reactor, producing high-pressure steam. There are emissions from the dehydration units. Reactor exhaust gas (after scrubbing) is combusted as it contains unreacted input material butane and carbon monoxide.

2.1.2.9.3 Phthalic anhydride

Phthalic anhydride is manufactured by the gas (or liquid) phase catalytic oxidation of ortho-xylene (or naphthalene) with air. The reactor gases are cooled and crude product desublimes in condensers before vacuum distillation to the required purity. The off-gases are either water scrubbed or incinerated.

Environmental issues

Air: Off-gas from the switch condenser scrubber contains phthalic anhydride, maleic anhydride, various acids, sulphur dioxide and carbon monoxide. Combustion products from incinerated residues and overheads from the distillation columns. Special control techniques include the wet scrubbing of switch condenser off-gases, with recovery of maleic anhydride by processes such as azeotropic dehydration; catalytic incineration of scrubber tail gas, or condenser off-gas if no scrubber is installed; incineration or fuel use of all hydrocarbon residues.

Water: Acidic scrubber liquor from the switch condenser off-gas scrubber or waste water from maleic anhydride recovery.

Wastes: Solid organic residues from distillation columns and stills.

2.1.3 Sulphurous hydrocarbons

The Industrial Emissions Directive (IED) (Section 4.1(c) of Annex I) gives no examples to explain the term ‘sulphurous hydrocarbons’.

Products such as the main thioalcohols may be considered commodity chemicals. For example, methanethiol is produced on a fairly large scale and used to manufacture the amino acid methionine (for which an EU capacity of 150 kt/yr exists). However, many other products will be produced at less than the nominal 20 kt/yr threshold for LVOC and are confined to specialist producers. Some of the more important products include:

- amino acids containing sulphur: methionine, cysteine;
- mercaptans: methanethiol, ethanethiol, butanethiol;
- dialkyl sulphides: dimethyl sulphide, diethyl sulphide;
- thiuram sulphides: tetramethyl thiuram monosulphide;

- acids: thioacetic acid, thioglycollic acid;
- dithiocarbamates: dimethyl and dibutyldithiocarbamates;
- heterocyclics: thiophene, thiazole;
- others: dimethylsulphoxide;
- linear alkyl benzyl sulphonates and linear alkylphenyl ethoxylates (APEO) (manufacture of detergents).

There are no sulphurous hydrocarbons described in an illustrative chapter in this document so the following chemical products are described here in outline only.

2.1.3.1 Sulphur compounds

2.1.3.1.1 Carbon disulphide

Carbon disulphide is manufactured by the reaction of vaporised sulphur and hydrocarbons (such as methane, ethane, propylene or natural gas). The gas mixture is heated to 580–650 °C and subjected to pressures between 2.5 barg and 5 barg to produce carbon disulphide and hydrogen sulphide. Uncondensed carbon disulphide is recovered from the hydrogen sulphide by absorption in odourless kerosene, followed by steam stripping, and the combined carbon disulphide streams are purified by distillation. The hydrogen sulphide is converted back to sulphur in a Claus plant.

Environmental issues

Air: Carbon disulphide and hydrogen sulphide are steam-stripped from the stabiliser feed drum overflow and sent to the flare system. Gases leaving the absorber column contain hydrogen sulphide, sulphur and carbon disulphide, and pass through a wire-mesh filter to remove entrained droplets before sulphur recovery in a Claus unit. The carbon disulphide surge tank vent is kept live with a methane (natural gas) blanket and this leads to a continuous discharge (possibly contaminated with carbon disulphide) to the flare system. Compressed air is used to strip carbon disulphide from the surge tank catch pot overflow, and the resulting gas stream will require treatment if it contains a significant concentration of carbon disulphide. Odourless kerosene from the production plant may be used to absorb carbon disulphide vapours emitted during the filling of tankers. Jacketed pipework from sulphur condensers discharges to the flare stack. During furnace start-up, a methane feed is established, and sulphur slowly brought online until the desired conversion is achieved.

Water: The aqueous layer from the stabiliser feed drum is degassed with steam and passed to a catch pot to which cold water is added. A purge of the lean oil system is completed to prevent the build-up of sulphur compounds and this is stripped using a polysulphide caustic liquor.

Wastes: The sulphur filters are coated with diatomaceous earth and this is periodically removed (together with some sulphur and inorganic impurities).

2.1.3.1.2 Dithiocarbamates

Dithiocarbamates are produced by the reaction of an aqueous alkaline solution of secondary or tertiary amines with carbon disulphide. Aqueous dithiocarbamates can be added to an aqueous metal salt to produce a metal dithiocarbamate slurry that is then filtered and dried. Zinc, nickel and copper dithiocarbamates are the main products.

2.1.3.1.3 Thiols

Thiols can be manufactured by a number of processes. Ethanethiol is prepared by the vapour phase reaction between ethylene and hydrogen sulphide over an acid catalyst. Methanethiol is similarly prepared from the corresponding alcohol. Other primary thiols are prepared by the UV-light-promoted addition of hydrogen sulphide to primary alkenes. Tertiary alkanethiols are prepared from the corresponding tertiary alkene and hydrogen sulphide, in a continuous flow reaction over a solid catalyst. Thiophenol is prepared by the red phosphorus reaction of benzenesulphonyl chloride, or by the high-temperature reaction of monochlorobenzene and hydrogen sulphide. Process equipment and storage vessels for thiols are constructed of carbon steel, aluminium, stainless steel or other copper-free alloys. Thiols stored in carbon steel are kept dry and blanketed with an inert gas to prevent the formation of iron sulphur complexes. Rubber is not suitable for hoses or gaskets.

Environmental issues

Air: The opening of drums prior to charging into reactors creates vapours that are locally extracted and passed to carbon adsorbers or incinerated. Used drums are gently heated in a drum decontamination plant and the extracted vapours are adsorbed, incinerated or caustic scrubbed. Blending tanks are vented to a carbon adsorber, incinerator or caustic scrubber. Road tankers are equipped with a carbon adsorber to remove residual odours. Spent tanker wash-down methanol is usually incinerated.

Water: The final water flushing of tankers containing unspent hypochlorite is discharged to effluent treatment.

Wastes: Effluent treatment sludges and filter cakes containing dithiocarbamates and other sulphur complexes are sent to landfill.

2.1.3.1.4 Thiophene

There are three commercial processes for the production of thiophene. One route is the vapour phase reaction of furan and hydrogen sulphide over a hetero-polyacid-promoted metal oxide catalyst at 300–400 °C. The second route is the continuous reaction of carbon disulphide and C_4 compounds (1-butene, butadiene, n-butanol and 2-butenal) over an alkali-promoted metal oxide catalyst at 500 °C. The third process involves the continuous reaction of butane and sulphur at 500–600 °C, over a mixed metal oxide catalyst.

2.1.3.2 Generic issues in the production of sulphur compounds

The following techniques are relevant to most processes involving organic chemicals containing sulphur.

Waste gases:

- Waste process gases are likely to contain hydrogen sulphide and, where practicable, undergo sulphur recovery.
- During normal operation, waste streams containing mainly carbon disulphide are adsorbed in odourless kerosene. The resulting stream containing hydrogen sulphide, sulphur and carbon disulphide can be incinerated to give sulphur dioxide as well as carbon oxides and water vapour. Methods to minimise the release of sulphur oxides are considered. Where appropriate, sulphur recovery units are installed upstream of any incineration equipment.
- Contaminated extraction air can be dealt with most easily by incineration. Otherwise, carbon or biological filters may be considered. Amine, caustic scrubbing or other systems may be appropriate for particular releases.

- Odour problems are particularly prominent in the manufacture of thiols and other organic sulphur compounds. Adsorption beds and biofilters may be used to eliminate odours from fugitive releases in enclosed areas.
- Cyclones are often used to remove surplus liquid from gas streams.
- Many sulphur compounds have low odour thresholds and conventional equipment designs (e.g. flanged pipework, centrifugal pumps) may have an unacceptable level of releases. This results in the use of all-welded pipework, canned pumps and scrubbing equipment.

Effluents:

- Liquid effluents will originate from scrubbing systems, process wastes and routine cleaning of equipment. The effluents may contain carbon disulphide, or hydrogen sulphide, mercaptans or other organic sulphur compounds.
- Effluents are likely to require primary and secondary treatment prior to discharge to the environment.
- Steam or air stripping can remove contaminants such as hydrogen sulphide and carbon disulphide and prepare the effluent for biological treatment, but the resulting off-gas will require incineration. Air-stripped H_2S cannot be sent for sulphur recovery in a Claus unit for safety reasons.
- Aqueous wastes contaminated with kerosene (carbon disulphide process) will require oil separation. Where possible, contaminated kerosene is regenerated on site by stripping with a polysulphide caustic liquor.
- Spent scrubber liquors can be treated with hypochlorite to form inert chlorates of sulphur. The use of hypochlorite or other easily handled oxidants (such as hydrogen peroxide or ozone) may be considered for the elimination of odours in effluent.

Wastes:

- Wastes are likely to contain organic sulphur compounds. Operators may need to ensure that the sulphur compounds are removed prior to landfilling or that the wastes are suitably contained to prevent the release of the sulphur component and to limit odours.

2.1.4 Nitrogenous hydrocarbons

The Industrial Emissions Directive (IED) (Section 4.1(d) of Annex I) defines this subgroup as ‘nitrogenous hydrocarbons such as amines, amides, nitrous compounds, nitro compounds or nitrate compounds, nitriles, cyanates, isocyanates’. Nitro compounds that are used in explosives production are included in Section 4.6 of Annex I to the IED and are covered in the OFC BREF, not the LVOC BREF. [205, COM 2006]

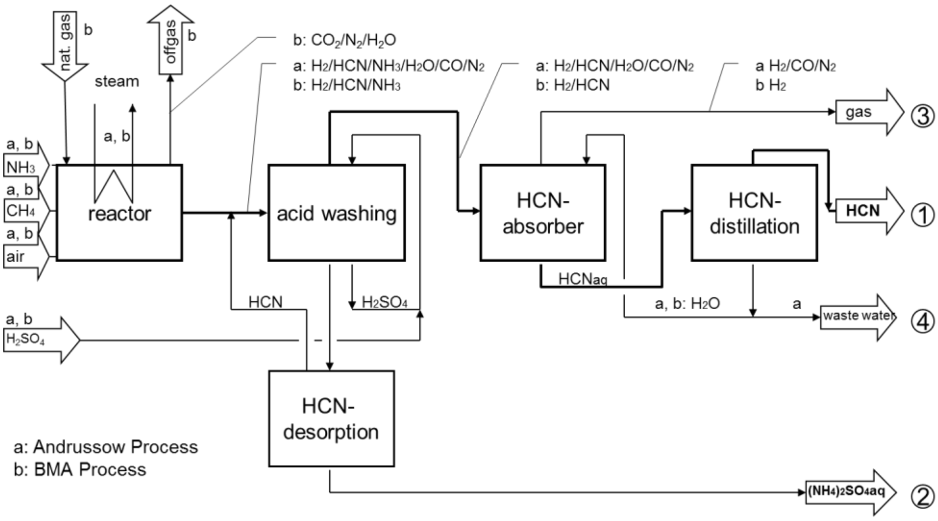
Processes for the production of the following nitrogenous hydrocarbons are described in illustrative chapters of this document:

- **Ethanolamine** (see Chapter 9).
- Toluene diisocyanate (TDI) and methylenediphenyl isocyanate (MDI) (see Chapter 10).

The following chemical products are not described in an illustrative chapter in this document and so are described here in outline only.

2.1.4.1 Hydrogen cyanide

<table>
<tr><th colspan="2">Hydrogen cyanide (HCN) [132, Gail et al. 2011]</th></tr>
<tr><td>Uses</td><td>Production of sodium cyanide and potassium cyanide (see SIC BREF).
Production of methyl methacrylate (to produce the polymer), adiponitrile (to produce nylon-6,6), methionine (an amino acid), EDTA and NTA (chelating agents).</td></tr>
<tr><th colspan="2">Gas phase reaction of methane and ammonia</th></tr>
<tr><td>Prevalence</td><td>Most HCN is produced by the Andrussow process and the Degussa process.</td></tr>
<tr><td>Summary</td><td>Ammonia and methane are reacted to HCN (as described below, under Process options).



Source: [195, CEFIC 2011]

Figure 2.3: Production of hydrogen cyanide</td></tr>
<tr><td>Process options</td><td>• Andrussow ammonoxidation process:
Reaction of methane and ammonia in the presence of oxygen (air) at about 1 200 °C and around atmospheric pressure over a platinum catalyst:
$CH_4 + NH_3 + 1.5\ O_2 \rightarrow HCN + 3\ H_2O$
The reaction itself and side reactions (partial oxidation of methane and ammonia) are exothermic. The reaction is followed by quick cooling (heat exchanger with steam production), acid washing with sulphuric acid or monoammonium phosphate solution to remove excess ammonia, absorption of HCN in water, product recovery by stripping/distillation and condensation.
• Degussa (BMA) process:
Reaction of methane and ammonia at about 1 200 °C and around atmospheric pressure in externally heated tube bundles coated with a platinum catalyst:
$CH_4 + NH_3 \rightarrow HCN + 3\ H_2$
The reaction is endothermic. Energy is provided by a gas-fired process furnace.
Downstream processing similar to the Andrussow process.

Other process routes of less relevance:
• Shawinigan process:
Reaction of hydrocarbons, e.g. propane, with ammonia to HCN and H_2 in a fluidised bed of coke which is heated by electrodes. Thermal reaction without catalyst at about 1 500 °C.
• Production via formamide.
• Ammonoxidation of methanol.

HCN is also obtained as a by-product in the production of acrylonitrile.</td></tr>
<tr><td>Yield</td><td>• Andrussow process: 60–70 % with respect to methane; about 70 % with respect to ammonia.
• Degussa (BMA) process: 90–94 % with respect to methane; about 80–87 % with respect to ammonia.</td></tr>
</table>

Co-products	Hydrogen (Degussa process).
By-products	Ammonia sulphate or ammonia phosphate from ammonia scrubbing.
Raw materials	• Methane and ammonia: high purity required to protect catalyst. • Air (for Andrussow process).
Energy	• Heat recovery from high-temperature process with production of steam. • Degussa (BMA) process: energy (heat) produced by process furnace.
Air	• Andrussow process: Process off-gas containing H_2, CO and N_2 can be used for heating or methanated and recycled as feedstock to the process. • Degussa (BMA) process: The process off-gas contains mainly hydrogen which is used as a fuel or reused (if needed, after purification).
Water	• Waste water from the HCN absorber and product recovery. • Main potential pollutant is HCN which, depending on the concentration/load, may require pretreatment. Emissions to air are prevented by control of the pH. • Other pollutants may be ammonia and organic compounds from side reactions.
Waste	Spent catalyst.
Other	HCN is volatile, extremely poisonous and flammable. BP 25.6 C.

2.1.4.2 Amines

Amines are derived from ammonia by replacing one or more of the hydrogen atoms with alkyl groups. Amines are classified as primary, secondary or tertiary depending on whether one, two or three hydrogen atoms are replaced. **Ethanolamine** is described in Chapter 9.

2.1.4.2.1 Ethylamines and isopropylamines

Ethylamines and isopropylamines are manufactured by the gas phase reaction of anhydrous ammonia and either ethanol or isopropanol at elevated temperature and pressure in the presence of a hydrogenation catalyst (e.g. Raney nickel).

Ethylamines and isopropylamines are usually produced on the same plant on a campaign basis. Primary, secondary and tertiary ethylamines are produced concurrently but tertiary isopropylamine is limited by steric hindrance. Diethylamine is generally the most important product, but the manufacture of the various products is governed by the relative market demands and the ability to recycle surplus product. A basic reactor system design is used worldwide with variations on the associated distillation system.

2.1.4.2.2 Methylamines

The unit process of ammonolysis is important in the production of amines, especially the methylamines of monomethylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA). Methylamines are produced in equilibrium in the catalysed vapour phase alkylation of ammonia with methanol at 260–320 °C and a pressure greater than 20 barg. The exothermic reaction is carried out over a fixed bed of amorphous silica-alumina catalysts. The crude reaction mixture consists of excess ammonia, mono-, di- and trimethylamines, reaction water and uncovered methanol, and is usually purified in a distillation train.

Environmental issues

Air: Process vents that contain methylamines are routed via an absorption system to enable recovery (in a stripper) and recycling. Due to the low odour threshold of MMA, DMA and TMA, leaks are minimised through the good design of storage and handling facilities, seals on pumps, and the minimisation of flanges in pipework. Biotreatment or incineration may be necessary as back-up systems to remove odour.

Water: Waste water is generated in the reaction and arises from scrubber water purges (containing soluble amines and ammonia). Water use in the scrubbing systems is minimised. Biological treatment of waste water.

Wastes: Spent catalyst.

2.1.4.2.3 Quaternary ammonium salts

The alkylation of amines forms quaternary ammonium salts (general formula R_4N^+X- where X is typically a halide ion and R is an aliphatic or aromatic group). Amines react with an alkyl halide to form the next higher amine in the series and the reaction can proceed to the final stage to produce the quaternary salt. Trimethylamine (TMA) is reacted with ethylene dichloride (EDC) to produce the chlorinated quaternary salt as an aqueous solution. The process involves the exothermic batch reaction of the two liquid feeds, with an EDC excess, carried out at 2.5 barg and 100 °C.

2.1.4.2.4 Aniline

One of the most important aromatic amines is aniline. It is produced either by the reduction of nitrobenzene (the Bechamp process) or by the catalytic hydrogenation of nitrobenzene (in the gaseous or liquid phase). The production of nitrobenzene and aniline are often integrated. The production of nitrobenzene is described in Section 2.1.4.4.

Environmental issues

Air: NO_X emissions from nitration processes are often treated by scrubbing with water or a weak nitric acid solution, prior to discharge to atmosphere. This allows recovery of material for reuse in the process. Depending on the effectiveness of upstream treatment, caustic scrubbing, if required, neutralises any remaining NO_X and can be used as a polishing step, but it does not allow recovery of acid. Vent gases (mainly methane and hydrogen) have a high calorific value and can be used as fuel or incinerated.

Water: Alkali water (‘red water’) is particularly toxic and contains nitrophenols and picrates that leach from the organic phase during washing. Typical concentrations range from 1 000 ppm to 10 000 ppm. Various abatement techniques have been employed including wet air oxidation, incineration and charcoal adsorption followed by incineration, or, where a facility exists with large enough flows from other sources to reduce the concentration of nitrophenols fed to the biomass, by biotreatment. The acidic water stream is usually managed by steam stripping and neutralisation, and then treatment in a conventional biotreatment plant prior to discharge.

Wastes: Catalyst residues (e.g. nickel, palladium, copper, silica) may be disposed of by landfill or recycled, including incineration, metal recovery, or export for energy recovery with the metals and/or solids being incorporated into a final product, e.g. cement.

2.1.4.2.5 Cyclohexylamine

Aniline may be subsequently used to produce cyclohexylamine by the liquid phase hydrogenation of aniline in the presence of a catalyst (cobalt, nickel or ruthenium/palladium).

2.1.4.2.6 Ethylenediamine

The production of ethylenediamine (1,2-diaminoethane) first involves the reaction of ethylene dichloride (EDC) and ammonia to form the intermediate diethylenetriamine hydrochloride.

The intermediate is neutralised with sodium hydroxide and converted into amines, salt and water. Ethylenediamine is separated by crystallisation and distillation, whilst the ammonia and sodium hydroxide are recovered. The by-products are diethylenetriamine (DETA), higher polyamines and ammonium salts. Vinyl chloride is also formed due to the partial decomposition of EDC.

An ethylenediamine process in Sweden does not use chlorinated reactants. The plant is run in two continuous stages. In the first stage, monoethanolamine (MEA) is formed from ethylene oxide and ammonia and, in the second, MEA is again reacted with ammonia to form ethylene amines. Ammonia that has not reacted is recirculated in each stage. Intermediate and final products are purified by distillation.

2.1.4.2.7 Melamine

2,4,6-triamino sym-triazine is used to produce melamine resins, glue and decorative surfaces, either from dicyanamide or urea.

- Dicyanamide can be exothermically converted to melamine in a liquid-phase reaction (using, for example, a methanol solvent mixed with ammonia, or liquid ammonia) but this requires the recovery and cleaning of solvents. In the solid phase reaction, the main problem is to remove reaction heat and so minimise by-product formation and prevent melamine decomposition.
- Melamine is produced from urea either under high pressure or using catalysts in a highly endothermic reaction. Much of the urea is decomposed to ammonia and carbon dioxide, and is recovered, most obviously for urea production. The process variants that use high pressure include the Allied Chemicals process, the Montecatini process and the Nissan process. The catalytic low-pressure processes include the Chemie Linz process, the Dutch Staatsmijnen process and the BASF process.

2.1.4.3 Amides

Amides are characterised by an acyl group (-$CONH_2$) attached to an organic, e.g. formamide ($HCONH_2$), carbamide (urea) ($CO(NH_2)_2$).

2.1.4.3.1 Acrylamide

Acrylamide is manufactured by the reaction of acrylonitrile and water in a continuously stirred tank reactor operating at 100 °C and 4 barg and with a copper-based catalyst. Hydrogen is used to activate the catalyst. The product is steam stripped from the resulting aqueous solution. Unreacted acrylonitrile can be recycled within the process to give almost complete chemical conversion.

Environmental issues

Air: Acrylonitrile. Residual atmospheric emissions are treated in a scrubber.

Water: Copper from catalyst after separation by precipitation/flocculation.

Wastes: AMD polymer, copper sludge, waste water treatment sludge.

Energy: Exothermic process. Energy recovery is practised.

2.1.4.3.2 Urea

Urea ($CO(NH_2)_2$) is mainly used in the production of: fertiliser, additives to agricultural fodder, resins and glues (condensation reactions with formaldehyde), melamine, dyes and varnishes. Urea is produced by the exothermic reaction of liquid ammonia and liquid carbon dioxide at high pressure (200–250 bar) and temperature (160–200 °C) to form ammonium carbamate. The use of ammonia and carbon dioxide raw materials can be optimised by recovery and recycling, and 'Total Recycle' processes now exist (either by conventional recycling or by stripping). The ammonium carbamate decomposes endothermically at a lower pressure to urea and water. The urea solution is concentrated to molten urea in an evaporator (short residence times are used to minimise decomposition to ammonia and cyanic acid). Alternatively, the urea is crystallised and subsequently separated from the solution by centrifuge. The process produces waste gas and waste water which need to be treated.

Further information can be found in the LVIC-AAF BREF and in the EFMA's (European Fertiliser Manufacturer's Association) booklet entitled 'Production of Urea and Urea Ammonium Nitrate'. The LVIC BREF contains a chapter on the production of urea and urea ammonium nitrate, including best available techniques.

2.1.4.4 Nitro compounds

The main nitration reactions carried out on a large scale are the nitration of benzene to produce nitrobenzene and the nitration of toluene to dinitrotoluene (which is described in detail in Chapter 10 and is used to manufacture polyurethanes via toluene diisocyanate) and trinitrotoluene (used as an explosive). The common features of nitration reactions are the following:

- large amounts of acid gas are evolved from the process;
- large excesses of acid are used to drive the reaction;
- gas streams rich in nitrogen oxides (NO_X) are formed and are treated to recover nitric acid and/or abate NO_X emissions.

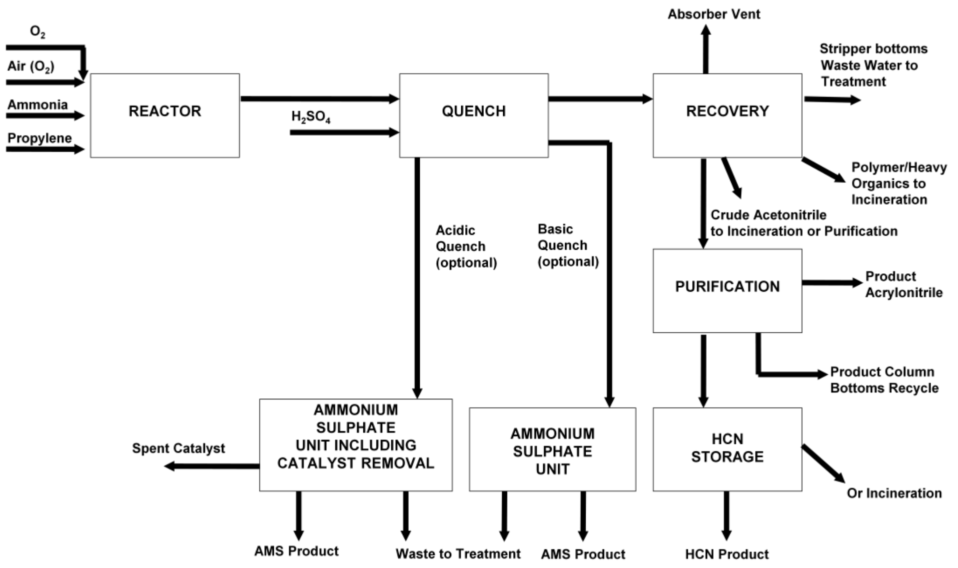
In aromatics nitration, the reactor is charged with an organic material plus a nitrating agent (often a 'mixed acid' of sulphuric acid and nitric acid). A wide range of operating conditions may be used but typically atmospheric pressure and a temperature around 100 °C are used. On completion of the reaction, the mixture is cooled. The organic phase and the acidic aqueous phase are separated. The organic phase is washed to remove acid. The product is separated from the cooled reaction mixture using pressure filtration. Releases from these steps typically include:

- acidic vapours;
- unreacted excess nitrating agent;
- VOC emissions;
- acidic waste waters mainly from washing.

2.1.4.5 Nitriles

2.1.4.5.1 Acrylonitrile

Acrylonitrile is the most commercially important nitrile product and is described below in outline only.

Acrylonitrile	
Uses	• Polymerisation to polyacrylonitrile and co-polymers, such as styrene acrylonitrile, acrylonitrile butadiene styrene (ABS). • Dimerisation of acrylonitrile produces adiponitrile, which is used in the synthesis of certain polyamides. • Precursor in the industrial manufacture of acrylamide and acrylic acid.
Ammoxidation of propylene (BP/SOHIO process)	
Prevalence	Used at all installations in the EU and most of the installations worldwide (LVOC 2003: 95 % of worldwide capacity).
Summary	 **Figure 2.4: Process flow diagram for acrylonitrile production** **Reaction** Acrylonitrile (C_3H_3N) is produced by the exothermic catalytic ammoxidation of propylene. Propylene is reacted with a slight stoichiometric excess of oxygen and ammonia in a fluidised-bed reactor: $C_3H_6 + NH_3 + 1.5\ O_2 \rightarrow C_3H_3N + 3\ H_2O$ -515 kJ/mol C_3H_3N The catalyst is a mixture of heavy metal oxides (mainly molybdenum, bismuth, iron, antimony and/or tellurium) on silica. The conversion to acrylonitrile requires operating temperatures of 400–500 °C, pressures of 150–250 kPa and a residence time of a few seconds. Large quantities of hydrogen cyanide and acetonitrile by-products are formed in the reactor, as are smaller quantities of acrolein, acetic acid, acrylic acid, propionitrile, and methacrylonitrile. The reaction also produces a large volume of reaction water – in total about 1.5 tonnes per tonne of acrylonitrile, of which about 1 tonne comes from the main reaction and about 0.5 tonnes from side reactions. The reactor off-gas contains carbon oxides (from the total oxidation of propylene) and propane (due to impurities in the propylene feed). Some catalyst fines are entrained with the reaction gas; most of it is returned to the reactor after capture by cyclones. Make-up catalyst is regularly added to acrylonitrile reactors to replace lost catalyst and maintain the activity and selectivity of the catalyst. **Quench system** The reactor off-gas must be quenched to the condensation temperature and the excess ammonia removed. Due to the presence of impurities, it is impossible to recycle the ammonia and it needs be removed with sulphuric acid. The two alternatives for the quench system are: • quench and acid treatment in one step (‘acidic quench’);

- quench and acid treatment in two separate steps (‘basic quench’).

In the **‘acidic quench’**, reactor off-gas is contacted with a circulating solution of sulphuric acid and ammonium sulphate in water. Fresh sulphuric acid is added to keep the system acidic and to avoid ammonia breakthrough. Water or, preferably, recycle streams from the plant are added to balance the evaporative losses incurred by quenching hot reactor off-gas. A purge is taken to avoid over-saturation of ammonium sulphate. The quench also removes the catalyst which is then removed from the purge by settling and/or filtration.

Advantages	Disadvantage
• Higher recovery efficiency of acrylonitrile due to low pH • Lower polymer production in the quench section • Opportunity to reuse waste water streams	• Additional energy consumption for crystallisation unit

In the first step of the **‘basic quench’**, reactor off-gas is quenched with water. Water losses are made up by adding fresh water or recycling plant waste water streams. Mainly the catalyst fines are removed from the reactor off-gas. However, the addition of water causes the formation of high-boiling oligomeric compounds and organic ammonium salts which must be purged from the system, together with organic acids.

In the second step, the gas is treated isothermally with sulphuric acid to remove excess ammonia. Fresh acid has to be added to maintain the acidity, but no additional water is required.

Advantages	Disadvantages
• Separate removal of catalyst fines and ammonia • Only a small waste stream containing ammonium sulphate	• Lower recovery of acrylonitrile due to high pH in the quench • Higher polymer formation in the quench

Ammonium sulphate unit

The ammonium sulphate in the quench purge is recovered by crystallisation to produce a saleable by-product. The crystallisation stage generates a waste liquor stream. The effluent streams from the crystallisation process that contain some ammonium sulphate, organics and possibly catalyst fines are incinerated or routed to the final waste water treatment.

Recovery section

Having passed the quench section, organics are typically recovered from the reactor off-gases by absorption (scrubbing with chilled water). The remaining waste gas is sent to treatment.

The scrubber liquor is passed to an extractive distillation column (recovery column) where the acrylonitrile and hydrogen cyanide products are separated in the overheads from the acetonitrile. The acetonitrile is preferentially refined for sale as a product, but it may be stripped and incinerated (with energy recovery). The recovery column bottoms contain high-boiling organic compounds (for incineration) and some ammonium and/or sodium salts of organic acids which are sent as an aqueous stream to waste water treatment).

Purification

The overheads from the recovery column, containing acrylonitrile, hydrogen cyanide and a small amount of water, are distilled to produce acrylonitrile and hydrogen cyanide products. In some plant designs, the ‘heads column’ (to refine the hydrogen cyanide) and the ‘drying column’ (to remove the water) are combined to reduce energy consumption.

The hydrogen cyanide may be incinerated, or transformed into other products on site, or sold (if a market is available). If stored, it has to be maintained at a low temperature and kept acidic, by the addition of acetic acid, phosphoric acid, sulphuric acid and sulphur dioxide, to prevent polymerisation. Due to the reactive and toxic nature of hydrogen cyanide, it is not stored for longer than a few days. If the material cannot be sold or used,

	then it is incinerated. All sites must therefore have the capability to destroy all of the hydrogen cyanide produced. The hydrogen cyanide by-product may be used in other chemical processes to produce: • sodium cyanide (NaCN) by reaction with caustic soda solution; • acetone cyanohydrin (ACH) with acetone; • benzaldehyde cyanohydrin (BCH) with benzaldehyde; • 1,4-diamino butane (DAB) with acrylonitrile and hydrogen; • pyrrolidine (PRD) as a by-product of DAB. The final step is the purification of the acrylonitrile by rectification in the acrylonitrile column. The drying column and the acrylonitrile column may be operated at low pressure to decrease the distillation temperature and to reduce acrylonitrile polymer formation. In order to protect the final product against possible polymerisation reactions during storage, small quantities of inhibitors, such as MEHQ (monomethyl ether of hydroquinone), are added to the acrylonitrile. The residue from the bottom of the acrylonitrile column contains some high-boiling-point nitriles.
Yield	• 85 % (conversion of propylene to saleable products – ACN and organic by-products). • 70-80 % (conversion of propylene to ACN). Main side reactions: oxidation of propylene to CO, CO_2, HCN or acetonitrile
By-products	• Hydrogen cyanide (from $C_3H_6 + 3\ NH_3 + 3\ O_2 \rightarrow 3\ HCN + 6\ H_2O$; -942 kJ/mol C_3H_6), which is either transformed into other products on site; sold as a product (if a use is available); disposed of by incineration; or a combination of all three. • Acetonitrile (from $C_3H_6 + 1.5\ NH_3 + 1.5\ O_2 \rightarrow 1.5\ CH_3CN + 3\ H_2O$; -545 kJ/mol C_3H_6), which is purified and sold as a product, and/or disposed of by incineration. • Ammonium sulphate (from neutralisation of excess ammonia), which may be recovered as a product (e.g. as a fertiliser).
Raw materials	• Propylene. • Ammonia. • Air or pure oxygen. • A number of auxiliary chemicals are used within the process, and these may include: ○ sulphuric acid (for neutralisation of unreacted ammonia); ○ catalyst (heavy metal oxides such as Mo, Bi, Fe, Sb, or Te on silica); ○ hydroquinone (as an in-process acrylonitrile stabiliser); ○ monomethyl ether of hydroquinone (as an acrylonitrile product stabiliser); ○ acetic acid (for in-process pH control, and hydrogen cyanide stabilisation); ○ soda ash (for in-process pH control); ○ sulphur dioxide (hydrogen cyanide stabiliser); ○ phosphoric acid (hydrogen cyanide stabiliser).
Energy	The ammoxidation of propylene to acrylonitrile is an exothermic reaction. The process delivers more energy (mainly steam) than it uses (steam, electricity). The net enthalpy excess of an acrylonitrile core plant is in the range of 340–5 700 MJ/t acrylonitrile. The reaction heat is used to produce steam for uses such as covering the heat needs of the acrylonitrile process; driving the reaction air compressor (via a turbine); and exporting high- or low-pressure steam to the site. Heat is also recovered, e.g. from the waste gas treatment and the stripped scrubbing water, to preheat the recovery column feed and vaporise ammonia and propylene. The latent heat of vaporisation of propylene and ammonia is used to chill the scrubbing water.
Air	The main emission to air is the reactor off-gas after having passed the quenching and absorption sections. It contains non-condensable components (nitrogen, oxygen, carbon monoxide, carbon dioxide, propylene, propane and argon) as well as vaporised water and traces of organic contaminants (acrylonitrile, hydrogen cyanide and other organics), and, in a few cases, the acetonitrile produced at the reaction. The volume of the stream can be reduced by the use of enriched air instead of normal air for the reactions. The off-gas stream can also be reduced by improved catalyst efficiency. The VOC load has been reported to be typically in the range of 15–80 kg/t acrylonitrile (exceptionally up to 130 kg/t if acetonitrile is not recovered), with CO at 50–100 kg/t acrylonitrile, CO_2 at 70–400 kg/t acrylonitrile and NO_X at 0.03–0.04 kg/t acrylonitrile. The waste gas is typically routed to a thermal or catalytic oxidiser with heat recovery. For smaller streams (e.g. from storage), scrubbers are sometimes used. Acrylonitrile concentrations of < 0.5 mg/Nm^3 can be achieved using oxidisers and < 5 mg/Nm^3 using

scrubbing systems.

Water

The main waste water arisings are from the quench section and the process stripper bottoms. Regarding final treatment, the main pollutant parameters are COD/TOC and TN_b.

Quench section

The reaction generates water, which is purged in the form of a stripped effluent. The quench effluent stream(s) contain ammonium sulphate and (generally high-boiling) organic compounds. In most cases, the ammonium sulphate is recovered as a crystal co-product or is treated to produce sulphuric acid. The remaining stream containing high-boiling components can be treated to remove sulphur compounds and is then incinerated or biologically treated.

The stream containing the light components is biologically treated or recycled to the acrylonitrile plant for rework. Table 2.1 gives the effluent data before and after treatment.

Table 2.1: European ranges for quench effluent before and after treatment

		Untreated (raw quench effluent)	**After treatment * (final emission)**
Effluent (combined streams)	**Units**	**Range**	**Range**
Total flow	kg/t acrylonitrile	350–900	-
Ammonium sulphate	Wt-%	15–37	-
TOC	ppm wt	15 000–25 000	-
TOC	kg/t acrylonitrile	5.3–18	0–1 **

* Treatment may be biological or by incineration.

** At the biological treatment, the elimination rate for TOC is expected to be ≥ 90 %.

Source: [181, CEFIC 2000]

Stripper bottoms

The water used to absorb the organic species in the absorbers has the acrylonitrile and hydrogen cyanide removed in the recovery column. The remaining water is treated in the stripper column where the light components are removed and recovered as crude acetonitrile. The stripper bottom is concentrated by evaporation. The condensates are routed to biological treatment. The concentrate which mainly consists of heavy organic compounds is incinerated or recycled. The effluent concentrations before and after treatment are given in Table 2.2

Table 2.2: European ranges for stripper bottom effluent before and after treatment

		Untreated (raw stripper bottoms)	**After treatment * (final emission)**
Effluent (combined streams)	**Units**	**Range**	**Range**
Total flow	kg/t acrylonitrile	500–2 000	-
TOC	ppm wt	4 000–20 000	-
TOC	kg/t acrylonitrile	8–15	0.1–0.4 **

* Treatment may be biological or by incineration.

** For biological treatment; the elimination rate for TOC is expected to be ≥ 90 %.

Source: [181, CEFIC 2000]

Residues

By-product recovery

Pure hydrogen cyanide is recovered from the process, ideally for reuse and/or sale. In any case, facilities are needed to enable the continuous incineration of all recovered hydrogen cyanide.

Acetonitrile can be purified to a commercial-grade product. Otherwise, unpurified acetonitrile is burnt as fuel.

Excess unconverted ammonia is reacted with sulphuric acid and purified, producing an ammonium sulphate solution that can be sold as fertiliser. Crystallisation is the only way to obtain solid reusable ammonium sulphate. Alternatively, the ammonium sulphate can be converted into sulphuric acid in a dedicated unit.

	Liquid residues Heavy residues are recovered from the quench system (catalyst fines and heavy organics) and from the bottom of stripper columns (heavy organic compounds/polymers). The heavy residue streams can be first concentrated and then incinerated (either on or off site), preferably with heat recovery. **Solid wastes** Spent catalyst is separated from the aqueous quench effluent by settling and/or filtration and disposed of or routed to a treatment for metal recovery.
Storage	Owing to the hazardous properties of acrylonitrile and hydrogen cyanide, safety considerations are very important in their storage and handling. Acrylonitrile has the ability to self-polymerise if initiators are present, and is flammable. Stabilising agents may therefore be added to the product, and measures taken to prevent the accidental ingress of impurities that could either strongly react or catalyse a runaway reaction. Acrylonitrile is typically stored in tanks under nitrogen at atmospheric pressure. A minimum amount of oxygen has to be present in the solution to ensure acrylonitrile stability. Tank vents are typically routed to water scrubbers. Pure hydrogen cyanide is not stored in large volumes, but a small volume buffer tank is typically used to aid its continuous reuse or destruction. When hydrogen cyanide is sold, storage capacity is minimised, consistent with shipping requirements.

2.1.4.5.2 Adiponitrile

Adiponitrile is an intermediate in the synthesis of nylon. It can be produced by the hydrocyanation of butadiene or the electro-hydrodimerisation of acrylonitrile. The electro-hydrodimerisation of acrylonitrile is carried out in reactors that contain lead-plated carbon steel electrodes. The crude adiponitrile stream is vacuum-distilled to produce a product stream and high/low-boiling fractions for incineration. A crystalliser is used to reclaim the majority of the phosphate and borate species from the electrolyte. The aqueous phase from the crystalliser is sent for lead removal, in which sodium hydrogen sulphide is added to form a lead sludge for separation by centrifuge.

2.1.4.5.3 Hexamethylenediamine

Adiponitrile may be catalytically hydrogenated to produce hexamethylenediamine (HMD) either by a high-pressure process or a low-pressure process. In the high-pressure process, liquid ammonia is used to suppress the formation of by-products and, with typical hydrogenation temperatures of 80–150 °C, this results in operating pressures in the range 200–340 barg that maintain the ammonia in the liquid phase. In the low-pressure process, alcohols and/or an aqueous alkali are used to suppress the formation of by-products. The hydrogenation catalyst may be a catalyst slurry or a fixed bed of reduced cobalt, iron, ruthenium or Raney nickel.

2.1.4.6 Cyanates / isocyanates

Cyanates and isocyanates contain the radical –NCO. Mono-isocyanates are used commercially but the term usually refers to diisocyanates. Toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) are described in Chapter 10 of this document.

2.1.4.7 Other

2.1.4.7.1 Caprolactam

Caprolactam is one of the main raw materials for the production of polyamide-6 (nylon). Caprolactam is produced via the intermediate cyclohexanone (ketohexamethylene), some of which is used as a solvent in the production of paint. A caprolactam production unit typically consists of four stages:

1) Cyclohexanone (ANON) plant: cyclohexanone is produced catalytically from phenol and hydrogen. By-products are cyclohexanol and residues (tar). Cyclohexanol is converted into cyclohexanone whilst the generation of hydrogen takes place. Tar is incinerated for heat generation purposes. Waste gas from the reactors contains hydrogen and methane. Methane is an impurity of the hydrogen gas. The waste gas is used in the site fuel gas system or flared.
2) Hydroxylamine phosphate oxime (HPO) plant: oxime, the basic intermediate for caprolactam production, is produced via the phosphate route. This utilises two circular countercurrent liquid streams of an inorganic liquid (ammonium nitrate, phosphoric acid and water) and an organic stream (mainly consisting of toluene).
3) Hydroxylamine sulphate oxime (HSO) and caprolactam purification plant: oxime from the HSO route plus the oxime from the phosphate route are converted to caprolactam via the sulphate route.
4) Caprolactam finishing plant: caprolactam is extracted with benzene. A water wash then removes ammonium sulphate and organic impurities. The remaining benzene is evaporated in a stripper. Further purification is achieved by ion exchange, by catalytic hydrogen treatment, by evaporation and by distillation.

Environmental issues

Air: The cyclohexanone plant has emissions of cyclohexanone, cyclohexanol, benzene and cyclohexane from tank vents and vacuum systems. The HPO plant has emissions of cyclohexanone from tank vents and vacuum systems; toluene tank vent emissions; and NO_X and NO_2 from the catalytic NO_X treatment unit. The HSO plant has emissions of cyclohexanone and benzene from tank vents and vacuum systems; SO_2 emissions; and NO_X and NO_2 from the catalytic NO_X treatment unit. Waste gases from the HPO and HSO plants are used as fuel or flared. Waste gases with nitric oxide and ammonia are converted to nitrogen and water over a catalyst. Benzene tanks are connected to a vapour destruction unit. Vents on oleum, phenol and ammonia storage tanks are equipped with water scrubbers. Balancing lines are used to reduce losses from loading and unloading.

Water: After effluent stripping with steam, the main residual contaminants are caprolactam, cyclohexanone and oxime, and effluent can be treated biologically. The main TOC loads are from the cyclohexanone production. For the manufacture of caprolactam from cyclohexanone, the specific water volume is in the range of 0.1–1 m^3/t and the COD load is 1–10 kg/t. Although ammonia can be separated as a saleable product, effluents may still contain considerable ammonia loads which can be reduced by biological nitrification/denitrification.

Wastes: Tar from cyclohexanone production is incinerated. Catalysts are recovered.

Energy: Waste heat recovery is widely applied.

2.1.4.7.2 Pyridine

Pyridine (C_5H_5N) is manufactured worldwide by the catalysed ammonolysis of acetaldehyde and formaldehyde. **Methylpyridine** is a by-product of the 2,2-bipyridyl manufacturing process, which involves the use of pyridine. **Dimethylpyridine** can be produced as a by-product from a wet pyridine recovery plant.

2.1.5 Phosphorus-containing hydrocarbons

The Industrial Emissions Directive (IED) (Section 4.1(e) of Annex I) does not give any examples of ‘phosphorus-containing hydrocarbons’.

These are a specialised group of products and most are of importance in agricultural insecticides. However, the production of these types of products is not covered in the scope of this document. Phosphorus-containing compounds that are used in plant protection products and biocides are included in Section 4.4 of Annex I to the IED and are covered in the OFC BREF [205, COM 2006].

2.1.6 Halogenic hydrocarbons

The Industrial Emissions Directive (IED) (Section 4.1(f) of Annex I) does not give any examples of ‘halogenic hydrocarbons’.

Chlorinated products have the most commercial importance, and there are few large volume brominated products. The most commercially important halogenation reaction is the production of **ethylene dichloride/vinyl chloride monomer (EDC/VCM)** and this is considered in detail as an illustrative process in **Chapter 11**. Other commercially or environmentally important halogenation reactions are:

- the further chlorination of EDC to trichloroethylene and perchloroethylene;
- hydrochlorination of methanol to methyl chloride (and further chlorination to methylene chloride);
- hydrofluorination of chlorocarbons (e.g. chloroform) to hydrochlorofluorocarbons (HFCs).

The following chemical products are not described in an illustrative chapter in this document and so are described here in outline only.

2.1.6.1 Allyl chloride

Allyl chloride is produced by the chlorination of propylene. The substantial quantities of chlorinated by-products (HCl, dichloropropane, 1,3-dichloropropylene) are separated by distillation and incinerated. HCl is recovered from the incinerator, for sale. Waste gases are scrubbed with an alkali liquor and this produces calcium and sodium hypochlorite. Some plants may incinerate waste gas and this avoids waste water generation.

2.1.6.2 Chlorofluorocarbons (CFCs)

CFCs are used as cooling fluids and raw material for production of TFE (tetrafluoroethylene) monomer. CFCs are produced from chloroform and hydrogen fluoride, with the help of a catalyst. Hydrogen chloride is formed as a by-product and is purified for sale as a 30 % HCl solution in water.

Environmental issues

Air: Waste gases are thermally incinerated. A 30 % solution of HCl in water is recovered for sale. Chlorine vapours are sent to chlorine destruction. Pollutants are VOCs, aromatic halogenated hydrocarbons, freons, and trichloromethane – mostly from fugitive sources.

Water: Air strippers remove organic compounds (e.g. chloroform) from waste water and pass vapour to the incinerator. The main pollutants are inorganic chlorine and fluorine compounds.

Wastes: The used catalyst is regenerated externally.

Energy: Endothermic process.

2.1.6.3 Epichlorohydrin

Epichlorohydrin is produced by a two-step aqueous phase reaction. In the first stage of epichlorohydrin (chloropropylene oxide) production, allyl chloride and hypochlorite are reacted to produce dichlorohydrin and HCl. In a combined hydrolysis/rectification unit, the dichlorohydrin is further reacted with dichloro isopropanol to form epichlorohydrin, which is instantly separated from the aqueous solution. The by-products include trichloro propane, tetrachloro propylethers and chloroether. The waste water organic load can be reduced by extension of the product rectification column. Lime and other inorganic solids are separated by filtration. The organic load (TOC) consists mainly of glycerine which is easy to biodegrade. As an alternative to biological treatment, the treatment with hypochlorite is applied to remove COD and AOX (90 % reduction and residual AOX of 3 mg/l). Emissions after treatment are about 3.5 kg COD/t of product, 150 g AOX/t of product and 3 g EOX/t of product. Application of sodium hydroxide instead of calcium hydroxide in the aqueous process steps may reduce the release of heavy metals and the related toxicity of the waste water effluent.

2.1.6.4 Chloro-acetic acid

The chlorination of acetic acid produces (mono)chloro acetic acid. The HCl by-product is cooled, condensed and recycled to the reactor, and any residual acidity is removed in a scrubber. The dichloroacetic acid and hydrogen by-products are converted to monochloro acetic acid, HCl gas and some unwanted aldehydes (removed in alkaline scrubber). Excess hydrogen is vented to atmosphere. Waste water contains high loads of organo-chlorine compounds but is amenable to biological treatment.

2.1.6.5 Ethyl pentachlorothiophene (EPCT)

EPCT is produced by the reaction of phosphorus pentasulphide and ethanol to form diethyldithiophosphoric acid (DETA). DETA is chlorinated to produce EPCT and a sulphur precipitate. See also Sections 3.2.5 and 3.2.6.

Environmental issues

Air: Breathing releases from the ethanol storage tank are released directly to the atmosphere. Off-gases from the reactor are incinerated with contaminated combustion air drawn from the building caustic scrubber discharge and storage tank vents.

Water: Spent scrubber liquor is discharged frequently. Hydrochloric acid (32 %) is generated in the adsorber (water scrubber) from hydrogen chloride fumes and either sold commercially or used to neutralise alkaline liquid waste streams.

Wastes: Cartridges from the DETA filter are collected and sent for off-site disposal. The residues generated in the chlorination are discharged to steel drums and allowed to cool before sealing and landfill disposal.

2.1.7 Organometallic compounds

The Industrial Emissions Directive (IED) (Section 4.1(c) of Annex I) does not give any examples of ‘organometallic compounds’.

The production of organo-lead, organo-lithium, organo-magnesium and organo-tin compounds was described in the 2003 LVOC BREF. At that time lead alkyls were still being produced in significant volumes for use as fuel additives, though production was declining. Since then, production of lead alkyls has reduced further and there is no information to suggest that any organometallic compounds are currently being produced in sufficient quantities to be considered LVOC.

2.2 Unit processes in LVOC production

There are many different types of chemical reaction that are used to produce LVOC. Some reactions (e.g. oxyhalogenation) are specific to one or two products, whilst others (e.g. oxidation, halogenation, and hydrogenation) are used in many processes. For this reason, the majority of emissions from the production of LVOC originate from a few, frequently used, unit processes.

Table 2.3 provides an overview of some key features of the most environmentally important unit processes. This is followed by brief descriptions of the main unit processes and a generic consideration of their potential environmental impacts.

Table 2.3: Unit processes used in organic chemical production

Process	**Feed material**		**Conditions**		**Products**
	Reagents	**Substrates**	**Catalysis**	**Phase**	
Oxidation	Oxygen (Air)	Paraffins, Olefins, BTX-Aromatics	Heterogeneous	Gas	Acids, Anhydrides, Epoxides
			Homogeneous	Gas-Liquid	Alcohols, Aldehydes, Ketones, Acids
			None	Gas-Liquid	Hydroperoxides
Ammoxidation	Oxygen, NH_3	Olefins, Alkyl-aromatics	Heterogeneous	Gas	Nitriles
Chlorination	Chlorine	Olefins, Aromatics,	Homogeneous	Gas-Liquid	Chloro-organics
		Olefins, Paraffins	None	Gas-Liquid	Chloro-organics
Hydrogenation	Hydrogen	CO, Aldehydes, Nitriles, Nitro compounds	Heterogeneous	Gas	Alcohols, Amines
Hydroformylation (Oxo-synthesis)	H_2, CO	Olefins	Homogeneous	Gas-Liquid	Aldehydes, Alcohols
Dehydrogenation		Paraffins, Olefins, Alkyl-aromatics, Alcohols	Heterogeneous	Gas	Olefins, Diolefins, Aromatics, Aldehydes Ketones
Alkylation	Olefins, alcohols, chloro-organics	Aromatics	Heterogeneous	Gas	Alkyl-aromatics
			Homogeneous	Gas-Liquid	Alkyl-aromatics
Source: Griesbaum in [179, CITEPA 1997]					

2.2.1 Oxidation

Pure oxygen and atmospheric oxygen are by far the most important oxidising agents used in LVOC production. Although atmospheric air is available at a much lower cost than pure oxygen, the inert nitrogen component present in air will dilute the reaction products and generate much larger waste gas streams. Hydrogen peroxide is widely used as an oxidising agent and its production is described in Chapter 12.

Heterogeneous catalysts based on noble metals play a dominant role in industrial-scale oxidations and an important example is the silver-catalysed gas phase reaction between ethylene and oxygen to form ethylene oxide (see Chapter 7). Ethylene is still the only olefin that can be directly oxidised to its epoxide with high selectivity. Other important industrial oxidation processes are the production of acetic acid (see Section 2.1.2.3), formaldehyde (see Chapter 6) phenol (see Chapter 8), acrylic acid (see Section 2.1.2.3), acetone and adipic acid (see Section 2.1.2.3).

Oxidation reactions are exothermic and heat can be reused in the process. Fire and explosion risks exist with heterogeneously catalysed direct oxidation processes and reactions involving concentrated hydrogen peroxide or organic peroxides.

Environmental issues of oxidation processes

The oxidation of organic compounds produces a number of by-products (including water) and wastes from partial and complete oxidation. In the organic chemical industry, compounds such as aldehydes, ketones, acids and alcohols are often the final products of the partial oxidation of hydrocarbons. However, careful control of partial oxidation reactions is usually required to prevent the material from oxidising to a greater degree than desired as this produces carbon dioxide and many undesirable gaseous, liquid, or semi-solid toxic by-products [92, Sikdar et al. 1998].

Air: Emissions of volatile organics can arise from losses of unreacted feed, by-products and products such as aldehydes and acids. Some carbon dioxide is normally produced in the oxidation of organic compounds because it is not possible to prevent the full oxidation of some carbon. Aldehydes, especially formaldehyde, require strict handling to minimise occupational exposure and this limits atmospheric emissions. Acid gases usually require removal from waste streams.

Water: To enable biological degradation in a WWTP, it is necessary to neutralise any acidic components and to remove/destroy any chlorinated species that may inhibit biological activity.

Wastes: Oxidation reactions may produce tars and ashes. Waste will also arise from the replacement or regeneration of spent catalysts.

Energy: In general terms, oxidation reactions are exothermic and they provide good opportunities for the recovery and reuse of heat.

2.2.2 Halogenation

Halogenation is the introduction of halogen atoms into an organic molecule by addition or substitution reactions. In organic synthesis, this may involve the addition of molecular halogens (e.g. Cl_2, Br_2, I_2 or F_2) or hydrohalogenation (with HCl, HBr or HF) to carbon-carbon double bonds. Substitution reactions involve replacing hydrogen atoms in olefins, paraffins or aromatics with halogen atoms. Chlorination is the most important industrial halogenation reaction. Chlorinated organic products include chlorinated aromatics, phosgene, chlorinated methanes, chlorinated ethanes; toxicity issues related to these compounds may demand additional control measures. The production of 1,2-dichloroethane (EDC) by direct chlorination is described in Chapter 11.

Halogenation processes are typically carried out in large-scale plants where an organic feedstock is reacted with a halogen or halide in a pressurised continuous reactor at an elevated temperature in the presence of a catalyst. A range of halogenated organic products are formed, which are separated by condensation and distillation in a train of columns depending on the complexity of the mixture. Unwanted by-products are recycled to the process where possible. Unreacted halogens and halides are recovered and returned to the process or another productive use wherever practicable. Where it is necessary to vent a gas stream, the release of VOCs is abated by an appropriate technique (e.g. incineration, adsorption). Emergency vents are directed to a collection system with suitable abatement facilities. Residues such as heavy ends from distillations are incinerated.

Although halogenation is characterised by a very wide variety of reaction options, a number of environmental issues are associated with virtually all options, namely:

- the potential for release of organo-halogens to air, water and land;
- the potential for formation of dioxins;
- sophisticated storage and handling techniques may be required;
- halides and halogen gases are formed and require abatement by water and/or caustic scrubbing.

The choice of halogenating agent is obviously dependent on the reaction chemistry, but a consideration of the strengths and weaknesses of the alternative agents gives an insight into some generic factors in their use (see Table 2.4).

Table 2.4: Comparison of halogenating agents used for LVOC production

Halogenating agent	Advantage(s)	Disadvantage(s)
Chlorine	Many reactions will generate only gaseous by-product streams, which are easily removed from the off-gas. On completion of the reaction, only small amounts of chlorine usually remain.	Sophisticated storage and handling facilities are normally required.
Aluminium chloride	Readily available. Does not require sophisticated storage facilities. Can be used to carry out chemical reactions to produce substances that would be difficult to make using other approaches.	Fumes readily in contact with moist air, generating hydrogen chloride and aluminium hydroxide. Generates a considerable volume of aqueous effluent containing aluminium salts. This effluent is usually highly acidic. Charging of solids to the reaction vessel may require special solids-handling equipment.
Hydrogen halides	Readily available in anhydrous form or aqueous solution. May generate no gaseous by-product.	Sophisticated storage and handling facilities are often required.

Halogenation processes will nearly always involve a reaction vessel (to combine an organic feed with the chosen halogenating agent) and a separation technique (to segregate waste from the product). The main releases from reactors will be VOCs (potentially organo-chlorines), halides/halogens, and an aqueous solution of reaction medium (HCl or inorganic salts). Separation processes may create wash waters (from filtration) and VOCs (from evaporation).

Environmental issues of halogenation processes

Air: The treatment of waste gases first requires a distinction between acidic streams, reaction gases and neutral waste streams. Air streams from tanks, distillation columns and process vents can be collected and treated using techniques such as low-temperature condensation or incineration. The treatment of acid streams is more problematic because any equipment in contact with acid gases and water must be constructed of acid-resistant materials or internally coated. The halogen content of waste gas represents a valuable raw material, and pollution control techniques offer an opportunity for its recovery and reuse (either as hydrogen halides or aqueous solutions). The techniques may include:

- product recovery (by vapour stripping of liquid streams followed by recycling to the process);
- scrubbing the acid gas with an easily halogenated compound (preferably a raw material used in the process);
- absorbing the acid gas in water to give aqueous acid (often followed by caustic scrubbing for environmental protection);
- washing out organic constituents with organic solvents;
- condensing out organic by-products for use as feedstock in another process (e.g. conversion of 1,1,2-trichloroethane to 1,1-dichloroethylene).

Water: There are also significant issues with waste water streams as the biological degradability of halogenated hydrocarbons (especially aromatics) decreases as their halogen content increases. Only chlorinated hydrocarbons with a low degree of chlorination are degradable in biological waste water treatment plants and then only if their concentration does not exceed certain levels. Waste water containing chlorinated compounds usually requires expensive preliminary purification prior to biological treatment, by stripping, extraction and adsorption (on activated carbon or polymeric resins). Waste water contamination can be substantially reduced by avoiding the water quenching of reaction gases to separate hydrogen chloride (for example in the production of chlorinated ethanes and ethylenes).

Wastes: Solid wastes may arise from sources such as reactor residues or spent catalysts. Incineration is a common method for destruction of the organic components, although attention has to be paid to incineration conditions in order to avoid the formation of PCDD/F.

2.2.3 Hydrogenation

Catalytic hydrogenation refers to the addition of hydrogen to an organic molecule in the presence of a catalyst. It can involve the direct addition of hydrogen to the double bond of an unsaturated molecule; amine formation by the replacement of oxygen in nitrogen-containing compounds; and alcohol production by addition to aldehydes and ketones. These reactions are used to readily reduce many functional groups, often under mild conditions and with high selectivity. Hydrogenation is an exothermic reaction and the equilibrium usually lies far towards the hydrogenated product at most operating temperatures. It is used to produce a wide variety of chemicals, such as cyclohexane (see Chapter 4), hydrogen peroxide (see Chapter 12), phenol (see Chapter 8) and toluene diamine (TDA) (see Chapter 10). Hydrogenation catalysts may be heterogeneous or homogeneous. Heterogeneous catalysts are solids and form a distinct phase in the gases or liquids. The general safety precautions that apply to highly flammable gases and vapours apply particularly to hydrogen. Hydrogen is combustible in air and oxygen over wider concentration limits than most other gases. Flammable mixtures in a confined space will explode if ignited by a flame or spark and special precautions are therefore necessary to prevent hydrogen gas leaks from tanks and equipment.

Environmental issues of hydrogenation processes

Air: VOC emissions from hydrogenation reactions are relatively low although hydrogen-rich vent streams are typically abated in combustion units. Possible issues with hydrogen may arise from sulphur impurities in the feed raw materials or from the dust and ash by-products of the hydrogen production itself. Small quantities of sulphur compounds (e.g. SO_2, H_2S) can, for example, be absorbed in dilute caustic solutions or adsorbed on activated charcoal. Larger quantities may need to be converted to liquid or solid sulphur.

Water: Hydrogenation of oxygenated compounds (e.g. in aniline or TDA production) may generate water, which ends up as waste water. Specific waste water volumes from hydrogenation reactions are generally low. Hydrogenated oxo-products often show good biodegradability and low toxicity, whereas aniline compounds may need measures additional to biotreatment.

Wastes: The spent catalysts are sometimes treated as wastes or reclaimed for precious metals. Hydrogenation reactions generate few or no unwanted by-products. The formation of so-called green oil (polymerisation product of acetylenes and dienes) is a possible side effect in hydrogenation reactors.

2.2.4 Esterification

Esterification typically involves the formation of esters from an organic acid and an alcohol. The most common method of esterification is the reaction of a concentrated alcohol and a concentrated carboxylic acid with the elimination of water. Esterification is an equilibrium reaction. Only strong carboxylic acids react sufficiently quickly without a catalyst, so a strong mineral acid (such as sulphuric acid or hydrogen chloride) must usually be added to aid the reaction. Acid anhydrides are used, e.g. in dialkyl phthalate production, and triglycerides are transesterified to produce fatty acid methyl esters (FAME) for use as biodiesel. The main products from esterification reactions are dimethyl terephthalate, ethyl acrylate, methyl acrylate and ethyl acetate, butyl acetate and FAME.

Environmental issues of esterification processes

Air: Solvent vapours can be collected and treated (e.g. by incineration, adsorption).

Water: Effluent generation is generally low as water is the only by-product of esterification reactions. The choice of solid polymer-based ion exchange resins avoids the need for catalyst neutralisation and the associated waste water treatment. Most esters possess low toxicity because they are easily hydrolysed on contact with water or moist air, and so the properties of the acid and alcohol components are more important.

Wastes: Waste streams can be reduced by recovering (and reusing) any organic solvents, water and alcohol components. Any wastes from waste water treatment can be incinerated (if they have high boiling points) or recovered by distillation for reuse (for low-boiling-point components).

2.2.5 Alkylation

Alkylation is the introduction of an alkyl group into an organic compound by substitution or addition. There are six types of alkylation reaction:

- substitution of hydrogen bound to carbon (e.g. ethylbenzene from ethylene and benzene);
- substitution of hydrogen attached to nitrogen;
- substitution of hydrogen in a hydroxyl group of an alcohol or phenol;
- addition to a metal to form a carbon-metal bond;
- addition to a tertiary amine to form a quaternary ammonium compound;
- miscellaneous additions to sulphur or silicon.

The principal use of alkylation is in refineries for the production of alkylates that are used in gasoline which is within the scope of the REF BREF. Other major alkylation products include ethylbenzene (see Chapter 5), isopropylbenzene (cumene), linear alkylbenzene, tetramethyl lead and tetraethyl lead. Alkylation is commonly carried out in a liquid phase at temperatures higher than 200 °C and at above-atmospheric pressures. Catalysts are hydrofluoric, sulphuric or phosphoric acid. Higher temperatures cause the expected lowering of product specificity and increased by-product formation. Some more recent alkylation processes (e.g. for ethylbenzene and cumene) use zeolite catalysts as they can be more efficient and may have lower emissions. Lewis acids, like aluminium trichloride or boron trifluoride, may also be used as catalysts.

Environmental issues of alkylation processes

Air: Emissions to air of VOCs can arise from alkylation reactions; see Chapter 5 on ethylbenzene and the thumbnail description of isopropylbenzene (Section 2.2.1).

Wastes: Older processes that are not based on zeolite catalysts tend to generate more waste. Alkyl halides and sulphates cause waste product disposal problems [92, Sikdar et al. 1998].

2.2.6 Sulphonation

Sulphonation is the process by which a sulphonic acid group (or corresponding salt or sulphonyl halide) is attached to a carbon atom. It is also the treatment of any organic compound with sulphuric acid, regardless of the products formed. It is used to produce many detergents (by sulphonating mixed linear alkyl benzenes with sulphur trioxide gas or oleum) and isopropyl alcohol (by the sulphonation of propylene). The most widely used sulphonating agent for linear alkylbenzenes is sulphur trioxide.

The reactions cover a wide variety of raw materials and products, but most are typified by the need for a large excess of acid (to drive the reaction) and the evolution of acid gas. Sulphonation often generates a sulphur trioxide (SO_3)-rich gas stream, which can be treated in a ceramic-packed scrubber containing 98 % sulphuric acid, followed by a candle filter to eliminate mist.

In the **sulphonation of aromatics**, the reactor is charged with organic material plus the sulphonating agent (often a ‘mixed acid’ of sulphuric acid and nitric acid). A wide range of operating conditions may be used but typically atmospheric pressure and a temperature of 100 °C are used. On completion of the reaction, the mixture is quenched in water or ice (possibly in a separate vessel). Releases from the reactor may include:

- acid vapours (largely sulphuric acid) from the reaction and quenching;
- unreacted sulphonating agent arising from the use of an excess to drive the reaction;
- VOC emissions;
- acidic waste waters.

In the separation stage, the quenched mixture is separated using pressure filtration. Releases from this activity may include the following:

- Filtrate contaminated with unreacted raw material and acid. Some may be recycled, but most is neutralised with lime to form gypsum.
- Dilute acidic wash waters (from washing the product on the filter) that will require neutralisation.

Sulphur trioxide gas is normally used in the **sulphonation/sulphation of aliphatics**. The reaction generates acidic vapours, VOCs and acidic waste waters. The most important products are the linear alkyl sulphonates (LAS) used in detergents. Waste gas streams may also arise from neutralisation of the acid reaction product and any on-site sulphur trioxide production.

Environmental issues of sulphonation processes

Air: Acid vapours (largely sulphuric acid) from the reaction and quenching. Unreacted sulphonating agent arising from the use of an excess to drive the reaction. (SO_2 and SO_3 in air from SO_3/air reactors – plants often integrated with sulphur burners and SO_2 to SO_3 conversion). VOC emissions depend on species being sulphonated, most are big molecules.

Water: Acidic waste waters from the reactor and dilute acidic wash waters (from washing the product on the filter) that will require neutralisation. Filtrate from the separation stage contaminated with unreacted raw material and acid.

Wastes: Oleum is an extremely strong oxidising agent, so, when it is used as a sulphonating agent, it may produce tar by-products that require disposal. The spent oleum will also need to be regenerated or disposed of.

2.2.7 Dehydrogenation

Dehydrogenation is the process by which hydrogen is removed from an organic compound to form a new chemical (e.g. to convert saturated into unsaturated compounds). No C-C bond cleavage takes place during dehydrogenation. It is used to produce aldehydes and ketones by the dehydrogenation of alcohols. Important products include acetone, cyclohexanone, methyl ethyl ketone (MEK) and styrene. One illustrative chapter of this document on ethylbenzene dehydrogenation reviews this unit process in more detail (see Chapter 5). It is also used in the EU for producing propylene from propane.

Environmental issues of dehydrogenation processes

Air: Large hydrogen-rich vent streams are produced and can be used as a hydrogen feed for other processes or as a fuel. Volatile hydrocarbons will be contained in purge and vent gases and will require collection and treatment possibly combined with beneficial energy production). Sulphur dioxide emissions can originate from acid gas incinerators.

Water: Quench water, dilution steam and decoking water discharges are the principal process streams that require treatment. Waste water streams with a high pollution load may require pretreatment prior to acceptance in a biological degradation plant. Other liquid wastes such as ‘green oil’ (from acetylene conversion in the production of ethylene) can be burnt to recover steam or energy.

Wastes: Process wastes include caustic or amines used in sulphide scrubbing, cleaning acids, catalysts, tars, polymers, waste oils, coke and extracting agents (e.g. N-methylpyrolidone) that cannot be recycled.

2.2.8 Cracking

Cracking is a process for splitting large hydrocarbon molecules to produce a mixture of smaller chain hydrocarbons that can be separated and subjected to further processing. The process is applied to appropriate hydrocarbon feedstocks (e.g. naphtha, ethane, LPG) in order to produce the very large volumes of ethylene, propylene, butenes and butadienes that are required as feeds for the chemical industry. Thermal pyrolysis or the cracking of EDC to vinyl chloride and HCl occurs as a homogeneous, first-order, free-radical chain reaction (see illustrative process in Chapter 3 for lower olefins and Chapter 11 for EDC cracking). Cracking may be achieved by catalytic or thermal process routes.

Olefins are usually produced by the steam cracking of petroleum fractions. A hydrocarbon stream is heated, mixed with steam and, depending on the feedstock, further heated to incipient cracking temperatures of 500–680 °C depending on the material being processed. Typical outlet temperatures are 775–875 °C. The conversion of saturated hydrocarbons to unsaturated compounds is highly endothermic, and so high energy inputs are necessary. High-temperature cracking is also used to produce pyrolysis gasoline from paraffin gases, naphthas, gas oils or other hydrocarbons.

Environmental issues of cracking processes

Air: Nitrogen oxides originate from furnace operations in crackers.

Wastes: In principle, all the co-products and by-products from the cracking process can be processed for use as raw materials for subsequent chemical conversions or for use as fuel.

Energy: Cracking is a significant user of energy.

2.2.9 Hydrolysis

Hydrolysis involves the reaction of an organic compound with water to form two or more new substances. Hydration is the process variant in which water reacts with a compound without causing its decomposition. These routes are used in the manufacture of alcohols (e.g. ethanol), glycols (e.g. ethylene glycol, propylene glycol) and propylene oxide. Ethylene glycol production is covered as an illustrative process in Chapter 7).

Environmental issues of hydrolysis processes

Air: The VOC arisings from reactors are generally low.

Water: In most cases, hydrolysis and hydration products are biodegradable.

2.2.10 Carbonylation

Carbonylation (carboxylation) is the combination of an organic compound with carbon monoxide. It is used to make aldehydes and alcohols containing one additional carbon atom. One of the major products is acetic acid. Hydroformylation (the ‘oxo’ process) is a variant where olefins are reacted with carbon monoxide and hydrogen (‘synthesis gas’) in the presence of a cobalt or rhodium catalyst (e.g. in the production of n-butyraldehyde, iso-octyl alcohol and isodecanol). A description of the production of ethylhexanol can be found in Section 3.3.2.1

Environmental issues of carbonylation processes

Air: The process typically generates large volume, hot vent streams containing some VOCs in addition to CO_2, CO, H_2 and other non-VOCs. Residual gas is recovered and used as fuel or flared.

Water: Heavy metals (from catalyst) to be removed from waste water prior to biological treatment.

Wastes: Spent catalysts.

2.2.11 Oxyacetylation

Oxyacetylation involves the addition of oxygen and an acetyl group to an olefin to produce an unsaturated acetate ester. It is used to produce vinyl acetate from ethylene, acetic acid and oxygen.

2.2.12 Nitration

Nitration involves the replacement of a hydrogen atom (in an organic compound) with one or more nitro groups (NO_2). By-products are unavoidable due to the high reaction temperatures and the highly oxidising environment, although many nitration reactions are carried out at low temperatures for safety reasons. The nitration can be of aliphatics (e.g. nitro-paraffins) but the nitration of aromatics is more commercially important (e.g. explosives and propellants, such as nitrobenzene and nitrotoluenes). However, the production of explosive nitro compounds is not covered by the scope of this document. Nitro compounds that are used in explosives production are included in Section 4.6 of Annex I to the IED and are covered in the OFC BREF [205, COM 2006]. Nitration is used to produce dinitrotoluene as an intermediate in toluene diisocyanate (TDI) production (see the illustrative processes in Chapter 10).

Environmental issues of nitration processes

Air: Acid vapours (largely nitric or sulphuric acid) from the reaction and quenching. Unreacted nitrating agent arises from the use of an excess to drive the reaction. VOC emissions. Gas streams rich in nitrogen oxides.

Water and waste: Aromatic nitration may produce large quantities of waste mixed acid that requires neutralisation and disposal, or recovery (e.g. by distillation) and reuse. Products and by-products are often poorly biodegradable and toxic, so measures such as extraction or incineration of aqueous wastes are required [92, Sikdar et al. 1998].

See also information on the production of nitro compounds in Section 2.1.4.4.

2.2.13 Dehydration

Chemical dehydration is a decomposition reaction in which a new compound is formed by the expulsion of water. The major product of this process, urea, is produced by the dehydration of ammonium carbamate.

2.2.14 Ammonolysis

Ammonolysis is the process of forming amines using, as aminating agents, ammonia or primary and secondary amines. Ammonolytic reactions also include hydroammonolysis, in which amines are formed directly from carbonyl compounds using an ammonia-hydrogen mixture and a hydrogenation catalyst.

The major products of ammonolysis are carbamic acid, ethanolamines (see Chapter 9) and alkylamines.

Environmental issues of ammonolysis processes

Air: Based on ethanolamine production, the VOC arisings from reactors are small, although there are waste gases associated with distillation. Off-gas containing ammonia or amines is washed or incinerated, in order to avoid odour problems and to recover ammonia. Hydrogen cyanide and acetonitrile are produced in the production of acrylonitrile and the hydrogen cyanide may be recovered.

Water: Unreacted ammonia can be recovered from alkaline effluents by stripping and is recycled back to the process. Ammonia remaining in the effluent can be neutralised with sulphuric acid (producing ammonium sulphate precipitate for use as fertiliser) or biologically treated. Waste waters containing impurities such as methanol and amines can be disposed of by incineration or biological treatment.

Wastes: Solid wastes from stripper bottoms are incinerated. Spent catalysts.

2.2.15 Condensation

Condensation is a chemical reaction in which two or more molecules combine and expel water, an alcohol, or another low-molecular-weight compound. Each of the reactants contributes a part of the separated compound. There is some overlap with addition reactions since the initial step in condensation is addition. Condensation is used in the production of acetic anhydride, bisphenol A, and ethyl hexanone.

Environmental issues of condensation processes

Air: Reactor emissions are generally low and are typically abated in a combustion unit. Distillation operations may be a source of emissions.

Water: Specific waste water volumes are generally low; effluents mainly consist of reaction water if recycling after phase separation is not possible. The effluent is composed of high-boiling components (condensation products/by-products) that often show moderate or poor biodegradability, and low-boiling components (educts) with better biodegradability.

2.2.16 Fermentation

Fermentation processes that are primarily used to produce food or drink are be covered in the FDM BREF. Where the primary product is used as a chemical or a fuel, it is considered to be within the scope of the BREFs for the chemical industry. Fermentation is a process of chemical change caused by microorganisms, producing carbon dioxide, heat and organic chemicals such as ethanol, butanol/acetone, citric acid, and xanthan gum, (see thumbnail description of bioethanol in Section 2.1.2.1.3. A wide variety of lignocellulose biomass materials can be used as feedstocks, including sugar beet and wheat straw. Fermentation produces a dilute product stream containing 10 % or less of the desired product, which must then be concentrated or separated, e.g. ethanol is usually separated from the fermentation liquor by distillation, which is an energy-intensive process. Process variants include:

- type of organism: prokaryotic (bacteria, cyanobacteria) or eukaryotic (yeast, algae, etc.);
- type of nutrient: carbon source (corn sugar, starch, cellulose), nitrogen source (soybean, corn streep), phosphorus source, etc.;
- reactors can operate in batch or continuous modes and can be fermenters or bioreactors;
- type of products: biomass (yeast), metabolic products (enzymes), modifying compounds, manufacture recombinant products.

Environmental issues of fermentation processes

Air: Fermenter off-gas can have strong odours during waste broth heat inactivation and during the cultivation itself. Process parameters and stack locations can reduce odour. Off-gas can be treated through scrubbing or other means. Thermal oxidisers could abate odour and VOC emissions. Dust can originate from fermentation and from other parts of the plant, such as grain-handling areas.

Water: Fermented broths can have appreciable aquatic toxicity, both to organisms in municipal sewage treatment facilities and to freshwater/saltwater species in local waterways. Often, some aquatic toxicity is observed if the active product component is anti-parasitic or anti-infective, i.e. compounds screened to kill other life forms. Releases of large broth quantities to the environment can raise the biochemical oxygen demand (BOD) in the receiving water.

Waste: Broth waste disposal concerns have been addressed most successfully by using fermenter waste as an animal feed additive or a crop fertiliser when applicable.

2.3 Current emission and consumption levels

The character and scale of emissions from LVOC processes are highly variable. Emissions depend on factors such as: raw material composition, product range, nature of intermediates, use of auxiliary materials, process conditions, extent of in-process emission prevention and type of end-of-pipe treatment.

Process emissions can have very specific causes:

- The raw materials may contain contaminants that pass through the process unchanged and exit with the waste water or waste gas (e.g. the MDI process has emissions that result from the presence of phenol (in aniline feedstock) and methanol (in formaldehyde feedstock)).
- The process may use air as an oxidant and this creates a waste gas (mainly consisting of nitrogen) that requires venting to the atmosphere (e.g. oxychlorination in the EDC process, methanol oxidation in the formaldehyde process, and cumene oxidation in the phenol process).
- The process reactions may yield water which mixes with the product (e.g. formaldehyde production) and requires separation (e.g. as in MDA, TDA or EDC production).
- By-products may be formed by the process reactions or from unwanted side reactions. These by-products have to be separated from the desired products and can often be used as a raw material (e.g. in lower olefin crackers) or as a fuel.
- Losses from the recovery of materials for reuse, e.g. unreacted feedstocks and solvents.

Consumption and emission levels are specific to each process. The data collection of the BREF review focused on the processes for producing the chemicals using a standardised questionnaire:

- lower olefins;
- aromatics;
- ethylbenzene;
- styrene from ethylbenzene dehydrogenation;
- co-production of styrene and propylene oxide;
- formaldehyde;
- ethylene oxide and ethylene glycol;
- phenol;
- ethanolamines;
- TDI and MDI;
- EDC and VCM.
- hydrogen peroxide;

The emissions and waste streams from each process will also vary over time, depending on the operating scenario. The possible sources of emissions and waste streams therefore require consideration during:

- normal operating conditions or routine operation (i.e. expected emissions under stable running);

- other than normal operating conditions or non-routine operation (e.g. start-up, shutdown, maintenance, decommissioning); and
- emergencies (e.g. fires, explosion).

However, LVOC processes also utilise many common activities so it is possible to consider in a generic manner where emissions and waste streams may arise and what those streams might contain. The emissions and waste streams described in this chapter are not exhaustive, nor will all streams occur in every process, but this chapter provides a checklist of possible emission sources and components against which a regulator can assess a process to elucidate specific details.

LVOC plants are usually described as being made up of equipment and process units that are 'ISBL' (inside battery limits) and 'OSBL' (outside battery limits). These definitions are not rigorous and may depend on the nature of the overall facility within which the plant is located. Some sites include production activities that are directly associated with the main process, but at other sites the same activities may be undertaken in separate facilities (i.e. physically remote and/or operated by another company).

LVOC processes typically require the principal utilities (steam, power and cooling water) and provision for waste water/waste gas treatment. In only a limited number of cases are LVOC plants totally independent stand-alone units with dedicated services. More typically, LVOC plants are part of an integrated (petro-)chemical and/or refining complex, where common utilities are provided by central facilities (e.g. dedicated power/steam generation plant, effluent treatment and flaring facilities).

Integration with other units may allow certain low-value streams to be processed into saleable co-products or by-products or utilised as feedstocks or fuels, thus eliminating the requirement for disposal.

For these reasons, information provided on emissions is often not reported on a consistent basis so direct comparisons between installations should be made with caution. However, where practicable, information from the data collection has been drawn together from across the different illustrative processes to make comparisons.

2.3.1 Emissions to air

2.3.1.1 Emission sources

The components of the generic LVOC production process provide a useful structure for identifying the potential sources of emissions to air. Waste gas streams can roughly be divided into ducted (channelled) and non-ducted (diffuse) emissions (see the CWW BREF). In practice, only ducted emissions can be treated. As far as diffuse emissions are concerned, the objective of waste gas management is their prevention and/or minimisation. Capturing diffuse emissions with subsequent treatment can often be carried out in order to reduce emissions.

- Raw material supply and work-up:
  - channelled emissions, from locations such as:
    - vents on distillation columns and stripping columns for the removal of impurities in raw materials;
    - vents on pre-mixing vessels;
    - purge vents or preheating equipment vents, which are used only in start-up or shutdown operations.

- Synthesis:

  - channelled emissions, from locations such as:
    - discrete vents serving reaction equipment (e.g. purges, inert vents from condensers, let-down vessels, process scrubbers);
    - vents associated with catalyst preparation and catalyst regeneration;
    - solvent regeneration equipment;
    - safety relief systems (e.g. pressure relief valves, bursting discs);
  - diffuse emissions, including:
    - emissions during normal operating conditions from flanges, valves, pump seals, etc.;
    - emissions during other than normal operating conditions such as start-up and shutdown and equipment undergoing maintenance.

- Product separation and refinement:
  - channelled emissions, from locations such as:
    - separation equipment (e.g. distillation columns, stripping columns, crystallisers, condensers);
    - drying and solids-handling equipment;
    - solvent regeneration and purification beds;
  - diffuse emissions arising from point, linear, surface or volume sources, including fugitive emissions, such as leaks from pumps and compressor seals, valves, flanges, connectors and pipework, drains or vent plugs or seals.

- **Materials storage and handling: detailed information on emission sources may be** found in the EFS BREF [191, COM 2006] but, in general terms, emissions may arise from:
  - channelled emissions, from locations such as:
    - storage tank vents;
  - diffuse emissions arising from point, linear, surface or volume sources, such as:
    - non-channelled emissions from storage equipment and during handling operations (e.g. the filling of drums, trucks and containers);
    - particulate losses from conveyors;
    - evaporative losses from spills.

- Emission abatement:
  - channelled emissions, from locations such as:
    - waste gas combustion units (e.g. flares, incinerators) which may produce secondary pollutants that did not exist in the original waste stream (e.g. PCDD/F, particulates), as well as combustion gases;
    - waste water strippers (using air or steam to transfer dissolved organics into the gaseous phase);
    - emission control equipment, (filters, incinerators/oxidisers or adsorbers likely to contain unabated pollutants or pollutants generated in the abatement system);
  - diffuse emissions arising from point, linear, surface or volume sources, such as:
    - waste water collection systems (VOCs from drains, balancing tanks);
    - waste water treatment facilities;
    - solid waste storage and treatment.

- Energy, utilities and infrastructure:
  - channelled emissions, from locations such as:

    - storage tanks (losses from displacement during filling and breathing during ambient temperature changes - mainly VOCs with the rate of loss depending on the vapour pressure);
    - containers and vessels during loading and unloading (tankers for road, rail and sea);
    - storage tanks (blanketing gases);
    - energy-providing units, such as process furnaces, steam boilers, combined heat and power units, gas turbines and gas engines;
    - on-site burning of waste gases or the incineration of liquid or solid wastes;
    - general ventilation systems;
  - diffuse emissions arising from point, linear, surface or volume sources, such as:
    - secondary emissions arising from the handling and disposal of waste water (e.g. volatile material from sumps, drains, sewers and waste water handling facilities);
    - fugitive losses (especially VOCs) from equipment (e.g. compressors, pumps) and fittings (e.g. flanges, valves);
    - cooling water contaminated with process streams (e.g. from equipment leakage) passing through cooling towers;
    - workspace and cleaning in preparation for access (e.g. maintenance).

- **Management systems**: Inadequacies of management systems or failure of operational control may be a source of process upsets or incidents, with possible subsequent emissions. Detailed information on Environmental Management Systems can be found in the CWW BREF.

The main category of air pollutants from the production of LVOC is volatile organic compounds (VOCs), but there may also be significant emissions of dust, acid gases and combustion gases, as described below.

2.3.1.2 Pollutant type: Organic compounds (VOCs)

Emissions of organic compounds are of significant environmental concern because some have the potential for photochemical ozone creation potential (POCP), ozone depletion potential (ODP), global warming potential (GWP), toxicity, carcinogenicity and local nuisance from odour. The prevention of VOC emissions is therefore one of the most important issues facing the operation of LVOC processes.

VOCs are defined in Article 3(45) of the IED as organic compounds having a vapour pressure of 0.01 kPa or more at 293.15 K, or having a corresponding volatility under the particular conditions of use. For the measurement of organic pollutants in waste gas streams, e.g. as TVOC (total volatile organic compounds), the volatility of the pollutants is neither assessed nor relevant. **Therefore, in this document, the term VOC means any non-solid organic compound found in waste gas, irrespective of its volatility.**

The term VOCs covers a diverse group of substances and includes all organic compounds released to air in the gas phase, whether hydrocarbons or substituted hydrocarbons. Their properties, and hence need for control, vary greatly and so systems have been developed to categorise VOCs according to their harmfulness.

Some VOCs may also be highly odorous, for example aldehydes, mercaptans, amines and other sulphur-containing compounds. This may necessitate additional stringency in the prevention measures (e.g. high-integrity equipment to reduce fugitive emissions) and the abatement of losses. VOCs typically arise from: process vents; the storage and transfer of liquids and gases; fugitive sources; and intermittent vents. Losses are greatest where the feedstock or process stream is a gas; in these cases, VOC losses can exceed 2 % of total production. Point sources of VOCs have been well controlled over recent years and fugitive losses (from pumps, valves, tanks, etc.) have become the major source of VOC emissions from many plants.

Some unit processes (e.g. hydroformylation, dehydrogenation, condensation) have reactors with large VOC emission factors but their high calorific values usually make them suitable for abatement in combustion devices. Other unit processes (e.g. ammination, ammonolysis, cleavage, esterification, fluorination, hydration, neutralisation, oligomerisation, phosgenation, cracking, sulphurisation) are reported to have no reactor vents (and hence no VOC emissions), but may have significant VOC emissions from subsequent distillation units.

Data for VOC emissions have been reported for the processes used to produce:

- TDI/MDI (see Section 10.3.1);
- ethylene oxide (see Section 7.3.1);
- formaldehyde (see Section 6.3.1);
- phenol (see Section 8.3.1);
- hydrogen peroxide (see Section 12.3.1);
- EDC/VCM (see Section 11.3.1).

2.3.1.3 Pollutant type: Dust

In general, emissions to air of dust are not usually a major issue in the production of LVOC, but they may derive from activities such as:

- the conditioning of solid raw materials;
- the drying of solid products;
- catalyst regeneration;
- waste handling.

2.3.1.4 Pollutant type: Combustion gases

This BREF addresses combustion operations where the main purpose is to generate energy. This document only addresses those combustion operations where the main driver is a chemical conversion or reaction (e.g. lower olefin crackers or EDC cracking). (See Chapters 3 and 11).

Combustion gases may originate from primary sources, such as process furnaces, steam boilers, turbines and engines, but also from pollutant abatement (e.g. oxidisers, incinerators and flares). Whilst process furnaces are usually dedicated to one process, steam- and electricity-producing units often serve a complete chemical complex and their emissions cannot be easily allocated to one process.

Combustion units will generate emissions to air that are related to combustion conditions (e.g. CO_2, H_2O, NO_X, C_XH_Y, CO, dust) and fuel composition (e.g. SO_2, fuel NO_X, metals, dust) [93, InfoMil 2000].

Common gaseous fuels in the LVOC sector are natural gas and low-boiling gaseous fractions arising from the processes (e.g. hydrogen, C_1-C_4 hydrocarbons). In general, gaseous fuels combust cleanly and result in the lowest emissions. Gaseous fuels are normally low in sulphur and have a low content of bound nitrogen, hence the SO_X and fuel NO_X emissions from gas firing are relatively low. Emissions may be increased by air preheating (higher thermal NO_X emissions) and sulphur or nitrogen compounds in the fuel (may cause fuel NO_X and fuel SO_2

emissions). The temperatures in high-temperature process furnaces may also increase thermal NO_X emissions.

Liquid fuels may occasionally be used in the LVOC industry. Common liquid fuels are residual higher boiling fractions from the process and industrial gas oil or fuel oil. Emissions depend mainly on the concentration of impurities in the fuel. In particular, 'heavy' liquid fuels may cause emissions of dust and heavy metals (due to ash content), emissions of NO_X and SO_2 (due to nitrogen and sulphur content) and have an increased potential for soot formation.

Further information on emissions from combustion processes can be found in the LCP BREF.

Data for emissions of NO_X and CO have been reported for the process furnaces used to produce:

- lower olefins (see Section 3.3.1);
- VCM (see Section 11.3.1).

Data for emissions of NO_X, CO and PCDD/F from waste gas treatment (oxidisers, incinerators) have been reported for the processes used to produce:

- TDI/MDI (see Section 10.3.1);
- formaldehyde (see Section 6.3.1);
- EDC/VCM (see Section 11.3.1).

2.3.1.5 Pollutant type: Acid gases

The acid gases generated in the production processes are mainly hydrogen chloride and hydrogen fluoride formed as by-products during halogenation and other reactions. There is also the potential for releases of halogenating agents as well (e.g. hydrogen chloride, chlorine, bromine), as well as releases of SO_2 from some processes.

Data for emissions of chlorine and hydrogen chloride have been reported for the processes used to produce:

- TDI/MDI (see Section 10.3.1);
- EDC/VCM (see Section 11.3.1).

2.3.1.6 Pollutant type: Dioxins

Polychlorinated dibenzodioxins (dioxins), polychlorinated dibenzofurans (furans) and polychlorinated biphenyls (PCBs) may be generated as pollutants from production processes that use chlorine. Dioxins can be destroyed by high-temperature incineration. It is important to prevent de novo synthesis of dioxins during the cooling of exhaust gases from incinerators and from thermal oxidisers treating chlorine-containing waste gases.

Data for emissions of PCDD/F after waste gas treatment (oxidisers, incinerators) have been reported for the processes used to produce:

- TDI/MDI (see Section 10.3.1);
- EDC/VCM (see Section 11.3.1).

2.3.2 Emissions to water

2.3.2.1 Emission sources

Whilst waste water can arise directly from chemical reactions, e.g. as condensate or reaction water, the majority of waste water in the chemical industry originates from subsequent physico-chemical work-up of synthesis mixture.

The component parts of the generic LVOC production process provide a useful structure for identifying the potential sources of emissions to water. For all sources, attention should not only be paid to effluent streams that enter surface waters (rivers, lakes, seas), but also to the prevention of discharges to soil and groundwater – either directly or indirectly (via the contamination of soil). Information on emissions to water may be found in the CWW BREF, but in general the sources include the following:

- Raw material supply and work-up:
    - storage tank overflows;
    - mixing vessels (e.g. overflows, wash-down).

- Synthesis:
    - water is added (as a reactant solvent or carrier);
    - reaction water is formed in the process (e.g. from a condensation reaction);
    - water is present in the raw material;
    - process purges and bleeds (especially of ‘mother liquors’);
    - quenching of organic vapour streams.

- Product separation and refinement:
    - water is used for product washing and picks up traces of products/wastes;
    - spent neutralising agents (acid or alkali);
    - regeneration of ion exchange resins;
    - solvent recovery;
    - vacuum generation.

- **Materials storage and handling:** more detailed information on emission sources may be found in the EFS BREF but, in general terms, emissions may arise from:
    - spills during loading/unloading;
    - leakage from tanks and pipe systems;
    - spillage from drums and other containers.

- **Emission abatement:** detailed information may be found in the CWW BREF but, in general terms, emissions may arise from:
    - acids or alkalis used to neutralise process waters;
    - air abatement systems as a cross-media effect (e.g. spent scrubber liquor);
    - dewatering of sludges;
    - water bleed from seal drums and knock-out drums.

- **Energy/utilities:** detailed information may be found in the LCP BREF but, in general terms, emissions may arise from:

  - hydrocarbon contamination of cooling water systems (e.g. from equipment leakage);
  - bleed from boiler feed water (containing corrosion inhibitors, biocides and scale);
  - bleed from the water demineralisation plant;
  - cooling system blowdown;
  - steam condensate contaminated with raw material, product, or waste (e.g. from equipment leakage).

- Infrastructure:
  - cleaning operations (washing of vessels, pipes and other equipment to facilitate access, e.g. for maintenance purposes);
  - firefighting water;
  - rainwater run-off from roofs and hardstanding;
  - diffuse sources (e.g. leaks, spills from process equipment);
  - oil from mechanical equipment (e.g. compressors);
  - contamination of condensate from steam ejectors used to create a vacuum;
  - water gland seals on vacuum pumps;
  - vapour condensates in pipe runs;
  - general site effluents from offices, canteens, laboratories and workshops;
  - water curtains for hydrocarbon containment and/or acid gas absorption.

- **Management systems:** Emissions may occur from process upsets or incidents that are attributable to the inadequacies of management systems or the failure of operators to adhere to procedures. Detailed information on Environmental Management Systems can be found in the CWW BREF.

2.3.2.2 Effluent loads

Waste water volume: There are only a very few processes (e.g. the chlorohydrin process for propylene oxide and epichlorohydrin) that show specific waste water volumes > 10 m^3/t of product. These processes involve hydrolysis reaction steps where, after the separation of the product, the aqueous solution is discharged without recycling.

TOC/COD: There are not many processes that show COD loads > 10 kg/t at the plant outlet prior to biological treatment. Most of the processes show the following characteristics:

- reaction in aqueous solution (chlorohydrin processes, manufacture of acetaldehyde) or aqueous removal of soluble by-products from gas phase reactions (e.g. acrylonitrile) or organic phases (e.g. nitration of aromatics, esterifications);
- no pretreatment to reduce TOC/COD.

Effluent loads typical of LVOC processes are given in the table below

.

Table 2.5: Emissions and abatement techniques of LVOC production installations in 2011

Product	Waste water volume (m^3/t)				Emissions prior to biological treatment											
					COD (kg/t)				AOX (Adsorbable organically bound halogens)(g/t)					AOX (mg/l)		
	< 0.1	0.1–1	1–10	> 10	< 0.1	0.1–1	1–10	> 10	< 0.1	0.1–1	1–10	10–100	> 100	< 1	1–10	> 10
1. Olefins																
C1=;C2=;C3=		x				x										
1.3-Butadiene		x			x											
Acetylene			x				x									
2. BTX																
Benzene / Toluene	x				x											
Ethylbenzene / Cumene		x			x				x							
Styrene			x		x											
3. EDC/VC, chloroorganics																
EDC (by direct chlorination)	x				x				x					x	x	
EDC (by oxychlorination)		x				x				x					x	
Methyl chloride			x			x	x			x				x		
Epichlorhydrin				x			x						x		x	
Chlorobenzene		x			x						x					x
Ethylchloride			x		x						x				x	
4. Oxygenated																
Formaldehyde	x	x			x	x										
Methanol / Butanol / Butene		x			x											
Ethylene oxide		x					x									
Phenol			x				x									
Propylene oxide (by chlorohydrine process)				x				x					x			x
Acetic acid		x						x								
EG/PG		x				x	x									
Phthalic anhydride			x				x									
Adipic acid			x				x									
Acrylic acid / ester		x					x									
Acetaldehyde			x					x					x			x (> 100 mg/l)

Product	Waste water volume (m^3/t)				Emissions prior to biological treatment											
					COD (kg/t)				AOX (Adsorbable organically bound halogens)(g/t)					AOX (mg/l)		
	< 0.1	0.1–1	1–10	> 10	< 0.1	0.1–1	1–10	> 10	< 0.1	0.1–1	1–10	10–100	> 100	< 1	1–10	> 10
2-Ethylhexanol		x				x										
Isopropanol			x				x									
Ethanol			x			x										
Bisphenol A		x				x										
Glycolether		x			x				x							
Methylmethacrylate		x					x									
Acetic anhydride / Acetic acid		x					x									
Ethylacetate		x				x										
FAME		x					x			x						
Methyl ethyl ketone	x				x											
Chloroacetic acid			x				x						x			x (> 100 mg/l)
1.4-Butandiol / Formaldehyde			x					x								
Maleic anhydride				x			x									
Cyclohexanol / Cyclohexanone		x					x									
5. Organic nitrogen																
Nitrobenzene		x					x			x						
Acrylonitrile			x					x								
Caprolactam		x					x				x					
Aniline			x			x	x			x						
TDA			x					x								
TDI (+ Phosgene)			x				x					x			x	
Ethanolamine		x				x										
MDA			x			x										
MDI (+ Phosgene)		x			x					x						

Source: UBA, Germany 2000, revised by TWG 2015

2.3.2.3 Pollutant types

The nature of pollutants in effluents is very specific to the process, but several generic effluent characteristics are encountered in LVOC processes:

- Mixtures of oil/organics in water: oils are so widely used in processes that they pose a high risk of contaminating effluents. Other organic contaminants may arise from raw materials, by-products and the use of solvents. These may occur as an emulsion or as a distinct phase.
- Biodegradable organics (typically as measured as BOD).
- Recalcitrant organics, i.e. they are not amenable to conventional biological degradation. They may be measured by bioelimination tests regarding parameters such as chemical oxygen demand (COD), total organic carbon (TOC), adsorbable organically bound halogens (AOX) or extractable organically bound halogens (EOX).
- Volatile organic compounds.
- Heavy metals – typically resulting from the use of catalysts.
- Nitrogen compounds (NH_4-N, NO_3-N, NO_2-N) and phosphate – where used in a process.
- Acid/alkaline effluents.
- Suspended solids.
- Heat.

2.3.3 Raw material consumption

Chemical plant operators will obviously seek a highly efficient use of raw materials to achieve a more profitable business. Annex III to the IED mentions the consumption and nature of raw materials as a criterion when selecting the best available technique.

The overall yield of a chemical process is influenced by many design and operational features such as chemical reaction selectivity or fractionation yields. In many chemical processes, the measures taken to reduce the generation of co-products, by-products or residues will also reduce raw material usage.

The purity or source of the raw materials can have an impact on:

- the price and availability of the feedstock;
- the need to pretreat the feedstock;
- equipment reliability (due to corrosion);
- the lifespan of the catalyst (poisons);
- the nature of certain emissions (e.g. light components to vent);
- process reliability;
- the need for post-treatment;
- the nature and type of emissions.

2.3.4 Energy consumption

Chemical plant operators will obviously seek a lower energy usage to have a more profitable business. Annex III to the IED mentions the use of energy as a criterion when selecting the best available technique.

The consumption and recovery of energy is an important issue for the LVOC sectors. Generic techniques are described in the ENE BREF.

This document contains, for every illustrative chapter, a list of measures to reduce the usage of energy. It also covers the opportunities to recover energy from process heat.
There is a clear and direct relationship between the amount of energy used in a process and the emissions to air generated by producing that energy (in a combustion process). These emissions to air are in the form of NO_X, CO_X, SO_X, etc. The techniques and measures to reduce the emissions on the energy supply side (operation of the furnace or boiler) are found in the LCP or REF BREFs. The techniques and measures to reduce the energy demand are given in this document.

2.3.5 Water usage

The CWW BREF deals with the horizontal or general measures that every chemical plant can apply during its design or operation to reduce water usage. These include the optimisation of the cooling water treatment (cycles) and the selection of vacuum systems not based on steam (condensate) usage.

This document contains other measures on the process-specific features than an operator can determine in order to achieve lower water usage. The treatment at source of effluent generated in the process can enable the recycling of water in operations that have an intensive water usage such as washing.

2.3.6 Waste generation

The sources of liquid and solid residues are very specific to a process. In some cases, useful materials can be recovered from residues, with the remaining material being waste. The key pollutants in wastes can be derived from: the raw materials and processes applied; construction materials; corrosion/erosion mechanisms; and materials related to maintenance. In generic terms, wastes may include the following:

- Raw material supply and work-up:
  - off-specification raw materials.

- Synthesis:
  - Spent catalyst and catalyst support. Catalysts may become spent because of chemical deactivation, physical degradation or fouling. The composition of catalysts varies greatly and is often subject to a high level of confidentiality. Many are based on precious metals so it is economically viable to recover them, either on or off site, rather than send them for disposal.
  - Wastes due to shutdown (e.g. organic residues).
  - Contamination arising from corrosion and erosion products inside equipment (e.g. oxides of iron and other metals).
  - Product separation and refinement.
  - Spent purification media. A variety of media are used to remove impurities such as water or unwanted by-products (e.g. activated carbon, molecular sieves, filter media, desiccants, ion exchange resins).
  - Unwanted compounds produced by side-reactions.
  - Process residues (e.g. heavy organic residues from distillation columns (e.g. tars and waxes), sludges in vessels). These may have value as a by-product, as a feedstock for another process or as a fuel.

  - Spent reagents (e.g. organic solvents – these may be valuable to recover/reuse, or to use a fuel to capture the calorific value).
  - Off-specification products.

- **Materials storage and handling:** detailed information on emission sources may be found in the EFS BREF but, in general terms, emissions may arise from:
  - waste packaging (e.g. spent drums, sacks);
  - product polymerisation in tanks.

- Emission abatement:
  - adsorbents used for spill clean-up;
  - solids produced by the abatement of air pollutants (e.g. dust from electrostatic precipitators, bag filters);
  - sludges from waste water treatment;
  - solids produced by the abatement of water pollutants (e.g. catalyst solids settled from waste water, filter cake).

- Energy/utilities:
  - ashes/soot from furnaces, heaters and other combustion equipment.

- Infrastructure:
  - decommissioned plant equipment;
  - construction materials (e.g. metal, concrete, insulation);
  - general site wastes from offices, canteens and laboratories;
  - spent cleaning agents (e.g. phosphoric acid);
  - spent oils (lubrication, hydraulic, etc.);
  - spent heat transfer fluids;

- **Management systems:** Emissions may occur from process upsets or incidents that are attributable to the inadequacies of management systems or the failure of operators to adhere to procedures.

2.4 Techniques to consider in the determination of BAT

This section describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this document. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers environmental management systems, process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations).

The techniques described or listed here are considered to be broadly applicable to all LVOC processes. They are described here to avoid repetition across the illustrative chapters and could be considered BAT in one or more of the processes described in the illustrative chapters. However, because of the large variability of feedstocks, processes and operating conditions in the LVOC sector, the applicability of some techniques may need to be reviewed on a case-by-case basis. Techniques that are specific to a particular process or group of processes are described in the relevant illustrative chapter.

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 2.6 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

However, where a technique has already been fully described in another BREF, this description is not repeated here, the technique is simply listed and a reference made to the relevant BREF (in most cases this is the CWW BREF). For some techniques, additional information may be provided, e.g. on applicability within the LVOC sector. Only those techniques which are specific to LVOC processes are described in full.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied in the sector. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

Table 2.6: Information for each technique

Heading within the sections	Type of information included
Description	A brief description of the technique with a view to being used in the BAT conclusions.
Technical description	A more detailed and yet concise technical description using, as appropriate, chemical or other equations, pictures, diagrams and flow charts.
Achieved environmental benefits	The **main** potential environmental benefits to be gained through implementing the technique (including reduced consumption of energy; reduced emissions to water, air and land; raw material savings; as well as production yield increases, reduced waste, etc.)
Environmental performance and operational data	Actual and **plant-specific** performance data (including emission levels, consumption levels – of raw materials, water, energy – and quantities of wastes generated) from well-performing installations/plants (with respect to the environment taken as a whole) applying the technique accompanied by the relevant contextual information. Any other useful information on the following items: • how to design, operate, maintain, control and decommission the technique; • emission monitoring issues related to the use of the technique; • sensitivity and durability of the technique; • issues regarding accident prevention. Links between inputs (e.g. nature and quantity of raw material and fuel, energy, water) and outputs (products, emissions, residues/wastes) are highlighted, in particular where relevant to enhancing an understanding of different environmental impacts and their interaction, for example where trade-offs have been made between different outputs such that certain environmental performance levels cannot be achieved at the same time. Emission and consumption data are qualified as far as possible with details of relevant operating conditions (e.g. percentage of full capacity, fuel composition, bypassing of the (abatement) technique, inclusion or exclusion of other than normal operating conditions, reference conditions), sampling and analytical methods, and statistical presentation (e.g. short and long-term averages, maxima, ranges and distributions). Information on conditions/circumstances hampering the use of the (abatement) technique at full capacity and/or necessitating full or partial bypassing of the (abatement) technique and measures taken to restore full (abatement) capacity.
Cross-media effects	Relevant negative effects on the environment due to implementing the technique, allowing a comparison between techniques in order to assess the impact on the environment as a whole. This may include issues such as: • consumption and nature of raw materials and water; • energy consumption and contribution to climate change; • stratospheric ozone depletion potential; • photochemical ozone creation potential; • acidification resulting from emissions to air; • presence of dust in ambient air (including microparticles and metals); • eutrophication of land and waters resulting from emissions to air or water; • oxygen depletion potential in water; • persistent/toxic/bioaccumulable components (including metals); • generation of residues/waste; • limitation of the ability to reuse or recycle residues/waste; • generation of noise and/or odour • increased risk of accidents.

	The Reference Document on Economics and Cross-media Effects (ECM) should be taken into account.

Technical considerations relevant to applicability	It is indicated whether the technique can be applied throughout the sector. Otherwise, the main general technical restrictions on the use of the technique within the sector are indicated. These may be:
	• an indication of the type of plants or processes within the sector to which the technique cannot be applied;
	• constraints to implementation in certain generic cases, considering, e.g.:
	  • whether it concerns a new or an existing plant, taking into account factors involved in retrofitting (e.g. space availability) and interactions with techniques already installed,
	  • plant size, capacity or load factor,
	  • quantity, type or quality of product manufactured,
	  • type of fuel or raw material used,
	  • climatic conditions.
	These restrictions are indicated together with the reasons for them.
	These restrictions are not meant to be a list of the possible local conditions that could affect the applicability of the technique for an individual plant.

Economics	Information on the costs (capital/investment, operating and maintenance including details on how these costs have been calculated/estimated) and any possible savings (e.g. reduced raw material or energy consumption, waste charges, reduced payback time compared to other techniques), or revenues or other benefits including details on how these have been calculated/estimated. Cost data are preferably given in euro (EUR). If a conversion is made from another currency, the data in the original currency and the year when the data were collected is indicated. The price/cost of the equipment or service is accompanied by the year it was purchased. Information on the market for the sector in order to put costs of techniques into context. Information relevant to both newly built, retrofitted and existing plants. This should allow assessment, where possible, of the economic viability of the technique for the sector concerned. Information on the cost-effectiveness of the technique (e.g. in EUR per mass of pollutant abated) and related assumptions for their calculation can be reported. The Reference Document on Economics and Cross-media Effects (ECM) and the Reference Document on the General Principles of Monitoring (MON) are taken into account with regard to economic aspects and monitoring costs, respectively.
Driving force for implementation	Where applicable, specific local conditions, requirements (e.g. legislation, safety measures) or non-environmental triggers (e.g. increased yield, improved product quality, economic incentives – e.g. subsidies, tax breaks) which have driven or stimulated the implementation of the technique to date. This subsection should be very short using bullet point lists.
Example plants	Reference to a plant(s) where the technique has been implemented and from which information has been collected and used in writing the section. An indication of the degree to which the technique is in use in the EU or worldwide.
Reference literature	Literature or other reference material (e.g. books, reports, studies) that was used in writing the section and that contains more detailed information on the technique. When the reference material consists of a large number of pages, reference will be made to the relevant page(s) or section(s).

2.4.1 Management techniques

The techniques listed below are described in full in the CWW BREF and are considered generally applicable across the LVOC sector.

- Environmental Management Systems (EMS).

- Strategic management tools:
    - risk assessment;
    - benchmarking;
    - life cycle assessment (LCA).

- Transparent information on:
    - the site and its environmental circumstances;
    - the production processes;
    - pollutant characteristics of the individual production processes;
    - the characteristics of the emitted streams;
    - local factors.

- Inventory management tools:
    - site inventory;
    - stream inventory or register:
        - reduction of water usage and waste water discharge;
        - waste gas emission quantification;
    - mass balances.

- Operational management tools:
    - Management of changes involving process and/or plant modifications.
    - Selection of appropriate performance indicators, including the setting and regular review of benchmarks and targets. (The ability to benchmark may be restricted where there are only a small number of comparable plants in the sector due to the variability in feedstocks, processes, operating conditions and commercial confidentiality issues, if the plants are owned by different operators).
    - Monitoring, both emissions monitoring and monitoring of performance indicators (further details are provided on emissions monitoring in subsequent sections of this chapter).
    - Implementation of the selected emission control options .
    - Quality control methods (NB. quality control methods in the CWW BREF are limited to waste water treatment).

- Reliability tools:
    - corrosion avoidance best practices;
    - reliability programme to maximise uptime;
    - standby/back-up treatment systems (based on risk assessment).

- Safety and emergency tools:
    - management of firefighting water and major spillages;
    - pollution incident response planning.

2.4.2 Techniques to minimise emissions to air from process heaters/furnaces

In LVOC installations, there are two principal types of combustion operations:

- combustion to generate energy as a utility;
- combustion to provide heat to a specific chemical process (such as EDC pyrolysis or lower olefin cracking).

Emissions from combustion plants where the principal objective is the production of energy as a utility, e.g. as steam, heat, electricity or combined heat and power, are outside the scope of this document. Full descriptions of all the emission control techniques that can be applied to such plants can be found in the LCP BREF.

This document covers the second type of operations. The techniques that are applied in the generation/supply of heat to a specific chemical process can be found in this section. The techniques or measures to minimise the energy demand can be found in the illustrative chapters.

Process off-gases, liquid residues or solid residues with a high calorific value may be burnt as fuels in a combustion unit and the heat recovered as steam or for electricity generation, or burnt as fuels in a process heater/furnace to provide heat to a process.

2.4.2.1 Techniques to reduce NO_X emissions

The techniques are essentially the same as those applied in large combustion plants; however, there may be differences in the applicability of techniques because of the specific requirements of the chemical process. Unless otherwise stated, all the technique descriptions (10-heading format) can be found in the LCP BREF and so are not repeated here.

Primary techniques for NO_X

- **Choice of fuel:** Increasing the use of gas (i.e. natural gas and/or fuel gas) instead of liquid fuels will reduce the formation of NO_X. However, the applicability may be limited by several factors: if the fuel gas has a high hydrogen content this could result in higher combustion temperatures and hence increased NO_X formation; the design of the burners in the case of existing plants; or the overall hydrocarbon balance of the site (liquid or solid residues, produced on site, that have a high calorific value will be burnt on site to provide energy where it is not economical to recover substances from the residues).

- **Low-NO_X and ultra-low-NO_X burners:** 'Low-NO_X' burners have the potential to reduce NO_X formation because of their ability to reduce both peak flame temperature and peak oxygen concentration through the use of the staged addition of either air or fuel. The effect can be enhanced by the recycling or entrainment of combustion gases as in the case of 'ultra-low-NO_X' burners. For existing process furnaces/heaters, the applicability may be restricted by their design.

- **Flue-gas recirculation:** Recirculation of part of the flue-gas within the combustion chamber to replace part of the fresh combustion air, with the effect of reducing the oxygen content and therefore reducing the temperature of the flame. This will reduce the potential for NO_X formation. Flue-gas recirculation can be an inherent feature of ultra-low-NO_X burners (as discussed above), sometimes referred to as internal flue-gas recirculation, or it can be implemented as a distinct strategy that is not directly linked to ultra-low-NO_X burners (external flue-gas recirculation). For existing process furnaces/heaters, the applicability may be restricted by their design (e.g. not applicable to existing EDC crackers).

- **Staged combustion:** Staged combustion achieves lower NO_X emissions by staging the injection of either air or fuel in the near-burner region. The division of fuel or air reduces the oxygen concentration in the primary burner combustion zone, thereby lowering the peak flame temperature and reducing thermal NO_X formation. The applicability may be restricted by space constraints when upgrading small process furnaces, limiting the retrofit of fuel/air staging without reducing capacity. For existing EDC crackers, the applicability may be restricted by the design of the process furnace.

- **Use of inert diluents:** 'Inert' diluents, e.g. steam, water, nitrogen, are used (either by being premixed with the fuel prior to its combustion or directly injected into the combustion chamber) to reduce the temperature of the flame. Steam injection may increase CO emissions. The technique is generally applicable.

Secondary techniques for NO_X

- **Selective non-catalytic reduction** (SNCR). SNCR is a non-catalytic process for removing nitrogen oxides from combustion flue-gases by gas phase reaction with ammonia or urea at high temperatures (850–1 100 °C). Reductions of 25 % to 75 % can be achieved, reducing NO_X emissions to less than 200 mg/m^3. Wet scrubbers can be used downstream of SNCR to remove ammonia slip and so enable the deliberate overdosing of ammonia into the SNCR system. The ammonia recovered in the scrubber can be recycled to the SNCR unit. Applicability to existing process heaters/furnaces may be restricted by the temperature window (900–1 050 °C) and the residence time needed for the reaction.

- **Selective catalytic reduction** (SCR), also known as catalytic $DeNO_X$. The ammonia/urea vapour is mixed with the flue-gas through an injection grid before being passed through a catalyst to complete the reaction. Various catalyst formulations are available for different temperature ranges: zeolites for 300–500 °C, traditional base metals employed at 200–400 °C, and metals and activated carbon for the lowest temperature applications at 150–300 °C. The catalyst's minimum operating temperature depends on the concentration of SO_3 (see the CWW BREF). With SCR, removal efficiencies of 80 % to 95 % can generally be achieved for inlet concentrations over 200 mg/Nm^3. Residual NO_X stack levels of 10–20 mg/Nm^3 can be achieved by using SCR in gas-fired boilers and furnaces and NO_X emissions of < 100 mg/Nm^3 can be achieved when firing heavy residues. Applicability to existing process furnaces/heaters may be restricted by space availability.

It is important to take account of emissions to air of ammonia from the application of both SCR and SNCR. The dosing of ammonia or urea should be optimised for achieving effective NO_X reduction without excessive ammonia slip; typical emissions of ammonia from these units are in the range of 5 mg/Nm^3 to 15 mg/Nm^3.

Data for emissions of NO_X in connection with abatement techniques have been reported for the process furnaces used to produce:

- lower olefins (see Section 3.4.1);
- VCM (see Section 11.4.1).

2.4.2.2 Techniques to reduce CO emissions

Primary techniques for CO: Optimised combustion

Technical description
Optimised combustion (in order to reduce emissions to air of CO and unburnt substances) is achieved by good design and operation of the equipment which includes optimisation of the temperature and residence time in the combustion zone, efficient mixing of the fuel and combustion air, and combustion control. Combustion control is based on the continuous monitoring and automated control of appropriate combustion parameters (e.g. O_2, CO, fuel to air ratio, and unburnt substances). See the LCP BREF.

Achieved environmental benefits
Reduced emissions to air of CO and VOCs.

Cross-media effects
Increased oxygen levels may have the effect of increasing NO_X emissions.

Secondary techniques for CO
There are no secondary techniques used to reduce CO emissions from process heaters and furnaces.

Data for emissions of CO in connection with abatement techniques have been reported for the process furnaces used to produce:

- lower olefins (see Section 3.4.1);
- VCM (see Section 11.4.1).

2.4.2.3 Techniques to reduce SO_X emissions

Primary techniques for SO_X: Choice of fuel

This technique consists of the use of fuel (including support/auxiliary fuel) with a low content of potential pollution-generating compounds (i.e. lower sulphur content in the fuel). Gaseous fuels generally have a lower sulphur content than liquid fuels. For existing plants, the applicability may be restricted by the design of the burners.

The applicability may be limited by the need to take into account the overall hydrocarbon balance of the plant: Some LVOC processes produce liquid residues or by-products which are used as internally generated, non-commercial fuels because it would not be economic to recover any of the compounds they contain, e.g. lower and heavy ends from the styrene monomer / propylene oxide process and ethylene cracker residue. These streams usually have a sulphur content < 1 000 ppm so burning them as fuels creates SO_X emissions. However, if these streams were not burnt as fuels they would have to be incinerated on site or off site, which would create emissions, and the plant would have to burn more conventional fuel, which would increase costs, emissions and raw material usage and decrease energy efficiency.

Secondary techniques for SO_X: Wet scrubbing with caustic
SO_X is removed by wet gas scrubbing using an alkaline absorbent, such as sodium hydroxide (caustic soda). The SO_X will principally be removed as sulphite/sulphate, and the absorbent is not regenerated. For existing plants, the applicability may be restricted by space availability.

2.4.2.4 Techniques to reduce dust emissions

Primary techniques for dust

- Choice of fuel: Switching from liquid fuels to gaseous fuels. Typically, dust emissions from the combustion of gaseous fuels are very low, and no secondary treatment is required. For existing plants, the applicability may be restricted by the design of the burners. The applicability may be limited by the need to take into account the overall hydrocarbon balance of the plant as described above in Section 2.4.2.3.
- Atomisation of liquid fuels: Use of high pressure to reduce the droplet size of liquid fuel. Current optimal burner design generally includes steam atomisation.

Secondary techniques for dust

- Fabric, ceramic or metal filters. Fabric filters: Porous woven or felted fabric through which gases flow to remove particles by use of a sieve or other mechanisms. Fabric filters can be in the form of sheets, cartridges or bags with a number of the individual fabric filter units housed together in a group. Ceramic filters: Use of ceramic material. In circumstances where acidic compounds such as HCl, NO_X and SO_X and dioxins are to be removed, the filtering material is fitted with catalysts and the injection of reagents may be necessary. Metal filters: In metal filters, surface filtration is carried out by sintered porous metal filter elements.
- Wet dust scrubbing. Removal of dust by scrubbing where the solvent used is water or an aqueous solution, Wet dust scrubbing entails separating the dust by intensively mixing the incoming gas with water, mostly combined with the removal of the coarse particles through the use of centrifugal force. In order to achieve this, the gas is released inside tangentially. The removed solid dust is collected at the bottom of the dust scrubber.Wet scrubbing will also remove gaseous pollutants by absorption. For example, wet scrubbing with caustic will remove both dust and acid gases, such as HCl.

More information on all the above techniques can be found in the LCP BREF.

2.4.2.5 Monitoring of combustion-related emissions to air

According to the LCP BAT conclusions, BAT is the continuous monitoring of emissions to air from combustion plants when the thermal capacity is 50 MW or more. This conclusion is generally applicable to large combustion plants on LVOC sites.

Where the main purpose of a combustion plant is to carry out a chemical conversion, e.g. lower olefin furnace for thermal cracking or EDC cracking/pyrolysis, then the operation of these plants is within the scope of the LVOC BREF and described in Chapters 3 and 11. The monitoring of emissions to air from these plants should not be less rigorous than that for combustion plants covered by the LCP BREF.

Where continuous monitoring of pollutants is applied, it will also be necessary to continuously monitor those parameters needed for the standardisation of emission measurements to reference conditions, e.g. temperature and O_2 content.

2.4.3 Techniques to reduce emissions to air other than from process heaters/furnaces

Emissions to air from LVOC production sites can include some or all of the following substances:

- hydrogen;
- volatile organic compounds (VOCs);
- inorganic compounds, e.g. hydrogen halides, hydrogen sulphide, sulphur dioxide, nitrogen oxides, ammonia and carbon monoxide;
- dust;
- odour (see Section 2.4.9).

This section elaborates further on some of the techniques which are applied widely across the LVOC sector to prevent, minimise, recover or abate these emissions. These techniques are sometimes applied to individual streams, sometimes to combined streams. Where waste gas streams contain several types of pollutants, a number of techniques may need to be applied sequentially. Therefore, waste gas treatment at LVOC sites is likely to be multi-component and may require the use of an integrated waste gas management and treatment strategy.

Full details on most of these techniques are available in the CWW BREF.

2.4.3.1 Techniques to reduce entrainment

From the CWW BREF, it is already BAT to use techniques to reduce solids and/or liquids entrainment, such as settling chambers and mist filters.

2.4.3.2 Waste gas collection systems

According to the CWW BAT conclusions, it is BAT to establish and maintain an inventory of waste gas streams as part of the site's environmental management system. Based on the application of the CWW BAT conclusions, decisions can be made on the selection of waste gas collection and treatment systems. This section seeks to elaborate further, where appropriate, on their application within the LVOC sector and specific examples may also be found in the illustrative chapters of this document.

2.4.3.2.1 Channelled waste gas streams

Description
Channelling of waste gas streams.

Technical description
Emissions from a number of different process emission points are collected into a common pipework system. Once collected, emissions can be treated using recovery or abatement techniques. The waste gas collection system can be a site-wide system or restricted to emission points from a specific process, or a combination of these. A more detailed description of waste gas collection systems is given in the CWW BREF.

Achieved environmental benefits

- The treatment of minor sources of waste gases that might otherwise be emitted unabated.
- The application of a more effective recovery or abatement technique that would be unavailable if applied to each individual stream.

- Possible material or energy recovery.

Environmental performance and operational data

Accurate information on the effectiveness of this technique is difficult to obtain because it depends on site-specific factors such as the layout of the plant or the diffuse nature of the sources of these emissions. The level of reduction achieved depends on the end-of-pipe technique that is subsequently applied.

Cross-media effects

None.

Technical considerations relevant to applicability

This technique requires a site infrastructure including pipework systems, fans and a shared abatement system. These systems are most easily incorporated at the design stage and are therefore generally applicable to new plants. The applicability may be limited by concerns regarding operability (access to equipment) or health (where operator access is required inside the enclosure which contains elevated levels of harmful substances), or for safety reasons, for example if the collection of emissions from different sources could result in concentrations above the lower explosive limit in the vent system or if the common vent system provides a route for fire and/or explosions to spread from one process unit to another. For existing sites, the applicability may be limited by various constraints but efforts should be made to incorporate these techniques over time as part of the process of continuous improvement. This technique is generally applicable for processes involving acidic and toxic compounds like EDC/VCM, TDI, MDI, etc.

Economics

The cost of techniques will be site-specific. Costs will be lower for new plants.

Driving force for implementation

To comply with the environmental legislation.

Example plants

Channelling is used to collect waste gas streams throughout the whole LVOC sector, e.g.:

- for thermal abatement (see Section 2.4.3.5.5 and 2.4.3.5.6);
- for other abatement techniques such as adsorption (see Section 2.4.3.5.3) or scrubbing/absorption (see Section 2.4.3.6.1).

Reference literature

For further information on this technique, please refer to the CWW BREF.

2.4.3.2.2 Dedicated gas collection system for diffuse emissions

Description

Dedicated gas collection system for diffuse emissions.

Technical description

Diffuse emissions are reduced by capturing and channelling them for treatment close to their source, e.g. through the design and operation of systems to collect waste gas emissions from certain process operations, such as road tanker loading/unloading and sampling, into a closed loop system or into a separate header. This technique can be operated in combination with the use of channelled emission streams (see Section 2.3.1.1).

Achieved environmental benefits

A reduction in diffuse emissions.

Environmental performance and operational data

These localised dedicated systems may also enable feedstock (or energy) recovery close to the source.

Cross-media effects

A reduction in diffuse emissions can also result in improved process safety and reduced operator exposure to harmful substances.

Technical considerations relevant to applicability

The techniques is generally applicable. It is especially applicable in those cases where hazardous, toxic or mutagenic compounds are present in the diffuse emission streams or when closed loop systems are easier and less expensive than final treatment of the emissions.

Economics

The cost of techniques will be site-specific. Costs will be lower for new plants.

Driving force for implementation

- To comply with environmental legislation/protection in a cost-effective manner.
- Improved operator health and safety.

Reference literature

For further information on this technique, please refer to the CWW BREF.

2.4.3.3 Monitoring of emissions to air

2.4.3.3.1 Monitoring of emissions to air from abatement

All emissions to air from channelled sources should be monitored to measure the concentration of the pollutants arising from the process. In addition, monitoring is needed to verify the proper operation of the abatement equipment. This can be either direct measurement of the pollutant concentration or the monitoring of process parameters, which can provide useful alternative information on the performance of the abatement plant.

As well as monitoring emissions from the end-of-pipe abatement device, it may be appropriate in some circumstances to monitor the emissions from key process operations, either unabated or after only pretreatment. This type of monitoring can generate important information on raw material and/or product losses, or on process efficiency. This is particularly the case where many process vents are combined prior to treatment/abatement.

The type of monitoring that should be used, i.e. continuous or periodic (and the frequency of periodic monitoring), will be dependent on a number of factors, e.g. the scale and environmental significance of the emission, and the variability of the emission. In some countries, a threshold approach is followed based on the mass emission rate, with continuous monitoring required above the mass emissions threshold.

A number of chemical plants include their own on-site waste incineration plant for the thermal treatment of liquid and solid wastes. These incineration plants may also function as abatement devices for gaseous emissions. Detailed monitoring requirements for waste incineration plants are set out in Annex VI to the IED and the BAT conclusions of the WI BREF.

Monitoring requirements are considered further, where relevant, in the description of abatement techniques and the processes described in the illustrative chapters.

2.4.3.3.2 Monitoring of diffuse emissions to air

Diffuse emissions are non-channelled emissions that are not released via specific emission points such as stacks. Diffuse emissions in the LVOC sector are most commonly of VOCs and can result from:

- 'area' sources such as container filling areas or waste water treatment facilities; or
- 'point' sources such as pipe flanges, valves, pumps and other pressurised components.

Fugitive VOC emissions can be reduced by the detection and subsequent repair or replacement of leaking components. This is achieved by adopting a structured approach, commonly known as a leak detection and repair (LDAR) programme. Two monitoring methods are currently available for the identification of leaks:

- sniffing using hand-held analysers; or
- optical gas imaging, using a hand-held infrared detector.

In order to assess the overall effectiveness of the techniques applied to prevent and reduce diffuse VOC emissions, two further monitoring methods are available:

- differential absorption LIDAR (DIAL) method;
- solar occultation flux (SOF) method.

Techniques to prevent and reduce diffuse VOC emissions in the chemical/petrochemical sector are described in the CWW BREF and are particularly relevant for LVOC installations.

2.4.3.4 Techniques for inorganic compounds

2.4.3.4.1 Recovery and use of hydrogen

The recovery and purification of hydrogen for use either as a product, feedstock or fuel is described in the REF BREF and so is not repeated here. This technique has some applicability in several LVOC processes.

- Excess hydrogen from hydrogenation reactions can be recycled to the feed to maximise the efficiency of its use, e.g. for the production of aromatics, TDI/MDI, phenol and H_2O_2.
- Other options to recover and purify hydrogen from process streams and from waste gas streams are to use an adsorption technique, i.e. pressure swing adsorption (PSA), or cryogenic separation of methane and hydrogen. These can be applied to hydrogen-rich streams not necessarily resulting from hydrogenation reactions such as lower olefins.

Description
Build and operate a system (piping, compressors, etc.) to enable the reuse of hydrogen-rich streams in the feed of hydrogenation reactions.

Technical description
Hydrogen is recovered from hydrogen-rich streams for reuse in the feed of hydrogenation reactions. A recycle compressor might be required.

Achieved environmental benefits
Reduced raw material usage.

Environmental performance and operational data

Emission values for VOC emissions from hydrogenation at H_2O_2 plants are given in Section 12.3.1.2.

Cross-media effects

This technique may lead to increased energy consumption from the use of compressors and coolers.

Technical considerations relevant to applicability

It is generally applicable to hydrogenation reactor off-gases. The applicability may be restricted where the energy demand for recovery is excessive due to the low hydrogen content or when there is no demand for hydrogen.

Economics

This technique has lower raw material costs due to lower hydrogen consumption, but higher capital investment costs and higher energy costs.

Driving force for implementation

Lower feedstock cost.

Example plants

Hydrogenation reactions normally operate in hydrogen molar ratio excess, generating a flue-gas from the reaction outlet that is rich in H_2. Hence most processes that use hydrogenation also carry out hydrogen recovery, including cyclohexane (see Chapter 4), phenol (see Chapter 8), toluene diamine (TDA) (see Chapter 10) and hydrogen peroxide (see Chapter 12).

Reference literature

For further information on this technique, see the REF BREF.

2.4.3.4.2 Recovery and reuse of spent air

Description

Recovery and reuse of spent air from oxidation reactions.

Technical description

In oxidation reactions using air, oxygen is consumed and, once the VOCs have been removed using an appropriate abatement technique, this results in a nitrogen-rich stream that can be further purified and used.

The key issue is process safety. Any residual oxygen must not be allowed to enter the nitrogen header system for the site. Continuous monitoring and process trips are required. Quality may also be a concern, e.g. nitrogen of a lower purity cannot be used in finished product tanks.

Achieved environmental benefits

Energy use will be reduced because less nitrogen will need to be produced by the nitrogen-manufacturing plant.

Environmental performance and operational data

No information provided.

Cross-media effects

None.

Technical considerations relevant to applicability
The technique is applicable where there are available uses for low-purity nitrogen which do not compromise process safety.
Some plants will need to invest in safety systems to ensure a sufficiently low oxygen content in the reused gas.

Economics
The technique may not be economically viable; in order to operate such a system safely, the investment costs may be higher than continuing the normal use of nitrogen.

Driving force for implementation
Marginal reduction in operating costs.

Example plants
Some formaldehyde plants.

Reference literature
[88, Wallace 2005].

2.4.3.4.3 Recovery of HCl

See Section 0 (Techniques for acid gases).

2.4.3.4.4 Recovery of H_2S to produce sulphur

The recovery of hydrogen sulphide is usually based on wet scrubbing using an absorbent, which is then regenerated in a separate column to produce a hydrogen-sulphide-rich stream. This is then sent to a sulphur recovery unit (SRU) which produces elemental sulphur. The technique is described in the REF BREF and so is not repeated here.

This technique is sometimes applicable in some LVOC processes, including lower olefin production. The technique may not be applicable:

- to processes that are not located near a refinery that has an SRU;
- to processes with emissions below 1 t/day of sulphur compounds.

2.4.3.5 Techniques for channelled emissions of organic compounds (VOCs)

Techniques to be considered include:

- the prevention, detection and control of diffuse emissions;
- appropriate waste gas collection systems (see Section 2.4.3.1);
- compression;
- condensation and cryogenic condensation;
- absorption (see Section 2.4.3.5);
- adsorption;
- use as fuel in a combustion unit;
- catalytic oxidation;
- thermal oxidation.

These techniques have widespread application in the LVOC sector and examples of their application can be found in a number of the illustrative chapters. Absorption (or wet scrubbing) is more likely to be applied for the treatment of acid gases and so is described in Section 2.4.3.5.3. A more comprehensive list of techniques can be found in the CWW BREF. Where techniques are only used in one or two LVOC processes, their application is described in the relevant illustrative chapter. These techniques are also used in vapour recovery units installed on storage facilities.

2.4.3.5.1 Prevention, detection and control of diffuse emissions

Diffuse emissions are non-channelled emissions that are not released via specific emission points such as stacks. In LVOC production sites, diffuse VOC emissions can arise from:

- 'area' sources such as container-filling areas and waste water treatment facilities;
- 'point' sources such as pipe flanges, valves, pumps and other pressurised components on a process plant; (diffuse emissions from point sources are referred to as fugitive emissions.)

Whilst the diffuse emissions from an individual source may be very small, these small losses aggregated over an LVOC production site could be significant.

The CWW BREF presents an overview of diffuse emissions from the chemical industry as a whole and describes a number of techniques to prevent and/or reduce diffuse emissions of VOCs, specifically:

- techniques related to the process and plant design;
- installation and commissioning;
- plant operation, in particular adopting an LDAR (leak detection and repair) programme;
- assessing the effectiveness of preventative and reduction measures;
- indirect cooling.

All of these are generally applicable to the LVOC sector and are described in detail in the CWW BREF and so are not repeated here.

The techniques that are generally considered to have the potential for achieving a high level of environmental protection in the LVOC sector for the storage, transfer and handling of liquids and solids are those described in the EFS BREF. Again, these are not repeated here.

2.4.3.5.2 Condensation

Condensation is a technique that eliminates organic vapours from a waste gas stream by reducing its temperature below its dew point. In the LVOC sector, it is a recovery technique generally applied close to the source of the emission as an initial treatment step. Further treatment of the waste gas stream is normally applied downstream.

Description
Condensation is carried out by means of either direct cooling (i.e. contact between the gas and cooling liquid) or indirect cooling (i.e. cooling via a heat exchanger). The choice of coolant will depend on the temperature that needs to be achieved.

Technical description
A full description of the different types of condensation systems available is given in the CWW BREF, ranging from the simplest water-cooled systems through to the use of refrigerants and closed-cycle inert gas condensation systems.

Achieved environmental benefits

Condensation enables the recovery of raw materials and products. This in turn will reduce the required size/capacity of subsequent downstream waste gas treatment equipment.

Environmental performance and operational data

Additional performance information can be found in the CWW BREF.

Cross-media effects

Indirect cooling is preferred because direct cooling results in an additional separation stage and waste water effluent. Cooling water systems can consume significant quantities of water, if the water is not recycled. Refrigerated systems will consume material and energy. There is also the possibility of diffuse emissions of refrigerant gases

Technical considerations relevant to applicability

Condensation is a compact and robust technology with a high removal efficiency and the ability to recover VOCs for reuse. Simple cooling water systems are easily retrofitted. More complex refrigerant-based systems can be skid-mounted for retrofit or a new plant. Cryogenic condensation is not suitable for wet gas streams because of ice formation. The applicability may be limited by coolant availability. The applicability may also depend on the level of site cooling integration and optimisation (e.g. using pinch analysis).

Economics

At its simplest, condensation is usually a low-cost technique. There is the potential benefit of product recovery. Further information is provided in the CWW BREF.

Driving force for implementation

The main driver for using condensation or cryogenic condensation is economic, to recover materials for reuse and reduce the pollutant load on the end-of-pipe treatment.

Example plants

Condensation is used in many LVOC processes, including the following:

- In phenol production, cumene is oxidised by air to produce cumene hydroperoxide. Condensation is used to recover unreacted cumene.
- In toluene diisocyanate (TDI) production, toluene is nitrated to produce dinitrotoluene (DNT). Condensation is used to recover educt and products.

Reference literature

For further information on this technique, please refer to the CWW BREF.

2.4.3.5.3 Adsorption

In the LVOC sector, adsorption is an end-of-pipe technique for the abatement of low concentrations and loads of VOCs, odours or other potentially harmful emissions, e.g. PCDD/F. The technique can also be used to pretreat process air (e.g. for drying) or treat intermediate process streams to remove low levels of undesirable contaminants. Adsorption is also used as a pretreatment to recover organic material and to reduce the load to the final waste gas abatement. A full description of the adsorption process is given in the CWW BREF. A summary of this description and its applicability to LVOC is given below.

Description

Adsorption is a technique for removing compounds from a process off-gas or waste gas stream by retention on a solid surface (typically activated carbon).

Adsorption is a separation method in which molecules of a compound within a fluid are retained on a solid surface that prefers specific compounds to others and thus removes these compounds from the fluid. It is typically used to remove a gaseous compound such as a VOC from a waste gas stream by adsorption onto activated carbon.

In regenerative adsorption, when the surface has adsorbed as much as it can, the adsorbed material is desorbed as part of the regeneration cycle of the adsorbent. When desorbed, the contaminants are usually present in a much higher concentration; this means they can either be recovered or disposed of more effectively.

In non-regenerative adsorption, the used adsorbent is disposed of.

Technical description

A full description of the adsorption process and the types of adsorption equipment available is given in the CWW BREF. The parameters of these techniques that are more relevant to performance are briefly mentioned here:

- Design: The process off-gas usually goes through condenser(s) where some of the pollutants are condensed and recycled to the process, before the adsorbers. Design criteria for the adsorbers include the final desired emission concentration and the size and number of beds required.
- Regeneration fluid selected by the design: Normally low- or medium-pressure steam, although vacuum or inert gas regeneration can also be used.
- Adsorbent material: Activated carbon (e.g. from charcoal) is the most common adsorbent. Other materials like zeolites and polymers are efficient and can be made highly selective to specific organic species. The adsorbent material is periodically regenerated, normally with steam, to recover the pollutants. The condensing of the steam results in an aqueous effluent (after separation of insoluble compounds).
- Adsorption management: This feature involves all actions taken by the operator to optimise adsorption performance. These include the monitoring of adsorption performance trends to optimise operation and regeneration times; procedures that include measures (such as changeover or plant shutdown) in the event that the emission threshold value is approached to prevent pollutant breakthrough; ensuring sufficient fresh adsorbent is available (in place) for unplanned early exhaustion of adsorption capacity.
- Adsorber cooling after regeneration: At the end of the steam regeneration the adsorber bed is both hot and wet. If it was put back online without being cooled, the waste gases would initially be in contact with the hot, wet active carbon bed and there would be a short period when VOCs were not optimally adsorbed. This would result in a high VOC concentration in the discharge but only for a few minutes in an adsorption step that typically lasts for several hours. To reduce the peak emissions at the beginning of the adsorption, the adsorber bed can be cooled using air recycled from the discharge, but additional electric power is needed (this is listed above as a technique).

Achieved environmental benefits

- Reduced organic load to final waste gas treatment.
- Reduced emissions to air.
- Reduced consumption of organic material when organic material is recovered for reuse.

Environmental performance and operational data

For performance data, see Chapter 8 (phenol) and Chapter 12 (hydrogen peroxide).

Over time the adsorbent will become saturated. If the regeneration cycle is not started before this occurs, there will be a breakthrough of VOCs.

Additional performance information can be found in the CWW BREF.

Cross-media effects

- Where the adsorbent is not regenerated, the material will need to be disposed of as a waste.
- Energy consumption for the regeneration of the adsorbent, usually as steam.

Technical considerations relevant to applicability

- Adsorption is widely used in the LVOC sector. The technique is generally applicable to those waste streams with only low concentrations of pollutants. Higher concentrations will result in more frequent regeneration of the adsorbent and other techniques are likely to be more appropriate. It can often be installed locally to individual emission sources.
- GAC (granular activated carbon) is not adapted for humid gas streams and is not suitable for some compounds, e.g. ketones and methane.

Economics

Adsorption is relatively low-cost in comparison with some other techniques, e.g. thermal oxidation. There is also the potential benefit of product recovery.

Driving force for implementation

- Raw material recovery from low-concentration waste gas streams.
- Abatement of VOC emissions.

Example plants

Adsorption is used in the following LVOC processes:

- In hydrogen peroxide (H_2O_2) production, regenerative adsorption is used to both recover hydrocarbons from the oxidiser off-gas stream and abate VOC emissions to air.
- In phenol production, adsorption is used to recover unreacted cumene from the oxidiser off-gas stream and to reduce the VOC load to final treatment. It is also used as final abatement for the waste gas from hydrogenation.

Reference literature

For further information on this technique, please refer to the CWW BREF.

2.4.3.5.4 Use as fuel in a combustion unit

Description

Process off-gases with a high calorific value are burnt as a fuel in a combustion unit (gas engine, boiler, etc.) and the heat is recovered as steam or for electricity generation. For a more detailed description of combustion units, see sections on combustion engines and steam processes in LCP BREF. Alternatively, they may be burnt in a process heater or furnace to provide heat to the process.

Technical description

Process off-gases may have a high calorific value due to the presence of organic solvents, unreacted organic raw materials, by-products or flammable diluents. The process off-gas is channelled to a gas engine or boiler where it is burnt to produce electricity and/or steam. The boiler may also use a conventional fuel, in which case the off-gases may require separate burners to ensure efficient combustion. The capacity to vent the off-gases or burn them in a flare may be required to cover process start-ups, shutdowns and other than normal operating conditions of the process and the combustion unit.

Achieved environmental benefits

- Reduced emissions of VOCs to air.
- Improved energy efficiency - lower energy consumption for steam production or electricity generation on site.

Environmental performance and operational data

See Chapter 6 on formaldehyde and Chapter 7 on ethylene oxide (EO).

Cross-media effects

No information provided.

Technical considerations relevant to applicability

Process off-gases should only be used as fuel when it is uneconomic or impractical to recover and use the substances that have a high calorific value.

The technique is applicable to formaldehyde plants using the silver process, but not the metal oxide process.

For existing plants, the introduction of the technique will be restricted to major plant upgrades. And it is only applicable if there is an on-site demand for the steam or electricity.

The technique is effective for the destruction of highly odorous substances, such as mercaptans.

It is applicable to streams with a relatively low calorific value if the stream is hot or if it contains elevated levels of oxygen.

The substances in the process off-gas must be readily combustible.

The technique is not applicable to streams containing halogenated organics which will increase releases of acid gases and PCDD/F and might cause corrosion of the gas engine or boiler.

Economics

Significant benefits from steam and/or electricity generation.

Driving force for implementation

- Environmental legislation.
- Cost reduction.

Example plants

This technique is used for the inerts purge of ethylene oxide plants.

It is also used in formaldehyde plants using the silver process.

Reference literature

[93, InfoMil 2000].

2.4.3.5.5 Catalytic oxidation

In the LVOC sector, catalytic oxidation is an end-of-pipe technique for the abatement of VOCs. It will normally be applied to a combined waste gas stream drawn from different parts of the same LVOC process or from a number of different LVOC processes. A full description of the catalytic oxidation process is given in the CWW BREF. A summary of this description and its applicability to LVOC is given below.

Description

Catalytic oxidation is the oxidation of the VOC content of waste gases and/or odorants in a waste gas stream by heating a mixture of the contaminants with air. It operates in a similar way to thermal oxidation except that, after passing through the flame area, the waste gas passes through a catalyst bed, enabling conversion at lower reaction temperatures than in thermal oxidisers.

Technical description

A full description of the catalytic oxidation process and the types of catalytic oxidation equipment available is given in the CWW BREF. A range of different types of catalyst are available depending on the specific application.

Achieved environmental benefits

Catalytic oxidation can achieve a high level of destruction of the VOC species present in the waste gas stream.

Heat from catalytic oxidation can be recovered to be used on or off site.

Environmental performance and operational data

Data for emissions of VOCs when using catalytic oxidation as an abatement technique have been reported for the production of:

- ethylene oxide (see Section 7.4.1);
- formaldehyde (see Section 6.4.1);
- phenol (see Section 8.3.1);
- EDC/VCM (Section 11.3.1).

NO_X emissions from catalytic oxidation will generally be low (provided the concentration of nitrogen-containing compounds in the waste gas is low) and less than from thermal oxidation, depending on the temperatures and the need for support fuel.

For the data collection for phenol and EDC/VCM plants, only a few plants reported using catalytic oxidation, which in these cases showed higher VOC emissions than thermal oxidation.

The performance of a catalytic oxidiser depends on many factors, e.g.:

- the choice of catalyst;
- the design of the oxidiser including the number of catalyst beds.

Cross-media effects

The catalyst will require periodic regeneration or replacement.

Technical considerations relevant to applicability

This technique is suitable for the reduction of VOC emissions to air from those LVOC processes with moderate to high VOC loadings, with only minor fluctuations in flow and load. The lower operating temperature allows the use of smaller oxidisers than thermal oxidisers, and produces lower NO_X and CO emissions and generally requires the use of less support fuel.

However, the waste gas may need pretreatment to remove components that could be poisonous to the catalyst or act as an inhibitor, e.g. halogenated VOCs, particulates, some metals, phosphorus and inorganic halogens.

Economics

Catalytic oxidisers have higher investment costs than thermal oxidisers.

Driving force for implementation
Environmental legislation.

Example plants
Catalytic oxidisers are used in the following LVOC processes:

- Ethylene oxide production using the oxygen-based process. The overhead stream from the carbon dioxide stripper contains carbon dioxide and small amounts of VOCs (principally ethylene, methane and ethylene oxide). It can be treated using a catalytic oxidiser then dried to produce an almost pure carbon dioxide stream that can be sold.
- Formaldehyde production using the metal oxide process. The adsorber off-gas has a low calorific value. A catalytic oxidiser is used to abate VOCs (principally formaldehyde, methanol and dimethyl ether).

Reference literature
For further information on this technique, please refer to the CWW BREF.

2.4.3.5.6 Thermal oxidation

In LVOC production, thermal oxidation is an end-of-pipe technique for the abatement of VOCs. It is normally applied to a combined waste gas stream drawn from different parts of the same LVOC process or from a number of different LVOC processes. Ideally, some of these vent streams will have already received some level of treatment to reduce the loading to the thermal oxidiser and recover materials for reuse, e.g. KO drums, condenser or absorber. A full description of the thermal oxidation process (including regenerative thermal oxidation) is given in the CWW BREF. A summary of this description and its applicability to LVOC is given below.

Description
Thermal oxidation (often referred to as 'incineration', although the term 'incineration' should be limited to combustion of liquid and solid waste) is the oxidation of the VOC content of waste gases and/or odorants in a waste gas stream that is heated above its auto-ignition temperature in a combustion chamber for sufficient time to ensure complete combustion to carbon dioxide and water.

Technical description
Techniques to reduce VOC emissions to air from the process under normal operating conditions include:

- combustion control: controlling the oxygen concentration and the temperature profile within the oxidiser;
- oxidiser design: sizing (e.g. residence time), design features (mixing);
- oxidiser type: regenerative, once-through, etc.

The combustion is optimised to maximise the removal of organic compounds, while minimising emissions to air of CO and NO_X.

Techniques to reduce NO_X emissions within the thermal oxidiser include:

- the use of low-NO_X burners;
- the reduction of the need for support fuel, e.g. by using a regenerative thermal oxidiser (RTO);
- the choice of a support fuel with a low nitrogen content.

Other techniques to reduce NO_X emissions are:

a) removal of NO_X precursors from the process off-gas streams: remove (if possible, for reuse) most of the NO_X precursors prior to thermal treatment, e.g. by scrubbing, condensation or adsorption (see for example Section 10.4.1.1 for DNT plants);
b) final abatement by SCR or SNCR (see Section 2.4.2.1).

A full description of the thermal oxidation process and the types of thermal oxidation equipment available is given in the CWW BREF.

Achieved environmental benefits
Thermal oxidation can achieve almost complete destruction of the VOC species present in the waste gas stream.

Environmental performance and operational data
The VOC destruction rate is 98 % to > 99.9 %, with residual VOCs (expressed as TOC) of 0.5–30 mg/Nm^3.

Data for emissions of VOCs when using thermal oxidation as an abatement technique have been reported for the production of:

- TDI/MDI (see Section 10.4.1);
- formaldehyde (see Section 6.4.1);
- phenol (see Section 8.4.1);
- EDC/VCM (see Section 11.4.1).

NO_X emissions from thermal oxidation depend on the concentration of nitrogen-containing compounds in the waste gas, the flame temperature and the need for support fuel. Low NO_X emissions can be achieved with regenerative thermal oxidation, especially when replacing the combustion of support fuel with electric heating (see example in Section 10.4.1).

Data for emissions of NO_X and PCDD/F when using thermal oxidation as an abatement technique have been reported for the production of:

- TDI/MDI (see Section 10.4.1);
- EDC/VCM (see Section 11.4.1).

Cross-media effects
- Thermal oxidation will also generate emissions typical of combustion plants, i.e. CO and NO_X. NO_X emissions may require subsequent abatement..
- In the unfavourable event that the VOC content of the waste gas stream is not sufficient to support combustion, support fuels are used. The use of a support fuel will have a negative effect on the overall energy efficiency of the process and may increase emissions to air (e.g. NO_X, CO).
- Any sulphur present in the waste gas (or support fuel) will be emitted as SO_2, and halogens as hydrogen halides. Further treatment of the exhaust gas may be needed to abate these emissions.
- If the VOCs have a high chlorine content, the thermal oxidiser will need to be designed and operated to prevent and minimise the formation of dioxins and furans, e.g. by rapid cooling of the exhaust gases.
- Abatement of the exhaust gases emitted from the thermal oxidiser may produce liquid and/or solid wastes requiring further treatment or disposal.

- Heat from thermal oxidation can be used to generate steam and electricity to be used on or off site if the heat available is sufficient to justify the additional investment.

Measures to reduce the cross-media effects can be found in the LCP, CWW and REF BREFs. The following table is not exhaustive.

Table 2.7: Techniques to reduce emissions from thermal oxidisers

Type of technique	Optimisation measure	Pollutant reduced
Fuel type	Low H_2 content	NO_X
	Low sulphur content	SO_X
Design/Conditions	Low residence time	PCDD/F
	Rapid quenching	PCDD/F
	> 850 °C	PCDD/F
	Mixing	VOCs
Type of oxidation	Catalytic oxidation	PCDD/F, NO_X
	Thermal oxidation	VOCs
Instr&Control	Monitoring of O_2 excess in outlet	CO, VOCs, PCDD/F
	Monitoring	VOCs, PCDD/F, etc.
	Temp. profile control	VOCs, NO_X
Burners	Low-NO_X burner	NO_X
Post-treatment	Wet gas scrubber	Sulphur, halogens
	Adsorber	PCDD/F
	SNCR	NO_X SO_X
Upstream treatment	Wet gas scrubber	HCl, Cl_2

Technical considerations relevant to applicability

Thermal oxidisers can be used to reduce emissions from almost all VOC sources, including reactor vents, distillation vents, solvent operations and operations carried out in ovens, dryers and kilns. They can handle minor fluctuations in flow and load, but large fluctuations may require the use of a flare. They are best suited to those processes with moderate to high VOC loadings where recovery of the VOCs is not possible. Low VOC loadings will result in high consumption of support fuel.

The applicability for low-NO_X burners and RTOs may be restricted by design and/or operational constraints at existing units. The applicability of SCR to existing units may be restricted by space availability. The applicability of SNCR to existing units may be restricted by the residence time needed for the reaction.

Economics

- Thermal oxidisers are a significant part of the site infrastructure, with associated capital and operating costs. Further information is provided in the CWW BREF.
- Boiler plants can be used for the thermal oxidation of VOCs if the temperature and residence time are in the correct range. This can be an attractive option when a suitable boiler plant is located on the same site.

Driving force for implementation

The reduction of VOC emissions to air from those LVOC processes with moderate to high VOC loadings, with only minor fluctuations in flow and load.

Example plants

Thermal oxidisers are used in the following LVOC production processes: EDC/VCM, TDI, MDI, and FA.

Reference literature
For further information on this technique, please refer to the CWW BREF.

2.4.3.6 Techniques for acid gases

The technique considered in this section is absorption (wet gas scrubbing) and examples can be found in a number of the illustrative chapters. A more comprehensive list of techniques can be found in the CWW BREF. Where techniques are only used in one or two LVOC processes, their application is described in the relevant illustrative chapter.

2.4.3.6.1 Absorption (wet gas scrubbing)

In LVOC production, absorption or wet gas scrubbing can be either:

- a technique for the recovery of a chemical component from a gas stream (e.g. the recovery of HCl); or
- an end-of-pipe abatement technique to reduce emissions to air.

The most common application of wet scrubbers in LVOC production is for the removal of hydrogen halides, SO_2, ammonia, hydrogen sulphide and some VOCs. Wet scrubbers can also remove some dust (although this is not their principal aim). A full description of wet scrubbing is given in the CWW BREF. A summary of this description and its applicability to LVOC is given below.

Description
Absorption is the mass transfer of a soluble component of a waste gas stream into a solvent, which in the case of wet scrubbing is water or an aqueous solution. Physical scrubbing is when the component is dissolved in the solvent, whereas chemical scrubbing is when the component reacts with a chemical present in the solvent. Physical scrubbing can be used for both material recovery and abatement, whereas chemical scrubbing is normally only used for abatement. In physico-chemical scrubbing, the chemical reaction is reversible so that the gaseous component can be recovered.

Technical description
A full description of the wet scrubbing process and the types of wet scrubbing equipment available is given in the CWW BREF. The abatement efficiency of wet scrubbers is dependent on the residence time of the gas in the absorption section, the type of scrubber used, e.g. the column internals (random packing, structured packing, etc.), the scrubbing liquid used and the liquid to gas ratio. If the scrubbing liquid is recirculated, the refreshment rate of the liquid and the addition rate of any chemicals can also be important.

Achieved environmental benefits
- Recovery of chemicals for use/reuse.
- Reduced emissions to air.

The first stage in the recovery of HCl is usually wet gas scrubbing. The HCl is recovered from the scrubber liquor and purified so that it can be used as a raw material or product (e.g. in the TDI/MDI process (see Chapter 10) and the EDC/VCM process (see Chapter 11)).

Wet scrubbers can often be installed close to individual emission sources.

Environmental performance and operational data
- The treated waste gas from scrubbers will be fully saturated with water vapour.

- Where the resulting scrubber liquor is treated to recover the absorbed component, or stripped to remove VOCs, the recovery process may generate emissions to air that may also need to be abated.

Data for emissions of HCl and chlorine after wet scrubbing have been reported for the processes used to produce:

- TDI/MDI (see Section 10.4.1);
- EDC/VCM (see Section 11.4.1).

Additional performance information can be found in the CWW BREF.

Cross-media effects

Scrubbing generates a process water stream, which will require further treatment or disposal. Effluent volumes can be minimised through recirculation, but this can reduce the effectiveness of scrubbing. A pumped recirculation and forced bleed will be necessary to prevent the accumulation of salts or other contaminants in the recirculating scrubber liquor.

Technical considerations relevant to applicability

- Wet scrubbing is widely used in the LVOC sector.
- This technique is applicable for the treatment of gaseous streams containing high concentrations of suitable VOCs.
- The use of absorption is subject to the availability of a suitable solvent, with a high solubility for the gas, low vapour pressure and low viscosity.
- Wet scrubbers are typically used to remove water-soluble organic compounds, e.g. alcohols, hydrogen halides or ammonia, with the main aim being the recovery and reuse of these components.
- Alkaline scrubbers are typically used to remove acid gases, such as hydrogen halides, sulphur dioxide and hydrogen sulphide.

Economics

Wet scrubbers are relatively low-cost and there is the potential benefit of product recovery. Further information is provided in the CWW BREF.

Driving force for implementation

- Raw material recovery from waste gas streams, e.g. hydrogen halides and water-soluble VOCs.
- Abatement of inorganic pollutants.

Example plants

Wet scrubbers are used to reduce emissions to air, e.g. in the following LVOC processes:

- The phosgenation of toluene diamine (TDA) to toluene diisocyanate (TDI). This produces HCl, which is recovered by wet scrubbing using water.
- The combined waste gas streams from EDC and/or VCM production are treated by using a thermal oxidiser or a liquid/waste gas incinerator followed by two-stage wet scrubbing. The first stage uses water in an HCl absorber and the second stage uses a caustic scrubber.
- Wet scrubbing with water is used to recover ammonia in the production of ethanolamines.

Reference literature

For further information on this technique, please refer to the CWW BREF.

2.4.3.7 Techniques for dust

The techniques listed below are described briefly in Section 13.10.1 and a full description is provided in the CWW BREF. Where relevant, the techniques can be applied across the LVOC sector. Dust emissions associated with decoking are described in Chapters 3 and 11. Dust emissions may also arise during the periodic replacement of catalysts or adsorption media, but are not normally significant for LVOC processes. The techniques are:

- settling chamber/gravitational separator;
- cyclon;
- electrostatic precipitator;
- wet dust scrubber;
- bag (fabric) filter;
- ceramic and metal filter;
- third stage blowback filter (see the REF BREF);
- centrifugal washer (wet dust scrubbing).

2.4.4 Techniques to reduce emissions to water

Emissions of water from LVOC production sites can include some or all of the following substances:

- volatile organic compounds (VOCs);
- inorganic compounds, e.g. hydrogen halides, hydrogen sulphide, sulphates/sulphites, nitrates/nitrites and ammonia;
- suspended solids;

LVOC production sites usually have a central waste water treatment plant (WWTP) receiving waste water from all the processes operating at the site. Operators should adopt an integrated waste water management and treatment strategy by using an appropriate combination of techniques based on their site-specific requirements.

Table 2.8: Holistic approach to waste water management at chemical sites

Technique	Description	Remarks
Process-integrated techniques	Techniques to prevent or reduce the generation of water pollutants	Where used in LVOC processes, this is within the scope of the LVOC BREF
Recovery of pollutants at source	Techniques to recover pollutants prior to their discharge to the waste water collection system	
Waste water pretreatment	Techniques to abate pollutants before the final waste water treatment. Pretreatment can be carried out at the source or in combined streams.	Where used in LVOC processes, this is within the scope of either the LVOC or CWW BREFs
Final waste water treatment	Final waste water treatment by, for example, preliminary and primary treatment, biological treatment, nitrogen removal, phosphorus removal and/or final solids removal techniques before discharge to a receiving water body	These techniques are described in the CWW BREF and so are not repeated here

The techniques listed below are described in full in the CWW BREF and, where appropriate, are considered generally applicable across the LVOC sector:

- selection of waste water control system;
- selection of waste water collection and segregation system, including equalisation tanks and buffer storage tank;
- connection to a central waste water treatment plant outside the chemical site;
- anaerobic treatment;
- biological removal of sulphur compounds/heavy metals;
- aerobic treatment, e.g aerobic biologically activated sludge process;
- removal of nitrogen by biological nitrification/denitrification;
- removal of phosphorus by biological treatment;
- removal of phosphorus by chemical precipitation;
- retention ponds;
- sand filters;
- rainwater and firefighting water collection and treatment;
- collection and treatment of unintended operational releases (spillages).

2.4.4.1 Water minimisation

Techniques that reduce water usage are not only beneficial in terms of reduction of consumption but also for reducing the pollutant load sent to treatment and to improve pretreatment efficiency. Although the pollutant concentration may increase in the first instance, this may open up opportunities for material recovery. Overall, water minimisation will result in a reduced waste water volume and therefore will reduce the required size of waste water treatment plants.

2.4.4.2 Process-integrated prevention techniques

The techniques listed below will prevent or reduce pollutant loads at source, and are fully described in the CWW BREF and, where appropriate, are considered generally applicable across the LVOC sector:

- use of heat exchangers in preference to open cooling towers;
- countercurrent product washing;
- countercurrent extraction;
- reactive extraction;
- substance recovery from mother liquors and substance retention;
- use of high-purity materials.

2.4.4.3 Source segregation of waste water

Description
Source segregation of waste water.

Technical description
For some effluent streams, it will be more effective to keep streams segregated in a dedicated and closed system so that specific pretreatments can be applied.

Achieved environmental benefits
Isolation of compounds that are toxic or difficult to treat, thereby enabling specific recovery techniques or pretreatments to be applied to these streams. Segregation of more concentrated waste water streams to facilitate materials recovery.

Environmental performance and operational data
No information provided.

Cross-media effects
None.

Technical considerations relevant to applicability
No information provided.

Economics
No information provided.

Driving force for implementation
No information provided.

Example plants
Waste water from aromatics plants is segregated from other sources of waste water in order to facilitate the removal and recovery of raw materials or products.

Reference literature
No reference literature provided.

2.4.4.4 Liquid phase separation

Description

Optimised liquid phase separation.

Technical description

Separation of organic and aqueous phases with appropriate design and operation (e.g. sufficient residence time, phase boundary detection and control) to prevent any entrainment of undissolved organic material.

The organic phase is recovered for reuse or disposal.

The aqueous phase is reused (if needed after treatment) or discharged as waste water to further treatment.

See also the CWW BREF.

Achieved environmental benefits

- Reduction of the organic load discharged to waste water treatment.
- Reduced emissions to water.
- Reduced consumption of organic material (if reused).
- Reduced consumption of water (if reused).

Environmental performance and operational data

No information provided.

Cross-media effects

None.

Technical considerations relevant to applicability

Not directly applicable to emulsions which need to be destroyed first.

Economics

The economic balance will depend on the benefits derived from the reuse of the organic material.

The costs for phase separation are comparatively low, and it is generally more cost-efficient to prevent emissions of organic pollutants by optimised phase separation than to enlarge capacities of waste water treatment.

Driving force for implementation

- Protection of the environment.
- Economic benefits from material recovery.

Example plants

The separation of aqueous and organic phases is widely used in the LVOC sector, e.g. after mixed-phase reactions to recover product (e.g. production of DNT, Chapter 10), after washing of organic product (e.g. production of DNT, Chapter 10), after condensation (e.g. production of phenol, Chapter 8), after extraction (e.g. production of phenol, Chapter 8; production of DNT, Chapter 10; production of hydrogen peroxide, Chapter 12). It is also used at aromatics plants (Chapter 4) and at styrene plants (Chapter 5) for example.

Reference literature

No reference literature provided.

2.4.4.5 Waste water pretreatment techniques

Depending on the composition, waste water from LVOC plants may (and often does) need pretreatment, e.g. to prevent emissions of volatile compounds, to remove heavy metals or organic compounds that are not biodegradable or to protect the final biological treatment.
The techniques listed below are described in full in the CWW BREF and, where appropriate, are considered generally applicable across the LVOC sector:

- adsorption;
- chemical oxidation;
- chemical hydrolysis;
- chemical precipitation;
- chemical oxidation
- chemical reduction;
- coagulation and flocculation;
- crystallisation;
- distillation/rectification;
- electrocoagulation;
- electrodialysis;
- electrolysis;
- evaporation;
- extraction;
- filtration;
- flotation;
- grit separation of solids;
- hydrocyclone;
- ion exchange;
- microfiltration and ultrafiltration;
- nanofiltration (NF) and reverse osmosis (RO);
- oil-water separation;
- pertraction;
- pervaporation;
- sedimentation of solids;
- stripping;
- waste water incineration;
- wet air oxidation.

Techniques that have been identified to be relevant for individual illustrative processes are given in the table below.

Technique	Description	Chapter(s)
Adsorption	Separation method in which compounds (i.e. pollutants) in a fluid (i.e. waste water) are retained on a solid surface (typically activated carbon).	12
Chemical oxidation	Organic compounds are oxidised with ozone or hydrogen peroxide, optionally supported by catalysts or UV radiation, to convert them into less harmful and more easily biodegradable compounds.	3, 10
Coagulation and flocculation	Coagulation and flocculation are used to separate suspended solids from waste water and are often carried out in successive steps. Coagulation is carried out by adding coagulants with charges opposite to those of the suspended solids. Flocculation is carried out by adding polymers, so that collisions of microfloc particles cause them to bond to produce larger flocs.	11
Distillation	Distillation is a technique to separate compounds with different boiling points by partial evaporation and recondensation. Waste water distillation is the removal of low-boiling contaminants from waste water by transferring them into the vapour phase. Distillation is carried out in columns, equipped with plates or packing material, and a downstream condenser.	7, 10
Extraction	Dissolved pollutants are transferred from the waste water phase to an organic solvent, e.g. in countercurrent columns or mixer-settler systems. After phase separation, the solvent is purified, e.g. by distillation, and returned to the extraction. The extract with the pollutants is disposed of or returned to the process. Losses of solvent to the waste water are controlled downstream by appropriate further treatment (e.g. stripping).	8, 12
Evaporation	The use of distillation (see above) to concentrate aqueous solutions of high-boiling substances for further use, processing or disposal (e.g. waste water incineration) by transferring water to the vapour phase. Typically carried out in multistage units with increasing vacuum, to reduce energy demands. The water vapours are condensed, to be reused or discharged as waste water.	7, 10
Filtration	The separation of solids from a waste water carrier by passing them through a porous medium. It includes different types of techniques, e.g. sand filtration, microfiltration and ultrafiltration.	11
Hydrolysis	A chemical reaction in which organic or inorganic compounds react with water, typically in order to convert non-biodegradable to biodegradable or toxic to non-toxic compounds. To enable or enhance the reaction, hydrolysis is carried out at elevated temperature and maybe pressure (thermolysis) or with the addition of strong alkalis or acids or using a catalyst.	5, 8
Precipitation	The conversion of dissolved pollutants (e.g. metal ions) into insoluble compounds by reaction with added precipitants. The solid precipitates formed are subsequently separated by sedimentation, flotation, or filtration.	11
Sedimentation	Separation of suspended particles and suspended material by gravitational settling.	11
Stripping	Volatile compounds are removed from the aqueous phase by a gaseous phase (e.g. steam, nitrogen or air) that is passed through the liquid, and are subsequently recovered (e.g. by condensation) for further use or disposal. The removal efficiency may be enhanced by increasing the temperature or reducing the pressure.	3, 4, 5, 6, 10, 11
Waste water incineration	The oxidation of organic and inorganic pollutants with air and simultaneous evaporation of water at normal pressure and temperatures between 730 °C and 1 200 °C. Waste water incineration is typically self-sustaining at COD levels of more than 50 g/l. In the case of low organic loads, a support/auxiliary fuel is needed.	12

2.4.4.6 Monitoring of water emissions

The monitoring of waste water streams is described in the CWW BREF. The data collection showed that, in most units, key process parameters that are relevant to the operation of downstream waste water treatment are monitored, including flow and pH. Additional monitoring of waste water streams should be applied in the following circumstances:

- When a technique is used to recover or reuse a material from a waste water stream; or when a technique to treat a pollutant at source or a specific pretreatment is applied prior to the waste water entering the common waste water system. Then monitoring of this waste stream should be carried out in order to optimise the performance of this technique.
- For those pollutants that are likely to be present and are not abated by the central waste water treatment system, e.g. PCDD/F and/or adsorbable organically bound halogens (AOX), and whose presence may harm the downstream process. Then monitoring of this waste stream should be carried out to protect the downstream facilities.
- For those pollutants that are likely to be present in the final effluent discharge and were not considered in detail in the CWW BREF.

The above bullet points should be applied to the inventory of waste water streams. Monitoring frequency is considered in the CWW BREF. The toxicity assessment of the final effluent and the applicability of whole effluent assessment are fully described in the CWW BREF and are not repeated here.

2.4.5 Techniques to reduce raw material consumption

2.4.5.1 Process optimisation

There are a number of process optimisation measures (design and operational) that can lead to lower emissions and waste from the process, and thus a lower load to be handled by the recovery and treatment systems downstream of the reaction section. These include the following:

- Process chemistry/route: using process intensification techniques to select the process that maximises the overall conversion of raw materials into the desired product and minimises the use of solvents, catalysts and energy, since this will typically be the process with the lowest overall environmental impact.
- Process design, including use of industry codes of practice.
- Process control, including computerised process control.
- Distillation system design and operation: techniques that avoid high-temperature operation and reduce liquid hold-up will minimise residue/oligomer formation in distillation systems:
    - Structured packing rather than trays will reduce the pressure drop, which will reduce the process temperature.
    - Vacuum rather than atmospheric operation will reduce the process temperature. Note: reducing the process temperature means that the operating temperature of the condensers will be reduced and additional energy may be required to provide chilled water or refrigerant capacity.
    - Addition of inhibitors.

2.4.5.2 Catalyst selection and optimisation

2.4.5.2.1 Catalyst selection

Correct catalyst selection will increase resource efficiency by reducing the production of by-products and wastes and increasing the lifetime of the catalyst which will result in reduced spent catalyst waste for regeneration or disposal and lower emissions to air. This is important in many of the processes described in the illustrative chapters, e.g. for hydrogenation reactions or the production of ethylbenzene, styrene, certain aromatics, ethylene oxide or formaldehyde.

Catalyst selection should take into account the following factors:

- the activity of the catalyst;
- the selectivity of the catalyst, (to eliminate or reduce by-product formation);
- the operating life of the catalyst (vulnerability to catalyst poisons);
- the use of less toxic metals (using precious metal catalysts such as silver and platinum, rather than heavy metal catalysts, to eliminate or reduce emissions or wastes contaminated with heavy metals).

An example of catalyst selection is the use of zeolite catalysts instead of aluminium trichloride for ethylbenzene production (see Chapter 5). Using zeolites will prevent or reduce emissions to air of organic compounds and acid gases, the generation of waste water and the amount of waste being sent for disposal.

2.4.5.2.2 Catalyst protection

Description
Measures taken upstream of the catalyst to reduce impurities in the feed that will cause catalyst degradation. These measures will reduce the production of spent catalyst waste for regeneration or disposal.

Technical description
The techniques to protect catalysts and prevent their degradation include:

- physical treatment of the feed to reduce impurities, e.g. decanters and filters to remove water, gums and suspended solids;
- chemical treatment of the feed to reduce impurities such as: carbonyls, chlorides, water, sulphur and sulphur compounds, for example by installing a guard bed containing a chemical adsorbent upstream of the catalyst;
- selection of corrosion-free materials of construction and the use of anti-corrosion treatments upstream to avoid corrosion products acting as a ‘catalyst’ to polymerisation reactions in the reactor;
- lower operating temperatures to avoid oligomer or gum formation.

Achieved environmental benefits
Minimisation of the generation of spent catalyst waste.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Generally applicable.

Economics
Reduced costs of catalyst regeneration/replacement and reduced plant downtime needed to change catalyst.

Driving force for implementation
Improved plant economics, reduction in the use of resources and reduction in waste generation.

Example plants
Formaldehyde production plants using the silver process are constructed using alloys that do not cause metal poisoning of the silver catalyst.

Reference literature
No reference literature provided.

2.4.5.2.3 Process optimisation

Control of reactor conditions (e.g. flow, temperature, pressure), to achieve the optimal balance between conversion efficiency and catalyst life. The aim is to minimise the thermal and mechanical degradation of the catalyst.

2.4.5.2.4 Monitoring of catalyst performance

Monitoring of the conversion efficiency to detect the onset of catalyst decay using suitable parameters (e.g. the heat of reaction and the CO_2 formation in the case of partial oxidation reactions).

2.4.5.3 Use of mercury-based compounds

There are only a few LVOC production routes that involve the use of mercury-based catalysts or amalgams, in particular the following:

- Vinyl chloride monomer (VCM) production: Mercuric chloride ($HgCl_2$) on a carbon carrier is used as a catalyst for the production of VCM from acetylene. This production route is mainly used in China and Russia. In 2016, only one plant in the EU used this production route (Fortischem in Novaky, Slovakia), while all other installations in the EU produce VCM from ethylene using mercury-free catalyst systems.
- Acetaldehyde production: Mercury sulphate ($HgSO_4$) can be used to catalyse the production of acetaldehyde, but this production route is no longer used in the EU or the US and several alternative production routes are available. In the 1950s and 1960s, emissions of methylmercury from the production of acetaldehyde caused the 'Minamata disease' in the Minamata Bay, Japan.
- Alcoholates (e.g. sodium methylate): Alcoholates can be produced from sodium or potassium amalgam and an alcohol. In 2016, two installations in the EU used this process route (Evonik in Lülsdorf and BASF in Ludwigshafen, both in Germany). Mercury-free production routes are available, e.g. by direct reaction of an alcohol with an alkali metal (e.g. used by EnviroCat in La Rochelle, France) or by reaction of an alcohol with caustic soda followed by azeotropic distillation (e.g. used by Evonik in Mobile, Alabama, US and in Puerto General San Martin, Argentina).
- Sodium methylate is used for the production of fatty acid methyl esters (FAME, i.e. biodiesel) (see thumbnail descriptions).

The use of mercury catalysts for the production of polyurethane polymers is outside the scope of this document.

In 2013, the Minamata Convention on Mercury was signed which includes provisions for the aforementioned mercury-based process routes including the following [96, UNEP 2013], [97, COM 2016].

- VCM production: reducing the use of mercury in terms of per unit production by 50 % by the year 2020 against 2010 use; taking measures to reduce emissions and releases;
- acetaldehyde production: phase-out of this production route by 2018 except where a Party to the Convention registers an exemption;
- sodium or potassium methylate or ethylate production: reducing the use of mercury, aiming at the phase-out of its use as fast as possible and within 10 years of the entry into force of the Convention; reducing emissions and releases in terms of per unit production by 50 % by 2020 compared to 2010.

In May 2017, Regulation (EU) 2017/852 of the European Parliament and of the Council of 17 May 2017 on mercury, repealing Regulation (EC) No 1102/2008, was published for the transposition of the Minamata Convention into EU legislation. Concerning the production of VCM and acetaldehyde, the Regulation prohibits the use of mercury-based catalysts as of 1 January 2022 and 1 January 2018, respectively. Concerning the production of sodium or potassium methylate or ethylate, the Regulation prohibits the use of mercury electrodes from 1 January 2028. Also, direct and indirect releases of mercury and of mercury compounds into air, water and land in terms of per tonne of substances produced have to be reduced by 50 % by 2020 as compared to 2010. Moreover, at the date of entry into force of the Regulation, the capacity of installations using mercury and mercury compounds for the production of sodium or potassium methylate or ethylate that were in operation before that date shall not be increased and no new installations shall be allowed. The use of mercury electrodes for the production of other chemicals (e.g. thionites) is prohibited from 1 January 2022 (except for chlor-alkali production which is prohibited from 11 December 2017). The Regulation entered into force on 13 June 2017. [204, COM 2017].

On 18 May 2017, the European Commission and seven Member States deposited at the UN Headquarters in New York their instruments of ratification of the Minamata Convention on Mercury, which triggered the entry into force of the Convention, as the 50 ratifications threshold has been exceeded.

2.4.5.4 Storage and loading

The techniques generally considered to have the potential for achieving a high level of environmental protection in the LVOC sector for the storage, transfer and handling of liquids and solids are those described in the EFS BREF.

2.4.6 Techniques to reduce energy consumption

2.4.6.1 Generic techniques on energy efficiency

The efficient use of energy is one of the principal cost factors for the LVOC sector. The use of fossil fuels for energy generation is also one of the key factors affecting the sustainability of the sector. Most LVOC production sites generate a significant part of their own demand for heat and electrical power. However, the combustion of fossil fuels to provide heat and power at LVOC sites is outside the scope of this document and is covered in the LCP BREF and the REF BREF.

Energy management of LVOC production sites needs to be considered on a site-wide basis. Techniques to minimise energy consumption are set out in the CWW BREF and REF BREF and so are not repeated here. In addition, reference should also be made to the ENE BREF, a horizontal BREF which provides more general guidance on energy efficiency.

Most of these techniques are only applicable to new plants or major retrofits of existing plants.

Energy management techniques for LVOC include the following:

- Use of combined heat and power (CHP): Co-production of electricity and steam for use in the process.
- Use of a combined cycle gas turbine: A technique to generate electricity at a higher efficiency than conventional steam boilers.
- Heat integration: A group of techniques to maximise the use of excess heat from a process or processes in other parts of the process or processes where heat input is required.
- Application of pinch technology: A structured design methodology for optimising the overall level of heat integration that can be achieved on a site-wide basis.
- Energetically coupled distillation: If distillation is carried out in two steps (two columns), energy flows in both columns can be coupled. The steam from the top of the first column is fed to a heat exchanger at the base of the second column. Steam usage is reduced by about 50 %.
- Recovery of energy from waste gas streams.
- Recovery of the exothermic heat of reaction through the generation of low-pressure steam.
- Use of energy recovery devices, such as a waste heat boiler, to provide space heating or district heating.
- Process optimisation using control and maintenance techniques.
- Management and reduction of steam consumption.
- Energy benchmarking.

2.4.6.2 Energy efficiency techniques in LVOC

Improved energy efficiency has the economic benefit of reducing energy costs and the environmental benefit of reducing heat releases and carbon dioxide emissions.

Where the purpose of a combustion plant is to provide direct heating for a chemical process, this is within the scope of the LVOC BREF. Examples of this can be found in Chapters 3 and 11, which describe the operation of thermal crackers.

As well as energy integration on a site-wide basis, energy integration can also be applied to individual processes. Some examples of this can be found in some of the illustrative chapters of this document.

Although less obvious than emissions to air and water, ‘heat’ is defined as pollution under Article 3 of the IED. The existence of significant heat releases may be indicative of a process that has poor energy efficiency. The techniques for minimising heat releases from the LVOC industry are very dependent on the local circumstances of a process. In general, new plants provide better opportunities for energy savings than existing plants.

‘Hard’ techniques could include the installation of new technology, process adaptations, heat exchange and the thermal insulation of vessels and pipework.

Conventional stand-alone power stations have overall energy efficiencies of only 35–40 %, but power and heat integration on large-scale integrated chemical plants can produce overall energy efficiencies of 70–90 %. LVOC processes can also provide opportunities for improved efficiency by considering energy integration beyond the site boundary (e.g. heat transfers to other sites – i.e. 'industrial ecology', district heating, CO_2 export).

There is also an important role for 'soft' techniques based on environmental management systems. This may include the full attribution of energy costs to each process, the internal reporting of energy use/efficiency, external benchmarking, and energy audits. Such energy audits should be an integral part of approving any significant process change.

It may not be feasible, due to technical or economic reasons, to use the lowest levels of energy that originate from a process. This energy is then transferred into the environment, e.g. by air-cooling and/or water-cooling systems.

A number of LVOC waste gas, liquid residue and solid residue process streams will contain by-products that have a higher value when used for energy recovery as a fuel substitute rather than isolating and purifying these for sale or reuse.

2.4.6.2.1 Recovery of energy from waste gas streams

In some cases, the economic value of recovering these as fuel may be low or complex because the streams are at a lower pressure than the fuel header at the site. It is best practice in these cases to recompress these streams in order to recover the calorific value, e.g. in a steam boiler. This will result in reduced fuel use and lower overall emissions to air. The applicability may be limited by the presence of contaminants, which will polymerise and block compressors, or by safety considerations.

Gas recompression to recover energy
An example can be found in Chapter 4 on aromatics. Some units may be designed to operate under vacuum or at low pressures. In this case, the overhead vents have a lower pressure than the vent header or fuel gas header; the vent gas could be recompressed and sent to the fuel gas network, a furnace or the flare (least preferable option). Low-pressure off-gases from low-pressure separators or from stripping columns need to be recovered as well, and they are generally used as fuel gases.

2.4.6.2.2 Recovery of energy from liquid and solid residues

Before recovering energy from liquid and solid residues by using them as fuels, the first priority should be to optimise the process conditions to maximise the product yield and minimise the production of liquid and solid residues. The second option to consider is to recover and reuse the substances directly in the process or indirectly in other processes which may be on or off site. The ability to use residues as by-products will vary between plants because it depends on the presence of other processes on the same site or located nearby.

However, in some cases, residues will have a higher value as a fuel substitute than if they are isolated and purified for reuse. In order to use liquid and/or solid residues as non-conventional fuels, they will need to be of a suitable quality. Otherwise the residue must be considered a waste and its combustion will be classed as waste (co-)incineration. Quality specifications for non-conventional fuels are outside the scope of the LVOC BREF.

2.4.7 Techniques to reduce water usage

Two techniques are considered:

- water-free vacuum generation;
- reuse of water.

Further techniques to reduce water usage are considered in the relevant illustrative chapters.

2.4.7.1 Water-free vacuum generation

Description
Water-free vacuum generation.

Technical description
Water-free vacuum generation can be achieved by using mechanical pumping systems in a closed circuit procedure, discharging only a small amount of water as blowdown, (e.g. closed-cycle liquid ring vacuum pumps) or by means of dry-running pumps. In some cases, waste-water-free vacuum generation can be achieved by, for example, liquid ring vacuum pumps using solvents as the ring medium or making use of the product as a barrier liquid in a mechanical vacuum pump, or by use of a gas stream from the production process.

Achieved environmental benefits
Reduced water consumption, reduced waste water volumes, and the possibility to recover/reuse materials from the ring medium.

Environmental performance and operational data
The waste water discharge amounts to less than 5 % of that of once-through systems.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
The technique is generally applicable when equipment is new or replaced. It is not applicable for large flows or when gases contain particulates, significant quantities of condensable liquid or corrosive substances.

Economics
No information provided.

Driving force for implementation
No information provided.

Example plants
Aromatic plants.

Reference literature
[198, UBA DE 2009].

2.4.7.2 Reuse of water

Description
Reuse of water.

Technical description
Reuse of water from washing, rinsing and equipment cleaning within the production process. With further treatment of some waste water streams, they can be used as boiler feed water, displacing other sources of water, thereby reducing consumption.

Achieved environmental benefits
Reduced water consumption, reduced waste water volumes, and the possibility to recover/reuse materials from the wash water.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
The technique is generally applicable for new units provided that the waste water can be treated sufficiently to achieve the required quality. For existing units, the applicability may be limited by the availability of facilities for collection, buffering and/or the storage of waste water.

Economics
No information provided.

Driving force for implementation
No information provided.

Example plants
Aromatic plants.

Reference literature
No reference literature provided.

2.4.8 Techniques to reduce waste generation

LVOC production sites have the potential to generate a wide range of wastes, many of which are classified as hazardous, e.g. solvents (halogenated, non-halogenated), organic liquids, wash water, sludge from effluent treatment, salt solution, residues from distillation columns, tars, waxes, sludge, chars, spent catalysts and off-specification products.

The following hierarchy of measures should generally be applied:

- prevention;
- preparation for reuse;
- recycling;
- energy recovery;
- disposal.

Residues from LVOC processes may be by-products or wastes. By-products with some economic value may be produced as a consequence of the process route followed and, whilst these are not intentionally produced, they are an integral part of the production process and can often be used directly as raw materials in other LVOC processes. However, where the further use of liquid and solid by-products is uncertain, they may need to be regarded as wastes.

Techniques to maximise the conversion of raw materials to products, co-products and by-products generally fall within the prevention part of the waste hierarchy. As such, this is linked closely with resource efficiency.

Techniques for reuse, recycling or recovery of residues include:

- reuse: regeneration of adsorption media and catalysts;
- recycling: of spent catalysts;
- recovery: sending liquid or solid residues from the chemical process to be burnt as fuel in a combustion plant in order to recover their calorific value.

The CWW BREF describes techniques for the reuse/recycling of used containers/drums and 'soft' packaging materials so the techniques are not repeated here.

The CWW BREF describes techniques for the treatment and disposal of waste water treatment sludge so the techniques are not repeated here.

Where reuse, recycling or recovery is not achieved, disposal will normally be by landfill or incineration.

2.4.8.1 Waste prevention

2.4.8.1.1 Use of inhibitors in distillation systems

Description
Addition of polymerisation inhibitors to distillation systems.

Technical description
Selection (and optimisation of dosage) of polymerisation inhibitors that prevent or reduce the generation of residues (e.g. gums or tars).

The optimisation of dosage may need to take into account that it can lead to a higher nitrogen and/or sulphur content in the residues which could interfere with their use as a fuel. For example, sulphur was used extensively as a polymerisation inhibitor/retarder. It is effective but the residue leaving the distillation train contained so much sulphur that it was not environmentally acceptable as fuel. Newer inhibitors, mostly nitrogen-containing organic compounds such as dinitrophenol and dinitrocresol, have been developed to replace sulphur.

Achieved environmental benefits

- Higher product yields.
- Reduction in the generation of waste (or non-conventional fuels if the oligomer is burnt).

Environmental performance and operational data
It is important to select the most suitable inhibitor and optimise the dosing regime: a higher dose rate will reduce gum or oligomer formation but can also increase the sulphur content of the process outputs.

Cross-media effects
Potential for increased emissions to air from the combustion of the inhibitor-containing residue.

Technical considerations relevant to applicability
No information provided.

Economics
Higher yield resulting in lower operating costs.

Driving force for implementation
Lower operating costs.

Example plants
Styrene production plants.

Reference literature
No reference literature provided.

2.4.8.1.2 Minimisation of residue formation in distillation systems

Description
Minimisation of high-boiling residue formation in distillation systems.

Technical description
A group of distillation strategies, covering both design and operation, that reduce temperatures and residence times, e.g. installing packing rather than trays to reduce the pressure drop liquid hold-up and operating under vacuum rather than at atmospheric pressure to reduce the operating temperature.

The feed purity should also be taken into account, since the presence of some impurities can promote the formation of cross-linked polymer which results in heavy insoluble fouling.

Achieved environmental benefits

- Higher product yields.
- Reduction of the generation of oligomers that are then used as non-conventional fuels.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
The technique is only applicable to new distillation units or major plant upgrades.

Economics
Lower operating costs.

Driving force for implementation
Higher product yields and lower operating costs.

Example plants
No information provided.

Reference literature
No reference literature provided.

2.4.8.1.3 Material recovery

Measures to recover feedstock, co-products or by-products from residues. See the CWW and LCP BREFs for use of tar as a fuel for energy generation.

Description
Recovery of material from residues, e.g. by distillation or cracking.

Technical description
Organic materials (i.e. raw materials, products and by-products) are recovered from residues by separation (e.g. distillation) or conversion (e.g. thermal/catalytic cracking, gasification, hydrogenation).

For material recovery in phenol production, see Section 8.4.5.

For material recovery in TDI production, see Section 10.4.5.

Achieved environmental benefits
The amount of residues and the consumption of feedstock are reduced.

Environmental performance and operational data
No information provided.

Cross-media effects
Increased consumption of energy (steam).

Technical considerations relevant to applicability
Generally applicable to new plants or retrofits of existing plants.

Economics
Recovery is carried out when the value of the substances recovered exceeds the energy and processing costs of recovering them, taking into account:

- increased energy and processing costs (for recovery operations);
- reduced material costs;
- reduced costs of residue disposal.

Driving force for implementation
Economics.

Example plants
No information provided.

Reference literature
Provided in the material recovery sections of a number of the illustrative chapters.

2.4.8.1.4 Catalyst and adsorbent regeneration

Description
Catalyst and adsorbent regeneration.

Technical description
The technique involves the regeneration of catalysts and adsorbents, e.g. using thermal or chemical treatment, to enable their reuse in the process. The treatment required will be specific to the process and/or the catalyst.

Catalyst regeneration can be carried out on or off site. Regeneration of adsorbents (e.g. activated carbon) for reuse in the process is typically carried out on site.

Achieved environmental benefits
Reduction of wastes (spent catalyst material and adsorbents).

Environmental performance and operational data
No information provided.

Cross media effects
Catalyst regeneration processes can generate emissions to air and/or water as well as waste.

Technical considerations relevant to applicability
The applicability may be restricted where regeneration results in significant cross-media effects.

Economics
The economic balance will depend on the costs for regeneration (including the abatement costs for any emissions to air and water and the disposal costs for any wastes) versus the costs for fresh catalyst/adsorbent and disposal of spent catalyst/adsorbent. There are also potential benefits from recovered desorbed material.

Driving force for implementation
Economics.

Example plants
Most of the illustrative processes in this document use catalysts which are regenerated. Regenerative adsorption is used in the production of phenol and hydrogen peroxide for example.

Reference literature
No reference literature provided.

2.4.8.1.5 Use of residues as a fuel

Description
Use of residues as an internal fuel.

Technical description
Some organic residues, e.g. tar, can be used as fuels in a combustion unit located on site.

Achieved environmental benefits

- Reduction of residues that have to be disposed as wastes.
- Reduction in the use of conventional fuels.

Environmental performance and operational data
No information provided.

Cross media effects
Increase in air emissions compared to using conventional fuels.

Technical considerations relevant to applicability
The applicability may be restricted by the presence of certain substances in the residues, making them unsuitable to use in a combustion unit and requiring disposal, e.g halogenated organics or organo-sulphur compounds that will form acid gases, chlorinated organics that might produce PCDD/F.

Economics
The economic balance is based on the costs of recovering compounds from residues and the value of these compounds compared to the value of the residue as a fuel.

Driving force for implementation
Economics.

Example plants
The technique is used, for example, in the production of ethylbenzene and SMPO (Chapter 5) and formaldehyde (Chapter 6).

Reference literature
No reference literature provided.

2.4.9 Techniques to reduce odour

Many of the substances processed or produced in the LVOC sector have the potential to be odorous, for example sulphides, amines and formaldehyde. The subject of odour is complex due to a combination of factors, including the different perceptions of odour by different people and the generally very low concentrations at which odour is perceptible.

The CWW BREF describes a number of techniques for measuring and treating odorous pollution. These are generally not repeated here, except that some of these techniques are also applied more widely for pollution abatement.

Techniques for the treatment of specific odorous streams are:

- adsorption (see Section 2.4.3.5.3);
- thermal oxidation (see Section 2.4.3.5.6);
- absorption or wet gas scrubbing (see Section 2.4.3.6.1);
- biofilters (see the CWW BREF).

Another approach to odour described in the CWW BREF is odour masking, where an odour-masking agent seeks to replace the existing odour with one that is more pleasant. This technique is not generally applied in LVOC production.

If odorous substances are present, the operators should have an odour management plan as part of the environmental management system (EMS). The plan may include all or a combination of the following elements:

- an odour management strategy;
- protocols for carrying out odour monitoring;
- a protocol for response to identified odour events;
- an ongoing odour prevention and elimination programme designed to identify the location, nature, emission and dispersion of on-site odours; to characterise the odours and implement elimination or reduction measures;
- an implementation plan and timetable;
- a reporting programme;
- a review programme.

Further details on odour management plans can be found in the CWW BREF. No further elaboration on odour control is included in this document.

2.4.10 Techniques to reduce noise and vibration

Noise and vibration are defined as pollution under Article 3(2) of the IED. Some noise is a constant feature of most LVOC installations, but particular issues may arise from equipment such as compressors, pumps, flares and steam vents. The techniques listed below are described in full in the CWW BREF and are considered generally applicable across the LVOC sector.

A combination of techniques can be used to reduce noise and vibration, for example:

- noise prevention by suitable construction (e.g. prevention of resonant vibration);
- selection of equipment with inherently low vibration (e.g. steadily running machines instead of pulsating machines; screw compressors instead of reciprocating compressors);
- sound absorbers (e.g. for safety valves, combustion machines);
- anti-vibration mountings (e.g. pumps mounted on rubber foundations);
- noise control booth / encapsulation of the noise sources (e.g. compactors, centrifuges);
- disconnection of vibration sources and surroundings (e.g. separate foundations for reciprocating compressor and any connected pipes); and
- consideration at the design stage of proximity to potential receptors (e.g. residential areas).

The application of the techniques listed above should be informed by the noise management plan, which is part of the environmental management system (EMS) and can include all or a combination of the following elements:

- a noise management strategy;
- protocols for carrying out noise monitoring;
- a protocol for response to identified noise complaints;
- an ongoing noise prevention and reduction programme;
- an implementation plan and timetable;
- a reporting programme;
- a review programme.

Further details on noise management plans can be found in the CWW BREF and so are not repeated here.

2.4.11 Techniques to reduce other than normal operating conditions

Emissions (to air or water) or waste can arise during other than normal operating conditions. The type (pollutants, flow, etc.) of these emission streams may be different from those that occur during normal operating conditions. Operators should take measures to reduce both the frequency of these events and the impact they have on the environment.

Competent authorities may wish to set permit conditions to control other than normal operating conditions, possibly including emission limit values. Where relevant, these would be expressed as BAT-AEPLs since BAT-AELs only apply under normal operating conditions.

Other than normal operating conditions can be broadly divided into planned and unplanned events.

2.4.11.1 Planned other than normal operating conditions

Planned events include:

- start-up and shutdown;
- reduced rate or idling operation;
- replacement/renewal of catalysts or media used for the abatement of emissions;
- decoking of crackers (see Chapters 3 and 11); and
- the definitive cessation of activities (which is not covered in this BREF).

Techniques that can be applied are:

- optimisation of the run time of the plant;
- planning of events for shutdown periods;
- including in the process design features for start-up and shutdown, e.g. ensuring shared vent/treatment systems can deal with start-up/shutdown loads.

2.4.11.2 Unplanned other than normal operating conditions

Unplanned events include:

- malfunction of process utilities (e.g. loss of electricity, water, vacuum);
- malfunction of process equipment (e.g. leakages);
- malfunction of abatement plant;
- operator error and accidents.

This section contains techniques which are applied widely across the LVOC sector to reduce either the frequency or consequences of these events. These techniques are sometimes applied individually, sometimes in combination. Full details on almost all of these techniques are available in the CWW BREF. This section seeks to elaborate further, where appropriate, on their specific application within the LVOC sector. Further elaboration and some specific examples may also be found in the illustrative chapters of this document.

Techniques considered in this section are:

- corrosion prevention;
- reliability programmes;
- back-up systems.

The application of the techniques listed above should be informed by a risk assessment to identify those assets whose malfunction or failure poses the greatest risk to the environment. The identification of critical assets enables the application of appropriate measures to reduce the likelihood of failure or minimise the consequences should failure occur. Techniques that could be applied include the following:

- HAZOP (Hazard and Operability) studies – the scope of these studies can be extended to include environmental as well as safety risks.
- FMEA (Failure Mode Effects Analysis) or QRA (Quantitative Risk Assessment) based on operational or industry data. Quantitative techniques are only likely to be applicable to those risks showing the most significant consequences from malfunction or failure.

Each of the illustrative chapters in this document identifies those assets considered ‘critical to the environment’ based on the answers given in the questionnaires.

2.4.11.2.1 Corrosion prevention

Description
Corrosion prevention.

Technical description
A group of techniques that prevent or reduce corrosion, which include material choice, personnel training, preventive maintenance and analysis of any incidents and malfunctions.

Achieved environmental benefits
Reduced levels of corrosion will lead to fewer leaks of chemicals from equipment to the environment (air, water or land) and reduce the likelihood of equipment failure. Tools to prevent and minimise leaks include: periodic thickness testing, fugitive emissions reduction programme, field detectors and alarms, cooling water monitoring and treatment and the monitoring of process streams for contaminants and corrosion products. Operating procedures should also describe how personnel training is carried out for this topic.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Applicable to those assets, systems, units or equipment that have been identified as ‘critical to the environment’ through a risk assessment or identified in the relevant chapter of this document.

Economics
No information provided.

Driving force for implementation
Reduction of corrosion leads to higher plant uptime and fewer shutdowns.

Example plants

- TDI and MDI production. The use of hydrochloric acid and high reaction temperatures necessitates the use of corrosion-resistant metallurgy.
- Aromatics production. Anti-corrosion treatment is used upstream to avoid corrosion products acting as a catalyst to polymerisation reactions in the reactor.
- Formaldehyde manufacture. Formaldehyde solutions corrode carbon steel so all exposed pipework must be made of corrosion-resistant materials such as stainless steel.
- Ethylene production. The chlorine content in fresh benzene is controlled by lab analysis; recycled and fresh benzene must be dried thoroughly prior to entering the reactor to prevent corrosion.

Reference literature
No reference literature provided.

2.4.11.2.2 Asset reliability programme

Description
A group of managerial and operational techniques to improve plant and equipment reliability that are part of the safety (and environmental) management system.

Technical description
These managerial and operational measures normally include continuous improvement using statistical tools. Provision of quantitative minimum targets (e.g. mean time between failures or failure rate) is not sufficient; reliability requirements should drive a system design to incorporate features that prevent failures from occurring or limit consequences of failure. These procedures will also describe how to achieve a lower environmental impact during these events by using one or more of the following techniques:

- a loss prevention strategy;
- protocols for monitoring plant and equipment reliability;
- an ongoing preventative maintenance programme;
- analysis of incidents and malfunctions;
- an implementation plan and timetable;
- a reporting programme;
- a review programme.

Achieved environmental benefits
No information provided.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Applicable to those assets, systems, units or equipment that have been identified as ‘critical to the environment’ through a risk assessment or identified in the relevant chapter of this document.

Economics
No information provided.

Driving force for implementation
No information provided.

Example plants
No information provided.

Reference literature
No reference literature provided.

2.4.11.2.3 Back-up systems for environmental protection

Description
Back-up systems whose primary purpose is to maintain environmental protection when the primary sytem fails.

Technical description
The technique consists of the building and maintenance of a back-up system, e.g. a waste gas treatment system, to ensure the availability of this critical service.

Achieved environmental benefits
Environmental protection is achieved for a greater proportion of the operating time of the plant.

Environmental performance and operational data
No information provided.

Cross-media effect
No information provided.

Technical considerations relevant to applicability
The need for a back-up or standby plant will be determined by the results of an environmental risk assessment. Back-up systems are only likely to be required for those plant items identified as critical to environmental protection.

Back-up systems may be installed to improve the economic performance of the plant, by reducing shutdowns or the production of off-specification products. Alternatively they may be installed to improve plant safety, by reducing shutdowns or deviations from normal operating conditions. These production back-up and safety back-up systems may have a secondary benefit of maintaining good environmental performance.

Economics
Back-up or standby systems installed primarily for environmental protection may add significantly to the cost, especially for small emissions released during start-ups and shutdowns.

Driving force for implementation
Improvement of environmental performance and compliance with regulatory requirements.

Example plants
Some plants producing EDC/VCM have both a thermal oxidiser as the end-of-pipe treatment for vent gases and an incinerator for destroying liquid wastes. In the event that the thermal oxidiser is out of service, the incinerator can be used to combust the waste gases, and the liquid wastes stored until the thermal oxidation plant comes back on stream.

Reference literature
No reference literature provided.

2.5 Emerging techniques

This generic section on emerging techniques contains several techniques that are not limited to specific chemical processes but could instead be generally applicable for the whole sector.

2.5.1 Waste gas treatments

2.5.1.1 Wet scrubbing with NO_X removal using ozone

Description
Ozone is added in a wet scrubber to remove NO_X, in order to oxidise the NO_X to soluble, higher nitrogen oxides. Ozone is generated on site using an ozone generator. Nitric acid is formed.

Commercially developed
Yes. Reference plant: Texas City, US (Marathon).

Technical considerations relevant to applicability
There is an explosion risk associated with adding oxygen/ozone to a stream containing flammable hydrocarbons that may reduce the applicability for LVOC processes.

Level of environmental protection
Reduction of NO_X.

Cost savings compared to existing BAT
Ozone generation is expensive so this technique may be limited to streams with a low flow rate.

Chance of becoming BAT in the future
High.

When it might become commercially available
Now.

References
[174, Billemeyer 2008].

2.5.1.2 Ceramic filters

Description
Ceramic membrane filters, which are superior in terms of resistance against heat, corrosion and solvents, are widely used for filtering. As the structure of the membrane is hardly changed by pressure and heat, it can be used for a long time.

Ceramic filters can also contain embedded nano-catalyst particles, e.g. in order to reduce NO_X emissions by SCR. This allows for lower temperatures in comparison to conventional SCR units.

Commercially developed
Yes. Widely used according to the reference literature. The REF BREF refers to NGK in Japan as a reference plant.

Level of environmental protection
No information on dust removal was provided. For SCR, NO_X removal rates of over 90 % can be achieved.

Cost savings compared to existing BAT
No information provided.

Chance of becoming BAT in the future
High.

When it might become commercially available
Now.

References
[173, Gravley et al. 2013].

2.5.2 Waste water treatments

2.5.2.1 Falling film contactor to remove impurities by extraction

Description
A falling film contactor increases the mass transfer rate between immiscible liquids (typically a hydrocarbon and water/aqueous solution) using a vertical cylinder containing metal fibres.
When used for waste water treatment, pollutants in the water are transferred into the hydrocarbon phase.

The aqueous phase adheres to (wets) the metal fibres and it flows down the length of the fibres by a combination of gravity and interfacial drag between the two immiscible phases. Hydrocarbon also flows through the cylinder co-currently and in between the aqueous-wetted fibres. The large surface area and tight packing of the metal fibres bring the ultra-thin falling films of the aqueous phase into close contact with the hydrocarbon phase. The interfacial surface area produced is an order of magnitude greater than in conventional extraction devices, allowing impurities to easily diffuse between phases. The use of a falling film also improves the efficiency of the subsequent phase separation process.

Commercially developed
Yes. Reference plant: Petrotel (Lukoil).

Level of environmental protection
No information provided.

Cost savings compared to existing BAT
No information provided.

Chance of becoming BAT in the future
No information provided.

When it might become commercially available
Readily available.

References
[175, Merichem Comp 2015].

3 LOWER OLEFINS

3.1 General information

The lower olefins are a very important group of substances for the chemical industry; they are the primary feedstock for most plastics, polymers and man-made fibres. Lower olefins comprise a range of unsaturated hydrocarbons, primarily **ethylene** (which is the largest volume industrially produced organic material), **propylene**, **butylenes** and **butadienes**.

The majority of **ethylene** that is produced is used for the manufacture of polyethylene, although ethylene also plays an important role in the manufacture of polystyrene (via ethylbenzene and styrene – see Chapter 5), glycols (via ethylene oxide – Chapter 7) and PVC (via 1,2-dichloroethane and vinyl chloride – see Chapter 11). The primary use of **propylene** is the manufacture of polypropylene. However, the manufacture of other important products, such as acrylic esters (via acrylic acid), phenol and acetone (via cumene), acrylonitrile fibres, butanol and ethylhexanol (via butyraldehyde) and propylene glycol (via propylene oxide), also relies on propylene. The primary use of **butadiene** is the manufacture of styrene/butadiene rubbers and polybutadiene rubbers and latexes. However, butadiene also plays a role in the production of adiponitrile, which is the precursor in the manufacture of nylon. The primary use of **butylenes** is the manufacture of synthetic rubbers.

Steam cracking is currently the most commonly applied technology for the production of lower olefins in Europe and is the process described in detail in this chapter. In 2013, there were in excess of 45 (ethylene) steam crackers (with one or more furnaces) operating in plants within the EU. Steam cracking involves the high-temperature pyrolysis ('cracking') of a mainly saturated hydrocarbon feedstock in the presence of steam. The cracked co-products that result are predominately lower olefins, but a range of other co-products will also be formed during the process, including hydrogen, methane, alkynes and alkanes. The range of saturated hydrocarbon feedstocks that can be used for steam cracking is potentially very wide. In Europe, liquid naphtha (from crude oil refining) is by far the most important feedstock; other feedstocks (such as gas oil, LPG and ethane) can also be used. Whilst these other feedstocks are less significant in Europe, the increasing use of ethane derived from US shale gas is having a significant impact on the development and economics of the sector [70, Zimmermann et al. 2009], [71, Grub et al. 2011], [83, CEFIC 2013], [78, CEFIC 2013].

In 2013, the production capacity of lower olefins in Europe was approximately 25 million tonnes of ethylene, which was about a quarter of global capacity. However, production capacity is increasing in all parts of the world except Europe, which is static or in slow decline and so the European share of global production is expected to fall. Lower olefin production in 2013 included approximately 19 million tonnes of ethylene and approximately 10 million tonnes of propylene, with smaller quantities of butadiene and butylenes produced. European production of lower olefins is summarised in Table 3.1 below [73, Siemens 2007].

Table 3.1: Producers of lower olefins in the EU (2015)

Country	City	Operator	Capacity (t/yr)
Austria	Schwechat	OMV	500 000
Belgium	Antwerp	BASF	1 080 000
	Antwerp	TOTAL Olefins Antwerp	610 000
	Antwerp	TOTAL Olefins Antwerp	550 000
	Kallo	Borealis	480 000
Czech Republic	Litvinov	Unipetrol	544 000
Finland	Porvoo	Borealis Polymers Oy	420 000
France	Berre	LyondellBasell	470 000
	Dunkirk	Polimeri Europe France	380 000
	Feyzin	A.P. Feyzin	250 000
	Gonfreville	Total Petrochemicals	525 000
	Lavera	Naphtachimie	740 000
	ND Gravenchon	ExxonMobil	425 000
Germany	Boehlen	Dow Olefinverbund GmbH	565 000
	Burghausen	OMV	450 000
	Köln-Worringen	INEOS Olefins	1 165 000
	Gelsenkirchen	BP Refining & Petrochemicals	1 050 000
	Heide	Klesch	100 000
	Ludwigshafen	BASF SE	620 000
	Munchmunster	LyondellBasell	400 000
	Wesseling	LyondellBasell	1 040 000
	Wesseling	Shell Deutschland Oil GmbH	260 000
Hungary	Tiszaujvaros	TVK	665 000
Italy	Brindisi (BR)	Versalis	468 000
	Priolo Gargallo (SR)	Versalis	558 450
	Porto Marghera (VE)	Versalis	563 200
The Netherlands	Geleen	SABIC Hydrocarbons	1 351 000
	Moerdijk	Shell Nederland Chemie	910 000
	Terneuzen	Dow Benelux b.v.	1 825 000
Poland	Plock	PKN Orlen	700 000
Portugal	Sines	Repsol Polímeros, Lda	1 000 000
Slovakia	Bratislava	Slovnaft	220 000
Spain	Puertollano	Repsol Petroleo	102 000
	Tarragona	Dow Chemical Ibérica	675 000
	Tarragona	Repsol Petroleo	702 000
Sweden	Stenungsund	Borealis AB	625 000
United Kingdom	Grangemouth	Ineos Olefins	700 000
	Mossmorran	ExxonMobil/Shell	770 000
	Wilton	SABIC UK Petrochemicals	865 000
TOTAL			25 323 650

Source: [128, Petrochemicals Europe 2016] amended by TWG comments.

Lower olefin production via the steam cracking process is a mature technology that has been the industry standard for over 50 years. Steam crackers are very large complex plants that involve significant investment costs and, since their products are commodities, any investments in new production capacities are heavily dependent on global market prices and economics – therefore no new crackers have been built in Europe in the past 10 years. However, improvements continue to be made in furnace design and in product separation. The steam cracking process is generally considered to be of strategic importance in maintaining a strong chemical industry.

However, lower olefins are sold on chemical specification and competition between producers is geared heavily towards price and margins are low.

Of the lower olefin production plants in the EU, the majority of installations are located on large chemical sites and/or refinery sites. Among the responders to the data collection, 29 plants reported sharing the site with other activities, while 7 plants were reported as stand-alone [83, CEFIC 2013].

Key environmental issues

The key environmental issues for the production of lower olefins are:

- emissions to air of nitrogen oxides (NO_X) and other combustion gases from the cracking furnaces;
- energy consumption and efficiency.

Other environmental issues include:

- emissions to air of dust from the decoking of cracker tubes;
- emissions to air of VOCs from diffuse sources;
- emissions to water of organic substances and suspended solids;
- the production of hazardous wastes [72, MIGA 2000].

3.2 Applied processes and techniques

3.2.1 Process options

The principal options for the production of lower olefins are:

- steam cracking;
- fluid catalytic cracking;
- ethanol dehydration;
- propane dehydrogenation;
- Fischer-Tropsch conversion of syngas;
- methanol-to-olefins.

Of these, the most commonly applied process is steam cracking and this is the only process described in detail in the subsequent sections of this chapter. The others are briefly reviewed below.

i) Fluid catalytic cracking (FCC)

A way to produce **ethylene** and **propylene** is as co-products during fluid catalytic cracking and in particular by the use of Enhanced FCC. As FCC is integrated within refinery operations, it is described in the REF BREF. FCC is therefore not considered further in this chapter.

ii) Ethanol dehydration

Ethylene can be produced by the catalytic dehydration of ethanol. In this process, heated ethanol is passed through a heated heterogeneous acidic catalyst. Unreacted ethanol is then recycled, while the ethylene is separated off with other gaseous impurities. The increase in bioethanol production has sparked interest in this route. However, the centres of bioethanol production are largely outside Europe, and it is not certain that this route will take hold to a great extent in Europe. In 2013, there were no ethanol dehydration facilities operating in Europe. This process is therefore not considered further in this chapter.

iii) Propane dehydrogenation

Propylene can be produced by the dehydrogenation of propane. In this process, heated propane (or a propane-rich feed) is passed through a heated heterogeneous catalyst. The process gases are then compressed and cooled to allow the separation of hydrogen, methane, and C_2 components. The C_3 fraction that remains is fractionated to allow the propylene to be isolated, and the remaining C_3 components to be recycled to the start of the process.

In 2007, there were only two propane dehydrogenation plants operating in Europe. In view of this limited application, this process is not considered further in this chapter.

iv) Fischer-Tropsch conversion of syngas

A range of alkenes can be produced during Fischer-Tropsch reactions. In overall terms, the Fischer-Tropsch process involves the catalysed reaction of CO and H_2 to form hydrocarbons. The majority of the hydrocarbons that are formed are alkanes; however, the relative quantity of alkenes produced can be enhanced under certain circumstances, and with certain catalysts.

In 2013, there were no plants in Europe employing Fischer-Tropsch conversion of syngas for the production of lower olefins. This process is therefore not considered further in this chapter.

v) Methanol-to-olefins

Both **ethylene** and **propylene** can be produced by a methanol-to-olefin process. In this process, methanol is passed through a heterogeneous catalyst, and a mix of both ethylene and propylene result. In 2013, there were no methanol-to-olefin plants operating in Europe. This process is therefore not considered further in this chapter.

3.2.2 Steam cracking process

Steam cracking is currently the most commonly applied technology for the production of lower olefins employed in Europe. It involves the high-temperature pyrolysis (‘cracking’) of a saturated hydrocarbon feedstock in the presence of steam. The cracked co-products that result are predominately lower olefins (ethylene, propylene, butylenes and butadienes), but a range of other co-products and by-products will also be formed during the process, including hydrogen, methane, alkynes and alkanes.

A typical steam cracker furnace is shown in Figure 3.1 below.

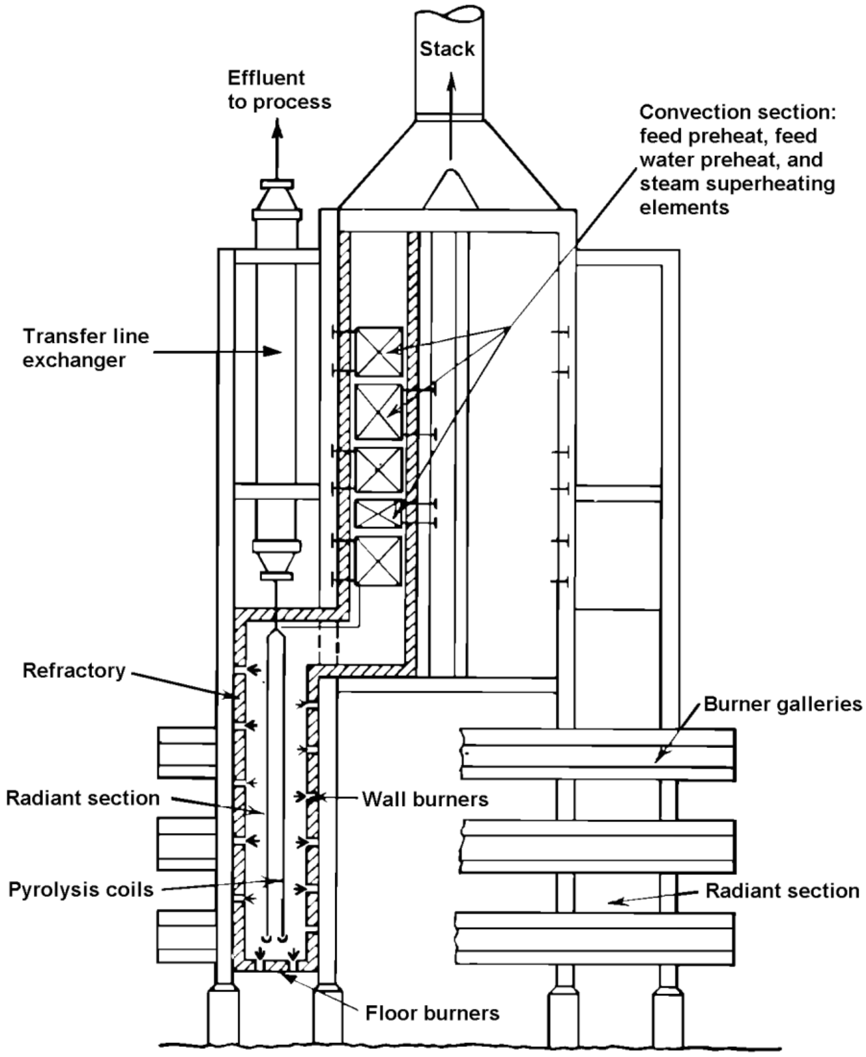


Figure 3.1: Typical ethylene steam cracker furnace

Although the range of saturated hydrocarbon feedstocks that can be used for steam cracking is very wide, an individual steam cracker will have a fixed operating window in terms of the feedstocks that it can utilise. The choice of feedstock (and therefore potentially of plant design) is heavily influenced by market factors and the availability of supplies [70, Zimmermann et al. 2009], [71, Grub et al. 2011].

Most of the technologies used in steam cracking processes are licensed by a small number of contracting firms [70, Zimmermann et al. 2009]. Although these firms' designs differ from each other in some respects, they all include the following general sequence of process steps, as typically seen in Figure 3.2 and Figure 3.3:

- pyrolysis;
- primary fractionation;
- gas clean-up;
- co-product fractionation.

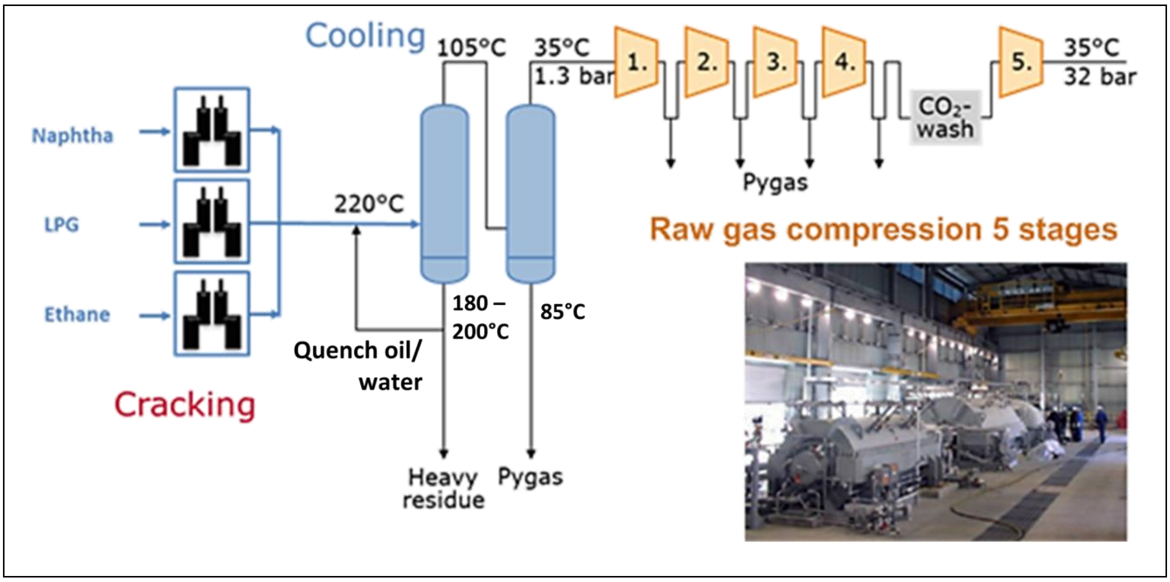


Figure 3.2: Process flow diagram for lower olefin production stages of cracking, cooling and raw gas compression

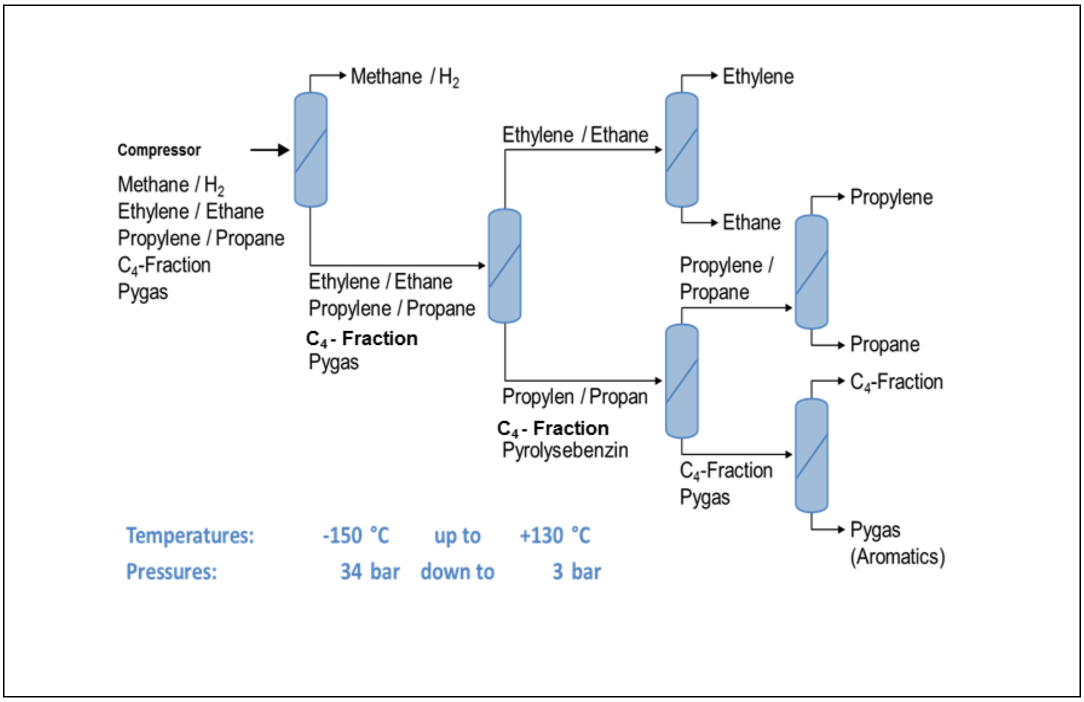


Figure 3.3: Process flow diagram of the lower olefin separation stage (with front-end demethaniser)

3.2.2.1 Pyrolysis of hydrocarbon feedstock

The saturated hydrocarbon feedstock is preheated (usually in separate heat exchangers by waste heat) and vaporised with superheated steam before passing into radiant tubes where the cracking reactions take place. A number of factors (e.g. the temperature profile and residence time of the feedstock and the quantity of steam within the tubes) influence how the cracking reactions proceed, and therefore the mix of co-products that is ultimately obtained.

As steam cracking is a highly endothermic and high-temperature process, the tubes must be externally heated on a continuous basis. This is achieved by locating the tubes within a furnace that is heated using oil-fired or gas-fired burners. Numerous burners are located within these furnaces in order to ensure that the desired temperature profile is achieved within the tubes. Tube metal temperatures of up to 1 100 °C are achieved; the highest reported bridgewall temperature under normal operating conditions is 1 280 °C.

Although a range of feedstocks can be used, an individual steam cracker will have a fixed operating window in terms of the feedstocks that it can utilise. Furthermore, there is an upper boiling point limit of approximately 600 °C with the current technology, and the use of heavier feedstocks would necessitate the use of different furnace or pretreatment technology to that currently employed in order to handle higher boiling feedstocks. Various techniques employing fluidised beds, molten salts, recuperators, and high-temperature steam have been investigated, but none of these have attained commercial significance.

Typical feedstocks and their sulphur contents, as gathered in the data collection, are shown in Table 3.2 below.

Table 3.2: Feedstock characterisation and sulphur content (breakdown of the data reported by the plants, representing averages over a year)

Feedstock and sulphur content	Minimum	Maximum	Average
Use of heavy (> naphtha) feedstock (% per year)	0	93.8	13.4
Avg. S content of heavy feedstock (wt-%)	0.00	0.2	0.042
Use of naphtha feedstock (% per year)	0.8	100.0	61.1
Avg. S content of naphtha feedstock (wt-%)	0.001	0.08	0.018
Use of gas feedstock (% per year)	0	100.0	21.5
Avg. S content of gas feedstock (wt-%)	0.00	0.019	0.004
Source: Data collection, [79, Kaiser 2013]			

Emissions to air from the cracking furnace are the most significant environmental impact of lower olefin production. The primary function of the cracking furnaces is to generate the process conditions necessary for the reaction to proceed; it is therefore an example of a combustion process that is within the scope of the LVOC BREF. Where energy recovery from cracking furnaces is integrated with other combustion plants, and depending on the thermal capacity and the level of integration, reference may also need to be made to the LCP BREF. For more information regarding these issues, see Sections 3.4.3.1 and 3.4.4.1.

3.2.2.2 Primary fractionation

The cracked gases are cooled in order to stabilise the cracked gas composition and allow further processing. This is initially achieved by the indirect cooling of the cracked gases in heat exchangers, which is normally followed by direct-contact cooling involving oil and/or water (water quench), with the exact arrangement depending largely on the type of feedstock.

The cooled cracked gases are then compressed using multistage compressors in order to facilitate the subsequent handling and separation of the various co-products within the cracked gases. The compressors can be driven by steam turbines or electric motors.

Depending upon the feedstock used, the cracked gases may contain a number of high-boiling components. These will condense out during the cooling and compression steps. Heavier hydrocarbon components such as oil and heavy gasoline are removed at this stage.

3.2.2.3 Clean-up of cracked gases

The cracked gases also contain carbon dioxide and some sulphide species. As these components will cause downstream processing problems (e.g. plugging due to hydrates or hydrogenation catalyst poisoning), and/or adversely affect product quality, they are removed. This is normally achieved by scrubbing the cracked gases with a caustic solution. In some installations, a regenerative amine scrubber is also used prior to the caustic scrubber to reduce the load on the caustic scrubber and facilitate the recovery of sulphur. However, amine scrubbing alone is not normally sufficient to achieve the required level of removal.

The clean-up of the cracked gases is incorporated into the final gas compression stages before co-product fractionation. The exact sequence and positioning will vary from one plant to another, and be dependent on the feedstock profile and technology provider's experience/preference. The acid gas removal system is typically located between the third and fourth, or between the fourth and fifth, compression stages (see Figure 3.2). In all process configurations, acid gas removal must be located upstream of the drying unit in order to avoid the formation of ice and hydrates in the following co-product fractionation steps. The spent caustic is stripped with methane, which is recycled back to the main fuel gas compressor.

The cracked gas also contains some water, being saturated with water before compression and after each intercooler stage. This moisture must be removed before fractionation in order to avoid downstream processing problems such as formation of hydrates and ice. Typically, this is accomplished by chilling and by adsorption on molecular sieves. Older plants also used absorption by a glycol scrubbing system or adsorption on alumina. Drying takes place before the first co-product fractionation step, typically after the last compression stage [70, Zimmermann et al. 2009].

3.2.2.4 Co-product fractionation

A typical distribution of product yield corresponding to different feedstocks is shown in Table 3.3 and Figure 3.4 and Figure 3.5. These co-products are separated using a sequence of splitters and fractionating columns.

The order in which the various co-product fractions are separated is determined by the precise way in which the splitters and fractionating columns are arranged. The options include:

- first separating off methane and hydrogen only (i.e. using a ‘front-end demethaniser’); or
- first separating off methane, hydrogen and C_2 components (ethylene, acetylene and ethane) (i.e. by using a ‘front-end de-ethaniser’); or
- first separating off methane, hydrogen, C_2 and C_3 components (ethylene, acetylene, ethane, propylene, propane and propadiene) (i.e. using a ‘front-end depropaniser’).

The type of front-end splitter arrangement that is used affects the degree of initial refrigeration required, and the subsequent interactions between the refrigeration plants and the fractionation columns. The configuration and the steps may vary from one plant to another. In order to separate methane and hydrogen, a temperature as low as -150 °C is required (see Figure 3.3).
The **alkynes** present in the cracked gases are commonly hydrogenated between the appropriate fractionation steps. Where a front-end de-ethaniser or depropaniser arrangement is used, some of the hydrogen required for this will be present in the cracked gases themselves. However, where a front-end demethaniser is used, all of the **hydrogen** that is separated off will need to be purified before it can be used for hydrogenation. Additional hydrogen may need to be supplied; however, the hydrogen will mostly be supplied from the hydrogen purification stage within the steam cracker process. The amount of **ethane** and **propane**, which are present in the cracked gases, may be increased as a result of any hydrogenation reactions that are incorporated within the process. The ethane and propane that are separated off are normally recycled back to the steam cracker feed. The **methane** that is separated off is normally used as fuel.

The **ethylene** and **propylene** co-products are recovered as the top products from their respective fractionation columns. If the bottom product from the depropaniser is sent to a debutaniser, the top product from the latter is a **mixed C_4 co-product fraction** that requires further processing. The bottom product from a debutaniser (or a depropaniser without a subsequent debutaniser) is called ‘**pyrolysis gasoline**’.

As **butadiene** forms an azeotrope with **butane**, its isolation requires the use of liquid-liquid extraction (e.g. using CAA - cuprous ammonium acetate) or extractive distillation (using a polar solvent such as acetone or DMF - dimethylformamide).

After isolation, the **ethylene** and **certain butenes** obtained can be catalytically converted to **propylene** in order to alter the relative quantities of the various co-products. This process is termed ‘metathesis’. However, this is not commonly incorporated into the steam cracking process.

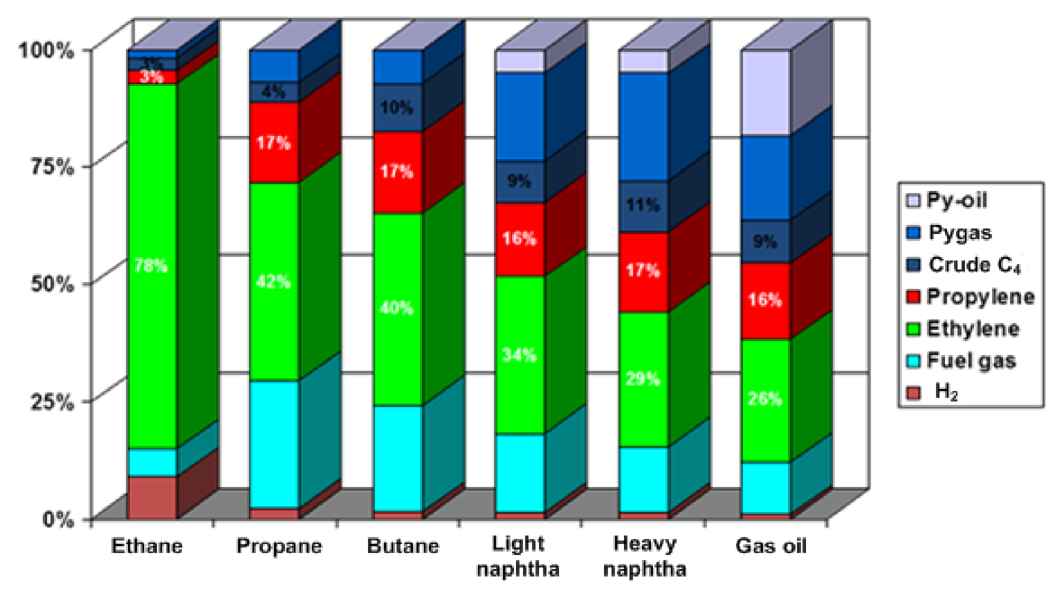


Figure 3.4: Typical total yield of co-products from different feedstocks including C_2-C_4 recycles

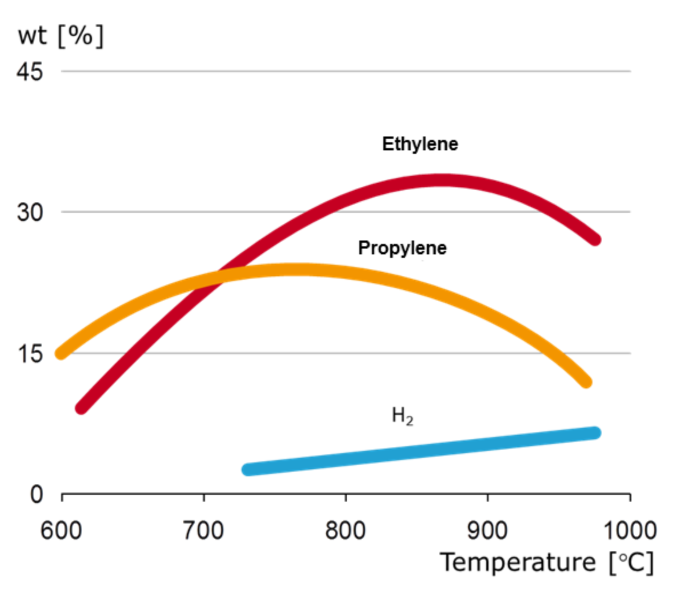


Figure 3.5: Effect of process conditions on product mixture

Table 3.3: Typical 'once-through' product yields (1) from a furnace (%) for different feedstocks

Product	Feedstock (2)				
	Ethane	Propane	Butane	Light naphtha	Gas oil
Hydrogen	4.3	1.3	1.2	0.8	0.5
Methane	4.2	25.2	20.1	13.5	10.9
Acetylene	0.4	0.5	0.8	0.7	0.2
Ethylene	56	40.9	40.4	28.4	20.6
Ethane	30	3.6	3.5	3.9	4.8
Propadiene	0.1	0.5	1.2	0.4	0.5
Propylene	1	11.5	14.4	16.5	14
Propane	0.2	5	0.1	0.5	0.8
Butadiene	1.6	4.5	4.3	4.9	4.9
Butylenes	0.2	1	1.3	5.2	3.9
Butane	0.2	0.1	2	1	0.1
C_5/C_6	1.8	5.9	10.7	3.9	1.9
C_7+ non-aromatics	NA	NA	NA	1.2	2.1
Aromatics	NA	NA	NA	10.5	12.5
< 430 °C	NA	NA	NA	5.2	2.6
> 430 °C	NA	NA	NA	3.4	19.7
Total	100	100	100	100	100

(1) The quoted yields are exemplary and do not reflect the overall yields which are achieved by recycling of species such as ethane.
(2) Not all products indicated in the table are produced at each plant; the products produced are dependent on the feedstock slate and product demand.
Source: 2003 LVOC BREF [190, COM 2003]

3.2.3 Other than normal operating conditions

3.2.3.1 Decoking of the cracker tubes

In addition to start-up and shutdown operations, there is a specific other than normal operating condition that will result in different emissions to those experienced under normal operating conditions. The internal walls of the cracker tubes (radiant coils) gradually become coated with coke during the cracking process. In order to maintain cracker throughput and heat transfer, this coke must be periodically removed.

The periodic removal of coke build-up on the inner surface of the cracker tubes (normally) involves heating the tubes to a temperature much lower than that normally employed for cracking. Air is used to burn off the coke, simultaneously passing steam through the tubes to avoid localised overheating as a consequence of the energy generated from the exothermic reaction of the coke with the hot air. Coil outlet temperatures of up to 800 °C are experienced in steam/air decoking [70, Zimmermann et al. 2009]. According to the data collection, almost all plants carry out steam/air decoking, with only two or three plants using steam-only decoking. Coil outlet temperatures above 1 000 °C are reported to be necessary for effective steam-only decoking.

The decoking process requires lower furnace temperatures and a lower firing rate than normal operating conditions (which should result in lower NO_X emissions), but it is also normally accompanied by higher excess oxygen concentrations (which would give rise to higher NO_X concentrations). In practice, NO_X levels during decoking are similar to those during normal operation.

Decoking is a periodic process. It is considered to be taking place whenever the air/steam mixture is being passed through the tubes. The duration and frequency of these decoking operations vary significantly between crackers, as they depend on a range of operating factors, like the feedstock used, the severity of the cracking conditions, the sulphur content of the feedstock and the furnace design. This in turn impacts on the nature and quantity of coke build-up.

The decoking time typically lasts between 18 and 48 hours. [27, Step 1966] Operators reported varying decoking times and frequencies, such that the total time spent in decoking ranged between 79 hrs/year and 564 hrs/year and the percentage of decoking time was, on average, approximately 3 % of the furnace run time, ranging between 0.9 % and 7.1 % (*Source*: data collection).

During decoking, the outflow of cracker furnaces is diverted to end-of-pipe abatement equipment, either dry cyclones or wet abatement devices for dust. This equipment may be shared between several of the cracker's furnaces. Alternatively this can be routed back to the cracker furnace, although this is less common. The amount of dust for combustion or abatement will vary through the decoking process. In a small number of cases, the exhaust gas is released to atmosphere unabated.

The impact of decoking will therefore be a change in the emissions to air from the cracker furnace and an emission to air from the decoking abatement equipment. Whilst the periodic decoking of the cracker tubes is an inevitable part of the operating cycle of cracker furnaces, the process is considered to be an other than normal operating condition (OTNOC) in that:

- during decoking, the furnace is not being used for production;
- the frequency of decoking and the time needed for decoking represent a relatively small proportion of total operating hours.

These are characteristics similar to those of start-up and shutdown, which are given as examples of other than normal operating conditions in the IED.
Where a number of cracker furnaces share the same flue, it may be that only one of the furnaces is in OTNOC, whilst the remainder are operating normally. The OTNOC condition could therefore impact on the total emissions measured from these plants.

3.2.3.2 Generic other than normal operating conditions

Start-up and shutdown: A start-up period is the period of time that elapses between the first introduction of fuel to the furnace after a shutdown and the establishment of stable production conditions, which can be defined for steam crackers in terms of the following interrelated parameters:

- **Hydrocarbon feed rate:** A hydrocarbon feed of > 70 % of the maximum load is widely considered to represent the end of the start-up phase.
-
- **Product composition:** The achievement of a stable and desired product yield in the process gases leaving the cracker and entering the quench section.
-
- **Firing duty:** Reaching > 70 % of rated thermal output can be used as an indication of when the start-up of a furnace has ceased and normal operation has commenced.
-
- **Downstream operations:** All downstream equipment is in full operation and no process streams are sent to flare – the composition of any recycled fuel gas could be highly atypical during start-up.

Planned shutdowns (e.g. to allow maintenance activities to be carried out) will involve the gradual reduction of both the hydrocarbon and fuel feed rates. A shutdown period is deemed to commence once the hydrocarbon feed rate falls below 70 % of the maximum load, and to finish when the fuel feed to the furnace ceases.

The need for flaring of raw materials can be reduced during start-up and shutdown by reducing the flow rate to the cracked gas compressor (typically to 75 % load) and recycling the off spec streams.

Standby: The furnace is deemed to be in standby mode whenever fuel is being fed to the furnace and the steam cracker is not undergoing normal operation, start-up, shutdown, or decoking. No feedstock is fed to the cracker furnace during this period. This situation could arise between the completion of a decoking exercise and the re-establishment of normal production operations, which are defined in the description of start-up above. During standby periods the fuel addition rate will be significantly reduced, and this will result in significantly lower mass emissions of NO_X. The data collection showed an average total standby duration of 2.18 % a year.

Malfunctions: There are a range of possible malfunctions that could directly or indirectly affect pollutant emissions to air. These could include the failure of air fans, the sticking of dampers/valves, or the sudden (rather than gradual) failure of abatement plant performance.

It is possible that furnaces associated with a cracker will be operating under different regimes (i.e. one or more under normal operating conditions and one or more under other than normal operating conditions) at any one time. Consequently, where emissions from two or more cracker furnaces are handled together, e.g. in a common flue or stack, there may be difficulties in the interpretation of emissions data when monitoring compliance with the BAT-AELs.

3.2.4 Equipment important for environmental protection

The following systems perform critical operations for environmental protection and should have the longest uptime possible:

- process and combustion control equipment (e.g. oxygen and temperature sensors, flue-gas analysers);
- cooling facilities in fractionation sections;
- end-of-pipe abatement equipment.

3.3 Current emission and consumption levels

3.3.1 Emissions to air

Emissions to air arise from the following principal sources:

- combustion of fuels to provide heat to the steam cracker;
- decoking of the cracker furnace tubes.

Other less significant sources of emissions to air may include fugitive releases of VOCs from storage and from equipment operated under pressure.

Whilst emissions to air from combustion processes (other than the steam cracker) are outside the scope of the LVOC BREF, where cracking furnaces are integrated with other energy facilities, depending on the thermal capacity and the level of integration, reference may also need to be made to the LCP BREF, e.g. when a combustion plant and cracker exhaust share the same exhaust flue.

3.3.1.1 Emissions to air from steam cracker furnaces under normal operating conditions

From the data collection, the rated thermal inputs of steam cracker furnaces are in the range of 8–120 MW; the average capacity is around 40 MW. The configuration and layout of these cracker furnaces also show great variability, e.g. a little over half of crackers are fitted with wall burners, around 20 % with floor burners and the rest with both floor and wall burners. Of the 485 cracker furnaces in the survey, only 86 (approximately 18 % of the total) discharge through a dedicated chimney stack, the remainder have two or more cracker furnaces sharing a stack, and only 41 (approximately 8 % of the total) furnaces share a stack with other types of combustion plant.

The combustion gases from a steam cracker furnace are mainly NO_X and CO, but also potentially SO_2 and dust, depending on the type and composition of the fuel burnt. Where selective catalytic reduction (SCR, see Section 2.4.2.1) is used for NO_X abatement, emissions will also contain some ammonia [26, Cheremisinoff 2002].

A general overview of the emissions from cracking furnaces to air compiled in the data collection process is shown in Table 3.4 below. Values in the table show the range of the results obtained (OTNOC events included).

Table 3.4: **Emissions to air from steam cracker furnaces**

Compound	**Emission range (min.–max.) (mg/Nm^3, dry, 3 % O_2)**	**Type of monitoring**	**Analytical methods used (not exhaustive)**
NO_X (expressed as NO_2)	0.1–454 (1)	Continuous	UV, IR, NDIR
	90–160 (2)	Periodic	Chemiluminescence EN 14792; Electrochemical cell
CO	0.1–1881 (1)	Continuous	NDIR; IR
	5–20 (2)	Periodic	EN 15058; ISO 12039
SO_2	2.5–38.5 (1)	Continuous	NDIR IR; EN 14791
		Periodic	NI
Dust	2.8–7.1 (1)	Periodic	EN 13284

(1) Lowest to highest of full data set (maximum values including OTNOC events).
(2) 25th to 75th percentile range of average values.
Source: Data collection

3.3.1.1.1 NO_X emissions

The levels of emissions obtained via the data collection are shown in Table 3.4 above and Figure 3.6 below.

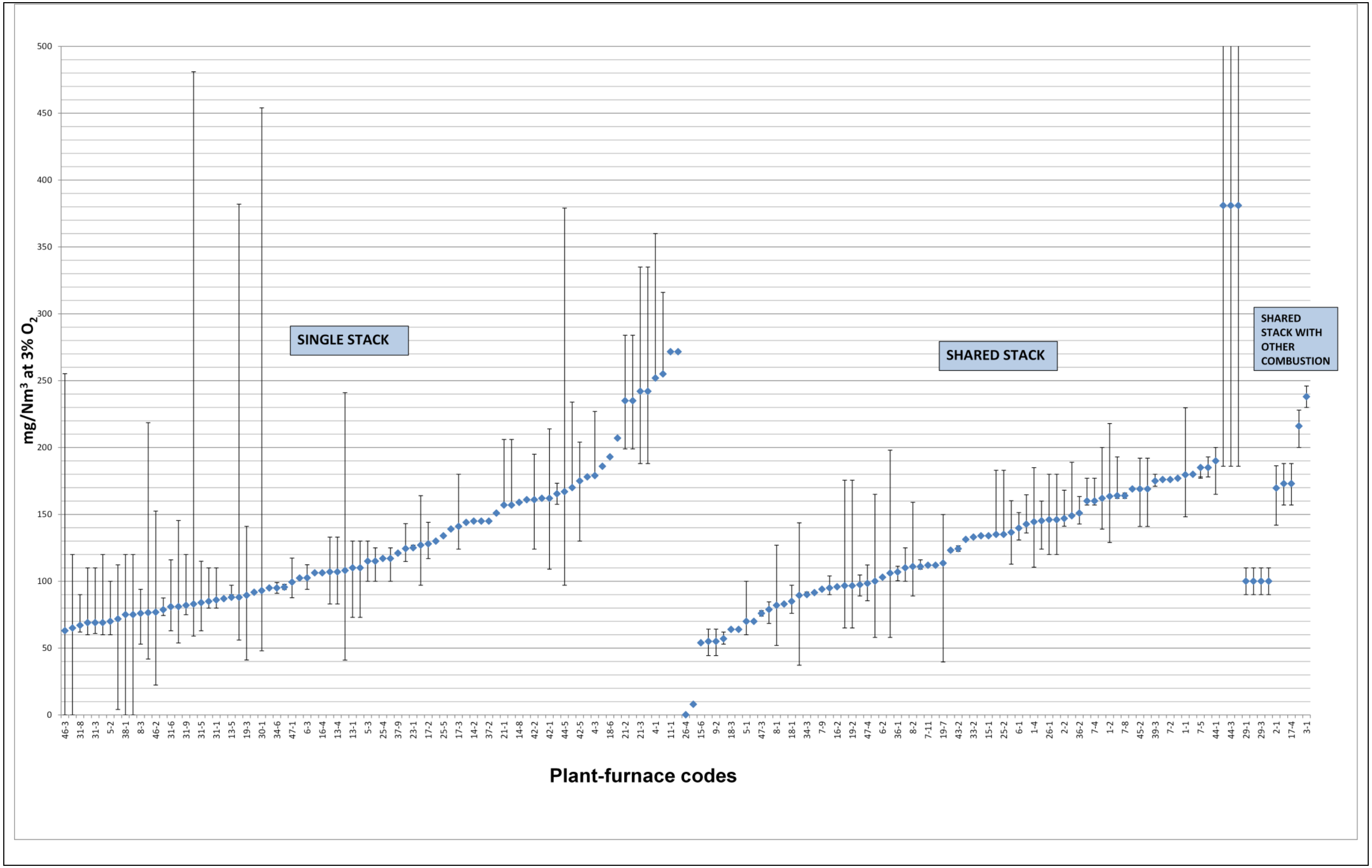


Figure 3.6: NO_X emissions from steam cracker furnaces

NO_X emissions could be directly or indirectly affected by the following contextual factors:

Feedstock: The cracking temperature and the heat for cracking will vary with feedstock. A shorter feedstock chain length can result in both a higher cracking temperature and a higher heat for cracking, but with a lower residence time. Also, the higher the degree of saturation of the feedstock, the higher the heat for cracking. However, a heavier feedstock is likely to produce greater amounts of coke than a lighter feedstock, and the coke produced from a heavier feedstock will also probably have a lower thermal conductivity. The feedstock used is therefore likely to affect both the amount of fuel that is consumed and the furnace temperature profile, although other factors such as load changes and variable severity of cracking may have a greater impact. The feedstock can also have an impact on NO_X emissions if it results in a significant amount of hydrogen in the fuel gas that is being recycled to fire the furnace [81, InterEnerStat 2010], [70, Zimmermann et al. 2009], [28, Ren et al. 2008].

Table 3.5: Use of different feedstock types in lower olefins production

Feedstock type	Number of plants *
Heavy feedstock	11 out of 44
Naphtha	42 out of 44
LPG	39 out of 44
Ethane	32 out of 44
Other (jet fuel and kerosene, FCC gasoline, raffinate, C_5 cut, C_3 cut, off-gas, refinery gas, condensates, pentane, hexane)	14 out 28

* The number of plants using this feedstock type out of the number replying to this question in the questionnaire - many plants use a combination of feeds.

Coke deposition: The amount of coke that builds up on the inner tube wall will adversely affect radiant heat transfer, necessitating a higher furnace temperature (and therefore a higher fuel firing rate) in order to give the driving force necessary to achieve and maintain the desired cracking temperature profile within the tubes.

Fuel: For the steam cracker furnaces covered by the data collection, information on the fuel types used in the furnaces was also collected. The most commonly used fuel is fuel gas recovered from the process streams (or where relevant from a neighbouring refinery). All sites reported using fuel, many use only fuel gas. Use of natural gas and, more rarely, liquid fuels (i.e. pyrolysis gas and recovered pyrolysis oils) is also reported. Natural gas is sometimes also used to augment the supply of fuel gas and at start-up when fuel gas may not be available [82, Brayden et al. 2006]. The hydrogen content of the fuel gas ranged from 0.5 % to 60 % although more typically it is in the range from 5 % to 25 %.

Firing rate: Increasing the firing rate for a given furnace increases the combustion intensity, which has the potential to increase NO_X due to the consequent temperature increase and the possibility of flame-flame interactions. Furnaces should be operated at > 90 % load during periodic emission measurement. Some data sets are based on low throughput data because the ethylene demand in 2013 was low.

Excess air (oxygen): The typical operating range is 2–3 % oxygen excess. Lower excess oxygen improves furnace energy efficiency and lowers the NO_X level but increases the CO level. There is also a serious safety risk (explosion) if substoichiometric conditions occur in a firebox, therefore a minimum level of excess air should be maintained at all times. Higher excess air typically gives higher NO_X levels. Excess air should be controlled at the lowest practical level while respecting limits for safe operation and low CO emissions.

Temperature: An increased firebox temperature will increase the potential for NO_X formation. However, the temperature is not homogeneous within the furnace, and it is likely to be measured at different locations in different furnaces, if at all; it is more normal to measure the temperature of the flue-gas leaving the furnace. However, it is possible to use predictive software to estimate the average flue-gas radiating temperature.

Energy integration: Preheating the combustion air using the flue-gases and/or within the convection zone of the furnace will reduce the fuel demand and could help reduce total cracker emissions. These techniques are also referred to as configuration optimisation. One possible approach involves the use of a gas turbine, the combustion gases from which could be used as cracker furnace combustion air – this could help with the overall emissions and energy efficiency of the process which also includes the combined production of compression power, electricity and steam. However, any form of air preheating can have an impact on NO_X emissions from the steam cracker furnaces.

Plant age and investment history: The age of the furnace (rather than necessarily the cracker) and its post-commissioning investment history will have an indirect effect on emissions, as these will determine the range of techniques that are (or could be) employed, and their effectiveness.

Process perturbations: Any significant disturbance caused by a change in feedstock, feed rate, fuel quality, etc. is likely to have a knock-on effect for the combustion conditions (probably requiring load changes). NO_X emissions are therefore likely to vary due to the inevitable inertia of the combustion control system, which may well be amplified by the size and complexity of the plant. These circumstances do not qualify as other than normal operating conditions, and could last long enough to materially affect an emission concentration that is measured over a 30-minute averaging period. The highest NO_X emissions under normal operating conditions could therefore occur during these circumstances.

3.3.1.1.2 CO emissions

Under normal operating conditions the objective is to achieve low CO emission concentrations, as this is indicative of the achievement of good combustion conditions. In fact, the concentration of CO is often used as a measure of the effectiveness of combustion control, and permits can therefore contain ELVs for CO, or implicitly anticipate their use as part of an operator’s combustion management strategy. However, there can be tension between CO and NO_X emissions, as they can be partially mutually exclusive.

The levels of emissions obtained via the data collection are shown in Table 3.4 above and Figure 3.7 below.

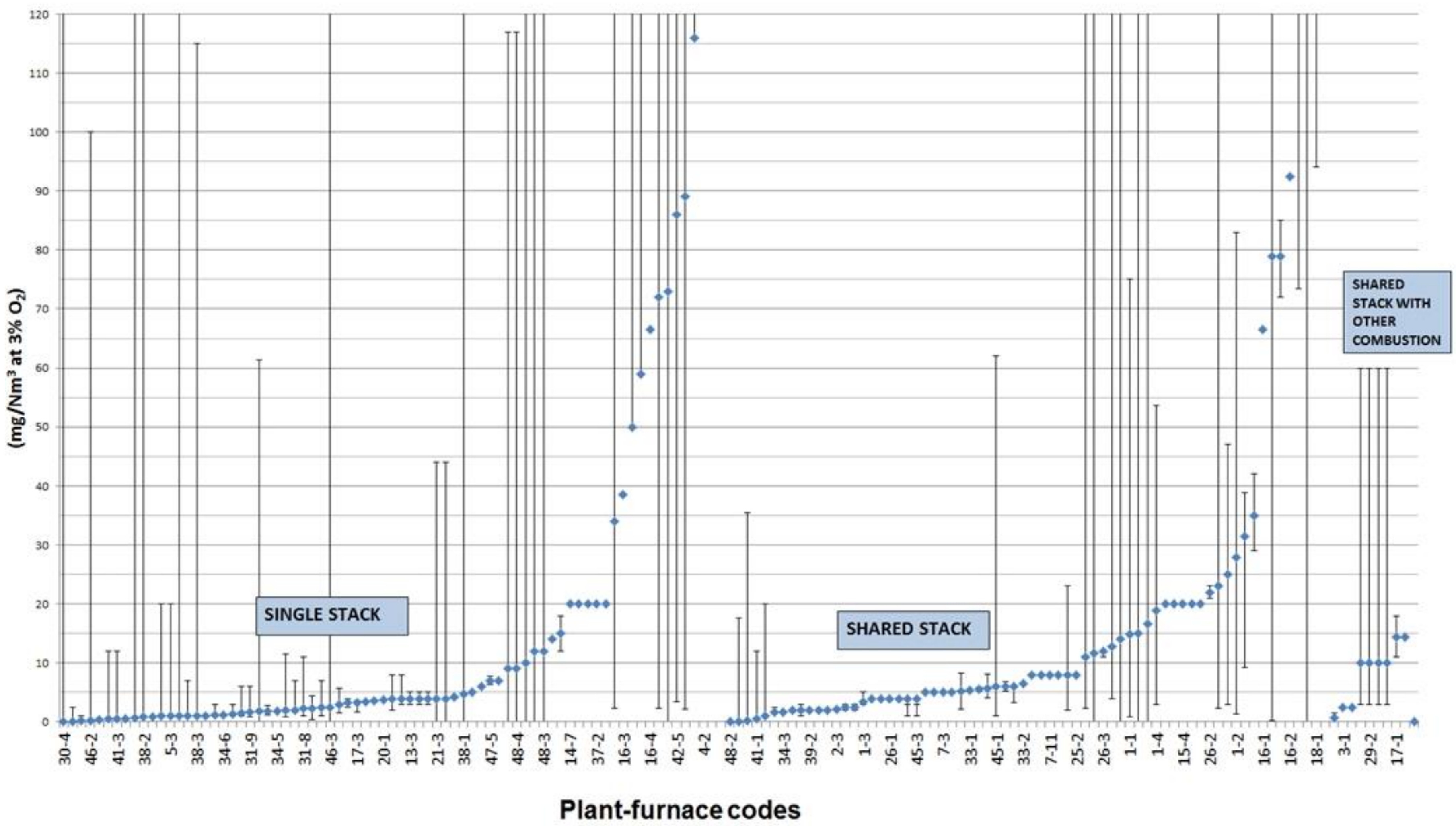


Figure 3.7: CO emissions from steam cracker furnaces

3.3.1.1.3 SO_2 emissions

SO_2 emissions are, in general, totally dependent upon the quantity of sulphur present in the fuel. Lower olefin cracker furnaces operate without abatement of sulphur dioxide emissions, therefore control of sulphur dioxide emissions is achieved by the use of gaseous fuels or fuels with a low sulphur content.

All or part of the fuel used in a cracker furnace is fuel gas from the cracking process. Because H_2S (and other acid gases) must be removed from the cracked gases prior to their downstream processing, this fuel gas should contain low levels of sulphur. However methane used for stripping spent caustic scrubbing liquors, which is then used as part of the fuel in a cracker furnace, will contain some sulphur.

Data on SO_2 emissions from steam cracker furnaces are shown in Table 3.4 above.

3.3.1.1.4 Dust emissions

Dust in emissions to air from combustion processes can include ash components present in the fuel and/or soot formed under certain combustion conditions where liquid fuels are used.

Lower olefin cracker furnaces operate without abatement of dust emissions; therefore control of dust emissions is achieved through the use of gaseous fuels. From the data collection, liquid fuels in steam crackers are only used at three locations and in each case the amount of fuel consumed is less than 20 % of the total, the main fuels being fuel gas and natural gas.

3.3.1.1.5 Ammonia emissions

Ammonia emissions will be a potential issue only where SCR is employed to reduce emissions of NO_X. At the time of writing (2013), very few steam cracker furnaces in Europe use SCR for reducing NO_X emissions; a total of 4 plants, 25 furnaces of 9 different types reported having SCR systems. Based on the data provided by the operators, NH_3 concentrations at the SCR outlet are in the range of 4.6–15.8 mg/m^3 (3 % O_2, dry basis, by continuous monitoring, half-hourly averaging periods).

In order to ensure the efficient reduction of NO_X to nitrogen and water, there will be a residual level of ammonia present in the emitted combustion gases. This is known as ammonia slip. The objective is not to avoid ammonia emissions altogether, but rather to limit them to an accepted cross-media effect of employing SCR to give a net overall benefit. Ammonia slip and NO_X emission are generally cross-related such that an excess of ammonia is likely to result in a low NO_X emission. The results from the data collection on ammonia slip from SCR are shown in Table 3.6 below.

Table 3.6: Ammonia slip from SCR (with half-hourly averaging periods)

	NH_3 concentration at SCR outlet (mg/Nm^3, 3 % O_2, dry)	Average NO_X concentration (mg/Nm^3, 3 % O_2, dry)
Average	9.1	55.0
Maximum	15.8	64.2
Minimum	4.6	44.4
Source: Data collection.		

3.3.1.2 Emissions to air from decoking

Emissions from the furnace side of a steam cracker during the decoking process may differ from those shown in Table 3.4. This is because the decoking process requires a lower furnace temperature and firing rate (20–50 %) than during cracking.

Steam and air are passed through the tubes, and decoking occurs through the (partial) oxidation of the coke and its physical removal by the steam/air flow. Emissions from the process side of the cracker, from decoking the cracker tubes, will contain both dust and carbon monoxide.

The rate of coking and the type of coke formed will be influenced by the nature of the feedstock used and the cracking severity. The coke formed in ethane cracking is very hard and during decoking a significant amount of coke is removed from coils through a spalling mechanism, i.e. the coke breaks away from the tube in small pieces/particles before it has time to burn, and dust emissions can therefore be high. It is also possible for coke particles to break away from the cracker tubes during normal operation and pass out of the cracker with the cracked gases. These will be removed prior to the compression section either in the initial separation columns or via a knockout drum.

Decoking can last for up to 48 hours, with a highly variable dust emissions profile, so measuring emissions over short time periods could give highly variable results. The moisture and oxygen content of the off-gas also change during the decoking cycle.

Minimising emissions from decoking is achieved through a combination of techniques to minimise the rate of coke build-up in the tubes (coke prevention techniques), in order to reduce the frequency of decoking operations, and abatement techniques. These are summarised in Table 3.7 below.

Table 3.7: Coke prevention and abatement techniques and number of sites that reported using these techniques

Technique		**Number (out of 43)**
Coke prevention	Doping feedstock with sulphur compounds	39
	Materials of construction for tubes that retard coke formation (1)	7
	Low-nickel tube composition (1)	3
Decoking method	Maximise burnout of coke with air/steam	39
	Steam-only decoking	2
Abatement	Dry cyclones	12
	Centrifugal washers (Wet cyclones)	18
	Reroute to furnace firebox (2)	4
	No abatement	5

(1) These two are described under the same heading in Section 3.4.1.5.3.
(2) One plant uses a dry cyclone followed by rerouting to the furnace firebox.
Source: Data collection.

As can be seen from Table 3.7, 39 out of 43 installations responding to the questionnaire use sulphur doping to minimise coke build-up and then maximise coke removal during decoking so that the frequency with which decoking is required is minimised.

The principal emissions from decoking are of dust and carbon monoxide. Collected emissions data for both parameters are scarce. Most plants have some form of abatement for the decoke stream (see Table 3.7 above).

3.3.1.2.1 Dust emissions to air from decoking

The commonly applied abatement techniques are dry dust abatement (cyclones), wet dust abatement and routing off-gas from the decoking process to the firebox of the furnace. Burning the decoke off-gas may give rise to an increase in dust emissions from the cracker furnace. There are limited data on dust emissions during decoking.

Table 3.8: Dust emissions to air from decoking

Abatement technique	**Dust emissions**	
	mg/Nm^3 (average over the decoking cycle)	mg/Nm^3 (maximum during the sampling period)
Wet abatement	17–80 (1)	56–170 (2)
Firebox	30	109–235
Dry cyclone	No data (3)	No data (3)

(1) One outlier of 560 mg/Nm^3.
(2) One outlier of 1600 mg/Nm^3.
(3) One plant reported a single value of 720 mg/Nm^3, but it is not clear if it is an average or a maximum value.
Source: Data collection.

Emissions data in the table above are from a small number of periodic emission measurements with sampling durations of 30 or 60 minutes, which do not necessarily represent the highly varying emission profile of the whole decoking cycle, which is longer.

The reported average values of dust emissions over the decoking cycle range between 17 mg/Nm^3 and 720 mg/Nm^3, while most values lie in the 20–90 mg/Nm^3 range. Reported mass emissions of dust over the decoking cycle are between 5 kg and 80 kg. Measurements that have been taken are generally periodic sampling with gravimetric analyses. Average and maximum values provided are shown in Table 3.8. No data have been provided to show the variation of emissions over a decoking cycle, which would be necessary for a more detailed analysis of the emission data.

Lack of a unified approach to monitoring (sampling, measurement protocol) and data processing (normalisation, averaging) makes these data difficult to interpret. Therefore the distinction and/or correlation between average and maximum values are unclear.

3.3.1.2.2 Carbon monoxide emissions to air from decoking

The CO level will depend on the relative airflow rate. As this has to be restricted during the early part of the decoking process for safety purposes (in order to avoid generating too much heat and damaging the tubes), CO is likely to be highest at the start of the decoking. The ability to allow more air into the process as the decoking progresses means that CO levels could be very low by the end of the cycle.

The carbon monoxide emissions data reported are not sufficiently reliable to present in this document.

3.3.1.3 Emissions to air from clean-up of cracked gases

Hydrogen sulphide and carbon dioxide are removed from the cracked gases by scrubbing the cracked gases with a caustic solution. In some installations, a regenerative amine scrubber is also used prior to the caustic scrubber to reduce the load on the caustic scrubber and facilitate the recovery of sulphur. However, amine scrubbing alone is not sufficient to achieve the required level of removal. Scrubbing applied in this manner is not an abatement process, as it is removing unwanted components (H_2S and CO_2) from the process stream.

In the data collection, all the crackers reported using caustic scrubbing. Only three crackers additionally use regenerative amine scrubbing, each of which has available a nearby refinery with an SRU (sulphur recovery unit) for processing the off-gas from the amine solvent. Meanwhile, a number of other plants close to a refinery do not use amine scrubbing.

This process does not in itself result in an emission to air. However, emissions to air could potentially arise from one or more of the following downstream processes:

- The thermal regeneration of the amine solvent (when used): this process takes place within a refinery and is described in the REF BREF, therefore it is not considered further in this document.
- The stripping of neutralised spent caustic scrubbing liquor: this process is carried out using the gaseous stream (e.g. methane) as the stripping medium (see Section 3.4.2.3.2). The resultant gas stream is used as fuel and so any VOCs or H_2S removed will be burnt in the cracker furnace.

The total sulphur removed is reported to be between 4 t/year and 1 175 t/year by caustic scrubbing and between 134 t/year and 988 t/year by amine scrubbing. The amount of sulphur removed will be dependent on the amount present in the feedstock and any additional sulphur doping of the feedstock.

3.3.1.4 Diffuse and fugitive emissions to air

As large sections of the process are conducted under significant pressure, there is the potential for diffuse and fugitive emissions of substances to air from the processes under normal operating conditions.

Fugitive emissions generally arise from the seals on items of process plants such as valves, pumps, pipe flanges, compressors, etc. The VOCs that may be present in fugitive emissions will be varied, reflecting the range of substances that could possibly be present in the cracked gases and to some extent also the range of feedstock components. For gaseous feedstocks, it is likely that all of the organic species will qualify as VOCs according to the criteria in the fugitive emissions monitoring standard (EN 15446), more details of which are provided in the CWW BREF. Heavier (e.g. naphtha and gas oil) feedstocks are likely to give rise to some cracked gas components that are relatively non-volatile, although they are also likely to result in the presence of aromatics, in respect of which there might be obvious health impact issues. The issue of fugitive emissions of VOCs from chemical plants is addressed in Chapter 2 and the CWW BREF.

As the various co-products are also stored under pressure, diffuse emissions of VOCs may also arise from product storage. The EFS BREF provides general information regarding emissions to air from storage.

The data collection resulted in estimated values of diffuse and fugitive VOC emissions from lower olefin production plants ranging from 30 t/year to 1 925 t/year.

3.3.1.5 Emissions to air from hydrogenation catalyst regeneration

Alkynes present in the cracked gases can be hydrogenated to increase ethylene and propylene yields. The hydrogenation catalyst used for this reaction will eventually need to be regenerated. This is done on site by most of the operators, using various techniques like thermal oxidation, steam and air purging, and treating it with hydrogen. Emissions to air from the regeneration operation will be relatively minor as the process will only be in operation for a limited period of time and the duty is small. These emissions should be sent to a suitable abatement system which will normally be a shared facility for the site.

3.3.2 Emissions to water

Emissions to water arise from the following principal sources:

- quench water bleed from the steam cracker;
- the treatment of spent scrubber liquor from the clean-up of the cracked gases.

In addition, waste water will arise from the decoking of the cracker furnace tubes, where a wet abatement technique is used.

Emissions to water from cooling systems associated with steam and energy generation are not included in this chapter. Emissions to water from these operations are described in the ICS BREF and the LCP BREF.

Among the lower olefin producers, eight plants reported having a dedicated waste water treatment facility. Physical, chemical and biological treatment is carried out at these sites. Other operators use shared site-wide waste water treatment facilities, but generally the effluent is first either subject to pollutant recovery at source or pretreatment.

According to the data collection, the following pollutant recovery/pretreatment operations are carried out before the effluent is directed to downstream treatment:

- 23 installations (out of 33 responding to this question) strip the scrubbing liquor; this process is carried out using methane as the stripping medium;
- 11 installations (out of 24 responding to this question) report using wet air oxidation of this stream to convert sulphides to sulphates;
- 24 installations (out of 32 responding to this question) carry out decantation;
- 11 installations (out of 31 responding to this question) carry out emulsion management; and
- 9 installations (out of 32 responding to this question) carry out centrifugation.

More information on these techniques can be found in Section 3.4.

Downstream treatment is mostly shared treatment; it includes biological and chemical oxidation and is described in the CWW BREF.

3.3.2.1 Emissions to water from steam cracking

The water used for the generation of the cracking steam normally includes water recycled from the water quench circuit (which will also include dilution steam) that condenses during the quenching process. However, in order to avoid the excessive build-up of salts and solids, a portion of the water is bled from this circuit.

The quench water may be contaminated with any heavy hydrocarbons that condense, and the nature of these will be influenced by the process conditions and the feedstock used. Many of the organic substances present will have some solubility in the quench water, particularly at the temperatures involved. The bleed from the circuit will therefore contain some level of organic contamination. An aqueous effluent containing significant quantities of these organic substances should be pretreated to a degree that would be suitable for the resultant effluent to be discharged to a downstream waste water treatment. This would be due to its high COD to BOD ratio, and the presence of substances that are inhibitory or toxic to the biological treatment process.

Operators of olefin plants (apart from three operators) report that pretreatment of the water bleed is carried out. As pretreatment, stripping (all but one), decantation, emulsion management (16 out of 39 operators who responded to the question) and centrifugation (7 out of 38 operators) are carried out before the waste water is sent to final waste water treatment.

3.3.2.2 Emissions to water from clean-up of cracked gases

The waste water stream that arises from the caustic scrubber to remove acid gases (H_2S and CO_2) from the cracked gases stream is spent caustic scrubber liquor.

This waste water stream will contain sodium sulphide. However, it will also contain a number of organic substances because of their solubility in the scrubbing liquor, and possibly as a result of the formation of emulsions. The spent scrubbing liquor may also contain some insoluble sludge and possibly some mercury if the caustic has originated from a mercury cell process, although the use of caustic from mercury cells will end as the technique is not BAT. Being a caustic solution, it will also have an elevated pH.

Furthermore, the presence of sulphidic substances raises the possibility of odorous emissions during the handling and treatment of the spent liquor. Pretreatment such as stripping or oxidation can be applied to reduce the organic content and oxidise sulphides (see Section 3.4.2.3).

3.3.2.3 Emissions to water from dust abatement of decoking

The most commonly applied dust abatement technique is the use of wet abatement (18 out of 46 sites). The aqueous effluent is generally sent to a shared treatment facility, after some pretreatment. The pretreatment operations reported are filtration, decantation and the use of a CPI (corrugated plate interceptor).

The waste water stream may be a continuous flow during the decoking process due to either a once-through use of water or a constant bleed from a water recycle loop. But the discharge could also be intermittent if the waste water is disposed of on a batch basis, e.g. after a decoking cycle.

The waste water will contain captured (potentially very fine) dust. In addition, any organic species that are volatilised or formed during the decoking operation may also be dissolved or present in the waste water.

The concentration of pollutants will depend upon the method of operation (e.g. once-through, recycle with bleed or batch) and any treatment that is used to remove some of the solids from the waste water. The techniques that can be used include filters, settling, and hydrocyclones.

3.3.3 Raw material consumption

3.3.3.1 Feedstock consumption

Essentially all of the feedstock is converted either into ethylene and propylene or a range of by-products that all have the potential to be used beneficially. The relative quantity of each of the various co-products/by-products depends upon a range of factors (feedstock, cracking severity, subsequent upgrading, etc.). In principal, the process is almost 100 % efficient. However, a number of factors can result in a loss of yield:

- there may be limited demand for side products which then would require disposal;
- raw material wastage due to excessive plant start-ups, shutdowns, trips, etc.;
- heavy residues (e.g. green oil, sludges) from the cooling stage, which it might not be possible to view as valuable by-products.

It is likely that the methane/hydrogen fraction is burnt as fuel in the cracker furnace, displacing natural gas. Nearly all of the lower olefin plants recover methane and hydrogen and burn them as a fuel, mostly in the steam crackers.

The alkynes present in the cracked gases are commonly hydrogenated between the appropriate fractionation steps to increase the yield of ethylene and propylene. The amount of ethane and propane may be increased as a result of any hydrogenation reactions that are incorporated within the process.

The ethane and propane that are separated off are normally recycled back to the steam cracker feed. Reuse of ethane and propane as part of the feedstock of the cracker is more beneficial than their use as fuel.

Controlling the product mix through the manipulation of feedstock and cracking conditions is viewed as extremely commercially sensitive by all operators. Consequently, data on the yields of co-products and by-products were not provided; however, Table 3.3 gives a general profile regarding co-products corresponding to the feedstock.

However, one important knock-on effect of this was difficulty in expressing specific loads in terms of a particular co-product or group of co-products, although most plants express their capacity in terms of their ethylene production.

3.3.3.2 Sulphur-doping chemicals consumption

In order to retard the build-up of coke on the inner tube walls, feedstock can be doped with a sulphur-containing chemical (e.g. dimethyl disulphide or H_2S). The consumption of these substances is influenced by a range of factors, including the quantity of such species already present in the feedstock, the nature of the feedstock generally (i.e. its tendency to coke), the nature of the cracking process (i.e. its severity), and the nature of the furnace (i.e. materials of construction).

The use of sulphur dosing should be optimised to minimise the need for decoking, taking into account that any sulphur added will need to be removed downstream prior to fractionation.

3.3.3.3 Acid gas scrubbing media consumption

Two scrubbing media are used:

- regenerative amines;

- caustic solution.

a) Regenerative amine solvent consumption

The regeneration of the amine solvent normally takes place in a refinery; the sulphidic species are stripped out and sent to the refinery's SRU. The regenerated amine is returned to the olefin plant. Although the amine solvent is regenerated, it cannot be completely recycled. This is because a portion needs to be purged in order to prevent the accumulation of impurities that arise from reactions with certain components present in the cracked gases. Therefore, a make-up stream of fresh amine solvent is required. Amine scrubbing is only carried out at three lower olefin installations and no data on amine consumption were provided.

b) Caustic consumption

The caustic scrubbing solution cannot be regenerated. As with any recirculatory scrubbing system, a purge is needed to prevent the accumulation of impurities to a level that would affect the effectiveness of the scrubbing process. Therefore, a make-up stream of fresh caustic and water is required. The quantity of caustic that is required is influenced by a range of factors, including the nature of the feedstock and the extent of any prior scrubbing with a regenerative amine solvent. No data on caustic consumption were provided.

3.3.3.4 Hydrogenation

Hydrogen consumption occurs when hydrogenation is carried out to upgrade the alkynes present in the cracked gases. The quantity required will be influenced by a range of factors, including the nature of the feedstock and the configuration of the co-product fractionation steps.

Because hydrogen is generated in the cracker as a by-product, this hydrogen can be recovered from the cracked gases and purified for use in hydrogenation. The data collection results show that the quantity of hydrogen generated is sufficient to meet the needs of hydrogenation with an excess, which can be used in other processes or recycled back to the cracker furnace (without purification) as part of the fuel. Nevertheless, other than normal operating conditions or process fluctuations may have an effect on this balance. This varies slightly from site to site, as shown in the responses to the data collection, summarised in the table below. Note: increasing the hydrogen content of the fuel could result in higher NO_X emissions arising from an increased combustion temperature.

Table 3.9: Use of hydrogen from the cracker

Responses	**Recover**	**Use on/off site**	**Recycle back to hydrogenation**	**Use as fuel**	**Burn in cracker**	**Flare**	**Buffer storage**
Number of plants that apply the technique	33	33	30	28	25	2 (+2 optional)	2
Number of plants that do not apply the technique	3	2 (1 off site)	3	5	8	30	27

Source: Data collection.

The catalyst used for any hydrogenation of alkynes will have a finite life and will therefore need to be periodically replaced (see Section 2.4.5.2). The frequency of replacement will depend upon a range of factors, such as the type of catalyst employed, details of process design and operation, and the cracker feedstock.

3.3.4 Energy consumption

Worldwide average cumulative process energy use for the steam cracking process has been reported as 12 GJ/t of high-value chemicals, which include light olefins (ethylene, propylene, butadiene and butylene) and non-olefin chemicals (mostly aromatics and a small amount of C_5+ hydrocarbons), and 26 GJ/t of ethylene [183, US EPA 2004], [68, Ren et al. 2006], [28, Ren et al. 2008].

A breakdown of contributions to total specific energy consumption for ethylene production (26 GJ/t of ethylene, with feedstock energy excluded) by different feedstocks (ethane, naphtha) cracking was reported to be: 55–65 % (13.5–16.2 GJ/t of ethylene) for feedstock heating (including losses), heat of reaction and dilution steam in cracker; 13–22 % (3.5–5.2 GJ/t of ethylene) for fractionation and compression of cracker gases; and the remaining 20–30 % (6.3–7.3 GJ/t of ethylene) for separation of products [183, US EPA 2004].

3.3.4.1 Energy consumption of cracking furnaces

Steam cracking is the single most energy-consuming process in the chemical industry. The energy demand for cracking comprises the following elements:

- heating and, in the case of liquid feedstocks, vaporising the feedstock; and
- satisfying the energy demand of the endothermic cracking reactions to maintain the desired radiant coil outlet temperature.

The energy demand will be influenced by a range of factors, such as feedstock type, cracking conditions, degree of air preheat, and heat transfer efficiency.

More than 90 % of the total energy input is introduced into the furnaces by the combustion of fuel. An important influence on overall energy consumption will be the level of heat recovery from the cracker furnace. More than 40 % of the energy input to the furnaces is recovered and used to drive compressors and pumps. Other uses of recovered energy can be process steam and/or electricity.

Heat integration (referred to as configuration optimisation) is important to maximise the level of energy recovery. The extent to which this might be achieved may be limited by the constraints of the original design and safety considerations.

According to the data collection, other techniques applied by the operators to reduce energy consumption are:

- air preheat (in 16 plants out of 42 that replied to the question);
- burner location/type (in 26 plants out of 34 that replied to the question);
- insulation (in all plants);
- use of the methane/hydrogen fraction as part of the process fuel (in all plants).

3.3.4.2 Energy consumption for steam generation

Steam is required for the cracking process itself. The specific quantity and quality of steam required for the cracking process will be dependent upon the type of feedstock that is used, and the nature of the process conditions that are desired. For liquid feedstocks, the steam to feedstock ratio is up to 0.85, whereas for an ethane feedstock the steam to feedstock ratio can be lower [70, Zimmermann et al. 2009].

Steam may also be required for a number of ancillary operations; most plants use steam for driving the turbines associated with the refrigeration compressors.

All or some of the energy utilised for the generation of steam can be provided by heat recovered from the steam cracker furnace. However, some or all of the energy could be provided by a conventional steam boiler or gas turbine. The main techniques for reducing the energy consumed for steam generation are heat integration and recycling of condensate, which are applied by all operators, according to the data collection.

3.3.4.3 Energy consumption for compression, refrigeration and fractionation

The cracked gases must be compressed, refrigerated and then separated/fractionated. The energy required for any one of these activities depends not only on the design and operation of that activity, but also on how it relates to the design and operation of the other two. Because of the limited degrees of freedom, it is not worth investigating them on an individual basis.

Given the nature of the energy demand, a certain proportion will be supplied in the form of electricity, which may be generated at the installation.

The techniques that can be employed to reduce the energy consumed include the following:

- Efficient fractionation columns: columns with a good separation capability need lower reflux ratios, and therefore have a lower energy demand. All operators report applying this technique.
- Fractionation section configuration: having either a front-end de-ethaniser or a front-end depropaniser in place of a front-end demethaniser, or incorporating a front-end depropaniser in place of a front-end de-ethaniser, may reduce energy consumption, but is determined by the desired product profile. This is however a design issue and something that cannot easily be changed for existing plants.

3.3.5 Water usage

3.3.5.1 Water consumption for steam generation

In general, there are at two different steam systems in use in lower olefin plants:

- Dilution steam system: dilution steam is used to produce the desired products inside the radiant coils. This steam is condensed inside the water wash column prior to cracked gas compression, and is generally reused as dilution steam after purification and evaporation.
- Turbine steam system: this is generally produced by recovering waste heat and is used to drive the raw gas compressors; after condensation, the water is generally reused as boiler feed water (after pretreatment).

The primary way of minimising water usage in the generation of steam is to reuse condensates. However, these two water circuits have different water quality requirements.

In the specific context of the steam cracker, most of the dilution steam is condensed prior to compression (during either a direct-contact water quenching step or indirect cooling). The excess quench water or, as the case may be, the condensed dilution steam normally makes up a significant proportion of the recycled condensate. However, as this will be contaminated with hydrocarbons, it will need to be cleaned by stripping, which will necessitate the consumption of energy.

However, the condensate that could be used may not be restricted purely to that from the steam cracking operations, as there may be other activities on the site that generate usable condensate.

3.3.5.2 Water consumption for direct-contact cooling

The cracked gases need to be cooled down before entering the cracked gas compressor. Most (but not all) gas crackers employ direct-contact water quenching for reducing the temperature of the cracked gases. Although water quenching is typical for gas crackers, naphtha crackers apply oil quenching.

The water used for the generation of the water quench cracking steam normally includes water recycled from the cracking dilution steam circuit, which condenses during the quenching process. However, in order to avoid the excessive build-up of solids within such a recycle, a portion of the water is bled from this circuit.

The last step of the cooling is usually done in a quench water column. Not all crackers have this and apply countercurrent cooling instead of cooling water or air for the last step of the cooling. However, as the cracking process uses dilution steam to improve the selectivity of the process, water and hydrocarbons will always be separated off prior to entering the cracked gas compressor. So, in all cases, water contaminated with hydrocarbons will be generated, which can be recycled to the process (after suitable treatment).

Water usage is typically reduced by recycling the water after appropriate treatment. The quality of the recycled water might deteriorate over time, so measures that can restore the quality of the effluent would reduce consumption.

The water used is normally recycled, so there is a relatively minor top-up to make up for the quantity that is bled, e.g. to control the build-up of solids – see Section 2.4.7.2.

3.3.5.3 Water consumption for acid gas removal

The amount of water consumed in this respect will depend on the amount of caustic that is used, the concentration at which it is delivered, and the concentration at which it is used. The amount of caustic used will be dependent upon a range of factors, such as the sulphur level in the feed, the extent (if any) to which scrubbing with a regenerative amine solvent is practised, and the rate or frequency at which the caustic scrubbing liquor is respectively bled or replaced.

One way of reducing the quantity of caustic used (and therefore potentially the amount of dilution water that needs to be consumed) would be to maximise the quantity of acid gases that are removed by first using a regenerative amine solvent. However, only three lower olefin plants report using amine treatment prior to caustic scrubbing.

Caustic used for acid gas removal is not regenerated and the spent caustic solution will be subject to final treatment. No data on caustic consumption were provided.

3.3.5.4 Water consumption for dust abatement during decoking

The use of wet arrestment for the abatement of dust entrained in the air/steam effluent from tube decoking (see Section 3.2.3.1) will, by definition, necessitate the consumption of water.

The instantaneous water usage rate will depend upon the design and mode of operation of the abatement plant and, in particular, the extent to which water recycling has been employed. However, the long-term water usage will be influenced by the frequency and duration of decoking operations. As these may be very infrequent, the quantity of water consumed in this respect may be low when judged in the context of the total water usage figure.

3.3.6 Co-products, by-products and waste generation

3.3.6.1 Co-products and by-products

Ethylene and propylene are the desired principal co-products. The main by-products are as follows:

- Hydrogen/methane fraction: it is likely that this fraction will be used as fuel gas in the cracker furnace, replacing natural gas. Any excess can be fed into the fuel gas system for the LVOC plant (or refinery). Hydrogen can also be recovered and purified for use in hydrogenation reactions. Table 3.10 below shows the ways in which methane is handled in lower olefin plants in the EU.
- Ethylene/ethane fraction: ethylene is the desired product, although ethane can also be considered a valuable co-product. Ethane is typically recycled to the cracker feed.
- Propylene/propane fraction: propylene is the desired product, although propane can also be considered a valuable co-product. Propane is recycled to the cracker feed or collected separately for use in LPG.
- C_4 fraction: further processing of this fraction can yield a number of beneficial products.
- Pygas fraction: this is an important feedstock for aromatics plants.

Controlling the product mix through the manipulation of feedstock and cracking conditions is viewed as extremely commercially sensitive by all operators.

However, many of the above by-products have the potential to be considered waste, e.g. due to processing problems or a mismatch between plant output and product demand, when they would have to be disposed of, e.g. by flaring.

Some heavy residues from the initial cooling stage may also be considered a waste in certain circumstances.

Table 3.10: Methane from cracker

Responses (out of 34)	**Isolated with hydrogen**	**Combusted in cracker**	**Used as fuel**	**Flared**	**Buffer storage**
Number of plants that apply the technique	13	30	26	2	3
Number of plants that do not apply the technique	5	2	1	23	20
No information	16	2	7	9	11
Source: Data collection.					

3.3.6.1.1 Pyrolysis oils and pyrolysis gasoline

Pyrolysis oils and pyrolysis gasoline are handled according to the site conditions. Pyrolysis oil is used either as a fuel (on or off site), or for the production of carbon black, or sent to a refinery for viscosity adjustment, or as feed for the FCC unit.

Pyrolysis gasoline is either sent to an aromatic plant for conversion into various products (see Chapter 4) or to a refinery. When the final use of pyrolysis gasoline is for fuel for motor vehicles (gasoline and diesel), it needs to undergo treatment and upgrading processes typical of a refinery.

Table 3.11 below shows the ways in which pyrolysis oils and pyrolysis gasoline are handled in lower olefin plants in the EU.

Table 3.11: How pyrolysis oils and pyrolysis gasoline are handled

Responses (out of 34)	**Used as a fuel (1)**	**Sold as a by-product**	**Used on site (aromatics unit, refinery or power plant on the same site)**	**Disposed of on site**	**Disposed of off site**	**Storage on site**
Number of plants that apply the technique	19	29	21	4	2	32
Number of plants that do not apply the technique	14	4	7	23	25	0
No information	1	1	6	7	7	5

(1) Only pyrolysis oil is able to be used as fuel untreated.
Source: Data collection.

3.3.6.1.2 Alkynes and dialkenes

These are recovered and hydrogenated in the majority of the plants (only two plants report not doing this) to increase the ethylene and propylene yield. In the data collection, 12 plants report recycling back to the process and 18 plants report that they do not. Another alternative for operators of lower olefin plants is to send these by-products as a raw material to other installations.

3.3.6.1.3 Alkanes (ethane, propane and butane)

These gases, mostly ethane and propane, are recycled back to the furnaces as part of the feedstock at the vast majority of installations and so remain within the process. There is also an option to convert some of these fractions to other end-products such as butane to butadiene. In some cases, propane is sent to other plants for LPG production; 20 operators reported that they have storage facilities. All operators reported that no flaring of these by-products is carried out.

3.3.6.2 Decoking sludge

Decoking sludge will arise where the dust in the air/steam decoking stream is collected. The sludge could arise from the use of cyclones, filters, etc., or could form part of any suspended solids captured in scrubbing liquors.

The quantity of sludge that arises will depend on the frequency and duration of decoking, and the nature of the decoking process (i.e. the degree of burnout achieved), and the mode of abatement employed – the higher the capture efficiency, the higher the sludge volume will be. The frequency and duration of the decoking process will be influenced by a range of factors, including the feedstock and cracking severity.

Table 3.12 below shows the ways in which decoking sludge is handled in lower olefin plants in the EU.

Table 3.12: How decoking sludge is handled

Responses	**Incinerated**	**Treated (on/off site)**	**Disposed of on site**	**Disposed of off site**	**Interim storage**
Number of plants that apply the technique	14	10 (1 on site, 6 off-site)	3	22	10
Number of plants that do not apply the technique	17	16	24	8	15
Source: Data collection.					

3.3.6.3 Regenerative amine solvent

The regeneration of the amine solvent normally takes place in a refinery; the sulphidic species are stripped out and sent to the refinery's SRU. The regenerated amine is then returned to the olefin plant. Although the amine solvent is regenerated, it cannot be completely recycled. This is because a portion needs to be purged in order to prevent the accumulation of impurities that arise from reactions with certain components present in the cracked gases.

3.3.6.4 Spent hydrogenation catalyst

When hydrogenation is used to upgrade alkynes, the catalyst used will need to be replaced periodically. The frequency will depend on the nature of the catalyst, the toxicity nature, the operating conditions, etc. Catalysts used in hydrogenation contain substances like palladium, silver, molybdenum, cobalt and nickel.

Regeneration of catalyst is carried out on site at most lower olefin plants using various techniques like thermal oxidation, steam and air purging, and treating with hydrogen. In the questionnaire, 18 (out of 26 companies responding to the question) reported treatment of the catalyst, 10 of them off site, while 30 (out of 33 companies responding to the question) reported catalyst recovery, but all carried out off site by third parties. There is only one operator reported to be disposing of catalyst on site, while 14 operators have off-site disposal. Interim spent catalyst storage is reported by 10 operators (out of 21 responding to the question). The used catalyst is normally returned to its supplier for recovery of the metal component.

Catalyst regeneration processes can also generate emissions to air or water.

3.3.6.5 Other waste

Reported waste from lower olefin production plants includes oil-contaminated solid waste, sulphur-rich hydrocarbons from caustic treatment, heavy ends from primary fractionation and a solid-rich waste stream. These types of waste are generic to the chemical sector.

In order to reduce these waste types, the first option should be to optimise the process conditions to maximise the product yield.

The other options are to recover and reuse the substances in the process directly or indirectly. In some cases, residues may have a higher value as a fuel substitute than if they are isolated and purified for reuse. This can be on site or off site depending on the conditions and characteristics of the site. As LVOC production takes place at installations on large sites with integration/synergies between different processes, sometimes with a refinery nearby, there may be a number of options for making the most of these residues. Therefore the ability to use these residues as by-products varies between plants.

3.4 Techniques to consider in the determination of BAT

This section describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this chapter. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations). Cross references to other chapters are used, where relevant to avoid repetition.

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 2.6 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

3.4.1 Techniques to reduce emissions to air

3.4.1.1 Techniques to reduce NO_X emissions

NO_X emissions from cracking furnaces arise from the combustion of the fuel in the furnace side of the crackers. Techniques to prevent or minimise NO_X emissions are those used for combustion. These are classified as process-integrated techniques, primary and secondary measures for NO_X. The techniques, briefly mentioned below, are described in more detail in Section 2.4.2.1 and in the LCP BREF and the REF BREF. However, application of these techniques and the achieved emission and performance levels are discussed in this section.

Data on emissions of NO_X from steam cracker furnaces are already shown in Section 3.3.1.1.1. Figure 3.6 shows NO_X emissions data for those plants that discharge through a dedicated stack, and for those from that discharge through flues/stacks which are fed from two or more cracker furnaces (these data need to be treated very carefully as the crackers may be applying different techniques and operating in different modes). Only where there is a one-to-one relationship between the cracker furnace and the emission can the data be used with confidence to seek to establish clear correlations between emission levels and techniques applied. However, both data sets show a very similar distribution.

The control of the efficiency of the measures applied is improved by monitoring NO_X emissions continuously.

3.4.1.1.1 Primary measures for NO_X

Description

NO_X emissions are reduced by the following techniques:

- choice of fuel;
- staged combustion;
- external or internal flue-gas recirculation;
- the use of low-NO_X burners or ultra-low-NO_X burners; and
- the use of inert diluents.

Technical description

All techniques reduce NO_X emissions by lowering peak flame temperatures.

- **Choice of fuels:** Gaseous fuels are used. The potential for increased NO_X emissions from fuels which lead to a high peak temperature (e.g. hydrogen) can be limited or avoided by other primary techniques. See also Section 3.4.1.3.1.
- **Staged combustion:** Staged combustion burners achieve lower NO_X emissions by staging the injection of either air or fuel in the near burner region. The staging of fuel or air reduces the oxygen concentration in the primary burner combustion zone, thereby lowering the peak flame temperature and reducing thermal NO_X formation.
- **Flue-gas recirculation:** Recirculation of part of the flue-gas to (external recirculation) or within (internal recirculation) the combustion chamber to replace part of the fresh combustion air, with the effect of reducing the oxygen content and therefore cooling the temperature of the flame.
- **Low-NO_X burner (LNB) or ultra-low-NO_X burner (ULNB):** The technique is based on the principles of reducing peak flame temperatures, delaying but completing the combustion and increasing the heat transfer (increased emissivity of the flame). It may be associated with a modified design of the furnace combustion chamber. The design of ultra-low-NO_X burners (ULNB) includes (air/)fuel staging and exhaust/flue-gas recirculation.
- **Use of inert diluents**: 'Inert' diluents, e.g. steam, water, nitrogen, are used (either by being premixed with the fuel prior to its combustion or directly injected into the combustion chamber) to reduce the temperature of the flame. Steam injection may increase CO emissions.

These techniques are also described in Section 2.4.2.1, and in more detail in the LCP and REF BREFs. Furnaces may have combustion air preheating or may be integrated with a gas turbine and use its hot exhaust air for the combustion. Both configurations improve the overall energy efficiency with a consequent reduction in overall fuel consumption. This may reduce total mass emissions of NO_X, although air preheating may also lead to increased emissions due to higher peak flame temperatures [76, Walker et al. 2004].

Achieved environmental benefits

Reduction of NO_X emissions.

Environmental performance and operational data

The techniques listed above are employed in different combinations. Regarding emission data, it is often impossible to discriminate particular effects of the single techniques. But it can still be observed that there is a difference between the performance of the plants that employ a combination of several of the measures mentioned here and the plants that have a less efficient combination or small number of those measures. Plants that use no or only one NO_X reduction technique have a higher average NO_X emission of 138 mg/Nm^3 compared with 103 mg/Nm^3 reported by those using three or more techniques.

The graph in Figure 3.8 (data collection) below shows separately the NO_X emissions of those that do and do not apply a combination of the techniques. From the data collection, it was not clear if outliers are due to OTNOC events. It can be noted that some plants that do not use the primary techniques discussed nevertheless achieve levels below 100 mg/Nm^3. A clear distinction between individual plants applying the primary measures and those that do not could therefore not always be observed.

The use of a particular fuel is also one of a number of factors and techniques that can influence NO_X emissions. In the data collection, as reported in Section 3.3.1.1.1, no clear correlation between H_2 levels and NO_X emissions could be found.

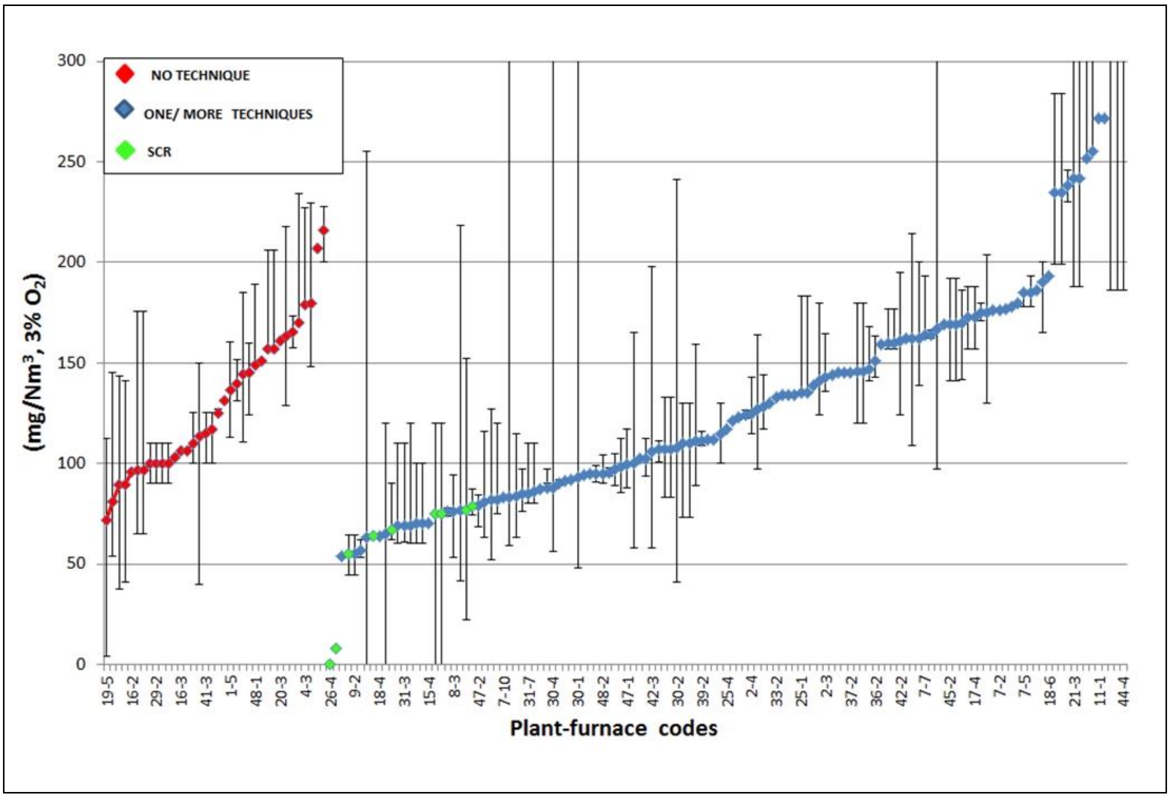


Figure 3.8: NO_X emissions with application of a combination of the relevant techniques

Cross-media effects

Potential low increase in energy consumption.

Technical considerations relevant to applicability

- **Choice of fuels:** In the case of existing plants, the switch from liquid to gaseous fuels may be restricted by the design of the burners.
- **Staged combustion:** The applicability may be restricted by space constraints when upgrading small process furnaces, limiting the retrofit of fuel/air staging without reducing capacity.
- **Flue-gas recirculation and low-NO_X burner (LNB)/ultra-low-NO_X burner (ULNB):** For existing process furnaces/heaters, the applicability may be restricted by their design.

Economics

No information provided.

Driving force for implementation

Environmental legislation.

Example plants

The majority of plants that participated in data collection use a combination of relevant techniques – see Figure 3.8 above. Example plants include: Dow, Terneuzen (Netherlands); Borealis, Porvoo (Finland); Borealis, Stenungsund (Sweden) and Ineos, Rafnes (Norway).

Reference literature

No specific reference literature provided. The techniques are described in the LCP BREF and the REF BREF.

3.4.1.1.2 Secondary measures for $NO_{X:}$ Selective catalytic reduction (SCR)

The only end-of-pipe technique that was reported to be in use by lower olefin plants is SCR.

Description

Use of selective catalytic reduction (SCR) to reduce NO_X in the flue-gas.

Technical description

SCR is the reduction of NO_X to nitrogen in a catalytic bed by reaction with ammonia (in general, aqueous solution) at an optimum operating temperature of usually around 300–450 °C. One or more layers of catalyst may be applied.

The ammonia/urea vapour is mixed with the flue-gas through an injection grid before being passed through a catalyst to complete the reaction. Various catalyst formulations are available for different temperature ranges: zeolites for 300–500 °C, traditional base metals employed at 200–400 °C, and metals and activated carbon for the lowest temperature applications at 150–300 °C.

Achieved environmental benefits

Reduction of NO_X emissions.

Environmental performance and operational data

The catalyst's minimum operating temperature depends on the concentration of SO_3 (see the CWW BREF). With SCR, removal efficiencies of 80 % to 95 % can generally be achieved for inlet concentrations over 200 mg/Nm^3. Residual NO_X stack levels of 10–20 mg/Nm^3 can be achieved by using SCR in gas-fired boilers and furnaces and NO_X emissions of < 100 mg/Nm^3 can be achieved when firing heavy residues.

The dosing of ammonia or urea should be optimised for achieving effective NO_X reduction without excessive ammonia slip; typical emissions of ammonia from these units are in the range of 5 mg/Nm^3 to 15 mg/Nm^3.

According to the data collection, a total of 4 plants (crackers), with 25 cracker furnaces of 9 different types reported having SCR systems. Emission measurement results reported by the plants show that obviously lower emissions of NO_X are achieved by the application of SCR. The difference in the emissions from cracker furnaces with and without SCR is demonstrated in the graphs in Figure 3.8 in Section 3.4.1.1.1 and Figure 3.9 bellow. Figures show the emissions from the cracker furnaces (from the data collection), indicating which are equipped with SCR systems and achieve significantly lower NO_X emissions of < 80 mg/Nm^3.

There are other plants that are not equipped with SCR but that also achieve similar low emissions. These plants use more of the primary measures for NO_X and process control and optimisation techniques together with continuous monitoring of the process and emissions.

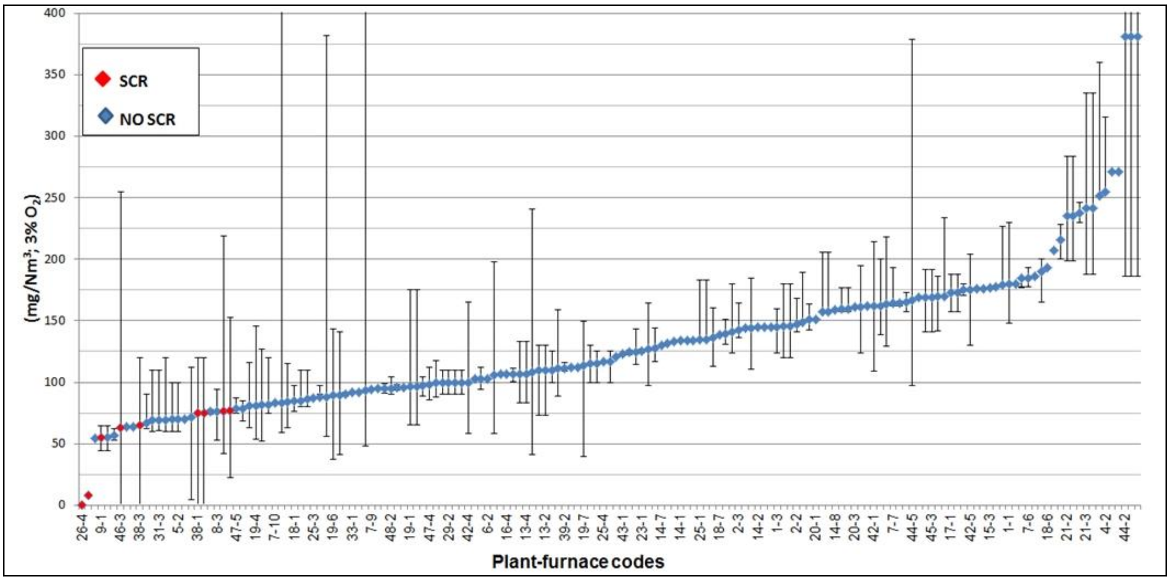


Figure 3.9: **Effect of SCR on reduction of NO_X emissions from the cracker furnaces**

Cross-media effects

- Potential emissions (slips) of ammonia.
- Spent catalyst.

Technical considerations relevant to applicability

Applicability to existing process furnaces/heaters may be restricted by space availability.

Plants which burn liquid fuels with no end-of-pipe abatement may be unable to use SCR for NO_X reduction due to the risk of fouling/poisoning the catalyst.

The technical considerations relevant to applicability in existing furnaces are the space requirements of SCR, and the high complexity of the convection section of the furnaces, which would demand a major redesign (revamp) of the furnace. As an alternative, the primary measures for NO_X emissions reduction, process control and optimisation techniques, together with continuous monitoring of the process and emissions, may give a comparable improvement in environmental performance with less design and construction changes.

Economics

No information provided.

Driving force for implementation

Environmental legislation.

Example plants

Of 42 sites responding to this part of the questionnaire, 16 perform continuous monitoring of NO_X and CO, 19 perform periodic monitoring, and 7 use a mixture of continuous and periodic monitoring. The frequency of periodic monitoring ranges from 90 times a year to once every three years. More typically, 6 sites carry out monitoring once per year, 5 sites carry out monthly monitoring, and 12 sites carry out monitoring every 3–6 months.

The stacks of cracker furnaces in BP plants, Gelsenkirchen (Germany); Shell, Moerdijk (Netherlands); and two LyondellBasell plants in Wesseling (Germany) are equipped with SCR.

Reference literature

[206, ICIS 2017], [207, CRI 2017], [208, Brundrett et al. 2001]

The techniques are also described in the LCP BREF.

3.4.1.1.3 Continuous monitoring of NO_X emissions

Technical description

This technique involves the continuous monitoring of NO_X emissions.

Continuous measurements of NO_X may be carried out with chemiluminescence, Fourier-transform infrared spectrometry, non-dispersive infrared spectrometry, non-dispersive UV spectrometry (NDUV), or differential optical absorption spectroscopy [89, COM 2017].

A number of EN standards for the quality assurance of continuous measurement devices are available (i.e. EN 15267-1, -2, -3, and EN 14181).

Achieved environmental benefits

Potential for reduction of NO_X emissions (in combination with primary and/or secondary measures).

Environmental performance and operational data

Continuous measurements of NO_X (and also of CO and other process parameters) provide emission data at a much higher frequency than periodic measurements and therefore allow for a better process control. This information can ultimately be used to reduce NO_X emissions. The questionnaires completed for the review of the LVOC BREF show that those installations that operated a continuous measurement system have lower emissions of NO_X (e.g. the 75th percentile of average emissions reported from installations with continuous measurements is 127 mg/Nm^3 compared to 170 mg/Nm^3 for those performing periodic measurements).

Plants with continuous monitoring have an average NO_X emission of 97 mg/Nm^3 compared with 144 mg/Nm^3 for plants using periodic monitoring. Although this should not be interpreted as a direct causal relationship (since monitoring would be only one element combined with others to control NO_X emissions), it can nevertheless be taken as an indication of environmental benefits.

Cross-media effects

None.

Technical considerations relevant to applicability

Most cracker furnaces discharge through a shared stack. Monitoring is normally carried out on each stack rather than on each furnace, which may be constrained by the space available to install the monitoring equipment in compliance with the relevant EN standard. In some cases, sampling according to EN standards (for both periodic and continuous monitoring) requires modification of the dimensions of the stack.

Economics

Costs for the installation of continuous monitoring arise mainly from the instrumentation (analyser, shelter, sampling line and DCS).

In the event that there is still a need for a sampling platform and/or suitable sampling points to fulfil the standard requirements established in EN 15289, the costs may increase significantly but to a similar extent as for the adaption of periodic monitoring to the standard requirements.

The costs may be significantly higher for existing stacks than for new stacks [67, CEFIC 2013].

Driving force for implementation

The main driving force seems to be national environmental legislation. From the data collection, the use of continuous monitoring differs depending on the Member State or the location of the installation. This is demonstrated in the following table for locations/installations in the Member States where data for more than 10 stacks have been reported.

Table 3.13 Percentage of LO furnace stacks with continuous monitoring for different Member States and categories of total thermal input

	Germany	Spain	Belgium	France	Netherlands
Total number of stacks considered	51	16	13	29	23
Rated thermal input					
≥ 100 MW	100 %	100 %	60 %	42 %	38 %
≥ 50 MW, < 100 MW	92 %	80 %	50 %	8 %	18 %
< 50 MW	60 %	14 %	0 %	20 %	50 %
Source: Data collection					

Continuous monitoring is also a requirement in combination with the use of SCR.

According to the data collection, all of the stacks using SCR (covering all categories of rated thermal input <50 MW, >50,<100 MW and >= 100 MW) apply continuous monitoring.

Example plants

Of 42 sites responding to this part of the questionnaire, 16 perform continuous monitoring of NO_X and CO, 19 perform periodic monitoring, and 7 use a mixture of continuous and periodic monitoring. (For comparison: The frequency of periodic monitoring ranges from 90 times a year to once every three years. More typically, 6 sites carry out monitoring once per year, 5 sites carry out monthly monitoring, and 12 sites carry out monitoring every 3–6 months.)

Approximately half of the cracker furnace stacks in the data collection currently use continuous monitoring. For stacks with more than 50 MW_{th} of thermal rated input, this share is 40 % for single stacks and 53 % for shared stacks. The findings from the data collection are summarised in the following table.

Table 3.14: NO_X monitoring at single and shared stacks

Number of single stacks performing NO_X monitoring					
	< 50 MW_{th}	50–100 MW_{th}	> 100 MW_{th}	No data	Total
Continuous monitoring	17	9	11	0	37
Periodic monitoring	17	19	11	0	47
Total	34	28	22	0	84
Number of shared stacks performing NO_X monitoring					
Continuous monitoring	14	11	17	1	43
Periodic monitoring	28	12	13	0	53
Total	42	23	30	1	96
Source: LVOC BREF review data assessment, emissions to air, March 2016					

Example site with cracker furnaces with single stacks, conducting continuous monitoring of NO_X is: LyondellBasell, Weselling (Germany).
Example sites with cracker furnaces with shared stacks, conducting continuous monitoring of NO_X are: Sabic, Geleen (Netherlands) and Total, Feyzin (France).
Example sites with cracker furnaces with both single and shared stacks, conducting continuous monitoring of NO_X are: BP, Gelsenkirchen (Germany); Borealis, Stenungsund (Sweden); Ineos, Cologne (Germany) and Dow, Tarragona (Spain).

Reference literature
Reference document on emissions to air and water from IED-installations (ROM).[89, COM 2017]

3.4.1.2 Techniques to reduce CO emissions

The main technique to reduce CO emissions is to optimise the combustion (see Section 2.4.2.2 and the LCP BREF for more detailed information).

3.4.1.2.1 Optimised combustion

Description
Ensure an optimised combustion in the process furnaces.

Technical description
Optimised combustion is achieved by good design and operation of the equipment, which includes optimisation of the temperature and residence time in the combustion zone, efficient mixing of the fuel and combustion air, and combustion control. Combustion control is based on the continuous monitoring and automated control of appropriate combustion parameters (e.g. O_2, CO, fuel to air ratio, and unburnt substances).

The technique includes advanced process control systems and on-line optimisation: Plants utilise multi-variable control techniques incorporating on-line analysers, performance controls, constraint controls, etc. often with on-line optimisation for maximising asset utilisation and performance.

Achieved environmental benefits
Reduced emissions to air of CO and VOCs.

Environmental performance and operational data
Reported CO emission data are summarised in Section 3.3.1.1.2.

The distribution of CO emissions from steam cracker furnaces can be seen in Figure 3.7. By use of combustion control techniques, CO emission values of below 20 mg/Nm^3 are observed. The reported data show that combustion control measures are generally implemented in these plants, providing generally lower CO emissions. The measures reported are combustion air control and control of excess O_2 throughout the combustion.

According to the data collection, continuous monitoring of CO is carried out at about half of the stacks.

Table 3.15: CO monitoring at single and shared stacks

No of single stacks performing CO monitoring					
	< 50 MW_{th}	50–100 MW_{th}	> 100 MW_{th}	No data	Total
Continuous monitoring	18	14	12	0	44
Periodic monitoring	16	15	9	0	40
Total	34	29	21	0	84
No of shared stacks performing CO monitoring					
Continuous monitoring	14	12	19	1	46
Periodic monitoring	27	10	10	0	47
Total	41	22	29	1	93
Source: LVOC BREF review data assessment, emissions to air, March 2016					

Cross-media effects
None known.

Technical considerations relevant to applicability
No information provided.

Economics
No information provided.

Driving force for implementation
Environmental legislation. Note that continuous monitoring of combustion plants with a rated thermal input of 50 MW or more is BAT in the LCP BREF and the REF BREF.

Example plants
Almost all plants use measures to control combustion, although they may differ in detail. For example, oxygen is monitored continuously at almost all plants; continuous monitoring of CO is carried out at about half of the stacks.

Reference literature
No reference literature provided.

3.4.1.3 Techniques to reduce SO_2 emissions

Techniques used to prevent and minimise emissions of SO_2 at lower olefin plants are:

- the use of fuel gas which is produced as a by-product from the cracking process and has a very low sulphur content;
- the use of gaseous fuels, such as natural gas, which have a very low sulphur content;
- where liquid fuels are used, the use of fuels with a low sulphur content.

The use of secondary abatement techniques such as wet or dry scrubbing is not reported at any site.

In the data collection, the maximum sulphur content reported by the plants is 0.05 % (from a liquid fuel with a share of 28 %). SO_2 emissions data collected from plants are limited; reported values are shown in Table 3.4 and range between 2.5 mg/Nm^3 and 38.5 mg/Nm^3.
The use of end-of-pipe abatement techniques for SO_2 emissions, such as wet or dry scrubbing, and for dust emissions, such as fabric filters, is not reported at any site.

3.4.1.3.1 Choice of fuel

Description
Use of fuels with a low content of potential pollution-generating compounds (e.g. sulphur compounds and ash).

Technical description
This technique involves the use of fuel gas instead of liquid fuels. Fuel gas usually has a low content of nitrogen and sulphur compounds, and complete combustion is achieved more easily than with liquid fuels.

Fuel gases can be natural gas or by-products from the cracking process (e.g. the methane/hydrogen fraction, if the hydrogen is not recovered to be used as feedstock, see Section 3.4.3.2) or from other processes. Whilst hydrogen is in principle a very clean fuel, higher levels of hydrogen in the fuel gas will result in higher combustion temperatures which might in turn result in higher levels of NO_X. These higher NO_X values will have to be addressed using other preventative or end-of-pipe techniques. However, the presence of hydrogen can result in more stable combustion with lean fuel mixtures and this could offset NO_X formation to a certain extent under specific circumstances. The presence of hydrogen can promote efficient combustion, thereby possibly helping to reduce residual VOCs and CO.

Where low-NO_X burners are used, additional upgrading of the fuel gas may be required to reduce the fouling and plugging of the small bore burner tips. A filter and coalescer system is typically used to remove any traces of solids and liquid aerosols from the fuel gas.

In the event that the switch from liquid to gaseous fuel is not possible, liquid fuels with a low sulphur content are used.

Achieved environmental benefits

- Low emissions of SO_2 and dust.
- Change from liquid to gaseous fuels may also lead to lower NO_X emissions.
- Potential to improve combustion, with reduction of emissions of VOCs and CO.
- Reduction of consumption of energy by use of by-products as fuels.

Environmental performance and operational data
SO_2 emissions are generally totally dependent upon the quantity of sulphur present in the fuel. The sulphur content in the recycled methane/hydrogen fraction from the cracking process will be low because hydrogen sulphide (from the feed to the reactor) needs to be removed from the cracked gases prior to their downstream processing. However, the methane used to strip H_2S from the scrubber liquor will, if burnt in the cracker furnace, result in SO_2 emissions.

SO_2 emissions data collected from plants are limited; reported values are shown in Table 3.4 and range between 2.5 mg/Nm^3 and 38.5 mg/Nm^3. From the data collection, the maximum sulphur content reported was 0.05 % from a plant using 28 % liquid fuel.

Cross-media effects
The combustion of a hydrogen-rich gas in the cracker from the recycled methane/hydrogen fraction has the potential to result in higher NO_X emissions.

Technical considerations relevant to applicability
The switch from liquid to gaseous fuels may be restricted by the design of the burners in the case of existing plants.

Economics
Increased resource and energy efficiency from the use of the methane/hydrogen fraction from the cracker.

Driving force for implementation
Lower costs.

Example plants
All plants operate with recovery and use of by-products as fuels, many plants use these in combination with natural gas. There are very few crackers in Europe that use liquid fuels.

Reference literature
No reference literature provided.

3.4.1.4 Techniques to reduce dust emissions

Techniques used to prevent and minimise emissions of dust at lower olefin plants are:

- the use of fuel gas which is produced as a by-product from the cracking process;
- the use of gaseous fuels, such as natural gas.

The use of secondary abatement techniques is not reported at any site.

In the data collection, limited emission data were received from spot sampling; values between 2.8 mg/m^3 and 7 mg/m^3 were reported.

3.4.1.5 Techniques to reduce emissions from decoking

3.4.1.5.1 Doping of the raw material feed with sulphur compounds

Description
Doping of feedstock with a sulphur-containing substance.

Technical description
Nickel and nickel oxide sites present in the cracker tube material can catalyse the formation of coke. As nickel sulphides do not catalyse coke formation, doping the feed with sulphur compounds (such as dimethyl disulphide or H_2S) when they are not already present at the desired level can also help retard the build-up of coke, as this will promote the passivation of the tube surface by formation of nickel sulphides.

Some feedstocks will already contain sulphur compounds, so the need for (and the extent of) doping will be variable. There is an optimum concentration range: A sulphur content above 400 ppm may increase coking.

Achieved environmental benefits
Reductions in coke formation will reduce the frequency and/or duration of decoking events and therefore the potential total mass emission of dust and the generation of wastes from dust abatement. Consequently, this would also reduce the amount of energy used during decoking.

Environmental performance and operational data
No information provided.

Cross-media effects
The addition of sulphur compounds to the feedstock increases the amount of hydrogen sulphide and other sulphur compounds that will need to be removed downstream. This is likely to increase the amount of spent scrubbing liquors requiring treatment. If they are stripped with methane used as a fuel, they will end up as an SO_2 emission in the furnace flue-gas.

Technical considerations relevant to applicability
Generally applicable.

Economics
As doping should be at a low concentration, the operating costs should not be high. However, installing the capability to dose at low rates will require some capital investment.

Driving force for implementation
Economic: Plant downtime is reduced.

Example plants
All plants responding to the questionnaire use this technique.

Reference literature
Data collection (questionnaires). [79, Kaiser 2013]

3.4.1.5.2 Optimisation of thermal decoking

Description
Optimisation of thermal decoking to achieve high levels of coke burnout.

Technical description
Optimisation of operating conditions, i.e. airflow, temperature and steam content, across the decoking cycle, to maximise coke removal.

The oxidation of coke with air is exothermic. Care must be taken to avoid high temperatures in the coils that could damage the integrity of the plant. A high burnout temperature might test the operating limits of the plant. Therefore this technique will only be applied towards the end of the decoking cycle when the residual coke level is low.

Achieved environmental benefits
Maximising the extent to which the coke is burnt out will maximise the period of normal operation and therefore the frequency of emissions from decoking. There will also be a reduction of dust emissions towards the end of the decoking cycle.

Removal of coke improves the efficiency of the cracking process (energy demand, process control).

Environmental performance and operational data
This technique will be used in combination with other techniques.

Cross-media effects
Increase in CO emissions.

Technical considerations relevant to applicability
Applicable to those processes that use thermal decoking (air and steam).

Economics
Economic benefits are derived from maximising the productivity and output of the plant by ensuring the longest possible period of normal operation between decoking cycles.

Driving force for implementation
Economics: The period of time the plant is in normal operation is maximised.

Example plants
All plants responding to the questionnaire use this technique.

Reference literature
[27, Step 1966].

3.4.1.5.3 Selection of materials of construction for cracker tubes (radiant coils) that retard coke formation

Description
Selection of tube materials that retard coke formation.

This technique relates to the use of materials with low nickel levels for the construction of the radiant coils, or the use of an appropriate surface coating that blocks access to available nickel (oxide) sites.

Technical description
Nickel (e.g. nickel oxides) present at the surface of the tubes catalyses coke formation. Employing materials that have lower nickel levels, or coating the interior tube surface with an inert material, can therefore retard the rate of coke build-up.

The technique will mainly be efficient to retard the initial coke formation. Efficiency is low for the period when a small coke layer has been formed that covers the inner surface of the coils.

The selection of tube material and coating material needs to be suitable for normal operating conditions and the conditions during decoking, e.g. in terms of resistance against thermal fluctuation. Radiant coils contain nickel because this is almost the only material which can withstand the high operating temperatures (tube skin temperature up to 1 250 °C), high thermal stresses (during furnace emergency shutdown) and high mechanical stresses (due to supersonic flow inside the coils). Therefore, the lifetime of nickel-free coils and coatings is often shorter or the effectiveness is reduced over time. Because of damage to the inner coating of the tubes during the operation due to high stresses, recoating may already be required after one or more decoking cycles.

Achieved environmental benefits
This should reduce the frequency and/or duration of decoking events, and therefore the potential total mass emission of dust. Consequently, this would also reduce the amount of energy used during decoking and the amount of waste from dust abatement.

Reducing the rate of coke build-up improves energy efficiency by limiting the insulation effect of coke build-up.

Environmental performance and operational data
No information provided.

Cross-media effects
No significant cross-media effects.

Technical considerations relevant to applicability
Only applicable to new units or major plant upgrades.

Economics
Implementation depends on the cost-benefit analysis. The production of the special materials of construction and coatings can be more expensive. These increased capital and operating costs could be compensated by productivity benefits. For new steam crackers, the costs are the differential costs (if significant); for existing steam crackers, the issue is the cost of replacing or recoating all the tubes.

Driving force for implementation
Economics: The period of time the plant is in normal operation is maximised.

Example plants
This technique is used by 10 plants responding to the questionnaire.

Reference literature
[70, Zimmermann et al. 2009], [80, Lemme 2011].

3.4.1.5.4 Dust abatement techniques from decoking

The principal techniques used for the abatement (see Table 3.7) of dust from decoking are:

- dry cyclones;
- wet dust scrubbing.

3.4.1.5.4.1 Dry cyclones

Description
Removal of dust entrained in the air/steam exhaust stream using a cyclone.

Technical description
Dry cyclones are equipment for dust removal from a process off-gas or waste gas stream based on imparting centrifugal forces, usually within a conical chamber.

Heavier/larger particles are removed from the base of the cyclone; the exhaust stream is then either vented to atmosphere or can be routed to the furnace firebox.

Dry cyclones are also used as pretreatment before wet dust abatement.

Achieved environmental benefits
Reduction in dust emissions.

Environmental performance and operational data
See Section 3.3.1.2.1. Data were reported for only one plant. The reported emission value seems high in comparison to the values reported for wet dust abatement but data are difficult to compare due to the lack of a defined methodology to assess dust emissions over the decoking cycle. Industry claims that well-designed and operated dry cyclones are able to achieve a similar abatement performance to wet abatement.

Cross-media effects
Collected coke will need to be disposed of as a waste.

Technical considerations relevant to applicability
Generally applicable. In the case of a high moisture content of the decoking off-gas, wet dust scrubbing may be the preferred option.

Economics
No information provided.

Driving force for implementation
Environmental legislation.

Example plants
A number of lower olefin plants apply this technique.

Reference literature
No reference literature provided.

3.4.1.5.4.2 Wet dust scrubbing

Description
Use of centrifugal cyclones (wet cyclones), water scrubbers or spray towers to capture dust.

Technical description
Wet dust scrubbing entails separating the dust by intensively mixing the incoming gas with water, mostly combined with the removal of the coarse particles through the use of centrifugal force. In order to achieve this, the gas is released inside tangentially. The removed solid dust is collected at the bottom of the dust scrubber.

Technical alternatives are: i) injection of water upstream of the cyclone, or ii) scrubbing of the cyclone exhaust gas with water in the decoking drum (installed downstream of the cyclone).

Spray towers are used in combination with cyclones.

Achieved environmental benefits
Reduction of dust emissions.

Environmental performance and operational data
See Section 3.3.1.2.1.

Cross-media effects
Collected coke will need to be disposed of as a waste.

An additional waste water effluent will arise which will need treatment. There is potential for recycling.

Technical considerations relevant to applicability
Generally applicable.

Economics
No information provided.

Driving force for implementation
Environmental legislation.

Example plants
A number of lower olefin plants apply this technique.

Reference literature
No reference literature provided.

3.4.1.5.5 Rerouting of the decoking exhaust gas to the furnace firebox

Description
Rerouting of the decoking exhaust gas to a cracker furnace firebox.

Technical description
The exhaust gas from the decoking process is routed to the furnace firebox to be burnt as part of the fuel during the decoking cycle. The technique can be applied as a stand-alone technique or in combination downstream of other dust abatement techniques, e.g. dry cyclones.

Achieved environmental benefits
Reduced CO emissions in comparison with other techniques and a further reduction in dust emissions when applied in combination with other techniques.

Environmental performance and operational data
No information provided.

Cross-media effects
In order to ensure that the dust is fully oxidised, it may be necessary to operate the furnace at a higher oxygen concentration than might otherwise be the case. The fired duty of the furnace will also increase due to the energy required to reheat the steam/air mixture to firebox temperature, which may impact on energy efficiency. Also, if steam-air admission nozzles are not well-positioned, there is a risk of higher CO emissions because of partial flame quenching.

Technical considerations relevant to applicability
Dust could result in fouling of the convection section and therefore reduce the energy efficiency, or impact on the heat distribution within the furnace, which could affect the performance or reliability of the furnace during normal operation.

Retrofitting this approach to an existing furnace may be constrained by a range of factors and safety considerations.

Special design, operation and maintenance measures are required where this technique is used in conjunction with selective catalytic reduction of NO_X to minimise risks of catalyst bed fouling with uncombusted coke dust, reduced catalyst performance and lifetime. To prevent this, a dust filter is used prior to the SCR unit.

Economics
No information provided.

Driving force for implementation
Environmental legislation.

Example plants
This technique is reported as being applied at four sites.

Reference literature
[171, De Haan et al. 2012]

3.4.1.6 Techniques to reduce emissions to air arising from the clean-up of cracked gases

Caustic scrubbing is used for the removal of acid gases from the process gas stream. This is required in a steam cracker to avoid poisoning of downstream catalyst systems and blockage of the chilling train. This is also the main reason why the fuel gas produced within the steam cracker is sulphur-free (< 1 ppm H_2S). In a small number of cases, an amine scrubbing stage precedes the caustic scrubber.

After the scrubbing stage, the caustic scrubbing liquor will contain sulphidic species and hydrocarbons. These can be recovered from the scrubbing liquor recycle or spent scrubbing liquor by stripping (see Section 3.4.2.3.2). Stripping the scrubbing liquor with methane and using the resultant gas for combustion avoids any direct emissions to air of H_2S and VOCs but will result in some indirect emissions of SO_2.

Where amine scrubbing is used, sulphur is recovered from the amine liquid, normally in the sulphur recovery unit of a nearby refinery. The amine liquid is regenerated for reuse in the amine treatment. See the REF BREF for further information.

3.4.1.7 Fugitive emissions to air

VOCs from various vents are usually combined and channelled to end-of pipe treatment, as these are shared by different units on big chemical sites. Emission values for lower olefin plants were not reported.

The techniques used to minimise fugitive VOC releases from lower olefin plants are reported in the table below. For further information on techniques to prevent/reduce fugitive emissions related to the process and plant design in order to reduce fugitive emissions, please refer to the section on generic techniques in this document and in the CWW BREF.

Table 3.16: Techniques used by LO operators to manage fugitive VOC emissions

Responses	LDAR	Helium test for flange tightness	High-integrity equipment			Solar occultation flux	Field continuous monitoring	Maintenance intervention strategy
			Gaskets	Flange standards	Pump seals			
Number of plants that apply the technique	30	17	31	21	27	2	7	24
Number of plants that do not apply the technique	11	24	3	5	1	27	22	1
Source: Data collection and industry comments								

3.4.2 Techniques to reduce emissions to water

During the data collection, 8 plants reported having a dedicated waste water treatment facility, and 16 operators reported dedicated pretreatment and 18 shared pretreatment. No data on emissions to water were reported.

3.4.2.1 Process water (purge from dilution steam generation)

3.4.2.1.1 Maximisation of the recovery of hydrocarbons from the quench water and condensates and reuse of the quench water in the dilution steam generation system

Technical description

The technique consists of ensuring an effective separation of organic and aqueous phases. The recovered hydrocarbons are recycled to the cracker or used as raw materials in other chemical processes. Organic recovery can be enhanced, e.g. through the use of steam or gas stripping, or the use of a reboiler. Treated quench water is reused within the dilution steam generation system. A quench water purge stream is discharged to downstream final waste water treatment to prevent the build-up of salts in the system.

Dilution steam generation systems are used to recycle the majority of the contaminated condensate from the crackers. These units typically include a gasoline wash system to extract heavy hydrocarbons, a coalescer/phase separation system, stripping to remove light hydrocarbons, and a regeneration column or regeneration exchangers where the partially cleaned water is reboiled and returned to the cycle. Hydrocarbons recovered in the process are retained to join the gasoline and/or fuel oil product or feed streams. Dilution steam generation systems can considerably reduce the requirement for boiler feed water in a plant since the condensate from the 'clean' steam used to reboil the process water can be recovered. Dilution steam generation gives the additional advantage of significantly reducing the quantity of process water that needs to be treated, whilst at the same time lowering the hydrocarbon and phenol load [84, US DoE 2000].

Techniques used for recovery and reuse of hydrocarbons and condensate from the dilution steam generation system are:

- multiple use and recirculation operations;
- feedstock recovery by stripping;
- recovery of liquid hydrocarbons for use in other processes (e.g. C_5, BTX).

See Chapter 2 and the CWW BREF.

Achieved environmental benefits

- Recovery of organic material.
- Reduction of water consumption and of the amount of waste water discharged to waste water treatment.

Environmental performance and operational data

No information provided.

Cross-media effects

Enhanced treatment may imply consumption of energy.

Technical considerations relevant to applicability

Generally applicable.

Economics

Benefits from water savings and recovery of organic material.

For existing crackers, the implementation is accompanied by potentially high costs – depending on the extent of re-engineering needed.

Driving force for implementation
No information provided.

Example plants
No information provided.

Reference literature
No reference literature provided.

3.4.2.1.2 Treatment techniques

Techniques to recover hydrocarbons and to reduce the organic load sent to a shared waste water treatment are:

- steam stripping;
- phase separation by oil-water separators (API), including emulsion management;
- use of a hydrocyclone.

The treatment can be carried out on combined streams coming from different units.

3.4.2.2 Abatement of emissions to water from decoking

A small waste water stream will arise when wet dust abatement is used at decoking (see Section 3.4.1.5.4.2). Wet abatement dust removal is used by around half of the operators that participated in the data collection, and aqueous effluent is generally sent to shared treatment, after some pretreatment. The pretreatment operations reported are filtration, decantation and the use of a CPI (corrugated plate interceptor) for oil-water separation.

These can be seen in detail in the CWW BREF.

3.4.2.3 Techniques to reduce emissions to water from acid removal systems

3.4.2.3.1 Maximisation of the use of amine scrubbing for the removal of acid gases

Description
Scrubbing of the cracked gases with a regenerative (amine) solvent to remove acid gases, mainly H_2S, to reduce the load on the downstream caustic scrubber.

Technical description
The cracked gases are contacted in a column with an amine scrubbing medium (e.g. monoethylamine) into which some of the hydrogen sulphide (and CO_2) in the gases is absorbed.

Amine treatment is the first step in a two-step process to recover sulphur from the process gas stream. It is similar to wet gas scrubbing but uses an amine absorption liquid instead of caustic. The second stage of the sulphur recovery process is normally located within refineries. Most refineries have a sulphur recovery unit, where elemental sulphur is recovered from the amine liquid. The amine liquid is regenerated for reuse. A small stream is purged in order to limit the concentration of high-boiling compounds in the amine solution. The technique is described in full in the REF BREF.

Achieved environmental benefits
The quantity of caustic required for hydrogen sulphide (and carbon dioxide) removal is reduced. Depending on the concentration at which the caustic for acid gas removal is delivered, the use of amine scrubbing may also help reduce water usage.

The mass emission of sulphide (and organics) in emissions to water and the volume of effluent will both be reduced. The emissions to air (of hydrogen sulphide and VOCs) resulting from the handling and processing of the spent scrubbing liquor will also be reduced.

The ability to isolate the hydrogen sulphide allows for the possibility of recovering sulphur as a useful by-product.

Environmental performance and operational data
The quantity of scrubbing liquor will be dependent on the amount of H_2S and CO_2 requiring removal from the cracked gases. Whilst low-sulphur feedstock will require less scrubbing, this should be balanced with the possible need to reduce the rate of coke generation. A sulphur concentration of 40 ppm is targeted for a cracker feedstock. Reported sulphur levels in feedstock are in the ~ 50–85 ppm range.

Cross-media effects
Some of the solvent can react with carbon dioxide in the cracked gases to form non-regenerable salts, and a portion of the solvent needs to be bled from the circuit in order to control the concentration of this salt. This will result in the generation of a waste stream.

The regeneration of the solvent will involve heating and therefore the consumption of steam.

Where no sulphur recovery plant is available, the incineration of any isolated hydrogen sulphide would result in sulphur dioxide emissions to air.

Technical considerations relevant to applicability
The technique may not be applicable if the lower olefin cracker is located far from a sulphur recovery unit. The applicability for existing plants may be restricted by the capacity of the sulphur recovery unit.

Economics
Benefits are derived from the recovery of sulphur and reduced costs for downstream treatment.

The capital costs will include the cost of significant absorption and desorption columns, and the original scrubbing medium charge. The ongoing operating costs will include the make-up of the scrubbing medium, and energy, particularly for acid gas desorption.

Driving force for implementation
No information provided.

Example plants
Three plants report using this technique.

Reference literature
[70, Zimmermann et al. 2009].

3.4.2.3.2 Stripping of the spent caustic scrubbing liquor

Description
Stripping of the spent caustic scrubbing liquor.

Technical description

Volatile compounds are removed from the aqueous phase by a gaseous phase that is passed through the liquid. The removal efficiency may be enhanced by increasing the temperature or reducing the pressure.

The stripping of scrubber liquors is carried out using a suitable gaseous stream (typically methane), which is then combusted (e.g. in the cracker furnace).

Achieved environmental benefits

Stripping will reduce the organic content of the effluent, thereby reducing the potential for fugitive emissions to air from the effluent and reducing the load on the downstream effluent treatment plant. The removal of dissolved H_2S will reduce the odour potential of the effluent.

Cross-media effects

Any H_2S stripped from the scrubber liquor will be released to the atmosphere as SO_2 when burnt.

Example plants

Most lower olefin plants apply this technique.

3.4.2.3.3 Chemical oxidation of the spent caustic scrubbing liquor

Description

Sulphides (hydrogen sulphide and organic sulphides) present in the spent scrubbing liquor are oxidised to sulphate, e.g. using air at an elevated pressure and temperature (i.e. wet air oxidation) or an oxidising agent such as hydrogen peroxide.

Technical description

An oxidant such as hydrogen peroxide (and a catalyst) is mixed with spent caustic scrubbing liquor. The resulting mixture is maintained at a moderate temperature in a stirred tank reactor before being cooled. The temperature needs to be controlled for safety reasons since the oxidation reactions (including the potential oxidation of residual hydrocarbons) are exothermic.

Oxidising agents such as hydrogen peroxide can be hazardous and have to be stored and handled accordingly to avoid the risk of accidents.

See also the CWW BREF.

Achieved environmental benefits

Achieved environmental benefits include the reduction of emissions of volatile compounds to air and the reduction of odour emissions.

Sulphides will be converted to sulphates. This should remove the immediate problem of odorous emissions to air, but the presence of sulphates in the pretreated effluent means that the potential for the formation of sulphides still exists, and the likelihood of this will depend on the handling of the effluent, and the operation of the WWTP, which falls within the scope of the CWW BREF.

Environmental performance and operational data

No information provided.

Cross-media effects

- Consumption of an oxidising agent.
- Waste from spent catalyst: When the treated spent scrubbing liquor is neutralised, some catalyst may precipitate, and this would have to be disposed of.

Technical considerations relevant to applicability
Generally applicable.

Economics
Ongoing cost of the oxidising agent.

Driving force for implementation

- Protection of the workforce by reducing the risk of exposure to hydrogen sulphide.
- Improvement of the operability and robust operation of any downstream biological effluent treatment plant.

Example plants
No information provided.

Reference literature
No reference literature provided.

3.4.2.3.4 Wet oxidation of the spent caustic scrubbing liquor

Description
Sulphides (hydrogen sulphide and organic sulphides) present in the spent scrubbing liquor are oxidised to sulphate using air at an elevated pressure and temperature (i.e. wet air oxidation).

Technical description
Air (or another gas containing oxygen) is injected into a continuous flow of pressurised spent caustic scrubbing liquor. The resulting mixture is heated, and then maintained at the desired temperature and pressure for a fixed period of time whilst passing through a plug flow reactor.

The temperature range employed is between 269 °C and 290 °C for high-pressure wet oxidation and between 120 °C and 220 °C for low-pressure oxidation. The operating pressure ranges from 80 bar to 120 bar for the high-pressure process and from 8 bar to 29 bar for the low-pressure process. The spent scrubbing liquor's residence time within the plug flow reactor is normally between 45 and 90 minutes, although longer times are required for low operating temperatures. For low-pressure oxidation, a catalyst (e.g. Fe(II)) is required.

See also the CWW BREF.

Achieved environmental benefits
Achieved environmental benefits include the reduction of emissions of volatile compounds to air and the reduction of odour emissions.

Sulphides will be converted to thiosulphates, sulphites and/or sulphates. This may remove the immediate problem of odorous emissions to air, but the potential for the formation of sulphides still exists, and the likelihood of this will depend on the handling of the effluent, and the operation of the WWTP, which falls within the scope of the CWW BREF. The potential conversion of sulphides only to sulphites may not necessarily avoid problems with the operation of any downstream biological effluent treatment plant.

Besides COD, TOC may also be reduced, including the organic load from phenols and oils. This could also help reduce the possibility of the performance of any downstream waste water biological treatment plant being adversely affected by receipt of this effluent.

Environmental performance and operational data
The operating regime of the wet air oxidation plant will have a significant bearing on performance. Increasing the operating temperature, retention time or partial oxygen pressure

will increase the proportion of sulphides converted to sulphates (and correspondingly reduce the proportion of sulphides converted to thiosulphates and sulphites), and will also increase the reduction in COD that is achieved.

Cross-media effects

There will be an energy demand for pumping, heating and pressurisation. However, the oxidation is exothermic and carried out under pressure, so a high degree of heat recovery should be possible, and the process could be autothermal in some circumstances.

The depressurisation of the treated liquor could liberate some VOCs to air, which may need to be destroyed by incineration, which necessitates further energy (fuel) consumption.

Technical considerations relevant to applicability

Under higher temperature operation, bisulphate formation in the absence of sufficient residual caustic could result in acid corrosion. The plant's materials of construction must be appropriate.

Economics

Low-temperature (and therefore low-pressure) plants do not need to be constructed to withstand such high pressures, so their capital costs may be lower. However, the need to supply greater airflows in order to maintain efficient mass transfer means that their operating costs can be much higher.

Driving force for implementation

- Protection of the workforce by reducing the risk of exposure to hydrogen sulphide.
- Improvement of the operability and robust operation of any downstream biological effluent treatment plant.

Example plants

This technique is reported to be used by 11 plants responding to the questionnaire.

Reference literature

No reference literature provided.

3.4.2.3.5 Use of low-sulphur raw materials in the cracker feed

Description

Use of raw materials that have a low sulphur content or have been desulphurised.

Technical description

The amount of sulphides discharged to waste water treatment from the spent caustic scrubber liquor originating from the removal of acid gases from the cracked gases is reduced by the control of the sulphur content in the feedstock. The average amount of sulphur in the feedstock ranges from 0.004 wt-% in gaseous feed to 0.042 wt-% in heavy naphtha, as reported in Table 3.2.

Achieved environmental benefits

Reduction of sulphides discharged to waste water treatment

Environmental performance and operational data

The total amount of sulphur removed by caustic scrubbing was reported in Section 3.3.1.3 to be between 4 t/year and 1 175 t/year and the total amount removed by amine scrubbing between 134 t/year and 988 t/year.

Cross-media effects

None.

Technical considerations relevant to applicability
The applicability may be restricted by the need for sulphur doping in order to reduce coke build-up. If the feedstock does not contain enough sulphur compounds – ideally around 400 ppm (0.04 wt-%) of sulphur content – they may need to be added, to minimise coke build-up. For more details see Section 3.4.1.5.1.

Economics
Lower costs of spent scrubbing liquor treatment.

Driving force for implementation
Reduced volume of scrubbing liquor sent to downstream treatment.

Example plants
Plants reported that they monitor the feedstock sulphur content.

Reference literature
No reference literature provided.

3.4.3 Techniques to reduce raw material consumption

Besides the recovery of hydrocarbons from quench water and condensates (see Section 3.4.2.1.1), the following techniques have been identified to reduce raw material consumption.

3.4.3.1 Process optimisation

Description
Process optimisation.

Technical description
This technique involves determining the optimum operating conditions (e.g. temperature, residence time, steam addition) to produce the desired product mix from the raw material feed.

Achieved environmental benefits

- Efficient use of raw materials and energy.
- Efficient use of feedstock and energy will reduce emissions to all environmental media.

Environmental performance and operational data
Process management in the steam cracker is also dependent on the type of the feedstock and the product spectrum desired. Generally speaking, ethylene is the most favoured product and maximising the ethylene yield is a major driving force for optimising the process conditions in crackers [28, Ren et al. 2008].

Cross-media effects
None.

Technical considerations relevant to applicability
Some of the main process conditions involved are furnace configuration, coil design, temperature (and temperature profile), run length and residence time. Severity or cracking severity is a key parameter. It is defined as the propylene to ethylene ratio (and sometimes methane to propylene ratio) for liquid feedstocks and the conversion ratio for gaseous feedstocks [70, Zimmermann et al. 2009]. The complexity of the interrelations between these parameters makes it difficult to provide a one-size-fits-all solution to cracking optimisation.

Due to the specific conditions mentioned above, the techniques for improving efficiency and reducing emissions and raw material demand may have limitations in terms of applicability. However, there are cases of particular solutions for performance optimisation being developed and implemented (catalytic cracking, hydropyrolysis, catalytic pyrolysis, etc.) [74, Ren 2004].

Economics
The cost and availability of fuels and feedstocks vary considerably among plants and geographic locations. The availability of providers or clients for feedstock or by-products can affect the design choice of the olefin manufacturing plants [68, Ren et al. 2006].

Driving force for implementation
Economic: Yield is maximised and costs are minimised.

Example plants
All plants.

Reference literature
[75, Shore et al. 1977], [68, Ren et al. 2006].

3.4.3.2 Recovery and reuse of hydrogen

Description
Recovery of hydrogen from the methane/hydrogen fraction (that would otherwise be used as fuel) for use as feed for hydrogenation reactions.

Technical description
Some of the hydrogen that is continuously produced in the steam cracker is separated and purified for use in the hydrogenation reactors within the steam cracker and other production plants (e.g. aromatics plants). This separation of hydrogen can be done through cryogenic separation in the chilling train of the steam cracker followed by pressure swing absorption (PSA).

Care has to be taken to ensure that resulting changes in fuel composition do not impact negatively on the control of the temperature of the cracking furnace.

In the event that hydrogen separation is not applicable (see below), hydrogen can be converted to methane by methanation (by catalysed reaction with CO).

Achieved environmental benefits
Achieved environmental benefits include the reduced consumption of hydrogen, and the reduction of potential NO_X emissions which are related to the use of hydrogen as a fuel.

Recovery of hydrogen results in the combustion of fuel gas which has a low hydrogen (H_2) content in the cracker furnace. This in turn could lead to a reduction in NO_X emissions from the cracker furnace due to the avoidance of elevated peak flame temperatures that can result from the presence of hydrogen (H_2) in fuel gas under some firing conditions.

Environmental performance and operational data
No information provided.

Cross-media effects
Energy consumption for hydrogen separation and purification.

Technical considerations relevant to applicability
The applicability may be restricted where the energy demand for recovery is excessive due to the low hydrogen content or when there is no demand for hydrogen.

Economics

Hydrogen is a useful chemical feedstock; its value to an operator may exceed the cost of other supplies, even when including the cost of separation.

On the other hand, fuel gas (including its hydrogen content) is available as a by-product and can be used to displace natural gas (or other fuels) which have to be purchased. Therefore investment in additional NO_X prevention and/or abatement techniques may be more economic than separating hydrogen from the fuel gas.

Driving force for implementation

Economic factors.

Example plants

Used in many crackers in the EU – see Table 3.9.

Reference literature

No reference literature provided.

3.4.4 Techniques to reduce energy consumption

3.4.4.1 Heat integration

Description

A group of techniques to maximise the use of excess heat from a process or processes in other parts of the process or processes where heat input is required. It reduces the wastage of energy by maximising its recovery for beneficial use, either within or outside the steam cracking process.

Technical description

Heat or energy integration does not necessarily address the reduction of energy consumption by the individual component activities, as it is primarily concerned with minimising the amount of energy that is wasted by the process as a whole. It can therefore help reduce the overall energy consumption of the process.

Within a steam cracker, heat (energy) integration can be achieved in a number of ways:

- generating and/or superheating steam in the convection zone of the cracker furnace and/or during the indirect cooling of the cracked gases;
- preheating the cracker furnace combustion air in the convection zone of the furnace and/or by heat exchange with the combustion gases prior to their emission to air;
- preheating the feedstock;
- recycling hot condensate and/or hot direct cooling (quench) water for steam generation;
- upgrading waste steam, e.g. using vapour recompression, to a state that would make it suitable for beneficial reuse;
- combusting by-product streams that would otherwise be disposed of;
- integration of a steam turbine; (use of the waste heat of a gas turbine if present on the site).

There are often complex interactions in the compression / refrigeration / fractionation elements of the chemical production processes and this should be taken into account to achieve efficient heat integration.

Heat integration can involve activities other than those directly associated with steam cracking.

Achieved environmental benefits

It can increase the efficiency of energy use by the process, although this may not be the case when the benefits are derived by other processes. Furthermore, it does not necessarily minimise energy consumption, as it is primarily designed to minimise energy wastage.

Environmental performance and operational data

No information provided.

Cross-media effects

The preheating of combustion air can increase the potential for NO_X formation.

Technical considerations relevant to applicability

Some of the techniques described above may only be possible to implement for new plants and for major retrofits.

Economics

Energy is one of the major costs associated with steam cracking, so there is an economic imperative to minimise energy wastage in overall terms.

Driving force for implementation

Economics.

Example plants

All steam crackers implement some energy recovery techniques.

Reference literature

[77, Manley 1998], [69, Mafi et al. 2009], [28, Ren et al. 2008], [74, Ren 2004].

3.4.4.2 Burner location

Description

Location of burners at positions within the cracker furnace that maximise heat transfer.

Technical description

Computational fluid dynamics (CFD) calculations are performed to optimise the burners' size and arrangement. Burners should be low-NO_X or ultra-low-NO_X burners.

Achieved environmental benefits

More efficient use of energy by having burners in the optimum location.

Environmental performance and operational data

No information provided.

Cross-media effects

None.

Technical considerations relevant to applicability

It may not be feasible to retrofit a different burner arrangement to an existing furnace, and it may therefore be feasible only where a furnace is being replaced.

Economics

Retrofitting a different burner arrangement to an existing furnace would be costly (if feasible).

Driving force for implementation

Economics.

Example plants
No information provided.

Reference literature
No reference literature provided.

3.4.4.3 Fractionation column configuration

Description
Use of a configuration with a front-end de-ethaniser or depropaniser.

Technical description
Incorporating either a front-end de-ethaniser or a front-end depropaniser in place of a front-end demethaniser; or incorporating a front-end depropaniser in place of a front-end de-ethaniser.

Achieved environmental benefits
The energy demand of the fractionation section is greatly influenced by the initial temperature required at the start of the fractionation process, where the entire cracked gas flow is present. The use of a front-end de-ethaniser or depropaniser can accommodate a higher starting temperature, and therefore can result in lower overall energy consumption.

Environmental performance and operational data
No information provided.

Cross-media effects
No significant cross-media effects known.

Technical considerations relevant to applicability
Several modifications of the three basic layouts are available. Other design criteria which may be relevant include operability, hydrogenation strategy, run length and fouling behaviour. An existing cracker cannot change its original fractionation layout.

Economics
As significant re-engineering would be required to implement this technique at an existing cracker, the technique is only applicable for new steam crackers.

Driving force for implementation
Energy savings and economics.

Example plants
No information provided.

Reference literature
[70, Zimmermann et al. 2009]

3.4.4.4 More efficient fractionation columns

Description
Provision of fractionation columns with a high separation efficiency.

Technical description
The separation efficiency of a fractionation column can be increased by a range of factors, including the number of plates or the height of structured (or random) packing.

Achieved environmental benefits

Columns with a greater separation ability require a lower reflux ratio. This technique can therefore reduce energy consumption.

Environmental performance and operational data

No information provided.

Cross-media effects

No information provided.

Technical considerations relevant to applicability

The column height will be limited by physical engineering considerations, including available foundations. Higher packing or more plates results in a higher pressure drop and higher bottom temperatures. The temperature may be limited due to fouling. The pressure drop and the higher bottom temperature can cause a higher energy demand.

As significant re-engineering would be required to implement this technique at an existing cracker, the technique is only applicable for new steam crackers.

Economics

Economic benefits are derived from from fractionation products with a higher purity and from energy savings.

Driving force for implementation

Economic benefits.

Example plants

No information provided.

Reference literature

[69, Mafi et al. 2009].

3.4.5 Techniques to reduce water usage

The primary way of minimising water usage in the generation of steam is to reuse condensates. In the specific context of the steam cracker, most of the dilution steam is condensed prior to the downstream compression of the cracked gases (during either a direct-contact water quenching step or indirect cooling). The excess quench water or, as the case may be, the condensed dilution steam normally makes up a significant proportion of the recycled condensate.

The reuse of these aqueous streams is described in Section 3.4.2.1.1.

Of course, the condensate that could be used may not be restricted to just that from the steam cracking operations, as there may be other activities on site that generate condensate that could also be used.

3.5 Emerging techniques

No emerging techniques on an industrial scale have been found regarding production of lower olefins by steam cracking. Regarding other process routes (not mentioned in Section 4.2), some interesting examples are described briefly below.

3.5.1 Olefin metathesis

Description
An alternative route to propene is by applying the metathesis reaction for the conversion of a mixture of ethene and 2-butene into propene.

Commercially developed
The Phillips triolefin process, which utilises a heterogeneous catalyst system, was originally developed by Phillips Petroleum Co., US, and operated from 1966 to 1972 for the conversion of propene into ethene and butene, due to the lower propene demand at that time. A plant is reported to be in operation by OMV in Germany.

Level of environmental protection
No information provided.

Cost savings compared to existing BAT

- The conversion of butene is above 60 % per pass.
- The selectivity for propene is > 90 %.

Chance of becoming BAT in the future
The technique can only be used to produce propylene, so is not a replacement technology for steam crackers.

When it might become commercially available
A semi-works unit using the OCT (olefins conversion technology) process is used at Sinopec’s olefin plant in Tianjin (China), for the metathesis of butene to produce 3-hexene, which is then isomerised into 1-hexene (co-monomer used in the production of polyethene).

References
[199, Nickel 2010], [200, CBI 2014]

3.5.2 Production of ethene by oxidative coupling of methane followed by dehydrogenation

Description
Production of ethane by catalysed partial oxidation of methane with oxygen, followed by catalysed dehydrogenation of ethane to ethene:

$$4\ CH_4 + O_2 \rightarrow 4\ {\bullet}CH_3 + 2\ H_2O$$
$$2\ {\bullet}CH_3 \rightarrow H_3C\text{-}CH_3$$
$$H_3C\text{-}CH_3 \rightarrow H_2C{=}CH_2 + H_2$$

Methane is separated from natural gas and is purified. Oxygen is separated from air cryogenically. The catalysts used are mostly oxides of alkali, alkaline earth and other rare earth metals. Hydrogen and steam are sometimes added to reduce coking on catalysts. After one pass, roughly 80 % of the total oxygen feed by mass is consumed. The per pass ethylene yield, on a mass basis, of methane is about 30 %.

Commercially developed
No.

Level of environmental protection
Not yet established.

Cost savings compared to existing BAT
Not yet commercially developed.

Chance of becoming BAT in the future
Low due to:

- low yields:
    - there is a trade-off between methane conversion and selectivity to ethylene;
    - under 600 °C, the rate of reaction is slow, but, above 600 °C, undesired oxidations dominate the reactions;
- separation:
    - relatively high energy use in separation and recycling;
- catalysts:
    - additional oxygen and hydrogen are required for reducing coking on catalysts;
    - high temperatures of 750–1 000 °C require catalysts with high thermal stability;
- other issues:
    - possible explosion due to the mixture of oxygen and hydrocarbons;
    - CO and CO_2 emissions, aromatic hydrocarbons, acid gas and organic acid.

When it might become commercially available
No information provided.

References
[28, Ren et al. 2008], [172, Guo et al. 2014].

4 AROMATICS

4.1 General information

Aromatics plants produce a number of intermediate chemicals such as benzene, toluene, ortho- and para-xylene (commonly known as BTX aromatics) and cyclohexane. Aromatics plants can have a number of different complex configurations. They operate downstream of refineries and upstream of other LVOC plants. Most aromatics plants are built geographically close to, or inside, refineries. Aromatics plants can also be located alongside steam crackers.

Benzene (C_6H_6) is an important chemical in that it is used as a raw material to produce a wide range of other chemical products. Around half of benzene production is used to produce styrene monomer via the production of ethylbenzene (see Chapter 5). Other uses of benzene include the production of aniline (which is used in the production of MDI, see Chapter 10) and isopropylbenzene (cumene) (which is used in the co-production of phenol and acetone, see Chapter 8).

Toluene (C_6H_5-CH_3) is used as a raw material to produce benzene and xylene. A further important use is the production of toluene diisocyanate (TDI) (see Chapter 10).

Xylene ($C_6H_4(CH_3)_2$) produced from aromatics plants can exist in three isomeric forms; para-xylene, ortho-xylene and meta-xylene. Most producers focus on para-xylene, which is an important raw material in the production of polyethylene terephthalate (PET) which is used in the production of plastic bottles.

Cyclohexane (C_6H_{12}) is also produced from benzene and, although it is not an aromatic substance, its production is described as part of this chapter because the process is closely integrated with the aromatics plant.

Aromatics processes use three main feedstocks: refinery reformates, steam cracker pyrolysis gasoline (pygas) and benzene from coal tar processing. Note that the BTX produced as a coke oven by-product in iron and steel production is covered in the IS BREF [189, COM 2013]. Aromatic complexes are designed and built with different plant arrangements depending on the feedstocks used and the mix of final products.

The European aromatics industry is a very large business. The market is complex as it concerns six main products that are produced in different processes from different feedstocks. In 2013, the production capacity of aromatics in the EU-15 plus Norway and Turkey was 16.3 million tonnes, which was 14 % of global capacity (118 million tonnes). This included 10.07 million tonnes of benzene, 2.108 million tonnes of toluene, 2.737 million tonnes of xylene and 1.372 million tonnes of cyclohexane [128, Petrochemicals Europe 2016].

There are more than 35 aromatic complexes operating in the EU, as shown in Table 4.1 below.

Table 4.1: European producers of aromatics

Country	City	Operator	Capacity (^{1})		
			Benzene	Toluene	Xylene
Austria	Schwechat	NI	NI	NI	NI
Belgium	Antwerp	BASF	NI	NI	NI
Belgium	Geel	BP	60	0	0
Belgium	Antwerp	Total	240	210	550
Belgium	Zelzaete	VFT	90	0	0
Croatia	Rijeka	INA	0	70	0
Croatia	Sisak	INA	0	88	0
Finland	Porvoo	Borealis	150	0	0
France	Lavera	Gexaro	240	0	0
France	Carling (^{2})	Total	325	0	0
France	Feyzin	Total	70	40	0
France	Gonfreville	Total	274	30	180
Germany	Gelsenkirchen	Arsol	410	0	0
Germany	Mannheim	BASF	300	0	0
Germany	Gelsenkirchen	BP	250	0	0
Germany	Lingen	Deutsche BP	75	60	0
Germany	Bohlen	Dow	300	0	0
Germany	Cologne	INEOS	280	140	0
Germany	Heide	Klesch	120	125	0
Germany	Burghausen	OMV	160	0	0
Germany	Schwedt	PCK	70	52	NI
Germany	Godorf	Shell	510	130	280
Germany	Wesseling	Shell	160	100	218
Hungary	Szazhalombatta	MOL	NI	110	NI
Italy	P. Marghera	Versalis	180	55	0
Italy	Priolo	Versalis	425	180	130
Italy	Sarroch	Sarlux	NI	0	345
The Netherlands	Terneuzen	Dow	915	0	0
The Netherlands	Rotterdam	ExxonMobil	650	100	NI
The Netherlands	Geleen	Sabic	350	0	0
The Netherlands	Moerdijk	Shell	550	240	NI
Poland	Plock	PKN Orlen	0	180	0
Portugal	Porto	Galp Energia	57	154	265 o-Xylene 55 p-Xylene 135
Romania	Bucharest	OMV	NI	NI	NI
Slovakia	Bratislava	Slovnaft	0	86	0
Spain	Algeciras	CEPSA	245	200	NI
Spain	Huelva	CEPSA	400	0	0
Spain	Puertollano	Repsol	125	0	0
Spain	Tarragona	Repsol	NI	NI	NI
United Kingdom	Immingham	ConocoPhilips	200	0	0
United Kingdom	Stanlow	Essar Energy	240	80	0
United Kingdom	Grangemouth	INEOS	295	0	0
United Kingdom	North Tees	Sabic	510	330	0

(^{1}) No data provided on cyclohexane production.
(^{2}) To close in the near future.
NB: NI: No information provided.

Interface with the Refinery BREF

Most aromatics plants are built geographically close to or inside a refinery, although they may often manufacture products that belong to a different business sector (i.e. chemicals instead of fuels). They can share most of the environmental abatement systems with the refinery and other utilities, such as fuel gas. In many cases, they operate under a refinery permit and there are no sampling routines (or sampling points) in between these units and the refinery vent header or collective effluent stream. In many cases, there are no data (flow or composition) for the emissions, to disaggregate the contributions of the aromatics plants (this document) and the refinery (covered by the REF BREF [188, COM 2015]) as a whole. The REF BREF does not deal specifically with pollutants arising from aromatics plants which are sent to refinery abatement systems.

Key environmental issues
The key environmental issues for the production of aromatics are as follows:

- The aromatics plants' main environmental emissions are to air and are related to combustion processes for energy supply (NO_X, SO_X, dust, etc.). Some old installations may still have some direct emissions to atmosphere or flare. Fugitive emissions and emissions from storage of VOCs (e.g. benzene) are also relevant. There is interest in material recovery since some streams not only have calorific value, but also contain valuable materials such as hydrogen.
- There are a number of effluents discharged to water from different process sections. The most relevant pollutants, due to their amount, are hydrocarbons, but some solvents used in the extraction processes (e.g. sulfolane and dimethyl sulphoxide) are also important because of their toxicity.
- Residues and waste are generated, such as spent catalysts, spent clay and solvent regeneration residues.

4.2 Applied processes and techniques

The following descriptions of the applied processes and techniques are based to a large extent on input from industry [129, CEFIC 2015].

4.2.1 Process options in aromatic complexes

Aromatics plants can have very different configurations, depending on the desired product portfolio, the quality and quantity of the feedstock(s) available, technology selection, by-product utilisation and site integration synergies. Therefore, there is no such a thing as a typical aromatics plant.

The key characteristic of aromatics plants however is that the main products are usually benzene and/or para-xylene. The raw material used to produce these products predominantly comes from steam crackers and/or refinery catalytic naphtha reformers. Pygas from steam crackers accounts for approximately 28 % of the overall feed to aromatics plants. Reformate/naphtha from catalytic reformers accounts for approximately 68 % of the feed to aromatics plants. Coke accounts for 3 % of the overall feed to aromatics plants. C_3-C_5 is a negligible feedstock in the world market share of aromatics. This chapter does not cover coke oven feedstock or C_3-C_5 feedstocks.

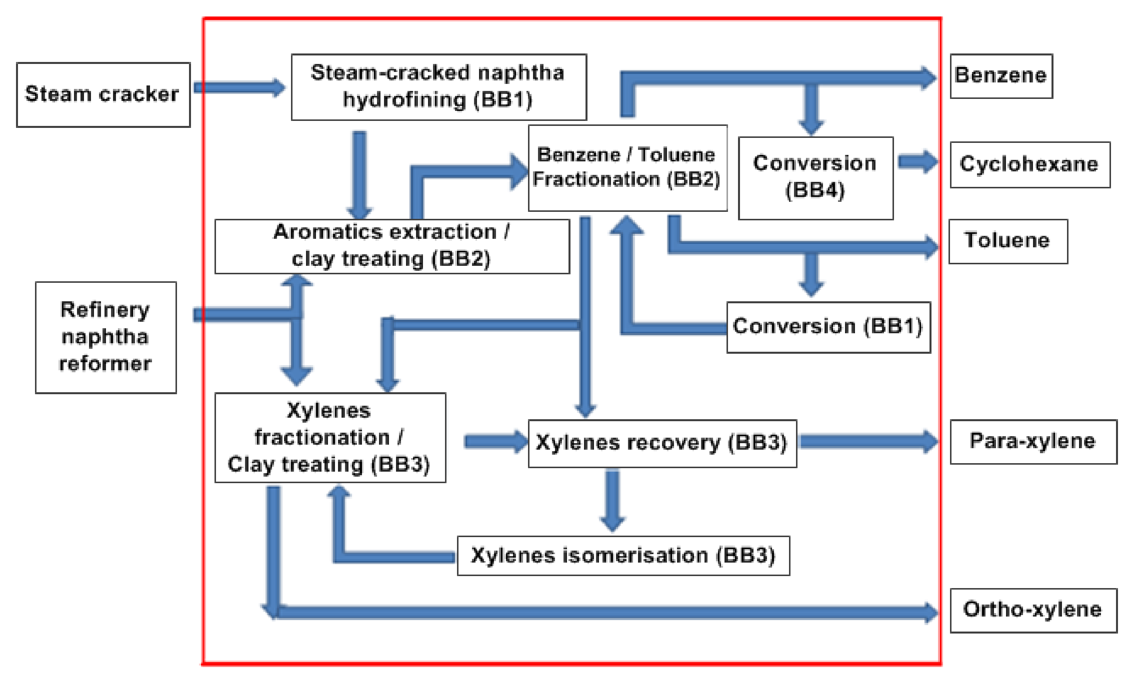
The aromatics process comprises three basic steps:

- feedstock treatment or conversion (hydrogenation of pygas);
- fractionation and purification steps to separate the pure products;
- conversion steps to transform less valuable products into ones with higher margins.

The process units (or building blocks - BB) which are the most common and significant for European aromatics plants are:

- BB1: steam-cracked naphtha hydrofining;
- BB2: aromatics extraction and clay treatment; benzene/toluene fractionation;
- BB3: xylenes fractionation and clay treatment; para-xylene recovery; xylene isomerisation;
- BB4: other conversion processes.

The typical configuration of these processing units is shown in the figure below. The processing units are described in more detail in Section 4.2.2.



Source: [129, CEFIC 2015]

Figure 4.1: Configuration of typical aromatics processing units

Aromatic complexes are made up of a number of basic unit operations, such as distillation, hydrogenation in fixed-bed reactors, extraction, etc. Each of these unit operations has a specific type of impact on the environment. This means that some of the emissions (and their abatement techniques) are repeated under a number of the headings below. The techniques commonly applied to these basic chemical unit operations are, on most occasions, generic and not specific to the production of aromatics.

The most common types of basic operations and emission sources are as follows:

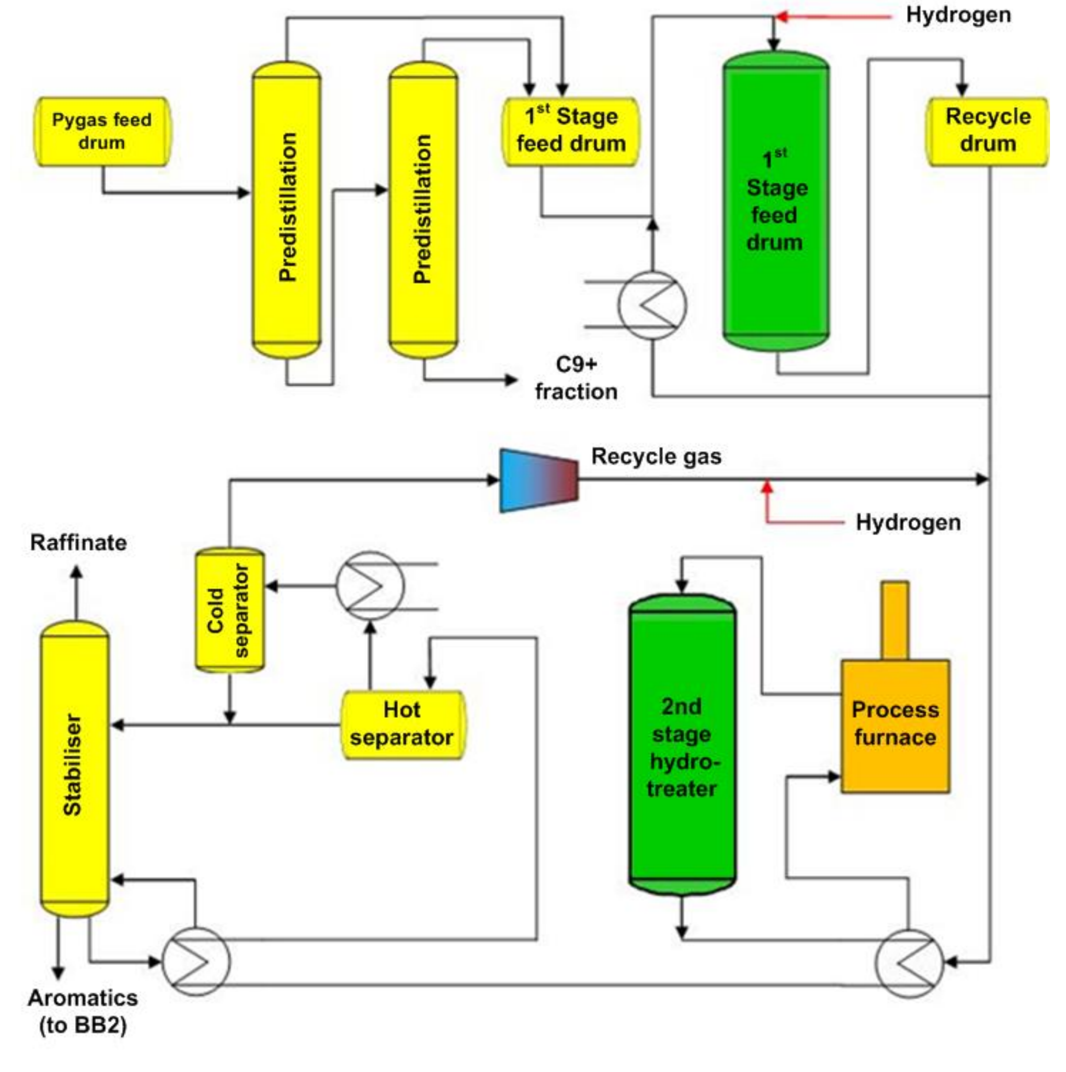
- Distillation: when a vacuum is used, there can be an overall net gas outflow which will include VOCs. Energy usage is typically high in these separation operations and depends on design and operating decisions.
- Clay purification: spent clay will be generated by most units.
- Recycling H_2-rich gas: even if the excess hydrogen from hydrogenation reactors is recycled, it will require a purge stream. Energy usage for compression.
- Purifying H_2 gas: the PSA contains solid granular alumina, a molecular sieve, and activated carbon, which need periodic replacement and should be disposed of via certified contractors. There are also specific emissions related to H_2 recovery, such as spent adsorbent material. Energy usage for compression.
- Preheating reaction feeds: boilers or furnaces are used as reaction feed heaters and will generate combustion-related emissions (CO, CO_2, NO_X, etc.)
- Catalyst regeneration processes emit dust and other pollutants to air if no precautions are taken.
- Fugitive emissions: most process systems work under pressure, leading to emissions from valves, flanges, compressor bearings, etc.
- Water washes of non-aromatics (raffinate) streams.
- Spent catalyst and solvent regeneration residue.

4.2.2 Building blocks of the aromatics process

4.2.2.1 Steam-cracked naphtha hydrofining (BB1)

Steam-cracked naphtha (also called pyrolysis gasoline or pygas) consists of a mixture of paraffins, olefins, diolefins, aromatics and alkenyl aromatics, ranging from C_5 to C_{10}+ components. The feed composition is dependent on the feed and operating conditions of the steam cracker and can vary substantially. Pygas contains a large amount of aromatics, including benzene, toluene and mixed xylenes. Before these valuable aromatic products can be extracted, however, full hydrogenation of any (di)olefins present and complete removal of any sulphur species present are required. To achieve this, the pygas is processed in a hydrofining unit, which typically consists of a predistillation section, a hydrogenation section and a stabilisation section.

The typical configuration of the steam-cracked naphtha hydrofining process is shown in the figure below. Other hydrogen treatment options upstream of the aromatic feed are considered in the REF BREF.



Source: [129, CEFIC 2015]

Figure 4.2: Typical configuration of a steam-cracked naphtha hydrofining process

4.2.2.1.1 Predistillation section

The pygas feed is sent to two distillation columns in series to remove the heavier C_{9+} fraction, which is rich in dicyclopentadiene (DCPD). The second column is operated under vacuum to minimise the bottom temperature and thereby avoid polymerisation reactions. The overhead C_{9+} content and in particular the DCPD content should be kept low, because DCPD (and its decomposition product cyclopentadiene) will also be hydrogenated in the following hydrogenation, resulting in unnecessary additional hydrogen consumption.

The overhead streams of both columns are condensed and collected together in a feed drum for the first-stage hydrogenation reactor.

4.2.2.1.2 Hydrogenation section

The liquid pygas, now free of C_9+ components, is mixed with hydrogen and sent to a first-stage trickle-bed hydrogenation reactor which has a palladium- or nickel-based catalyst to selectively hydrogenate (di)olefins and unsaturated aromatics (especially styrene). The heat generated by the exothermic hydrogenation reactions is recovered or dissipated and the reactor temperature is controlled by a reactor product recycling step with a heat exchanger. The reactor system is normally designed for a ratio of recycled to fresh feed of between 2:1 and 3:1. Catalyst activity is monitored by measuring the reactor bromine number and styrene conversion. The reactor product is collected in a recycle drum and then partly recycled to the reactor; the other part is routed to the second-stage hydrofining reactor.

Due to side reactions, the surface of the catalyst becomes gradually covered with heavy hydrocarbons, thereby reducing its activity. Raising the reactor inlet temperature (but within certain limits) will compensate for some activity loss. The catalyst will need to be regenerated if a further reactor temperature increase is not possible. *In situ* catalyst regeneration is done by oxidising the heavy hydrocarbon deposits on the catalyst with a superheated steam-air mixture. Alternatively the spent catalyst is unloaded for *ex situ* regeneration off site.

The feed to the second-stage reactor is mixed with hydrogen recycle gas, partially vaporised by heat exchange with the reactor effluent and then fully vaporised and raised to the second-stage vapour phase hydrofining reactor feed temperature. The second-stage hydrogenation reactor uses a combination of two different catalysts: a nickel/molybdenum catalyst converts all olefins into paraffins while a cobalt/molybdenum catalyst converts all sulphur species, mainly into hydrogen sulphide (H_2S). Both catalysts work in the form of metal sulphides given the presence of H_2S. When there are insufficient sulphur species present in the steam-cracked naphtha feed, a small amount of dimethyl disulphide may be injected to ensure the catalyst metals remain sulphided (any excess will again be converted to H_2S).

Catalyst activity is monitored by measuring the reactor olefins and sulphur species conversion. Side reactions also occur in the second-stage hydrofining reactor, gradually covering the catalyst surface with heavy hydrocarbons and reducing its activity. The reactor inlet temperature can be raised (but within certain limits) to compensate for some activity loss. If conversion levels are too low and a reactor temperature increase is no longer possible, regeneration or replacement of the catalysts by fresh catalysts is needed.

The reactor outlet product is cooled down by a feed-effluent heat exchange and other forms of heat integration and sent to a hot vapour-liquid separator drum. The vapour from this drum is further cooled down and sent to a cold vapour-liquid separator from which the recycle gas is routed to the compressor. A recycle gas purge is maintained to the site fuel gas system to avoid accumulation of light hydrocarbons. Hydrogen is added to the recycle gas to make up for the reactor hydrogen consumption.

The first- and second-stage hydrogenation reactors function together in achieving the desired hydrofined product quality. The first-stage hydrogenation can already convert some olefins to reduce the load of the second stage. Conversely, the second stage can handle some diolefins conversion, delaying the first-stage catalyst regeneration.

4.2.2.1.3 Stabilisation section

In order to remove the C_5- components in the hydrofined pygas, the hot and cold separator liquid streams are sent to a depentaniser fractionation column. The C_5- distillate product condensed in the overhead system of this column has a very small benzene content and may be reprocessed by the steam cracker. The vapour not condensed in the overhead system (hydrogen, methane, butane and pentane) is compressed and sent to the fuel gas system. The bottom stream from the depentaniser, now free of diolefins, sulphur species and C_5- components, can be used as feed to an aromatics extraction process.

There are a number of variations on this typical steam-cracked naphtha hydrofining flow scheme, including:

- dependanising is done as a first step (before hydrofining);
- depentanising and C_7+ / C_9+ removal is done between the first- and the second-stage hydrogenation reactor;
- different catalyst systems are used for the first- and second-stage hydrogenation reactor;
- *in situ* regeneration of second-stage hydrogenation reactor catalyst (similar to first-stage hydrogenation reactor catalyst) is carried out;
- full hydrogenation/desulphurisation is carried out using only one integrated reactor system.

4.2.2.1.4 Regeneration of hydrogenation reactor catalyst

Coke deposition is considered to be the most common cause of deactivation in catalysts for pygas hydrogenation.

Coke can be removed from the catalysts by either *in situ* or *ex situ* regeneration. *In situ* regeneration can result, if the required facilities are available and the regeneration procedure is properly conducted, in almost complete restoration of the catalyst activity. The effectiveness of regeneration is limited in the event that metal or other poisons are present on the catalyst.

Two different *in situ* regeneration procedures are generally used: gas (e.g. nitrogen) and hydrogen stripping at higher than normal process temperatures (mild regeneration) and steam-air regeneration (full regeneration).

Hydrogen stripping at higher than normal process temperatures enables the removal of 'soft' coke (high H to C ratio) which has formed on the catalyst. Timely mild regeneration is required since, over time, 'soft' coke slowly condenses to form a more hydrogen-deficient 'hard' coke, which can only be removed with air burn-off treatments. The hot hydrogen stripping converts the coke deposits into hydrocarbon liquids, which can be drained from the process to be burnt as fuel. The purge gas is sent to a site fuel system.

In the presence of oxygen under typical steam-air regeneration conditions, the organic part of the spent catalyst is oxidised. It should be noted that CO_2 is a major product even when the availability of oxygen is limited. The off-gas from gas stripping and from steam-air regeneration is sent to a water-cooled condenser unit to recover hydrocarbons and steam. Because of the presence of oxygen, the water cooler/condenser column off-gas is routed to the firebox of the regeneration furnace to burn hydrocarbons and CO traces that may still be present.

Final regeneration and cool-down of the catalyst is done with air, and during which the condenser column off-gas is released to atmosphere (e.g. via the regeneration furnace stack) as only minimal traces of hydrocarbons are present at this stage.

The frequency of catalyst regeneration aiming at coke removal very much depends on the feed characteristics, catalyst selection and key reactor performance controls (bed grading, liquid space velocities, temperatures, etc.). Coke formation can be minimised through feed treatment and the control of operating conditions.

In contrast to full *in situ* regeneration, the spent catalyst in *ex situ* regeneration needs to be unloaded, for regeneration off site.

4.2.2.2 Aromatic extraction and benzene/toluene production processes (BB2)

The feed to the aromatics extraction process comes from hydrogenated and desulphurised steam-cracked naphtha and/or catalytically reformed naphtha. Depending on the aromatics extraction technology used, the catalytically reformed naphtha may require an additional hydrofining step to remove diolefins/olefins.

The processes normally have the following sections:

- Aromatic extraction section: where the aromatic species (benzene and/or toluene and/or xylenes) present in pygas or reformate streams are separated from the non-aromatics species present that boil at similar temperatures. This separation of aromatics is done by means of a solvent, based on liquid-liquid extraction or extractive distillation.
- Clay treatment: the extracted aromatics from the previous section may be further processed at relatively mild temperatures in clay beds where small traces of olefinic impurities are reacted to yield heavy boilers that are removed from the aromatics downstream.
- A distillation section: where the different aromatic species are separated, to yield essentially pure products with the required commercial specifications.

4.2.2.2.1 Aromatics extraction and clay treatment

Traditional distillation cannot separate aromatics from non-aromatics, due to their similar boiling points. Therefore, aromatics are recovered by liquid-liquid extraction and/or extractive distillation. Various commercial liquid-liquid processes using specific solvents exist.

In general, two types of solvents can be used for aromatic extraction processes. Dry solvents, such as N-methyl-2-pyrrolidone (NMP) or di-methyl formamide (DMF) are used mainly in extractive distillation processes. When dry solvents are used, both the aromatic product stream and the non-aromatics stream are obtained practically dry, so usually no process water drains are produced.

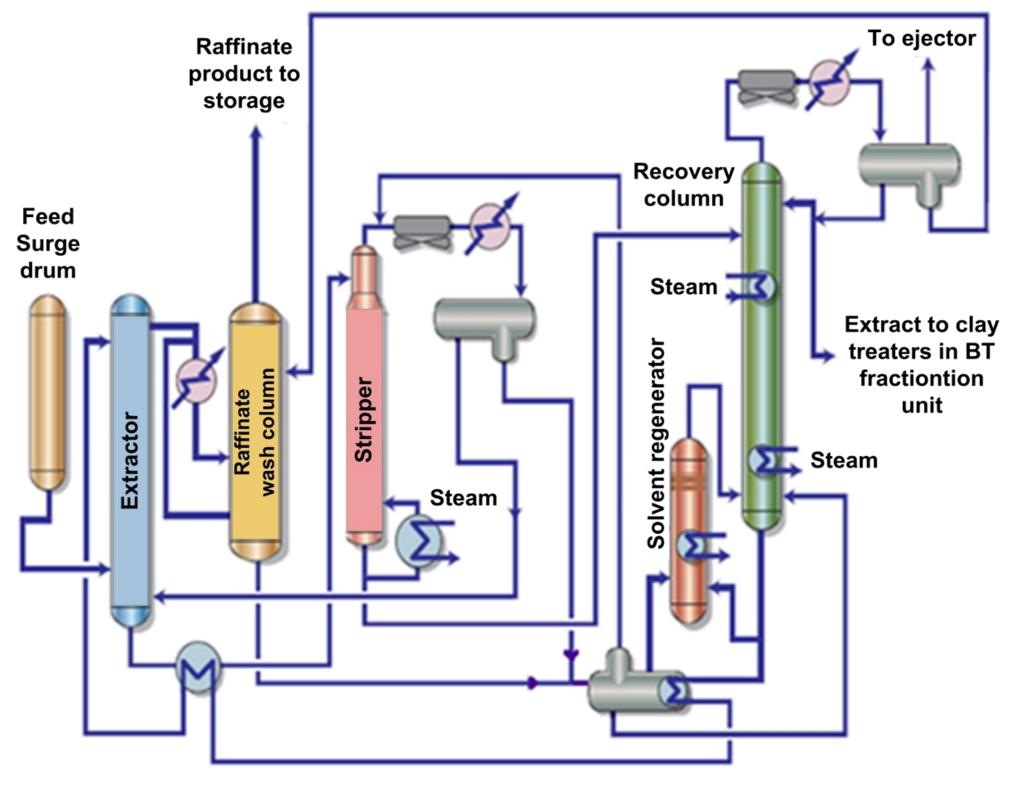
Wet solvents (solvent-water mixtures) are used for liquid-liquid extraction processes, such as in the case of sulfolane or dimethyl sulphoxide (DMSO), although some wet solvents can be used in extractive distillation processes (sulfolane). When wet solvents are used, the process implies phase separation and/or drying steps, and some of the water may be discharged as waste water.

The 'sulfolane liquid-liquid extraction' process is most common where benzene, toluene and mixed xylenes are being recovered. This is because the solvent sulfolane (tetrahydrothiophene 1,1-dioxide) exhibits a high selectivity and capacity for aromatics extraction. Other commercial extractive distillation processes exist, again using specific solvents. Where only benzene and toluene are recovered, the liquid-liquid extraction step can be omitted and extractive distillation suffices.

The sulfolane process is described in more detail below:

In the typical sulfolane liquid-liquid extraction process, feed enters the extractor and flows upward, countercurrent to a stream of lean sulfolane solvent. As the feed flows through the extractor, aromatics are selectively dissolved in the solvent. A raffinate stream, very low in aromatics content, is withdrawn from the top of the extractor.

The rich solvent, loaded with aromatics, exits the bottom of the extractor and enters the stripper. The non-aromatic components having volatilities higher than those of the dissolved aromatics are completely separated from the rich solvent in the stripper and removed overhead along with a small quantity of aromatics. This overhead stream is recycled to the extractor where the light non-aromatics displace the heavy non-aromatics from the solvent phase leaving the bottom of the extractor. The bottoms stream from the stripper, substantially free of non-aromatic impurities, is then sent to the recovery column where the aromatic product is separated from the solvent.



Source: UOP A Honeywell Company

Figure 4.3: Typical sulfolane aromatics extraction process

The recovery column is operated under vacuum to minimise solvent temperatures. Lean solvent from the bottom of the recovery column is returned to the extractor. The extract is recovered overhead and sent on to downstream distillation columns for recovery of the individual aromatics products. The raffinate stream exits the top of the extractor and is directed to the raffinate wash column. In the wash column, the raffinate is contacted with water to remove dissolved solvent. The solvent-rich water is vaporised in a water stripper by heat exchange with hot circulating solvent and then used as stripping steam in the recovery column. Accumulated solvent from the bottom of the water stripper is pumped back to the recovery column. Thus both the solvent circuit and the water circuit are designed as a closed internal circulation loop. The raffinate product exits the top of the raffinate wash column and is used for gasoline blending, steam cracking or aliphatic solvent applications.

Under normal operating conditions, the sulfolane solvent undergoes only minor degradation. Increased solvent degradation may occur when air leaks into the unit. A small solvent regenerator (typically a vaporiser, again operated under vacuum) is included in the design of the unit to maintain a high solvent quality. A small slipstream of circulating solvent is continuously directed to this solvent regenerator, to accumulate and allow removal of any solvent degradation products.

The extracted product may contain trace amounts of olefins and other impurities which would adversely affect final product qualities. To eliminate these trace impurities, the extract is clay-treated in mild conditions prior to fractionation. At some point, the activity of the clay will be exhausted and the clay will require regeneration or replacement. The clay-treated extract is directed to a fractionation section where high-purity benzene, toluene, and mixed xylenes are recovered.

4.2.2.2.2 Benzene/toluene fractionation

The production of aromatics products after extraction and removal of olefins by clay treatment requires the utilisation of several distillation columns. The configuration of this product fractionation section depends on the extracted aromatics. If benzene, toluene and mixed xylenes are jointly extracted, two fractionation columns are needed to produce pure benzene and toluene.

The arrangement of these distillation columns would then typically be as follows:

The first distillation column that processes the extracted aromatics is typically the benzene column, separating benzene as the distillate product with a 99.8 % to 99.95 % purity to meet commercial specifications. The bottom product then contains essentially toluene, mixed xylenes and some other heavy species. The column is operated such that both the specifications of toluene in the benzene product and that of benzene in the toluene product are achieved. The column reboiler is typically heated with steam or through heat integration with other columns.

The extracted aromatics feed to the benzene column may contain dissolved water, particularly when the extraction process uses a solvent that contains water (such as sulfolane or dimethyl sulphoxide (DMSO)). To remove the water, the distillate receiver at the top of the benzene column is provided with a water boot, allowing the condensed water phase to accumulate and to be drained to waste water treatment facilities. The dissolved water in the feed may also contain traces of chlorides and/or extraction solvent degradation products, potentially causing internal corrosion in the benzene column overhead section and condensing equipment. This corrosion concern is typically mitigated by preventing the formation/entrainment of any corrosive compounds and/or by the utilisation of chemical additives.

The bottom product from the benzene column is fractionated in the toluene column to recover the toluene product as the distillate product, leaving mixed xylenes and other heavy components as the bottom product. The column is operated such that both the specifications of mixed xylenes in the toluene product and that of toluene in the mixed xylenes are achieved. The column reboiler may be heated with steam, through heat integration with other columns or by a fired heater to provide the required reboiling duty.

Mixed xylenes may also be recovered as a commercial product from the toluene column bottom stream. In such cases, the toluene column is sent to an additional xylenes column to produce on-specification mixed xylenes as the distillate product and a small heavy bottom stream containing

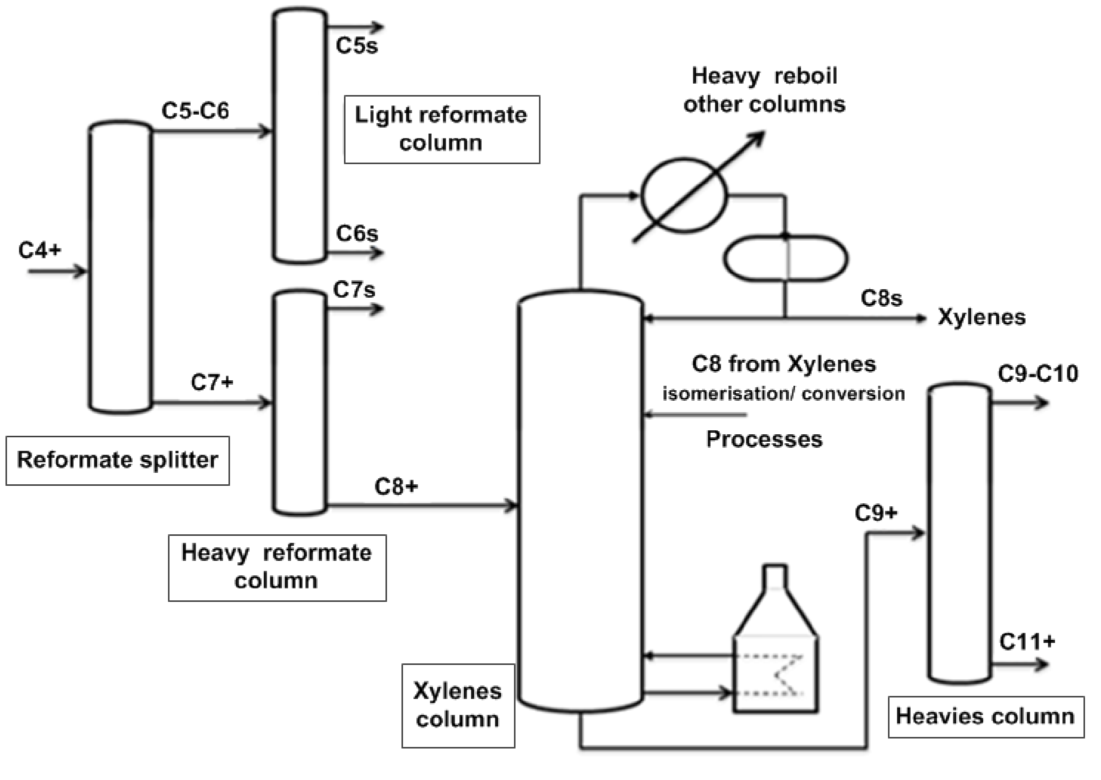
mainly heavier aromatics (C_9+) and by-products of the clay treatment (alkylated aromatics and oligomers). This bottom stream is typically sent for refinery reprocessing.
Where only one aromatic compound is extracted, the fractionation section may consist of only one column or may not need any column at all if the specification of that single aromatic product can be assured before extraction.

4.2.2.3 Xylene fractionation / clay treatment, xylene recovery and xylene isomerisation (BB3)

4.2.2.3.1 Xylenes fractionation / clay treatment

Mixed xylenes for individual C_8 aromatics isomers production are produced from refinery processes (catalytic naphtha reforming) and/or from xylenes isomerisation and/or aromatics conversion processes (toluene disproportionation).

Several fractionation schemes exist to recover mixed xylenes from the liquid naphtha reformer C_4+ fraction which contains the equilibrium xylenes, ethylbenzene and non-aromatics. A typical configuration is described and illustrated below, including potential interfaces with a refinery.



Source: [129, CEFIC 2015]

Figure 4.4: Typical xylenes fractionation

- The C_4+ reformate is first separated in a light reformate column to produce a C_5-C_6 distillate and a heavy reformate stream (C_7+ cut).
- The C_7+ stream is further separated in a heavy reformate column to produce a C_7 stream which can be used for gasoline blending or for toluene production.
- Both the light and heavy reformate columns are usually located in the refinery.

- The C_8+ bottom product from the refinery heavy reformate column is finally fractionated in the xylenes column to produce a mixed xylenes distillate stream (typically above 80 %) and a C_9+ bottom stream.
- The xylenes column is typically located in the aromatics plant. Supplementary feed to the xylenes column may come from chemical conversion processes in the aromatics plant producing mixed xylenes concentrates (xylenes isomerisation, toluene disproportionation).
- The xylenes column C_9+ bottom stream can be used for refinery gasoline-fuel blending purposes. This stream can be further fractionated in an aromatics plant heavies column if there is a demand to produce a C_9-C_{10} cut as a co-feed for a transalkylation process. The aromatics plant xylenes column typically has a fired heater reboiler and operates at an elevated pressure (up to 11 bar) in order to enable the condensing system to be heat-integrated (reboiling other columns) with significant savings in energy consumption.

Depending on the specifics of the aromatics plant, there are several variations of this typical scheme:

- If benzene and toluene are being extracted and recovered in the aromatics plant, the refinery light reformate column will produce a C_5-C_7 distillate product (instead of sending the C_7 cut to the gasoline pool) and the refinery heavy reformate column may not exist.
- If benzene, toluene and mixed xylenes are to be extracted and recovered in the aromatics plant, the refinery reformate splitter will produce a C_6-C_8 cut. In this case, a depentaniser may exist upstream of the refinery reformate splitter to remove C_5 hydrocarbons while the refinery heavy and light reformate columns may not exist.
- When ortho-xylene is a desired product from the aromatics plant, the xylenes column may actually be designed to split the C_8 isomers, producing a distillate product rich in meta-xylene, para-xylene and ethylbenzene, leaving ortho-xylene and C_9+ in the bottom. As the C_8 isomers' boiling points are very close, the xylenes column will require a significant number of trays in this case. An additional column before the heavies column is also needed to separate the ortho-xylene product from the C_9+.

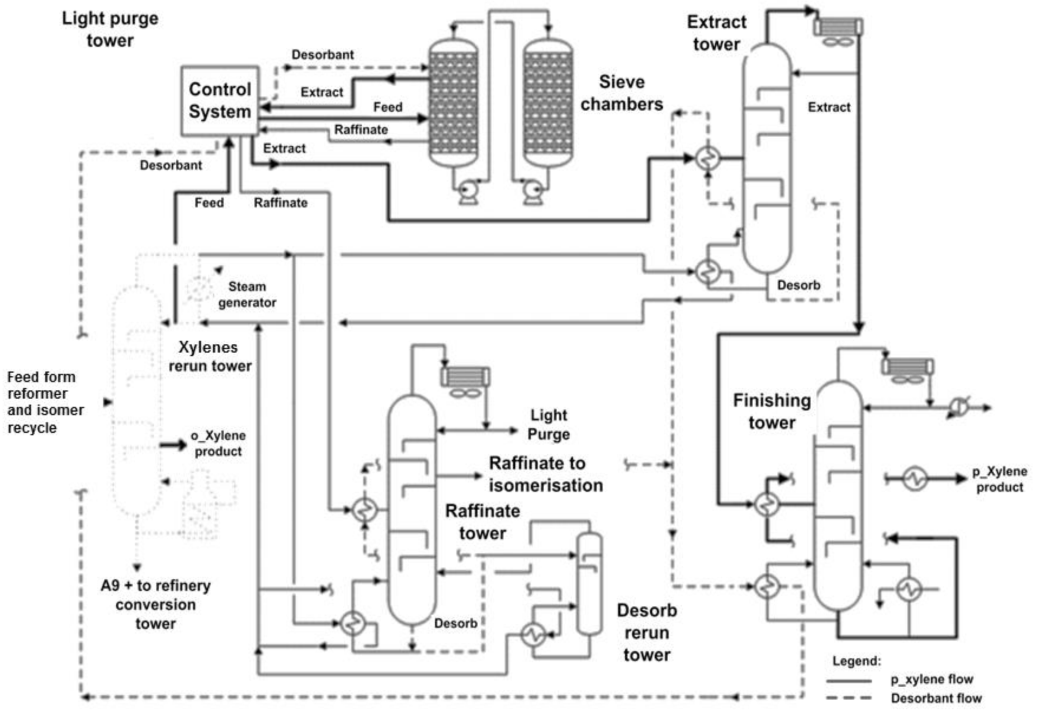
A clay treater is typically located in the feed to the xylenes column to remove traces of olefinic species that would affect the quality of the final xylenes products. At some point, the activity of the clay charge of the clay treater is exhausted and it requires regeneration or replacement.

As the xylenes column feed is essentially dry, no waste water is produced.

4.2.2.3.2 Para-xylene recovery

Xylenes separation focuses mainly on para-xylene, but producers may also produce ortho-xylene and, in some instances, meta-xylene is also extracted as a product. The xylene isomers have similar boiling points and so it is not possible to separate para-xylene by distillation. Separation is therefore achieved by adsorption or crystallisation. In order to improve the para-xylene recovery, the depleted para-xylene stream may undergo isomerisation to convert the ortho- and meta-xylene back to the equilibrium xylenes.

Para-xylene adsorption processes use adsorbent chambers which are divided into a number of adsorbent beds containing molecular-sieve-type material for selective para-xylene adsorption. Bed lines are provided to inject liquid into and to withdraw liquid from each bed.



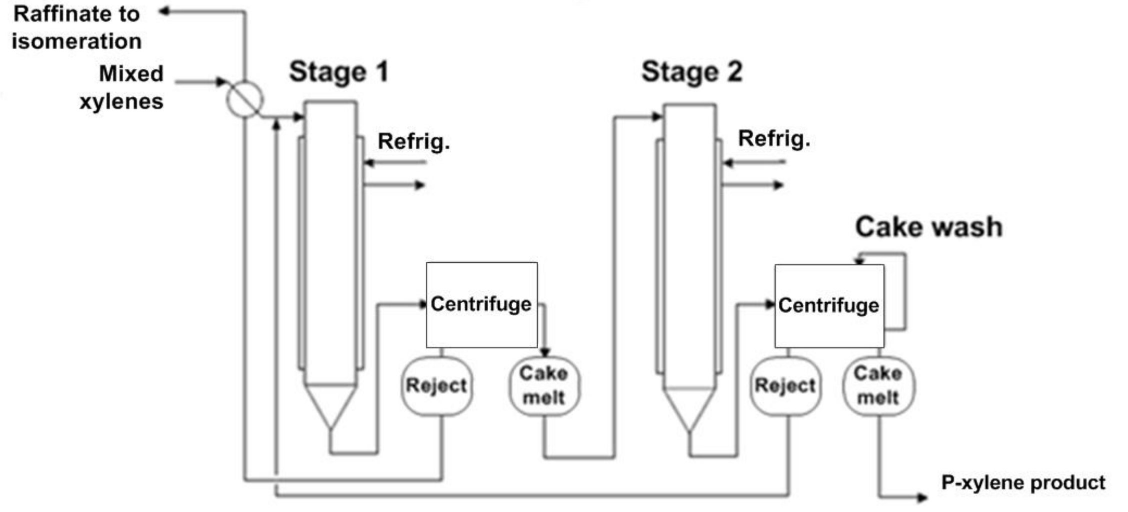
Source: [129, CEFIC 2015]

Figure 4.5: Typical para-xylene adsorption process

The two streams going in to the adsorbent chamber are the mixed xylenes feed and the desorbent (para-diethylbenzene or toluene) which is recycled from the fractionation section. The two streams coming out of the adsorbent chamber are the extract (para-xylene diluted with desorbent) and the raffinate (ethylbenzene, meta- and ortho- xylene diluted with desorbent). At any given time, only four bed lines are active, carrying these four streams into and out of the adsorbent chamber. The positions of the streams going in and out of the the chamber are periodically switched as the composition profile moves down the chamber. The extract is sent to the extraction column to separate the desorbent. Where para-diethylbenzene is used as the desorbent, the overhead product from the extraction column is sent to a finishing column where the pure para-xylene product is separated from any toluene which may have been present in the feed. The raffinate is sent to the raffinate column for separation of the desorbent. The overhead product of the raffinate column contains the unextracted C_8 aromatic components. This stream can be sent to a xylenes isomerisation unit to produce an additional mixed xylenes feed, from which para-xylene can be recovered again.

The desorbent from the bottom of both the extraction and raffinate columns is recycled back to the adsorbent chamber. In order to prevent accumulation of heavy components and desorbent degradation products, a slipstream of the recycle desorbent is taken to a small desorbent rerun column where those contaminants are rejected for refinery reprocessing. As the mixed xylenes feed is free of oxygen, clay-treated and rerun before being sent to the adsorption process, solvent degradation is normally only minor and the amount of heavy components to be removed from the desorbent is minimal. Filters may be installed in the desorbent circulation to remove any small particles (adsorbent fines). With these safeguarding measures, a good desorbent quality can be maintained , which will ensure that the molecular sieve material in the adsorbent chamber has a lifetime of more than 10 years. A very small amount of water may be injected into the feed to the adsorption chamber to maintain a high adsorbent selectivity. This water is accumulated in fractionator tower overhead systems and sent to the waste water treatment plant.

Para-xylene crystallisation processes make use of the high freezing point (+14 °C) of para-xylene compared to the other C_8 aromatics. The mixed xylenes feed is dried and cooled down by a low-temperature external refrigeration system to cause para-xylene to precipitate out of the solution as pure crystals, which can then be centrifuged.



Source: [129, CEFIC 2015]

Figure 4.6: Typical para-xylene crystallisation process

A disadvantage of para-xylene crystallisation processes is the inherent low per pass recovery rate as the minimum temperature is limited to prevent the crystallisation of other components. This disadvantage disappears when the mixed xylenes feed is rich in para-xylene (such as that produced from selective toluene disproportionation). In such cases, the crystallisation process design can be rather different, the per pass recovery rate can be high and the refrigeration requirement is reduced.

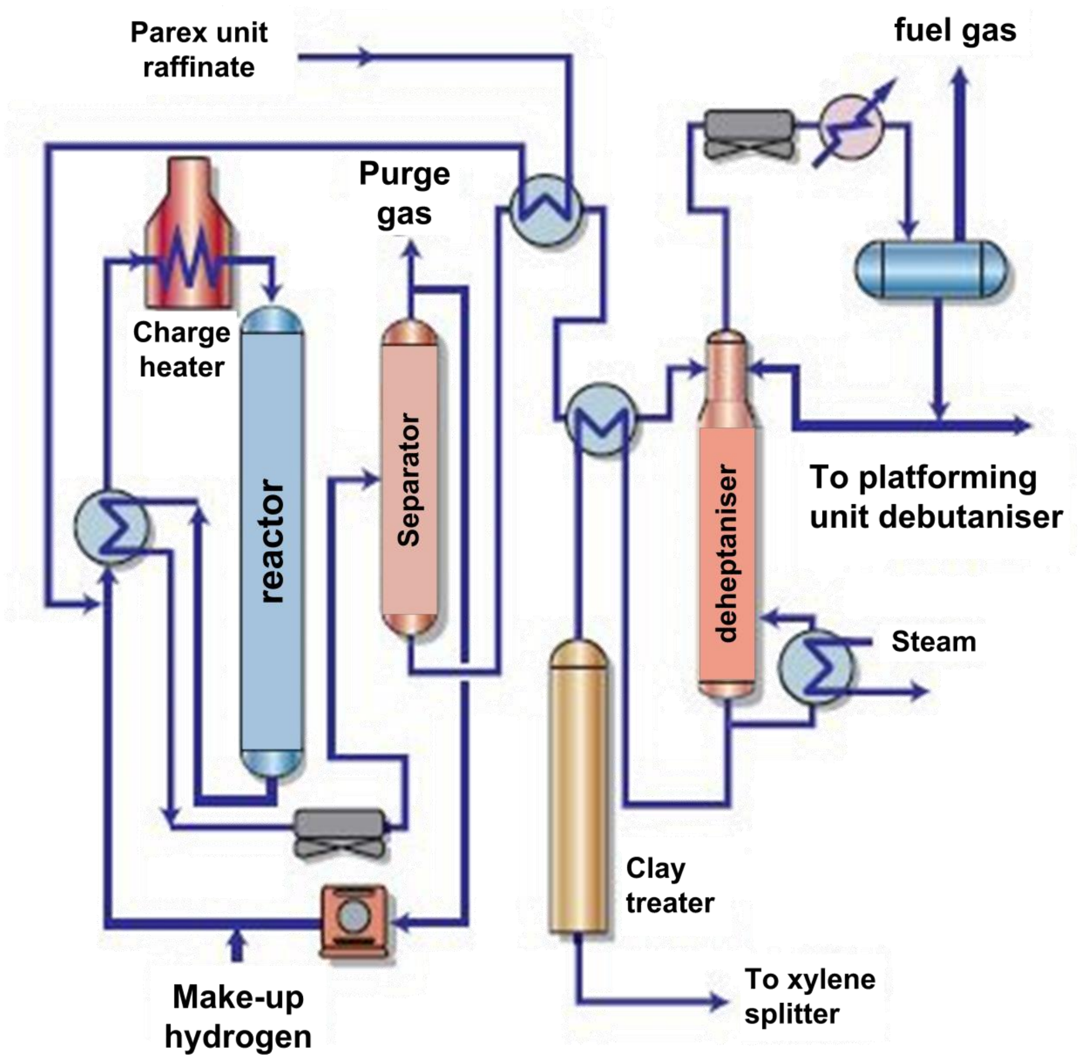
Hybrid configurations combining adsorption and crystallisation processes also exist.

4.2.2.3.3 Xylene isomerisation

Xylenes fractionation and para-xylene recovery are usually followed by a xylenes isomerisation process. This process aims to re-establish the para-xylene equilibrium concentration in the mixed xylenes from which the para-xylene has been recovered. By returning the xylenes isomerisation product to the xylenes fractionation, a recycle loop is created (called the xylenes loop), allowing all C_8 components in the overall aromatics plant feed to be completely transformed into valuable pure aromatic products. More specifically, the xylenes isomerisation process combines the following functions:

- Re-establishment of the thermodynamic chemical equilibrium between the three xylene isomers after para-xylene, and in some cases also ortho-xylene, is recovered.
- Conversion of ethylbenzene that would otherwise accumulate in the xylenes loop. Two alternative conversion technologies are available:
    - Dealkylation of ethylbenzene to give benzene and ethylene (the latter will be hydrogenated to ethane under the reaction conditions) is the most common technology in use.
    - Isomerisation of ethylbenzene to give a mixture of xylenes. This technology may be preferred when the xylenes feedstock is limited.

- Cracking of non-aromatic species that also accumulate in the xylenes loop into light hydrocarbon gases.



Note: Parex means para-xylene.
Source: CEFIC

Figure 4.7: Typical xylenes isomerisation process

In the typical xylenes isomerisation process, the para-xylene-depleted mixed xylenes feed is first combined with hydrogen-rich recycle gas and the mixture is preheated by exchange with the reactor effluent, vaporised in a fired heater, and raised to the reactor temperature. The hot vapour is then sent to the reactor, where it passes through a fixed bed of catalyst. The reactor effluent is cooled by heat exchange with the combined feed and then sent to the product separator. Hydrogen-rich gas is taken from the top of the product separator and recycled back to the reactor. A small portion of the recycle gas is purged to remove accumulated light ends from the recycle gas loop and hydrogen is added to make up for the reactor hydrogen consumption. Liquid from the bottom of the separator is charged to the deheptaniser column. The C_7-overhead from the deheptaniser is cooled and separated into gaseous and liquid products. The deheptaniser column off-gas is exported to the site fuel gas system. The liquid distillate is recycled to the debutaniser column of the upstream refinery catalytic naphtha reformer such that benzene formed in the reactor is recovered in the aromatics extraction unit. The C_8+ fraction from the bottom of the deheptaniser is clay-treated, combined with the fresh mixed xylenes feed coming from the reformate fractionation section and reprocessed in the xylenes column. The feed to the process may contain some traces of dissolved water that will accumulate in the boot of the distillate drum of the deheptaniser column.

4.2.2.4 Other conversion processes (BB4)

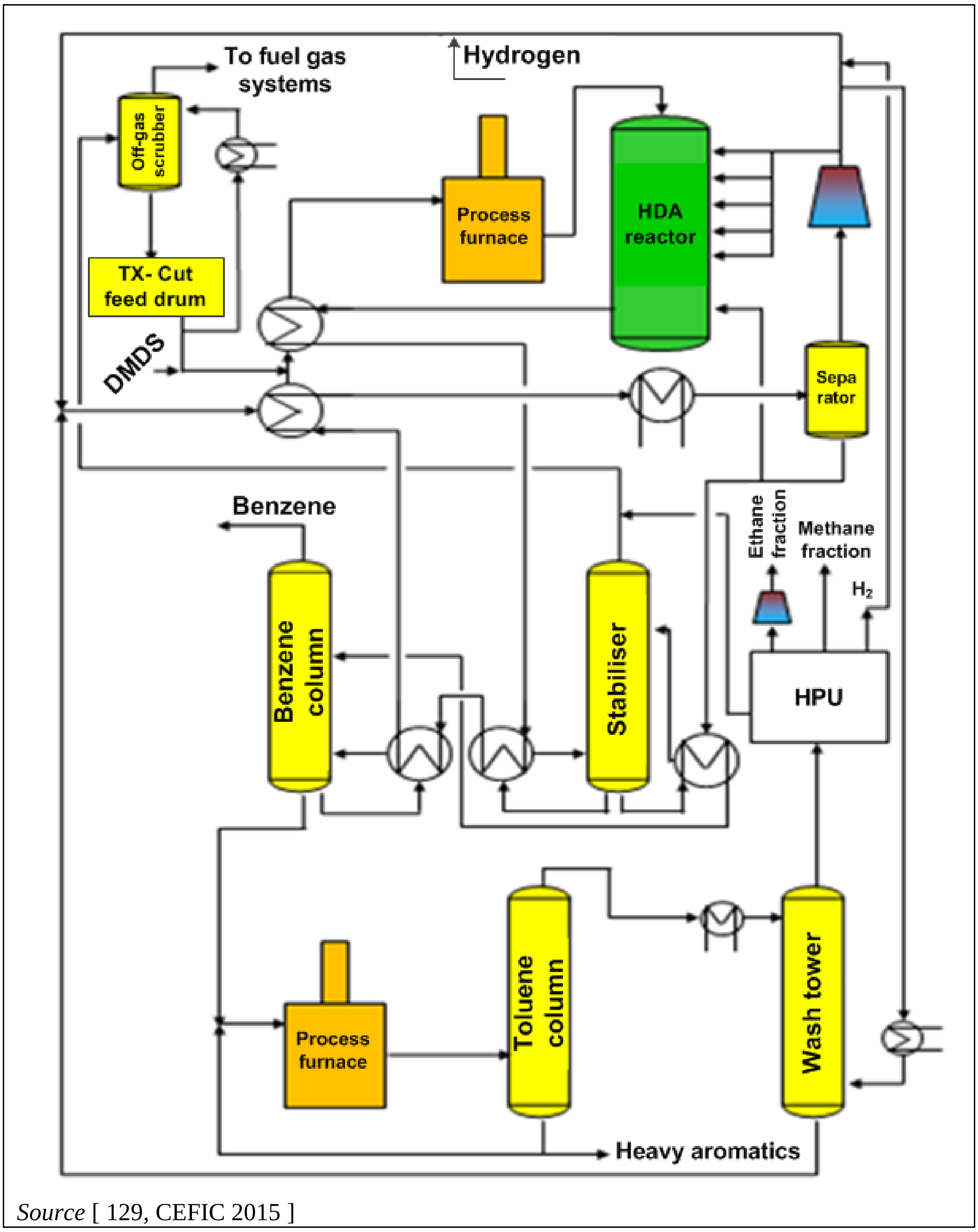
These units concern the conversion of toluene into more valuable products. Three of these conversion processes are considered in this section:

- toluene hydrodealkylation;
- toluene disproportionation;
- cyclohexane production.

A fourth process, toluene transalkylation, is not covered here as it is not carried out in Europe.

4.2.2.4.1 Toluene hydrodealkylation (HDA)

The hydrodealkylation process converts toluene or an aromatics TX concentrate (obtained from BTX fractionation and consisting of toluene, ethylbenzene, mixed xylenes, non-aromatics and C_9+) into pure benzene by removal of alkyl groups from the aromatic ring molecules. Some toluene ('wash toluene') is recycled inside the HDA process and used as a scrubber liquid to purify gaseous streams.



Source [129, CEFIC 2015]

Figure 4.8: Typical toluene hydrodealkylation process

The process comprises the following steps:

- feedstock takeover / off-gas scrubbing;
- hydrodealkylation reactor;
- hydrogen supply / recycle gas compressor / recycle gas purge scrubbing;
- stabilisation;
- benzene separation;
- heavy aromatics separation / wash toluene production;
- hydrogen recovery / hydrogen purification unit (HPU).

Feedstock takeover / off-gas scrubbing

Fresh feed from a TX-cut feed drum is mixed with preheated recycle gas and wash toluene after injecting a small amount of a dimethyl disulphide (DMDS)/toluene mixture. The ppm levels of DMDS in the feed will convert to hydrogen sulphide which minimises the formation of filamentary coke in the reactor and the downstream equipment. The total mixture is preheated by heat integration with the reactor outlet, vaporised and raised to the appropriate reactor inlet temperature by a fired heater. The feed system includes an off-gas scrubber to remove benzene from the stabiliser column off-gas (see 'Stabilisation'). The liquid recovered by the aromatics separator of the HPU (see 'hydrogen recovery / hydrogen purification unit (HPU)') is also depressurised and the released dissolved gases are routed to this scrubber. A small part of the TX feed is used as the scrubbing liquid and recycled to the feed drum. The purified scrubber off-gas is sent to the site fuel gas system by an off-gas compressor.

Hydrodealkylation reactor

The reactor is a tubular reactor with an inner insulation/lining of refractory concrete. As the hydrodelakylation reaction is exothermic, the reactor temperature is controlled by injecting quench gas at different points. The degree of dealkylation is controlled by varying the recycle gas amount and/or the reactor inlet temperature. The main reactions are the dealkylation of toluene and C_8/C_9 aromatics to benzene and methane/ethane. Paraffinic hydrocarbons present in the TX fraction are cracked to methane and ethane under the reaction conditions. Furthermore, a small amount of heavier aromatics are formed from side reactions. The hot reactor outlet stream is used in several heat exchangers to preheat and vaporise the reactor feed and to supply the heat duty for the stabilisation and benzene column reboilers.

Hydrogen supply / recycle gas compressor / recycle gas purge scrubbing

The reactor outlet is cooled down and sent to a vapour-liquid separator drum. The liquid from this separator is sent to the stabiliser. A small amount is continuously used as liquid quench for the reactor outlet. The vapour from the separator is recycled to the fresh feed by a recycle gas compressor. Hydrogen is added to the recycle gas to make up for the hydrogen consumed by the hydrodealkylation reactions. A recycle gas purge is maintained to control methane/ethane in the recycle gas and is cooled down and sent to a toluene washing tower to remove aromatics (see 'Heavy aromatics separation / wash toluene production'). The gas leaving the washing tower is sent to the HPU (see 'Hydrogen recovery / Hydrogen Purification Unit (HPU)'). The benzene content in this gas should be as low as possible to prevent the HPU from freezing up. The liquid bottom product from the washing tower is returned to the feed system.

Stabilisation

The liquid from the separator is preheated and sent to the stabiliser column which operates with a total reflux. Non-condensable vapours from the stabiliser are sent to the off-gas scrubber to wash out aromatics. The bottom product is sent to the benzene separation. The stabiliser column operation determines the type and quantity of non-aromatics in the final pure benzene product. In some cases, the stabiliser bottoms product requires an additional clay treatment step to remove traces of (di)olefins to produce on-specification benzene. The activity of the clay can be maintained by a steam-out to a closed system but at some point the clay charge is exhausted and needs to be replaced.

Benzene separation

The benzene column fractionates a high-purity benzene distillate product. The bottom product from this tower, consisting of toluene, C_8 aromatics and heavier aromatics, is sent to the heavy aromatics separation / wash toluene production section.

Heavy aromatics separation / wash toluene production

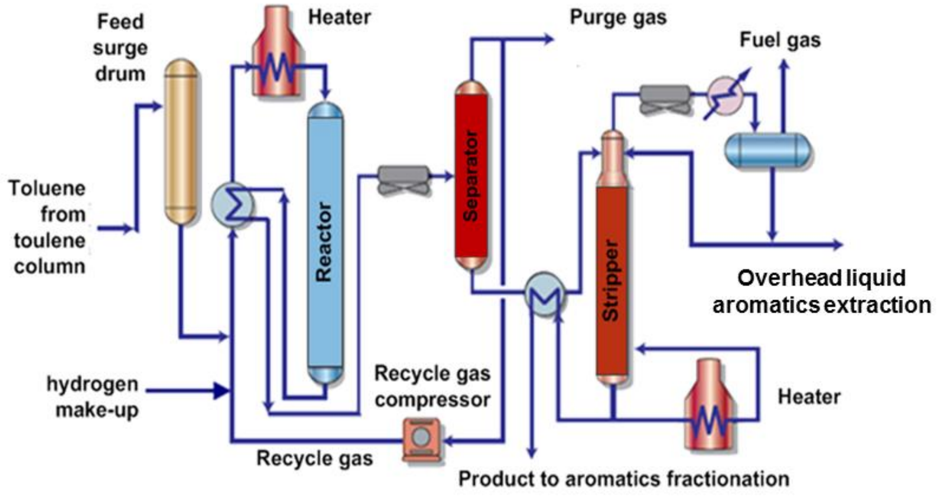
The toluene column recovers wash toluene from the combined benzene tower bottom stream and the bottom circulation product. A fired heater is used to heat up the combined feed to this tower .The wash toluene is cooled down and sent to the washing tower. The heavier aromatics fraction (HDA residue) bottoms product of the toluene column is reprocessed in the steam cracker. Some toluene column designs may also include steam injection to facilitate the separation.

Hydrogen recovery / hydrogen purification unit (HPU)

The gas from the toluene washing tower is sent to the HPU for hydrogen recovery. The HPU is a cold box which achieves separation by the auto-refrigeration, staged liquefaction and depressurisation/vaporisation of the ethane and methane in the gas, leaving a high-purity hydrogen product gas. The high-pressure gas enters the first HPU multi-stranded heat exchanger and is cooled against the cold product stream. In this first stage, aromatics that remained in the gas are condensed and separated to be returned to the off-gas scrubber. The gas leaving this first stage is cooled down further in a second multi-stranded heat exchanger. In this second stage, ethane and a part of the methane are condensed and separated and expanded into the ethane column where dissolved hydrogen and methane are distilled off. The remaining liquid ethane fraction is expanded, vaporised and heated up in the second and then in the first multi-stranded heat exchanger. It is then sent to the ethane compressor to be used as feed to the steam cracker or alternatively sent to the fuel gas system. As the heat source for the ethane column, a part of the second multi-stranded heat exchanger is used. The gas phase from the ethane separator is further cooled down in a third heat exchanger and the condensing methane is separated to yield high-purity (85–90 vol-%) hydrogen. The purified hydrogen is heated up in the third, second and first heat exchangers and returned to the recycle gas. The liquefied methane is depressurised/vaporised. A small part of the purified hydrogen is also depressurised into this stream to achieve a low methane separator temperature. This mixture is heated up in the third heat exchanger and sent to the overhead stream of the ethane column. The total methane fraction, consisting of the vaporised liquid from the methane separator and the overhead of the ethane column, is heated up in the second and first heat exchangers and is sent to the fuel gas system.

4.2.2.4.2 Toluene disproportionation (TDP)

When toluene product is available, additional valuable mixed xylenes and benzene can be produced by toluene disproportionation processes.



Source: UOP A Honeywell Company

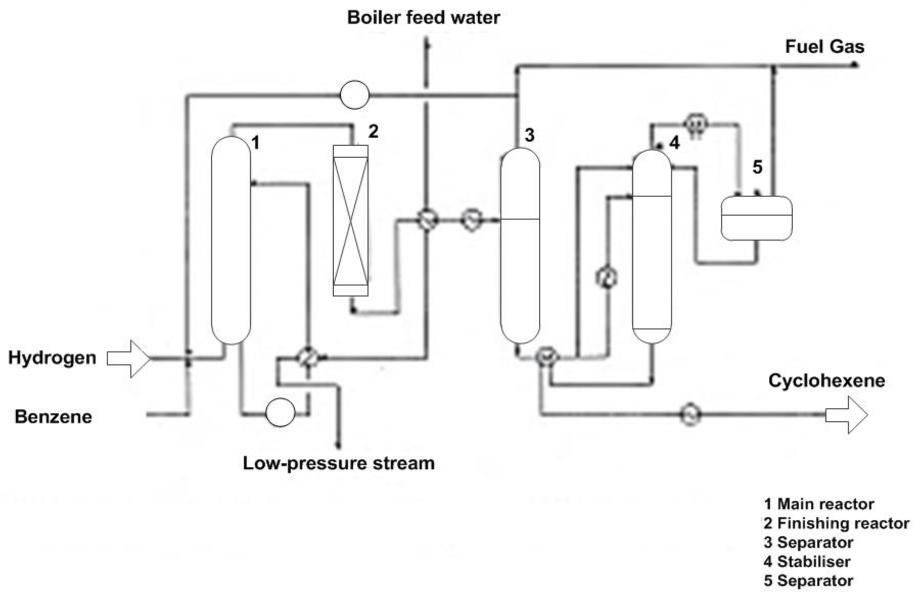
Figure 4.9: Typical toluene disproportionation process

Fresh toluene feed is combined with hydrogen-rich recycle gas, preheated and vaporised in a fired heater where it is raised to the reaction temperature (around 330 °C). The hot vapour feed is sent to a reactor (operating at a pressure of about 30 bar) with a fixed-bed catalyst, converting 30–50 % of the toluene into benzene and mixed xylenes. The reactor effluent is cooled by heat exchange with the combined feed and then sent to a product separator. Hydrogen-rich gas is taken from the top of the separator and recycled to the reactor. A small portion is purged to remove accumulated light ends from the recycle gas loop and a small amount of hydrogen is added to make up for the reactor hydrogen consumption. Liquid from the bottom of the separator is sent to a stripper column. The overhead from the stripper is cooled and separated into gas and liquid products. The stripper overhead gas is sent to the fuel gas system. Any benzene in the stripper overhead liquid may be recovered by refinery reprocessing and aromatics extraction. The benzene and mixed xylenes products, together with the unreacted toluene, are taken from the bottom of the stripper and sent to the aromatics fractionation and product recovery facilities.

Various toluene disproportionation processes have been developed, including selective toluene disproportionation processes that use a sophisticated catalyst which favours the formation of para-xylene as the main C_8 isomer in the mixed xylenes product. The increased para-xylene content of the mixed xylenes allows for a more efficient para-xylene product recovery step.

4.2.2.4.3 Cyclohexane production

Cyclohexane is produced by the catalysed hydrogenation of high-purity benzene (at least 98 wt-%). A variety of processes exist both for liquid and vapour phase benzene hydrogenation. In some process designs, prior to the benzene hydrogenation, the feed is first sent to a hydrodesulphurisation reactor to remove traces of sulphur compounds. Common to all processes is that benzene and an excess of hydrogen are contacted with a supported metal catalyst at a temperature of 80–300 °C and a pressure of around 30 bar. A high conversion rate is achieved by one or more reactors and facilities are included to manage and potentially recover the heat generated in each reactor by the highly exothermic hydrogenation reaction. Typically, hydrogen recycle gas compression facilities are also included, minimising the purge gas sent to the fuel gas system or hydrogen recovery. Light ends are removed from the cyclohexane product by a stabiliser and are typically sent to the fuel gas system.



Source [129, CEFIC 2015]

Figure 4.10: Typical cyclohexane production

4.2.3 Other than normal operating conditions

Measures that are commonly taken to reduce the occurrence and impact of other than normal operating conditions in aromatics plants are shown below.

4.2.3.1 Generic other than normal operating conditions

The following other than normal operating conditions can arise on any part of the process, and typically these account for less than seven days per year:

- shutdowns/start-ups for mandatory inspections;
- equipment failures (e.g. due to internal/external corrosion);
- equipment fouling/cleaning (in some aromatics extraction processes, chemical additives may be injected during the process to prevent corrosion, fouling or foaming issues resulting in other than normal operating conditions);
- hydrogen supply interruptions (where hydrogen is used);
- fuel supply interruptions (where fired heaters are used);
- nuisance trips (initiated by malfunctioning of safety instrumentation);
- equipment failures due to recycle gas compressor issues.

It is reported that, during these other than normal operating conditions, venting of equipment contents to flare may occur. For aromatics extraction processes, the solvent concentration in the waste water is monitored in order not to destabilise downstream waste water treatment operations.

Solvent regeneration is considered a normal operating procedure.

4.2.3.2 Specific other than normal operating conditions

For para-xylene recovery, other than normal operating conditions can also arise from fractionation tower upsets in adsorption processes or refrigeration circuit upsets in crystallisation processes.

For toluene disproportionation, other than normal operating conditions can also arise from splitter tower upsets.

For cyclohexane production, other than normal operating conditions can also arise from nuisance trips (initiated by malfunctioning of safety instrumentation).

For catalytic processes, other than normal operating conditions can also arise from catalyst regeneration or replacement. As described in Section 4.2.2.1.4 for pygas hydrogenation, aromatics plants operate with catalysts that deactivate over time. Several mechanisms are responsible for the deactivation, one of which is the deposition of carbonaceous residue (coke) on the surface of the catalyst. When deactivation reaches a level where conversion, selectivity or other process parameters are below the required specification, the catalyst must be replaced or regenerated. The regeneration and reuse of the catalyst is the preferable option.

However, the effectiveness of the catalyst regeneration depends on the nature of the deactivation. Some poisons are difficult (or even impossible) to remove from the catalyst. Similarly, deactivation as a result of catalyst sintering and thermal deactivation is usually irreversible.

The frequency of catalyst regeneration aiming at coke removal very much depends on the feed characteristics, catalyst selection and key reactor performance controls (bed grading, liquid space velocities, temperatures, etc.). Coke formation can be minimised through feed treatment and the control of operating conditions.

Only pygas treatment catalysts need frequent (mild) regeneration. Depending on the pygas feed quality, the first-stage hydrofining reactor catalyst will require full regeneration approximately once every two years. A spare reactor may allow the continuation of operations while the catalyst is regenerated *in situ* or is replaced by fresh catalyst. For the second-stage reactor, a spare reactor or regeneration system is not normally available and a unit shutdown is required every few years in order to regenerate or replace the catalyst.

4.2.4 Equipment important for environmental protection

The following systems perform critical operations for environmental protection and should have the longest uptime possible:

- closed vent and drain system(s);
- recompression system to avoid flaring low-pressure vent streams;
- PSA recovery system;
- waste gas treatment system;
- closed cooling water system;
- API oil-water separators;
- waste water treatment system;
- dedicated solvent recirculation systems.

4.3 Current emission and consumption levels

4.3.1 Emissions to air

Aromatics plants are usually integrated into the refinery auxiliary facilities (vent header, flare system, etc.). Therefore the process emissions to air from the plant's channelled sources will most commonly go to the end-of-pipe devices shared with or belonging to the refinery. It is possible that some older installations may still have some direct emissions to atmosphere or to flare. However, according to the CWW BAT conclusions, BAT is that emissions should be enclosed and treated where possible and that flaring should only be used for safety reasons or non-routine operations. Process vent streams not only contain calorific value but also valuable compounds such as hydrogen, which can be recovered for reuse.

The main environmental emissions to air from aromatics plants are related to combustion. Steam boilers or hot oil furnaces that supply heating fluid utilities can be dedicated solely to aromatics plants or shared with nearby installations. Some of these plants may also combust non-conventional (non-commercial) fuel, such as the tar stream generated in the fractionation section.

Combustion units generally provide energy for heating reaction mixtures (e.g. for hydrogenation) or for distillation reboilers. They are not designed to produce specific reaction conditions for chemical conversions, e.g. crackers, and so are (subject to consideration of thermal capacity) within the scope of the LCP BREF and outside the scope of the LVOC BREF.

Fugitive emissions and emissions from storage (e.g. benzene) are also relevant. Some plants may have feed/intermediate storage tanks between the different sections of the plant. These tanks have the potential to cause VOC emissions to arise from raw material, intermediates and product storage. The control of emissions from storage is described in the EFS BREF.

There is the potential for fugitive emissions of VOCs to air from aromatics production processes under normal operating conditions, particularly as parts of these processes operate under positive pressure. Fugitive emissions can arise from equipment such as pumps, seals and flanges, valves, etc. The control of fugitive emissions is described in the CWW BREF.

4.3.1.1 Emissions to air from steam-cracked naphtha hydrofining (BB1 units)

Modern pygas treatment units do not have direct emissions to air, although some older units may have these types of emissions either in one of the hydrogenation steps or in the fractionation. Emissions are channelled and the net emissions to air will depend on the type and efficiency of the end-of-pipe treatment. Sources include:

- hot separator downstream of the first step: VOCs, H_2S, CH_4, benzene, toluene and other light hydrocarbons; unsaturated olefins;
- cold separator downstream of the second step: VOCs, H_2S, CH_4;
- recycle compressor purge(s): VOCs, H_2S, CH_4;
- downstream stabiliser columns or flash vent: VOCs, H_2S, CH_4;
- vents from overhead column vessels and vacuum systems: VOCs.;
- purges/streams from gas recovery section: VOCs, H_2S, CH_4;
- waste gas from *in situ* catalyst regeneration;
- waste gas from exchange of catalyst.

4.3.1.1.1 Emissions from catalyst regeneration

Many operators subcontract the regeneration of catalysts to the catalyst provider or another service provider. Selecting *ex situ* regeneration will avoid emissions to air from regeneration at the installation but dust emissions during replacement may be an issue; the replacement operation can be done with the use of filters and vacuum devices to abate/collect the dust generated.

Some operators carry out certain steps or all of the hydrogenation catalyst regeneration *in situ* (see Section 4.2.2.1.4). The most common way to treat the resulting waste gas is to use a decoking drum, as wet dust abatement, in which the waste gas is simply washed with water; this will not be efficient enough to remove all VOCs from the waste gas. The spent washing liquor is routed to waste water treatment.

The preferred treatment options differ for the various regeneration steps. The off-gas leaving the condenser (see Section 4.2.3.2) is typically:

- sent to a furnace to abate hydrocarbons and CO (oxygen-containing off-gas from air/steam stripping); or
- treated (typically washed in a decoking drum (see above)) before being released to atmosphere; or
- sent to flare.

The treatment options in place are summarised in Table 4.2.

Table 4.2: Gaseous effluents during catalyst regeneration in selective hydrogenation

	Heating	**Stripping**	**Pre-oxidation**	**Burning**	**Cooling 1**	**Cooling 2**
Main gas components	N_2	Steam	Steam + air	Steam + air	Steam	N_2
Pollutants	Hydrocarbons	Hydrocarbons	CO, CO_2, hydrocarbons and impurities (1)	CO, CO_2, hydrocarbons, and impurities (1)	Impurities (1)	Impurities (1)
Route to	Thermal abatement (2)	Thermal abatement (2)	Decoking drum (3)	Decoking drum (3)	Decoking drum (3)	Thermal abatement (2)

(1) Impurities refer to compounds present in trace amounts in raw materials and which are adsorbed on the catalyst.
(2) Often flare; alternatives are combustion (furnace) or oxidiser.
(3) Before being routed to thermal abatement (see footnote (2)) or atmosphere.

The off-gas may also be sent to a site fuel gas system (used for off-gas from hot stripping with hydrogen).

4.3.1.2 Emissions to air from aromatic extraction and benzene/toluene production processes (BB2 units)

Emission of hydrocarbons to the air from this section is particularly important given the very high concentrations of benzene (which is classified as a CMR substance) and other aromatics that are managed there. Therefore, efforts need to be made by producers to minimise VOC emissions. Other substances of particular concern whose emissions should be prevented are extraction solvents, such as N-methyl-2-pyrrolidone (NMP), which has also been identified as a mutagenic substance. However, these solvents are typically high boilers with reduced volatility in comparison to the other chemical compounds managed in this section. Also, compounds from solvent degradation (such as SO_2 from sulfolane degradation) need to be considered.

Examples of emission sources are:

- extractive distillation column overhead vent;
- solvent recovery column overhead vent;
- fractionation overhead vent;
- stripper overhead vent;
- clay tower filling/emptying;
- vents from vacuum systems.

4.3.1.3 Emissions to air from xylene fractionation / clay treatment, xylene recovery and xylene isomerisation (BB3 units)

Process vents: modern units do not emit VOCs directly to air, although some older units may. Examples of these channelled streams are:

- recycle compressor purges;
- xylene isomerisation stabiliser/columns/flash vent;
- vents from overhead column vessels;
- purges/streams from gas recovery.

In the case of crystallisation processes, fugitive emissions also occur from the associated refrigerant system.

4.3.1.4 Emissions to air from other conversion processes (BB4 units)

Modern HDA units do not have direct VOC emissions to air, although some older units may have these types of emissions to air either in the stabiliser step or in the fractionation. Vent streams include:

- purge taken upstream of the recycle gas compressor;
- stabiliser column overheads;
- fractionation columns' overhead vents.

Vents from toluene hydrodealkylation processes include:

- benzene-methane fractionation vent;
- separator flash drum vent;
- vents from catalyst regeneration operations;
- stabilisation overhead vent;
- H_2 purification stabiliser overhead vents.

During the cyclohexane production process, small amounts of off-gas are produced which can contain some cyclohexane. In a typical plant set-up, this off-gas is collected and contained and used as heating gas for other processes. Modern cyclohexane plants do not have direct VOC emissions to air. The main gaseous stream is the off-gas from the reaction (which is routed to the recycling compressor).

4.3.2 Emissions to water

There are a number of effluent streams to water from the different process sections. The organic substances present will comprise a range of substances, some of which could cause harm if directly discharged into the water environment, either due to their toxicity or due to their oxygen demand. However, most of these substances will be biodegradable and a downstream biological effluent treatment plant is necessary. This will be a shared facility for the whole site, and, as aromatics plants are normally located inside refineries, the waste water treatment plant will often be located in the refinery.

The most important pollutants in the waste water are BTX and the solvents used in the extraction processes (e.g. sulfolane or DMSO) which may require pretreatment (e.g. stripping, see Section 4.4.2) and monitoring.

4.3.2.1 Effluent from steam-cracked naphtha hydrofining (BB1 units)

Normally the feed to the pygas unit is saturated with water. Water from the pygas feed accumulates at several drum water boot locations in the unit and is sent to the site waste water treatment plant.

Also, waste water that discontinuously arises from steaming or flushing is collected and sent to the site waste water treatment plant too.

Many of the organic substances that may be encountered will have some solubility in water, particularly given the increased temperatures involved, and the potential synergistic solubilising effect caused by the presence of other components.

There are only very few data from the questionnaires, and they indicate that the waste water volume flow from the unit may be relatively low (0.01–0.2 m^3/tonne of product, < 0.3 m^3/h from vacuum systems).

4.3.2.2 Effluent from aromatic extraction and benzene/toluene production processes (BB2 units)

Effluent streams include the following:

- In aromatics extraction processes, a steam ejector is used to maintain the recovery column / solvent regenerator vacuum, a condensate is produced which is directed to the waste water treatment plant as this condensate may be contaminated with hydrocarbons.
- A clay charge (or, in some cases, also reformate hydrofining catalyst) that requires replacement is steamed out to a closed condensation system to be freed of hydrocarbons before being discharged. The condensate is sent to the waste water treatment plant.
- In benzene/toluene production, when the feed comes from a ‘wet’ aromatics extraction process, water is drained from the water boot of the benzene column distillate receiver. A few hundred grams of water may be produced for every tonne of aromatics extract produced and this is sent to waste water treatment facilities.

These streams may contain BTX, solvent, methanol (or acetone), and strongly polar auxiliary agents (alcohols, ketones). Questionnaire responses mention solvents like DMSO or sulfolane and hydrocarbons, e.g. C_{6-9} aromatics.

4.3.2.3 Effluents from xylene fractionation / clay treatment, xylene recovery and xylene isomerisation (BB3 units)

In xylene fractionation / clay treatment, a clay charge that requires replacement is steamed out to a closed condensation system to be freed of hydrocarbons before being discharged. The condensate is sent to the waste water treatment plant.

In para-xylene crystallisation, in feed dryers' water is stripped with hot gas to a closed condensation system from which minor quantities of accumulated water are sent to the waste water treatment plant.

In xylene isomerisation, less than 100 grams of water are produced from the deheptaniser distillate drum for every tonne of xylenes processed and this water is sent to waste water treatment facilities.

4.3.2.4 Effluents from other conversion units (BB4 units)

The feed to the cyclohexane plant usually contains no, or only very little, water. The amount of water generated is low but also depends on the feed composition and the plant design.

Water can be purged out of the system via water boots or other draining systems.

In toluene hydrodealkylation, water produced from regeneration of a clay charge is collected and sent to the site waste water treatment plant. If steam injection is used in the toluene column, water is continuously removed from the overhead system and also sent to the site waste water treatment plant.

4.3.3 Raw material consumption

As described in Section 4.2, depending on the building block / process unit, raw materials for the aromatics processes are mainly different hydrocarbon feedstocks (which, besides aromatic compounds, may contain saturated hydrocarbons and olefins), solvents, hydrogen, air, water, catalyst and clay material. For most of these raw materials, hardly any data have been provided on specific consumption levels. Where material is lost as waste, data are summarised in Section 4.3.6.

4.3.4 Energy consumption

Combustion plants (e.g. for the generation of steam) associated with the manufacture of aromatics, including those using non-commercial fuels, are covered by the LCP BREF. Techniques that address the energy generation (supply) devices and operations (hot oil furnaces, steam boilers) such as low-NO_X burners are also covered in the LCP BREF.

Aromatics plants consume fuel and steam for heating (e.g. reactions, distillations) and electrical energy (e.g. for compressors and pumps).

It is difficult to make comparisons between different aromatics plants because of the widely differing configurations. Only a few operators provided data. The ranges in Table 4.3 show the order of magnitude of energy consumption for different processing units.

Table 4.3: Energy usage per tonne of product

		Pygas BB1	**BTX extraction BB2**	**Xylene fractionation BB3**
		(kWh/t)	(kWh/t)	(kWh/t)
Total	Max.	462	1564	2854
	Min.	418	633	1757
Steam	Min.	182	531	382
	Max.	363	622	1398
Electrical	Min.	15	11	292
	Max.	54	72	320
Fuel	Min.	40	149	1054
	Max.	226	875	3960
Source: Data from data collection (2012).				

4.3.5 Water usage

There are a number of potential uses for process water in aromatics production, although actual process water usage is generally not measured. These uses are listed below:

a) Extraction processes.
b) Solvent recovery processes. Water may be needed, e.g. for the washing of process streams (e.g. to remove salts), for the regeneration of ion exchange columns and as boiler feed water to produce steam for the treatment of spent clay and catalyst.
c) Caustic washes. Water can be introduced into the process along with some raw materials (e.g. sodium hydroxide solution). These raw materials may be delivered to the site in the desired concentration, or they may have to be diluted to the required concentration after receipt; the water usage for any use of this nature would therefore have to be judged in the context of the nature of the raw materials.
d) Some process water may be added to the fractionation and purification activities in order to modify a column's composition and temperature profile, in order to make the achievement of the desired outcome easier. The nature of the fractionation/purification activities could therefore have an impact on the process water usage.
e) Water that is used in the operation of vacuum systems (ejectors), to replace purges from steam/water circuits.
f) Boiler feed water.

4.3.6 By-products and waste generation

Residues and wastes generated include spent catalyst, spent clay and solvent regeneration residues. Waste generation is strongly related to process turnaround, which occurs at long time intervals.

4.3.6.1 By-products

Since composition can vary in the feeds, and the processes include purification steps, most of the units generate one or various by-product streams. Table 4.4 shows a few examples of such by-product streams (including additionally some gaseous streams).

Table 4.4: Other products from aromatics plants

Unit	Source	Stream
BB1 unit:		
Pygas hydrogenation		Fuel gas; drag stream
Pygas hydrogenation	Cold separator	Hydrogen
	Depentaniser	C_5; C_6; C_7+
BB2 unit:		
Aromatic extraction	Toluene column	C_8+ aromatics
Xylene	Xylene column	C_9+ aromatics
Extractive distillation	Ext. distillation top cut	Non-aromatic HC
BB3 unit:		
Xylene crystallisation	Centrifuge	Mother liquor
Xylene adsorption	Fractionation	Light ends
BB4 unit:		
HDA	Fractionation	Fuel; di-phenyl; hydrogen; ethane
TDP	Fractionation	Light ends; C_5+ aromatics; C_9+ aromatics

As illustrated by Table 4.4, in the majority of aromatics units there are distillation columns, some of them producing a small continuous by-product bottom stream of high boilers (distillation heavy cut, oligomers, etc.).

The amount of this material that is not waste and is further used ranges from 5 kg to 100 kg per tonne of product.

4.3.6.2 Waste from catalyst regeneration and spent catalyst

The hydrogenation catalysts used to upgrade the pygas in the first stage are typically nickel- or lead-based. The catalyst needs to be regenerated periodically and eventually replaced. The frequency with which this will be required will depend to a large extent on the presence of poisons, the operating conditions, and the nature of the catalyst. See Sections 4.2.2.1.2, 4.2.2.1.4 and 4.2.3.2.

Catalyst regeneration may result in the production of a small quantity of residue which is sent to incineration. Spent catalysts are sent to (external) metal recovery.

Example values from the data collection are as follows: 0.0015–0.04 kg/t of product for spent first-stage hydrogenation catalyst and 0.009–0.12 kg/t of product for spent second-stage hydrogenation catalyst.

The xylene isomerisation reactor catalyst charge load is normally replaced every 6 to 12 years. The spent catalyst is discharged for external disposal or incineration.

The catalyst for cyclohexane production generally consists of supported platinum, nickel or ruthenium. The typical life of the catalyst is 6 to 12 years; it is sent for metals reclaiming.

Toluene disproportionation catalysts normally have a lifetime of more than 10 years. When it is replaced, the spent catalyst is sent for external disposal.

4.3.6.3 Spent clay

Spent clay arises from the vessels in which small quantities of olefins are reacted to generate heavy boilers that can be easily separated from the pure aromatics streams by distillation. To replace the spent clay (when it loses efficiency for olefins removal), the vessel needs to be taken out of service and unloaded following similar procedures to those used to unload fixed-bed reactors or adsorbers. Most plants are provided with two clay treaters, so when one of them is taken off-line for unloading spent material and loading fresh clay, the other treater remains in operation, allowing the production of aromatics to continue.

Clay charges in pygas units have a typical lifetime of six months to two years. Clay charges from xylene fractionation and recovery have a typical lifetime of two to six years. Clay charges from xylene isomerisation units have a typical lifetime of two years. Spent clay may contain some heavy boiling hydrocarbons, gums and traces of aromatics, and should be managed in such a way so as to minimise the environmental and human impacts. They are discharged for external disposal or incineration. Maximising the lifetime of the clay charge by the selection of the clay material and appropriate operation of the clay treatment will minimise this solid waste.

Table 4.5: Ranges of consumption of clay from the data collection

Unit type	Spent clay (kg/t of product)
BB1	0.065–0.217
BB2	0.104–0.65
BB3	0.104
BB4	0.005

4.3.6.4 Solvent sludge from BTX extraction

Solid sludge is generated in the solvent regeneration (evaporator) of the extraction unit. A small non-vaporised residue is left in the bottom of the regenerator containing solids such as gums, the products of degradation and oxidation of the solvent, scale, heavy boilers entrained by the feed, other residues and some solvent that remains attached to the solids. This mixture forms a slurry paste accumulating to a few hundred kilograms which are periodically (once every 2 to 10 weeks typically) unloaded and sent for disposal.

Some units may have filters in the solvent loop instead of solvent regenerators. They are typically less effective than a regenerator and also imply the frequent removal of solids.

Some units that do not have regenerators and that work for some periods with poor-quality solvents may not generate solids during normal operating conditions, but could have periods of degraded operation, impacting on extraction capacity and/or energy consumption and/or solvent consumption (batch replacement of larger quantities of solvent from the solvent loop).

An example from the data collection gives as a figure for solid sludge from solvent regeneration 0.05–0.003 kg/t.

4.3.6.5 Adsorbents

Adsorbents are used, for example, in the para-xylene adsorption process and for gas purification, e.g. as a pretreatment upstream of hydrogen purification units. These adsorbents typically consist of alumina or molecular sieves and have a lifetime of more than 10 years. Para-xylene crystallisation process feed dryer materials similarly have a lifetime of over 10 years.

Spent adsorbent is usually disposed of as a waste.

4.3.6.6 Other waste steams

Oil-contaminated materials and oily sludge (from solvents, biotreatment and water filtration) are incinerated under carefully controlled conditions, with associated heat recovery.

There is a certain amount of solid waste and some sludge produced during the cleaning of some equipment in maintenance operations (e.g. ‘gums’ from unsaturated cuts, filter cartridges). The amounts may be generally negligible, episodic and not easily related to the process conditions. These materials are typically sent to incineration.

Sludge and solid polymerisation material that are recovered from process equipment during maintenance activities are typically incinerated off site but can be used on site as a fuel source.

4.4 Techniques to consider in the determination of BAT

This section describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this chapter. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations). Cross references to other chapters are used, where relevant to avoid repetition.

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 2.6 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

4.4.1 Techniques to reduce emissions to air

4.4.1.1 Generic techniques to reduce the organic load from process off-gases

In order to reduce the organic load from process off-gases and to increase the resource efficiency or, where this is not practicable, to recover energy from these process off-gases, a variety of techniques are used. The majority of the techniques used in aromatics plants are generic to the LVOC sector. The first priority should be to recover hydrocarbons and, where appropriate, hydrogen for reuse. Otherwise energy should be recovered (by combustion and heat recovery in a combustion plant or a thermal oxidiser). Flaring should only be used for safety reasons or for non-routine operations.

All of the techniques shown below are described in Section 2.4 of this document, in the REF BREF or in the CWW BREF. The techniques listed below are widely applied in aromatic complexes. However, not all techniques are applied in all plants; the combination of techniques that can be applied will be dependent on the configuration of the complex.

- Condensation and cryogenic condensation: Condensers are used to recover materials and/or reduce the VOC content in the process-related vent streams. Cryogenic separation (cold box) is used to recover expensive/scarce raw materials (e.g. hydrogen or methane) from recycle compressor purges or other vent streams. This technique is used, for example, in BB1, BB3 and BB4 units.
- Adsorption: Adsorption using activated carbon or other adsorbents enables the recovery of hydrocarbons (feedstock, by-products, products or solvents) from the gaseous stream.
- Recovery of energy from process streams (calorific value): The gaseous stream is sent to the fuel gas system/furnace to recover energy from the VOCs contained in such a stream.

Normal operating pressures should allow the fuel gas produced in the process to be fed directly to the fuel gas system.

- Gas recompression to recover energy or feedstock: Some units/unit operations are designed to operate under vacuum or low pressures. In this case, the overhead vents have a lower pressure than the vent header or fuel gas header; they can be recompressed and sent to the fuel gas network or a furnace. Gas recompression is used to fully recover some or all of the hydrocarbons that would otherwise be vented to the final treatment, or, on some occasions, to flare.
- Recovery of feedstock: Some gas streams contain valuable chemicals and are returned to the process for recovery.

4.4.1.2 Recovery/reuse of material from hydrogen-containing process off-gas

BB1 units:
The gases separated after the hydrogenation reactors (or purged if the unit is equipped with a recycle compressor) have reduced concentrations of H_2. However, techniques can be applied to recover energy or valuable feedstock and reduce emissions.

- In some cases, it is possible to use hydrogen-containing gases in other hydrotreatment units that could operate with lower hydrogen purities.
- In other cases, they are used as a fuel gas on site, given the higher quantities of hydrocarbons such as methane and ethane.
- In some units, it is possible to reconcentrate H_2 by using a PSA unit or a cold box (cryogenic separation). However, the latter option requires a very large investment and in general is not justified.

BB3 and BB4 units:
Recovery of diluted H_2, ethane and methane streams: the gases separated after the isomerisation reactor and hydrodealkylation reactor (or purged if the unit is equipped with a recycle compressor) have reduced concentrations of H_2, ethane and methane. However, they can still be further processed to prevent emissions and to reduce hydrogen consumption.

- In some units, it is possible to reconcentrate H_2 by using a PSA unit or a cold box (cryogenic separation).
- Furthermore, separated methane can be used directly as a fuel gas and the ethane fraction can be sent back to upstream steam crackers as feed, but also used as a fuel gas.

4.4.1.3 Routing of the process off-gas from the regeneration of the hydrogenation catalyst to a suitable treatment system

Description
The process off-gas is sent to wet or dry dust abatement devices to remove dust and then to a combustion unit or a thermal oxidiser to remove organic compounds in order to avoid direct emissions to air or flaring. The use of decoking drums alone is not sufficient.

Technical description
As described in Sections 4.2.2.1.4 and 4.3.1.1.1, the different steps of the mild and full regeneration of hydrogenation catalysts may require different forms of off-gas treatment. Depending on the off-gas composition, a condenser unit is used to recover hydrocarbons. Dust is removed, typically by wet dust abatement. Then, to minimise emissions, waste gas streams containing organic compounds are routed to a thermal abatement unit. In order to avoid flaring,

the waste gas is routed to an existing combustion unit or shared thermal oxidiser. For example, the off-gas from hydrogen stripping is sent to the site fuel gas system, and the oxygen-containing off-gas from steam-air stripping is routed to the firebox of a furnace.

Flaring is only used in events where there is no other treatment option available due to safety reasons.

Achieved environmental benefits
Lower emissions to air.

4.4.2 Techniques to reduce emissions to water

The main sources of waste water are:

- steam used during *in situ* hydrofining catalyst regeneration (BB1);
- vacuum systems (BB1, BB2);
- recovery column in the sulfolane process (BB2);
- raffinate water wash in the sulfolane process (BB2).

Aromatic products (e.g. BTX) and solvents are the main potential pollutants. Depending on the concentration, load, biodegradability and toxicity, pretreatment (see Section 4.4.2.1) and/or periodic monitoring of the waste water streams is carried out (for waste water management, see the CWW BREF). Monitoring may not be necessary where integrated techniques are in place that ensure that emissions are low. Solvents include sulfolane, dimethyl sulphoxide (DMSO), N-methyl-2-pyrrolidone (NMP) and N-formyl morpholine (NFM).

The majority of the techniques used in aromatics plants are generic.

4.4.2.1 Generic techniques to reduce the waste water and organic load from aromatics plants

The techniques listed below which are used in appropriate combinations are described in Section 2.4 or in the CWW BREF. In the event that they are not considered generally applicable for aromatics plants, the applicability of these techniques is set out below.

- Water-free vacuum generation (see Section 2.4.7.1): This technique involves the use of mechanical pumping systems in a closed circuit procedure, discharging only a small amount of water as blowdown, or the use of dry-running pumps. In some cases, waste-water-free vacuum generation can be achieved by use of the product as a barrier liquid in a mechanical vacuum pump, or by use of a gas stream from the production process.
- Source segregation of waste water (see Section 2.4.4.3): Waste water from aromatics plants is segregated from other sources of waste water in order to facilitate the removal and recovery of raw materials or products. For existing plants, the applicability may be restricted by the site-specific drainage system.
- Stripping to recover hydrocarbons (see Section 2.4.8.1.3): Stripping can be used on individual or combined streams. For small streams, stripping mainly for recovery may not be justified if the hydrocarbon concentration is too low, e.g. < 1 wt-%.
- Liquid phase separation with recovery of hydrocarbons (see Section 2.4.4.4): This involves the separation of organic and aqueous phases with appropriate system design and operation (e.g. sufficient residence time, phase boundary detection and control) to prevent any entrainment of undissolved organic material.

- Reuse of water (see Section 2.4.7.2): With further treatment, water effluents after stripping can be used as process water or as boiler feed water, replacing other sources of water.

4.4.2.2 Use of dry solvents or closed systems for aromatics extraction

Description
Use of dry solvents or closed systems in order to reuse water.

Technical description
For aromatics extraction, dry solvents and wet solvents are used. Dry solvents will generate no or a very small amount of waste water effluents. Wet solvents are operated with a closed loop recovery system for the recovery and reuse of water (e.g. after separation by drying/condensation).

Achieved environmental benefits
Reduced waste water volume and solvent emissions to water.

4.4.3 Techniques to reduce raw material consumption

4.4.3.1 Use of co-produced hydrogen

Description
Use of co-produced hydrogen as a chemical reagent or fuel, or, where that is not practicable, to recover energy from these process vents.

Technical description
Co-produced hydrogen, e.g. from dealkylation reactions, is recovered and used as a reagent, e.g. for hydrogenation reactions. Hydrogen may also be used as a fuel.

Where these options cannot be applied, the process off-gas is combusted (e.g. in a combustion unit or an oxidiser with heat recovery) to recover energy.

See techniques for recovery of hydrogen in Section 2.4.3.4.1.

See techniques for recovery of energy in Section 2.4.6.2.1.

Achieved environmental benefits
- Reduction of consumption of materials.
- Reduction of consumption of energy.

Technical considerations relevant to applicability
Use of hydrogen as a reagent is only applicable for sites where hydrogenation reactions are carried out (which is usually the case).

4.4.3.2 Other techniques

4.4.3.2.1 BB1 units

In order to minimise hydrogen usage, some plant designs allow the recovery of hydrogen-rich gas streams (e.g. from hydrogenation) as a feed for hydrogenation (e.g. recycling or second-stage hydrogenation) or other usages.

4.4.3.2.2 BB2 units

The techniques used to increase aromatics recovery (reduce feedstock consumption) from an aromatics extraction unit under normal operating conditions are as follows:

- Optimisation of the operating conditions (solvent ratio, temperatures, pressures in columns and internal recirculation loops) for the best compromise between energy consumption and aromatics recovery while assuring the required product quality.
- Use of control systems that allow the regulation of process conditions to achieve close to optimum operation (product recovery and energy consumption). Advanced process control systems may, in some cases, be adequate for this purpose.
- Minimisation of variations in feedstock (quality and flow rate) to enable the optimisation of the extraction section (energy and material recovery).

The solvent to BTX feed ratio is in the order of 2:1 to 6:1, depending on the nature of solvent. There are two main causes of solvent loss:

- Losses of solvent in improper process streams: solvent losses during normal operation depend on how the final separation equipment for each cut is operated (e.g. the raffinate/water decantation at the top of the raffinate water wash column).
- Degradation of solvent due to cracking at high temperatures or other degradation reactions. Other losses are due to the solvent degradation over time and they depend on the intrinsic stability of the solvent, the operating temperature and the various kinds of solids entering the unit (accumulating in the solvent).

One measure taken is to use continuous regeneration systems including small slipstreams of solvent to minimise its consumption. Another measure is to assure the tightness of the equipment operated under vacuum conditions to prevent air ingress which would accelerate solvent degradation and its consumption.

4.4.3.2.3 BB3 units

p-Xylene adsorption with molecular sieves achieves a high recovery rate per pass.

4.4.3.2.4 BB4 units

In HDA units, the feed purification or fractionation reduces hydrogen usage. In TDP units, the toluene can be fractionated prior to being fed into the TDP unit, in order to minimise hydrogen usage.

4.4.4 Techniques to reduce energy consumption

Energy consumption is a key economic and environmental issue for aromatics production. Generic techniques for energy saving, energy recovery and heat integration are important. Several techniques are discussed in terms of performance and costs in [136, Neelis et.al. 2008].

Distillation is one area where energy consumption can be optimised. This section therefore focuses on techniques to reduce energy consumption from distillation operations.

For energy recovery from hydrogen-rich streams, see Section 4.4.3.1.

4.4.4.1 Single extractive distillation column

Description
Extractive distillation process design with a single column configuration.

Technical description
In a conventional extractive distillation system, the separation would require a sequence of two separation steps (i.e. main distillation column with side column or stripper). In a single extractive distillation column, the separation of the solvent is carried out in a smaller distillation column that is incorporated into the shell of the first column.

Achieved environmental benefits
Lower energy consumption.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
This technique is applicable to new plants or major retrofits. The applicability may be restricted for existing smaller capacity units as operability may be constrained by combining a number of operations into one piece of equipment.

Economics
Benefits from reduced costs for energy.

Driving force for implementation
Economics (reduced costs for energy).

Example plants
Arsol Aromatics GmbH in Gelsenkirchen, Germany.

Reference literature
[176, ThyssenKrupp Uhde 2016], [177, Yildirim et al. 2011]

4.4.4.2 Distillation column with a dividing wall

Description
Distillation column with a dividing wall.

Technical description
In a conventional distillation system, the separation of a three-component mixture into its pure fractions requires a direct sequence of at least two distillation columns (or main columns with side columns). With a dividing wall column, separation can be carried out in just one piece of apparatus. One of the more effective methods of reducing both the capital and energy costs of separation units is the installation of a dividing wall column where appropriate.

Achieved environmental benefits
While results vary, a distillation column with a dividing wall will typically cut capital and energy costs by approximately 30 % compared to a traditional two-column system.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Applicability restrictions are similar to those for single extractive distillation (see above).

Consistency of feed composition: Significant fluctuations in feed composition complicate or even hinder the application.

Economics
Compared to a conventional distillation system, the investment costs are 20 % less, the energy costs 35 % less, and 40 % less space is required.

Driving force for implementation
Economics.

Example plants
Ruhr Oel refinery in Münchsmünster, Germany.

Reference literature
[177, Yildirim et al. 2011]

4.4.4.3 Energetically coupled distillation

Description
Energetically coupled distillation.

Technical description
If distillation is carried out in two columns, the energy flows in both columns can be coupled. The steam from the top of the first column is fed to a heat exchanger at the base of the second column.

Achieved environmental benefits
Lower energy consumption.

Technical considerations relevant to applicability
The technique is only applicable to new plants or major plant upgrades. The applicability depends on the set-up of the distillation columns and process conditions, e.g. working pressure.

Driving force for implementation
Economics (reduced costs for energy).

4.4.4.4 Distillation optimisation

Description
Distillation optimisation.

Technical description
For each distillation column, the number of trays, the reflux ratio, the feed location and – for extractive distillations – the solvents to feed ratio are optimised.

Achieved environmental benefits
Lower energy consumption.

Driving force for implementation
Economics (reduced costs for energy).

Technical considerations relevant to applicability
The technique is applicable to new distillation units. For an existing distillation column, the only variable that can be optimised is the reflux ratio which is to be set to the minimum needed to achieve the product specifications within operational constraints.

4.4.4.5 Recovery of heat from column overhead vapours

Description
Use of the heat from distillation column overhead vapours.

Technical description
This technique involves the recovery of the heat from condensing distillation column overhead vapours. The condensation heat, e.g. from the toluene and o-xylene distillation column, is used to supply heat elsewhere in the installation. The distillation column condenser duty is used, for example, to supply heat to the reboiler of another distillation column or to generate steam. The potential for energy recovery depends on the temperature of the overhead vapours.

Note that this technique highlights one of various generic options to recover energy in connection with distillation operations. For example, heat is also recovered from the bottom cut which normally has a higher temperature and therefore a higher heat content.

Achieved environmental benefits
Reduced consumption of energy.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
This technique is applicable to new plants or major retrofits. Applicability to existing units may be restricted by design, space availability and/or operational constraints.

Economics
No information provided.

Driving force for implementation
Economics.

Example plants
No information provided.

Reference literature
No reference literature provided.

4.4.5 Techniques to reduce waste generation

4.4.5.1 Catalyst selection and use

Both the generation of spent catalyst and the generation of organic waste (gums and oligomers) depend on the catalyst and the operating conditions.

The choice of the catalyst and the associated operating conditions are essential to the performance of any catalytic process. Criteria governing the choice of the catalyst for first-stage hydrogenation are:

- a high hydrogenation activity to fully hydrogenate the diolefins, alkenyl aromatics and other gum precursor compounds, at the lowest possible temperature;
- a low polymerisation activity to reduce gum formation to a minimum and allow long enough operating cycles even with highly reactive feeds;
- a high selectivity towards the hydrogenation of diolefins and alkenyl aromatics while minimising the hydrogenation of the olefins into paraffins.

Catalysts for first-stage reactors are of two basic types, palladium- or nickel-based catalysts. Both catalysts make use of an alumina carrier. Palladium catalysts are generally more active than nickel catalysts but are (typically) less tolerant to feed poisons. However, this depends to a great extent on the anticipated poisons (feed impurities) that can (occasionally) be present in the pygas feed. Nickel catalyst is disadvantaged in that it requires more stringent loading, activation and unloading procedures. The option of switching from palladium to nickel or vice versa in existing units is restricted due to differences in the activity and the handling procedures.

The catalyst type is generally dictated by the (anticipated) quality of the raw pygas feed. For clean feed applications, use of palladium catalysts will result in a smaller reactor volume requirement.

There are various measures that reduce spent catalyst generation:

- Feed pretreatment / optimisation of upstream conditions to reduce the ingress of impurities. For example, water or dust removal by applying decanters and coalescers/filters for protection from water and suspended solids from storage.
- Feed purification: First-stage hydrogenation and removal of the high-boiling fraction, as well as C_5 hydrocarbons. C_5 hydrocarbons can reduce the amount of fouling-forming compounds in the feed to the second hydrotreatment stage. The two distillation columns involving the removal of the heavy fraction, as well as C_5 hydrocarbons, can reduce the amount of fouling-forming compounds in the feed to the first-stage hydrogenation, but feasibility is dependent on the configuration of the plant. Stabilisation of the high-boiling fraction can be important to avoid issues in downstream processes or fuel oil blending, e.g. when hydrogenated C_5 hydrocarbons are routed to the petrol production in a refinery.
- Lower operating temperatures to avoid oligomer or gum formation.
- Proper liquid recycling to dilute the inlet concentration of diolefins to minimise polymerisation and subsequent coking.
- Proper regeneration of the catalyst.
- Timely regeneration as coke on the catalyst becomes harder and, as such, hydrogen stripping becomes less effective and steam-air stripping is required. The latter always comes with some (slight) catalyst deactivation and subsequently each restart requires a slightly higher start-of-run temperature.

Spent hydrogenation catalyst is removed from the reactors periodically and is normally returned to the catalyst manufacturer or specialised companies for regeneration or for recovery of the (precious) metal contained on the catalyst (nickel or palladium). This has economic reasons and environmental benefits. The catalyst support is sent to landfill.

For further information on catalyst regeneration, see Section 2.4.8.1.4.

4.4.5.2 Spent clay

The product used for aromatics extraction is often clay treated prior to fractionation to remove trace amounts of olefins and other impurities. The generation of spent clay depends on the olefin content of the feed and on the selection of the adsorption material. In order to prevent or reduce the amount of spent clay being sent for disposal, the following techniques are used.

4.4.5.2.1 Selective hydrogenation of raw materials reformate or pygas

Description
Selective hydrogenation of raw materials reformate or pygas.

Technical description
The main factor impacting the generation of spent clay is the amount of olefins that remain in the extracted aromatic product. The extraction section is capable of removing most of the olefins present in its feed with the non-aromatics stream. However, when non-hydrotreated feeds are used (such as those coming directly from naphtha reformers), some traces of olefins remain in the extracted aromatics.

Depending on the olefin content, hydrogenation can be used to remove olefins. This will extend the operational lifetime of the clay material.

Some of the heavy boilers formed inside the clay by alkylation and/or oligomerisation reactions of olefins foul its structure, which after a certain time causes it to lose its efficiency. When fully hydrotreated aromatics cuts are used as feedstock to the extraction section, clay treaters are typically not used, but, in cases where they may be available, they show very long operating cycles.

Achieved environmental benefits
Reduced generation of waste.

Environmental performance and operational data
Spent clay consumption depends largely on the bromine index of the feed. A typical reformate has a bromine index of 100, leading to a clay consumption of 1 tonne per 10 000 Mt of feedstock.

Cross-media effects
Consumption of energy for compression.

Technical considerations relevant to applicability
This technique is only applicable to plants using raw materials with a high olefin content. For feeds with reduced amounts of olefins, such as those coming from reformers, hydrogenation is not justified with respect to costs and cross-media effects (higher energy consumption).

Economics
Investment and operational costs for hydrogenation may exceed the costs for clay treatment, especially when the olefin content is low.

Driving force for implementation
No information provided.

Example plants
No information provided.

Reference literature
No reference literature provided.

4.4.5.2.2 Clay material selection

Description
Use of clays with a long operational lifetime or use of synthetic material that can be regenerated.

Technical description
After a certain time the clay material loses its efficiency by fouling, e.g. by heavy boilers formed inside the clay by alkylation and/or oligomerisation reactions of olefins, and needs to be removed. Waste from spent clay is reduced by the use of a clay that lasts as long as possible for its given conditions (i.e. having surface/structural properties that increase the operating cycle length) or by the use of a synthetic solid material that has the same function as the clay but that can be regenerated (e.g. Olgone process).

Achieved environmental benefits
Reduced generation of waste.

Economics
Synthetic materials are significantly more expensive than clays.

4.5 Emerging techniques

4.5.1 Ionic liquid for alkylation reactions

An ionic liquid is used as homogeneous catalyst for alkylation reactions at ambient temperatures and moderate pressures.

For information on this technique, please refer to the REF BREF.

4.5.2 Membranes for recovery of solvents

Use of membranes for solvent recovery in solvent extraction/dewaxing processes. The driving force is the reduction in energy consumption [197, Dekkers 2000].

4.5.3 Benzene from methane

Description
Methane condenses to benzene with H_2 as the co-product in a fixed-bed reactor or in a fluidised-bed reactor at temperatures of 700–800 °C.

The catalysts used are as follows:

- Molybdenum carbide: Dehydrogenation and C_1 coupling.
- Acidic zeolite: Oligomerisation/Aromatisation.

The selectivity to benzene is about 80 %, with other products being for example naphthalene and toluene.

A limitation of the technique is the low conversion rate of methane (e.g. < 15 %).

Commercially developed
Probably not.

Level of environmental protection
No data. No evidence of environmental benefits.

When it might become commercially available
This is dependent on the research activities and economic interest in basing benzene production on methane (e.g. natural gas) rather than crude oil.

References
[127, Lippert 2009].

5 ETHYLBENZENE AND STYRENE

5.1 General information

Ethylbenzene (C_6H_5-C_2H_5) is almost exclusively (> 99 %) used as an intermediate for the manufacture of styrene monomer, which is one of the most important large-volume commodity chemicals. Styrene production uses ethylbenzene as the starting raw material and is responsible for 50 % of the world's benzene production. The less than 1 % remaining of the ethylbenzene produced is used as paint solvent or as an intermediate for the production of diethylbenzene and acetophenone. European production capacity in 2014 was 7.5 million metric tonnes per year, which was about 16 % of the worldwide production capacity [137, Yang et al. 2016].

Styrene monomer (C_6H_5CH=CH_2) is a major industrial product with a production of more than 27 million tonnes per year worldwide with European production capacity being 5.7 million metric tonnes per year in 2012 [138, Mellor 2013]. Styrene is mainly used as raw material for polystyrene manufacturing. Polystyrene is the fourth most widely produced polymer following polyethylene, polypropylene and polyvinyl chloride. Styrene is also used in the production of other styrenic resins (co-polymers) such as acrylonitrile butadiene styrene (ABS), styrene butadiene latex (SBL), styrene butadiene rubber (SBR) and styrene acrylonitrile (SAN).

Almost all ethylbenzene is produced by alkylating benzene with ethylene. The newer technologies utilise synthetic zeolites to catalyse the reaction, although a considerable quantity of ethylbenzene is still produced by alkylation using an aluminium chloride catalyst. Ethylbenzene can then be converted into styrene monomer (SM) by dehydrogenation. Most styrene is produced in this way.

The other major process used to produce styrene monomer is its co-production with propylene oxide. In this process, ethylbenzene is first oxidised to form its hydroperoxide. The hydroperoxide is then converted to alcohol in an epoxidation reaction with propylene. Finally, the alcohol is dehydrated to form styrene, with propylene oxide as the principal co-product.

Propylene oxide (PO) is a major industrial product with a production of more than 7 million tonnes per year worldwide. Approximately 70 % of it is used to produce polyether polyols, which is a raw material for polyurethane production. The remainder is used to produce propylene glycol, which is a raw material for unsaturated polyesters, and an additive in food products and cosmetics. Co-production of propylene oxide with styrene monomer accounts for about one third of propylene oxide production worldwide. Other processes for the production of propylene oxide are considered in Section 2.1.2.8; they are the chlorohydrin process; epoxidation of propylene with hydrogen peroxide; epoxidation of propylene with organic peroxides; epoxidation using molten salts.

Table 5.1: Most of the European producers of ethylbenzene and styrene

Country	City	Operator	Ethylbenzene	Styrene by EB dehydrogenation	Styrene co-production with PO
			Capacity (kt/yr)	Capacity (kt/yr)	Capacity (kt/yr)
Belgium	Antwerp	Styrolution	890	500	NA
Czech Republic	Litvinov	Synthos	300	NI	NI
Czech Republic	Kralupy	Synthos	NI	170	NA
France	Gonfreville	Total	810	650	NA
Germany	Ludwigshafen	BASF	650	550	NA
Germany	Böhlen	Styron	400	400	NA
Italy	Mantova	Versalis	547	610	NA
The Netherlands	Maasvlakte	Lyondell Basell		NA	565
The Netherlands	Moerdijk	Shell	640	NA	990
The Netherlands	Terneuzen	Styron	550	250	
Spain	Tarragona	Repsol	505	NA	450
Spain	Puertollano	Repsol	NI	NA	150
United Kingdom	Stanlow	Essar	160	NA	NA
Total			6053	3130	2155

NB:
NI: No information.
NA: Not applicable.
Source: CEFIC and other TWG comments

Key environmental issues

The key environmental issues for the production of ethylbenzene are as follows:

- Emissions to air of VOCs, which are normally channelled and collectively treated.
- The $AlCl_3$ process generates solid and liquid waste from a neutralisation step.
- In some plant designs, the raw materials may be in a dilute feed, resulting in large streams being sent back to upstream units.
- The production of tars, which are separated in fractionation but generated upstream. Waste is also produced from catalyst regeneration.

The newer processes based on zeolites (especially the liquid phase one) generate less waste and less effluents.

The key environmental issues for the production of styrene by ethylbenzene dehydrogenation are as follows:

- Emissions to air from the steam superheater furnace used for the reaction.
- Another important emission to air comes from the reaction section off-gas. An off-gas recovery system is normally in place to recover hydrogen but other vents or purge streams containing VOCs will be generated.
- The reaction section will also generate the most significant effluent.
- Tar and/or polystyrene oligomers arise from the fractionation section.

The key environmental issues for the co-production of styrene with propylene oxide are as follows:

- The most significant off-gas streams are generated in the oxidation and epoxidation sections and are normally recovered for other uses before their end-of-pipe abatement and venting.
- There are two effluents for which treatment is technically complex and relevant: the acid purge from the oxidation step and the caustic wash from the epoxidation step.
- Tar and other residues arise from the various fractionation steps.

Fugitive emissions and emissions from storage are also important for all these types of plants.

5.2 Applied processes and techniques

Commercially, almost all ethylbenzene (EB) is produced by alkylating benzene with ethylene. The newer technologies utilise synthetic zeolites installed in fixed-bed reactors to catalyse the alkylation in the liquid phase. Another proven route uses narrower pore synthetic zeolites, also installed in fixed-bed reactors, to carry out the alkylation in the vapour phase. However, a considerable quantity of ethylbenzene is still produced by alkylation with homogeneous aluminium chloride catalyst in the liquid phase, though the recent trend in the industry has been to retrofit such units with zeolite technology.

The feedstock for all commercial styrene manufacture is ethylbenzene. Direct dehydrogenation of ethylbenzene to styrene accounts for approximately 85 % of commercial production. The reaction is carried out in the vapour phase with steam over a catalyst consisting primarily of iron oxide. The reaction is endothermic and can be carried out either adiabatically or isothermally. Both methods are used in practice.

The only other route for the commercial production of styrene involves its co-production with propylene oxide. This route offers a way to manufacture propylene oxide without the need for chlorine as in the chlorohydrin process; however, it is subject to market fluctuations in styrene and PO demand that may not match the stoichiometry of the process. The process requires a large capital investment and produces styrene at a higher cost than the conventional process, but revenue from sales of the PO co-product can make the overall operation profitable. About 15 % of the world's supply of styrene is now made by this process.

5.2.1 Process routes

5.2.1.1 Process routes for the production of ethylbenzene

Alkylation processes

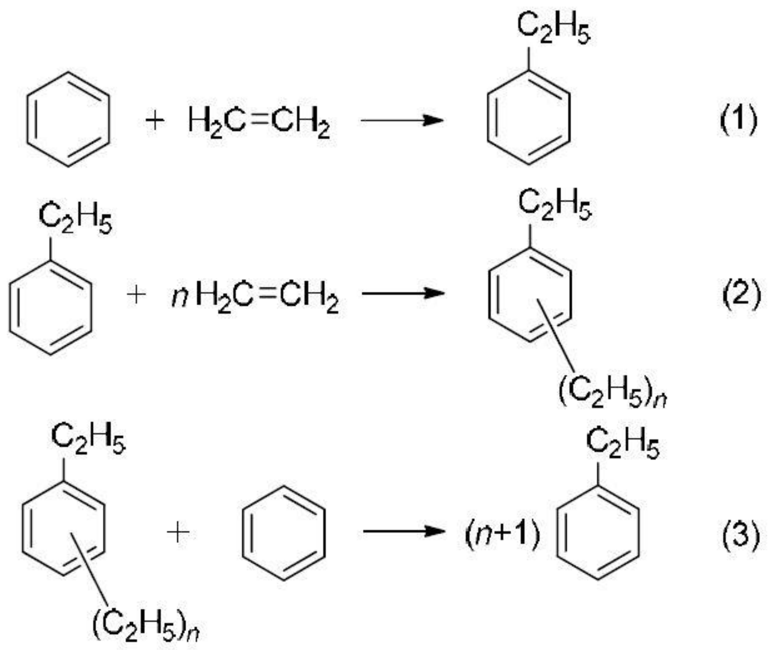
[51, Welch et al. 2012], [56, Vora et al. 2003], [137, Yang et al. 2016], [139, Perego et al. 2002].

Ethylbenzene (EB) is most commonly produced by benzene alkylation, and ethylene is the most frequently used ethylation agent (reaction (1) in Figure 5.1 below). The ethylbenzene formed can, under certain reaction conditions, react further with ethylbenzene to form polyethylbenzenes (PEB) (reaction (2) in Figure 5.1), such as diethylbenzenes (DEBs) and triethylbenzenes (TEBs). Transalkylation of PEB with benzene is performed to increase the yield of ethylbenzene (reaction (3) in Figure 5.1).

The highest benzene and ethylene conversions are theoretically achieved when the reactants are fed in stoichiometric ratios, but at these ratios the selectivity is extremely low, and the likelihood of forming di-, tri- or higher ethylbenzenes is much greater.

The alkylation reaction as ordinarily conducted is very fast. As soon as some monoethylbenzene is formed, the ethylene tends to add onto monoethylbenzene to give diethylbenzene. The more ethyl groups on the benzene ring, the more reactive the molecule becomes so that, unless steps are taken to prevent it, the alkylate ultimately would lead predominately to polyethylbenzenes. Fortunately, they can easily be reacted with benzene to (mono)ethylbenzene (transalkylation). Therefore most processes employ benzene to ethylene ratios higher than stoichiometric – from 1.5 to 6 times more benzene. The addition of a translalkylation unit in EB production increases the yield of EB by about 10 %.

Side reactions such as formation of xylenes depend on the reactor design and run length and are considered undesirable for downstream styrene processing. The same goes for any propylene present as a contaminant of the ethylene feed or formed by cracking of other non-aromatic impurities, which can react further to isopropylbenzene.



Source: [137, Yang et al. 2016]

Figure 5.1: Alkylation of benzene to form ethylbenzene

The principal options for the production of ethylbenzene via the benzene alkylation (Friedel-Crafts) route concern (i) the phase in which the reaction takes place – either vapour- or liquid-phase process, and (ii) the type of catalyst used – zeolite catalyst or Lewis acid catalyst.

Industrially used production routes are:

a) liquid-phase $AlCl_3$-catalysed process;
b) vapour-phase zeolite-catalysed process;
c) liquid-phase zeolite-catalysed process;
d) mixed liquid-vapour-phase zeolite-catalysed process.

a) Liquid-phase $AlCl_3$-catalysed process

Older $AlCl_3$-catalysed liquid-phase benzene alkylation was the first process to be developed for the industrial production of ethylbenzene in the 1930s and remained popular up to the 1980s. It was conducted at a benzene to ethylene molar ratio of ~ 2.5:1 and at a temperature of 130 °C. The products from intensive stirring and mixing of reactants are liquid benzene, liquid catalyst and gaseous pure ethylene. Because of its high conversion rate and yield, the aluminium chloride route is generally competitive in economic terms, but disposal of hazardous waste streams resulting from the use of dissolved Lewis acid catalyst and severe corrosion of equipment and piping has made the route increasingly costly [51, Welch et al. 2012], [56, Vora et al. 2003].

In 1974, advanced (modern) aluminium chloride alkylation technology that significantly reduced the $AlCl_3$ catalyst used was brought forward. The amount of catalyst needed was reduced to $AlCl_3$ dissolved in the feed (up to the solubility limit in the range from 0.001 moles to 0.0025 moles per mole of ethylene) by carefully controlling ethylene addition and elevating alkylation temperatures to 160–180 °C and pressures of 0.5–2 MPa. This temperature range ensures enhanced catalyst activity with the additional benefit that the heat of reaction can be recovered as low-pressure steam. The benzene to ethylene molar ratio is a bit lower than in older technology (~ 1.5:1), but the process is also capable of operating with diluted ethylene feed. The elimination of the separate catalyst liquid phase and the introduction of an additional transalkylation reactor increased the selectivity and overall yield, in addition to lessening the problem of spent catalyst treatment and waste disposal [140, patent US 3848012 A 1974].

An additional transalkylation reactor needs no additional catalyst since both alkylation and transalkylation use the same catalyst, $AlCl_3$, which is already dissolved in the alkylation reactor effluent. Another advantage of this process is that the reaction is very fast and produces almost stoichiometric yields of ethylbenzene with the conversion rate of ethylene being almost 100 %.

The major disadvantages of this process remain increasing environmental and economic constraints due to the catalyst. Although handling and disposal of $AlCl_3$ catalyst waste, along with equipment and piping corrosion issues, have been somewhat lessened in comparison to the older process, they still represent a major contribution to high maintenance and operating costs which will probably keep rising due to increasing environmental considerations.

b) Vapour-phase zeolite-catalysed process

The vapour-phase technology was developed in the 1970s using ZSM-5 synthetic zeolite catalyst in a fixed-bed reactor. Because of the excellent catalytic properties (pore structure and acidic nature) and its thermal stability, this zeolite is widely used in petrochemical processes and is suitable for alkylation of benzene with different ethylation agents from pure to diluted ethylene (including fluid catalytic cracking (FCC) off-gases) or even ethanol, which makes it commonly licensed technology for dilute-ethylene applications.

The first generation design carried out vapour-phase alkylation and transalkylation in a single fixed-bed reactor, as in older $AlCl_3$ technology. The use of FCC off-gases and other diluted gaseous ethylene feeds demands sophisticated feed pretreatment, to eliminate certain olefins and other impurities which could react (isomerisation and other side reactions) and form by-products, which would make the product impure and cause catalyst deactivation. In the most advanced, so-called third generation technology (from the 1990s onward), the propylene removal unit has been added to the feed pretreatment section and the transalkylation step is performed in a separate reactor at lower pressures and higher temperatures which enables the technology to achieve a yield of more than 99 % and a higher product quality.

The alkylation temperatures are typically in the range of 350–450 °C and pressures from 1–3 MPa, which enables > 99 % of the net process heat input and reaction heat to be recovered as steam. The reactor operates with a significant excess of benzene relative to ethylene (molar ratios of ~ 7:1).

Catalyst deactivates gradually as a result of coke formation (catalyst poisoning) and has to be regenerated after some time. The single-pass catalyst lifetime depends to a great extent on the specific plant design and operating conditions and can span from 6 to 9 months for alkylation and 18 to 24 months for transalkylation. Since *in situ* regeneration takes quite a long time – around 36 hours – the reactor section of the plant is often doubled to keep on-stream efficiency unaffected.

The operating costs are further added to by the high energy consumption of benzene distillation columns due to the high benzene to ethylene ratio and high reaction temperatures.

c) Liquid-phase zeolite-catalysed process

Plants using liquid-phase technology began to emerge from the 1990s onwards using ultra-stable Y-zeolite-based catalyst.

The technology, based on MCM-22 zeolite-based catalyst, and technology based on β-zeolite-based catalyst are the most recent liquid-phase processes. Both licensors usually recommend off-site regeneration of a catalyst because of its long regeneration cycle times.

In the early stages of technology development, the alkylation was performed in a liquid phase, while the transalkylation was initially operated in a gas phase with a ZSM-5-based catalyst and has recently changed to liquid phase with the new catalyst.

In both technologies, ethylene is injected into a fixed-bed alkylation reactor with multiple stages in the presence of excess liquid benzene (benzene to ethylene molar ratios are high: 4–6:1). The catalyst lifetime of both types of catalysts used is increased to three years (or, according to some reports, even more). Reaction temperatures are kept below the critical temperature of benzene – 289 °C, usually from 240 °C to 270 °C and pressures must be high enough to keep all the constituents in the liquid phase – in the order of 4 MPa. Total ethylbenzene yields of these technologies are more than 99 % and the ethylene feed is usually of polymer-grade purity. The MCM-22 and β zeolite both overcome the oligomerisation and cracking problems because they are highly active for alkylation and inactive for oligomerisation and cracking.

The advantages of these technologies over vapour-phase technologies are better thermal control, lower reaction temperatures, decreased side reactions (and by-product formation) and longer catalyst lifetimes. The prominent reactor design feature enabling this is a multipoint injection of ethylene feed – over several injection points (nozzles) along the alkylation section of the reactor instead of it all being supplied in the fixed-bed entrance. This allows the reaction heat to be absorbed and conducted through heat exchangers / coolers to the steam, thereby avoiding the problems of side reactions and prolonging the catalyst lifetime as well [51, Welch et al. 2012], [58, Aspen 1999], [59, CBI/UOP 2016].

Both technologies require considerable heat input due to excess benzene handling (distillation columns in recovery and pretreatment), although less than vapour-phase processes (the excess benzene ratios are halved in the liquid-phase process). Nevertheless, both technologies still provide a lot of opportunities for heat recovery and integration of heat demand and supply.

d) Mixed liquid-vapour-phase zeolite-catalysed process

The technology using catalytic distillation for the production of ethylbenzene was commercialised in 1994. The technology combines catalytic benzene alkylation and distillation in one reactor. Benzene and ethylene streams flow countercurrently: liquid benzene entering at the top and gaseous ethylene at the bottom of the reactive distillation column. The Y-zeolite-based catalyst was used initially but changed to β-zeolite-based catalyst later. The catalyst is stacked in bales and, as gaseous ethylene dissolves in benzene, it alkylates benzene to ethylbenzene and the heat released by the reaction drives the benzene distillation to the upper pre-reaction sections of the column. The ethylene being spent in this reaction provides a driving force for more ethylene from the vapour phase to dissolve in benzene and continue the alkylation. At the bottom of the column, liquid ethylbenzene is recovered from the mix of reaction products – mainly polyethylenes – which are transalkylated in a separate liquid-phase reactor. The reaction temperatures range from 150 °C to 195 °C in the alkylation section and are around 300 °C in the stripping/rectification section. The pressures range from 1.6 MPa to 2.1 MPa. The benzene to ethylene molar ratios are comparable to liquid-phase technologies in the range of 4–5:1. The total ethylbenzene yield is more than 99 %, which - together with the low energy consumption of 'self-sustaining' reactive distillation, the relatively long catalyst life of up to two years and the reduced need for benzene-related distillation units - makes this technology economically very attractive. The fact that ethylene feed is in a gaseous form makes it also suitable for diluted ethylene feeds, like FCC off-gas. [137, Yang et al. 2016]

The main advantage of liquid-phase over vapour-phase processes is that they proceed at lower temperatures and less xylene is therefore produced through cracking. Xylene is difficult to separate from ethylbenzene and poisons the styrene monomer. The xylene content in ethylbenzene produced by vapour-phase processes is difficult to limit to below 600 ppm, whereas only about 10 ppm is easily achieved in liquid-phase processes. Moreover, the benzene to ethylene feed ratio is significantly lower in liquid-phase processes. Less excess benzene has to be recycled and circulated. Other advantages of liquid-phase ethylation are better thermal control and longer catalyst lifetimes which allow off-site regeneration and facilitate easier pollution control.

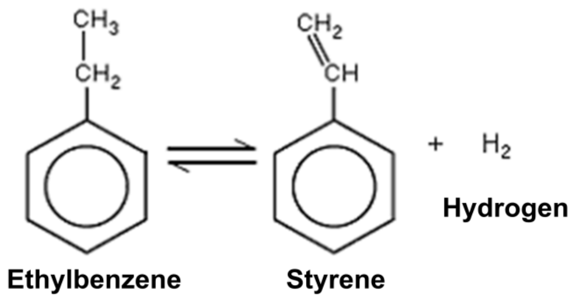
Separation process

The alternative to alkylation is the extractive process via separation from mixed xylene streams. Several facilities were built during the 1960s in the United States, Europe and Japan that recovered ethylbenzene by the fractionation of the mixed xylenes produced in refinery catalytic reforming units. The separation generally requires three distillation columns in series, each with over 100 stages (so-called superfractionation). This practice has largely been discontinued due to the poor economics that result from the high energy and investment costs, as well as the small economies of scale in comparison to the older alkylation routes. It will therefore not be discussed further in this chapter.

5.2.1.2 Process routes for the production of styrene

a) Production of styrene by ethylbenzene dehydrogenation

The majority of commercial styrene production (~ 85 %) is carried out by the direct dehydrogenation of ethylbenzene. The reaction is the reversible, endothermic conversion of ethylbenzene to styrene and hydrogen (see Figure 5.2).



Source: [184, CEFIC 2016]

Figure 5.2: Conversion of ethylbenzene to styrene and hydrogen

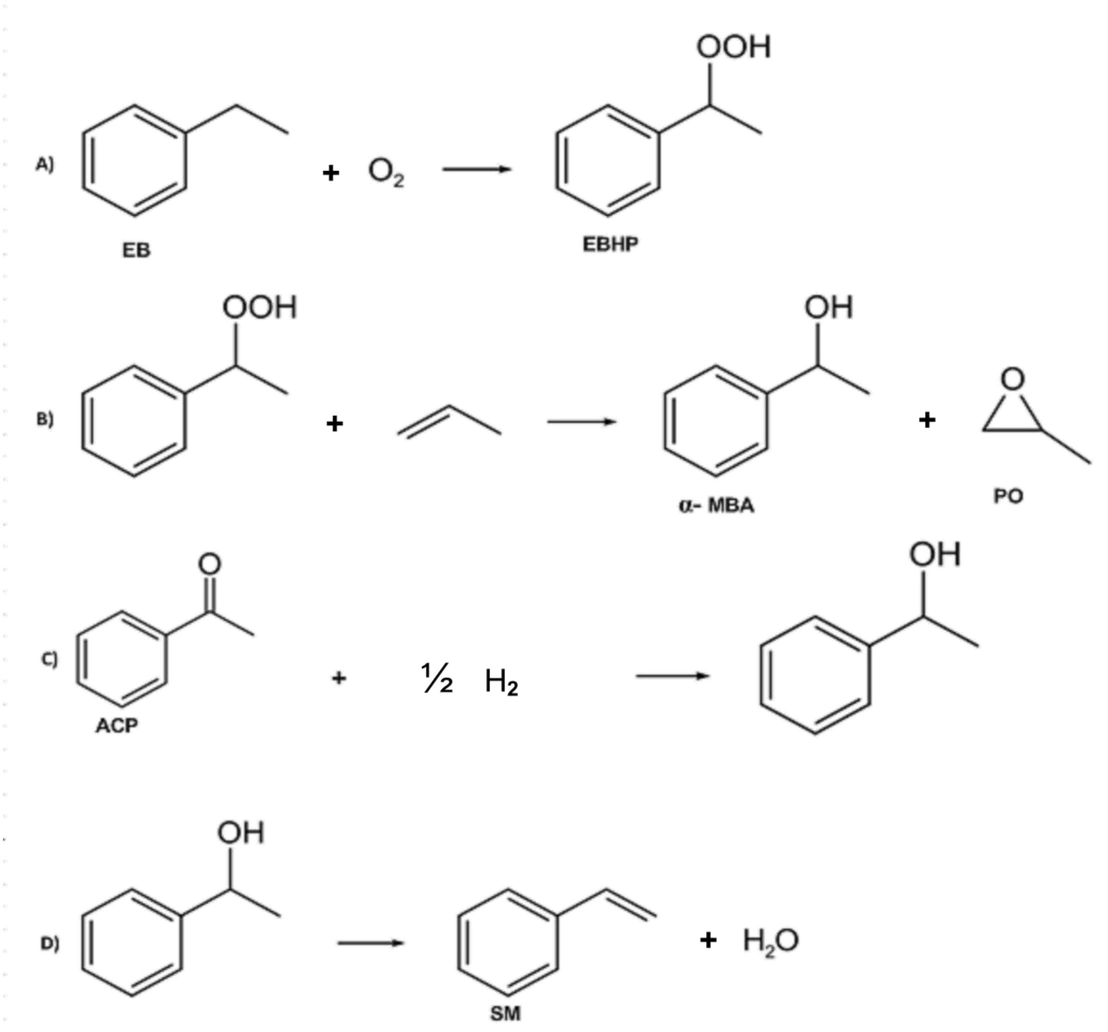
The reaction proceeds thermally with a low yield and catalytically with a high yield. It is usually conducted at low pressure to ensure that the forward reaction (in the direction of products) is more favourable than the reverse one. Competing reactions are the thermal degradation of ethylene to benzene or carbon and hydrogen and the catalytic hydrogenation of styrene to toluene and methane. Carbon acts as a poison to iron oxide catalyst. By incorporation of potassium into the catalyst, it becomes self-cleaning through enhancing carbon oxidation with steam to form carbon dioxide and hydrogen, which are removed with reactor off-gases.

Catalysts used are typically a mixture of iron and chromium oxide with potassium oxide or carbonate added. Typical operating conditions in commercial reactors are around 620 °C and low pressure. The overall yield depends on the relation between catalytic conversion to styrene and thermal cracking to by-products. Under typical equilibrium conditions, a reversible ethylbenzene conversion of 80 % is achieved. However, the time and temperature necessary to achieve this give rise to excessive thermal cracking, so commercial units typically operate at conversion levels of 50–70 wt-%, with yields of 88–95 mol-%.

The steam introduced into the reactor lowers the partial pressure of ethylbenzene and shifts the equilibrium towards the styrene, minimising the loss due to thermal cracking. It also supplies the heat needed for the reaction and cleans the catalyst by reacting with carbon to produce carbon dioxide and hydrogen [63, James et al. 2012].

b) Production of styrene in co-production with propylene oxide

Styrene is co-produced in the **peroxidation** process with propylene oxide. In this process, ethylbenzene is oxidised in air to form ethylbenzene hydroperoxide (EBHP) (A in Figure 5.3). This hydroperoxide is then used to oxidise propylene to propylene oxide over epoxidation catalyst (Mo-based homogeneous or Ti-supported silica-based heterogeneous) and produce small amounts of α-methylbenzyl alcohol (α-MBA, also known as 1-phenylethanol) and acetophenone (ACP) (B in Figure 5.3). To improve yields, ACP is converted to α-MBA over a catalyst – a mixture of zinc and copper oxide (C in Figure 5.3). The resulting α-MBA is then dehydrated in the presence of acid catalyst to give styrene (D in Figure 5.3) [63, James et al. 2012].



Source: Adopted from [185, Wikipedia 2016]

Figure 5.3: Reactions in the peroxidation process

The ethylbenzene process produces 2–2.5 kg of styrene per kilogram of PO. Obviously, the presence of these co-products can be a disadvantage if the demands for SM and PO are not properly balanced. Economic operation requires integration into a refinery complex, where mixed butanes and ethylbenzene are readily available; or integration in a petrochemical process which is generally more efficient.

c) Production of styrene from other feedstock

Alternative processes for the production of styrene are described briefly below.

Styrene from pyrolysis gasoline: An aromatic mixture (‘pyrolysis gasoline’) which includes styrene is obtained from the thermal cracking of naphtha or gas oil. Recovery of the styrene has been proposed on the basis of extractive distillation with dimethylformamide or dimethylacetamide, by adsorption, by complex formation, or by membrane separation. However, so far none of these methods have been commercially exploited. This process is therefore not considered further.

Styrene from butadiene: Another route to produce styrene which is being heavily researched starts with the Diels-Alder dimerisation of 1,3-butadiene to 4-vinylcyclohexene. This reaction is exothermic and can be carried out either thermally or catalytically. Thermal processes require a temperature of about 140 °C and a pressure of about 4 MPa. This route to styrene is not yet economically attractive, but the availability and price of butadiene in the future could make it so. This process is therefore not considered further.

Styrene from toluene: There have been many attempts to find a route to styrene starting from toluene. Toluene is readily available, is usually at least 15 % cheaper than benzene, and is not as toxic. However, no process has yet become commercially competitive. Monsanto has worked extensively on a process for styrene starting with air oxidation, but no commercial plants have yet been announced. This process is therefore not considered further.

5.2.2 Ethylbenzene production by the alkylation route

5.2.2.1 Process description

The basic process steps in an ethylbenzene plant are the pretreatment of feedstock, the alkylation and transalkylation units and the separation of products in a fractionation unit. $AlCl_3$-catalysed processes have catalyst-related handling units (for preparation and replacement of catalyst, for removal or separation of spent catalyst from reaction effluents, and for recovery and/or treatment of spent catalyst).

The main processes in the production of ethylbenzene through the alkylation route are the aluminium-chloride-catalysed and zeolite-catalysed processes. Block schemes of both processes are presented in Figure 5.4 and Figure 5.5, with major unit processes and operations presented in groups according to their function in the process. The possible unit configurations pertaining to specific technology according to the catalyst used and the phase in which the reaction proceeds are discussed next.

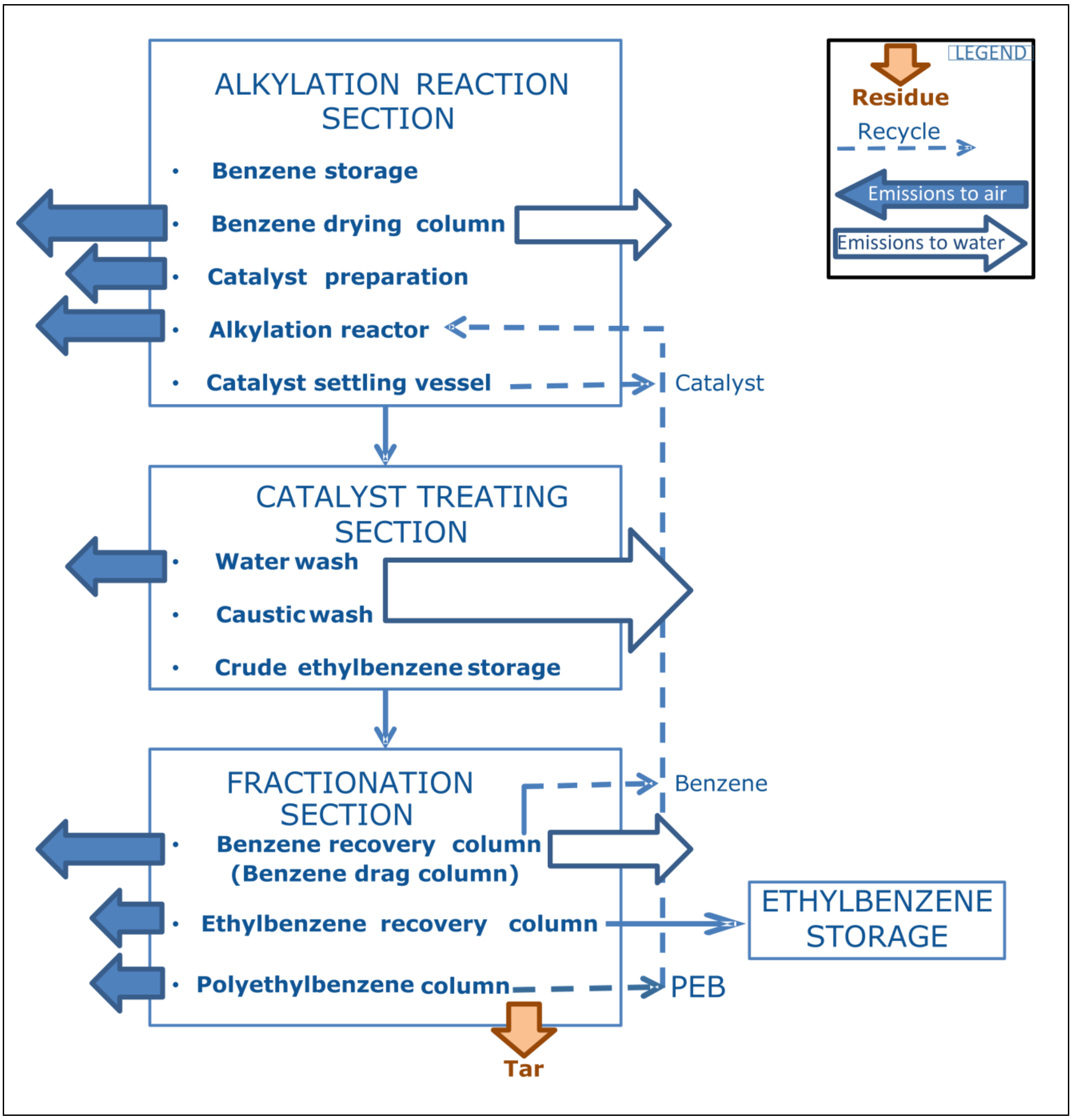


Figure 5.4: Block flow diagram of $AlCl_3$-catalysed ethylbenzene production

The obvious difference between both processes is that they use different catalysts, which in turn determines some specific units and arrangements needed to accommodate the process. The aluminium chloride process therefore has additional **units related to catalyst handling**, which the zeolite process does not need. This catalyst-handling section is comprised of (i) catalyst preparation/replacement units and (ii) catalyst removal/separation or so-called spent catalyst treatment units. In older aluminium chloride technologies, the catalyst removal units serve both (i) to separate the catalyst liquid complex from the reactor effluent and (ii) to remove the catalyst dissolved in the organic products mix. The modern aluminium chloride technologies use only the latter. The catalyst removal/separation units consist of different wash sections (acid/water, caustic) in which the organic product phase is separated from the catalyst and other acid by-products, which are both neutralised. The aqueous effluents from these units are used to either recycle the catalyst back to the reactor, reused in wash sections or these by-products are concentrated and used/sold for other applications.

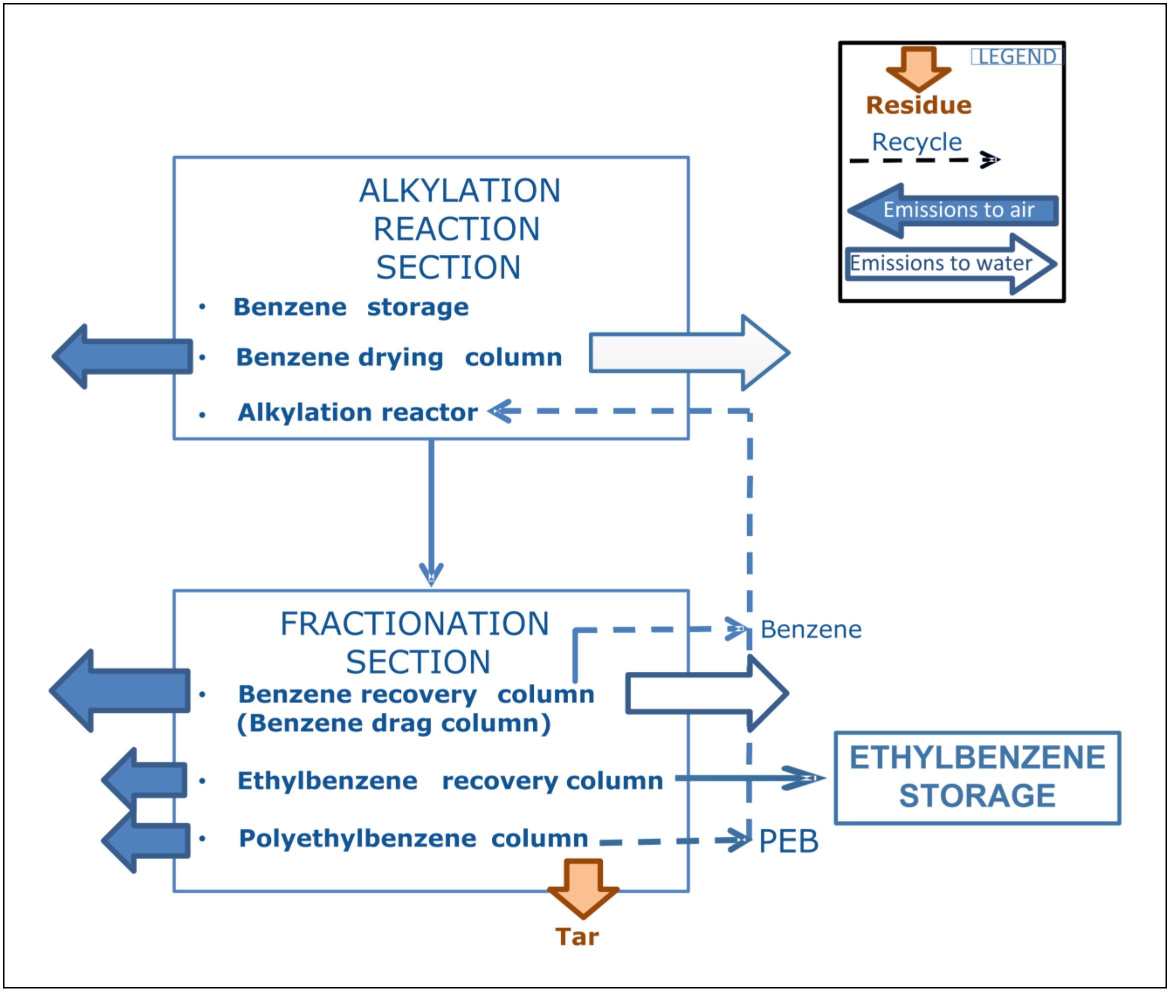


Figure 5.5: Block flow diagram of zeolite-catalysed ethylbenzene production

Despite some differences between the aluminium chloride and zeolite processes that originate from the different catalysts used, there are also a lot of similar process steps, the first being **the alkylation and transalkylation** reactions that take place in both processes. These proceed either within the same or in separate **reactors**. Both processes also have **benzene-related units** either for pretreatment/drying of the feed or for separating excess benzene from the reaction products (benzene recovery column) or lighter benzene feed or reactor effluents (benzene drag or lights column) in order to recirculate them back to the reactors (either alkylation or transalkylation). The next feature both processes have in common are the purification or **fractionation units** where the reaction products are separated from co-products, unreacted feed, by-products and residues. The fractionation units are distillation columns with settlers and/or decanters following overhead condensation sections. The separation and distillation columns are lined up in the following sequence: first the unreacted benzene is separated in the benzene recovery column, then the ethylbenzene is separated from heavier reaction products and lastly the polyethylbenzenes (PEB) are separated from residues and other heavier by-products and recirculated to the transalkylation reactor.

5.2.2.1.1 Pretreatment of the feedstock

The feedstock

The **ethylene** used in the process can be supplied as polymer-grade, chemical-grade or sometimes in the diluted form, e.g. fluid catalytic cracking (FCC) off-gases or partially purified off-gases from ethylene fractionation units of lower olefin production (steam cracking naphtha or gas oil) with typically 10–25 mol-% of ethylene. Chemical-grade, FCC and partially purified ethylene are often referred to as ‘diluted ethylene’, in the sense that the feedstock contains a significant proportion of non-ethylene molecules: typically 20 % to 80 % by mass.

The **benzene** feed used for the process can also come in varying purities from so-called crude or impure benzene (85–96 wt-% benzene) recovered from other lower olefin, aromatic or refinery (pyrogas) processes to high-purity (99.99 wt-%) benzene.

The other components of such crude benzene feed are aliphatic or non-aromatic compounds (cyclohexane, dimethylpentane, methylcyclohexane, n-heptane, etc.) and other impurities (e.g. sulphur or nitrogen compounds), which can, depending on the reaction conditions (T, p), cause catalyst poisoning or fouling, form by-products in side reactions, enhance corrosion of the equipment and piping, etc. These issues can be successfully avoided in zeolite-catalysed processes (vapour- or liquid-phase) with the lowering of the reaction temperature.

The non-benzene and non-ethylene components of the feed will have to be separated from the reaction products and can cause increased process off-gas and effluent streams.

Feedstock impurities or non-ethylene and non-benzene components are sometimes separated from the feed (before reaction) and sometimes from the products / reactor effluents (after the reaction). This can greatly affect the processing operations, catalyst (activity, selectivity and lifetime), reaction yield, side reactions, by-products, waste gases, waste waters and residues. The units needed for their removal, separation and further treatment are discussed below.

Units used for feedstock pretreatment

For pretreatment of benzene feedstock, a **benzene drying column** and **settler or decanter** are most commonly used. Depending on the feed constituents (like light/gaseous hydrocarbons), the benzene drag column can also serve as the entry pretreatment for benzene feeds. For benzene feed with very little impurities, the **benzene drying column** is used primarily to remove and lower the water content to 0.01 wt-% or lower. Some plant configurations use (additional to or instead of the benzene drying column) **decanters** for water content removal.

For pretreatment of ethylene feedstock, **guard beds** or **ion exchange resin filters** are used for the removal of feedstock impurities – compounds of sulphur, nitrogen and hydroxyl compounds. Feedstock guard beds are fixed beds of absorbent material like alumina, clay or metal oxides. In the ethylbenzene process, it is not unusual to use the same catalyst as used in the alkylation/transalkylation reactor to capture feed impurities through adsorption and thereby enhance the reactor catalyst life. Specifically, zeolite catalysts are very sensitive to contamination by polar molecules present in benzene and ethylene.

The **benzene drying column** is a distillation column usually designed as a straightforward stripping section for distillation, operating at medium or low pressures. The overhead condenser of this distillation column can be used to recover heat and generate steam. Two phases are collected in the overhead: the water phase and the hydrocarbon phase; and they are separated using a **decanter**. The recovered benzene is sent to the reactor and waste water to further treatment. This upper stream cut may, in cases of diluted benzene feeds, also consist of small amounts of gaseous phase, although it is more common to separate these constituents from reactor effluents in the post-alkylation benzene recovery column.

5.2.2.1.2 Alkylation and transalkylation units

The alkylation reaction occurs by mixing an excess of benzene with ethylene in the presence of catalyst in the alkylation reactor. The reaction is exothermic and although there is an excess of benzene, and some specific reactor design features to avoid side reactions, a portion of the ethylene (depending also on catalyst selectivity) reacts further with ethylbenzene to form isomers of diethylbenzene and triethylbenzene along with smaller amounts of heavier aromatics.

Having a stoichiometric excess of benzene in the alkylation loop minimises the formation of polyethylbenzenes (PEB).

These by-products are separated and recycled to the transalkylation reactor where, in the presence of usually the same catalyst as used for the alkylation reaction, the polyethylenebenzenes are reacted with benzene to ethylbenzene.

Reactor design

$AlCl_3$ alkylation reactors can be very diverse in their design in order to ensure the efficient mass transfer, control of reactant temperature and sufficient heat recovery. Reactors can be simple continuous stirred tank reactors (CSTR) with one chamber or multiple chambers, with different inlet nozzles, spargers and agitators, or tube-in-shell plug flow reactors with design features ensuring more tubular flow together with good mixing and contact of reactants during the reaction. Reactors can be operated in single- or multiple-pass mode in order to control the reaction temperatures (exothermic reaction) and ensure sufficient contact times. In older $AlCl_3$ processes, the catalyst complex liquid phase prevents operation at temperatures higher than 130 °C, which then results in the need for longer contact/residence times of 30–60 minutes. In modern $AlCl_3$ processes, which use smaller amounts of catalyst dissolved in reactants, the temperatures can be higher, i.e. 150–190 °C or even more than 200°C, and contact times much shorter (in multiple-pass reactors, e.g. in a range of seconds) [140, patent US 3848012 A 1974], [141, patent W O9116285 A1 1991].

Some arrangements use the same reactor for the alkylation and transalkylation reactions, and some use separate reactors. Due to the $AlCl_3$'s corrosive behaviour, corrosion-resistant materials and coatings have to be used in the reactor and piping parts in contact with the catalyst. Materials used include Hastelloy, stainless steel and glass and enamel coatings.

Zeolite alkylation reactors: Large-scale industrial processes may employ a fixed-bed continuous reactor operating in an up-flow or down-flow mode or a moving-bed reactor operating with concurrent or countercurrent catalyst and hydrocarbon flows. These reactors may contain a single catalyst bed or multiple beds and may be equipped for inter-stage (multipoint) addition of ethylene and inter-stage cooling (heat exchangers). They may be operated in a single- or multiple-pass mode, depending on the kinetics of reaction and other feed and design characteristics. Plain carbon steel can be used as the material for the reactors and piping due to the non-corrosive nature of the reaction effluents, reactants and catalysts.

5.2.2.1.3 Catalysts and catalyst-related units used in ethylbenzene production

5.2.2.1.3.1 AlCl3 catalyst

[140, patent US 3848012 A 1974], [142, Weissermel et al. 2008].

Anhydrous $AlCl_3$ is the well-known Friedel-Crafts catalyst. It is a representative of acid halides (Lewis acids) which have an electron-deficient central metal atom capable of electron acceptance from (basic) reagents. In many Friedel-Crafts reactions, substantial amounts of $AlCl_3$ must be used, greatly exceeding the amounts needed to be considered catalytic. This is because the Lewis or Brønsted acids are tied up, either forming stoichiometric complexes with the reagents and products (such as carbonyl compounds) or participating as counter-ions in 'red oil' formation (systems composed of carbocationic complexes resulting from protonation or alkylation of aromatics). In the alkylation of benzene with ethylene in the older process, the catalyst complex 'red oil' is used, while the modern process aims to avoid its formation and lower the amount of the catalyst needed.

At temperatures higher than 130 °C, a rapid decrease of the $AlCl_3$ catalyst complex's activity occurs. Also, some non-aromatic and polyaromatic hydrocarbons can form which are caustic in nature and preferentially dissolve in the highly acidic catalyst complex. With continued recirculation of the catalyst complex, these heavy aromatics tend to degrade and polymerise to sludge-like product referred to as 'flux oil' or tars. The gradual decrease in catalytic activity can be counteracted by partially removing the catalyst and replacing it with fresh catalyst.

In the modern $AlCl_3$-catalysed process which uses only catalyst dissolved in the reaction effluent, a continuous make-up of fresh catalyst is required; this makes any treatment to remove low concentration poisoning substances from the reactants unnecessary, with the only exception being water, which can be present in the benzene in too high a concentration causing an excess of catalyst consumption.

5.2.2.1.3.2 $AlCl_3$ catalyst replacement/preparation unit

[143, Reddy et al. 2013].

The catalyst complex ('red oil') (older process) or feed/recycle stream with dissolved catalyst (modern process) is prepared by dissolving a granular anhydrous (hygroscopic) aluminium chloride powder in the benzene feed or in the (poly)ethylbenzene recycle stream. The catalyst complex contains up to a third of $AlCl_3$, while for the dissolved catalyst stream much less is needed. Specifically, the $AlCl_3$ solubility in (poly)ethylbenzene(s) is in the range from 0.001 moles to 0.0025 moles per mole of ethylene (entering the reaction) and the $AlCl_3$ solubility in benzene is 1.24 g/100 g of benzene at 80 °C and increases with temperature. The promoter ethyl chloride, which forms HCl in the reaction environment, or HCl is also added to the catalyst effluent. The mixing of catalyst, promoter and feed takes place in a separate vessel/reactor before being delivered to the alkylation/transalkylation reactor. The reaction temperature is 140–200 °C, the pressure 0.5–1 MPa, and the residence time at least 15 minutes (preferably 30–60 minutes) [140, patent US 3848012 A 1974].

The handling of powder $AlCl_3$ by pneumatic conveyor and the charging of it to the mixing vessel are possible sources of dust and HCl emissions. Also, a minimal amount of HCl can be present in the waste gases collected from $AlCl_3$ handling due to its reaction with water vapour in air (humidity), or from the reaction between the promoter and catalyst due to the mixing and evaporation from the mixing vessel.

The catalyst complex 'red oil' can also be prepared *in situ* by reacting aluminium metal and HCl gas and dissolving product ($AlCl_3$) in ethylbenzene in a vessel/reactor in the following ratio: solid aluminium powder fed at 5 wt-%, liquid polyethylbenzene fed at 57 wt-% and HCl gas fed at 38 wt-%, at a temperature of 75 °C, pressure of 207 kPa and with a contact time of 30 minutes [141, patent W O9116285 A1 1991].

Dust and HCl emissions in off-gases from aluminium chloride catalyst replacement units can be abated by scrubbing with water, which can be reused in the wash section downstream of the reactors.

5.2.2.1.3.3 Spent $AlCl_3$ catalyst treatment units

The catalyst dissolved in the organic reactor effluent is removed by first washing it with water (water wash unit), which causes the majority of aluminium chloride to dissolve in the aqueous phase. This is then followed by a second (or more) washing step with diluted NaOH solution (caustic wash unit) to remove the remaining dissolved aluminium chloride catalyst.

The acidic aqueous effluent from the water wash and the salty alkaline effluent from the caustic wash are decantated (in the decanter/settler after the washing step) from the organic effluent phase, which proceeds to the fractionation section for further treatment. Both aqueous effluents from spent catalyst treatment can be further treated.

The acidic aqueous effluent is an aqueous solution of aluminium chlorides and organic acids, saturated with VOCs, mostly benzene and ethylbenzene. The VOC content can be reduced by steam stripping. If an ethylbenzene plant is next to the styrene monomer plant, this stream can be stripped jointly with the water effluent of the dehydrogenation section. The off-gases from the stripping process (VOCs) are then routed to the combustion unit or thermal oxidiser.

The remaining $AlCl_3$ solution can be concentrated by evaporating the low-boiling solution of HCl and water. The concentrated $AlCl_3$ solution can be reused in the WWTP. The vapour phase from evaporation is scrubbed with water to form diluted HCl solution which can be reused in the catalyst preparation (as a promoter) or as a pH stabiliser for the caustic wash effluent. The off-gas from the scrubber may still contain some HCl, but the mass flow and concentration are very low because of the high solubility of HCl in water [144, Campbell 1977].

The alkaline caustic effluent contains diluted NaOH solution, salt (NaCl), and aluminium hydroxide ($Al(OH)_3$) and is saturated with hydrocarbons (benzene and ethylene). Again, hydrocarbons can be removed by steam stripping and the remaining effluent is neutralised either with HCl solution from concentrating $AlCl_3$ solution or fresh acid – before being treated in a common WWTP.

5.2.2.1.3.4 Zeolites

[146, patent WO 2007081923 A2 2007].

Increasing environmental concern and the development of green processes based on heterogeneous catalysis are driving forces, not only for the improvement of conventional zeolites but also for discovering new molecular sieves with novel pore architectures.

Acidity in zeolites is generated by Brønsted and Lewis acid sites. The former are attributed to protons compensating for the negative lattice charge of an oxygen atom in the vicinity of an aluminium atom, while the latter are believed to result from lattice defect sites and/or extra-framework aluminium species. Zeolites are thermally stable up to 800 °C, allowing high-temperature reactions and the thermal regeneration of spent catalysts by burning of the carbonaceous residues in oxygen-containing gas streams. Zeolites can be synthesised in a wide variety of pore sizes. The number and strength of Brønsted acid sites, as well as crystal sizes, may be adjusted.

The pore dimensions are of the same order of magnitude as those of the molecules of reagents and reaction products. The high selectivity of these materials in alkylation or transalkylation reactions, for example in alkylation of benzene to ethylbenzene or transalkylation of benzene with diethylbenzene, lies both in its particular acid characteristics and also in the shape selectivity aligned to the specific pore structure of the catalyst

The aluminosilicates with three-dimensional frameworks consisting of SiO_4 and AlO_4 tetrahedra (primary building blocks) form single or double 4-, 5-, 6-rings (secondary building blocks) – a distinguishing characteristic of zeolite microporous structure. The most widely used systems are based on silica and alumina. However, a large variety of other elements have been integrated into the zeolite framework.

The zeolite catalysts most widely commercially used for benzene ethylation are ZSM-5, Y, beta and MCM-22. Apart from ZSM-5 which is used for the vapour-phase ethylbenzene process, they are used for liquid-phase and Y zeolite is also used for mixed-phase (catalytic/reactive distillation) processes.

Table 5.2: Structural parameters of typical zeolites used for benzene alkylation

Molecular sieve (zeolite)	IZA code (structure)	Main window (number of rings)	Channel dimensionality	Pore / Channel size (Nm)
MCM-22	MWW	10	2D	0.40 × 0.55
ZSM-5	MFI	10	3D	0.54 × 0.56
Beta	BEA	12	3D	0.76 × 0.64
Y	FAU	12	3D	0.74
Source: [147, Cejka et al. 2010]				

Zeolite catalysts are used in formulations that are prepared in the form of powder or pellets, which are bonded or packed into beds. Typical catalyst formulations may include some 20–50 wt-% binder like clay, alumina or silica, which bonds the catalyst and offers it structural integrity and additional porosity, and 50–80 wt-% molecular sieve (zeolite). The catalyst may be bound to, supported on or extruded with any support material like alumina, silica, aluminosilicate, titanium or clay – to increase its mechanical strength and attrition resistance.

[137, Yang et al. 2016], [147, Cejka et al. 2010].

The ZSM-5 zeolite has the MFI structure (framework type) with a three-dimensional 10-ring pore structure (medium pore) and is very effective in vapour-phase benzene alkylation. It is highly siliceous zeolite, thermally and hydrothermally stable with adjustable acid amounts and strengths. Because of its unique pore structure and acidic properties, ZSM-5 zeolite is widely used in petrochemical processes such as fluid catalytic cracking (FCC), methanol-to-propylene conversion, methanol-to-gasoline conversion, etc.

The Y zeolite is a faujasite (FAU framework type) molecular sieve with a three-dimensional 12-ring pore structure (large pore). Due to its nanocrystalline structure, larger intercrystalline void spaces, large pore volume, more acid sites located on the external surfaces, higher activity and better stability, it is used at lower temperatures in liquid- as well as mixed-phase (catalytic distillation) processes. Although the required benzene to ethylene feed ratio is high (~ 7:1), Y zeolite is competitive because of its thermal stability and long catalyst life (about one year).

The β zeolite has a three-dimensional (BEA framework type) 12-ring pore structure (large pore), silica-rich framework, and easy-access active sites in the pores which are connected in narrow helical channels. The β zeolite gives a higher overall ethylene conversion and ethylbenzene selectivity than Y zeolite. The benzene to ethylene feed ratio is reduced compared to Y zeolite to 4:1 and the catalyst life is prolonged to two years.

MCM-22 zeolite is a well-known representative of the MWW structure (framework type) zeolites formed by stacking basic layers with the MWW structure. MCM-22 zeolite has a peculiar structure consisting of two independent pore systems accessible via 10-ring windows. These different types of pore systems play important roles in the catalytic abilities of this zeolite. MCM-22 zeolite shows comparable activity to that of Y zeolite in liquid-phase benzene alkylation, but is less active than β zeolite. The advantage of MCM-22 zeolite is that its ethylbenzene selectivity is higher than those of Y and β zeolites, which results in less polyethylbenzenes being formed (that could be transalkylated to ethylbenzene), therefore smaller amounts of EB are produced overall during benzene alkylation with MCM-22 than with Y and β zeolites. What makes this catalyst attractive is its low benzene to ethylene feed ratio (3:1 to 4:1), and its stability (lifetime more than three years).

ZSM-5 zeolite with its medium pore structure is suitable for vapour-phase processes, while in liquid-phase processes its diffusion resistance to mass transfer is stronger and large pore zeolites like Y, β and MCM-22 are preferable. Again, β and MCM-22 are more suitable than Y zeolite since MCM-22-zeolite-catalysed processes can be operated at lower benzene to ethylene feed ratios, and β zeolite has the highest catalytic activity and poison tolerance.

5.2.2.1.3.5 Zeolite catalyst's deactivation and regeneration

[148, Argyle et al. 2015], [149, Flego et al. 1999].

Deactivation mechanisms
Catalyst deactivation, the loss over time of catalytic activity and/or selectivity, is a problem of great and continuing concern due to the costs of catalyst replacement and process shutdown.

The catalyst inevitably decays; however, the loss of activity in a well-controlled process typically occurs slowly. On the other hand, process upsets or poorly designed hardware can bring about rapid failure of catalyst performance.

The most important mechanisms of zeolite catalyst deactivation in benzene alkylation are poisoning and fouling.

Poisoning is the strong chemisorption of reactants, products or impurities on sites otherwise available for catalysis. Whether a species acts as a poison depends upon its adsorption strength relative to the other species competing for catalytic sites. Catalyst poisons can be classified according to their chemical make-up, selectivity for active sites and the types of reactions poisoned. Organic bases, hydrocarbons and heavy metals are common poisons for silica-alumina zeolite catalysts used for alkylation reactions.

Fouling is the physical (mechanical) deposition of species from the fluid phase onto the catalyst surface, which results in activity loss due to the blockage of sites and/or pores. Owing to the limited channel dimensions in which the acid sites are situated and in which the molecules react, deactivation is a particularly significant phenomenon. It can be caused both by fouling of the single acid sites and also by physical blockage of the channels of the porous system; this is due to the formation of substances with a high molecular weight which obstruct the free passage of reagents and products and hinder the reaction process. The organic deposits are of two types: light phases (benzene, ethylene, ethylbenzene, diethylbenzenes) which desorb easily between 80 °C and 350 °C; and heavy oligomers, polyalkylated products and polycondensed aromatic rings (anthracenes), which can be removed only by combustion. The deposits of these substances on catalyst are referred to as **coke** or pitches. If not desorbed or removed by combustion, they lower catalyst activity and can also contaminate the product stream, from which they are separated in distillation columns (like PEB) as so-called heavies, bottom fraction, tar or flux oil.

Regeneration procedures for various zeolites
[146, patent WO 2007081923 A2 2007].

There are two types of *in situ* zeolite catalyst regeneration: heat treatment with gases and heat treatment with aromatic hydrocarbons.

Heat treatment with gases
The catalyst can be regenerated *in situ* by purging with a stream of hot gas when the reactor is taken off-line. The purging stream (regeneration gas) may include any suitable inert gas (e.g. nitrogen). The regeneration procedure consists of the incremental heating of the catalyst to temperatures higher than the reaction temperature and purging with hot gas. For example, the catalyst is heated first to 370 °C and purged with nitrogen gas containing about 2 % oxygen, for a time sufficient to provide an off-gas stream with an oxygen content of about 0.5 %. The catalyst may than be heated to a second temperature, e.g. 50 °C higher than the first and so forth up to about 600 °C, for a time sufficient to provide an off-gas stream with an oxygen content of about 2.0 %. Upon regeneration, the catalyst may be reused for alkylation/transalkylation.

An alternative regeneration procedure is to introduce nitrogen into the reactor at a temperature of 550–575 °C and keep it at this temperature during the whole treatment, while at the same time the oxygen/air concentration in the regeneration gas is incrementally increased in small increments from 1 % to 99 % and left at each concentration increment for a certain amount of time. At the end of the regeneration, when the exotherm has moved completely through the catalyst bed, the air injection is terminated and only nitrogen is left flowing through. The temperature is then reduced to the reaction temperature and the catalyst bed is ready for another alkylation run [150, patent WO 2005042159 A1 2015].

Heat treatment with aromatic hydrocarbons
The regeneration procedure of heat treatment with aromatic hydrocarbons consists of alternating cyclic washes at high temperatures with aromatic hydrocarbons– in the case of ethylbenzene production with benzene. It reacts with otherwise insoluble pitches (coke), by means of a series of alkylation/transalkylation reactions catalysed by the zeolitic material itself, transforming the pitches into molecules of a lower molecular weight, soluble in the aromatic hydrocarbons (benzene) and, above all, capable of diffusing through the zeolitic pores. The treatment is carried out at temperatures between 200 °C and 290 °C, preferably from 15 to 45 hours, at a pressure ranging from 20 bar to 40 bar. The process works for all zeolite catalysts used for liquid-phase reactions: Y, β, ZSM-5 and MCM-22. It is particularly convenient for use in catalytic fixed-bed continuous reactors in a weight hour space velocity (WHSV) range from 2 to 8 hours [151, patent EP 1068898 B1 2004].

Regeneration of guard beds in alkylation process
Guard beds containing a zeolite material are used for feedstock pretreatment to remove catalyst poisons (adsorption) from olefin (ethylene) streams prior to their introduction into the reactor. To ensure the continuity of operation, the regeneration takes place in a so-called swing system in which one or more guard beds are kept on stream to remove the contaminants while one or more of the remaining beds are being purged or regenerated. The regeneration medium is a product stream from the olefin alkylation process – reactor effluent consisting of benzene and (poly)ethylbenzene(s). The regeneration is carried out at an elevated temperature, typically around 150–250 °C, and relatively low pressures may assist desorption (1 000–4 000 kPag or 145–580 psig). The contaminants that can be encountered in light aromatics streams (like ethylene feed) are sulphur or nitrogen compounds, water, oxygenates, etc. which adversely affect the catalyst and should therefore be removed from the feed stream before it enters the main reactor. The volume of guard-bed zeolites will normally not exceed about 20 % of the total catalyst bed volume used in reactors [152, patent US 20080029437 2008].

5.2.2.1.4 Fractionation units

[146, patent WO 2007081923 A2 2007].

Passing from reactors to the fractionation units, the pressure and temperature of reactant effluents sometimes have to be adjusted in a **flash (knock-out) tank**, where the lighter fractions (together with some products and reactants) of the reactor effluent are vaporised, separated and ducted away for recycling to other units for recovery or used as feedstock or for further treatment and/or use as fuel. **Heat exchangers** are used for temperature adjustments between different units in the reactor and fractionation sections.

Typical reaction effluent from the $AlCl_3$-catalysed process consists of 45 wt-% benzene, 37 wt-% ethylbenzene, 15 wt-% diethylbenzenes, 2 wt-% polyethylbenzenes and 1 wt-% of tarry residues. It is separated into components in a downstream distillation unit of the fractionation section. These considerable amounts of unreacted benzene that have to be separated from the reactor effluent and recirculated (recycled) to the reactor are even more pronounced in zeolite-catalysed processes. This is accomplished in the **benzene recovery column** – the first distillation column of the fractionation section downstream of the reactors. In processes where the reactor effluents are gaseous (e.g. vapour-phase or mixed-phase processes as described in Section 5.2.1.1), the benzene purge is first cooled and liquefied in a **condenser** and then treated in the benzene recovery column in the same way as the reactor effluent from the liquid-phase processes. The benzene recovery column is often coupled with a **benzene drag or lights**

column, intended to separate lighter fractions still present in the unreacted benzene feed after the recycling column separates it from the reaction products.

The fractionation unit's design may have different arrangements of distillation columns, settlers and decanters, from plant to plant. In the most common arrangement, the distillation consists of a three-column train. From the first one, the benzene is recovered from the top to be recycled back to the reaction sections (benzene recovery column). From the top of the second column, pure ethylbenzene is separated (**ethylbenzene recovery column**). In the third column, sometimes operated under vacuum, the separation of heavier by-products is carried out (**polyethylbenzenes recovery column**). Transalkylable polyethylbenzenes are removed from the top of the column, while high-boiling by-products (flux oil or tar) are extracted from the bottom. In this heavy cut stream (tar), diethylbenzene and triethylbenzene are present in low concentrations, since they have already been minimised and recovered by distillation.

A key process feature in the design of fractionation units from the economics and environmental point of view is whether the process can handle a wide range of ethylene feed compositions, e.g. from 10 mol-% to 100 mol-% ethylene, and/or benzene feed compositions, e.g. from 85 wt-% to 100 wt-% benzene – considering possible side-effects on catalyst degradation, fouling, poisoning, lifetime and/or selectivity, the overall process yield, by-products formation, and more complex off-gas, waste water and residues treatment. The important factor in these deliberations is the presence and possible integration and compatibility with other on-site activities, unit processes and operations – in terms of their material and energy flows.

There is a wide variation in distillation column operating conditions (number of trays, feed tray location, reboilers (low-pressure steam), condensers (cooling water), etc.), particularly in revamped (upgraded) facilities and there is also a wide variation in excess benzene from plant to plant. These details are to a certain extent deemed confidential by licensors and operators. They are based on unit optimisation and may lead to all kinds of intertwining flows, connections and modifications. For example, at least some overhead fractions can be recycled as input to reactors or other distillation units. Also, any process stream may be split into multiple process stream inputs for serial or parallel units. Respectively, additional process equipment, such as heat exchangers, may be employed throughout the process/technology steps.

Benzene drag column

This distillation column is normally used downstream of the reactor section to remove the unreacted benzene. It is operated at medium pressures, and typically about 60 trays are used. The temperatures in the benzene recovery distillation column are about 130 °C at the top and about 170 °C at the bottom, and the pressure may be atmospheric pressure. The reaction products are to be found in the distillation tower bottoms. The excess benzene is condensed out at the top of the column in the overhead condenser, which is used also for heat recovery / steam generation.

EB recovery column

This column is designed for lower pressures (1.1–1.7 bar) which enable heat recovery from the condenser and simultaneously lower the bottom temperatures in the reboiler. The temperatures in the ethylbenzene recovery distillation column are about 120 °C at the top and about 240 °C at the bottom, and the pressure may be from 100 kPa to about 300 kPa. Current designs use structured packing and trays to increase capacity.

PEB recovery column

Many designs for this column include trays due to the high frequency of fouling incidents. For upgrades, packing can be utilised with success. Although the feed streams from the bottom of the EB distillation column have a low tendency to polymerise, they have high boiling temperatures. To prevent fouling and cracking of the distillation feed, the temperature of distillation is kept below 300 °C which is achieved by lowering the pressure of the column (sometimes to vacuum). The temperatures in the polyethylbenzenes recovery distillation column are about 120 °C at the top and about 240 °C at the bottom, and the pressure may be vacuum pressure. The pressure of the columns is set according to the available heat source and the integration of the steam generated in the overhead condensers into the local steam supply. Most of the steam produced in the overhead condensers can be used in the other on-site units, like styrene monomer (SM) dehydrogenation.

5.2.2.2 Other than normal operating conditions

5.2.2.2.1 Specific other than normal operating conditions

According to the data collection, deviations from stable and normal operating conditions can arise for the following reasons:

- Zeolite process:
    - catalyst end of run (life): beyond the threshold of optimal operation the catalyst needs to be replaced or regenerated;
    - replacement of spent zeolite catalyst: 5–12 days/yr;
    - *in situ* catalyst regeneration operations: 21 days/yr.
- $AlCl_3$ process:
    - malfunction of spent catalyst concentration and preparation units: 2 days/yr.
- Both processes:
    - malfunction of benzene drying column (which can cause zeolite catalyst poisoning and/or corrosion issues) or any other column/part of fractionation units: up to 7 days/yr.

The cumulative average duration of these occurrences ranges from 9 to 19 days per year, except for *in situ* catalyst regeneration which alone can last up to 21 days per year.

5.2.2.2.2 Generic other than normal operating conditions

According to the data collection, the following operations deviate from standard operating procedures in ethylbenzene manufacturing plants:

- routine start-up: 2–3 days/yr;
- shutdown for maintenance, e.g. equipment flushing can cause a higher load to the WWT: 5–21 days/yr;
- process control systems failure: 1–2 days/yr;
- plant idle due to loss of containment – leak due to corrosion: according to the data collection, two leaks on average in 5 years;
- service or utility failure: steam and electric power shortages: 1–2 days/yr.

The cumulative average duration of these occurrences ranges from 9 to 28 days per year.

Another disruption of normal operation reported by operators was low plant rate due to force majeure (disruptions that occur in final product processing or raw material supply). According to the data collection, in the period 2008–2013, such conditions lasted on average 10 days per year and in one case even up to 50 days per year).

5.2.2.3 Equipment important for environmental protection

The following units carry out important functions to protect the environment (minimise effluents and waste generation) and require the best availability possible:

- Air:
    - In various distillation columns: cooling water supply for the header/condenser of the column; condenser fouling can result in a loss of efficiency and increased emissions to air.
    - End-of-pipe abatement treatment reliability: proper combustion in furnace, thermal oxidiser or flare (note that flares should only be used for non-routine operations and/or as a safety device and not as an abatement system).
    - For $AlCl_3$-catalysed processes: reliable functioning of the caustic scrubber for scrubbing of the acid alkyation/translalkylation off-gases before sending them to end-of-pipe abatement.
    - For $AlCl_3$-catalysed processes: wet scrubbing of dust and HCl emissions from catalyst replacement and spent catalyst treatment units.
    - Continuous leak detection and repair system for VOC and benzene leakage: fugitive emissions sensors at valves, piping, vessels, reservoirs and other potential leakage points.

- Water:
    - Benzene drying column: for separation of the water content in the benzene feed.
    - Decanter of the benzene recovery column: separation of organic and aqueous phases.
    - For $AlCl_3$-catalysed processes: aqueous-phase separators (condensers, decanters), neutralisation and concentration of aqueous effluents from spent catalyst treatment units.

- Waste:
    - Catalyst management systems (various sensors – e.g. bed temperature, effluent temperature) and procedures (control sampling and testing) are important for control of catalyst activity, avoidance of (heavy) by-product (tar) formation and maximisation of catalyst lifetime.

5.2.3 Styrene production by the ethylbenzene dehydrogenation process

5.2.3.1 Process description

5.2.3.1.1 Dehydrogenation reactor section

[60, Chen et al. 2006], [61, Woodle 2006], [62, Nexant 2009], [63, James et al. 2012], [64, patent US 5461179 A 1995] [153, patent WO 2008148707 A 2008].

The majority of all styrene plants in operation carry out the dehydrogenation reaction **adiabatically** in multiple reactors or in reactor beds operated in series. The necessary heat of reaction is applied at the inlet to each stage, by injection of superheated steam into the reaction stream or by indirect heat transfer; also, between the stages the reaction gas is heated in heat exchangers.

The purified ethylbenzene is therefore preheated with steam (to 160 °C) and by heat exchangers (to 520 °C). Superheated steam (720 °C) and ethylene vapours are then mixed and fed into the reactor. Typically, 1–1.8 kg steam is required for each kilogram of ethylbenzene to ensure sufficiently high temperatures throughout the reactor. The superheated steam supplies the necessary reaction temperature of 550–620 °C throughout the reactor. The dehydrogenation reaction requires low pressures and is generally carried out under high vacuum (or as low as safety measures allow). Ethylbenzene conversion is typically 60–65 %. Styrene selectivity is greater than 90 %. The three significant by-products formed are toluene, benzene and hydrogen.

In contrast, in isothermal reactors, the heat needed for the reaction is continuously provided by the heating medium. The isothermal reactor is designed like a tube-in-shell heat exchanger: a fixed-bed dehydrogenation catalyst and reactant gas are on the tube side, and a suitable heat transfer medium is on the shell side. The steam to EB mass ratio can be lowered to about 1:1, and steam temperatures are lower than in the adiabatic process. A disadvantage is the practical size limitation on the reactor-exchanger, which restricts the size of a single-train plant to about 150 000 t/yr, translating into increased capital costs for large plants. Only Plant #3 reported using this process.

As temperatures well above 850 °C may be encountered, the potential for thermal cracking of ethylbenzene and formation of by-products is increased. Therefore, the temperature profile management in heaters and reactors should be momentary (in real time) and residence times of reaction gases minimised.

The dehydration of ethylbenzene to styrene occurs in the reactor over a fixed bed of dehydration catalyst. All commercial catalysts are formulated around an iron oxide base; inherent to this ferric compound is the reduction to lower oxides at the dehydrogenation reaction temperature. The most widely used additives are chromic oxide as the stabiliser and potassium oxide as the coke retardant. Thus, the catalyst is self-regenerative, thereby allowing coke to build up only to an equilibrium level.

Catalysts are formulated in specialised shapes, such as ribbed extrudates, to gain the advantage of increased surface area without incurring the penalty of increased pressure drop and reaction pressure.

The catalyst is a significant cost in the production of styrene owing to the large quantity required: about 120 m^3 or 120–160 tonnes depending on the density of the catalyst, for a plant with a 300 000 t/yr capacity. Therefore, the best catalyst or a combination of catalysts for a particular application must be selected to optimise ethylbenzene conversion, styrene selectivity, catalyst activity, and catalyst stability. A catalyst lifetime of two years is achievable.

Carbon (coke) deposition can be reversed to a large degree by steaming the catalyst, but the effect is only short term; frequent steaming is not deemed to be economical. Steaming is ineffective for extending the catalyst life because it does not prevent chemical decomposition of the catalyst. A more efficient method of preventing decomposition and disintegration of the dehydrogenation catalysts is to continuously or intermittently add an effective amount of an alkali metal compound to a reactant stream without interrupting the dehydrogenation reaction.

5.2.3.1.2 Process off-gas recovery unit

The reaction product leaves the top of the reactor and is cooled first by the incoming ethylbenzene and then by steam in heat exchangers. The mixture then goes through a water-cooled and/or air-cooled condenser, where the steam and crude styrene vapour are condensed, and then flow to the separator, where the hydrocarbon and water phases are separated.

The process water condensate is decanted and fed to the stripper, where dissolved aromatic organics are removed and returned to the process. The purified water is sent to the plant boiler for use as boiler feed water.

The remaining off-gas stream, containing hydrogen, carbon monoxide, carbon dioxide and hydrocarbons, is compressed, and then cooled in the recovery section to recover aromatic organics, which are returned to the process. After removal of organics, the hydrogen-rich gas is usually sent to a steam superheater, where it is used as a fuel.

5.2.3.1.3 Fractionation (styrene purification) section

Inhibitors are added to liquid crude styrene, before entering the fractionation section, to prevent styrene polymerisation in the process equipment. Typical crude styrene from dehydrogenation consists of styrene (~ 64 %), ethylbenzene (~ 32 %), toluene (~ 2 %), benzene (~ 1 %) and other similar compounds (~ 1 %) [63, James et al. 2012].

After adding a polymerisation inhibitor (usually a phenol), the styrene is vacuum-distilled in a series of four or five columns (often packed columns) to reach the required 99.8 % purity. Benzene and toluene are separated first in the benzene-toluene distillation column. The ethylbenzene is separated next in the ethylbenzene recycle column. Finally, the styrene monomer product is separated from the tars in the styrene finishing column.

The separation is difficult due to the similar boiling points of styrene and ethylbenzene. The typical capacity per plant ranges from 70 000 to 100 000 metric tonnes per year in each reactor and most plants contain multiple reactors or units.

The main dehydrogenation reaction by-products are benzene, toluene and some non-aromatics with boiling points spread between those of benzene and toluene. The amount of benzene/toluene produced depends on the dehydrogenation conditions and catalyst. A lower steam to olefin ratio (to save steam) generally increases the amount of benzene/toluene. The amount increases during run length as a consequence of catalyst ageing.

Toluene generation is relatively constant over the entire run length and depends on the catalyst and dehydrogenation operating conditions, while benzene increases over the time the catalyst charge spends on-stream.

The recovered toluene can be sent to the aromatics plant for further treatment; recovered benzene can normally be recycled to the ethylbenzene plant, while recovered ethylbenzene is recycled back to the process.

Figure 5.6 below shows a block flow diagram with major emission streams in the ethylbenzene dehydrogenation process.

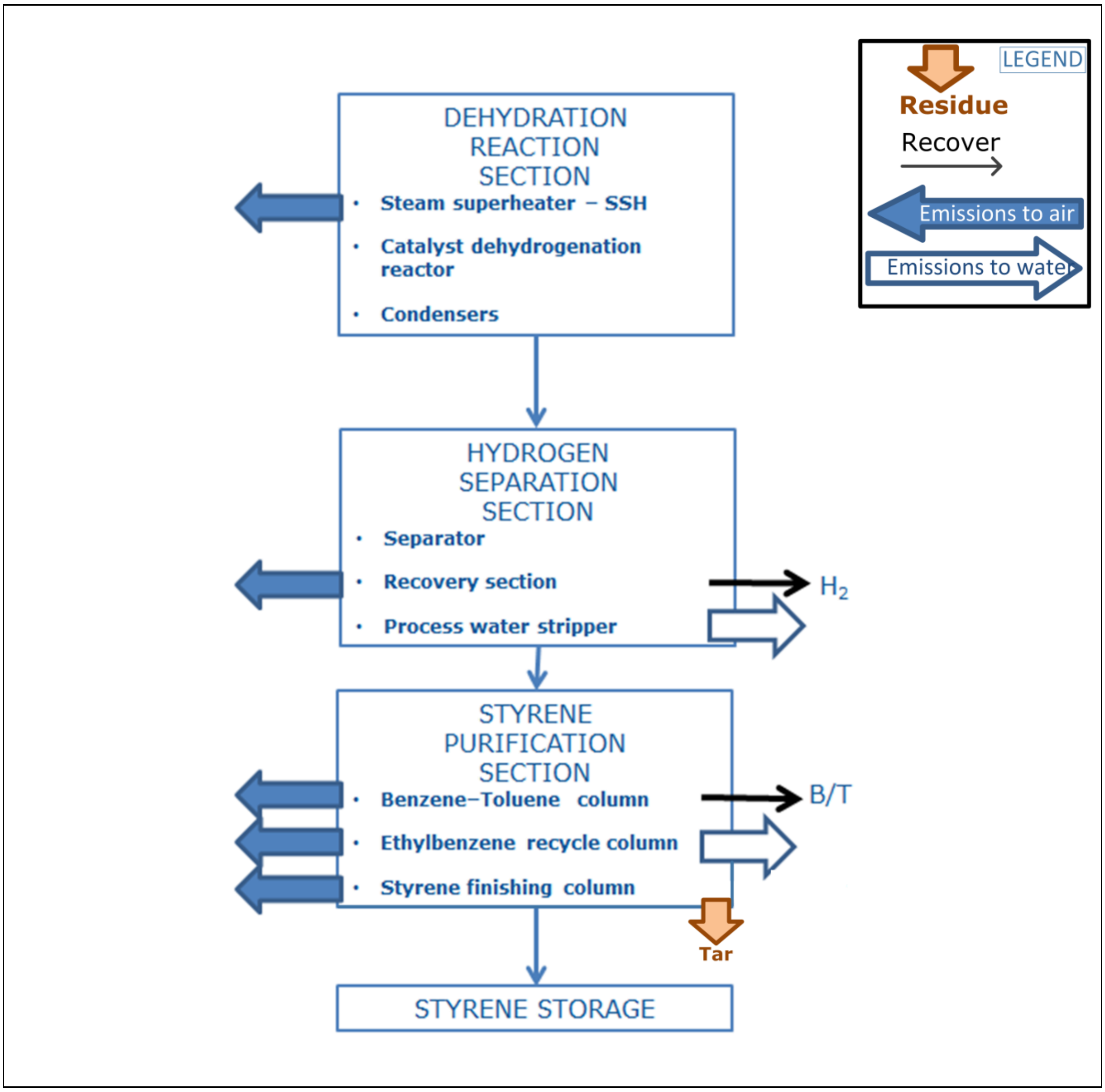


Figure 5.6: Block flow diagram of ethylbenzene dehydrogenation process

5.2.3.2 Other than normal operating conditions

5.2.3.2.1 Specific other than normal operating conditions

Deviation from stable and normal operating conditions can arise for the following reasons:

- malfunction/stoppage of end-of-pipe abatement technique;
- catalyst end-of-life and catalyst fluidisation;
- reaction poisoning leading to higher off-gas rates;
- decoking and shut blowing of the steam superheater;
- coke filter cleaning;
- leak due to corrosion;
- leak to vacuum (air ingress) in the purification unit;
- equipment fouling;

Information from the data collection indicates that these types of other than normal operating conditions can occur (on average) for up to as many days as follows:

- phase separation (downstream reaction) flaws: 4 days/yr;
- distillation flaws: 5 days/yr;
- equipment fouling (gums, etc.): 9 days/yr;
- malfunction/stoppage of end-of-pipe abatement technique: 1 day/yr;
- compressor trip: 4 days/yr;
- decoking of steam superheater: 6 days/yr.

However, in most cases, these events will be for considerably shorter periods of time.

5.2.3.2.2 Generic other than normal operating conditions

The following operations deviate from standard operating procedures in ethylbenzene dehydrogenation plants:

- Routine start-up: the hydrogen (off-gas) is sent to a flare during this upset condition.
- Shutdown for maintenance: equipment flushing, higher load to WWT.
- Low plant rate due to force majeure. (Disruptions that occur in final product processing or raw material supply.)
- Containment losses greater than normal in systems that operate under vacuum. This will increase ejector water/steam usage, and net emissions to water or air.
- Plant is idle due to loss of containment: corrosion or rupture disc.
- Service or utility failure: malfunction of cooling water and/or chilled water, power, distributed control system, instrument air.

Information from the data collection indicates that these types of other than normal operating conditions can occur for up to as many days per year as follows:

- routine start-up: 4 days/yr;
- shutdown for maintenance: 10 days/yr;
- idle; unplanned partial stoppage: 10 days/yr;

- malfunction of cooling water and/or chilled water: 8 days/yr.

However, in most cases, these events will be for considerably shorter periods of time.

According to the data collection, suboptimal operation at a low plant rate due to force majeure in the period 2007–2012 lasted, on average, 10 days per year and in the case of one plant up to 72 days/yr (in 2012).

5.2.3.3 Equipment important for environmental protection

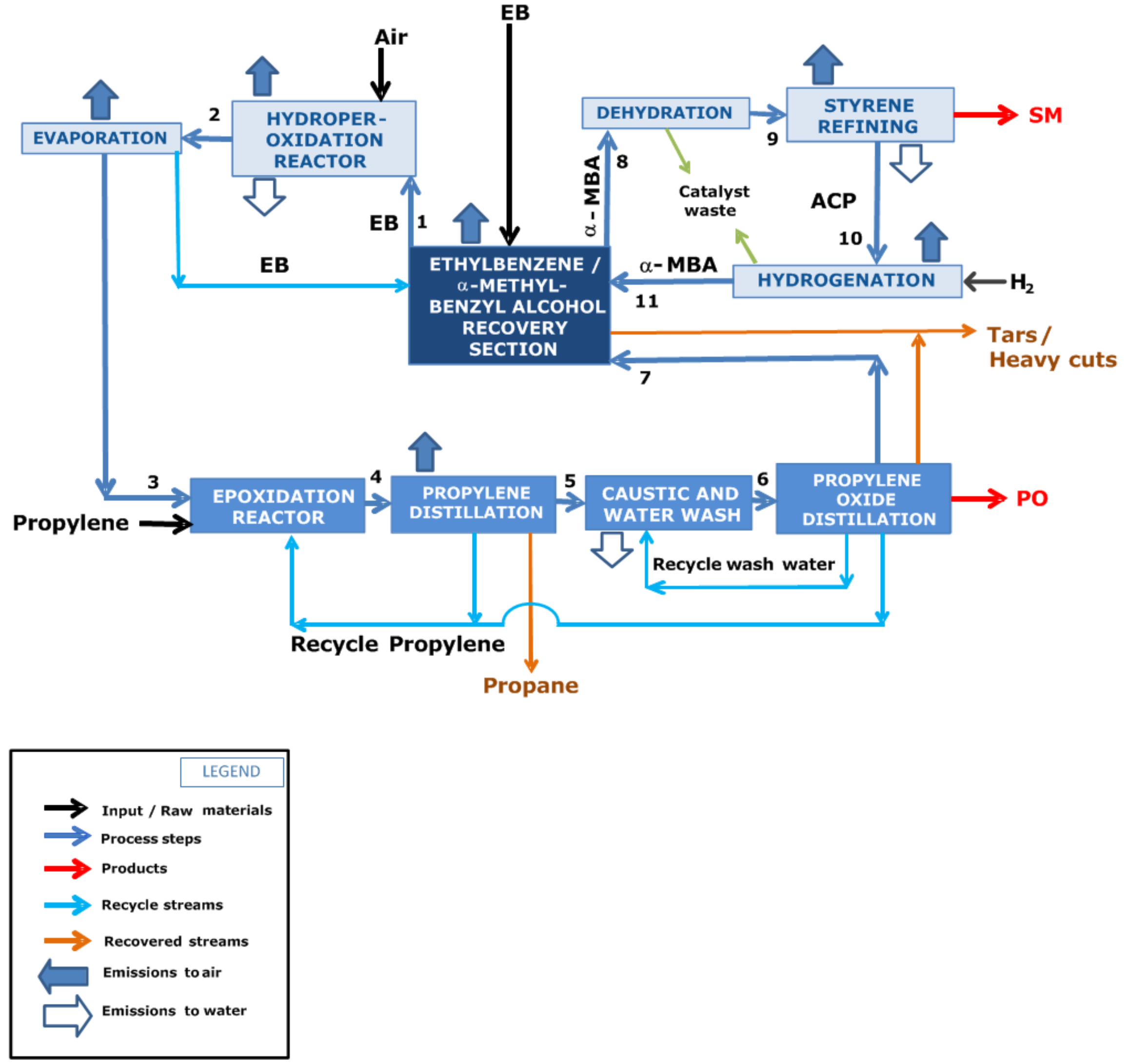
The following units/equipment perform important operations for environmental protection and require the longest uptime possible:

- steam superheater;
- condensers on the H_2 recycle stream;
- adsorption system on the H_2 recycle stream ;
- decanter downstream of the reaction;
- stripper downstream of the reaction;
- catalyst (lifetime and activity);
- styrene monomer inhibitor management.

5.2.4 Styrene co-production with propylene oxide

5.2.4.1 Process description

The peroxidation process for the co-production of styrene and propylene oxide (SMPO) includes several basic operations. In Figure 5.7, a flow diagram shows the major emissions, input and output streams.



NB: Numbers represent the process steps and acronyms have the following meaning: EB – ethylbenzene, SM – styrene monomer, PO – propylene oxide, ACP – acetophenone, α-MBA – α-methylbenzyl alcohol.

Figure 5.7: Block flow diagram of ethylbenzene peroxidation process

5.2.4.1.1 Ethylbenzene oxidation section

The initial step in the process is the oxidation of ethylbenzene with air to produce ethylbenzene hydroperoxide (EBHP) and minor amounts of α-methylbenzyl alcohol (α-MBA) and acetophenone (ACP). Selectivity to by-products generated in the oxidation reaction is: ACP 5–10 %; α-MBA 5–10 %; organic acid impurities 1 %. The oxidation takes place at 2 bar and 140–150 °C in the liquid phase.

The process off-gas exiting the reactor contains inert gas (principally nitrogen) and a mixture of organic vapours. The stream is cooled and scrubbed to recover aromatics before the remaining off-gases are ducted to an end-of-pipe abatement. The mixed organic condensate is fed to an evaporation system where some of the unreacted ethylbenzene, along with low-boiling contaminates, is removed. The recovered ethylbenzene is sent to the ethylbenzene recovery system for further purification prior to reuse. The remaining concentrated solution of ethylbenzene hydroperoxide (EBHP) and reaction by-products is sent to the epoxidation reaction section.

5.2.4.1.2 Epoxidation of propylene

Next, propylene is mixed with the concentrated EBHP solution and epoxidised over a catalyst (Mo-based homogeneous or Ti-supported silica-based heterogeneous) at high pressure (35–40 bar, 100 °C) to form propylene oxide (PO) and acetophenone (ACP) as the main by-product of this reaction. After epoxidation, the pressure is reduced and most of the residual propylene and other low-boiling compounds are separated from the reaction mixture by distillation. The off-gas stream from this distillation contains a small amount of unreacted propylene and – depending on the compounds that entered the process with the propylene feed – ethane, propane and minor amounts of other gases (light ends). Propylene can be recycled to the epoxidation reaction and propane and ethane can be recovered in the depropaniser and de-ethaniser and fed to the plant fuel gas network and used as a fuel.

The crude epoxidate stream from the epoxidation reactor is next treated to remove the acidic impurities and residual (homogeneous/dissolved) catalyst by washing with caustic solution.

The washed epoxidate stream is then distilled to separate and purify the propylene oxide (PO). The purified propylene oxide is sent to storage.

Again, the recovered propylene is recycled to the epoxidation process; residual water is returned to the epoxidate washing operation; and residual liquid impurities (tars/heavy cuts) are collected and either used as a fuel, recovered or disposed of.

The organic layer remaining after PO removal goes to the **ethylbenzene/α-MBA recovery section**. In this recovery section, the organic layer is again washed in caustic and water and then distilled. The (vacuum) distillation removes the remaining ethylbenzene and then separates the organic residues from the α-MBA and ACP. The recovered ethylbenzene, along with ethylbenzene from other parts of the process and fresh ethylbenzene, is treated prior to reuse in the oxidation reactors and the organic liquid residues (tars/heavy cuts) are either used as fuel, recovered or disposed of.

5.2.4.1.3 Dehydration of acetophenone (ACP) and α-methylbenzyl alcohol (α-MBA)

The mixed stream of α-MBA and ACP from the ethylbenzene/α-MBA recovery section is then dehydrated over a solid catalyst (a mixture of zinc and copper oxide) to produce styrene. The residual catalyst solids and high-boiling impurities are separated from the organic product stream and collected for disposal.

The crude styrene passes through a series of vacuum distillation columns where pure styrene monomer is separated and recovered for sale.

5.2.4.1.4 Hydrogenation section

After the pure styrene monomer is removed, the residual organic stream contains crude acetophenone (ACP), along with a mixture of various impurities. A solid catalyst (e.g. palladium on activated carbon or copper oxide with other metal oxides (zinc, silicon, chromium)) is used for hydrogenation of crude ACP stream. The reaction to convert the ACP to α-MBA proceeds with hydrogen gas under pressure. The residual hydrogen stream containing some organic vapours is either used for hydrogen recovery or vented to the plant fuel gas network and used as a fuel. The crude α-MBA from the hydrogenation section is returned to the **ethylbenzene/α-MBA recovery section** to join the stream for the dehydration section.

5.2.4.1.5 Fractionation units

The styrene monomer and propylene oxide co-production process includes a large number of feedstock and intermediate recycle streams that are generated in the separation and fractionation units following the oxidation, epoxidation and dehydration units, as described below.

Downstream of the oxidation stage, the ethylbenzene hydroperoxide is concentrated by removing ethylbenzene via distillation.

After epoxidation, the crude epoxidate is washed. The washed stream is then distilled to separate the styrene monomer and propylene oxide co-products. Downstream of the epoxidation stage, propylene is recovered via distillation.

Styrene purification: Downstream of the α-methylbenzyl alcohol (α-MBA) dehydration, styrene is purified in distillation operations. The post-dehydration section may include a distillation column train in order to purify the styrene monomer product. Depending on the technology or design configuration, there can be two or three columns in this section. The first column runs to remove the compounds that are lighter than the styrene monomer (mainly ethylbenzene and other light ends). A second column runs to distil the styrene product from the top. The bottoms stream with a high content of acetophenone (ACP) is sent to the hydrogenation section. In some cases, a third column can be installed in order to reduce the styrene losses towards the hydrogenation section.

Propylene oxide purification: Propylene oxide distillation trains may have different configurations to separate propylene oxide from propylene and residual liquids which are removed from the process. Propylene would normally be recycled back to the epoxidation so potentially there may be no off-gases from this unit.

By-product recovery and conversion: Separation of ethylbenzene in excess from the α-MBA/ACP stream takes place in a vacuum distillation section. The 1,2-propylene glycol (MPG) by-product is also purified via a vacuum distillation step prior to ACP hydrogenation [55, US EPA 1993].

5.2.4.2 Other than normal operating conditions

5.2.4.2.1 Specific other than normal operating conditions

Deviation from stable and normal operating conditions can arise because of the following events (which are usually some kind of malfunction or failure):

- oxidation section:
  - oxidation reactivity loss;
  - oxidation feed control malfunction;
  - large excess of wash water feed;
  - elevated temperatures;
- post-oxidation wash section:
  - phase separation;
- epoxidation section:
  - epoxidation reaction conditions;
- post-epoxidation wash, fractionation and dehydration section:
  - distillation flaws;
  - malfunction or failure of process off-gas post-condensers;
  - charcoal absorbers' end of run (not in every plant design);

- hydrogenation section:
    - hydrogenation start-up;
- fractionation section:
    - charcoal decanter malfunction (not in every plant design);
    - neutralisation decanter malfunction;
    - equipment fouling;
    - malfunction/stoppage of end-of-pipe abatement technique.

According to the data collection, the most frequent events that happen are flaws in distillation columns (up to 11 times per year) (like malfunction of cooling water or high temperatures), neutralisation decanter malfunction and equipment fouling (up to 7 times per year). The cumulative occurrence of the above events was up to 10 days per year (homogeneous epoxidation can have more flaws).

5.2.4.2.2 Generic other than normal operating conditions

The following operations deviate from standard operating procedures in SMPO plants:

- Routine start-up: the hydrogen (off-gas) is sent to a flare during this upset condition. This operating condition may last from a few hours to some days.
- Shutdown for maintenance: equipment flushing, higher load to WWT.
- Low plant rate due to force majeure. (Disruptions that occur in final product processing or raw material supply.)
- Containment losses greater than normal in systems that operate under vacuum. This will increase ejector water/steam usage, net emissions to water or air.
- Plant idle.
- Service or utility failure: malfunction of cooling water and/or chilled water, power, distributed control system, instrument air.

According to the data collection, the cumulative occurrence of these events lasted up to 15 days per year (without the low plant rate event, which lasted on average 8 days per year).

5.2.4.3 Equipment important for environmental protection

The following systems perform important operations for environmental protection and should have the longest uptime possible:

- Air:
    - off-gas header/manifold treatment system;
    - chilled water-cooled post-oxidiser condensers;
    - charcoal adsorber regeneration programme.

- Water:
    - charcoal decanter;
    - neutralisation decanter.

5.3 Current emission and consumption levels

5.3.1 Emissions to air

All plants that participated in the data collection had both ethylbenzene and styrene monomer plants integrated (on site) with common (shared) off-gas and waste water streams collection and treatment (recovery or abatement) systems.

Table 5.3: Generic information about processes used in ethylbenzene and styrene monomer plants (configurations) that participated in the data collection

	Plant #1	**Plant #2**	**Plant #3**	**Plant #4**	**Plant #5**
Ethylbenzene unit					
Catalyst	$AlCl_3$	Zeolites	Zeolites	Zeolites	Zeolites
Process	Liquid-phase	Liquid-phase	Liquid-phase	Liquid-phase	Liquid-phase
Alkylation reactor	Fluid catalyst beds	Fixed catalyst beds	Fixed catalyst beds	Fixed catalyst beds	Fixed catalyst beds
Transalkylation reactor	Same reactor as for alkylation	Fixed catalyst beds	NI	Fixed catalyst beds	Fixed catalyst beds
Feedstock treatment	Benzene drying column	Water decantation. Guard beds: Clay / Ion exchange resin	Benzene drying column. Guard beds: molecular sieves	Guard beds: Clay	Benzene drying column: valve trays. Guard beds: molecular sieves (2 for benzene, 1 for ethylene)
Downstream purification	Wash section Distillation columns	Distillation columns with: sieve trays and multiple downcomer trays	Distillation columns with: sieve trays	Distillation columns	Distillation columns
Styrene monomer unit					
Process	Ethylbenzene catalytic dehydration	Ethylbenzene hydroperoxidation (co-production with propylene oxide)	Ethylbenzene catalytic dehydration	Ethylbenzene catalytic dehydration	Ethylbenzene catalytic dehydration
Dehydrogenation	Adiabatic (iron oxide catalyst)	*Oxidation.* (*) *Epoxidation*: homogeneous catalyst. *Washing section*: neutralisation and gravity decanters. *Fractionation section*: distillation columns (trays and packed)	Adiabatic (iron oxide catalyst)	Adiabatic (iron oxide catalyst)	Adiabatic (iron oxide catalyst, fixed bed)
Fractionation	Vacuum distillation columns (packed)	*Dehydration:* (*) liquid-phase, homogeneous catalyst *Fractionation section*: distillation columns (random	Shared with isothermal units	NI	NI

		and structured packing) *Hydrogenation:* liquid-phase, heterogeneous catalyst			
NB: NI: No information. (*) Ethylbenzene hydroperoxidation has different process steps than ethylbenzene dehydration. *Source:* Data collection					

5.3.1.1 Emissions to air from ethylbenzene production

The sources of waste gas streams from ethylbenzene production units are:

- feedstock pretreatment units: waste gas stream from the benzene drying column;
- alkylation/transalkylation units: waste gas streams from reactor degassing through a flush tank and/or vented to a caustic scrubber; in the case of zeolite-catalysed processes, *in situ* catalyst regeneration can also produce a waste gas stream – usually all these streams are routed to a shared combustion treatment/unit;
- $AlCl_3$-catalyst-handling units: waste gas streams from the catalyst preparation/replacement reactor and waste gas streams from spent catalyst removal and treatment;
- fractionation units: waste gas streams from benzene recovery and/or the benzene drag column.

In some cases, depending on operation and design features, the waste gas streams could emerge from other (EB, PEB) distillation columns and can be merged with the benzene recovery column tops. These streams are also usually routed to a shared combustion treatment/unit.

The emissions to air from most sources of the plant (except from $AlCl_3$-catalyst-handling units) are relatively similar in terms of quantity and pollutant content. These waste gases consist mainly of VOCs – reactants (mainly benzene), feed impurities, products and by-products; or inerts (gases like N_2, O_2, CO, H_2, CH_4) which are either already present in the feed or added to the flow to regulate pressure. Due to the potentially hazardous nature of these emissions, treatment is required. Most ethylbenzene units will thus have a **shared end-of-pipe** abatement technique for these off-gases. They can be shared with different sources from the ethylbenzene plant or units with other LVOC processes. Some streams have sufficient calorific value to be used as fuels in the on-site combustion plants. If an ethylbenzene dehydrogenation unit is located on the same site, this is often the steam superheater (SSH) furnace. For lower calorific value streams, a thermal oxidiser with energy recovery can be used, or the off-gases can be used as part of the combustion air in furnaces. Flares should be considered only as a last resort abatement device and used only for safety reasons.

The emissions to air from $AlCl_3$-catalyst-handling units are acidic, containing chlorine or HCl and (catalyst) dust emissions.

In the data collection, information from five plants was reported (see Table 5.3): one using the $AlCl_3$-catalysed liquid-phase process and four using zeolite-catalysed liquid-phase processes. The former used the same reactor for alkylation and transalkylation, and the latter used separate fixed-bed reactors for the two reactions.

5.3.1.1.1 Emissions to air from alkylation and transalkylation units

$AlCl_3$-catalysed processes: In both older and modern $AlCl_3$-catalysed processes the reactor has a direct off-gas stream whose emissions will comprise organic and acid species. The off-gases of the alkylation and/or transalkylation section are released after the effluents leave the reactor, where they were heavily mixed in the presence of inert gas (nitrogen) needed to ensure high pressures. Leaving the reactor, this inert gas then needs to be treated to remove hydrocarbons and acidic species, usually in the caustic scrubber (with NaOH solution). The resultant waste gas can either be treated with the off-gases from other on-site units in a shared thermal oxidiser or, if its calorific value is high enough, it can be used as a fuel in the combustion unit. The composition and flow rate of these off-gases are usually not measured although emissions from the thermal oxidisers or combustion units can be monitored for VOCs and dust. According to the data collection (Plant #1), the amount of VOCs in this off-gas stream (before treatment) has been estimated at about 1.28 kg/tonne of ethylbenzene produced.

Zeolite-catalysed processes: Usually these processes have no direct off-gas stream from the reactor because it is routed to downstream fractionation units where off-gases are treated.

Both processes: The off-gases appear from a flash tank which is usually used between the reactor section and the fractionation section (units) in order to lower the pressure (and temperature) of the reactor effluent (stream).

The volumes of process off-gases from the alkylation and/or transalkylation reactor are proportional to the purity of the ethylene and benzene feed. If polymerisation-grade ethylene and high-purity benzene are used in the process, the off-gas volume roughly corresponds to the amount of non-reacting (non-ethylene and non-benzene) components in the raw material and is very low. If dilute ethylene and crude benzene feeds are used, the volume of off-gases is significantly higher.

These off-gases contain benzene and ethylbenzene but also lighter fractions like ethane, propylene and others, which attributes to the considerable calorific value of these off-gases – sometimes used as fuel gas.

Ethylbenzene plants that are integrated with styrene monomer plants using the ethylbenzene dehydrogenation process may have a shared absorber that collects all the process off-gas streams and recovers the valuable components from them using a wet gas scrubber.

5.3.1.1.2 Emissions to air from feedstock pretreatment and post-alkylation fractionation units

a) Emissions from the benzene (feed) drying column

Both processes: Emissions to air from this unit include benzene and other lighter hydrocarbons. Monitoring is normally not done on individual streams, so most installations have limited data. Most of the VOCs to be removed from the process are simply non-reacting inerts from the benzene feed.

In plants using diluted benzene feed, the feed can be routed through the benzene drag column, after going through the benzene drying column, to additionally purge lighter hydrocarbons. The purified benzene feed can then be recirculated to the reactor, and the purged lighter gaseous fraction can in normal operation be sent to some sort of combustion, or flared under other than normal operating conditions.

In some technology configurations, the benzene recovery column upper stream may also be rerouted through this column, acting as the benzene drag column.

According to the data collection, for zeolite-catalysed processes, the TVOC content in the off-gas streams from the benzene drying column is reported to be around 0.32–1.5 kg/tonne of EB (Plants #2 and #5), and ducted either to the plant fuel gas network or (in other than normal operating conditions) to flare.

In both ethylbenzene plant processes, the fractionation section that follows the alkylation/translalkylation section involves multiple distillation units, of which (at least) the polyethylbenzenes (PEB) recovery columns are operating under low pressure or vacuum.

The components are recovered from the overheads of consecutively linked distillation columns in the following order: first excess benzene, then ethylbenzene and lastly polyethylbenzenes. The largest quantity of emissions to air comes from the first – the benzene recovery column.

b) Emissions from the benzene recovery column (post-alkylation)
Both processes: This distillation column is used downstream of the reaction section to remove the unreacted benzene. The reaction products are to be found in the distillation tower bottoms and the excess benzene is condensed out at the top of the column – in the overhead condenser, which is used also for heat recovery (as steam generation).

In the case of high-purity feedstock, the emissions to air from the condenser will include some benzene, but also ethylene, ethylbenzene and other VOCs. This stream may also contain some process inerts (lighter hydrocarbons) originating from the ethylene feed, e.g. methane, as well as some light hydrocarbon compounds generated by alkylation/transalkylation side reactions. This stream sometimes has sufficient calorific value to be used to produce energy, e.g. generate steam. It will normally be fed into a common combustion gas system shared with on-site styrene monomer or other units (see Section 5.3.1.2.1 and Section 5.3.1.4). According to the data collection (Plant #1), the amount of VOC emissions (mainly benzene) before treatment is normally not measured, but has been estimated at approximately 7.2 kg/tonne of ethylbenzene produced.

In special cases where the benzene feed is of a low purity (e.g. crude benzene with 85–95 wt-% benzene), the liquid condensate of the top stream cut from the benzene distillation/condensation column will be substantial, mostly (85 wt-%) composed of non-aromatic hydrocarbon fractions (C_5-C_7) and some benzene (15 wt-%) and will usually be returned to the refinery or unit in which the crude benzene originates.

On the other hand, if diluted ethylene feed is used in the process, the stream cut from the benzene recovery column will create a stream of off-gas (consisting mostly of methane and hydrogen) which can be used as a fuel or sent to the suitable abatement treatment often ending in some sort of combustion [57, Netzer 1999].

c) Emissions from the benzene drag column (post-alkylation)
Both processes: Benzene drag is a purge from the top cut of the distillation column that normally goes to the fuel header. According to the data collection, the amount of VOCs in the off-gas stream from this distillation column is in a range from 0.07 kg to 7 kg/tonne of EB.

Emissions to air are similar in composition to the emission streams from benzene recovery and drying columns and are usually collected and treated jointly with those. Again, most installations have only limited (indirect) data and estimations on the composition of this stream.

d) Emissions from the ethylbenzene (EB) recovery column
Both processes: The next column that receives the bottoms of the benzene recovery column is the ethylbenzene recovery column, which is, under normal operating conditions, directly connected to the polyethylbenzenes (PEB) recovery column and is vented jointly with its off-gases; a separate off-gas stream may be present under other than normal operating conditions (like start-ups) and is usually flared.

e) Emissions from the polyethylbenzenes (PEB) recovery column

Both processes: The final column in the fractionation section is the PEB recovery column, which receives the bottoms of EB recovery column. The vacuum system of these columns will have a net emission from the vent outlet – regardless of whether pumps or ejectors are used to generate the vacuum. Emissions to air are likely to be predominately comprised of non-condensables from the condensers and/or vacuum systems, mainly diethylbenzenes, ethylbenzene and inerts.

According to the data collection (Plant #1), the amount of VOCs before treatment has been estimated at approximately 0.57 kg/tonne of ethylbenzene produced. The total (overall) unabated channelled TVOC emissions from the EB ($AlCl_3$-catalysed) Plant #1 are estimated to be 11.05 kg/tonne of EB.

Zeolite-catalysed processes: TVOC emissions from the fractionation unit's vacuum system (liquid ring) are reported to be around 0.005 kg/tonne of EB.

Plants #1, #3 and #5 (from the data collection) collect process off-gases and off-gases from fractionation (e.g. the benzene recovery column) from EB units in a fuel gas network (header) and burn it as a fuel (heat recovery) in the steam superheater of the SM unit together with the off-gases from the SM unit (for emission data for steam superheaters, see Section 5.3.1.2.1). Plant #2 sends off-gases from condensation (following the reaction and fractionation sections) to the fuel gas network where they are used as a fuel in furnaces or boilers.

5.3.1.1.3 Emissions to air from catalyst-related units

$AlCl_3$ catalyst replacement/preparation unit

The catalyst is prepared either by aluminium chloride powder handling and dissolution in the feed/recycled PEB stream or by the *in situ* reaction of aluminium powder with HCl and subsequent dissolution of aluminium chloride in the feed/recycled PEB stream, and waste gases with dust and/or HCl emissions are generated. This gas stream is treated in the water scrubber where dust and HCl emissions are dissolved in scrubbing water. This water can be reused in the wash section of the reactors.

According to the data collection (Plant #1), specific emissions of dust from these units are around 10 mg/tonne of EB, and specific emissions of HCl around 34 mg/tonne of EB.

Spent $AlCl_3$ catalyst treatment units

Spent $AlCl_3$ catalyst treatment units' processes as described in Section 5.2.2.1.3 generate the following emissions:

- water and caustic wash sections: some of the aluminium chloride (from the catalyst complex) reacting with water may still release HCl emissions, which are usually treated together with acid process off-gases from the alkylation/translalkylation reactor section;
- steam stripping VOCs from wash effluents: off-gases may still contain small amounts of VOCs, therefore they are sent to combustion or a thermal oxidiser;
- concentrating aluminium chloride solution: after water scrubbing of evaporation off-gases, minor HCl emissions may be left in the off-gases.

According to the data collection (Plant #1), specific emissions of HCl from these units are around 3 mg/tonne of EB.

Zeolite catalyst regeneration

Zeolite processes require catalyst regeneration. The regeneration process can require separate units if the catalyst bed is removed from the reactor for regeneration. These units can be part of the installation as a dedicated system installed in the plant, although most of the licensors

recommend off-site regeneration by third parties. With some zeolite catalysts and reactor designs, *in situ* regeneration (without catalyst removal from the reactor) is possible.
In *in situ* regeneration of zeolite catalyst at high temperatures with regeneration gas, as described in Section 5.2.2.1.3, an off-gas stream is generated. The compounds that make up coke are partially stripped out in the initial step when the regeneration gas consists of pure nitrogen and can be condensed from the regeneration gas and recovered. In further regeneration steps, when the oxygen is gradually introduced into the regeneration gas, the coke is burnt off and CO/CO_2, NO_X and dust emissions are expected in the off-gases. The pollutant loads correspond to the coke quantity and are expected to be relatively low.

The same *in situ* regeneration process can also be used for the regeneration of feedstock guard beds.

According to the data collection, most (three out of four) of the plants with zeolite-catalysed technology use a third party for the off-site regeneration. The one that has technology capable of *in situ* regeneration had not yet used it at the time of the data collection.

5.3.1.2 Emissions to air from ethylbenzene dehydrogenation

Figure 5.6 shows the main emissions to air from the ethylbenzene dehydration process.

5.3.1.2.1 Emissions to air from the steam superheater

The dehydrogenation reaction takes place in a sequence of two or more reactors with intermediate heating at temperatures between 500 °C and 650 °C. In order to produce such high temperatures, steam is heated to temperatures of up to 900 °C in a furnace called a steam superheater (SSH). Therefore the main emissions from the dehydrogenation section originate from the steam superheater, which, due to its main purpose (energy production, specifically steam production), falls within the scope of the LCP BREF.

The emissions to air are those normally associated with furnace flue-gases; however, these emissions may have more SO_2 and NO_X due to the reuse of process streams (gaseous by-products) as non-conventional fuel. Plants #1, #3 and #5 use steam superheaters as a combustion unit and end-of-pipe abatement unit where off-gas streams from the EB and SM plants are burnt as a fuel for heat recovery (see also Section 5.3.1.1.2). Some of the streams from distillation units in the fractionation sections of SM plants may have a higher nitrogen or sulphur content due to the use of polymerisation inhibitors/retarders, which will affect NO_X and SO_2 emissions. The hydrogen level in the fuel will also have an effect on the NO_X level.

Data on fuels used and emissions to air from a steam superheater (Plant #1) are shown below:

- nominal capacity (MW) : 95.5;
- H_2 content of fuel (vol-%): 10;
- hydrocarbon content (except C_2 compounds) of fuel (vol-%): 2.8;
- NO_X (mg/Nm^3), dry, 3 % O_2: < 140;
- CO (mg/Nm^3), dry, 3 % O_2: < 5;
- dust (mgN/m^3), dry, 3 % O_2: < 5;
- VOCs (mg/Nm^3), dry, 3 % O_2: < 5.

The amount of emissions from another steam superheater (Plant #5) are given below:

- CH_4: 1.3–2.3 g/tonne of SM;

- SO_2: 0.8–4 g/tonne of SM;
- NO_X: 39–83 g/tonne of SM;
- CO: 4–8 g/tonne of SM;
- PM: 0.6–1.9 g/tonne of SM;
- NMVOC: 0.5–2 g/tonne of SM.

Data collected on fuels used in the steam superheaters are presented in

Table 5.4 below.

Table 5.4: Fuel use in steam superheaters

Fuel used in SSH	Plant #1	Plant #3	Plant #4	Plant #5
Natural gas	No	Yes	Yes	No
Fuel gas ($CH_4 + H_2 + C_2$–C_4 + CO + CO_2)	Yes	Yes	No	Yes
H_2-rich stream from SM process	Yes, also for shutdowns	Yes	Yes	Yes
H_2 content of fuel gas (NOC) (vol-%)	10	NI	87	15
Other streams from SM process	B/T splitter vents	-	Tar	Dehydration vacuum system
Source: Data collection				

According to information collected in the questionnaires, the only combustion control used for steam superheaters by all plants (see

Table 5.4) is continuous or frequent periodic measurements of the oxygen content in the flue-gases with an on-stream analyser. Monitoring of NO_X, SO_2, CO and VOC emissions in flue-gases is conducted periodically.

5.3.1.2.2 Emissions to air from the dehydration reaction section

The dehydrogenation reaction takes place under vacuum conditions and in the presence of steam. After the dehydrogenation reactors, the product is condensed and the water decanted from the organics. The process off-gases comprise mainly hydrogen, but also some CO, CO_2 and VOCs (methane, ethylbenzene, styrene, aromatics). The amount of hydrogen produced depends on the dehydrogenation conditions and catalyst. A lower steam to olefin ratio, to save steam, generally increases the hydrogen content. The amount of hydrogen also increases with the run length as a result of catalyst ageing. The emissions in this stream are normally not measured as it is fed to a shared abatement device; oxygen may be monitored for safety purposes. Hydrogen can be separated, compressed and reused. The remaining purge would be abated for remaining VOCs before venting to air. The other option is to not treat this off-gas stream but route it wholly to the steam superheater to be used as a fuel. According to the data collection, this is done in Plants #1, #4 and #5.

5.3.1.2.3 Emissions to air from the vacuum systems

Depending on the plant design, the process will contain a number of vacuum systems. First, the dehydrogenation reaction can be carried out under vacuum. This vacuum system will generate a net emission to air. Second, a fractionation or purification section (also under vacuum) may be in place to split the feedstock from the styrene monomer product and by-products. Each distillation train will have a net off-gas stream (regardless of whether ejectors or pumps are used). Distillation columns will also include condensers and overhead receivers. Ejector systems will also include a decanter to split organic and aqueous phases.

There may be a number of different vacuum systems in operation (i.e. for the reaction section and for the fractionation section. The resulting waste gas stream is comprised of CO, CO_2, non-condensables and VOCs: light hydrocarbons formed in the dehydrogenation step, aromatics (BTX), ethylbenzene and styrene). The stream from the vacuum system that operates in the fractionation section is normally collected and sent as fuel gas to the SSH or to a shared abatement (e.g. thermal oxidiser). The emissions in this stream are also normally not measured as it is also fed to a shared abatement device; this stream is smaller than the one from the reaction section.

Emissions from vacuum systems collectively treated in a thermal oxidiser are reported by Plant #4 in Section 5.3.1.4.

5.3.1.3 Emissions to air from styrene co-production with propylene oxide

Figure 5.7 shows the main emissions to air from the ethylbenzene peroxidation process.

5.3.1.3.1 Emissions to air from the oxidation unit

The initial step of the process is the oxidation of ethylbenzene with air to produce its peroxide and minor amounts of α-methylbenzyl alcohol (α-MBA) and acetophenone (ACP), α-methylethanol, benzoic acid, and other organic acids. The selectivity to impurities generated in the oxidation is: 5–10 % ACP; 5–10 % α-MBA; 1 % organic acid impurities. According to the data collection (Plant #2), the average yearly amount of ACP sent from oxidation to the hydrogenation unit was 115.4 kg/tonne of SM+PO.

Process-integrated techniques for treating this stream include condensers, chilled condensers and an absorber or adsorber. The exhaust gas from the reactor columns contains nitrogen and excess oxygen brought into the process with the reaction air and a mixture of organic vapours. As the EB feedstock is manufactured by the alkylation of benzene, it may include residual levels of benzene. The main pollutants in this off-gas stream are: CO, $CO_{2,}$ ethylbenzene, methanol, some acetophenone (ACP) and methylbenzyl alcohol (α-MBA), due to entrainment, and methane [55, US EPA 1993].

According to data collected from Plant #2, this stream is treated first to absorb aromatic compounds in a scrubber using EB flux oil as the absorption medium and then in a catalytic oxidiser for abatement of the remaining VOCs.

5.3.1.3.2 Emissions to air from the epoxidation unit

From the epoxidation section off-gases it may be necessary to purge the impurities that enter the process with the propylene, with the use of distillation columns. For this reason, there can be two purge streams depending on the quality of the propylene feedstock: a de-ethaniser purge stream to remove the ethane and other light ends and a depropaniser purge stream to separate the propane. In some cases, both purges can be sent to the plant fuel gas manifold/header as fuel feedstock, as an abatement technique.

According to data collected from Plant #2 which uses a homogeneous catalyst in the epoxidation unit, the process off-gases from this unit (before the de-ethaniser, depropaniser and propylene purification) contain methane levels in the range of 2 632 g/Nm^3 and NMVOC levels of about 784 g/Nm^3 during start-up and 553 g/Nm^3 during stable operation (reference conditions: dry gas at 3 % O_2, flow rate 500 m^3/h, measured by gas chromatography/TCD, averaged over one hour).

5.3.1.3.3 Emissions to air from the fractionation units

The main emission sources from the vacuum distillation systems are as follows:

- Benzene distillation column: this vacuum header manifold is the only large benzene emission point of the plant. The benzene present results from feedstock (ethylbenzene) impurities and/or minor side reactions.
- Other columns: there will be slightly different compositions of VOCs present, depending on distillation conditions and targets. The VOCs could be present in small quantities in the air that could enter the vacuum systems.

The main components of atmospheric distillation systems are light hydrocarbons, aromatics and others (e.g. H_2O from dehydration and H_2 from hydrogenation).

Process-integrated techniques include condensers and overhead receivers. Individual streams are not normally monitored and most installations have scarce data. No emissions data for this stream were reported in the data collection.

5.3.1.3.4 Emissions to air from the hydrogenation unit

After the pure styrene monomer is separated, the residual organic stream contains crude acetophenone (ACP), along with a mixture of various impurities. The stream is treated by catalytic reaction under pressure with hydrogen to convert ACP to α-methylbenzyl alcohol (α-MBA). The residual hydrogen stream from the hydrogenation reaction outlet contains some organic vapours that need to be treated.

Hydrogenation units operate at pressures of 2.5–3.0 MPa and temperatures < 190 °C with an ACP conversion > 80 % (depending on the applied technology) and an MBA/ACP selectivity >> 90 %.

Existing processes require high-pressure hydrogen for ACP hydrogenation and large quantities of hydrogen in excess of the ACP. In addition, the yield in the hydrogenation reaction can be insufficient due to by-products such as ethylbenzene.

Process-integrated techniques normally implemented in the design are a condenser, flash and recycling of a hydrogen-rich stream. The expected composition of this stream is excess hydrogen with methane, ethylbenzene, ACP, α-MBA and water.

According to data collected from Plant #2, the unabated off-gas from the hydrogenation unit (used as a fuel in a conventional steam boiler) contains, on average, 2.165 kg VOCs per tonne of SM+PO and 67.3 g $VOCs/Nm^3$ of hydrogen, as an average over three years. The hydrogenation unit was operated at a 25.8 mol-% hydrogen excess.

5.3.1.4 Emissions to air from shared end-of-pipe abatement

Both ethylbenzene and styrene monomer plants often have an off-gas recovery network through which various continuous and discontinuous off-gas streams are collected and combusted as a fuel either in the steam superheater of the styrene monomer unit (see Section 5.3.1.2.1), a process furnace, a conventional steam boiler or a thermal or catalytic oxidiser.

Typical levels of pollutants in (overall) collected off-gas streams from ethylbenzene plants are: benzene < 8 g/t of ethylbenzene; VOCs 1–8g/t of ethylbenzene; and, where $AlCl_3$ catalyst is used, dust 0.02–2g/t of ethylbenzene The total flow is typically in the range of 30–300 kg TVOC/h [51, Welch et al. 2012]. Monitoring is normally carried out after abatement, downstream of any shared combustion unit, and measurement will usually be periodic. The average yearly amount of emissions from the combustion unit (boiler) burning off-gases from EB Plant #4 is for TVOC 1–8 g/tonne of EB and for dust 0.3–2 g/tonne of EB. The estimated amount of TVOC sent to the shared end-of-pipe abatement (combustion unit) from EB ($AlCl_3$-catalysed) Plant #1 is 2.0 kg/tonne of EB (with estimated total (overall) TVOC emissions from the plant being 11.05 kg/tonne of EB).

The off-gas streams from ethylbenzene dehydrogenation and SMPO plants will comprise VOCs, CH_4, SO_2, NO_X, CO_X and dust. Monitoring is normally after the abatement device, and by spot samples (periodic).

Average yearly emissions from the thermal oxidiser abating off-gases from SM Plant #4 are:

- SO_2: 1.4–3 g/tonne of SM;
- NO_X: 124–162 g/tonne of SM;
- CO: 4–8 g/tonne of SM;
- dust: 2–3 g/tonne of SM;
- NMVOC: 2–3 g/tonne of SM.

5.3.1.5 Emissions to air from combustion processes

Other than the steam superheater (Section 5.3.1.2.1) for ethylbenzene dehydrogenation, steam boilers or hot oil furnaces that supply heating fluid utilities to the ethylbenzene, ethylbenzene dehydration or SMPO plants can be dedicated to each plant or shared with other nearby processes. These units may also include the combustion of non-conventional (non-commercial) fuel, such as the tar streams generated in the fractionation sections. Some of the flue-gas streams may have a higher nitrogen or sulphur content due to the use of polymerisation inhibitors/retarders. For further information on combustion processes, see the LCP BREF.

5.3.1.6 Fugitive VOC emissions to air

Much of the process operates under pressure, which potentially generates some fugitive releases (losses). Other operations that could result in fugitive releases include maintenance during turnarounds. For more information on fugitive releases, see the CWW BREF.

Fugitive emissions from ethylbenzene plants are of methane, ethylbenzene, ethylene, benzene and other VOCs. Fugitive emissions of VOCs (including methane) are estimated at up to 50 g/tonne of ethylbenzene, and benzene at up to 10 g/tonne of ethylbenzene – both these figures exclude emissions from storage. Fugitive emissions from ethylbenzene dehydration plants include methane, ethylbenzene, styrene and aromatics and are estimated to be in the range from 3 g to 16 g/tonne of styrene monomer.

No data were available for SMPO plants.

5.3.1.7 VOC emissions to air from storage

Tanks and other storage assets are used for raw materials, consumables, end-products and for intermediates. These are typically atmospheric storage tanks. Most ethylbenzene plants include benzene storage (with the size depending on the logistics of the benzene), ethylbenzene storage and residue storage. Some ethylbenzene plants have dry benzene storage, ethylbenzene storage, alkylation reactor product storage, and polyethylbenzene storage.

The tanks, spheres and other storage assets that are used for raw materials, and consumable end-products and intermediates, can be located geographically far from the process in order to share abatement techniques with storage from other processes. Tank vent gases are, in some cases, partially recovered by condensation (chilled water) and non-condensable gases are treated by thermal oxidation. Other processes use storage tanks blanketed with nitrogen where vent gases are sent to the atmosphere or to an absorption column to remove hydrocarbons. For propylene oxide, a water scrubber can be used. For further information, see the EFS BREF.

5.3.2 Water usage

Water used as boiler feed water for steam generation

In the overhead condensers and in the steam generators of ethylbenzene plants, the removal of the heat of reaction can produce a huge amount of steam. The boiler feed water can be either taken from the grid or stripped condensate from other process units like the styrene monomer plants.

For styrene production by ethylbenzene dehydrogenation, boiler feed water for the steam consumed in the reaction constitutes the largest water usage, up to 4 m^3/tonne of styrene monomer. For SMPO plants, the process water usage is reported by CEFIC as up to 0.25 m^3/tonne of styrene monomer.

Water as part of aqueous solutions used in washing sections following reactions

In ethylbenzene production by $AlCl_3$-catalysed processes, the aqueous spent scrubbing liquor from water scrubbers used for purging acid (HCl) emissions in post-alkylation catalyst removal units (treatment of spent catalyst effluent) can be reused as washing water in the washing and neutralisation post-alkylation sections. According to information collected in the EIPPCB questionnaires, this effluent is generated in amounts of around 0.2 m^3/tonne of ethylbenzene.

5.3.3 Emissions to water

According to the data collection, all plants (#1 to #5) collect waste water streams from different sources/units of the ethylbenzene plant with waste water streams from different sources/units of the styrene monomer plant and treat them in a common waste water treatment plant. Nevertheless, some waste water streams need to be pretreated prior to the common WWTP (as indicated in Section 5.4.2). In the following subsections, more detailed information is provided on specific waste water streams. Besides waste waters from production processes, less relevant effluents may also arise from auxiliary systems like cooling water or heat/steam generation systems.

5.3.3.1 Emissions to water from ethylbenzene production

Major waste water streams arise in $AlCl_3$-catalysed processes due to the wash section and spent catalyst treatment section characteristic to these processes.

Apart from these, there are some minor water streams common to both $AlCl_3$- and zeolite-catalysed processes: aqueous condensates from benzene drying and recycling columns, and condensates from vacuum systems needed either for distillation columns in the fractionation section (see Table 5.5 below).

Emissions to water from the $AlCl_3$ catalyst wash units

Post-reactor wash sections generate two different aqueous streams as described in Section 5.2.2.1.3: the acidic aqueous stream from the water wash and the alkaline stream from the caustic wash.

The acidic aqueous effluent contains aluminium chloride and organic acids, while the alkaline effluent contains diluted NaOH, salt (NaCl) and some alumina (TSS). Both effluents are saturated with hydrocarbons (benzene and (poly)ethylbenzene(s)), which can be removed by steam stripping. The aluminium chloride is recovered from the acidic aqueous effluent as saturated aluminium chloride solution that can be used in the WWTP as flocculant. The alkaline effluent may be neutralised, if its pH is too high, with diluted HCl (condensate from the evaporation/concentration of the $AlCl_3$ solution) before being treated in a common WWTP.

Emissions to water from benzene drying

The overhead of the benzene drying column consists of benzene and water. Benzene is recycled and oily water sent to the oily water treatment unit of the site.

Another technique for drying benzene can be just phase separation using a decanter. The pollutants will be the same as in distillation. The amount of benzene and other hydrocarbons is low, as can be seen from Table 5.5 below, corresponding to the low water content in the feed. Water from the benzene drying column can be reused.

Table 5.5: Characteristics of effluents from different EB plant units

Effluent	Pretreatment techniques and effluent characteristics		Plant #1	Plant #4	Plant #5
Post-reactor (wash section)	$AlCl_3$ process: Decanter		Yes	NA	NA
	Flow (m^3/h)	Avg.	10	NA	NA
		Max.	15	NA	NA
	Pollutants		Benzene, ethylbenzene, polyethylbenzenes	NI	NI
Benzene drying column	Decanter		Yes	Yes	Yes
	Flow (m^3/h)	Avg.	0.5	0.03	0.04
		Max.	1	1	0.05
	Pollutants		Benzene	Benzene, COD, BOD	Benzene
Vacuum systems	Flow (m^3/h)	Avg.	2	NI	NI
		Max.	2	NI	NI
	Pollutants		Ethylbenzene, diethylbenzenes	NI	NI
Catalyst handling ($AlCl_3$) and/or regeneration (zeolite)	$AlCl_3$ catalyst preparation (#1). Condensation during zeolite regeneration (#5)		Yes	NI	Yes
	Flow (m^3/h)	Avg.	0.3	NI	0
		Max.	0.5	NI	2
	Pollutants		$AlCl_3$, HCl	NI	Benzene, ethylbenzene, polyethylbenzenes
Overall effluent (m^3/t of EB)			0.208	0.144 (5-year average) 0.117 (2011)	NI

NB: Plant #1 (*) This stream is delivered to spent catalyst treatment and not to a common WWT.
Source: Data collection

Condensates from steam jet vacuum systems used for process and operation units can become contaminated with hydrocarbons and generate a small but constant stream of waste water in both zeolite- and $AlCl_3$-catalysed processes.

Most ethylbenzene plants gather all waste water streams together and treat them collectively. Therefore, data availability on individual streams are scarce. According to the data collection, the net effluent generated is approximately 0.117 m^3/t of EB in zeolite-catalysed processes and 0.208 m^3/t of EB for $AlCl_3$-catalysed processes (see Table 5.5 above).

The liquid-phase zeolite process has very low or negligible emissions to water, depending on the design details; and the water effluent could be reused as boiler feed water. Therefore, the zeolite processes do not need much downstream treatment of waste water. The operating costs and environmental impact are lower as there is no requirement to wash and neutralise the reactor effluent or treat the exhausted catalyst.

Table 5.6 below provides information on emissions from the total (combined) waste water effluent from ethylbenzene (EB) and styrene monomer production (by ethylbenzene dehydration (EB-D) or co-production with propylene oxide (SMPO)), some before and some after treatment in a common waste water treatment plant.

Table 5.6: Combined effluents from ethylbenzene and styrene monomer production

	Plant #1		Plant #2	Plant #4	Plant #5
	EB	EB+EB-D	EB+SMPO	EB	EB+EB-D
Overall effluent flow (m^3/h)	10.8	147	58.3–59.4	20.7–58.3	130
Ethylbenzene (mg/l)	17 (*)	0.75	516 (**)	NI	NI
Styrene (mg/l)	NI	1.25	NI	NI	NI
Benzene (mg/l)	25 (*)	0.1	175 (**)	24.7–47	NI
Alcohols (mg/l)	NI	NI	7 609 (**)	NI	NI
Peroxides (mg/l)	NI	NI	1 567–1 893 (**)	NI	NI
Heavy metals (mg/l)	8 (Al) (*)	NI	NI	NI	NI
TSS (mg/l)	NI	5	NI	8.3 – 17	NI
COD	NI	NI	NI	193 – 450	
TOC (mg/l)	NI	NI	14332–24 815 (**)	NI	< 10

(*) Data after pretreatment (VOC stripping) before combining with the SM unit's effluents.
(**) Untreated waste waters before treatment in a common WWTP.
NB: NI: No information.
Source: Data collection

5.3.3.2 Emissions to water from the ethylbenzene dehydrogenation process

Emissions to water in ethylbenzene dehydration plants arise from the following principal sources:

- **Organic load separator from the reaction section:** An aqueous stream arises from the decanter downstream of the condensation system of reactor effluents. The pollutants expected here are aromatic compounds, benzene, ethylbenzene, styrene monomer, etc.

- **Organics to water from the fractionation section:** An aqueous stream arises from the vacuum system of the distillation columns that separate the final products from the by-products. If an ejector is used as the vacuum system, the flow will be larger. The pollutants are the same as those in the reaction section.
- **Others:** Auxiliary systems such as cooling water or energy generation systems may generate other aqueous waste streams; these are generally less significant effluents. See the CWW BREF.

Most ethylbenzene dehydration plants collect these aqueous streams together and treat them in a common steam stripper, which will normally be shared with other processes, in most cases with the ethylbenzene manufacturing plant upstream. Data available on individual streams are therefore scarce. According to the data collection, the flow is in the range of 38–175 m^3/h (2–2.3 m^3/ t of styrene monomer). One plant reuses the water after stripping as boiler feed water.

Table 5.7: Effluents from different sources of styrene production by ethylbenzene dehydration

Effluent	Pretreatment techniques and flow specifics		Plant #1	Plant #3	Plant #4	Plant #5
Downstream of the reactor	Decanter/settler		Yes	Yes	Yes	Yes
	Stripper		Yes	Yes	Yes	Yes
	Flow (m^3/h)	Avg.	147	135	35	130
		Max.	165	150	48	175
	Pollutants/ parameters		TOC (benzene, toluene, ethylbenzene, styrene),corrosion inhibitors (amines), COD, pH			
Vacuum system	Ejector		Yes	No	No	Yes
	Flow (m^3/h)	Avg.	7	NA	NA	2.7
		Max.	10	NA	NA	3.5
	Pollutants/ parameters		Benzene, toluene, ethylbenzene, styrene			
Overall	Flow (m^3/h)		199	NI	83.03 – 101.87	NI

NB: NI: No information. NA: Not applicable.
Source: Data collection

5.3.3.3 Emissions to water from styrene co-production with propylene oxide

The principal sources of emissions to water are:

- the acid purge from the oxidation unit;
- the aqueous stream from the epoxidation caustic wash;
- the aqueous stream from the SM production/purification section.

Table 5.8: Emissions and effluents from different process steps (Plant #2) after pretreatment and prior to the common waste water treatment plant

Effluent	Pretreatment techniques	Flow (m^3/h)		Concentrations of pollutants (mg/l)
		Avg.	Max.	
Post-oxidation	Peroxide removal (Section 5.4.2.3.1.4) Wet air oxidation (Section 5.4.2.3.1.3)	6	6.7 9 (*)	pH 1.8 TOC 24 763 COD 70 972 Peroxides 24 000 Alcohols 12 000 Ethylbenzene 300
Post-epoxidation caustic wash	Decanter: phase separation. Wet oxidation	10.7	11.7 14.8 (*)	pH 13.7 TOC 115 429 ACP 399 Prop. ox. 4 108 NaOH 16 973 Alcohols 21 547
Post-dehydration wash	NI	9	9.5 16 (*)	Pollutants: styrene, α-MBA, NaOH, salts, benzaldehyde, heavies
Vacuum systems	NI	NI	NI	Pollutants: ethylbenzene, styrene, α-MBA, ACP, benzaldehyde, glycols, peroxides, organic acids
Styrene monomer purification	Decanter: phase separation	0.22	0.26 1.04 (*)	NI
Overall (total) effluents: 0.8–1.4 m^3/tonne of product (SM+PO)		65 (**)	83.5 (**)	NA

(*) Peak at start-up.
(**) Waste waters from EB and SMPO processes together.
Source: Data collection

Acid purge from the oxidation unit: Organic acids are generated in the oxidation of ethylbenzene. The vapours from the oxidation reaction outlet are contacted directly with the recycle ethylbenzene inlet stream to recover heat. As a result of the contact, the water and the low-boiling organic acid are stripped and then condensed. This stream is the ‘acid purge’.

The typical composition of this aqueous stream is as follows: approximately 70 wt-% water; small amounts (< 1 wt-%) of ethylbenzene; organic acids like: formic acid, acetic acid, and propionic acids (but no benzoic acid or phenols) are present in quantities < 10 wt-%: ethylbenzene hydroperoxide and other peroxides constitute < 10 wt-%; monopropylene glycol < 3 wt-%; dipropylene glycol < 0.2 wt-%. This stream has a low pH (1.7–3) and low flow but a high COD content.

Aqueous stream from the epoxidation caustic wash: This stream will vary depending on the process design and the catalyst system (homogeneous/heterogeneous) selected.

Heterogeneous (silica-based) catalysis
Using a heterogeneous fixed-bed catalyst instead of a homogeneous catalyst generates a waste water stream without metallic compounds, which requires less treatment than the one using homogeneous catalyst. Heterogeneous catalyst with increased oxidation selectivity will also reduce the organic content and decrease the washing intensity required, which will reduce the waste water from this section.

The caustic wash produces an aqueous stream, also called the alkaline purge, with no catalyst present but heavily loaded with organic compounds and sodium. The typical composition of the stream is between 4 % and 8 % alcoholic compounds, mostly monopropylene glycol and methylbenzyl alcohol, between 3 % and 6 % organic salts, largely sodium benzoate and phenolate, and > 2 % sodium hydroxide. The treatment is very complex, mainly due to three aspects: its high organic matter content, which is translated into a high value of chemical oxygen demand (COD), the high flow of said stream and, finally, the fact that it may contain organic compounds that are not easily degradable.[52, Nijhuis et al. 2006], [53, DÜZENLI 2010], [54, Sainz-Pardo 2007].

Homogeneous (molybdenum-based) catalysis
The caustic wash is applied to remove catalyst and organic compounds like monopropylene glycol and phenols; and to neutralise organic acids from reactions upstream. A later phase separation (decanter) results in the phases below:

- Aqueous phase (the 'alkaline purge'): wash water, organic compounds, salts and epoxidation spent catalyst (aqueous effluent is not always monitored for the spent catalyst content). The waste water stream produced has a very large volume and contains metallic catalyst, neutralised acids and phenols. Peroxides in this stream can be removed together with the peroxides in the 'acid purge' from the oxidation unit. Also, organics can be recovered before sending the waste water stream to disposal, e.g. by incineration. The molybdenum catalyst can be recovered from the incineration blowdown, for example via ion exchange.
- Organic phase: propene, α-methylbenzyl alcohol, ACP, ethylbenzene, propylene oxide, monopropylene glycol.

The typical composition of this aqueous stream is: < 10 wt-% alcohols (monopropylene glycol, dipropylene glycol, tripropylene glycol, methylbenzyl alcohol); < 10 wt-% organic salts (sodium benzoate, phenolates); < 2 wt- % NaOH and metallic catalyst; 0–4 wt-% propylene oxide; and 0–2 wt-% acetophenone.

Aqueous stream from SM purification section: The co-product from the epoxidation, α-methylbenzyl alcohol (1-phenylethanol), can be dehydrated to styrene by two processes. The reaction also releases water as a dehydration reaction product.

- A vapour-phase reaction over a catalyst of silica gel or titanium dioxide at 250–320 °C and atmospheric pressure.
- A liquid-phase reaction with an organic acid at 175–210 °C and under vacuum.

The dehydration product is then distilled to recover purified styrene and to separate water and high-boiling organics for downstream distillation and partly for use as a fuel. Water may also be removed prior to distillation, mainly via decantation. Typical pollutants in the resulting waste water stream are: large molecular weight aromatics, acetophenone (ACP), gums, α-methylbenzyl alcohol, styrene, and ethylbenzene.

A caustic wash after the dehydration section may produce waste water with the following typical components: styrene, acetophenone (ACP), α-methylbenzyl alcohol (α-MBA), benzylic alcohol, 2-phenylethanol, phenoxypropanol, phenolic salts, heavy compounds, sodium hydroxide).

Others possible effluents are other caustic washes and condensates from adsorbent regeneration, vacuum systems, etc.

Most SMPO plants will have specific effluent treatments applied to the relevant individual streams mentioned in this chapter. Shared and common waste water treatments may operate downstream of those specific recoveries or treatment techniques. The collective stream at the plant battery limits will depend largely on the plant design (i.e. the catalyst system selected and the potential to internally recycle streams). According to the data collection (Plant #2), the total effluent from styrene co-production with propylene oxide is 0.78–1.38 m^3/tonne of products (SM+PO). It may contain organic compounds such as ethybenzene, styrene and benzene.

5.3.4 Raw material consumption

5.3.4.1 Benzene, ethylene and ethylbenzene

According to the data collected in the questionnaires, the average specific feedstock consumption is reported to be in the range of:

- benzene consumption: 0.735–0.746 tonnes per tonne of EB;
- ethylene consumption: 0.254–0.265 tonnes per tonne of EB.

The raw material consumption will depend on the purity of the feedstock. The major impurities in the ethylbenzene product can include non-aromatics (naphthenes) and toluene. These components can originate from the benzene feed or be generated in the reactor.

The most problematic contaminant is propylene because it forms isopropylbenzene that contaminates the styrene monomer product downstream.

Any other non-reacting inerts present in the feedstock are discharged from the process via the benzene distillation waste gas.

As can be seen from Table 5.9 below, all of the operators that took part in the data collection use high-purity feeds (> 99.5 wt-% or vol-%) which result in a reduced waste gas stream and less waste being generated.

Table 5.9: Raw material consumption in EB and SM production

Information	**Plant #1**	**Plant #2**	**Plant #3**	**Plant #4**	**Plant #5**
Ethybenzene production					
Catalyst	$AlCl_3$	Zeolites	Zeolites	Zeolites	zeolites
Reference year	NI	2007–2011 (avg.)	2012	2007–2011 (avg.)	2011
Specific consumption of benzene (t/t of EB)	NI	0.746	0.735	0.743	0.743
Excess benzene (benzene/ethylene molar ratio)	NI	4.17/1	3.27/1	NI	8/1
Benzene feed purity (wt-%)	99.95	99.85	99.8	99.5	99.8
Ethylene feed purity (vol-%)	99.95	99.93	99.9	99.8	99.9
Styrene production					
Process	EB-D	SMPO	EB-D	EB-D	EB-D
Reference year	2011		2011	2007–2011 (avg.)	NI
Specific consumption of ethylbenzene (t EB/t of SM or SM+PO)	1.066	0.782	1.077	1.042–1.075	NI
Ethylbenzene/steam molar ratio	1.5	NA	1.1–1.3	0.67–0.77	1.02
Inhibitors (kg/t of SM)	0.075	NA	0.01	NI	0.58 (Inhib. + retarder)

NB:
NA: Not applicable.
NI: No information.
Source: Data collection

In styrene production by ethylbenzene dehydration, the principal raw materials used are ethylbenzene and the catalyst. According to the data collection, the ethylbenzene consumption reported is: 1 040–1 100 kg per tonne of styrene monomer.

Table 5.10: Overview of resource efficiency techniques in styrene plants (ethylbenzene dehydration)

	Plant #1	Plant #3	Plant #4	Plant #5
Downstream heat recovery	Yes	Yes	Yes	Yes
Adiabatic (A) or isothermal (I)	Adiabatic	Adiabatic (A) / Isothermal (I)	Adiabatic	Adiabatic
Reactor configuration (bed number)	3	2 in series (A) / 1 (I)	3 in series	2
Catalyst	Iron oxide	Iron oxide	Iron oxide	Iron oxide
Oxidative reheat	No	No	No	Yes
Conversion vs selectivity (%)	68	63	72	62
Steam–feed ratio	1.5	1.1 (A)–1.3 (I)	0.67–0.77	1.02
Vacuum level (mbar)	500	350 (A)–450 (I)	500	300–350
Reaction energy (GJ/t)	14.57	12.5	7.92–8.16	NI
Source: Data collection				

In styrene production by peroxidation (SMPO), the ethylbenzene consumption is typically 1 100–1 200 kg per tonne of styrene monomer.

Solvents usage: Depending on the selection of the catalyst system, there may be three purposes for using solvents in SMPO plants:

- triphenylmethane: to carry dehydration catalyst;
- toluene: to carry epoxidation catalyst in the MTBE (methyl tert-butyl ether) process;
- extraction solvents like n-octane and others: for final extractive distillation to purify propylene oxide.

Some process design options do not use solvents in the dehydration and epoxidation.

5.3.4.2 Catalyst consumption

Zeolite-catalysed processes: Periodic replacement of the catalyst is required every two to three years. Catalyst deactivation is slow and occurs as a result of coke formation and requires periodic regeneration. *In situ* regeneration takes approximately 36 hours and may be necessary after 18–24 months of operation, depending on the operating conditions. *Ex situ* regeneration is also used. According to the data collection, 0.003 kg to 0.012 kg of catalyst per tonne of ethylbenzene is spent in the liquid-phase zeolite-catalysed processes.

The catalyst used in the gas-phase EB process is less sensitive to water, sulphur, and other poisons than the Lewis acid catalysts and zeolite catalysts operating in the liquid phase. The catalyst can also be deactivated by basic compounds. In the liquid-phase process, the catalyst can be poisoned by basic nitrogen compounds, sulphur and water.

$AlCl_3$-catalysed processes: Catalyst losses are compensated continuously. The poisoning of the catalyst (e.g. by alkaline substances) normally has no effect. Entrainment and losses to downstream process steps are relevant. About 10 kg $AlCl_3$ is required per tonne of EB in older $AlCl_3$-catalysed process and 0.25 kg per tonne of EB in the modern process.

The $AlCl_3$ concentration in the reactor effluent is reported to be in the range of 900–1 800 ppm (0.9–1.8 wt-%) and the HCl concentration ~ 1 400 ppm (1.4 wt-%) [141,patent W O9116285 A1 1991].

The transalkylation reactor effluent contains 0.14 wt-% $AlCl_3$ and the same concentration of HCl [154, patent JPH1171305 1999].

Catalyst usage in ethylbenzene dehydrogenation: The performance of the catalyst is the key economic factor of the process. The catalyst deteriorates over time and negatively impacts on the performance of the process (lower energy efficiency and increased by-product formation). The quantity of catalyst used for a given plant capacity is related to the liquid hourly space velocity (LHSV), i.e. the volume of liquid hydrocarbon feed per hour per volume of catalyst. To determine the optimal LHSV for a given design, several factors are considered: ethylene conversion, styrene selectivity, temperature, pressure, pressure drop, SHR, and catalyst life and cost. In most cases, the LHSV is in the range of 0.4–0.5 h^{-1}. This corresponds to a large quantity of catalyst, approximately 120 m^3 or 120–160 tonnes depending on the density of the catalyst, for a plant with a 300 000 t/yr capacity. The catalyst (particle) size is usually kept small and, to avoid pressure drops, catalyst is extruded in ribbed shapes to maximise its performance. No information on the amounts of catalysts used were provided in the data collection.

Catalyst usage in ethylbenzene peroxidation (SMPO): Catalysts are used for the epoxidation reaction and in some cases also the dehydration reaction. No information on the amounts of catalysts used were provided in the data collection. See also Section 5.4.2.3.2.

5.3.5 Energy consumption

The type of energy used in a plant is defined by the local conditions and plant configuration. The number of columns involved and the nature of the separations required means that the energy consumed for the fractionation processes is likely to be significant.

Most of the steam produced in the overhead condensers of ethylbenzene plants can be used in the styrene monomer dehydrogenation process and peroxidation (SMPO) process. Energy from the exothermic alkylation reaction can also be recovered inside its own reaction section, as inter-stage heat exchange between alkylation and/or transalkylation. Reaction heat can also be used to preheat the feed. Excess heat can be used to generate steam with a pressure of 2 bar in the overhead condenser of the benzene recovery column.

The values below show the average range of energy utilities used or recovered per tonne of EB:

- electricity (kWh): 25–32;
- steam (kWh): 100–2 600;
- heat recovery (kWh): 700–2 600;
- total (kWh): 760–2600.

Low-pressure steam production is not considered in the heat recovery of the total energy usage figures above.

In ethylbenzene dehydrogenation plants, the steam superheater (SSH) furnace required for the reaction section is the largest energy consumer. The capacity of the SSH furnaces installed in Europe ranges from 10 MW to 100 MW of rated thermal input depending on the plant capacity. The next largest energy consumers are fractionation operations, with the number of distillation columns involved also depending on the nature of the separations required, meaning that the energy consumed for fractionation processes is likely to be considerable. The main energy consumer of fractionation units is the ethylbenzene/styrene monomer splitter.

The values below show the range of energy utilities per tonne of styrene monomer from ethylbenzene dehydration plants:

- electricity (kWh): 50–170;
- steam (kWh): 1 850–2 900;
- fuel (kWh): 1 100–2 900;
- heat recovery (kWh): 210–840;
- total (kWh): 3 200–4 700.

In SMPO co-production, energy consumption is heavily dependent on the SMPO configuration. The energy mix used depends on availability, costs, supply, integration with other units, etc. Ranges for the consumption and recovery of energy per tonne of styrene monomer co-produced with propylene oxide are:

- electricity (kWh): 160–200;
- steam (kWh): 3 100–3 900;
- energy recovery (kWh): about 300;
- total (kWh): 2 900–3 800.

The use of energy for process compressors is important, as compressors are widely used:

- the oxidation reactors are supplied by compressed ambient air;
- temperature control in oxidation via off-gas recycling can require a compressor;
- propylene recovery downstream of epoxidation can require a compressor;
- the hydrogen fed to the ACP hydrogenation will possibly require a compressor (or come from the header outside of the battery limit) and/or the H_2 recycle stream;
- a considerable amount of energy is consumed by compressors in fractionation operations.

Energy can also be recovered from the process heat of both the ethylbenzene dehydration and peroxidation processes. In ethylbenzene dehydration, heat can be recovered from the overhead condensers of the distillation columns (e.g. the benzene and ethylbenzene columns). In the peroxidation process, the heat can be recovered from the oxidation reaction unit (exothermic reaction).

5.3.6 Co-products, by-products and waste generation

5.3.6.1 Co-products, by-products and waste generation in the production of ethylbenzene

The impurities and diluents in so-called dilute ethylene and benzene feeds can be the source of by-products if they react in side reactions and can be recovered from either feedstock or process streams (off-gases or effluents) to be used as material or as fuel to be combusted in process furnaces, boilers or thermal oxidisers. For example, when diluted ethylene is used as feedstock, ethane, methane, hydrogen and other lighter components can be recovered in the distillation/condensation steps. Likewise, purification of benzene feedstock (before feeding or in the benzene recovery column after the reaction) generates an organic gaseous stream and sometimes also a liquid one of non-aromatic hydrocarbons (different C_5-C_7 cyclo-compounds).

5.3.6.1.1 Spent catalyst waste

Zeolite-based processes: The catalysts used for alkylation/transalkylation (or feedstock guard beds for purification of the benzene and ethylene feed) are in the fixed beds and can usually be (at least partially) regenerated several times during a turnaround before they are completely replaced.

The amount of spent catalyst reported in the data collection was 0.003–0.012 kg per tonne of EB for zeolite catalyst.

$AlCl_3$ processes: Catalyst is prepared from $AlCl_3$ (anhydrous salt) and promoter (normally ethyl chloride, which forms HCl, in the reaction environment) and benzene. The fresh catalyst is a liquid, with partial solubility in the organic reaction phase (feedstock), which can be separated from it by settling.

In the modern $AlCl_3$-catalysed process, which uses only dissolved catalyst, the situation is different: due to the solubility of the catalyst in the reaction effluent, a continuous make-up of fresh catalyst is required. This makes any treatment to remove low-concentration poisoning substances from the reactants unnecessary; with the only exception being water, which can be present in the benzene in too high a concentration, causing an excess of catalyst consumption. The amount of spent catalyst solution reported in questionnaires (data collection) was 54.3 kg per tonne of EB (for modern $AlCl_3$ process – Plant #1). According to the data collection (see Table 5.6 – Plant #1), the average amount of recovered concentrated $AlCl_3$ solution is 10.8 kg/tonne of ethylbenzene.

When the resulting waste stream containing the $AlCl_3$ cannot be sold as a by-product, the aqueous phase from these washes can first be neutralised and then recovered as a saturated aluminium chloride solution (which may be reused) and wet aluminium hydroxide sludge (which may need disposal as a waste).

5.3.6.1.2 Tar

Both processes: The reaction by-products generate a residue stream, or flux oil, consisting primarily of polycyclic aromatics. The largest portion of these, considered as yield loss, leaves the process through the residue stream from the bottom of the polyethylbenzene recovery column. This liquid stream consists of a complex mix of relatively high molecular weight mono- or polycyclic hydrocarbons (compounds with 10 carbon atoms or more).

Additionally, in the older $AlCl_3$-catalysed process at temperatures higher than 130 °C, some non-aromatic and polyaromatic hydrocarbons can form which are basic in nature and preferentially dissolve in the highly acidic catalyst complex. With continued recirculation of the catalyst complex, these heavy aromatics tend to degrade and polymerise to a sludge-like product referred to as 'flux oil' or tars.[140, patent US 3848012 A 1974].

Data collected regarding by-products, residues and waste generated in ethylbenzene production show that tar is formed at an average amount of 12.4 kg per tonne of ethylbenzene in the $AlCl_3$-catalysed process and 3–5.6 kg per tonne of ethylbenzene in the zeolite-catalysed process.

Tar from ethylbenzene production is reported to be used as a flux oil in the styrene distillation in styrene monomer plants (Plants #1, #3, #4 and #5) or blended with heavy cuts/tars from other petrochemical (usually styrene monomer) or refinery units and burnt as fuel (Plants #2, #3, #4 and #5).

5.3.6.2 Co-products, by-products and waste generation in styrene production by ethylbenzene dehydration

According to the data collection, the principal co-products and by-products of this process are:

- hydrogen – up to 50 kg/tonne of SM;
- benzene – up to 20 kg/tonne of SM;
- toluene – 16–94 kg/tonne of SM.

According to the data collection (Plants #1, #3, #4 and #5), the process produces the following waste streams:

- spent catalyst waste – up to 0.45 kg/tonne of SM;
- coke from the reaction;
- tar – up to 12.9 kg/tonne of SM;
- gums, oligomers of polystyrene – up to 1.5 kg/tonne of SM;
- spent solvents 1.5–6 kg/tonne of SM.

Table 5.11 and Table 5.12 show data collected on tar generation, its use and the techniques used to prevent or reduce its generation.

Table 5.11: Tar generation and use in plants using the ethylenzene dehydration process

	Plant #1	Plant #3	Plant #4	Plant #5
Tar (kg/t) *	6.4	7.1	8.9–10.73	10.5–12.9
Ethylbenzene purity (%) **	97.5	99.2	99	99.8
Used as a fuel	No	Yes	Yes	Yes
Tar cracking	No	No	No	No

* Does not include the flux oil from ethylbenzene production used to dilute styrene column bottoms.
** Only fresh feed – does not include the ethylbenzene recycle stream.
Source: Data collection

Table 5.12: Tar avoidance in distillation

	Plant #1	Plant #3	Plant #4	Plant #5
Inhibitor dosing	Yes	Yes	Yes	Yes
Reduced pressure drop in distillation	Yes	Yes	Yes	No
Usage of inhibitor (kg/t of SM)	0.075	0.01	NI	0.58

Source: Data collection

These specific waste data are affected by factors such as feedstock purity, catalyst selectivity and lifetime, reactor and distillation column design and actual production rate (i.e. if the production requirement is low, the ratio of spent catalyst at the end of run to produce styrene will be higher).

Hydrogen: The off-gases from the dehydrogenation reaction contain mainly hydrogen. They may also contain N_2, CO_2, CO, CH_4, C_2H_4, C_2H_6, and traces of high-boiling organics and low-boiling aromatics (such as benzene and toluene).

The most frequent purification treatments are:

- absorption with flux oil (residue of ethylbenzene distillation) and condensation to remove aromatics;
- CO_2 methanation or absorption; CO and CO_2 (residual) methanation and/or pressure swing adsorption (PSA).

The purification treatments depend on the purity required by the final user(s).

The amount of hydrogen produced depends on the dehydrogenation conditions and catalyst. A lower steam to olefin ratio (to save steam) generally increases the hydrogen. The amount increases during the run length as a consequence of catalyst ageing.

Benzene/toluene: Also generated in dehydration is a mixture of benzene and toluene with some non-aromatics with boiling points between those of benzene and toluene. The toluene level is constant over the entire run length depending on the catalyst and dehydrogenation operating conditions, while the benzene increases over the time spent on-stream by the catalyst charge. The mixture is normally delivered to an aromatics unit to recover benzene and toluene at suitable purity levels. In some cases, the splitting of benzene from toluene can take place inside the styrene monomer plant. The benzene is recycled to the ethylbenzene production unit while the toluene is sent to the aromatics unit or refinery.

Spent catalyst waste: Catalyst life can range from 12 to 40 months. It is limited by the loss of potassium over the run length. The lifetime can be prolonged by the application of catalyst stabilisation technology. This is related to the plant run length, which may be linked to the major overhaul of upstream (ethylene plant, aromatics plant) or downstream units.

Coke from the reaction: Coke is mainly removed by the steaming of the catalyst during the normal shutdown procedure. No data on the amount of coke were provided in the questionnaires.

Tar: This is a mixture of polystyrene (PS), high boilers, aromatics (formed in the dehydrogenation), C_9 aromatics (mostly α-methylstyrene) and styrene, plus flux oil (the residue of the ethylbenzene distillation). Tar is isolated (separated from the product) in the fractionation section downstream of the reaction section. If divinylbenzene is present in the feed to the distillation section, PS levels could become high and make the heavy cuts heavily fouling. Tar is produced continuously during the operation. The amount may increase during the run as a consequence of the dehydrogenation catalyst ageing.

Gums and oligomers of polystyrene: This is a mixture of low molecular weight polymers and high boilers formed in the dehydrogenation reaction section. This is a waste material that is formed during the run but is removed from the various pieces of plant equipment during an overhaul or maintenance. Sometimes small amounts of this material are removed during operation when cleaning the filters.

Spent solvents: Solvents are used for scrubbing the reaction off-gases to reduce the hydrocarbon content of the H_2-rich purge. Spent solvents are in the reange of 1.2–6 kg per tonne of styrene monomer.

5.3.6.3 Co-products, by-products and waste generation in styrene co-production with propylene oxide (SMPO)

Ethane and propane that may be present in the propylene feed can be recovered as fuel gas. There are a number of process intermediates that are (normally) neither isolated nor purified: e.g. acetophenone (ACP) and α-methylbenzyl alcohol (α-MBA). According to data collected in the questionnaires (Plant #2), up to 115.4 kg ACP/tonne of styrene monomer and propylene oxide (SM+PO) is sent to a hydrogenation unit for conversion into α-methylbenzyl alcohol and to maximise styrene production.

The principal waste streams are:

- tars and heavy cuts from distillation columns (up to 300 kg/t of SM+PO (Plant #2));
- light end cuts from purification operations;
- spent resins and spent adsorbents;
- spent catalyst (epoxidation up to 0.151 kg/t of SM+PO and hydrogenation up to 0.013 kg/t of SM+PO (Plant #2));
- catalyst residues;
- spent solvents.

Tars and heavy cuts consist of:

- the heavy bottom cut from the α-methylbenzyl alcohol (MBA) distillation prior to dehydration (up to 158.06 kg/t of SM+PO) and from styrene monomer purification (up to 69.15 kg/t of SM+PO (Plant #2));
- heavies from the dehydration reaction (up to 5.3 kg/t of SM+PO (Plant #2));
- heavies from the hydrogenation feed purification (up to 63.57 kg/t of SM+PO (Plant #2));
- bottom residues (as a consequence of styrene monomer polymerisation under acid conditions); first they are recovered upstream of hydrogenation via fractionation;
- bottom cuts from propylene oxide purification.

Light end cuts (light hydrocarbons) from purification operations consist of:

- light hydrocarbons (methane and others) from the epoxidation reaction recovered by distillation;
- light ends (ethane, propane) from the propylene oxide purification.

Spent resins and spent adsorbents are generated due to:

- ion exchange in the purification of propylene oxide to remove methylformate;
- charcoal adsorption from oxidation off-gases resulting in activated carbon waste.

Hydrogen-rich purge: If low-purity hydrogen is used for hydrogenation then a hydrogen/methane purge stream from the hydrogenation reaction section is generated.

Spent catalyst: Deactivated catalyst (in the heterogeneously catalysed processes such as epoxidation and dehydrogenation) has to be replaced.

Catalyst residues: If homogeneous catalyst systems are used (in the epoxidation reaction or dehydrogenation) the catalyst leaves the unit partially in a heavies purge from the dehydration.

Spent solvents: Solvents are used in the reaction off-gas recovery system to reduce the hydrocarbon content of the H_2-rich purge.

5.4 Techniques to consider in the determination of BAT

This section describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this chapter. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations). Cross references to other chapters are used, where relevant to avoid repetition.

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 2.6 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

5.4.1 Techniques to reduce emissions to air

It is often advantageous for operators to integrate plants that produce ethylbenzene with those that produce styrene monomer – either through ethylbenzene dehydration or the SMPO process. For this reason, many ethylbenzene plants have an end-of-pipe abatement system, e.g. thermal oxidisers or energy recovery in a furnace or combustion plant, shared with other on-site units. The same applies to flares, which should only be used as a last resort abatement device, i.e. as a safety device.

The following techniques may apply to either the treatment of individual streams or to shared abatement devices or joint emission streams.

5.4.1.1 Techniques to reduce emissions to air from ethylbenzene production

5.4.1.1.1 Process selection: zeolite catalyst processes

Description
Use of the zeolite catalyst process technology to gradually upgrade the $AlCl_3$ catalyst process or to completely replace it.

Technical description
Zeolite catalysts are used in fixed-bed reactors for promoting alkylation reactions in the liquid or vapour phase. For more information on these processes, see Section 5.2.1.1. The zeolite catalyst process has been introduced as a (partial) replacement of existing $AlCl_3$ catalyst units – either for alkylation or transalkylation.

Achieved environmental benefits

- Reduction or prevention of emissions to air of organic compounds and acid gases.
- Reduction of generation of waste water.
- Reduction of wastes for disposal.

Environmental performance and operational data

Zeolite catalyst technologies have proven to be superior in environmental performance regarding emissions to air (no dust and HCl), reduced effluent to water and waste related to the catalyst (no need for catalyst removal from the products). See Sections 5.3.1, 5.3.2 and 5.3.6.1 for more details.

If the existing $AlCl_3$-catalysed alkylation unit is retrofitted with a zeolite-catalysed transalkylation unit, the fresh benzene feed can be introduced to the process through that transalkylation unit. Such retrofitting can lower the overall $AlCl_3$ consumption by 50–85 %.

Tar formation is also lowered by this process conversion since zeolite-catalysed processes produce less tar then $AlCl_3$-catalysed processes. Also, vapour-phase processes produce less tar than liquid-phase ones.

Cross-media effects

The higher reaction temperatures and the use of more excess benzene can increase the heat/steam demand significantly.

Technical considerations relevant to applicability

Applicable for new EB plants and major EB plant upgrades.

Economics

The high short-term investment costs are compensated by the lower long-term operating costs – as there is no need to remove and treat catalyst with the washing and neutralisation of the reactor effluent. Costs are reduced by the gradual introduction of zeolite-catalysed reactors – e.g. starting with additional transalkylation or partial alkylation.

Driving force for implementation

Lower environmental impact and operating costs.

Example plants

Out of five plants that took part in the data collection, four use zeolite-catalysed liquid-phase technology.

Plants retrofitting recently have moved increasingly in favour of zeolite-catalysed liquid-phase technologies due to products with fewer impurities. Data from 2002 show that 24 % of worldwide production was based on $AlCl_3$ technology and the rest was based on zeolite catalyst technologies (40 % vapour-phase and 36 % liquid-phase) [139, Perego et al. 2002].

Reference literature

[51, Welch et al. 2012], [155, patent US 005600048 A 1997], [154, patent JPH1171305 1999], [146, patent WO 2007081923 A2 2007].

5.4.1.1.2 Caustic scrubbing

Description

Acid (HCl) emissions from the alkylation reactor using $AlCl_3$ catalyst are pretreated by caustic scrubbing before final waste gas treatment.

Technical description

In the alkylation reactor, the feed (aromatic and olefin) and catalyst promoter are well mixed and stirred, at temperatures in the range of 160–180 °C. Off-gases from reactor reactions consist mainly of lighter hydrocarbons, but also contain some HCl and other acidic volatile by-products. Acid gases stem from catalyst and promotor reactions with reactants (for more information, see Section 5.2.2.1.2).

Acidic pollutants are removed from the off-gas by scrubbing using an alkali solution (e.g. NaOH solution), to protect downstream devices and reduce emissions to air.

For a more detailed description of caustic scrubbing, see the CWW BREF.

After scrubbing, the off-gas is routed to a final waste gas treatment for VOC abatement. Depending on the calorific value, it may be routed to a fuel gas system instead.

Achieved environmental benefits

Reduction of emissions to air of HCl and other acid gases.

Environmental performance and operational data

See Section 5.3.1.1.1.

Cross-media effects

The generation of a salty scrubbing liquor.

Technical considerations relevant to applicability

Generally applicable.

Economics

No information provided.

Driving force for implementation

Possible utilisation of scrubbed off-gases as a fuel.

Example plants

Plant #1 uses NaOH scrubbing of off-gases prior to combustion.

Reference literature

[51, Welch et al. 2012]

5.4.1.1.3 Wet scrubbing

Description

Dust and HCl are removed from off-gases from the $AlCl_3$ catalyst replacement operations prior to final waste gas treatment.

Technical description

During catalyst replacement operations in $AlCl_3$-catalysed processes, dust and HCl emissions arise from the dissolution of solid $AlCl_3$. They can be abated by scrubbing using water as the scrubbing medium. The scrubbing liquor can be reused in the wash section, either as the washing medium or for balancing the pH before or after the washing liquor neutralisation. For more information on dust and HCl emissions abatement using scrubbers, see the CWW BREF.

Achieved environmental benefits

Reduced emissions to air of dust, $AlCl_3$ and HCl.

Environmental performance and operational data

See Section 5.3.1.1.2.

Cross-media effects
Acid (HCl) aqueous effluent which can be reused in the post-alkylation wash section or for adjusting the pH of aqueous effluents from that section. See Section 5.4.5.1.2

Technical considerations relevant to applicability
Generally applicable for plants that still use the $AlCl_3$ catalyst process.

Economics
No information provided.

Driving force for implementation
Environmental legislation.

Example plants
Plant #1 uses water scrubbing.

Reference literature
See the CWW BREF.

5.4.1.1.4 Recovery of lighter hydrocarbons

Description
Non-ethylene and non-benzene hydrocarbons can be recovered from the feed or reaction off-gases.

Technical description
Techniques used for the recovery of hydrocarbons from feed pretreatment or treatment of off-gases are distillation followed by condensation, scrubbing or use as a fuel in combustion units. For descriptions of these techniques see the CWW BREF and for more information on recovery from ethylbenzene production see Section 5.4.5.1.1 of this document.

Achieved environmental benefits

- Reduced VOC emissions to air.
- Raw materials for other LVOC processes.

Environmental performance and operational data
Information on the content of this stream and potential emissions to air can be found in Sections 5.3.1.1.2, 5.3.1.3.1, 5.3.1.3.2 and 5.3.1.3.3.

Cross-media effects
Operating with diluted feedstock may lead to more waste gas, waste water and waste being generated.

Technical considerations relevant to applicability
Generally applicable.

Economics
Recovery of raw materials or heat (fuel) from these streams may have a significant influence on the overall operational cost – diluted feedstock is much cheaper than high-purity ethylene and benzene, which lowers the overall production costs significantly.

Driving force for implementation

- Reduced emissions of VOCs to air.

- Recovery of materials useful for other processes or as a fuel (heat recovery).

Example plants
Used in many plants.

Reference literature
[51, Welch et al. 2012], [62, Nexant 2009], [57, Netzer 1999], [156, patent US 6677496 B2 2004].

5.4.1.1.5 End-of-pipe abatement techniques

Description
After treatment for recovery of hydrocarbon compounds, off-gases from the fractionation section can be routed to the collective end-of-pipe abatement device.

Technical description
Techniques that can be applied to off-gases from these units are usually thermal or catalytic oxidation**.** For more information on these techniques, see Sections 2.4.3 and 2.4.6 of this document or the appropriate chapters of the CWW BREF.

5.4.1.2 Techniques to reduce emissions to air from ethylbenzene dehydrogenation

The gas stream generated after condensing the reactor effluent is treated to recover hydrogen and other hydrocarbons. These gas treatment systems will vary across plants, depending on their detailed engineering designs, but all of them will have a net off-gas that cannot be recovered (either a purge of the hydrogen recycle stream or another stream).

5.4.1.2.1 Process optimisation

Description
This is a group of process-related measures (design and operational) that will reduce the amount of light components generated in the reaction, and thus lessen the load to the off-gas recovery and abatement systems.

Technical description
Reducing the by-products generated in the reaction will reduce the gas treatment workload and thus improve the net result. These measures will not only affect the composition of this off-gas stream but also energy usage.

The measures to be taken into account for the design are as follows:

- Operating the reaction at the lowest possible pressure that still gives high selectivity and thus a lower steam consumption for a given yield target.
- Optimising the EB to steam ratio fed to the reaction: a higher steam to hydrocarbon ratio results in higher conversion, and also higher selectivity.
- Catalyst selection: different catalyst-promoter systems have been developed on an iron oxide basis and prolonged catalyst lifetimes of 1 to 2 years are achievable.
- Catalyst stabilisation techniques: continuously adding small amounts of alkali metal compounds to a reactant stream without interrupting the dehydration reaction. The advantage over self-cleaning (decoking) with steaming is that this technique also chemically removes deposited species and extends the catalyst lifetime considerably.

- Lower conversion leads to higher selectivity.
- Oxidative reheat: optimisation of the oxygen fed to the reaction. For more information, see Section 5.4.3.2.2.
- Reactor design: radial, diameter, number of reactors, adiabatic vs. isothermal.

Achieved environmental benefits
Reduced emissions of VOCs to air (from the reactor or end-of-pipe device) are achieved.

Environmental performance and operational data
No information provided.

Cross-media effects
This may lead to increased energy consumption. However, these measures will also have a beneficial effect on raw material consumption, waste generation and emissions to air.

Technical considerations relevant to applicability
Generally applicable.

Economics
Lower raw material costs.

Driving force for implementation
Lower feedstock costs.

Example plants
Generally used in plants.

Reference literature
[60, Chen et al. 2006], [61, Woodle 2006], [62, Nexant 2009], [63, James et al. 2012], [64, patent US 5461179 A 1995], [153, patent WO 2008148707 A 2008].

5.4.1.2.2 Recovery techniques

Description
The ethylbenzene dehydration off-gas stream is a valuable source of organic compounds and hydrogen which can be recovered.

Technical description
The following techniques can be used for organic compounds recovery:

- Condenser and post-condenser:
- A larger condensing duty will reduce VOCs. See the CWW BREF for more information on condensers.
- Absorption (scrubbing):
- By scrubbing off-gases with either commercial solvents or by reusing by-products from other LVOC processes (like bottom streams of ethylbenzene distillation units called flux oil) – see Section 5.4.5.2.2 – hydrocarbons can be absorbed. Hydrocarbons can then be stripped from the scrubbing medium and recycled to the process.

For more information on both techniques, see the CWW BREF.

The following techniques can be used with respect to hydrogen:

- recovery and purification of H_2 for chemical usage;

- use as a fuel.

The remaining off-gas is sent to an end-of-pipe abatement device, which may be shared with other parts of the process.

Achieved environmental benefits

- Reduction of emissions of organic compounds to air.
- Reduction of consumption of material (organics, hydrogen).
- Recovery of energy (hydrogen).

Environmental performance and operational data
For data reported on the amounts of recovered organic compounds and hydrogen, see Section 5.3.6.2.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Generally applicable.

Ethylbenzene flux oil can be used as a scrubbing medium if an ethylbenzene plant is on site (see Section 5.4.5.2.2.

Economics
Lower raw material and fuel costs.

Driving force for implementation
Economics (savings in raw material and fuel consumption).

Example plants
Used by all plants in the data collection. See

Table 5.4.

References
[63, James et al. 2012].

5.4.1.2.3 Combustion of process off-gases in steam superheater

Description
Combustion of process off-gases from ethylbenzene and styrene monomer production (with ethylbenzene dehydration) in a steam superheater for heat recovery.

Technical description
A steam superheater's principal objective is the production of energy, e.g. as steam, heat, electricity or combined heat and power, for the ethylbenzene dehydration reactor. Full descriptions of all the emission control techniques that can be applied for emission reduction and control can be found in the LCP BREF.

Achieved environmental benefits
Reduction of fuel used and efficient energy balance.

Environmental performance and operational data
See Section 5.3.1.2.1 for emissions data as reported by the operators that participated in the data collection.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
This technique is applicable for styrene production with ethylbenzene dehydration; when the ethylbenzene production plant is on the same site, its off-gases can be used as a fuel as well.

Economics
Lower fuel (energy) costs.

Driving force for implementation
Economics.

Example plants
According to the data collection, except for Plant #2, all the EB plants (#1 to #5) are integrated with a SM (EB-D) plant and use a steam superheater as a combustion unit for heat recovery using off-gas streams from reaction as fuel.

Reference literature
[63, James et al. 2012], [60, Chen et al. 2006].

5.4.1.3 Techniques to reduce emissions to air from styrene co-production with propylene oxide (SMPO)

5.4.1.3.1 Techniques to reduce emissions to air from the oxidation unit

In order to reduce the organic load sent to the final waste gas treatment from the oxidation unit in the SMPO production process, the following techniques are used.

5.4.1.3.1.1 Techniques to reduce liquids entrainment

Description
Use of generic techniques to reduce liquids entrainment. For more information, see Section 2.4.3.1.

Technical description
These are techniques that reduce the carry-over of droplets or particles in gaseous streams (e.g. from chemical processes, condensers, distillation columns) by mechanical devices such as settling chambers, mist filters, cyclones and knock-out drums.

Achieved environmental benefits

- Reduction of emissions of VOCs to air.
- Reduction of consumption of raw materials.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Generally applicable.

Economics
Lower raw material costs due to lower ethylbenzene losses.

Driving force for implementation
Lower feedstock and abatement costs.

Example plants
Plant #2 uses a knock-out drum before the off-gas is fed to the catalytic oxidiser after the oxidation unit, demisters installed in piping equipment and a chilled condenser downstream of the epoxidation unit.

Reference literature
[43, Trent 2001], [44, Kahlich et al. 2011].

5.4.1.3.1.2 Scrubbing

Description
The off-gases from the oxidation unit are scrubbed with a suitable solvent (e.g. the cool recirculated ethylbenzene) to absorb ethylbenzene, which is recycled to the reactor.

Vapour off-gases from the oxidation unit are contacted with the cool ethylbenzene recycle stream to absorb the ethylbenzene contained in the vapours and to recover the heat supplied to the recycled ethylbenzene stream. Then cleaner off-gases are exhausted and a water acid purge is generated from this absorption.

Technical description
Scrubbing of the off-gas with recirculated ethylbenzene:

- removes and recovers organic compounds from the off-gas;
- provides rapid and efficient heat exchange between the vapours and the recycle liquid to recover heat and cool the vapours;
- strips water and low-boiling organic acids from the recirculated ethylbenzene to the off-gas, which enables the reuse of the thus purified ethylbenzene as feed for the reactor.

Achieved environmental benefits
- Reduction of the net organic load to the final waste gas treatment.
- Reduction of the consumption of energy.

Environmental performance and operational data
No information provided.

Cross-media effects
Increase of the load of low-boiling organic compounds in the off-gas, from stripping of the solvent.

Technical considerations relevant to applicability
For existing plants, the use of the recirculated ethylbenzene stream may be restricted by the plant design.

Economics
Lower operating costs.

Driving force for implementation
Lower operating costs (energy and raw material usage and off-gas pretreatment).

Example plants
No information provided.

Reference literature
[46, patent US 4066706 A 1978], [63, James et al. 2012], [43, Trent 2001].

5.4.1.3.1.3 Recovery techniques

The following generic techniques can also be applied to reduce the organic load from off-gases from the oxidation unit:

- Condensation
- A larger condensing duty will reduce VOC losses at the off-gas outlet. See the CWW BREF on condensers.
- Adsorption
- Charcoal may be the most common adsorbent. See the CWW BREF on adsorption.

5.4.1.3.2 Balanced generation and recovery of organic compounds from the epoxidation unit off-gases

Description
Balancing the generation of organic compounds and their recovery downstream of the epoxidation reaction with a combination of design and operational measures that will lead to less light hydrocarbons being generated in the reaction and/or their recovery in the off-gas recovery system.

Technical description
Operational measures include balancing the excess propylene feed reduction and its purity: the higher the purity of propylene available, the lower the reaction effluent stream will be.

Design measures include the following:

- a recycle stream to the propane splitter is normally included in all designs;
- epoxidation catalyst system selection;
- ethane, propane and other light ends can be recovered in (de-ethaniser and depropaniser post-epoxidation recycle purge streams) and used as fuel.

Achieved environmental benefits
Reduced emissions of VOCs to air.

Environmental performance and operational data
Lower raw material consumption and recovered compounds are used as a fuel or raw materials for other LVOC processes.

Cross-media effects
This may lead to increased energy consumption.

Technical considerations relevant to applicability
Applicable for new installations and major plant upgrades of existing installations.

Economics
Lower raw material costs.

Driving force for implementation
Economics.

Example plants
No information provided.

Reference literature
[44, Kahlich et al. 2011]

5.4.1.3.3 Techniques to reduce emissions to air from the fractionation unit

Horizontal techniques that can be applied to off-gases from these units are:

- thermal or catalytic oxidation;
- use as a fuel in a combustion unit.

For more information on thermal and catalytic oxidation and energy recovery by combustion, see Sections 2.4.3 and 2.4.6 of this document or the appropriate chapters of the CWW BREF.

5.4.1.3.4 Techniques to reduce emissions to air from the hydrogenation unit

Description
Process optimisation by balancing process design and operational measures in order to generate less (gaseous) by-products in the hydrogenation unit and thus lower the load of the recovery and abatement units.

Technical description
Reduction of the amount of by-product in the hydrogenation unit off-gases is achieved by the following measures:

- Selection of a suitable catalyst for the hydrogenation reaction to improve yield and reduce excess hydrogen.
- Reduction of excess hydrogen to the lowest possible level that does not significantly affect the yield. See Section 5.4.5.3.1.
- Condensation of light organic compounds in condensers of off-gas recovery units.

Achieved environmental benefits
Reduction of emissions of VOCs to air.

Environmental performance and operational data
No information provided.

Cross-media effects
Condensation will require additional cooling water consumption.

Technical considerations relevant to applicability
Generally applicable.

Economics
Lower operational and raw material costs.

Driving force for implementation
Economics.

Example plants
No information provided.

Reference literature
[44, Kahlich et al. 2011]

5.4.1.3.4.1 Recycling or recovery of excess hydrogen from acetophenone hydrogenation

Description
Excess hydrogen from hydrogenation reaction off-gases can be recirculated back to the reaction or recovered for use as a chemical agent in other reactions or as a fuel.

Technical description
Hydrogen-rich off-gas streams can be either recirculated back to the hydrogenation reactor or reconcentrated by pressure swing absorption, or used as a fuel in combustion units. For more information, see Section 5.4.5.3.1.

Achieved environmental benefits
Reduced consumption of hydrogen.

Environmental performance and operational data
No information provided.

Cross-media effects
This may lead to increased energy consumption.

Technical considerations relevant to applicability
Generally applicable.

Economics

- Lower raw material costs due to lower hydrogen usage.
- Lower feedstock costs.

Driving force for implementation
Economics.

Example plants
No information provided.

Reference literature
[44, Kahlich et al. 2011]

5.4.1.3.4.2 Reduction of emissions to air from acetophenone hydrogenation during start-up

Description
Process off-gas from the acetophenone hydrogenation unit, during other than normal operating conditions (such as start-up events), is sent to a suitable treatment system to reduce VOC emissions.

Technical description
The off-gas from the hydrogenation unit will contain hydrogen and organic compounds. Emissions of VOCs are reduced by channelling the reactor off-gases during start-up periods to a

suitable waste gas abatement device rather than to atmosphere or flare. The off-gas stream can be sent to a thermal oxidiser with heat recovery or used as a fuel in a suitable combustion unit.

Achieved environmental benefits

- Reduction of VOC emissions to air.
- Recovery of energy.

Environmental performance and operational data

Complete oxidation of the organic compounds needs to be ensured with sufficiently high temperatures and residence times.

Cross-media effects

Emissions of combustion (CO, CO_2, NO_X).

Technical considerations relevant to applicability

Generally applicable.

Economics

Opportunities for minor fuel savings.

Driving force for implementation

Lower environmental impact.

Example plants

No information provided.

Reference literature

No reference literature provided.

5.4.1.4 Emissions from storage

Most plants include storage of benzene, ethylbenzene, styrene and residues. This is typically in atmospheric storage tanks. Some plants may also have dry benzene storage, ethylbenzene storage, alkylation reactor product storage, and polyethylbenzene storage.

The common techniques applied to reduce emissions are:

- vents are fitted with a condensing unit;
- vents are routed to a combustion plant or thermal oxidiser;
- floating roof.

Further information is available in the CWW BREF and the EFS BREF.

5.4.2 Techniques to reduce emissions to water

5.4.2.1 Techniques to reduce emissions to water from ethylbenzene production

5.4.2.1.1.1 Optimised phase separation

Description

Liquid-liquid phase separation is optimised to separate the organic phase from the catalyst complex or aqueous phase (from washing operations) and reduce emissions of organic compounds to the aqueous effluent from ethylbenzene production.

Technical description

Separation of organic and aqueous phases with appropriate design and operation (e.g. sufficient residence time, phase boundary detection and control) to prevent any entrainment of undissolved organic material to the aqueous phase.

In $AlCl_3$-catalysed and zeolite-catalysed processes, the main waste water effluents with organic load comes from the decanters of the benzene feed drying column and the benzene recovery column. Optimised phase separation in those decanters and settlers will reduce the amount of waste waters and their organic load sent to final waste water treatment units.

For more information on decanters, condensers and phase separation, see the CWW BREF.

Achieved environmental benefits

- Lower organic load sent to downstream waste water treatment.
- Less stripping of organic compounds from waste waters needed downstream.

Environmental performance and operational data

For more information on this waste water stream, see Section 5.4.3.3.1.

Cross-media effects

No information provided.

Technical considerations relevant to applicability

Generally applicable.

Economics

No information provided.

Driving force for implementation

- Environmental legislation.
- Lowering the waste water treatment plant load.

Example plants

According to the data collection, all plants strive to operate separation units at optimum performance to minimise the costs and avoid additional operations in the process.

Reference literature

No reference literature provided.

5.4.2.2 Techniques to reduce emissions to water from ethylbenzene dehydrogenation

5.4.2.2.1.1 Optimised phase separation

Description

Liquid-liquid phase separation is optimised to maximise the recovery of organic compounds and to reduce emissions of organic compounds to the aqueous effluent from ethylbenzene dehydrogenation.

Technical description

Separation of organic and aqueous phases with appropriate design and operation (e.g. sufficient residence time, phase boundary detection and control) to prevent any entrainment of undissolved organic material to the aqueous phase.

All plant designs will include a decanter or another phase separation device (such as a settling drum) for downstream reaction sections, like washing and fractionation units. In these separation devices, the organic phase will be separated and recirculated or sent to the further fractionation section, and the generated aqueous effluent may be further treated before being sent to the waste water treatment plant or reused. For more information on separation techniques (decanters and others), see the CWW BREF.

Achieved environmental benefits

Lower organic load to the waste water treatment plant downstream.

Environmental performance and operational data

The technique can be used in combination with organic compounds recovery by steam stripping and adsorption. See Section 5.4.5.2.2.

Cross-media effects

No information provided.

Technical considerations relevant to applicability

Generally applicable.

Economics

No information provided.

Driving force for implementation

- Environmental legislation.
- Lowering the waste water treatment plant load.

Example plants

No information provided.

Reference literature

No reference literature provided.

5.4.2.3 Techniques to reduce emissions to water from styrene co-production with propylene oxide (SMPO)

5.4.2.3.1 Techniques to reduce emissions to water from the oxidation unit

5.4.2.3.1.1 Reduction of emissions of organic peroxides by hydrolysis

Description
Pretreatment of waste water from the oxidation unit containing organic peroxides (acid purge) by hydrolysis before it is combined with other waste water streams and discharged to the final biological treatment.

Technical description
Hydrolysis is a chemical reaction in which organic or inorganic compounds react with water, typically in order to convert non-biodegradable to biodegradable or toxic to non-toxic compounds. To enable or enhance the reaction, hydrolysis is carried out at an elevated temperature and maybe pressure (thermolysis) or with the addition of strong alkalis or acids or using a catalyst.

To be able to mix the acid purge from the oxidation unit of styrene monomer co-production with propylene oxide (see Section 5.3.3.3) with other aqueous effluents (which are mainly alkaline), it is necessary to remove the peroxide prior to final biotreatment. For catalytic treatment, the acid waste water is contacted with a solid catalyst under appropriate conditions to decompose the peroxides contained therein. The oxygen formed by the decomposition is swept with nitrogen (e.g. with a nitrogen off-gas stream from the oxidation unit) to avoid the formation of flammable or explosive gas mixtures. Decomposition temperatures of e.g. 30–100 °C are used and residence times in the decomposition zone of 5 to 60 minutes are preferred.

As organic peroxides are decomposed to more readily (bio)degradable compounds, an aqueous purge stream can be further treated by downstream waste water treatment plants.

Achieved environmental benefits
Reduction or elimination of organic peroxides in the effluent from this section before it is combined with other streams and protection against malfunction of the biological waste treatment downstream, which can be caused by high concentrations of organic peroxides.

Environmental performance and operational data
No data were provided on concentrations of peroxides in the effluent.

Cross-media effects
Consumption of energy (heat) and potentially some VOC emissions to air.

Technical considerations relevant to applicability
Generally applicable if organic peroxides are present in the aqueous stream.

Economics
Operational costs are estimated to be low.

Driving force for implementation

- Environmental legislation.
- Protection of downstream biological waste water treatment plant.

Example plants
No information provided.

Reference literature
[45, patent US 20040031763 A1 2004]

5.4.2.3.1.2 Reduction of emissions of organic peroxides by process-integrated measures

This stream is normally called the acid purge (see Section 5.3.3.3). SMPO plants incorporate some or all of the following process-integrated measures into their design and operation:

- minimisation of the formation of acid compounds (improve oxidation selectivity by recycling of inert gas to control the reaction temperature);
- minimisation of the formation of acids by limiting ethylbenzene conversion and thus ethylbenzene hydroperoxide decomposition;
- process design to separate the ethylbenzene from the aqueous stream (e.g. by efficient chimney tray or decanter).

5.4.2.3.1.3 Combined wet oxidation and activated carbon treatment of effluents

Description
Use of an effective combination of waste water treatments: the acid purge is pretreated with wet oxidation followed by activated carbon treatment.

Technical description
Wet oxidation with compressed oxygen gas at elevated temperatures and pressure is used to pretreat the combined effluent of the acid purge stream and other waste water streams, which is high in COD. Even though the COD is reduced significantly, the wet oxidation effluent is not of a sufficient quality to be discharged, so it must be treated using the activated carbon system. Any off-gases from wet oxidation can be used as a fuel in a combustion unit.

Achieved environmental benefits
Reduction of emissions to water.

Environmental performance and operational data
The main advantage to wet oxidation, which is a liquid-phase oxidation, is its heat self-sufficiency: the heat of reaction is sufficient to maintain the reaction conditions without any heat addition.

Cross-media effects

- Waste generated in active carbon treatment (sludge).
- Emissions to air (off-gases).

Technical considerations relevant to applicability
Generally applicable.

Economics
No information provided.

Driving force for implementation

- Environmental legislation.
- Lower waste water treatment costs.

Example plants
No information provided.

Reference literature
[47, Gallego et al. 2002].

5.4.2.3.1.4 Use of the peroxide-containing acid purge for chemical oxidation to treat other waste water streams

Description
Use of peroxide effluent and its oxidative power instead of hydrogen peroxide in advanced chemical oxidation process.

Technical description
The advanced chemical oxidation process (AOP) uses hydrogen peroxide to generate highly oxidative hydroxyl radicals (Fenton's reaction using iron salts as catalysts). Instead, hydroxide radicals can be formed by the use of peroxides in the acid purge from the ethylbenzene oxidation unit . This enables the cost-effective consumption of oxidation reagent: lowering the COD load of the combined waste waters and removal of peroxides from the acid purge effluent at the same time. For more information on the advanced chemical oxidation process, see the CWW BREF.

Achieved environmental benefits
Reduction of the COD of treated waste waters.

Environmental performance and operational data
No information provided.

Cross-media effects
VOC emissions are generated.

Technical considerations relevant to applicability
Generally applicable.

Economics
Lower operational costs of waste water treatment.

Driving force for implementation
Economics.

Example plants
No information provided.

Reference literature
[49, Foret-Deisa 2006].

5.4.2.3.2 Techniques to reduce emissions to water from epoxidation

5.4.2.3.2.1 Catalyst removal prior to the post-epoxidation caustic wash

Description
Application of a two-step treatment in the post-epoxidation wash section to recover metallic catalyst from the epoxidation effluent.

Technical description
Using a two-stage treatment, most of the metallic catalyst can be selectively removed in a first stage, and acidic reaction products neutralised in a second stage. This procedure is selective in that one can obtain a relatively small volume of solution containing essentially all of the catalyst, which can be treated for recovery or disposal of the catalyst.

Removal of catalyst: The quantity of aqueous alkali solution added in this step is insufficient to neutralise a substantial quantity of the acidic substances present in the epoxidation effluent charged to this first treatment step. The aqueous phase containing catalyst is separated from the organic phase.

Neutralisation of acidic reaction products: The organic phase is again contacted with the aqueous alkali solution. The aqueous salt phase is separated from the remaining organic phase which is free of acidic compounds and can be further treated or used.

Achieved environmental benefits
Lower metallic emissions to the WWTP.

Environmental performance and operational data

- Lower metallic compounds load for the WWTP downstream.
- Lower catalyst consumption.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Applicable to new plants or major upgrades of existing plants using homogeneous catalyst for the epoxidation reaction.

Economics
Lower operational costs.

Driving force for implementation
Economics.

Example plants
No information provided.

Reference literature
[48, patent US 3988353 A 1976].

5.4.2.3.3 Techniques to reduce emissions to water from other washing operations

These techniques can be employed to reduce the quantity of organic compounds discharged to water without (or with minor) metal content. They apply to caustic and water wash post-epoxidation with heterogeneous catalysts that are similar to those applied in other SMPO washes (downstream of the dehydration process, in the SM purification area) as no metallic compounds are present.

Phase separation

- Phase separation equipment selection and design: stabilising walls' size, position and overall volume, proper design to minimise turbulence inside decanters, etc.
- Phase separation control: phase level indicator and control techniques selected, etc. See the CWW BREF on decanters and phase separation.

Chemical treatments

- Dissolved organics in the aqueous phase are further recovered by treatment with sulphuric acid and phase separation. See the CWW BREF on chemical recovery.

Distillation for reuse

- Distillation post-washing can enable the reuse of the aqueous phase for washing purposes. See the CWW BREF on stripping and distillation.

Liquid-liquid extraction

- Distillation post-washing can enable the reuse of the aqueous phase for washing purposes. See the CWW BREF.

5.4.2.3.4 Techniques to reduce emissions of solvents to water

Different techniques or measures can be applied in order to reduce the amount of solvent emissions:

- Dehydration process selection.
- Epoxidation process selection. The homogeneous catalyst route does not require solvents.
- Purification technique selection. Some plants use solvent extraction to purify and isolate products.
- Solvent selection: One operator uses octane for PO purification. Losses are very small as PO product has very pure product specifications > 99.99 %.
- Dedicated and closed drainage system for collection of waste water.

5.4.3 Techniques to reduce raw material consumption

5.4.3.1 Techniques to reduce raw material consumption in ethylbenzene production

5.4.3.1.1 Process optimisation: benzene feed purity and consumption

Description
A group of process design, operational and process integration and optimisation measures related to benzene feed purity and consumption.

Technical description
This technique involves finding balanced operating conditions regarding excess benzene feed, reaction yield, tar (by-products) generation and energy consumption (for excess benzene recovery).

<u>Lower excess benzene feed:</u> There is a wide variation in excess benzene from plant to plant. These details are held confidentially by the licensors. A high benzene to ethylene ratio in the feed mixture gives a low polyethylbenzene to ethylbenzene ratio in the reaction product, but requires larger equipment and increased energy consumption to recover the additional unreacted benzene by distillation for recycling to the reactor. Commercial plants typically operate at benzene to ethylene molar ratios of around 1.5:1 for $AlCl_3$-catalysed processes and 4:1 to 6:1 for zeolite-catalysed processes. To lower the excess benzene needed for reaction, multipoint ethylene injection is used, catalyst activity and selectivity monitored, and the functioning of the benzene recovery column optimised. For ethylene multipoint injection, see Section 5.4.6.2.4.

<u>Increase benzene feed purity:</u> This involves the use of benzene feed of a purity higher than 99 % (sulphur impurities below 0.1 %). Feed pretreatment (guard beds and drying column) is used in the pre-reaction section to remove impurities. The benzene feedstock contains C_6 non-aromatics, ranging from 50 ppm to 2 000 ppm, depending on the source of supply. The C_6 non-aromatics do not directly contaminate the product because their boiling points are typically 40–

60 °C lower than that of ethylbenzene. However, some of these non-aromatics are alkylated by ethylene in certain processes to form higher non-aromatics, which may contaminate the product. The non-aromatics may also be cracked in the reactors, and the resulting components react with benzene to form various alkylbenzenes, such as cumene, which may also contaminate the product. The only aromatic impurity in a significant concentration in the typical benzene feedstock is toluene, ranging from 50 ppm to 1 000 ppm. It reacts with ethylene to form ethyltoluene in the alkylator; ethyltoluene is converted back to toluene in the transalkylator. Toluene is distilled together with ethylbenzene and becomes a product impurity that is innocuous downstream in the dehydrogenation process. However, any ethyltoluene that is not separated from the ethylbenzene contaminates the styrene product as ethyltoluene and vinyltoluene.

Achieved environmental benefits

- Reduced raw material consumption.
- Reduced energy consumption.
- Reduced emissions to air.
- Reduced waste generation (tar formation).

Environmental performance and operational data

These measures will lead to improved plant performance: lower feedstock usage, better yield, energy and material balance of the site, lower environmental impact at the same or better performance/yield.

Cross-media effects

Increased energy usage at a higher benzene recycling rate.

Technical considerations relevant to applicability

Generally applicable.

Economics

Reduced raw material consumption and energy usage at a high yield.

Driving force for implementation

Lower operational cost.

Example plants

See data on feed purity in Section 5.3.4.1.

Reference literature

[51, Welch et al. 2012].

5.4.3.2 Techniques to reduce raw material consumption in ethylbenzene dehydrogenation

5.4.3.2.1 Process optimisation

The process design measures related to catalysts (selection, management and stabilisation) and the adiabatic dehydrogenation reactor described in Section 5.4.1.2.1 will also enable efficient use of raw materials (increase of yield).

5.4.3.2.2 Oxidative reheat approach

Description
In the oxidative reheat technique or oxidative hydrogen removal, oxygen is fed to the reaction. Heat for reaction is generated by the controlled combustion of H_2. Removing H_2 from the reaction mixture shifts the equilibrium towards EB conversion.

Technical description
This technique involves adding oxygen that reacts with H_2, generating heat and thereby encouraging conversion reactions of raw materials. Many efforts have been made to remove hydrogen from the process to favour the forward reaction. A new process employs a noble metal catalyst that selectively oxidises hydrogen, allowing the ethylbenzene conversion to be increased to over 80 % while maintaining good styrene selectivity. It is mainly offered as a retrofit to existing units as a way of gaining extra capacity.

Achieved environmental benefits

- High selectivity and thus high feedstock yields.
- Lower energy consumption.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Applicable to revamp projects where capacity increase at a nominal capital cost is desired.

Economics
It is claimed to have higher variable costs, but a lower capital cost than a conventional plant.

Driving force for implementation
Lower operating costs.

Example plants
Plant #5 reported using it.

Reference literature
[63, James et al. 2012].

5.4.3.3 Techniques to reduce raw material consumption in styrene co-production with propylene oxide

5.4.3.3.1 Process optimisation: reaction selectivity and reactant recovery

Description
Influencing the conversion yield and selectivity of products and by-products by optimising the control over reaction conditions (temperature, pressure, feedstock purity and ratios) and recovery and recycling of unreacted feed or by-products.

Technical description
The following techniques can be applied in various process sections:

a) Oxidation reaction selectivity:
Operators of the SMPO process can apply different techniques in order to increase the selectivity of the process:

- Carry out oxidation at progressively decreasing temperatures.
- Recycle inert gas to oxidation. The reactor configurations with up to nine separate reaction zones, over which the temperature is reduced from 140–150 °C to 130–140 °C with controlled recycle gas additions to avoid decomposition of the peroxide.
- Limit ethylbenzene hydroperoxide generation (conversion up to 13 % maximum) to avoid its decomposition.
- Purify recycled ethylbenzene from decomposition promoters such as acids and water.
- Use feedstock of a high purity.
- Reduce/control iron presence.

b) Selection of catalyst for epoxidation reaction.

c) Maximisation of reactant and by-product recovery in downstream fractionation sections (EB/MBA/ACP distillation and hydrogenation process):

- Recover/recycle overhead condensates.
- Minimise propylene oxide losses in crude propylene oxide distillation using an adequate cooling system on top.
- Recover unreacted propylene from the epoxidation downstream section. PO is purified with (extractive) distillation.

d) Process intensification:

- Convert MBA to SM in a dehydration step.
- Recover unreacted MBA to feed the dehydrator.
- Convert ACP into MBA in a hydrogenation step.

e) Solvents that are used to carry the dehydration catalyst and epoxidation catalyst can be recovered and reused. Extraction solvents are also used for propylene oxide purification.

Some of the techniques for reducing emissions to air (see Section 5.4.1.3) will also result in improved feedstock yields.

Achieved environmental benefits
Reduced raw material consumption.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Generally applicable.

Economics
Reduction of raw material consumption and higher yield.

Driving force for implementation
- Lower operating costs.
- Reduced emissions to air.

- Reduced waste generation.

Example plants
No information provided.

Reference literature
[63, James et al. 2012]

5.4.4 Techniques to reduce energy consumption

5.4.4.1 Techniques to reduce energy consumption in ethylbenzene production

Description
Techniques used to reduce the net energy demand by suitable operating conditions, energy recovery from the process streams and process integration.

Technical description
The energy demand can be reduced by process integration and balancing operating conditions as follows:

- Lowering of the excess benzene required (heat is also reduced as it is dealing with lower recycling volumes, lower energy consumption) by using multipoint injection. See Section 5.4.3.1.1.
- Process selection. See Section 5.4.1.1.1.
- Optimised fractionation – distillation columns' design: earlier designs utilised trays in this application. Current designs utilise structured packing and trays to increase capacity (only in the case of revamped units). Other designs may also include reactive distillation and energetically coupled distillation.

For more information on generic and horizontal techniques on energy efficiency, see Section 2.4.6 of this document.

Achieved environmental benefits
Lower energy demand will lead to reduced emissions of combustion-related pollutants to air such as NO_X and SO_X.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Applicable to new units or major plant upgrades of existing plants.

Economics
Lower operating costs.

Driving force for implementation

- Economics.
- Environmental legislation.

Example plants
Widely used techniques.

Reference literature
[51, Welch et al. 2012], [157, Yoon et al. 2007].

5.4.4.2 Techniques to reduce energy consumption in ethylbenzene dehydrogenation

Energy needed for sustaining the reaction in ethylbenzene dehydration can be provided by oxidative hydrogen removal. For more information see 5.4.3.2.2.

5.4.4.2.1 Heat recovery from condensation

Description
Improved methods and related apparatus for efficiently recovering the heat of condensation from the overhead vapour produced during the separation of various components of the dehydrogenation reaction effluent.

Technical description
This technique minimises undesired polymerisation reactions by using, at least, a compressor to facilitate azeotropic vaporisation of an ethylbenzene and water mixture within a certain range of pressure/temperature conditions. In this option, the EB/SM splitter overhead vapour is used to boil an EB-water azeotrope mixture, which is then fed to the dehydrogenation reactors. The condensation of the splitter overhead vapour produces approximately 500 kcal/kg of styrene. This energy-saving potential makes the azeotropic heat recovery option economically attractive, particularly in regions with moderate to high steam costs.

Achieved environmental benefits
Lower energy usage.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Applicable to new installations.

Economics
Lower operating costs.

Driving force for implementation
Lower operating costs.

Example plants
It is in operation in five countries worldwide.

Reference literature
[65, patent US 2010111785 A1 2011].

5.4.4.2.2 Flameless distributed combustion

Description
Flameless distributed combustion for heating reactor feed streams. It provides continuous heat input to the reaction and permits operation at lower temperatures.

Technical description
Heat transfer is primarily done by convection, as opposed to conduction in conventional heat exchangers. A process heater is provided utilising flameless combustion, as follows. The process heater has an oxidation reaction chamber, which has an inlet for the oxidant, an outlet for combustion products, and a flow path between the inlet and the outlet. A fuel conduit is capable of transporting a fuel mixture to a plurality of fuel nozzles within the oxidation reaction chamber, each nozzle providing communication from within the fuel conduit to the oxidation chamber, with each nozzle along the flow path between the inlet and the outlet. A preheater is in communication with the oxidation chamber inlet. The preheater is capable of increasing the temperature of the oxidant to a certain temperature, resulting in the combined oxidant and fuel from the fuel nozzle closest to the oxidation chamber inlet being greater than the autoignition temperature of the combined oxidant and fuel streams. Fuel and oxidant are mmixed in stages and at a temperature that results in oxidation of the fuel without producing a flame – replacing it with a flowing stream of very hot gases. ‘Flameless distributed combustion’ technology enables specific constraints in the conventional dehydrogenation system to be overcome, in particular designing for low steam to oil ratios.

Achieved environmental benefits
Lower energy usage is achieved. A low steam to oil ratio is desirable because of the substantial energy savings associated with superheating less steam. However, a practical lower steam to oil ratio limit exists due to the metallurgy of the steam superheater, steam transfer lines and inter-stage reheater. Flameless distributed combustion allows for operation at molar steam to oil ratios of less than 7:1 without a costly metallurgy upgrade. This is accomplished by heating the reaction mixture more directly through a combustion and convective heat transfer process.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Applicable to new units.

Economics
Lower operating costs.

Driving force for implementation
Lower operating costs.

Example plants
No information provided.

Reference literature
[66, patent US 2002015670 A1 2002].

5.4.4.3 Techniques to reduce energy consumption in styrene monomer co-production with propylene oxide

Description
Use of heat generated in the exothermic reaction.

Reactor effluent heat can be recovered through heat exchange with a combined feed.

Technical description
This techniques consists of designing, building and operating a device (heat exchanger, direct contact heating, etc.) to provide reaction heat to the EB recycle stream.

Achieved environmental benefits
Lower energy usage.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.
Technical considerations relevant to applicability
Applicable to new installations or retrofits.

Economics
Lower operating costs.

Driving force for implementation
Lower operating costs.

Example plants
No information provided.

Reference literature
Several patents on this process.

5.4.5 Techniques to improve resource efficiency

5.4.5.1 Techniques to improve resource efficiency in ethylbenzene production

5.4.5.1.1 Recovery of lighter hydrocarbons

Description
In processes where dilute ethylene feed and crude benzene feed are used as feedstock, non-ethylene and non-benzene hydrocarbons can be recovered from the feedstock or reaction off-gases.
Technical description
Feedstock pretreatment units like distillation columns and guard beds are used to purify the feed and separate impurities or other hydrocarbon compounds that can be used in other LVOC processes or as a fuel in furnaces or other combustion units.

In ethylbenzene production units such as the benzene drying column, a decanter and guard beds are used for feed pretreatment. And units like the benzene recovery column and benzene drag column, both with condensers and decanters, are used for process off-gas treatment. For more detailed descriptions of distillation and condensation used for substance recovery, see the CWW BREF.

Recovered compounds can also be used as a fuel in combustion units.

Achieved environmental benefits

- Reduced VOC emissions to air.
- Recovery of raw materials for other LVOC processes.

Environmental performance and operational data

Diluted ethylene feeds (like FCC off-gases or the stream from ethylene fractionation units of lower olefin production, etc.) can be a valuable source of gaseous light hydrocarbons (like methane, ethane, hydrogen), while co-boilers and close-boilers like cyclohexane and methyl-cyclopentane can be recovered from crude benzene. Information on the content of this stream and potential emissions to air can be found in Section 5.3.1.1.2.

Cross-media effects

Operating with diluted feedstock may lead to more waste gas, waste water and waste generation.

Technical considerations relevant to applicability

This technique is applicable on sites with other olefin or refinery processes where diluted ethylene or crude benzene feed streams are available.

Economics

Recovery of raw materials or heat (fuel) from these streams may have a significant influence on the overall operating cost – diluted feedstock is much cheaper than high-purity ethylene and benzene, which lowers the overall production costs significantly.

Driving force for implementation

- Reduced raw material consumption.
- Recovery of materials useful for other processes or as a fuel (heat recovery).

Example plants

Used in many plants.

Reference literature

[51, Welch et al. 2012], [62, Nexant 2009], [57, Netzer 1999], [156, patent US 6677496 B2 2004].

5.4.5.1.2 Reuse of spent scrubbing liquor in the wash section

Description

Scrubbing liquor from wet scrubbing of HCl emissions from catalyst replacement operations can be reused in post-alkylation wash section of $AlCl_3$-catalysed processes. For more information, see Section 5.4.1.1.3.

5.4.5.2 Techniques to improve resource efficiency in styrene monomer production by dehydrogenation of ethylbenzene

5.4.5.2.1 Recovery of organic compounds from waste water and reuse of water

Description

Organic compounds recovery from the aqueous effluents of ethylbenzene dehydration can be maximised by steam stripping and adsorption. Condensates free from organic compounds can be reused as process or boiler feed water.

Technical description

Steam stripping

Most plant designs will include (downstream of the decanter) a stripper to recover hydrocarbons from the effluent and will send them back to the process fractionation section. See the CWW BREF for more information on stripping.

Adsorption

The separated process water is additionally cleaned of hydrocarbons by adsorption on activated carbon or similar filtering (sorption) material. See the CWW BREF for more information on adsorption.

After stripping and/or adsorption, the waste water will be reused as process or boiler feed water and only smaller parts pass to the combined waste water treatment plant.

Reuse of water (condensates)

The steam which is added as a reactant to the reaction is condensed and hydrocarbons are separated from it (by decanters, etc.). The condensate is treated to reuse it as process or boiler feed water. Several treatments may be applied to purify it (i.e. stripping and adsorption in a charcoal bed). Frequent monitoring is normally applied.

Achieved environmental benefits

Reduction of emissions to water and usage of water.

Environmental performance and operational data

No information provided.

Cross-media effects

Energy use.

Technical considerations relevant to applicability

Generally applicable.

Economics

Treatments done to recover organic compounds and condensate normally cost less than treating waste waters with an organic load or purchasing raw fresh water for boiler feed usage.

Driving force for implementation

Lower water usage is achieved.

Example plants

All plants from the data collection use an on-site steam stripping unit shared with other plants or processes.

Reference literature

[63, James et al. 2012].

5.4.5.2.2 Recovery of organic compounds from ethylbenzene dehydration off-gases prior to recovery of hydrogen

Description

Condensation and scrubbing are used to recover organic compounds from ethylbenzene dehydrogenation off-gases prior to recovery of hydrogen.

Technical description

For more information on techniques for recovery of organic compounds from ethylbenzene dehydration off-gases, see Section 5.4.1.2.2. For reuse of tar from ethylbenzene production as a scrubbing medium for recovery of organic compounds from ethylbenzene dehydration off-gases, see Section 5.4.5.2.3.

Achieved environmental benefits

- Reduced VOC emissions to air.
- Recovered raw materials.

Environmental performance and operational data
No information provided.

Cross-media effects
Higher cooling water consumption for condensation.

Technical considerations relevant to applicability
Generally applicable.

Economics
This technique is favourable on integrated sites with complementary units that use benzene, toluene and other recovered organic compounds as raw materials.

Driving force for implementation
Economics.

Example plants
Some plants reported performing this.

Reference literature
[63, James et al. 2012].

5.4.5.2.3 Recovery of co-produced hydrogen from ethylbenzene dehydrogenation

Description
Hydrogen is recovered either to be used as a chemical reagent or as a fuel. For more information, see Section 5.4.1.2.2.

Technical description
Recovery and purification of hydrogen for chemical usage
The output off-gas from the unit for the recovery of organic compounds has a high hydrogen content that can be purified either in a pressure swing adsorption (PSA) unit and supplied to the hydrogen grid, or compressed and used as a chemical in a hydrogenation unit. See the CWW BREF on PSA.

Use as a fuel
Often the hydrogen from the reaction is used as fuel and supplies the majority of the energy used in the steam superheater (SSH). The off-gases from the styrene monomer plant can be collected and delivered to the SSH which can be used as a combustion and abatement unit. The off-gases collected in the ethylbenzene production unit, frequently integrated with the styrene monomer plant, can be combined with the styrene monomer off-gas and also delivered to the SSH and used as a fuel. Natural gas and/or liquid fuels are used as the SSH's main fuels. See the CWW BREF on recovery for fuel usage.

Achieved environmental benefits
Resource efficiency – less additional hydrocarbon fuels need to be used in the process.

Environmental performance and operational data
No information provided.

Cross-media effects
When used as a fuel, NO_X or CO emissions to air can be heightened if combustion conditions in the SSH are not properly controlled.

Technical considerations relevant to applicability
Generally applicable.

Economics
No information provided.

Driving force for implementation
Lower fuel consumption.

Example plants
All plants that took part in data collection used the hydrogen-rich stream from ethylbenzene dehydrogenation in the steam superheater as a fuel. See

Table 5.4.

Reference literature
No reference literature provided.

5.4.5.3 Techniques to improve resource efficiency in styrene co-production with propylene oxide

5.4.5.3.1 Minimisation, recycling or combustion of excess hydrogen in acetophenone hydrogenation

Description
Minimisation or recycling of the excess hydrogen used in acetophenone hydrogenation.

In the event that these techniques cannot be applied, the hydrogen-containing off-gas is used to recover energy.

Technical description
Hydrogenation can be carried out with a significant excess of hydrogen, which is recycled. Alternatively, processes may be designed not to recycle hydrogen and minimise the use of hydrogen instead.

For the first option, excess hydrogen is recovered and recycled to the hydrogenation feed.
A condenser and a recycle compressor are normally required. Sometimes the hydrogen has to be reconcentrated (by using pressure swing absorption). Hydrogen may also be reused in other hydrogenation units that could operate with lower hydrogen purities.

In the event that these techniques cannot be applied, the energy of the hydrogen-containing off-gas is recovered by using it as a fuel gas.

Achieved environmental benefits
Reduced consumption of hydrogen.

Environmental performance and operational data
No information provided.

Cross-media effects
This may lead to increased energy consumption.

Technical considerations relevant to applicability
When hydrogenation is carried out with a low excess of hydrogen, the applicability of hydrogen recovery for reuse may be restricted where the energy demand for recovery is excessive due to the low hydrogen content.

Sending process off-gas streams to a combustion unit may be restricted due to safety considerations.

Economics
Lower raw material costs due to lower hydrogen usage.

Driving force for implementation
Economics.

Example plants
No information provided.

Reference literature
[44, Kahlich et al. 2011].

5.4.5.3.2 Reuse of vacuum system condensates in washing operations

In SMPO production, where the vacuum system is based on ejectors, the water (condensate) from the vacuum system can be reused for washing operations.

5.4.6 Techniques to reduce waste generation

5.4.6.1 Techniques to reduce spent catalyst waste

5.4.6.1.1 Techniques to reduce spent zeolite catalyst waste from ethylbenzene production

Description
Reduction or prevention of spent zeolite catalyst waste by reducing catalyst degradation or deactivation and promoting its regeneration.

Technical description
Catalyst degeneration and deactivation by poisoning, fouling and mechanical disintegration can be reduced by controlling reaction conditions (temperature, pressure, reactants' flow through the reactor, by-product formation) and maintaining feedstock purity (removing impurities by pretreatment in the benzene drying column and guard beds).

The zeolite catalyst can be regenerated *in situ* by purging with a stream of hot gas (e.g. nitrogen) with an increasing oxygen content, or by means of alternating cyclic washes at high temperatures with aromatic hydrocarbons – in the case of ethylbenzene production with benzene. In order not to affect the on-stream time, the reactor section is usually doubled, so that the reactor can be taken off-line to undergo catalyst regeneration. The off-gases are either sent to a recovery unit to recover (condensate) the hydrocarbons or to end-of-pipe abatement (usually a thermal oxidiser).

Off-site regeneration of zeolite catalyst by a specialised recovery plant is also common.

Achieved environmental benefits
Reduced waste disposal to landfill.

Environmental performance and operational data
For information on use of feedstock pretreatment, see Section 5.2.2.1.1.

Cross-media effects

- Emissions to air.
- Increased energy consumption.

Technical considerations relevant to applicability
Generally applicable.

Economics
Possible investment in additional equipment, but lower catalyst replacement costs.

Driving force for implementation

- Longer uptime.
- Lower operating costs.

Example plants
All five plants taking part in the data collection reported having feedstock pretreatment and zeolite regeneration; one (Plant #5) reported carrying it out *in situ* while others do it via a third party.

Reference literature
[51, Welch et al. 2012], [56, Vora et al. 2003], [152, patent US 20080029437 2008], [158, Song et al. 2006], [159, Martínez et al. 2011], [148, Argyle et al. 2015].

5.4.6.1.2 Techniques to reduce the amount of waste being sent for disposal from spent $AlCl_3$ catalyst neutralisation in ethylbenzene production

Description
Recovery of residual organic compounds by stripping and then concentration of the aqueous phase from the post-alkylation wash section to give a usable $AlCl_3$ by-product.

Technical description
Aluminium-chloride-catalysed alkylation produces an aqueous effluent of spent catalyst in the post-alkylation wash section (after decantation). Organic compounds (mostly benzene and ethylbenzene) are removed and recovered from this stream by steam stripping. The spent catalyst solution is then concentrated by evaporation and reused in municipal waste water treatment or industrial flocculation applications. The vapour phase from evaporation is condensed or scrubbed to give a diluted HCl solution which can be used in the neutralisation of caustic wash effluent for example.

Achieved environmental benefits
Avoidance of other disposal routes (e.g. landfill) for this waste.

Environmental performance and operational data
See Section 5.3.6.1.1.

Cross-media effects
Minor emissions of HCl to air are possible from the condenser unit of evaporation.

Technical considerations relevant to applicability
Relevant for $AlCl_3$-catalysed plants with steam available on site (for stripping and evaporation).

Economics
Lower operating (waste treatment) costs.

The untreated $AlCl_3$ solution is classified as hazardous waste with high disposal costs. However, after removal of toxic organics, the $AlCl_3$ solution has value as a flocculant in waste water treatment [160, Siefert 2000].

Driving force for implementation

- Environmental legislation.
- Lower operating costs.

Example plants
Plant #1.

Reference literature
[51, Welch et al. 2012].

5.4.6.1.3 Techniques to increase the efficiency of ethylbenzene dehydrogenation catalysts

Description
Operation at higher temperatures to compensate for lower catalyst activity and achieve the same (high) conversion.

Technical description
The useful lives of dehydrogenation catalysts vary from one to four years, and in most cases 18 to 24 months, depending on the nature of the catalyst, the design and operation of the reactor system, and the quality of the feedstock. The lifetime of the catalyst can be prolonged by the application of catalyst stabilisation technology offered by one of the licensors.

The catalyst is a significant cost in the production of styrene owing to the large quantity required. In commercial practice, the reaction temperature is increased to compensate for the decrease in the activity of the catalyst and to maintain the desired conversion. This procedure continues until the temperature reaches the limit allowed by the mechanical design of the reactor system or when the styrene selectivity is deemed too low to be economical. Higher energy usage is required to operate at higher temperatures.

Typically, the dehydrogenation temperature is 550–620 °C. By increasing the temperature and by catalyst stabilisation, a desired conversion can be maintained in spite of some loss of catalyst activity.

Achieved environmental benefits
No information provided.

Environmental performance and operational data
No information provided.

Cross-media effects
Higher energy usage.

Technical considerations relevant to applicability
For existing plants, such operation may be restricted by the plant design.

Economics
Lower operating costs.

Driving force for implementation
The most important advantage is a significant reduction in the amount of catalyst used, thus lessening the costs related to it.

Example plants
No information provided.

Reference literature
[63, James et al. 2012], [60, Chen et al. 2006].

5.4.6.2 Techniques to reduce tar formation or to improve its reuse

5.4.6.2.1 Material recovery by tar distillation or cracking

Description
Recovery of organic material from tars from ethylbenzene production by distillation or cracking with steam.

Technical description
The tar is fed to the middle part of a continuous operation column-type reactor (i.e. a thermocracker), heated and treated with steam. Upon heating, the tar is refluxed, and the vapour which does not condense in the reactor is led into a phase separation stage to condense and recover organic compounds for reuse in other LVOC processes. The waste tar residue is removed from the bottom of the reactor.

Achieved environmental benefits
The amount of tar waste to be managed is reduced and the consumption of feedstock for other LVOC processes is reduced.

Environmental performance and operational data
No information provided.

Cross-media effects
Use of energy (steam).

Technical considerations relevant to applicability
No information provided.

Economics
Lower costs for raw materials.

Driving force for implementation
Recovered feedstock.

Example plants
No information provided.

Reference literature
No reference literature provided.

5.4.6.2.2 Reuse of tar from ethylbenzene production as an absorbent for scrubbing in styrene monomer production

Description

Tar from ethylbenzene production is used as an absorbent in the styrene monomer unit, instead of other commercial organic solvents.

Technical description

The tar (flux oil) is used as an absorbent in the scrubbers used in styrene monomer production by ethylbenzene dehydrogenation (see Section 5.4.1.2.2), instead of commercial organic solvents.

In styrene production, the recycle off-gases are scrubbed in a flux oil scrubber where cooled lean flux oil (consisting of heavier organic hydrocarbon compounds with greater viscosity) is used to substantially absorb all of any remaining aromatics from the recycle off-gas from the ethylbenzene dehydration.

The extent to which tar can be used depends on the scrubber capacity of the styrene monomer unit.

Achieved environmental benefits

Reduced consumption of commercial solvents and reduced overall residue (heavy cut) from integrated ethylbenzene and styrene monomer plants.

Environmental performance and operational data

No information provided.

Cross-media effects

No information provided.

Technical considerations relevant to applicability

Applicable when the styrene monomer plant is close to the ethylbenzene plant.

Economics

Low investment costs and lower overall operating costs.

Driving force for implementation

Lower operating costs of the styrene monomer unit.

Example plants

All of the plants using the ethylbenzene dehydration process reported using flux oil from the ethylbenzene plant as the scrubbing medium in the styrene monomer plant.

Reference literature

[51, Welch et al. 2012].

5.4.6.2.3 Use of tar and other residues as fuels

Description

Tars from ethylbenzene and/or styrene production can be used as a fuel and combusted to recover heat (typically for steam generation).

Technical description

The bottom cuts from the PEB distillation column and styrene purification column are sent to an appropriate combustion unit. Tars are a complex mixture of by-products (heavy aromatic compounds – mono- and polycyclic hydrocarbons with 10 or more carbon atoms). It is a high-quality fuel, which contains low amounts of sulphur and nitrogen compounds and has a low viscosity.

Achieved environmental benefits

- Reduction of waste.

- Recovery of energy.

For more information on the use of tar as a fuel, see Sections 5.3.6.1.2, 5.3.6.2 and 5.3.6.3. According to the data collected, most plants reported the use of tars as a fuel.

Environmental performance and operational data
No information provided.

Cross-media effects
Emissions to air from combustion.

Technical considerations relevant to applicability
Generally applicable for tars with low sulphur and nitrogen content (see also Section 5.4.6.2.5).

Economics
Lower costs for fuel/energy.

Driving force for implementation
Lower operating costs due to fuel savings.

Example plants
No information provided.

Reference literature
[63, James et al. 2012], [60, Chen et al. 2006].

5.4.6.2.4 Ethylene multipoint injection

Description
Multipoint injection of ethylene to avoid temperature increase and by-products formation during the reaction.

Technical description
The alkylation reaction is exothermic. Instead of supplying all the reactants in the fixed-bed entrance, one reactant (ethylene) is fed into several points (pipes/nozzles), allowing the temperature to decrease in between these injection points. Controlled lower reaction temperatures (without local maxima in some parts of the reactor) lower or prevent side reactions and the thermal cracking of reactants. With less by-products (high-boiling organic residues, coking precursors, etc.), less tar is generated.

Achieved environmental benefits
Higher yields and reduced by-products and waste generation.

Environmental performance and operational data
Multipoint injection of ethylene in the alkylation reactor can also extend catalyst life.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Applicable to major upgrades of existing plants and to new plants.

Economics
Reduced operating costs.

Driving force for implementation
Economics.

Example plants
Commonly used.

Reference literature
[51, Welch et al. 2012], [58, Aspen 1999], [59, CBI/UOP 2016].

5.4.6.2.5 Addition of inhibitors to distillation systems

Description
Addition of inhibitors to distillation systems in order to prevent or reduce oligomerisation and polymerisation reactions.

Technical description
In distillation systems in plants for styrene monomer production including its co-production with propylene oxide, inhibitors are added at the beginning of the fractionation train to avoid/reduce polymerisation reactions. Inhibitors or retarders are selected and the dosage optimised in order to reduce losses of styrene monomer and gum waste generation.

The term inhibitor is often used indiscriminately in the styrene industry to denote substances ranging from a true inhibitor to a retarder. True inhibitors prevent the initiation of polymerisation by reacting rapidly with free radicals; retarders reduce the rate of polymerisation. New inhibitor systems that are said to be capable of dramatically reducing polymer formation have been developed.

Sulphur was used extensively as a polymerisation inhibitor until the mid-1970s. It is effective but the residue leaving the distillation train is contaminated with sulphur and is not environmentally acceptable as fuel. Newer inhibitors, mostly nitrogen-containing organic compounds such as dinitrophenol and dinitrocresol, have been developed to replace sulphur. They are more expensive and some are highly toxic, but it is more acceptable to use the residues containing inhibitors of this type as fuel.

Achieved environmental benefits
Higher yields and reduced generation of residues.

Environmental performance and operational data
The most commonly used inhibitor for this service is 4-tertbutylcatechol (TBC), usually in 10–20 ppm concentrations.

Cross-media effects
Since the fractionation tars are normally used as non-conventional fuels, the nitrogen- and sulphur-based inhibitors used in fractionation may lead to increased emissions of NO_X or SO_X to air or limit their reuse as fuel.

Technical considerations relevant to applicability
No information provided.

Economics
No information provided.

Driving force for implementation
No information provided.

Example plants

- Styrene production by ethylbenzene dehydrogenation.
- Co-production of styrene with propylene oxide.

Reference literature
[63, James et al. 2012].

5.4.6.2.6 Minimisation of high-boiling residue formation in distillation systems

Description
The formation of organic residues (gums, tars, polymers) is reduced by lowering the operating temperature and residence time (or hold-up volume) of the distillation columns in the fractionation system.

Technical description
This technique involves the use of techniques that reduce temperatures and residence times (e.g. packing instead of trays to reduce the pressure drop and thus the temperature; vacuum instead of atmospheric pressure to reduce the temperature).

The measures relate to the design of the distillation column. Additional drivers for the use of structured packing are:

- reduction of inhibitor consumption because of the reduced mean residence time;
- increase in volume capacity, yield and purity;
- energy savings by increasing the number of stages and adding heat exchange technology.

Achieved environmental benefits

- Higher yields and reduced generation of residues.
- Lower energy consumption.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
This technique is applicable for styrene production units with either ethylbenzene dehydration or co-production with propylene oxide processes. It is only applicable to new distillation units or major plant upgrades.

Economics

- Lower purification costs.
- Lower residue handling costs.

Driving force for implementation
Lower operating costs.

Example plants
Several plants reported using distillation columns with structured packing (see Table 5.3).

Reference literature
[63, James et al. 2012].

5.4.6.3 Techniques to reduce coke formation in ethylbenzene dehydrogenation

Description
Reduction of coke formation by operating the ethylbenzene dehydration reactor at the lowest possible pressure.

Technical description
Coke is both a catalyst poison and a waste. The dehydration reaction section is operated under vacuum in order to increase the conversion, selectivity and self-cleaning capacity of the catalyst (iron oxide with chromium and potassium oxides incorporated) enabled by the addition of diluted steam. Steam reacts with coke deposited on the catalyst to give carbon dioxide which is removed with the reactor off-gases. Lower pressure means less steam needs to be added and therefore a lower amount of effluent is generated.

Achieved environmental benefits

- Less energy consumption and high yield (conversion).
- Longer catalyst lifetime and less spent catalyst waste.

Environmental performance and operational data
Less coke and gums formed.

Cross-media effects
Small increase of CO_2 emissions to air.

Technical considerations relevant to applicability
Generally applicable.

Economics
No information provided.

Driving force for implementation
No information provided.

Example plants
Plant #5 reported operating at low vacuum.

Reference literature
No reference literature provided.

5.4.7 Techniques to reduce other than normal operating conditions

5.4.7.1 Techniques to prevent or reduce corrosion in ethylbenzene production

Description
Corrosion prevention by limiting the content of chlorine and other impurities in process streams, selection of corrosion-resistant materials, process controls and preventive maintenance.

Technical description
Corrosion-related interferences of normal operating conditions can be minimised and/or prevented by applying the following techniques:

- Process selection: Changing the process from $AlCl_3$-catalysed to zeolite-catalysed lessens the problem considerably, since the presence of chlorine in process streams is very detrimental in terms of the corrosion rate. The zeolite process has inherently less corrosion issues than the $AlCl_3$ process.

- Selection of appropriate corrosion-resistant construction materials: In order to prevent and minimise emissions arising from corrosion events in the $AlCl_3$ process, it is important to select the correct materials of construction. Alkylation reactors are lined with brick or glass; high-alloy construction materials are also required for the piping and handling systems.
- Removal of water residues and chlorine impurities from the process streams: Because the alkylation mixture can tolerate only small amounts of water, the recycled benzene and fresh benzene must be dried thoroughly prior to entering the reactor. Water not only increases corrosion, but also decreases catalyst activity.
- Corrosion can also occur in the drag benzene column top due to the high chloride concentration in the water present. This effect can be avoided or reduced by material selection and/or chloride content control in the recovered and fresh benzene feed.
- Appropriate process controls: Control of process parameters like the temperatures, pressures and chemical composition of the streams improves the operation of the reactor, prolongs the catalyst (fixed-bed zeolite) lifetime and the reaction yield.
- Preventive maintenance.
- Regular periodic inspections and cleaning of critical parts (piping and equipment) lower the number of incidents and alert the operator in time to replace the critical parts.

For more information on these issues, see also Section 2.4.11.2.1.

Achieved environmental benefits
Less corrosion-induced loss of containment and spillages.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Generally applicable.

Economics
High costs due to the corrosion and environmental (spent catalyst handling and treating) issues of $AlCl_3$-catalysed technologies mean that their replacement by zeolite-catalysed ones is favoured.

Driving force for implementation
Less risk of loss of containment and possible damage/cost related to it.

Example plants
Commonly used in plants using $AlCl_3$-catalysed processes.

Reference literature
[51, Welch et al. 2012].

5.4.7.2 Techniques to reduce equipment plugging in ethylbenzene dehydrogenation

Technical description

The material that can plug the equipment is a waste that will need to be disposed of. In addition, plugging events may lead to higher emissions to air and/or water related to start-up and shutdown as well as equipment cleaning. Plugging events can be minimised by the following:

- Operation at as low a temperature as possible (by applying a vacuum).
- Use of polymerisation inhibitors. For more information on these additions, see also Section 5.4.6.2.5.
- Design measures to produce lower pressure drops across column internals.
- Design heat exchangers and distillation column internals to bear fouling.
- Preventive maintenance with regular periodic inspections and cleaning of piping and equipment.

Achieved environmental benefits

Resource efficiency: less raw material is wasted in form of fouling residues. Plugging events may lead to higher emissions to air and/or water related to other than normal operating conditions.

Driving force for implementation

- Longer uptime (on-stream).
- Lower maintenance costs (in the longer term).

5.4.7.3 Techniques to reduce neutralisation decanter malfunction in styrene co-production with propylene oxide

Description

Application of a group of managerial, design and operational measures to minimise the malfunction of this key unit.

Technical description

Adequate interphase level control instruments providing precise and trustworthy phase level measurement allow proper decanter operation. Appropriate design of internals in decanters (feed entry, baffles, compartments' volume, etc.) is also important, considering fluid velocities and residence times. Appropriate preventive maintenance and skilled and trained personnel will ensure stable and safe operating conditions.

Achieved environmental benefits

- Lower organic load in the waste water stream.
- Less water present in the organic phase downstream of the neutralising and washing section.

Environmental performance and operational data

No information provided.

Cross-media effects

No information provided.

Technical considerations relevant to applicability

The feed stream composition must be stable and well known to properly specify and design an interphase level measurement device. The techniques are generally applicable.

Economics
No information provided.

Driving force for implementation
No information provided.

Example plants
No information provided.

Reference literature
No reference literature provided.

5.5 Emerging techniques

The production of ethylbenzene by alkylating benzene with ethylene is the predominant process route (> 99 % of worldwide production) and apart from $AlCl_3$- or zeolite-catalysed technologies no new emerging technologies (on an industrial scale) were currently found. Both existing ones constantly undergoing improvements, with a lot of research and development, due to the increasing demand for energy-saving processes with a lower environmental impact.

Currently, styrene is produced by catalytic dehydrogenation, or by a peroxidation process together with propene oxide. These processes have several disadvantages such as high energy demands, low equilibrium conversions, lack in product flexibility and high capital costs. Improvements in the current processes are not expected, but other dehydrogenation processes show great potential and are in development. These are catalytic dehydrogenation in CO_2, catalytic oxidative dehydrogenation, and the combined catalytic dehydrogenation of ethane and ethylbenzene (SNOW process). [161, Nederlof 2012]

6 FORMALDEHYDE

6.1 General information

Formaldehyde (CH_2O) is an important organic base chemical and is widely used for the manufacture of numerous products, either as 100 % polymers of formaldehyde or a reaction product together with other chemicals. Formaldehyde is used in the production of the following:

- A huge variety of resins from the reaction of formaldehyde with phenol, urea, melamine, furfuryl alcohol or resorcinol. Resin products are used as adhesives, bonding agents, glues, paints, coatings, insulators and sealants.
- Formaldehyde is one of the feedstocks in the production of MDI (methylene diphenyl diisocyanate) used to produce polyurethanes (for foams, synthetic leather, and engineering plastics).
- Polyoxymethylene is a 100 % formaldehyde polymer used as an engineering plastic (e.g. for ski bindings, toothed wheels, kitchen articles).
- Water-soluble paints and coatings use formaldehyde polyols.
- Hydraulic fluids and lubricants based on polyol esters are used in the aircraft industry.
- Pharmaceuticals, food and feed use formaldehyde intermediates (e.g. provitamin B3).
- Chelating agents that are used in agricultural products, detergents, soaps, cleaners, the food industry, the mining industry, metal plating, pulp and paper, and textiles.

Formaldehyde is produced by the catalytic oxidation of methanol and is ordinarily produced as a solution in water, which is often referred to simply as ‘formalin’.

Formaldehyde production and consumption rates have significantly increased during recent years and the steep trend seems to be continuing. In the mid-2000s, China and the Asia Pacific region took over a dominion of global consumption and production capacities, reaching ~ 56 % in 2012. In the same year (2012), the consumption of formaldehyde in Europe was approximately 3.6 million metric tonnes per year (as 100 % formaldehyde) with an installed production capacity of ~ 6 million metric tonnes per year (as 100 % formaldehyde), which represented ~ 29 % of global consumption and ~ 27 % of global production capacity. However, this figure includes some production from countries outside the EU.

Formaldehyde is manufactured in 23 out of the 28 EU Member States, often as a part of integrated chemical complexes for resin production. European production of formaldehyde is summarised below.

Table 6.1: Location of EU producers of formaldehyde

Country	Number of production sites (1)	Country	Number of production sites (1)
Austria	1	Latvia	1
Belgium	4	Lithuania	1
Bulgaria	1	The Netherlands	4
Czech Republic	2	Poland	4
Denmark	1	Portugal	2
Finland	2	Romania	4
France	1	Slovakia	2
Germany	11	Slovenia	1
Greece	1	Spain	6
Hungary	1	Sweden	2
Ireland	1	United Kingdom	5
Italy	8		
(1) Estimated number of sites based on information reported by industry.			

The cost of formaldehyde production is dominated by the cost of methanol and energy. Methanol prices do not necessarily follow the same business cycle as the petrochemical industry, so the economics shows some decoupling from the rest of the industry. A significant number of operators are small and medium-sized businesses [42, Reuss et al. 2012], [86, UBA-Austria 1999], [164, Magnusson 2013], [165, Bahmanpour et al. 2014].

Key environmental issues

Formaldehyde gas is a strong irritant of the eyes, nose and mucous membranes at very low concentrations. Operational practices have therefore been developed to limit the occupational exposure of workers. Formaldehyde is toxic and a suspected carcinogen at high concentrations, but the strong irritating effect means that human exposure to high concentrations is self-limiting. Formaldehyde poses a moderate fire risk and is explosive in air in the range of 7–72 vol-% [42, Reuss et al. 2012]. Formaldehyde is soluble in water and most organic solvents.

The key environmental issues for the production of formaldehyde are as follows:

- The emissions to air from the reaction section and the related abatement systems. The main pollutants from these streams are VOCs (formaldehyde, methanol) and combustion-related emissions such as CO, CO_2 and NO_X.
- The major solid waste generated is the spent catalyst and there are no or only very small continuous process effluent flows to waste water treatment systems. But high formaldehyde loads are a challenge for biological reactors.

6.2 Applied processes and techniques

6.2.1 Process options

Formaldehyde is produced from methanol, either by catalytic oxidation under air deficiency (‘the silver process’) or under air excess (‘metal oxide process’). There are further options to design the silver process for either 'total' (i.e. high) methanol conversion or partial methanol conversion. European formaldehyde production capacity is split roughly equally between the silver and metal oxide routes. Both processes continue to be used for new capacity although there is more investment in the metal oxide process than in the silver process. High methanol conversion is the dominating process for new units using the silver process.

The main characteristics of the three process routes are summarised in Table 6.2.

Table 6.2: Typical main characteristics of the different process routes

Criterion	**Silver catalyst process**		**Metal oxide catalyst process**
	High methanol conversion	**Partial methanol conversion**	
Temperature	580–680 °C	600–650 °C	270–430 °C
Catalyst	Silver crystal (change every 3–9 months, regenerable)	Silver crystal or silver gauze (change every 8–16 months, regenerable)	Metal oxide (e.g. iron, molybdenum, or vanadium oxide) (change every 5–18 months, only recovery of molybdenum)
Reagent mix	Methanol in excess		Air in excess
Main reactions	$CH_3OH \rightleftharpoons CH_2O + H_2$ $H_2 + ½\ O_2 \rightarrow H_2O$		$CH_3OH + ½\ O_2 \rightarrow CH_2O + H_2O$
Side products	Hydrogen, carbon monoxide, carbon dioxide, formic acid, methyl formate		Carbon monoxide, dimethyl ether and formic acid
Product work-up	Absorption	Absorption and distillation	Absorption
Methanol conversion	97.5–99.5 %	77–87 % (primary)	98–99.5 %
Overall yield (mol-%)	89.5–90.5	91–92	88–91
Advantages	• Low waste gas volumes • Combustible tail gas used for steam/electricity generation • No catalyst losses and short shutdown time due to replacement • All oxygen spent in reaction – low safety risks due to methanol flammability • High product quality - no requirement for product distillation	• Generation of combustible tail gas • Economic for small plants	• High yield due to lower reaction temperatures and thus higher selectivity • High product quality • Generation of steam that can be exported • Economic for large plants (split into separate units) • Safer due to lower methanol amounts in the plant
Disadvantages	• Higher methanol consumption	• Methanol flamability – possible safety risks • Need for methanol distillation	• High investment costs due to higher gas volumes • High energy consumption due to higher gas volumes
Source: [42, Reuss et al. 2012] [163, Gerberich et al. 2013], amended by comments from industry			

These processes are described in more detail in the subsequent sections of this chapter.

Methanol is the main raw material for both process routes and is either produced on site or imported (by ship, barge, rail or road tank). Because of its flammability, methanol is stored in tanks at atmospheric pressure under air or nitrogen. The only other auxiliary raw materials are:

- air used to oxidise the methanol (in both processes);
- demineralised process water to absorb formaldehyde, control product concentration (this leaves with the commercial product) and to generate steam;
- optionally, very small quantities of sodium hydroxide which are injected in the absorption step of the metal oxide process and leave with the commercial product.

Both production routes share the same sequence of basic unit operations, namely:

- vaporisation of (aqueous) methanol in air;
- catalytic conversion of vaporised methanol to formaldehyde; and
- absorption of formaldehyde into water to produce formalin (sometimes formaldehyde might be contacted with a urea solution in order to produce urea formaldehyde within the process for subsequent conversion into resins).

Formaldehyde is normally produced commercially as 37–55 % aqueous solution (‘formalin’). The various concentrations of formaldehyde product are stored in tanks under atmospheric pressure.

The responses in the data collection show that in the EU:

- most installations operate with a 97–99.5 % conversion target;
- methanol purity typically ranges from 99.5 % to 99.9 %, although in some cases it can be as low as 97 %;
- the product is typically sold as a 30–55 % solution; where the product is used internally, this can be as high as 70 %;
- residual methanol in the product ranges from 0.5 % to 3 %; where the product is used internally, the residual methanol can be as high as 5 %; the remainder of the impurities are around 0.1 %.

6.2.2 Silver catalyst process

The silver process is an oxidative dehydrogenation of methanol with air over a crystalline silver catalyst. Catalysts other than crystalline silver can be used in the silver process (e.g. silver on a carrier), but to date the crystalline silver is superior in performance to other forms of silver catalysts. In the initial step, methanol is dehydrogenated (Equation 1) and there is a secondary combustion of a part of the formed hydrogen (Equation 2):

$$CH_3OH \rightleftharpoons CH_2O + H_2 \qquad \Delta H = +\,84\ \text{kJ/mol (Equation 1)}$$
$$H_2 + \tfrac{1}{2}\,O_2 \rightarrow H_2O \qquad \Delta H = -\,243\ \text{kJ/mol (Equation 2)}$$

6.2.2.1 High methanol conversion

The process for high methanol conversion consists of four main unit operations, namely:

- methanol vaporisation;

- catalytic methanol conversion to formaldehyde;
- formaldehyde absorption; and
- emission control.

Methanol vaporisation: Methanol is diluted by water or a methanol/formaldehyde/water mixture recycled from the absorption tower (so-called water ballast process) and fed into the bottom of a vaporiser column. This methanol/formaldehyde/water mixture is heated and passes to the top of the vaporiser column together with water from the scrubber on top of the absorption column. The heat required to evaporate the methanol/formaldehyde/water mixture is provided by heat exchangers that are linked to the absorption and catalytic conversion system. Overall, the feed to the vaporiser column is about 60 % methanol.

Fresh process air enters the bottom of the vaporiser column and passes countercurrent to the descending liquid. A gaseous mixture of methanol in air is formed by the actions of stripping and vaporisation. The methanol-rich gas mixture contains enough methanol, nitrogen and water to be safely above the upper explosion limit. After passing through a demister, the gaseous mixture is superheated with steam in order to avoid any partial condensation above the silver catalyst bed.

Catalytic methanol conversion: The catalytic reactor contains a silver catalyst bed with layers of silver crystals of a defined range of particle sizes supported on a perforated tray. The catalyst lifetime, typically three to nine months, is influenced by a number of operating conditions. Depleted catalyst can be completely recycled.

In order to minimise the over-oxidation of methanol and the decomposition of formaldehyde to carbon monoxide, carbon dioxide and hydrogen, the short residence time is very short (< 0.1 seconds). The reaction occurs at a slightly elevated pressure and temperatures of 650–700 °C.

Wall effects in the reactor can be responsible for poor product selectivity and are an important part of the reactor design. If the throughput and reaction temperature have been optimised, then the formaldehyde production capacity increases in proportion to the reactor's diameter. New reactors can typically be greater than 3 metres in diameter.

Immediately below the catalyst bed is a water boiler that produces steam and simultaneously cools the hot reaction gases to a temperature corresponding to that of the pressurised steam. An additional gas cooler rapidly reduces the reaction gas temperature to about 85 °C.

Formaldehyde absorption: The cooled reaction gas enters a multistage packed absorption column and is contacted countercurrent with aqueous formaldehyde solutions whose concentrations decrease from stage to stage. The excess heat from the first absorption circuit is often used to preheat the methanol/water feed in the methanol evaporation column in a recuperative heat exchanger. In the final absorption stage, the gas is scrubbed countercurrent with demineralised water. The concentration in the first absorption stage can be controlled at a concentration of 40–60 wt-% formaldehyde as required by the final product specification. The formaldehyde product contains up to 3 wt-% methanol; however, where the product is used internally, this can be as high as 5 wt-% methanol. Methanol acts as a stabiliser to prevent polymerisation.

Emission control: The reaction off-gas contains about 18–27 vol-% hydrogen and has a calorific value that makes it suitable for energy recovery, either in a dedicated thermal oxidiser, a gas engine (with the production of electricity) or a conventional boiler.

The silver process with high conversion can be summarised as shown in the diagram below.

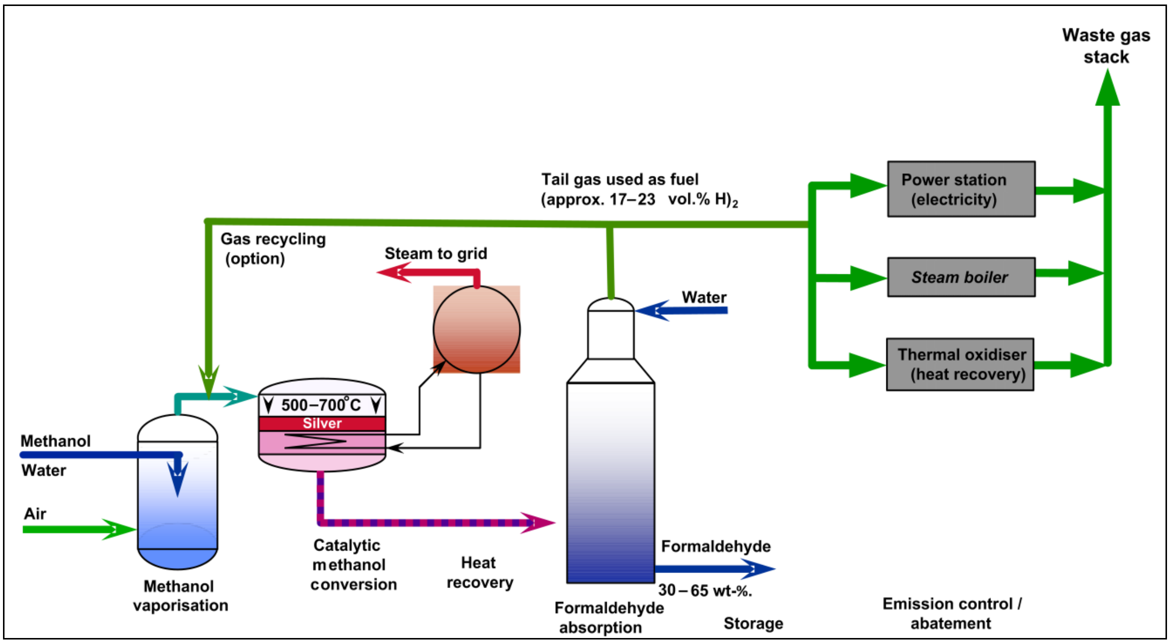


Figure 6.1: Process flow diagram for formaldehyde production using the silver process (high methanol conversion)

6.2.2.2 Partial methanol conversion

The silver process may also be operated to give partial (about 80 %) methanol conversion using methanol with only small amounts of water. The reaction over the silver catalyst takes place at the slightly lower temperature of 590–650 °C but again with methanol significantly above the upper explosion limit. The main difference is that the process solution from the absorber contains excess methanol and is fed to a vacuum distillation column where methanol is separated off and recycled to the vaporiser (so-called methanol ballast process). At the bottom of the distillation column, a product is obtained with about 62 % formaldehyde and up to 1.5 % methanol. The off-gas from the process is combusted to generate steam (about 1.5 t steam/t of formaldehyde) either in a dedicated thermal oxidiser (with energy recovery) or in a boiler.

6.2.3 Metal oxide catalyst process

In the metal oxide process, the formation of formaldehyde is accomplished by the direct oxidation of methanol with excess air over a metal oxide catalyst according to the formula:

$$CH_3OH + {}^1/_2\, O_2 \Rightarrow HCHO + H_2O \qquad \Delta H = -159 \text{ kJ/mol}$$

The process gives a high yield of formaldehyde on a single pass, and also a methanol conversion above 99 mol-%, making the recovery of methanol from the final product unnecessary. The actual formaldehyde yield is in the range of 88–91 mol-% of the theoretical amount. The process can be divided into four unit operations:

- methanol vaporisation;
- catalytic conversion of methanol to formaldehyde;
- formaldehyde absorption;
- waste gas treatment by catalytic oxidation.

Methanol vaporisation: Fresh air is mixed with recycled gas from the absorption tower and fed to the vaporiser/preheater. Pure methanol is flash-vaporised into the gas stream, most often using heat generated in the process. The methanol to air ratio is controlled to maintain a safe and accurate feed of the desired oxidation atmosphere. A high content of methanol is possible, as the recycle gas is high in nitrogen, thereby ensuring an atmosphere with an oxygen concentration below the lower explosion limit (in contrast to the silver process, which is operated above the upper explosion limit).

Catalytic conversion of methanol to formaldehyde: The methanol oxidation is an exothermic reaction that takes place over a solid oxide catalyst at atmospheric pressure and 270–430 °C. The catalyst is an mixture of ferric molybdate and molybdenum trioxide, but performance may be enhanced by small amounts of other metal oxides. Chromium oxide promoters are no longer used in Europe for catalyst enhancement because of their carcinogenic nature. The catalyst is simultaneously regenerated with atmospheric oxygen and has a typical lifetime of 5 to 30 months. The gas mixture entering the reactor tubes is preheated by a heat transfer fluid (hot oil).

As the gas reaches the catalyst, the reaction starts and heat is liberated. The reaction by-products are very small amounts of dimethyl ether, carbon monoxide and formic acid. To promote good heat transfer, the upper part (and sometimes the lower part) of the tubes is loaded with inert rings. The hot oil fills the reactor shell and removes the heat of reaction, which is used to produce steam in a heat transfer fluid condenser. Before the reaction gas enters the absorption tower, the gas is heat exchanged to reduce the inlet gas temperature to the absorber and to increase the reactor inlet temperature. A good heat transfer on the reactor downstream side and a minimisation of the residence time are therefore required to minimise the by-product formation.

Formaldehyde absorption: The cooled reaction gas enters the bottom of an absorption tower that consists of several different sections to obtain maximum absorption efficiency. Process water is fed to the top of the absorber and flows countercurrent to the gas flow at a rate that depends on the desired formaldehyde concentration of the final product. The heat of absorption is removed by both internal and external cooling. Part of the heat is utilised in the process in order to optimise the energy utilisation in the plant. Dependent on application, formaldehyde solutions of 37–60 wt-% are produced. As the conversion of methanol is highly efficient, the levels of methanol in the formaldehyde product can be as low as 0.2–0.3 wt-%.

The off-gas from the absorber contains traces of unreacted methanol, carbon monoxide, dimethyl ether and formaldehyde. Part of the off-gas stream is recycled to the process and the rest is sent to a catalytic oxidiser.

Catalytic oxidation of emissions: The absorber exhaust gas is not directly combustible as the oxide process is a full oxidation reaction and the waste gases have a low concentration of organics. The exhaust gas is therefore oxidised over a catalytic bed of noble metal catalyst. The exothermic reaction can produce steam in an integrated steam generator and also preheats the absorber off-gas. The profitability of producing steam is checked on a case-by-case basis. The metal oxide catalyst process can be summarised as follows.

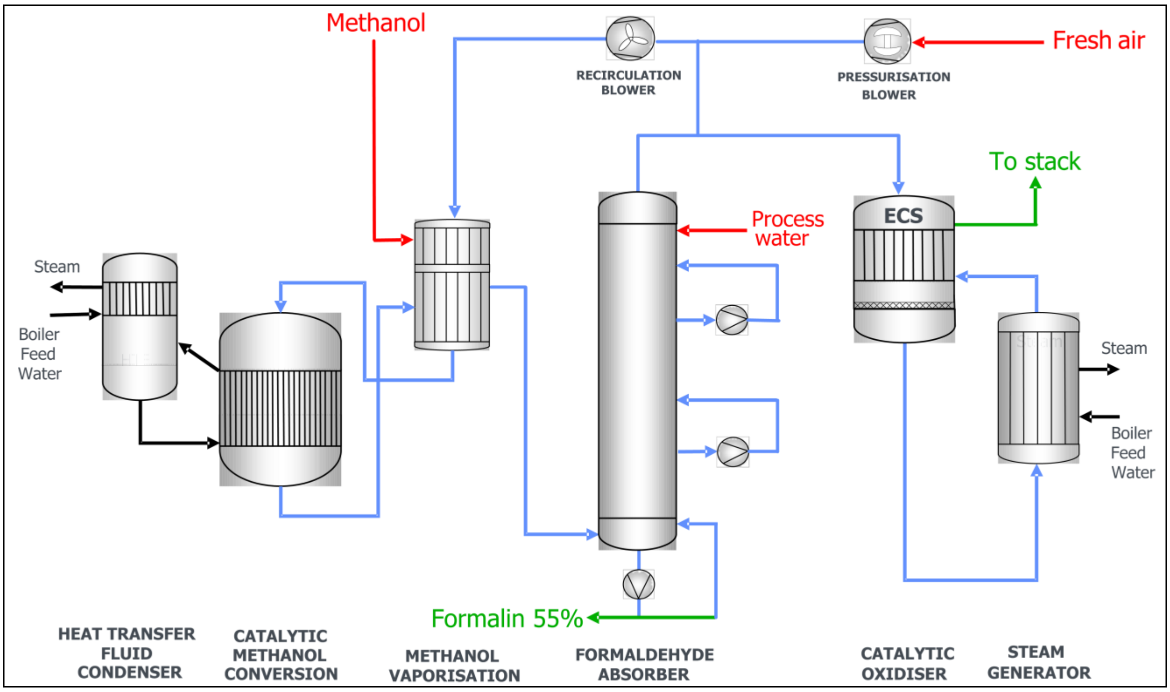


Figure 6.2: Process flow diagram for formaldehyde production using the metal oxide process

6.2.4 Other than normal operating conditions

6.2.4.1 Start-up and shutdown

The following operations deviate from the stable and normal operating procedures:

Start-up: For the silver process, filling the plant could result in the venting of some displaced gases if the off-gases cannot be burnt in the off-gas treatment system, and VOC emissions can be expected during start-up before the burning of the off-gas begins. Combustion begins once the oxygen in the off-gas after start-up is below 3 %. Formaldehyde emissions also occur during plant start-up. Start-up procedures will vary from plant to plant, but the reaction gases are routed to the absorption column.

The oxide process operates below the explosive limit of methanol with an excess of air resulting in stable reactor conditions during start-up, and so venting is not required and there are no intermittent start-up emissions. The reactor feed rate varies as the start-up proceeds. Initially, the reactor produces mainly CO and water vapour, but, as the temperature rises, the formaldehyde yield increases, increasing the amount of formaldehyde in the process off-gas [85, Rentz et al. 1999].

Shutdown: Both processes may be allowed to vent process off-gas to atmosphere at shutdown for a short time as a safety requirement in the event that no off-gas treatment is possible. When the plant is shut down its inventory will need to be removed, and a process of purging may be employed in order to eliminate hazardous substances.

6.2.4.2 Process-related other than normal operating conditions

Overheating during reaction (metal oxide process): If problems removing the heat of reaction result in too high a temperature rise, the amount of methanol that is converted to CO, etc. will rise. The process control system could constantly monitor the temperature, and make an appropriate intervention in the event of a problem, possibly including shutting down the process.

Overheating during absorption (both processes): Heat is generated during the absorption step. Consequently, if there is a problem with the removal of this heat the efficiency of the absorption process may reduce due to an increase in temperature. It is therefore expected that the plant's control system would constantly monitor the temperature, and make an appropriate intervention in the event of a problem, possibly including shutting down the process.

Malfunction of the absorber (both processes): Any problem with the supply of water to the absorption columns might result in a reduction in absorption efficiency. It is therefore expected that the plant's control system would constantly monitor the water feed rate, and make an appropriate intervention in the event of a problem, possibly including making use of a separate supply, e.g. in a dump tank.

Others: Where combustion may not be possible, other process-related other than normal operating conditions are: catalyst poisoning, malfunction or maintenance of the off-gas treatment system (e.g. thermal oxidiser, catalytic oxidiser, combustion plant, conventional boiler), and test runs (e.g. first start-up, tests of new process optimisations or catalysts).

6.2.5 Equipment important for environmental protection

The systems that carry out operations important for environmental protection are those controlling the reactor conditions, the absorption of the formaldehyde and for the combustion/oxidation of the waste gas stream.

6.3 Current emission and consumption levels

Data on emissions and consumption levels and other performance-related contextual information were collected by questionnaire in 2013. In 2014, upon request from the EIPPCB, additional information was provided by the industry and Member States' representatives in the TWG. Some additional information was also provided by the members of the TWG in their comments on D1. In further text, all of this information is referred to as the 'data collection'.

6.3.1 Emissions to air

6.3.1.1 Emissions from the silver process

The primary source of emissions to air from formaldehyde processes is the process gas from the absorber. The silver process operates above the upper explosive limit, which requires a reduced volume flow and reduced emission rate and that the process operates with no oxygen in the absorber. The primary source of formaldehyde process emissions is the gas from the reaction. The product fractionator / distillation column (where used) is another possible formaldehyde emission source, but most producers feed the fractionator gases to the absorber before venting. Some of the process gases leaving the final stage of the formaldehyde absorption step in both the high and partial methanol conversion routes may be recycled to the initial feed vaporisation step.

The process gas composition consists basically of nitrogen from the air along with some reaction by-products, hydrogen, carbon monoxide and carbon dioxide; with small traces of methanol, methyl formate and dimethoxymethane.

The total VOC load is low. Composition data from the 2003 LVOC BREF (now amended by the TWG comments) is shown below.

Table 6.3: Composition of the process gas from the silver process

Gas volume (Nm^3/t of product*)	1 500–1 700	
Nitrogen and argon (% v/v)	65–75	
Hydrogen (% v/v)	18–27	
Carbon dioxide (% v/v)	4	
Formaldehyde	0.04–1.6 kg/t of product*	25–1 000 mg/Nm^3
Methanol	0.5–8 kg/t of product*	300–5 000 mg/Nm^3
Carbon monoxide	1–14 kg/t of product*	600–9 000 mg/Nm^3

* Product is 100 % formaldehyde.
Source: Table 10.4 from 2003 LVOC BREF [190, COM 2003]now amended by comments from industry.

The concentration ranges of formaldehyde, methanol and CO are based on a nominal gas flow of 1 600 Nm^3/t. Data cover both full and partial oxidation processes.

According to the data collection, the hydrogen content is reported as being between 18 % and 27 % by volume.

The process gas burns without additional fuel at approximately 900 °C to 950 °C. This combustion also reduces the final VOC emission. There are a number of options for the burning of the tail gas, including:

- a dedicated waste heat boiler to recover steam;
- a conventional steam boiler;
- gas engines to directly produce electrical power.

Emissions data from the data collection for periodic monitoring of five silver process plants using a thermal oxidiser with a waste heat boiler are shown in the table below.

Table 6.4: Emissions to air from the silver process (thermal oxidiser)

Plant reference	Concentration (mg/Nm^3)				
	Oxygen content (% O_2)	Formaldehyde	CO	NO_X	TVOC
FA025	3	0.1	12	6	0.9
FA054	2.6	2.28–4	78.5	< 2	< 2
FA059	3	NI	3.9	65.7	NI
FA002	3.5	0.06	0.4–2.2	3.7–18	0.8–2.6
FA032, FA064, FA068	3	0.3–4	4–80	18–55	10–30
NB: NI – No information.					

Data from one plant using a conventional steam boiler and gas engines (for generating electricity) is shown in the table below.

Table 6.5: Emissions to air from the silver process (boiler and gas engines)

Plant reference	Concentration (mg/Nm^3)			
	Formaldehyde	CO	NO_X	TVOC
FA050 - Boiler (1)	NI	27–93	< 2–45	< 1 (2)
FA050 - Gas engines (3)	NI	13–16	5	20–23 (1)

(1) Reference conditions are 3 % O_2.
(2) Figure provided is TOC.
(3) Reference conditions are 5 % O_2.
NB: NO_X arises from the combustion process. CO is present from incomplete oxidation and from combustion.
NI – No information.

The lean gas from the plant FA050 (in Table 6.5) has a calorific value of approximately 2 000 kJ/m^3. Approximately two thirds of the lean gas produced is used for the production of electricity in gas engines. The rest is used for steam production in four steam boilers.

The gas engines produce electrical energy (2 450 kW at an electrical efficiency of 34 %). The exhaust gas of these gas engines is led to catalytic converters to oxidise the CO of the exhaust gas. Steam boilers use the waste heat of the gas engines' exhaust to produce 1 300 kg/h steam at 10 bar (855 kW). Further energy is recovered by preheating the boiler feed water with the cooling water of the gas engines (12 000 kg/h, $\Delta T = 60$ °C, 835 kW). The remaining energy is lost via the mixture cooler, oil- and water cooler and by radiation of the engines. The overall energy utilisation is 52–57 % and the heat utilisation is 22–28 %. Due to the low combustion temperatures, the formation of NO_X is low. The amount of CO and unburnt H_2 in the exhaust gases is reduced due to the use of catalytic converters. The rest of the lean gas is used for steam production in flame tube boilers [86, UBA-Austria 1999].

6.3.1.2 Emissions from the metal oxide process

The primary source of formaldehyde process emissions is the process gas from the absorber. The emission composition and flow rates are affected by the percentage of absorber process gas recycled.

Unlike the silver process, the process gases from the metal oxide catalyst process contain little or no H_2, and the levels of combustible substances such CO, formaldehyde, methanol and dimethyl ether should be low under normal operating conditions. Thermal oxidation of the process off-gas would require the use of support fuels; therefore alternative strategies (such as catalytic oxidation) could be employed instead. Some dimethyl ether can be formed as a reaction by-product, although this should be present in only small quantities under normal operating conditions.

By recycling a portion of the oxygen-lean vent gas, the oxygen concentration in the reactor feed mixture can be reduced, making it possible for the concentration of methanol to be increased and still be below the explosive limit. This reduces the volume of reaction gases and thus reduces the emission rate of formaldehyde from the absorber [85, Rentz et al. 1999].

No data on the composition of the process gas were provided during the BREF revision. Composition data from the 2003 LVOC BREF (now amended by the TWG comments) are shown below.

Table 6.6: Composition of the process gas from the metal oxide process

Gas volume (Nm^3/t of product*)	2 300–2 400
Nitrogen and argon (% v/v)	91–93
Oxygen (% v/v)	5–7
Carbon dioxide (% v/v)	4
Formaldehyde (mg/Nm^3)	150–700 (~ 9 % of TVOC)
Methanol (mg/Nm^3)	500–2 000 (~18 % of TVOC)
Dimethyl ether (mg/Nm^3)	6–10 000 (~73 % of TVOC)

* Product is 100 % formaldehyde.
Source: Table 10.4. from 2003 LVOC BREF [190, COM 2003] as amended by comments from industry.

Emissions data from the data collection of seven metal oxide plants using a catalytic oxidiser are shown in the table below.

Table 6.7: Emissions to air from the metal oxide process (catalytic oxidiser)

Plant Ref	Concentration (mg/Nm^3)				
	Oxygen content (% O_2)	Formaldehyde	CO	NO_X	NMVOC
FA045	3	0.04	90	NI	NI
FA031	NI	0.61	40	NI	NI
FA041	4	5–20	100–250	1–25	80–200
FA010	5	1–5	15–50	NI	5–50
FA006	NI	2–27	NI	NI	NI
FA051	6	0.1–4.7	1–10	< 10	1–15
FA037	5.3	1–10.4	5.2–36.3	NI	5.4–43.5

NB: NO_X is formed as a cross-media effect of the abatement technique. CO is present from incomplete oxidation, both as a pollutant from the process and as a cross-media effect of the VOC abatement technique.

6.3.1.3 Monitoring of emissions

Information on the monitoring of emissions to air gathered from the data collection is shown in the table below.

Table 6.8: Emissions to air - monitoring methods and frequencies

Parameter	Monitoring method	Frequency	Average sampling period
CO	NS-EN 15058 ASTM-D-6522_00	Periodic (once a year) or continuous	3 x 30 minutes
TVOC	VDI 3481 B1.3 EN 12619	Periodic or continuous	30/60 minutes
NMVOC	NIOSH 1610:2003	Periodic	3 x 20 minutes
Methanol	UNI EN 13649:2002 NIOSH 2000:1998	Monthly or every two months	3 x 20/30 minutes
Formaldehyde	NIOSH 3500, USEPA Method 0011; VDI 3862-6; VDI 3862-2	Monthly or every two months	3 x 20/30 minutes
NO_X	ASTM-D-6522_00	Yearly	1 hour
SO_2	ASTM-D-6522_00	Yearly	3 x 30 minutes
Dust	UNE-EN13284	Yearly	3 x 30 minutes
Source: Data collection			

The majority of plants report monitoring TVOC and only some NMVOC. In the absence of methane in the waste gas, TVOC is the more appropriate parameter to use. Only one plant monitors continuously. The frequency of periodic monitoring ranges from monthly to yearly.

Only a few plants that use waste gases as a fuel in shared combustion units (boilers) report monitoring the combustion parameters (NO_X, SO_2 and dust). For more information on methods and standards used for monitoring formaldehyde and TVOC, see the ROM. [89, COM 2017].

6.3.1.4 Fugitive emissions and emissions from storage

Fugitives: The silver and oxide processes both run close to atmospheric pressure and so there is little pressure gradient to force fugitive emissions. Emissions from maintenance activities are negligible because it is easy to rinse residues from process equipment (both formaldehyde and methanol are water-soluble), but minor emissions do occur for infrequent short periods (e.g. during filter cleaning). VOC releases mainly consist of methanol and formaldehyde, but may also include some dimethyl ether (for the metal oxide catalyst process) and methyl formate.

Flanges can be a significant source of fugitive losses and, to minimise losses, a European plant has installed a 50-metre, one-piece (i.e. flange-less) absorption column that reduces maintenance and fugitive losses. Another source of fugitive losses can be relief devices such as rupture discs and pressure relief valves. These devices require periodic inspection and replacement.

VOC emissions to air from storage: Vents containing VOCs may occur from loading and unloading operations or from the purge of the equipment prior to a maintenance operation. Emissions during methanol and formaldehyde handling can occur from the decoupling of pipe connections, when the connections are not properly emptied before decoupling.

Typical breathing and fugitive emissions from storage and handling are given in Table 6.9 below.

Table 6.9: VOC emissions from formaldehyde storage and handling

	Emission factor from storage vents (g/t product)	
	Prior to treatment	**After treatment**
Storage – silver process	30	3 (with scrubber) 0.6 (with thermal oxidation)
Storage – oxide process	30	3 (with scrubber)
Handling – both processes	10	0.4 (with vapour recovery)
Source: [85, Rentz et al. 1999]		

6.3.2 Emissions to water

Under normal operating conditions, the silver and metal oxide processes do not produce any significant continuous aqueous waste streams.

Some discontinuous waste water streams are present from rinsing and cleaning. The rinsing of process equipment, for example prior to maintenance, creates a weak stream of hydrocarbons. The number of cleaning operations is highly dependent on the maintenance regime, and the frequency of discharge may range from 10 times per year to once every five years. Effluents may also arise from spills, vessel wash water and contaminated condensate (boiler purges and cooling water blowdown that are contaminated by upset conditions such as equipment failure). Many of these streams can be reworked into the process to dilute the formaldehyde product.

Some of these recovered streams may contain substances that have negative effects on the catalyst activity and are therefore not suitable for recycling to the vaporiser unless these substances are purged from the streams prior to reworking. According to the data collection, these purges from the process waters recycled back to evaporators on average range from 0.4 m^3/h to 10 m^3/h with maximum amounts rising up to 30 m^3/h, depending on the flow characteristics of the process streams.

Other occasional waste water streams are waste waters from the regeneration of ion exchange resins which, according to the data collection, on average range from 0.2 m^3/h to 1.2 m^3/h with maximum amounts rising up to 30 m^3/h. These waters contain small amounts of formaldehyde together with sodium formate and hydroxide.

In some cases of water streams with a high formaldehyde content it may be necessary to apply on-site pretreatment for these constituents at their sources, before being routed to the biological treatment, due to the high inhibition effect of formalin to biodegradation. However, in most cases, the aqueous effluent streams are treated in central facilities together with other streams.

Direct discharge to surface water is normal for unpolluted waste water from the cooling tower, boiler drain liquid and unpolluted rainwater as this reduces the hydraulic load on the WWTP [93, InfoMil 2000].

6.3.3 Raw material consumption

Although the dehydrogenation reaction that is at the heart of the silver catalyst process is endothermic (see Section 6.2.2, Equation 1) it can proceed because of the exothermic oxidation of some of the hydrogen that is produced from the dehydrogenation reaction (Section 6.2.2, Equation 2). This does not result in the wastage of any of the methanol raw material. However, other oxidation reactions can occur, notably of methanol and formaldehyde, that result in the additional direct or indirect consumption of methanol.

In the metal oxide process, the conversion of methanol to formaldehyde is exothermic in overall terms. However, some of the formaldehyde that is produced can also be further oxidised, as a result. This heat is obtained at the expense of an indirect increase in the specific methanol consumption (see Section 6.3.4).

The issue of specific methanol consumption is therefore closely related to the net energy consumption/export of the process. This is because the major factor influencing the proportion of methanol that is converted into formaldehyde is generally the extent to which methanol is over-oxidised.

The silver process typically consumes more methanol than the oxide process. The economic significance of this difference will depend on the methanol price and is partly offset by the higher rate of steam production (see Table 6.10).

Another important issue of the methanol feed is its purity. According to the data collection, operators report that they can use methanol of 97– 99.9 vol-% purity; nevertheless, purities higher than 99 vol-% are preferred.

6.3.4 Energy consumption and production

All the formaldehyde process routes are net producers of steam either due to the exothermic reaction or due to combustion of calorific off-gas. There is a strong link between the consumption of methanol and the rate of steam production. Over-oxidation of methanol (or formaldehyde) produces carbon monoxide and carbon dioxide and these reactions are far more exothermic than the reaction producing formaldehyde. Therefore, when more methanol is combusted to carbon monoxide and/or carbon dioxide, more heat is generated and more steam is produced, but the methanol yield is lower. Also, in partial methanol conversion a methanol distillation column needs to be employed which means the use of more steam and cooling water. This relationship is shown in Table 6.10 for the production of one tonne of 100 % formaldehyde by the different routes.

Table 6.10: Relationship between yield, steam export and electricity consumption

	Silver process – High methanol conversion	**Silver process - Partial methanol conversion**	**Oxide process**
Conversion of methanol to formaldehyde (%)	87–90	87–90	91–94
Methanol consumption (kg/t of 100 % formaldehyde)	1 185–1 226	1 185–1 226	1 135–1 151
Net steam export (t/t of 100 % formaldehyde)	2.6 (1) [0.4–1.2 t/t (2)]	0.4–1.2	2.0
Electricity consumption (incl. off-gas combustion) (kWh/t of 100 % formaldehyde)	50–100	50–100	80–190

(1) Roughly 45 % of this figure is due to off-gas combustion.
(2) Without off-gas combustion.
Source: Table 10.3 from 2003 LVOC BREF [190, COM 2003] amended by the comments from industry.

An important source of energy in the silver process is the combustion of off-gas rich in hydrogen, either in gas engines producing electrical energy (see Section 6.3.1.1, example plant FA050) or in conventional boilers producing steam, leading to an overall energy utilisation of 52–57 % and the heat utilisation of 22–28 %.

Important energy efficiency improvements in the metal oxide process are achieved by the recirculation of process off-gases from the absorber to the evaporator and the pressurisation of the incoming air with a turbocharger.

In terms of energy use, the silver process has moderate electricity consumption, because the process operates close to atmospheric pressure and the smaller gas volumes allow the use of smaller blowers. Electricity consumption in the oxide process is higher because the process gas is lean in methanol and the air content of the circulating gas is higher (excess air), which results in higher gas volumes. Also, the air compression and turbocharger consume additional electricity.

6.3.5 Co-products, by-products and waste generation

Almost all of the spent catalyst from reactors and off-gas oxidation can be regenerated and as a result there are minimal catalyst wastes for disposal. Deactivated formaldehyde catalyst is usually sent to a reclaimer for recovery of the valuable metals - either by recycling in a metallurgical process or by electrolytic regeneration to produce new catalyst. More than 99 % of the silver is typically recovered from spent silver catalyst. Iron and molybdenum can also be reclaimed from spent oxide catalyst. After metal reclamation, the inert catalyst carrier requires disposal by the reclaimer.

According to the information provided in the data collection, the frequency of the spent catalyst replacement in the metal oxide process varies from once every six months to once every two years, while the frequency of its replacement in the silver process varies from once every four months to once a year. The average amount of spent catalyst from the metal oxide process was reported to be in the range of 0.02 kg to 0.15 kg per tonne of 100 % formaldehyde.

A small build-up of solid paraformaldehyde may occur (principally at cold spots in equipment and pipes) and is removed during maintenance activities. Paraformaldehyde is a polymerisation product of formaldehyde with a typical degree of polymerisation of 8–100 units. Filters may also be used in the purification of formaldehyde product that gather paraformaldehyde. According to the data collection, paraformaldehyde is generated on average in a range from 0.01 kg to 0.13 kg per tonne of 100 % formaldehyde. Some sites also operate an integrated paraformaldehyde production process as part of the formaldehyde plant.

In the oxide process, the heat transfer fluid is periodically checked and in rare cases is changed. Spent fluid is most frequently sent to a reclaimer (for recycling) or incineration.

Wastes generated at Dutch and German formaldehyde plants are given in Table 6.11.

Table 6.11: Wastes generated at Dutch and German formaldehyde plants

Source	Destination	Waste generated (kg/tonne of product*)	
		The Netherlands	Germany
Reactor catalyst (Silver)	Recycling	0.04–0.1	
Reactor catalyst (Fe/Mo oxide on carrier)	Recycling	0.06	0.01
Catalyst from off-gas oxidiser (Pt on carrier)	Recycling	0.002 (1)	
Oil/filters	Disposal	0.06	0.51
Domestic, sewer sludge	Disposal	NI	

(1) CEFIC give a figure of 0.015 kg/t of product, with the spent platinum catalyst being recycled.
* Product is 100 % formaldehyde.
NB: NI – No information.
Source: Table 10.10 from 2003 LVOC BREF [190, COM 2003] as amended by the comments from industry

In the data collection, one plant reported that spent ion exchange resins are generated at a rate of 0.03–0.06 kg/t of 100 % formaldehyde.

6.4 Techniques to consider in the determination of BAT

This section describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this chapter. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations). Cross references to other chapters are used, where relevant to avoid repetition.

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 2.6 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

6.4.1 Techniques to reduce emissions to air

The composition and the pollutant load of the waste gas will depend on the reaction conditions and the design and operation of the absorbers that are used in the production process to recover the product. A suitable combination of absorbers will have the dual benefit of maximising formaldehyde and possibly methanol recovery and of reducing the pollutant load to final abatement – absorbers are therefore at least part of the formaldehyde production process, rather than an end-of-pipe abatement technique.

Once formaldehyde has been absorbed from the reaction gas, wet off-gas remains. This resulting stream contains small amounts of VOCs (methanol, formaldehyde). Further components are typically carbon monoxide, carbon dioxide, nitrogen, and:

- oxygen and dimethyl ether in the case of the metal oxide process; and
- hydrogen in the case of the silver process.

As this stream is the major individual source of emissions to air, whatever abatement device selected is normally shared with the rest of the vents from the process. According to the data collection, all formaldehyde plants employ a treatment of the main off-gas stream from the absorption column. In some plants, this treatment is shared with other waste streams on site, either from other production processes or with smaller streams from other sources (e.g. storage).

The off-gas is combusted to reduce emissions to air and to recover energy, but the type of combustion depends on its heating value.

6.4.1.1 Reduction of VOC and formaldehyde emissions

6.4.1.1.1 Thermal oxidiser with energy recovery or combustion unit

Description

Process off-gases, containing VOCs and formaldehyde, with high calorific value are combusted in thermal oxidisers or combustion units (gas engines, boilers). The VOCs and formaldehyde are oxidised/burnt and the heat is recovered as steam or for electricity generation. For a more detailed description of thermal oxidisers see Section 3.5.1.2.5 of the CWW BREF and for a more detailed description of combustion units see Sections 2.3.2 (Combustion engines) and 2.4 (Steam processes) of the LCP BREF.

Technical description

In the **silver process**, the off-gas has high heating value (typically 2 200 kJ/Nm^3 or 4 700 MJ/t of 100 % formaldehyde) because it contains excess hydrogen. This is due to the fact that the silver process operates under air deficit and this leads to free hydrogen resulting from the methanol dehydrogenation reaction. The off-gas is therefore amenable to combustion. The combustion can be in a dedicated thermal oxidiser with steam production or in a central boiler plant. Thermal oxidation has an estimated efficiency of 99.8 % [93, InfoMil 2000].

Given the possibly high hydrogen content (and therefore probable high calorific value) of the process gas purge stream, it could alternatively be combusted beneficially alone or along with commercial and/or other non-commercial fuels in gas engines or conventional boilers in order to recover energy. Whilst the hydrogen content is useful for generating steam on site, it may be too low to be recovered as hydrogen gas for commercial purposes.

Achieved environmental benefits

- Reduction of emissions of VOCs to air.
- Lower energy consumption for steam production either for formaldehyde production or for other units/processes on site.

Environmental performance and operational data

Emissions data are given in Table 6.4 and Table 6.5.

Cross-media effects

Emissions of NO_X and additional emissions of CO_2.

Technical considerations relevant to applicability

This technique is applicable in plants using the silver process. For existing plants, changes in the process will be restricted to major plant upgrades and will be dependent on the demand for steam.

Economics

Significant benefits from steam and possibly electricity generation.

Driving force for implementation

- Environmental legislation.
- Energy balance/efficiency of the site.

Example plants

- Thermal oxidiser with energy recovery: Dynea, Lilleström (NO); Bordsochem, Kazincbarcika (HU); Covestro (Bayer MaterialScience), Uerdingen-Krefeld (DE); Ercros, Almussafes (ES), Ercros, Tortosa, (ES)
- Combustion units: Metadynea, Krems (AT).

Reference literature
[93, InfoMil 2000].

6.4.1.1.2 Catalytic oxidiser with energy recovery

Description
Process off-gases, containing VOCs and formaldehyde, are oxidised over a catalyst and the heat is recovered as steam. For a more detailed description of catalytic oxidisers see Section 3.5.1.2.5 in the CWW BREF.

Technical description
In the **metal oxide process**, the off-gas has a low calorific value (typically 500 kJ/Nm^3 or 1 100 MJ/t of 100 % formaldehyde). Off-gas from the oxide process can be burnt in an existing central boiler plant but this tends to reduce the steam production capacity. More efficient combustion is provided by catalytic oxidation. Catalytic oxidisers have typical operating temperatures of 450–500 °C and a conversion efficiency to carbon dioxide and water of 99.7–99.8 %. Typical Pd/Pt wire catalysts on an Al_2O_3 support have a four- to six-year lifetime.

The heat transfer fluid used in the oxide process has a vapour pressure and will incur breathing losses. Waste gases from the heat transfer fluid circuit in the metal oxide process are oxidised in the catalytic oxidiser.

Steam production from catalytic oxidisers is small and the feasibility of raising steam this way is determined by local circumstances. However, it is estimated that a catalytic unit can produce 5 000 tonnes of steam per year.

Achieved environmental benefits

- Reduction of emissions of VOCs to air.
- Lower energy consumption for steam production either for formaldehyde production or for other units/processes on site.

Environmental performance and operational data
Emissions data are given in Table 6.7.

Cross-media effects
Waste from spent catalyst.

Technical considerations relevant to applicability
This technique is applicable to plants with the metal oxide process. The ability to recover energy may be restricted in small stand-alone plants.

Economics
No information provided.

Driving force for implementation

- Environmental legislation.
- Energy balance/efficiency of the site.

Example plants
DuPont, Dordrecht (NL); Momentive, Rotterdam (NL); Alder, Trieste (IT); Akzo Nobel, Kristinehamn (SE); Celanese/Hostaform, Frankfurt (DE); Fantoni, Osoppo (IT).

Reference literature
No reference literature provided.

6.4.1.2 Reduction of fugitive emissions

For occupational health reasons, extensive measures have been taken at formaldehyde plants to prevent VOC releases (including fugitives). Formaldehyde leaks can be detected without a sophisticated monitoring system because of the strong odour (detectable at about 0.8 ppm). Fugitive emissions are monitored indirectly by tests on the workspace formaldehyde concentrations to which operators may be exposed.

The occupational exposure limits (OELs) depend on national regulations in the Member States. Limits are normally expressed as an 8-hour and/or 15-minute time-weighted average. Sometimes a maximum exposure level (MEL) is given. In 2014 in Belgium, the OEL was 0.3 ppm as an 8-hour average with a maximum of four peaks of 0.6 ppm as a 15-minute average and a maximum value of 1 ppm. Whilst the values in other countries may vary, these numbers are not unusual.

Formaldehyde solutions with high concentrations solidify when spilt. Vapour emissions from spills are therefore low and the resulting solid material can be easily removed. If vapours do escape from liquid formaldehyde spills then foams can be used to reduce the loss and water can be sprayed over the vapour cloud.

The main technique to minimise fugitive emissions is a leak detection and repair (**LDAR**) programme (see Section 3.5.4.4 of the CWW BREF). Although it is difficult to predict the exact reductions in fugitive emissions that can be achieved by LDAR, it is reported that a quarterly inspection and maintenance programme (I/M) for pumps and valves has an overall efficiency for formaldehyde emissions of about 57 % (see Table 6.6). Monthly I/M for pumps and valves has an overall efficiency of about 69 %. The use of double sealed pumps, application of a rupture disc to relief valves, and monthly I/M for other valves has an overall efficiency of about 91 %. Double mechanical seals and rupture discs are virtually 100 % efficient in reducing emissions from pumps and relief valves [85, Rentz et al. 1999].

6.4.1.3 Reduction of emissions from storage

The storage tanks for methanol raw material and the various concentrations of aqueous formaldehyde product have emissions from breathing and from loading/unloading activities. The techniques that are available for reducing emissions of VOCs from storage under normal operating conditions, most if not all of which are described in the EFS BREF, include the following (among others):

- formaldehyde and methanol can be effectively removed from displaced gases using a water scrubber;
- the methanol storage vents are treated by thermal or catalytic oxidation over a noble metal, adsorption on activated carbon, a condenser, or connection to the suction of the process air blower;
- the formaldehyde storage vents are treated by thermal or catalytic oxidation, absorption in water (or connection to the suction of the process air blower, provided the necessary safety precautions are in place);
- the back-venting of displaced gases, e.g. during tank filling, would help avoid emissions, although such an approach would not be feasible where pressurised nitrogen transfers are practised.

An appropriate formaldehyde storage temperature is maintained as low temperatures (and/or a concentration increase) cause the precipitation of paraformaldehyde, whilst formic acid tends to form at high temperatures. Stabilisers may be added to enhance storage but they should not interfere with further processing. Stabilisers are selected to be compatible with end-user requirements and examples are lower alcohols, urea and melamine [42, Reuss et al. 2012].

In general terms, the size of storage tanks should be minimised but cognisance should be taken of the dynamics between the supply of methanol and use of formaldehyde so that interruptions to the continuous process are minimised. Storage capacity should consider the rate of usage of downstream processes and recognised downtime for maintenance. The storage of formaldehyde and methanol may also be subject to the provisions of the Seveso Directive.

6.4.2 Techniques to reduce emissions to water

The formaldehyde process does not generate waste water during normal operation, but waste water may arise because of incidents or from the rinsing of equipment prior to maintenance activity. For reasons of environmental protection, chemical installations have kerbed concrete floors, bunds, drainage channels, and retention tanks or sumps to collect any spills from tanks, reservoirs or other storage and handling equipment and rainwater (with possible contamination).

6.4.2.1 Reuse of water

Description and technical description
Reuse of aqueous effluents (originating for example from equipment cleaning, spills and other incidents, contaminated cooling water, rainwater or condensates from columns) as process water in the absorption column to dilute the formaldehyde product. See the description and technical description for multiple use and recirculation operations in Section 3.3.1.4 of the CWW BREF.

Achieved environmental benefits

- Reduction of waste water generation.
- Reduction of emissions of organic pollutants to water.

Environmental performance and operational data
Data on the quantities and contents of these waste waters are given in Section 6.3.2.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
The impurities and the formaldehyde content in waste waters may affect the applicability due to the product quality specifications.

Economics
The benefits derived from water reuse may be reduced by the operating and equipment costs incurred by the need to remove impurities.

Driving force for implementation
Environmental legislation and economics.

Example plants
FA005, FA027, FA028, FA029, FA041, FA069.

Reference literature
No reference literature provided.

6.4.2.2 Chemical pretreatment

Description

Aqueous effluents (from cleaning, spills and condensates) with a high formaldehyde content are chemically pretreated to convert the toxic formaldehyde into less toxic substances.

Technical description

Formaldehyde is easily oxidised with ozone or hydrogen peroxide, optionally supported by catalysts or UV radiation, to convert it into less harmful and more easily biodegradable compounds. Industrially used alternatives are:

- oxidation with hydrogen peroxide in acidic media with metallic ions (like Fe^{2+} in Fenton's reagent) [166, Schulte et al. 1995]; or
- oxidation with hydrogen peroxide in alkaline media (like NaOH).

Oxidation with hydrogen peroxide in alkaline media results in the formation of hydrogen that requires additional safety measures. For a more detailed description of chemical oxidation, see Section 3.3.2.3.3.3 of the CWW BREF.

Another alternative for converting formaldehyde into less toxic substances is reaction with sodium sulphite in which a complex (sodium bisulphite formaldehyde) that is easily biodegradable is formed [91, El Morsy 2003].

Achieved environmental benefits

- Reduction of emissions of organic pollutants to water.
- Prevention of the accidental increase of emissions to water.

Environmental performance and operational data

No information provided.

Cross-media effects

Depending on the pretreatment process, waste gas and/or sludge can be generated.

Technical considerations relevant to applicability

This technique is only needed for effluents which, due to their formaldehyde content, could have a negative effect on the downstream biological waste water treatment.

Economics

No information provided.

Driving force for implementation

Environmental legislation (local water discharge standards).

Example plants

No information provided.

Reference literature

[166, Schulte et al. 1995], [91, El Morsy 2003].

6.4.3 Techniques to improve process performance and reduce raw material and energy consumption

Process losses of methanol and/or formaldehyde occur through miscellaneous vents to air and water, flushing of the process unit, and incidental spillages, but the main losses are due to the reaction selectivity.

The selectivity of the formaldehyde production reaction depends on a number of closely interrelated factors such as: temperature, gas flow rate and composition, catalyst characteristics and reactor design features, which need to be balanced through process optimisation. For more information on the reduction of raw material consumption and energy efficiency, see Sections 2.4.5 and 2.4.6.

6.4.3.1 Process optimisation

The optimal balance of formaldehyde yield, methanol consumption and heat/steam generation takes into consideration the integrated site demands and process yields and losses.

The methanol consumption rate can be reduced by reducing the proportion of methanol that is over-oxidised. However, doing so will reduce the amount of steam that is generated from the process, and this may cause problems with heat integration measures, particularly where formaldehyde production is combined with the manufacture of other processes with a net energy demand.

6.4.3.2 Overall site energy efficiency

Electricity and steam are the two main utilities in formaldehyde production. As all formaldehyde units produce more steam than they consume, it is important that there is efficient energy management at the overall site level. As long as the industrial site is able to consume the excess steam delivered by the formaldehyde unit, then the steam excess can be maximised through heat recovery techniques from the hot process streams.

Trade-off between selectivity and energy generation
Steam production and methanol consumption are directly linked to process selectivity. The process selectivity is, in turn, a function of the carbon loss (as carbon monoxide and carbon dioxide) in the reactors. The lower the carbon loss, the higher the selectivity (i.e. less methanol is needed to produce each tonne of formaldehyde). However, the full oxidation of carbon is very exothermic (compared to the reactions producing formaldehyde) so high carbon loss produces more steam. High steam production can therefore be an indicator of a poorly performing catalyst and the possible need for catalyst regeneration.

Best practice gas compressors
The major electricity consumer of a formaldehyde unit is the process air blower. This is especially characteristic of the metal oxide process. The usual ways to reduce the energy consumption of blowers are applied, i.e. choice and efficient design of the blower, reduction of pressure drops (particularly over the catalytic bed) and recycling of the process gas.

Energy recovery
The energy efficiency of formaldehyde production by the silver process can also be improved by using the lean gas to produce electricity in gas engines and steam in steam boilers (see Sections 10.3.1.1 and 10.3.4, example plant FA050).

6.4.4 Techniques to reduce residues and waste

6.4.4.1 Minimisation of spent catalyst

Description
Control and optimisation of reaction conditions that affect the performance of the catalyst.

Technical description
The life of both the silver and oxide catalysts is adversely affected by long exposure to excessively high reaction temperatures and high throughput rates. This causes the catalyst to sinter and become matted with carbon deposits that cause an irreversibly excessive pressure loss across the catalyst bed [42, Reuss et al. 2012].

Significant improvements have been made to the selectivity, activity, lifetime and structural stability of catalysts through research and development. In general, good catalysts provide improved yield, improved production capacity and product quality, have a reasonable lifetime and have a good price to performance ratio.

As changing a catalyst requires a total reactor shutdown lasting 0.5 to 2 days (every 3 to 9 months) for the silver process and 3 to 4 days (every 5 to 30 months) for the oxide process, this operation is carried out on a scheduled basis. Larger reactors generally require longer shutdowns.

The main technique to prevent catalyst ageing is therefore to **optimise reaction conditions** and hence catalyst life. One way of reducing the frequency is to carefully control the reaction conditions, and primarily the **temperature**. The temperature is regulated either by water and/or gas recycling (so-called methanol or water ballast process) or fresh steam input, both affecting the methanol to air ratio and heat in the reactor. Due to its considerable heat capacity, water vapour may remove a significant proportion of the reaction heat, thereby preventing detrimental overheating and sintering of the catalyst and also helping to burn away the coke build-up on catalyst surface.

Another important aspect of catalyst lifetime and performance is process **feed purity** – either recycled streams or fresh methanol – as the amounts of impurities can affect the catalyst either through coke build-up (by-products from C_2 alcohols) on the catalyst surface or by catalyst poisoning. Formaldehyde solutions corrode carbon steel and so all exposed equipment is made of corrosion-resistant alloys (e.g. stainless steel). Pipes that convey water or gases are made of alloys that do not cause metal poisoning of the silver catalyst [42, Reuss et al. 2012].

Conceptually, the consumption of formaldehyde catalyst (in terms of tonnes/tonne of formaldehyde produced) could be minimised by running the catalyst for longer before replacement with a fresh batch. However, an ageing catalyst gradually loses its activity and selectivity, and eventually the continued catalyst operation is not justified.

Achieved environmental benefits
Reduction of the amount of waste (spent catalyst).

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
This technique is generally applicable to both the silver and metal oxide processes, but, due to the high recycling ability of silver catalyst, it is more of an issue for metal oxide catalysts. For existing plants, it is to be considered at major upgrades.

Economics
No information provided.

Driving force for implementation
Economics of costs and yields.

Example plants
Example plants using the metal oxide process: FA008, FA022, FA028, FA029, FA041 and FA047.

Reference literature
[42, Reuss et al. 2012], [167, Qian et al. 2003], [163, Gerberich et al. 2013].

6.4.4.2 Reduction of paraformaldehyde-containing waste for disposal

Description
Solid paraformaldehyde could form in cold spots of pipes, in storage tanks, filters and spots/places where liquid formaldehyde leaks from equipment (e.g. drips from pumps). To reduce the amounts of paraformaldehyde-containing wastes that need to be disposed of, a set of measures could be implemented. Paraformaldehyde-containing waste can emerge during maintenance activities (e.g. from filters installed upstream of the pumps or external solid deposits that are swept up).

To minimise these amounts, several approaches are employed:

- minimisation of paraformaldehyde generation;
- material recovery;
- use of paraformaldehyde residues as a fuel.

Technical description
Minimisation of paraformaldehyde generation
Internal deposits of solids can be minimised by improved heating, insulation and flow circulation. However, even if the system is carefully heated and insulated, its formation cannot be totally prevented.

Paraformaldehyde solids formed in storage facilities can be minimised by storing them above a minimum storage temperature and for under a certain period of time, e.g. 37 % formaldehyde solution with less than 1 % methanol should be stored above 35 °C for less than three months. Lower temperatures (and/or a concentration increase) and longer storage periods cause the precipitation of paraformaldehyde. Stabilisers may be added to enhance storage but they should not interfere with further processing. Stabilisers are selected to be compatible with end-user requirements and examples are lower alcohols, most commonly methanol, urea or melamine [42, Reuss et al. 2012].

Material recovery
The solid paraformaldehyde can be dissolved, either in hot water (for recycling in the process) or in ammonia (for reuse, for example, in a hexamethylene tetramine unit).

If the recovered paraformaldehyde is of a suitable purity it can also be used as a feedstock in polymer resin production, where a low water content is more favourable in order to control the reaction rate. Paraformaldehyde is often used as a partial replacement of formalin in phenol-, urea- and melamine-formaldehyde resins [126, Reuss et al. 2012].

Use of paraformaldehyde residues as a fuel
If paraformaldehyde cannot be recovered, it can be used as a fuel in a suitable combustion unit.

Achieved environmental benefits

- Reduction of waste for disposal.
- Use of paraformaldehyde as a fuel improves energy efficiency.

Environmental performance and operational data
No information provided.

Cross-media effects
Minimisation of paraformaldehyde formation and its recovery improve the production yield.

Technical considerations relevant to applicability
Material recovery is not applicable when the recovered paraformaldehyde cannot be used due to impurities or is insoluble.

Economics
No information provided.

Driving force for implementation
Economics.

Example plants
Example plants that use on-site incineration if material recovery is not possible: FA026, FA028, FA033, FA060.

Reference literature
[42, Reuss et al. 2012], [163, Gerberich et al. 2013].

6.5 Emerging techniques

The existing process routes for the production of formaldehyde from methanol over catalysts compete in development and innovations to increase the yields, energy efficiency and overall economics of the processes.

A continuous improvement of the catalysts and reaction conditions can be observed. The improvement of catalysts might lead to a reduction in methanol consumption. Fundamental changes regarding the catalyst including the use of additives or carrier materials might also lead to a change in the by-products and solid wastes due to the catalyst recycling.

In recent years, there has been some progress in the research and development of different process routes to produce formaldehyde from other feedstock – like CO_2 and seawater, using boron-doped electrode to reduce the CO_2 in an electrochemical process [168,Nakata et al.2014].

Another option is the production of formaldehyde from synthesis gas via hydrogenation of carbon monoxide in a slurry reactor with catalyst powder in a 5 % methanol solution in water [169, Bahmanpour et al. 2015].

Due to these methods having lower yields and selectivities than those achieved in the currently employed process routes, they have not yet been commercialised or used on an industrial scale.

7 ETHYLENE OXIDE AND ETHYLENE GLYCOLS

7.1 General information

Although ethylene oxide (EO) and ethylene glycols (EG) can be produced separately, nearly all European installations produce a mix of products in integrated plants. These production processes are therefore considered together in this chapter.

Ethylene oxide is an important chemical intermediate used in the production of ethylene glycols (as described here), but also detergent ethoxylates, ethanolamines, glycol ethers and polyols. A very small portion of the EO produced is employed directly as a sterilising agent and as a fumigation chemical. It is produced by the oxidation of ethylene. Ethylene glycol is a collective term that refers to monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG). It is produced by reacting ethylene oxide with water. MEG is mainly used for the manufacture of polyester fibres and polyethylene terephthalate (PET); other uses include as an anti-freeze in cooling systems (e.g. car radiators). DEG is used in many applications like in the production of unsaturated polyester resins and in polyurethane systems, and TEG is used mainly in the production of polybutylene terephthalate foils and for gas purification and drying. [90, REBSDAT et al. 2012].

Industrial production of EO started in 1937 with a Union Carbide process based on ethylene and air. In 1958, oxygen (rather than air) processes were introduced by Shell Development Company, and now most European EO plants are based on pure oxygen feedstock. Ethylene glycols are produced by reacting EO with water. About 40 % of the European EO produced is converted into glycols, although worldwide the figure is about 70 %. [41, CEFIC 2010].

Although production plants can be designed to produce either just high-purity ethylene oxide or just ethylene glycols, it is more normal for a plant to produce a mixture of the two. This reflects the fact that the production of ethylene glycol is a major end use for ethylene oxide, and that the handling and transportation of ethylene oxide is hazardous. However, there are also process integration drivers for producing a mixture of the two at the same location - the manufacture of ethylene oxide inevitably results in the formation of some ethylene glycols, and the excess heat generated during the production of ethylene oxide can be used to offset the energy demand associated with the dewatering and separation of ethylene glycols.

The total European production capacity of EO (ex reactor) is about 3 000 kt/yr.

Table 7.1: European producers of ethylene oxide and ethylene glycol

Country	Company	Location	EO capacity* (kt/yr)
Belgium	BASF	Antwerp	500
Belgium	Ineos Oxide	Antwerp	420
France	Ineos Oxide	Lavera	220
Germany	BASF	Ludwigshafen	345
Germany	Ineos Oxide	Dormagen	290
Germany	Clariant	Gendorf	240
Germany	Sasol	Marl	216
The Netherlands	Shell	Moerdijk	305
The Netherlands	Dow	Terneuzen	170
Poland	PKN Orlen	Plock	Approx. 100**
Spain	IQOXE	Tarragona	130
Sweden	Akzo Nobel (S)	Stenungsund	115
Total			3 050

* Nominal 2014 EO capacities.
** 2012: EO 27 kt + glycols 74 kt [115, Orlen 2012].

EO and EG are sold on chemical specification, and competition between producers is heavily geared towards price and margins are low. The EG market is global and prices are strongly influenced by the price of ethylene. In 2010, the global market of MEG was 18 900 kt, growing on average at 3.7 % per year [103, Nexant Inc 2011].

Key environmental issues

The key environmental issue for the production of ethylene oxide and ethylene glycols is the emission to air from the EO section (VOCs and ethylene oxide).

7.2 Applied processes and techniques

7.2.1 Process options

The principal option for the production of ethylene oxide is the direct oxidation of ethylene, and this is the only process described in detail in the subsequent sections of this chapter. It has replaced the chorohydrin route which is also briefly reviewed below.

The principal option for the production of ethylene glycol is the thermal hydrolysis of ethylene oxide, and this is the only process described in detail in the subsequent sections of this chapter. An alternative is the hydrolysis of ethylene carbonate to produce monoethylene glycol (MEG) which is also briefly reviewed below.

7.2.1.1 Production of ethylene oxide

7.2.1.1.1 Direct oxidation of ethylene

Ethylene oxide can be produced commercially by the catalytic direct oxidation of ethylene using air or oxygen. However, the use of air has now been fully superseded by the use of oxygen in the EU-28.

Ethylene oxide (EO) is formed by reacting gaseous ethylene and oxygen over a solid, silver-containing catalyst. The exothermic reaction is carried out at an elevated temperature (200–300 °C) and pressure (15–25 bar) with a residence time of a few seconds. Very small amounts of acetaldehyde (from isomerisation of EO) and formaldehyde may also be produced.

$$C_2H_4 + \frac{1}{2}\,O_2 \rightarrow C_2H_4O \text{ (+105 kJ/mol)}$$

The main side products are carbon dioxide and water, which result from a highly exothermic reaction:

$$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O \text{ (+1323 kJ/mol)}$$

Ethylene oxide may also be oxidised to carbon dioxide and water.

The ratio between the above two reactions defines the selectivity of the process (i.e. the amount of ethylene converted to EO on a molar basis) and is mainly determined by the type of catalyst used. The selectivity to EO is 75–90 % (for the oxygen process) at an ethylene conversion of 8–10 %.

The reaction gases are recycled back to the oxidation reactor once the ethylene oxide product has been removed and there is therefore a need to control the build-up of carbon dioxide produced as a result of the full oxidation of some of the ethylene. Often, carbon dioxide is isolated for beneficial use.

In 2013, the direct oxidation route using oxygen was the only one in use in the EU, and it was anticipated that any new plant would also adopt the use of oxygen rather than air. Therefore it is the only route for the production of ethylene oxide that is considered further in this chapter.

7.2.1.1.2 Chlorohydrin route

This costly, two-stage process involves the liquid-phase reaction between ethylene and hypochlorous acid to form an ethylene chlorohydrin intermediate, followed by conversion to EO with hydrated lime. The EO selectivity is about 80 %. However, this route results in the formation of unwanted ethylene dichloride and calcium chloride. Due to the high cost of chemical feedstocks (especially chlorine) and the considerable effluent load, this route has been replaced by direct oxidation and is therefore not considered further in this chapter.

7.2.1.2 Production of ethylene glycols

7.2.1.2.1 Thermal hydrolysis of ethylene oxide

At the time of writing (2015), the thermal hydrolysis of ethylene oxide accounts for all of the ethylene glycols manufactured in the EU.

This route involves the following sequence of process steps:

- reaction of ethylene oxide with a significant stoichiometric excess of water at a temperature of 120–250 °C and a pressure above 10–40 bar;
- separation by distillation (and subsequent recycling) of the water from the ethylene glycols mixture;
- separation by distillation of the mono-, di-, tri- and polyethylene glycols, employing progressively higher levels of vacuum.

The process can be summarised as shown below.

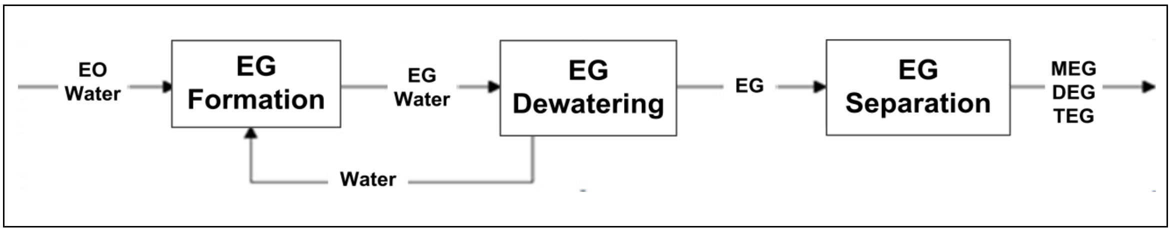


Figure 7.1: Process flow diagram for ethylene glycol production

In commercial units, the crude glycols mixture typically contains between 75 wt-% and 92 wt-% monoethylene glycol (MEG).

$$\underset{\text{EO}}{C_2H_4O} + \underset{\text{water}}{H_2O} \rightarrow \underset{\text{MEG}}{HO\text{-}C_2H_4\text{-}OH}$$

The main co-product in the MEG manufacturing process is diethylene glycol (DEG), which is formed by the reaction of MEG with EO.

$$\underset{\text{MEG}}{HO\text{-}C_2H_4\text{-}OH} + \underset{\text{EO}}{C_2H_4O} \rightarrow \underset{\text{DEG}}{HO\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}OH}$$

The DEG can react further again with EO (ethoxylation) to form triethylene glycol (TEG) and heavier glycols.

$$\underset{\text{DEG}}{HO\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}OH} + \underset{\text{EO}}{C_2H_4O} \rightarrow \underset{\text{TEG}}{HO\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}OH}$$

7.2.1.2.2 Hydrolysis of ethylene carbonate

Ethylene oxide can be reacted with carbon dioxide (using the CO_2 evolved from the oxidation of ethylene to ethylene oxide) to produce ethylene carbonate as an intermediate. The subsequent hydrolysis of ethylene carbonate results in the selective production of monoethylene glycol (which is quite often the preferred co-product) and is effectively a variation on the thermal hydrolysis route albeit requiring less water for the reaction.

The process is applied in some new plants outside Europe, e.g. by Lotte Petrochemicals in Daesan, South Korea; by Petro Rabigh, a Saudi Aramco/Sumitomo Chemical joint venture, in Rabigh, Saudi Arabia; and by Shell in Singapore [114, Shell 2009]. From an economic point of view, it may be the preferred route where (unlike in Europe) the market demand for DEG and TEG is low.

At the time of writing (2015), this route is not used in the EU and is therefore not considered further in this chapter.

7.2.2 Direct oxidation route

The manufacture of ethylene oxide using oxygen is shown in Figure 7.2 below.

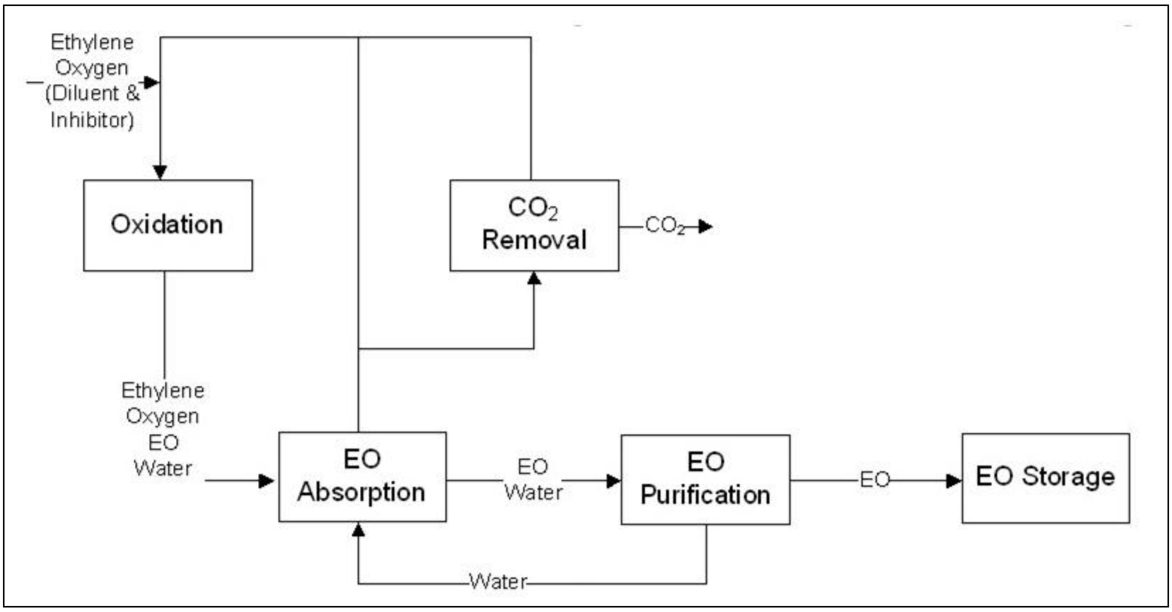


Figure 7.2: Process flow diagram for ethylene oxide production

EO/EG processes can be designed for the production of:

- glycols only (without high-purity EO recovery);
- high-purity EO only with a minimum production of unavoidable glycols;
- a product mix of high-purity EO and glycols in an integrated plant.

In practice, the third configuration is usually adopted because:

- MEG is the most important outlet for EO;
- the EO process intrinsically forms glycols, which require work-up;

- it provides efficient heat integration of the exothermic EO and energy-consuming EG stages (the reaction of EO and water to make glycols is exothermic but the glycol plant is a net consumer due to the large heat demand of the evaporation and distillation stages).

Although there are a number of different EO/EG manufacturing process licensors, the process technologies are broadly similar and the unit operations can be grouped into four stages:

- Stage 1: EO reaction, EO recovery and carbon dioxide removal;
- Stage 2: non-condensables removal and EO purification;
- Stage 3: glycols reaction and dewatering;
- Stage 4: glycols purification.

These steps are described in detail below.

7.2.2.1 Ethylene oxide reaction (Stage 1.1)

Feedstock ethylene is typically received by pipeline from a steam cracker. The oxygen can be provided by air (in an air-based process) but modern processes are based on pure oxygen supplied by pipeline from an air separation unit. Both the oxygen and the ethylene have to be extremely pure.

The reaction between ethylene and oxygen is carried out in a multi-tubular, fixed-bed type reactor, with a silver catalyst in the tubes and a coolant on the shell side. The heat generated by the exothermic reactions is removed by the coolant and is recovered by producing steam. The steam is used as a heating medium in various sections of the plant.

A large gas flow is circulated continuously through the EO reactors. Reaction products (EO, carbon dioxide and water) are removed from the circulating gas while unconverted oxygen and ethylene are recycled back to the reactor. There is a fire and explosion risk with heterogeneously catalysed direct oxidation processes and the recycle gas therefore contains a diluent which allows operation at oxygen levels that do not create a flammable mixture. All sites that responded to the questionnaire use methane as a diluent which, in comparison to nitrogen, allows for higher oxygen levels, is more effective in limiting temperature rise, requires less energy for the recirculation/compression of the process gases and allows the use of purge gases as fuels. (However, occasionally methane may not be available; in that case, nitrogen would be used for a limited period of time.) A small amount of an organic chlorinated compound (typically ethylchloride or dichloroethane) is added to the recycle gas for catalyst performance control and the chlorine will end up in various product and effluent streams, partly as inorganic chloride (e.g. NaCl).

A vent stream, the inerts purge, is taken from the recycle gas (about 0.1–0.2 vol-%) in order to reduce the build-up of inerts like ethane, argon and nitrogen, and impurities present in the ethylene and oxygen feedstocks. The inerts vent is typically used as fuel gas and burnt (e.g. in a cracker furnace or steam boiler).

Make-up ethylene, oxygen and diluent are added to the recycle gas loop.

Plants that in the past that used air instead of pure oxygen as a feedstock had a slightly different configuration: In order to dispose of the large volume of inert nitrogen that enters the process via the air feed, part of the recycle gas was routed to a second EO reactor (purge-reactor) to convert most of the ethylene. EO was recovered from the purge-reactor product gas via absorption in water, and the remaining gases (unconverted ethylene, nitrogen and carbon dioxide) were vented to atmosphere. When compared with pure oxygen plants, air-based plants had higher atmospheric emissions and lower yields.

7.2.2.2 EO recovery (Stage 1.2)

EO is completely miscible with water. At ambient temperatures and in the absence of catalysts, the reactivity of EO with H_2O (to form glycols) is very low over a wide pH range, which makes water a suitable scrubbing medium for EO removal/recovery. EO is recovered from the gaseous reactor effluent by absorption in water. The aqueous EO solution from the absorber is concentrated in a stripper (desorber). The top stream of the stripper is a concentrated EO-water mixture that is routed to a section for non-condensables removal and EO purification (Stage 2, see below). The bottom stream of the stripper is an EO-free water stream that is cooled and returned to the EO absorber.

Typically one or more bleed streams are taken from the EO recovery section to reduce the accumulation of glycols and/or salts, which are further processed to recover EO and/or glycols.

7.2.2.3 Carbon dioxide removal (Stage 1.3)

Part of the recycle gas that leaves the EO absorber is routed through a column in which carbon dioxide (generated in the oxidation process) is removed by absorption under pressure as hydrogen carbonate in a hot potassium carbonate solution:

$$CO_2 + K_2CO_3 + H_2O \rightarrow 2\ KHCO_3$$

The carbon dioxide is subsequently removed from the carbonate solution in an atmospheric stripper (back reaction). The carbon dioxide vent from the top of the stripper is either routed to atmosphere or recovered for further use (e.g. carbonated drinks), after treatment to remove VOCs. The regenerated carbonate solution from the stripper bottom is cooled and recycled to the carbon dioxide absorber. The carbon-dioxide-depleted overheads stream from the absorber is recombined with the recycle gas stream and routed to the EO reactor(s).

7.2.2.4 Non-condensables removal and EO purification (Stage 2)

The overhead stream of the EO stripper (desorber), an EO-steam mixture, is partially condensed and routed to a purification unit for removing traces of carbon dioxide, ethylene and other non-condensables, e.g. by stripping. The non-condensables are routed back to the recycle gas loop while the purified EO-water mixture is routed to a unit for high-purity EO recovery and/or to the glycols reactor.

Most plants in Europe have an EO purification unit in which high-purity EO is recovered via distillation from the purified EO-water mixture. The remaining process water is either recycled to the EO recovery section or routed to the glycols unit. The EO product is typically chilled and routed to storage.

EO is a gas at ambient temperatures. It is generally stored under a nitrogen blanket below the boiling point (10.8 °C), although it can also be stored at ambient temperatures and elevated pressures. Vent gases from EO storage and other EO-containing vent gases are typically routed to atmosphere via an absorber that recovers the EO and recycles it to the process. If not used immediately on site, EO is normally shipped in railroad tank cars that are loaded directly from plant storage tanks. The transfer generally occurs at about 350 kPa nitrogen pressure.

7.2.2.5 Glycols reaction and dewatering (Stage 3)

Glycols are manufactured by feeding a mixture of EO and water to a reactor that is operated at an elevated temperature (typically 150–250 °C). Under these conditions, reaction rates are fast and no catalyst is required. Sufficient residence time is provided to react all the EO to full conversion. A reactor pressure of 10–40 barg is typically applied to avoid vaporisation of the EO. The reactor feed contains an excess of water in order to limit the adiabatic temperature rise and to enhance the selectivity to MEG. Typically the glycol products consist of 75–92 wt-% MEG, with the remainder being DEG and some TEG. All (100 %) of the EO feed is converted into glycols (either MEG, DEG, TEG or heavy glycols).

The product stream from the glycols reactor contains the various glycol products and the excess water. The excess water is removed by multiple-effect evaporation with subsequent vacuum distillation and, after heat exchange, is recycled back to the glycols reactor. A bleed is taken from the recycled water to reduce the build-up of impurities. Low-pressure steam generated in this stage is used as a heating medium at various locations in the plant.

7.2.2.6 Glycols purification (Stage 4)

The water-depleted crude glycol stream is fractionated in a number of vacuum columns to recover the individual glycol products at a high purity level. Co-products in the MEG manufacturing process are, in decreasing amounts, diethylene glycol (DEG), triethylene glycol (TEG) and heavier glycols. The individual glycol products are recovered by subsequent fractionation. The glycol products are cooled and routed to storage. The bottom stream from the last vacuum column contains the heavier glycols and can be sold for further glycol recovery or sent for disposal (e.g. incineration).

7.2.3 Other than normal operating conditions

OTNOC operations cover planned and unforeseen events. They may result in higher or lower emissions and affect one or more environmental media. Emissions to the environment will depend on the systems in place to prevent an increase in emissions (e.g. redundancy or back-up systems for key abatement devices) and to prevent unforeseen events (see Section 2.4.11).
The following lists are examples of operations that deviate from the stable and normal operating procedures.

7.2.3.1 Specific other than normal operating conditions

The following operations deviate from the stable and normal operating procedures:

- Product isolation: A problem with the operation of the ethylene oxide scrubber would result in higher quantities of ethylene oxide in the recirculating gases and therefore in the purged gas stream. As ethylene oxide has a high vapour pressure, a problem with incomplete recovery of ethylene oxide from the recycled scrubbing water could also result in an elevated ethylene oxide level in the recirculating gases post-scrubbing.
- Heat removal: The oxidation is exothermic and this heat is normally removed by vaporising water to produce steam (or by heating oil). If the supply of water (or oil) were to be interrupted or reduced to a problematic level, or some other problem occurred that gave rise to the same outcome, this could result in the overheating of the reactor, which could in turn result in a runaway reaction, and therefore a need for the pressure relief system to operate.
- Overdosing: The overdosing of the organochlorine inhibitor would increase the amount of this that is present in the recirculating process gases and therefore the amount that would be present in the purge gas stream.
- Contamination: The presence of a substance that would catalyse the polymerisation of ethylene oxide could result in a runaway reaction that would probably require the operation of emergency relief systems, resulting in a release to the environment.

7.2.3.2 Generic other than normal operating conditions

The following generic events deviate from standard operating procedures in EO manufacturing plants:

- Routine start-up: The process of filling the plant could result in displaced gases that would ultimately need to be vented.
- Shutdown for maintenance preparation: When the plant is shut down its inventory will need to be removed, and a process of purging may be employed in order to eliminate hazardous substances (and ethylene oxide in particular), particularly where maintenance activities are anticipated. This involves equipment flushing, a higher load being sent to the WWT, and potential emissions to the surface water (rainwater) header.
- Malfunction of pressure control: A problem with a storage tank's pressure control system (possibly the nitrogen supply valve or a terminal PSV) could result in ongoing emissions. This could be a particular issue where pressurised nitrogen filling operations are practised.
- Malfunction of temperature control: A problem with the supply of chilled cooling service (due to a stuck valve, pump failure, control loop issue, etc.) could lead to 'boiling' and therefore an over-pressurisation that might lead to an emission.
- Malfunction of abatement: A problem with any scrubber or oxidiser whose duty it is to abate emissions from storage.
- Air leakage greater than normal into systems that operate under vacuum: This will increase the ejector water/steam usage, and net emissions to water or air.
- Plant idle due to loss of containment caused by corrosion or operation of a rupture disc.
- Service or utility failure: Malfunction of cooling water and/or chilled water, power, distributed control system (DCS), or instrument air.

7.2.4 Equipment important for environmental protection

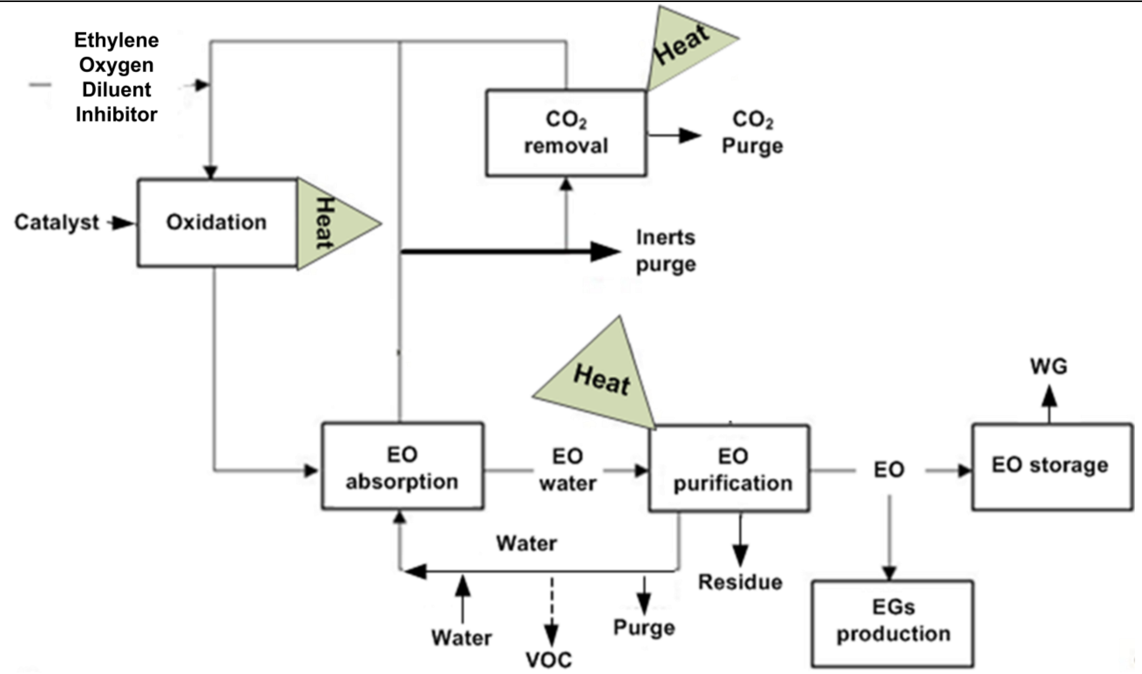
The following systems perform important operations for environmental protection and require the longest uptime possible:

- air:
  - vent gas treatment (scrubbers, oxidisers);
  - recycled gas control in oxidation loop;
  - CO_2 removal/treatment system;
- water:
  - stripping;
- waste:
  - catalyst management system/procedures.

7.3 Current emission and consumption levels

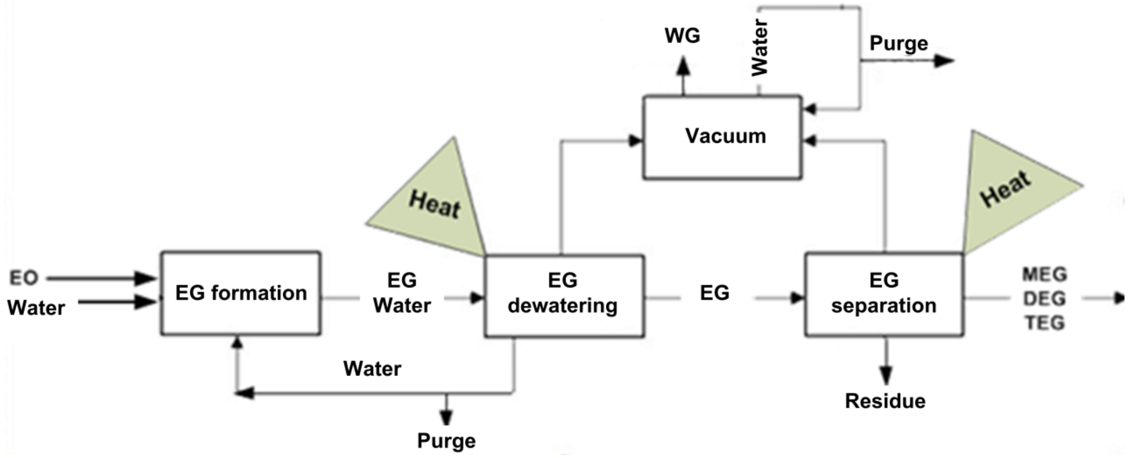
If not stated differently, the emission and consumption data in this chapter for the production of ethylene oxide refer to the oxygen-based process using methane as a diluent. In some places, information for the former air-based process is included mainly in order to illustrate the environmental benefits of the oxygen-based route.

The main sources of emissions to air and water are shown in Figure 7.3 for the EO plant and in Figure 7.4 for the EG unit.



NB: WG: Waste gas

Figure 7.3: Block flow diagram of an EO plant and its emission sources



NB: WG: Waste gas

Figure 7.4: Block flow diagram of an EG plant and its emission sources

7.3.1 Emissions to air

A rather dated report [130, EC VOC Task Force 1990] gives average VOC arisings (prior to treatment) from ethylene oxide plants as 20.5 kg/t of ethylene oxide product. In air-based plants VOCs mainly arise from the secondary absorber vent and the fractionating tower vent, whilst in oxygen-based plants the main sources are the vent gas scrubber and the carbon dioxide absorption system. A comparison of VOC arisings is given in the table below.

Table 7.2: Specific emissions to air from EO production

	Air-based plants	**Oxygen-based plants**
Methane (kg/t of EO product)	6	3
Ethylene (kg/t of EO product)	92	0.1–2.5
Ethylene oxide (kg/t of EO product)	1	0.5

7.3.1.1 Inerts purge from the reaction section

Contrary to the air-based process where the inerts purged from the gas loop form a large stream, the inerts purge from the oxygen-based process is only a small part of the recycled gas (e.g. 0.1–0.2 %) and consists mainly of hydrocarbons (e.g. methane, ethane) as well as some argon and nitrogen. Small amounts of ethylene dichloride or ethyl chloride, which are used in small quantities to modify the oxidation reaction, are also present. This stream is passed to the fuel gas network for combustion.

The purge can be located upstream (as shown in Figure 7.3) or downstream of the CO_2 removal step. According to the data collection, approximately half of the installations have the purge upstream of the CO_2 removal and half downstream.

The composition of the inerts purge is as follows:

- Some of the carbon dioxide that results from the full oxidation of a portion of the ethylene will be present irrespective of whether the purge occurs before or after the CO_2 removal step. Due to the desire to target selectivity rather than per pass conversion efficiency, the recirculating process gas will also contain significant unreacted/unoxidised ethylene, and there will also be unreacted oxygen present. The relative proportions of ethylene, oxygen and carbon dioxide will depend on the addition rates of the reagents, the conversion rate and selectivity of the oxidation reaction, and the location at which the purge stream is removed.
- The recirculating process gas, and therefore the purged gas, still contains some traces of ethylene oxide.
- The addition of an organochlorine inhibitor (such as ethylchloride or dichloroethane) to help minimise the proportion of ethylene that is fully oxidised to carbon dioxide will mean that this too will be present in the recirculating gases (no more than trace levels).
- A diluent, normally methane, will normally be added to allow the process to operate safely at a higher oxygen concentration. According to the data collection, under normal operating conditions all installations use methane as a diluent.
- Contaminants present in the raw materials (e.g. ethane and argon) and by-products formed within the process (e.g. acetaldehyde, formaldehyde, acetic acid and formic acid) will also be present at generally very low levels in the purge gas stream, although some of these (and also some ethylene) will be absorbed to a certain extent during the ethylene

oxide scrubbing step, and may ultimately form part of the light ends [40, US EPA 1986], [42, Reuss et al. 2012], [90, Rebsdat et al. 2012].

7.3.1.2 Emissions to air from the CO_2 removal section

A portion of the ethylene is fully oxidised to carbon dioxide, and some of this therefore needs to be removed from the recirculating process gas stream in order to maintain the CO_2 concentration at an appropriate level. Carbon dioxide is removed from the recirculating process gases by absorbing an appropriate proportion of the recycled process gas after ethylene oxide isolation into an appropriate medium (normally potassium carbonate), from which the carbon dioxide can subsequently be desorbed by stripping.

In the oxygen-based process, the overhead stream of the carbon dioxide stripper (shown as the CO_2 purge in Figure 7.3) contains carbon dioxide, water (steam) and small amounts of ethylene, methane, EO and aldehydes. It can be treated by thermal or catalytic oxidation. The resulting stream is essentially pure carbon dioxide (and water) containing traces of hydrocarbons (methane and/or ethylene). Where possible, it is sold to a customer. More often, the treated stream is vented to atmosphere. Specific emission levels are given in Table 7.3.

Table 7.3: Specific emissions to air from EO processes

	Before treatment		**After treatment**	
	All units	**Lowest 50 %**	**All units**	**Lowest 50 %**
Ethylene (kg/t of EO ex reactor)	0.1–2	NI	NI	NI
Methane (kg/t of EO ex reactor)	0–1	NI	NI	NI
Ethylene and methane (kg/t of EO ex reactor)	0.4–3	0.4–1	0*–3.1	0*–0.2

* In the case of treatment by catalytic/thermal oxidation, the emissions are considered to be zero.
NB: NI No information provided.
Source: [41, CEFIC 2010]

The following ranges have been derived (for the oxygen-based process) from the questionnaires.

Table 7.4: Specific emissions to air from the CO_2 purge of the EO processes

	Without/before final treatment		**After catalytic oxidation**	
	No of installations	**Emission (kg/t of EO ex reactor)**	**No of installations**	**Emission * (g/t of EO ex reactor)**
Methane	3	0.03–1.45	3	0.2–8
NMVOC	3	0.07–1.35	3	0.8–9

* Including installations where the CO_2 stream is marketed instead.

The reported common methods for monitoring these streams are as follows.

Table 7.5: Monitoring methods for emissions to air

	NMVOC	**Methane**	**Aldehydes**
Analytical method	DIN EN 13649 GC, GC/MS, HPLC	ISO 14965 EN GC	DIN EN 13649 GC/MS, HPLC
Frequency	Once a year	Once a year	Once a year
Sample size	1 000 cm^3	1 000 cm^3	1 000 cm^3
Reference	Dried CO_2	Dried CO_2	Dried CO_2

7.3.1.3 Emission of VOCs to air from EO isolation

The water into which the ethylene oxide is absorbed will also contain some of the various VOCs that are present in the recirculating process gas (e.g. ethylene, aldehydes, organochlorine inhibitor), and these are stripped from the desorbed ethylene oxide prior to its purification. The overheads from the column are also likely to contain some ethylene oxide. If they are not recycled to the process, the fact that they may contain ethylene oxide and other VOCs means that they would need to undergo appropriate treatment before release.

7.3.1.4 Emissions of EO to air from scrubbers

The common treatment system for EO-containing vent streams, e.g. from EO recovery/purification, is a wet scrubber that recovers EO. It has an overhead stream of nitrogen that contains some EO. If no further VOC abatement is required, this scrubber outlet stream is vented to atmosphere. The range of EO concentrations for all units is 0.1–40 ppm wt (around 0.13–54 mg/Nm^3), and the lowest 50 % of units contain 0.1–3 ppm wt (around 0.13–4 mg/Nm^3) [116, CEFIC 2000], [90, Rebsdat et al. 2012], [41, CEFIC 2010].

7.3.1.5 Emissions to air from EG fractionation

Non-condensable gases are vented from the vacuum system(s) serving the evaporators and distillation columns that are employed to respectively dewater and separate the individual ethylene glycols.

The substances present in the evacuated gases may include:

- ethylene glycols: these have very low vapour pressures and are unlikely to be emitted in material quantities where efficient condensation is employed;
- VOCs: any light ends (volatile aldehyde by-products that are produced during the hydrolysis step and any unreacted ethylene oxide) should be recycled with the water.

7.3.1.6 Emissions to air from open cooling of the EO absorbent

The aqueous bottom stream of the EO stripper (desorber) (see Section 7.2.2.2) needs to be cooled before being returned to the EO absorber in order to maintain scrubbing efficiency.

While most plants use indirect cooling, in some plants the water used to absorb EO is cooled down in a cooling tower. As this water contains some traces of organics, the air from the cooling tower contains VOCs. There is no direct treatment of the gas stream leaving the cooling tower and cooling tower vapours are vented to atmosphere. VOC emissions are instead reduced by improving the stripping at the EO stripper. The final emission to atmosphere is usually less than 0.03 kg VOC/t of EO ex reactor) (compared to emissions of up to 0.6 kg VOC/t of EO ex reactor without optimisation of the stripping [116, CEFIC 2000]). However, this emission quantification is difficult because the VOC content in the air stream is close to, or even below, the limit of detection, and the organics content in the absorbing water shows only little variation from the inlet to the outlet of the cooling tower.

7.3.2 Emissions to water

The aqueous effluent streams are typically treated biologically in central facilities together with other streams (see the CWW BREF) and this makes it difficult to establish the true contribution to the overall emissions. Discontinuous waste water streams are also present. The rinsing of process equipment, for example prior to maintenance, creates a weak stream of hydrocarbons. The number of cleaning operations is highly dependent on the maintenance regime and the frequency of discharge may range from 10 times per year to once every five years.

7.3.2.1 Effluents from EO production

The absorption of the ethylene oxide product in water will result in the inevitable formation of some ethylene glycols. As the absorption water is recycled, there is a likelihood of a build-up of ethylene glycols, and a purge stream (as shown in Figure 7.3) is consequently needed in order to limit the extent of this. Furthermore, there is potential for salts to also build up within this recycle loop.

The need for the purge stream is primarily to manage ethylene glycol levels, so ethylene glycols will therefore be present. The purge stream may also contain organic acids or their salts if the pH is adjusted.

The purge stream is removed after the concentration of the ethylene oxide prior to its purification. The purge stream should therefore contain only trace amounts of ethylene oxide under normal operating conditions.

The purge stream is usually concentrated at the EO unit (to attain marketable by-products) or routed to the EG unit for reuse and further processing. When the concentration of organics is too low for recovery and the purge stream does not meet the quality demands for reuse in an associated EG plant, it is discharged as waste water and routed to biological treatment.

7.3.2.2 Effluents from EG production

In order to maximise the formation of monoethylene glycol, a significant stoichiometric excess of water is normally used during the ethylene oxide hydrolysis reaction. Both the amount of effluent that is generated and the quantity of water that is consumed are minimised by recycling the water after it has been separated from the ethylene glycols. Aldehydes that are formed during the hydrolysis reaction will remain in the water and their levels therefore need to be controlled by purging some of the recycled water (see Figure 7.4). It is possible that this purge may be disposed of as an effluent. It will contain aldehydes and possibly ethylene glycols.

7.3.2.3 Emissions to water from vacuum systems

The separation of the individual ethylene glycols is achieved by multiple distillations that are conducted under vacuum conditions. The systems employed for generating the vacuum can comprise steam ejectors and/or liquid ring pumps, in which case an aqueous effluent may arise. As ethylene glycols are readily condensable (due to their low vapour pressures) and miscible with water, any that are present (i.e. uncondensed or entrained) in the evacuated gases are likely to be mainly transferred to any effluents that might arise from the vacuum systems, either condensate from steam ejectors or water purges from liquid ring pumps that use water (rather than glycol) as a sealing liquid.

7.3.3 Raw material consumption

7.3.3.1 Consumption of ethylene and oxygen

EO/EG production has two main raw materials, ethylene and oxygen (or formerly air). Typical ranges are given in Table 7.6.

Table 7.6: Raw material consumption of ethylene oxide processes

		Oxygen-based process	**Air-based process**
Ethylene	Selectivity (%)	75–90	65–75
	Consumption (kg/t of EO ex reactor)	700–850	800–900
Oxygen	Consumption (kg/t of EO ex reactor)	600–1 100	
Source: [116, CEFIC 2000] revised by CEFIC in 2014			

The raw material consumption and the energy consumption depend on the selectivity of the EO catalyst (see Section 7.4.3.1.1).

7.3.3.2 EO consumption at EG plants

The various co-products (mono-, di- and triethylene glycols) all have potential uses and values, and the ethylene oxide consumption therefore has to be seen in the context of the desired (or at least accepted) co-product profile.

The main reason for an increased ethylene oxide consumption rate per tonne of target product could be loss of material in the bottom product from the final separation column.

The loss of ethylene glycols in the purge from the water stream being recycled back to the glycol reactor will also result in an increase in the ethylene oxide consumption rate.

7.3.3.3 Other consumption at EO plants

Other consumption at EO plants includes the use of methane as a diluent, of an organochlorine inhibitor (such as ethylchloride or dichloroethane) and of potassium carbonate for the absorption of CO_2.

7.3.4 Energy consumption

The EO/EG process is both a consumer and a producer of energy:

- The EO reaction section is typically a net energy producer and this is used to generate steam. The steam production depends on the EO catalyst selectivity, which in turn depends on the type and age of the catalyst.
- The EG section is a net consumer of energy. A multi-effect evaporator system can be used in the glycols dewatering section to reduce energy consumption. Furthermore, the

heat released in the glycols reactor is used to reduce the energy consumption of the glycols dewatering section.

Catalyst selectivity and the relative sizes of the EO and EG sections influence the overall energy balance of the unit and define whether a plant is a net steam importer or exporter. Low catalyst selectivity (and therefore increased oxidation of ethylene to carbon dioxide) gives a higher level of reaction heat release and steam generation in the EO reaction section.

Apart from generating steam, the process also generates a number of gaseous and liquid effluent streams that may be recovered as fuel for furnaces, power plants or steam boilers. Optimisation of the energy balance is therefore typically on a site-integrated basis. Since each European plant has different characteristics, it is difficult to give a meaningful range of energy consumption figures. Even when they are available, care is required in interpretation as lower energy consumption could mean that a plant is converting more ethylene into carbon dioxide.

Fractionation operations

Energy is required for the removal of water from the ethylene glycols reaction mixture and the subsequent fractionation of the individual ethylene glycols which require an evaporation step followed by a series of distillations.

Vacuum generation

The separation of the individual ethylene glycols is achieved by distillation columns in series operating under vacuum. Vacuum generation options include liquid ring pumps and/or steam ejectors. Given the progressively high boiling points of the ethylene glycols, the level of vacuum is likely to be high, and this is likely to translate into a relatively high energy demand.

Gas recycling

The pursuit of selectivity rather than rate of conversion means that a significant proportion of the process gases need to be recirculated back to the reactor. This will require the operation of compressors and these will have a potentially significant energy demand.

7.3.5 Water usage

EO production

Water is used within the process to absorb ethylene oxide. The ethylene oxide is separated from the water later in the process and this allows the recycling of the water (after suitable cooling). Additional water is required to compensate for the purge stream from the recycled water that is necessary in order to limit the build-up of glycols that are formed during the absorption.

The net water usage may be marginally affected by the water that will arise as a consequence of the full oxidation of ethylene.

EG production

As ethylene glycols are produced via a hydrolysis reaction, there is a net consumption of water by the process due to the chemical reaction. However, in order to limit the formation of heavy glycols, a significant stoichiometric excess of water is normally used which is usually recycled after it has been evaporated from the ethylene glycols mixture.

The main reason for requiring additional water over and above that which has reacted will therefore be to compensate for the purge stream from the recycled water that is necessary to limit the build-up of aldehydes that are formed during the reaction.

7.3.6 Co-products, by-products and waste generation

7.3.6.1 Carbon dioxide

As explained in the process description (Section 7.2.2), carbon dioxide is the main by-product of the direct oxidation. A selectivity of 70–90 % would correspond to a maximal ratio of 0.86–0.22 tonnes of CO_2 per tonne of EO produced in the reaction.

The stream is purified and either liquefied by a downstream unit for marketing or released to atmosphere.

7.3.6.2 Glycol residue from the EO recovery and purification

A residue arises during the purification of ethylene oxide. Any stream with a high concentration of hydrocarbons is usually sold as a by-product (optionally after further processing in the EG plant) or otherwise incinerated as a waste. In the 2003 LVOC BREF, the rate of arisings was reported to be in the range of 0.5–10 kg/t of EO ex reactor, and the typical hydrocarbon content was 40 wt-% TOC [116, CEFIC 2000]. The data collection showed higher values for glycol residue from EO purification, ranging from 3 kg/t to 45 kg/t of EO.

7.3.6.3 EO spent catalyst

The selectivity of the catalyst will deteriorate over time, until it needs to be replaced with fresh catalyst. The EO catalyst loses its efficiency over time and it is periodically changed (typically every one to four years). The rate of generation is 0.12–0.8 kg/t of EO (0.12–0.3 kg/t of EO for the lowest 50 % of units) [116, CEFIC 2000]. The catalyst is sent to reclaimers for recovery of the silver content. The inert, inorganic support for the catalyst requires landfilling once the silver has been recovered.

7.3.6.4 Purge streams and heavies from EG fractionation and purification

The EG fractionation and purification result in some purge streams being generated along with a bottom stream of heavy glycols (oligomers) from the last column of the glycols separation unit. If customers can be found, the stream is usually sold. Alternatively it may be incinerated. The data collection shows residues from EG separation ranging from 1.4 kg/t to 21 kg/t of EO, including the cases in which the purge stream from the EO plant is routed to the EG plant.

7.4 Techniques to consider in the determination of BAT

This section describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this chapter. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations). Cross references to other chapters are used, where relevant to avoid repetition.

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 2.6 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

7.4.1 Techniques to reduce emissions to air

7.4.1.1 Process route selection: Use of oxygen instead of air

Description
Ethylene oxide production process based on oxygen feed instead of air.

Technical description
The oxidation reaction to produce ethylene oxide is carried out with oxygen instead of air to improve process efficiency (by increased selectivity). Methane is used as a diluent (instead of nitrogen) which allows the inerts purge to be used as a fuel gas.

Achieved environmental benefits

- Lower ethylene consumption, lower carbon dioxide formation and less off-gas.
- Allows the recovery of pure carbon dioxide which can be reused (e.g. for blanketing or sale).
- Lower emissions to air.
- Lower energy consumption.

Environmental performance and operational data
The selectivity and consumption ranges of the oxygen-based process are listed in Table 7.6 in Section 7.3.3.1, including the improvements in comparison to the air-based process.

Cross-media effects
The oxygen-based process requires pure oxygen as a feedstock, and energy is used in the manufacturing of the oxygen. Improved selectivity implies less heat formation/recovery (see Section 7.3.4).

Technical considerations relevant to applicability
This technique is applicable to new installations or major retrofits.

Economics
The additional costs of pure oxygen consumption are more than compensated by the reduced ethylene use and lower capital requirements per tonne of product. Costs for VOC abatement are also reduced.

Driving force for implementation
Economics.

Example plants
The first generation of EU plants used air but they have been replaced by, or converted into, plants using pure oxygen. EO plants in the EU now all use pure oxygen feed.

Reference literature
No reference literature provided.

7.4.1.2 Techniques to reduce VOC emissions from the reaction section

According to the data collection, all installations use the inerts purge as fuel gas. Most installations in the EU recover ethylene from the inerts purge beforehand, either via PSA (adsorption) or membrane separation.

7.4.1.2.1 Recovery of ethylene

Pressure-swing adsorption (PSA) is a separation method in which gas molecules are retained on a solid or liquid surface (adsorbent, also referred to as a molecular sieve) that prefers specific compounds to others and thus removes them from effluent streams. See the CWW BREF for further information.

Membrane separation is used to concentrate the organic content for recovery. See the CWW BREF for further information.

7.4.1.2.2 Routing of the inerts purge to a combustion unit

This technique involves the recovery of energy by reusing the stream as fuel, e.g. in site boilers. See the LCP BREF for a technical description.

7.4.1.3 Techniques to reduce emissions from the CO_2 removal system

Carbon dioxide is removed by absorption in a hot carbonate solution. Carbon dioxide is then stripped from the carbonate solution by means of lower pressure and heat. The vent stream is mainly composed of carbon dioxide and water, but also contains VOCs (mainly ethylene and methane).

The carbon dioxide stream is reduced by any technique that improves the selectivity of the oxidation reaction (see Section 7.4.3.1).

7.4.1.3.1 Recovery of the carbon dioxide for sale as a product

As the carbon dioxide is normally isolated in a relatively pure form, it can be used beneficially, typically after further treatment, e.g. by catalytic oxidation (see Section 7.4.1.3.3), in order to remove VOCs.

The beneficial use of CO_2 will reduce the CO_2 emissions to air from the installation. The feasibility will depend on the market situation and the availability of third-party investors to build a CO_2 recovery plant.

On a life-cycle basis, the achieved reduction of CO_2 emissions will depend on the way CO_2 is used (e.g. for soft drinks) and the alternative CO_2 sources for this use.

In the answers to the questionnaires, about 40 % of the sites reported that the CO_2 stream is marketed.

7.4.1.3.2 Staged carbon dioxide desorption

Description
Recovery of ethylene and methane from the carbonate solution before stripping out the carbon dioxide.

Technical description
Conducting the depressurisation necessary to liberate the carbon dioxide from the absorption medium in two steps rather than one results in the separation of two streams: the main VOC stream from the main CO_2 stream.

‘Flashers’ can recover a significant amount of the absorbed ethylene and methane from the carbonate solution prior to carbon dioxide removal in the carbon dioxide stripper. The overheads of the flasher can be recycled back to the process.

Achieved environmental benefits

- Lower emissions to air.
- Recovery of material.

Technical considerations relevant to applicability
Applicable to oxygen-based oxidation processes.

7.4.1.3.3 Use of oxidisers for end-of-pipe treatment

The off-gas from the CO_2 stripper consists mainly of CO_2 with VOCs (e.g. ethylene and methane) as pollutants. To achieve low levels of VOCs, it can be treated either with catalytic or thermal oxidisers, to reduce emissions to air or enable reuse of the purified carbon dioxide.

Catalytic oxidiser
See the description in the CWW BREF.

- This is used at at least four sites, according to the data collection; three of those sites are: Sasol, Marl (DE), IQA, Tarragona (ES) and Clariant, Gendorf (DE). It is used to purify the carbon dioxide for reuse/marketing or as final abatement before release to atmosphere.
- After catalytic oxidation, one site reported a load of 0.8 g NMVOC and 0.2 g methane per tonne of EO (from one periodic measurement); others reported NMVOC loads of 4–9 g/t

and 8–9 g/t of EO, and methane loads of 6–8 g/t and 1.3–1.9 g/t of EO from yearly and monthly measurements respectively.

Thermal oxidiser
See the description in the CWW BREF.

This is only used in one of the installations that participated in the data collection – Ineos Oxide, Antwerp (BE).

7.4.1.4 Techniques to reduce emissions to air from EO isolation

The techniques that can be employed to reduce VOC emissions associated with the light end fraction under normal operating conditions include the following:

Gas recompression to recover energy or feedstock

- Recycling of light ends: the light overheads mentioned in Section 7.3.1.3 can be collected and returned to the oxidation reactor loop after recompression. This will involve the recycling of non-condensables, but the features built into the management of the recirculation loop should be able to deal with this. The energy involved in recompression is not anticipated to be high.

Thermal oxidation

- See the CWW BREF.
- For safety reasons, the raw gas should not contain high concentrations of EO, which can be removed beforehand by wet scrubbing.

Catalytic oxidation

- See the CWW BREF.

7.4.1.5 Removal of EO to enable recovery of VOCs and to reduce EO emissions to air

Wet scrubbing is used to remove EO from process streams (to enable VOC recovery/reuse) and from waste gas streams (to abate EO emissions and, for safety reasons, before final treatment in oxidisers).

Scrubbing of process gas streams
Most of the individual process vent streams contain valuable components (ethylene, methane) in addition to EO. The streams are usually routed to a scrubber that is operated at the lowest possible pressure so that all process vents can be routed to it. EO is recovered by absorption in water and recycled back to the process. The scrubber overheads stream is compressed and also recycled back to the process, leaving no residual effluent stream or emission to atmosphere.

Scrubbing of waste gas streams
EO-containing vent streams (e.g. from the process or from storage) that are unattractive for recycling back to the process are typically treated by wet scrubbing. Where the plant configuration allows, the recovered EO solution can be recycled back to the process. If no EO recovery is foreseen, scrubbing may possibly be enforced by adding caustic or acid to enhance the reaction of EO to glycol. The spent scrubbing liquid is then sent to biological treatment.

Depending on the VOC content, the treated waste gas will be routed to further treatment (thermal or catalytic oxidiser).

7.4.1.6 Prevention of fugitive emissions

Due to its toxic and carcinogenic nature, threshold limit values for EO in ambient air are very low (in the order of 1 ppm). For occupational health reasons, extensive measures have been taken by the industry to prevent EO releases, including fugitive emissions, or to detect them at an early stage so that remedial measures can be taken promptly.

In addition to the generic techniques described in Chapter 2, the specific techniques to minimise fugitive emissions may include the following:

Prevention techniques for diffuse emissions of VOCs

- Careful material selection for seals, O-rings, gaskets, etc. in EO duty.
- Use of double seals or tandem seals on pumps in EO duty or use of canned or magnetic drive pumps.

High-integrity equipment

- High-integrity equipment includes: valves with double packing seals; magnetically driven pumps/compressors/agitators; pumps/compressors/agitators fitted with mechanical seals instead of packing; and high-integrity gaskets (such as spiral wound or ring joint) for critical applications.
- As the ethylene glycols separation is carried out under vacuum, reducing leaks (which are not considered an other than normal operating condition in this context) will reduce the quantity of non-condensable gases that enter the distillation plant, thereby reducing the gas volumes handled by the associated vacuum systems, and consequently the likely emissions from them. However, a significant amount of air ingress might affect the level of vacuum that is achieved, which could affect the nature of the process vapours, and may result in a plant shutdown.

Targeted monitoring of pollutants in ambient air (for health and safety)

- Application of metal strips around flanges, with a vent pipe sticking out of the insulation that is monitored for EO release on a regular basis.
- Installation of sensitive EO detection systems for continuous monitoring of ambient air quality (these systems also detect ethylene).
- Monitoring of EO plant personnel for EO exposure (as exposure means emission).

[94, CEFIC 2000], [95, Swedish EPA 2000].

7.4.1.7 Techniques to prevent or reduce VOC emissions from cooling of the EO absorbent

Emissions from open cooling of the EO absorbent as part of the EO absorption-desorption cycle can be reduced by control of the VOC content or preferably prevented by indirect cooling of the absorbent with heat exchangers.

7.4.1.7.1 Complete EO removal by stripping

Description
Emissions are controlled by stripping upstream of the open cooling system, to ensure that no EO is left and to reduce other VOCs.

Technical description
The technique involves maintaining appropriate operating conditions and using online monitoring of the EO stripper operation to ensure that all EO is stripped out; and providing adequate protection systems to avoid EO emissions during other than normal operating conditions.

Achieved environmental benefits
Lower emissions to air of EO and other VOCs.

Environmental performance and operational data
Reduction of VOC emissions to below 0.03 kg/t of EO ex reactor (see Section 7.3.1.6).

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Applicable where cooling is carried out in open cooling towers.

Economics
No information provided.

Driving force for implementation
No information provided.

Example plants
According to CEFIC, 2 out of 11 plants use open cooling systems for the EO absorbent. Both of them use extensive stripping to reduce EO/VOCs.

Reference literature
No reference literature provided.

7.4.1.7.2 Indirect cooling

Description
Use of indirect cooling of the EO absorbent instead of open cooling systems.

Technical description
Indirect cooling is carried out in a closed system with heat exchangers and a separate cooling medium (in this case, cooling water).

Achieved environmental benefits
No VOC emissions to air from the cooling system.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
The use of indirect cooling systems to decrease the temperature of liquids is a standard operation in the chemical industry (whereas open cooling systems for process liquids tend to be an exception). For closed cooling circuits, i.e. if the cooling water is recycled, coolers such as cooling towers need to be integrated or, for existing systems on site, adapted to the additional duty.

Economics
Replacing open EO cooling systems with indirect cooling is assumed to be a major investment.

Driving force for implementation
Environmental legislation.

Example plants
According to CEFIC, 9 out of 11 plants use indirect cooling for the EO absorbent.

Reference literature
No reference literature provided.

7.4.1.8 Storage

As a safety precaution, ethylene and oxygen are usually stored outside the EO/EG units and are fed by pipe to the process unit. See the EFS BREF.

Pressure vessels are under a nitrogen blanket and may be refrigerated.

- EO is typically stored in pressure vessels. The nitrogen serves as a diluent in order to keep the vapour phase outside the explosive area. An important issue is avoiding the ingress of air, which could form an explosive vapour mixture with EO, or of other impurities that are reactive with EO or that could catalyse EO runaway reactions.
- EG and heavier glycols are stored in atmospheric vessels because glycols have a lower vapour pressure and emissions to air are negligible.

EO tank vents and purge vents from loading operations are typically routed to a water scrubber that ensures nearly 100 % EO recovery (see Section 7.4.1.5).

7.4.2 Techniques to reduce emissions to water

This document addresses only effluent treatment at source and specific pretreatments. Most EO plants have a collective effluent header that is sent to a waste water treatment unit.

7.4.2.1 Techniques to reduce effluent from EO production

7.4.2.1.1 Use of the purge from the EO unit in the EG unit

Description
Use of the aqueous purge streams from the EO unit in the EG unit.

Technical description
The purge streams from the EO plant are sent to the ethylene glycols process (which has a continuous net water demand) and not discharged as waste water. The extent to which the purge can be reused in the EG process depends on EG product quality considerations.

Achieved environmental benefits
Reduction of emissions to water.

Environmental performance and operational data
No information provided.

Cross-media effects

Depending on the water balance, energy may be required for the removal of additional water from the recovered water/glycol stream.

Technical considerations relevant to applicability

This option is obviously dependent on ethylene glycol production being co-located with ethylene oxide production.

Quality considerations could impose constraints on the application of the technique if the purge stream contains impurities that may affect the quality of the final products. Depending on the plant (and its original design), it may not be possible to recycle this stream as the final products (such as high-purity MEG) would be off spec or of poor quality, making them impossible to sell.

Economics

Depending on the water balance, the benefits from recovery of glycols and reuse of water may be reduced by the operating costs for the removal of additional water from the recovered water/glycol stream.

Driving force for implementation

Economics.

Example plants

Some EU operators reported using this technique in the data collection.

Reference literature

No reference literature provided.

7.4.2.1.2 Distillation of aqueous streams

Technical description

Purge streams from the EO unit and the EG fractionation with high glycol contents can be routed to a distillation or evaporation unit which may be inside the glycol plant or a dedicated unit for the recovery of (most of) the glycols and (partial) recycling of water back to the process.

The technique is used in EO and EG units to concentrate aqueous streams to recover glycols or enable their disposal (e.g. by incineration) and to enable the (partial) reuse/recycling of water.

Achieved environmental benefits

- Reduction of emissions to water.
- Improved resource efficiency (recovery of product, reuse of water).

Environmental performance and operational data

No information provided.

Cross-media effects

Energy consumption of distillation (but reduced energy consumption at the waste water treatment plant and for waste incineration).

Technical considerations relevant to applicability

Regarding waste water management, the technique is used to avoid the discharge of high loads of TOC/COD to the biological treatment plant. At low concentrations, glycols are readily biodegradable.

Depending on the design of the EO plant, the implementation of the technique at an existing EO plant may imply a major revamp and investment, and a potentially lower performance in terms of energy efficiency and product quality.

Economics

Benefits from reduced costs for disposal (waste water, waste) and from recovered glycols (which however may have a comparatively low quality/value).

Driving force for implementation

Economics.

Example plants

Some EU operators reported using this technique in the data collection.

Reference literature

No reference literature provided.

7.4.3 Techniques to reduce raw material consumption

The main raw materials used in the EO/EG process are ethylene and oxygen.

7.4.3.1 Techniques to reduce ethylene consumption

The techniques that can be employed to reduce the specific ethylene consumption due to carbon dioxide formation under normal operating conditions include the following.

7.4.3.1.1 Catalyst selection

By far the most important factor causing raw material consumption to be higher than stoichiometric consumption is the limited selectivity of the EO catalyst. Significant progress has been made to improve catalyst performance, reducing raw material losses by more than 50 %, and further efforts are continuing, mainly driven by economic factors.

A lack of catalyst selectivity will result in a greater proportion of the ethylene being oxidised to carbon dioxide, thereby reducing the proportion of ethylene that is converted into ethylene oxide.

Catalyst selectivity, expressed as the number of moles of EO produced per mole of ethylene consumed, is a measure of the reactor performance and it shows how efficiently ethylene is used by the catalyst.

Catalyst selectivities have improved from 50 % to around 90 %. This has been achieved by optimising the support materials (e.g. aluminium oxide) and silver distribution, and by the use of promoters and moderators. Catalyst selectivity has a great impact on raw material consumption and the formation of carbon dioxide by-product.

Ageing of catalysts results in a decrease in activity and selectivity. Ageing may be caused by accumulation of catalyst poisons (e.g. sulphur from ethylene or methane), mechanical effects (e.g. abrasion, blocking of pores) and agglomeration of the silver particles; the latter may reduce the silver surface (and related catalyst activity) by 50 % which to a certain extent is compensated by raising the reaction temperature (e.g. to a maximum of 300 °C).

For fresh catalyst, improved selectivity brings not only higher EO yields, but also less heat generation which in turn increases catalyst lifetime. However, the catalysts with the highest selectivities tend to age more quickly and have to be replaced more frequently.
[90, Rebsdat et al. 2012], [41, CEFIC 2010].

7.4.3.1.2 Control of catalyst performance

Description
Control of catalyst performance in order to reduce the replacement frequency.

Technical description
Catalyst selectivity gradually decreases over time, resulting in increased raw material consumption per tonne of EO produced. Conceptually, lower raw material consumption over the lifetime of the catalyst could be achieved by more frequent catalyst changeout. In order to recognise a decrease in catalyst activity, updated balances of the reaction section are kept, based on suitable parameters such as the heat of reaction or the CO_2 formation.

Achieved environmental benefits

- Lower consumption of ethylene and oxygen.
- Lower emissions of CO_2 to air.

Cross-media effects
An increase in catalyst exchange frequency results in increased amounts of spent catalyst for recovery.

Economics
Benefits of maintaining a high catalyst performance include lower costs due to the reduced consumption of ethylene.

In terms of costs, increasing the catalyst exchange frequency implies higher catalyst costs and reduced economic performance from the reduced throughput due to the process downtime needed for the exchange of the catalyst.

The decision as to what level of performance will trigger the exchange of the catalyst will depend on an assessment also taking into account economic factors.

7.4.3.1.3 Use of inhibitors

The addition of an organochlorine inhibitor (such as ethylchloride or dichloroethane) to the reactor feed, in order to increase selectivity and reduce the proportion of ethylene that is fully oxidised to carbon dioxide, is common practice. According to the data collection, most plants use ethylchloride (0.5–2.5 kg/h).

The inhibitor will also be present in the recirculating process gas and may contribute to emissions to air via the inerts purge from the reaction cycle.

7.4.3.1.4 Process optimisation

The techniques that can be employed to reduce the specific ethylene consumption by limiting formation of carbon dioxide, losses of ethylene from the process or losses of ethylene oxide product are as follows:

Methane quality
The presence of heavy components can adversely affect the performance of the catalyst inhibitor, which can therefore increase the extent of carbon dioxide formation.

Construction materials
Aldehyde formation from ethylene oxide can be catalysed by a range of materials. The careful selection of construction materials (and possibly an appropriate maintenance regime) can therefore limit the formation of such impurities. However, the increase of ethylene consumption due to the formation of aldehydes is considered to be of only minor significance.

Reaction conditions
The selectivity of the process for ethylene oxide will be influenced by pressure, temperature, etc. The reaction conditions are optimised in a way that minimises carbon dioxide formation.

Raw material quality
Reducing the inert components in the ethylene and oxygen raw materials will limit the extent to which process gas needs to be purged in order to control the build-up of such inerts, and this will therefore limit the amount of ethylene that has to be wasted from the process. It may also limit the emissions of VOCs to air from the process where the purge stream is not used beneficially. However, the raw materials will need to be bought to general specifications, and there will therefore be a limitation on what can be achieved in this respect.

Dynamic control of purge rate
Having a sound basis for determining the required purge rate and ensuring that this is not exceeded is a key means of limiting the purge rate. Having a fixed purge rate may result in greater purge rates than may be really required.

The techniques that can be employed to reduce the specific ethylene consumption rate include the below techniques:

Glycol formation
Reducing the amount of ethylene glycols and heavy organics that are formed during ethylene oxide isolation will reduce ethylene consumption when judged in terms of ethylene oxide production. However, it is possible that some of the ethylene glycols formed could be used to supplement ethylene glycol production where ethylene oxide and/or ethylene glycols are produced at the same site.

Storage losses
The emissions of ethylene oxide from storage may be low not simply because of good venting design, but possibly because of good vent scrubbing arrangements. Recycling the spent scrubber liquor to the process to recover ethylene glycols reduces losses of product and reduces the load discharged to waste water treatment, although the effect may be low.

7.4.3.2 Techniques to reduce consumption of EO in EG production

The ethylene oxide consumption rate can be reduced by reducing the proportion of ethylene oxide that is transformed into heavy organics that leave as the bottom product from the final separation column, and which would ordinarily (but not necessarily) be considered a residue. The techniques that can be employed to reduce specific ethylene oxide consumption due to reducing heavy/heavier glycol formation under normal operating conditions include the following:

a) Hydrolysis reaction optimisation
Using a significant water excess favours the formation of monoethylene glycol rather than the heavier glycols (see Section 7.4.5.2.1).

b) Efficient fractionation

The more efficient the final separation columns, the lower the losses of glycols in their bottom product. In attempting to maximise the separation potential, it is possible that a higher energy demand will arise due to the use of an increased reflux ratio and/or higher vacuum.

7.4.4 Techniques to reduce energy consumption

Electricity and steam are the main utilities used in EO/EG plants and they usually represent a considerable share of production costs.

Setting a criteria or target

The reaction by-products generate energy. This leads to an interrelationship or trade-off between EO catalyst selectivity and heat balance: the more efficient the catalyst, the less steam that is produced in the EO reactors. Each installation (case by case) will decide whether energy or feedstock yield is more relevant.

The plant energy balance also depends on the relative sizes of the EO and EG sections. If the EO/EG process is a net steam exporter, the way to reuse this energy in the complex becomes of prime importance. To a certain extent, the EO/EG complex may play the role of a boiler plant for the site and this may hinder the use of more selective catalysts which would allow less steam to be exported.

The steam consumption of the EO/EG process is mainly due to distillation, and sometimes to turbines driving the gas compressors.

The methods for minimising the steam consumption of distillation when designing a new unit are well known. For existing distillation columns, retraying and repackaging techniques can be used, and technologies that often have a minor impact on steam consumption are principally used to debottleneck the capacity.

Unless steam turbines are used, the major electricity consumer of the EO/EG process is the recycle gas compressor at the EO unit. The usual ways to reduce the energy consumption of compressors are applicable (i.e. efficient design, reduction of pressure drops, etc.).

7.4.4.1 Fractionation

The techniques available for reducing the overall energy consumption associated with ethylene glycols dewatering and fractionation include the following:

Reduced water levels

Limiting the water excess in the glycols reaction will reduce the amount that needs to be evaporated off. However, this will likely increase the relative quantity of heavy glycols formed, and it will also have the knock-on effect of increasing the energy required by the subsequent fractionation step due to the need to progress more material through the chain of fractionation columns.

Hydrolysis of ethylene carbonate

Instead of hydrolysing ethylene oxide, hydrolysing ethylene carbonate requires a lower water excess and therefore would result in a lower overall energy consumption. The ethylene carbonate could be produced using the CO_2 isolated from the oxygen process (CO_2 is liberated during the hydrolysis, so it can be recycled), although this would require particular process conditions.

Evaporation configuration
The use of a multiple-effect evaporator would be more energy-efficient by allowing the steam use to be reduced. This may involve the need for vacuum pumps and/or vapour recompression.

Distillation column design
A column with a good inherent separation capability (due to efficient packing, height, etc.) may reduce the required reflux ratio, thereby reducing the vaporisation energy requirement during the fractionation.

Heat integration between distillations systems
This technique involves using heat from one column as a (partial) input of heat to another column – potential differences in vacuum levels might affect temperature differences. This may be done with the support of methodologies such as the pinch analysis (between the EO and EG production units, and externally between the EO/EG complex and the surrounding facility).

Earlier designs utilised trays in this application. Current designs utilise structured packing and trays to increase capacity (only in the case of revamped units).

7.4.4.2 Energy from vacuum generation

Combination of steam ejectors and liquid ring pumps
The use of steam ejectors and liquid ring pumps in combination can be more energy-efficient.

Plant integrity
Reducing the number of leaks (which in this context are not considered as contributing to an other than normal operating condition) will reduce the quantity of non-condensables that need to be handled and therefore reduce the load of the vacuum systems.

7.4.5 Techniques to reduce waste generation

7.4.5.1 Techniques to consider on spent catalyst

Conceptually, the consumption of EO catalyst (in terms of t/t of EO produced) could be minimised by running the catalyst for a longer time before replacement with a fresh batch. However, an ageing catalyst gradually loses its selectivity and therefore has to be replaced. The frequency of replacement depends on the catalyst selection (see Section 7.4.3.1.1) and the control of its performance (see Section 7.4.3.1.2).

Typically, the spent EO catalyst is sent to an external reclaimer for recovery of the valuable silver. After silver reclamation, the inert carrier requires disposal.

7.4.5.2 Techniques to reduce organic wastes from EO and EG units

7.4.5.2.1 Hydrolysis reaction optimisation

Description
The relative amount of heavy glycols formed in the glycol unit can be influenced to some extent by varying the water to EO ratio in the glycol reactor feed.

Technical description
Higher water to EO ratios result in lower co-production of heavier glycols but on the other hand require more energy for the glycol dewatering. The enforcement of the hydrolysis reaction may not always be desirable due to the fact that it will also reduce the formation of the co-products DEG and TEG, which are usually sold.

Achieved environmental benefits
Reduced quantity of heavy glycols, possibly requiring disposal.

Environmental performance and operational data
For data on the amount of residue generated per tonne of ethylene oxide, see Sections 7.3.6.2 and 7.3.6.4.

Cross-media effects
Increased energy consumption for the glycol dewatering.

Technical considerations relevant to applicability
Generally applicable.

Economics
Higher water to EO ratios result in lower co-production of heavier glycols but on the other hand require more energy for the glycol dewatering.

Driving force for implementation
Economic benefits.

Example plants
In the questionnaires, almost all operators confirmed the use of control/optimisation of the hydrolysis ratio as a technique to prevent wastes.

Reference literature
No reference literature provided.

7.4.5.2.2 Isolation and sale of by-products from EO units

Description
The concentrated organic fraction obtained after the dewatering of the liquid effluent from EO recovery is distilled to give valuable short-chain glycols and a heavier residue (containing heavy glycols and organic salts) for sale or disposal (incineration).

Environmental performance and operational data
For data on the amount of residue generated per tonne of ethylene oxide, see Section 7.3.6.2.

Only one operator reported amounts of waste for disposal (incineration), which were in the range of only a few g/t of EO, which indicates for this site, too, that most of the residue is marketed.

Technical considerations relevant to applicability
Depending on the design, the implementation of the technique at an existing EO plant may imply a major revamp and investment, with a potentially lower performance in terms of energy efficiency and product quality.

In terms of waste reduction, there is no need for the isolation of by-products if the organic fraction can be marketed as a whole.

Example plants
According to the questionnaires, at most of the sites the residue from the EO purification is sold. Some operators answered that they would incinerate residues from the EO and/or EG unit if they could not be sold.

7.4.5.2.3 Isolation of by-products from EG units for sale

Description
For EG units, the heavy glycols fraction can either be sold as such or further fractionated to yield pure valuable glycols.

Technical description
The bottom stream of the last distillation column of the glycol fractionation unit contains the higher boiling ethylene glycols (heavy glycols). The composition of this stream depends on the extent of separation of the lower boiling glycol products. Typical compounds are triethylene glycol, tetraethylene glycol and higher ethylene glycols.

The stream can be either sold as such or fractionated to yield pure marketable glycols. If the stream is not marketed as such, the recovery of glycols is maximised, in order to minimise the waste to be disposed of.

Environmental performance and operational data
For data on the amount of residue generated per tonne of ethylene oxide, see Section 7.3.6.4.

Only one operator reported amounts of waste for disposal (incineration), which were in the range of only a few g/t of EO, which indicates for this site, too, that most of the residue is marketed.

Technical considerations relevant to applicability
In terms of waste reduction, there is no need for the isolation of by-products if the organic fraction can be marketed as a whole.

Example plants
According to the questionnaires, at most sites (i.e. all sites that provided information), the heavy glycol residues from the EG unit are marketed. Some operators answered that they would incinerate residues from the EO and/or EG unit if they could not be sold.

7.5 Emerging techniques

7.5.1 Co-production of diphenyl carbonate (DPC) and ethylene glycol

Description
Carbon dioxide, phenol and ethylene oxide react to form DPC and ethylene glycol.

The main product is DPC (mainly for the production of polycarbonate), and the environmental benefits relate to the production of DPC by a phosgene-free route. In the context of the EO/EG process, the co-production of EG may substitute some part of the EG directly produced from EO.

Alternatively, the process can be carried out with propylene oxide instead of ethylene oxide which then would not be related to EG production.

Commercially developed
By Shell.

Level of environmental protection
Environmental benefits are:

- substitution of phosgene (avoiding the emissions and safety issues related to phosgene production and handling);
- consumption/transformation of carbon dioxide.

When it might become commercially available
In a few years; pilot plant in operation.

References
[105, Shell 2011].

7.5.2 MEG production via dimethyl oxalate

Description
Monoethylene glycol (MEG) is produced by the reduction of dimethyl oxalate (DMO) with hydrogen. DMO is obtained by a more complex process from carbon monoxide (syngas) which allows the production to be based on coal (alternatively natural gas or possibly biomass) as the carbon source instead of ethylene.

The process implies the following steps:

1) Synthesis/regeneration of methyl nitrite from methanol and nitrogen oxide:

$$2\ NO + 0.5\ O_2 + 2\ CH_3OH \rightarrow 2\ CH_3ONO + H_2O$$

Gas-liquid reaction. Small losses of NO may occur by oxidation.

2) Synthesis of DMO by carbonylation of methyl nitrite:

$$2\ CH_3ONO + 2\ CO \rightarrow 2\ CH_3OCOCOOCH_3 + 2\ NO$$

Catalysed gas-phase reaction (e.g. using Pd), condensation of DMO (e.g. by scrubbing with methanol).

3) Production of MEG:

$$CH_3OCOCOOCH_3 + 4 H_2 \rightarrow CH_2OHCH_2OH + 2 CH_3OH$$

Catalysed vapour-phase process, e.g. using Cu-Cr-BA- or Cu-Cr-Zn-based catalyst, followed by multistep distillation to remove organic impurities (e.g. methyl glycolate, dimethyl carbonate, methyl formate, 1,2-butanediol).

Methanol and NO are recycled within the process. The resulting total balance is:

$$2 CO + 0.5 O_2 + 4 H_2 \rightarrow CH_2OHCH_2OH + H_2O$$

Level of environmental protection

No information provided. A comprehensive environmental process evaluation would have to consider all process steps starting with the upstream non-LVOC processes.

The LVOC process is more complex and involves other potential pollutants. Therefore there is no straightforward indication that emissions will be lower compared to the production of glycol from ethylene oxide.

When it might become commercially available

Soon, driven by the interest in having coal-based processes in China. A pilot plant is in operation. In 2011 Henan Coal Chemical group and Tomgliao Jinmei Chemical Industry announced plans to produce 1.8 million tonnes in China, starting with four installations with capacities of 200 kt/yr each in 2011.

References

[104, Naqvi 2013], [104, Naqvi 2013], [103, Nexant Inc 2011].

8 PHENOL

8.1 General information

Phenol (C_6H_5-OH) is an important chemical intermediate for pharmaceutical and many industrial products including phenolic resins, aniline, caprolactam, and bisphenol A to produce epoxy resins and polycarbonates. All these products have considerable economic importance because they are used for the production of a wide range of consumer goods and process materials, e.g. adhesives, laminates, impregnating resins, raw materials for varnishes, emulsifiers and detergents, plasticisers, herbicides, insecticides and rubber chemicals.

Starting from cumene (isopropylbenzene, 1-methylethylbenzene), phenol is mainly produced by the two-step process. This involves the oxidation of cumene to cumene hydroperoxide, which is then cleaved to produce phenol. The economic yield from this process is strongly influenced by the price of the by-product acetone, which varies considerably.

In 2014, the production capacity of phenol in western Europe was approximately 2.6 million tonnes, which was 21 % of global capacity. European production of phenol in 2011 is summarised in Table 8.1 below.

Table 8.1: European producers of phenol

Country	City	Operator	Process	Capacity (kt/yr)
Finland	Porvoo	Borealis (SF)	Cumene ox.	185
Spain	Huelva	CEPSA Quimica	Cumene ox.	600
Germany	Leuna	DOMO Caproleuna	Cumene ox.	195
Belgium	Antwerp	INEOS Phenol	Cumene ox.	680
Germany	Gladbeck	INEOS Phenol	Cumene ox.	650
France	Roussillon	NOVAPEX S.A.S.	Cumene ox.	186
Italy	Mantova	Versalis	Cumene ox.	310
Germany	Castrop-Rauxel	Rütgerswerke	Coal tar	10

In 2012, global phenol production was estimated to be growing at around 10 % per year, mainly in Asia [120, Meehan et al. 2012].

Key environmental issues
The key environmental issues for the production of phenol are as follows:

The key emission to air is from the spent air downstream of the cumene oxidisers. Cumene and other VOCs are present in this stream. There are numerous sources of emissions to water. The aqueous streams are normally treated to decompose peroxides, to recover phenol, cumene and acetone and to reduce the organic load (TOC) sent to the final waste water treatment.

The largest residue from the reaction sections is a stream of tars (residue or acetophenone fraction) that is separated in the fractionation section. Reaction selectivity is a key parameter to minimise tar at source. Salts (e.g. sodium sulphate) generated in neutralisation and other sections also need to be addressed. Fugitive emissions and emissions from storage may also be relevant.

8.2 Applied processes and techniques

8.2.1 Process options

The principal options for the production of phenol are:

- oxidation of cumene;
- direct oxidation of benzene with O2 or H2O2;
- direct oxidation of benzene with N2O;
- production of phenol from coal tar;
- oxidation of toluene via benzoic acid;
- benzene sulphonation;
- hydrolysis of chlorobenzene.

[5, Weber et al. 2010], [6, Liptáková et al. 2003], [7, Lemke et al. 2002].

Of these, the process which is most commonly applied worldwide and which is predominant in Europe is the oxidation of cumene and this is the only process described in detail in the subsequent sections of this chapter. It involves the oxidation of cumene to cumene hydroperoxide (CHP), which is then cleaved to produce phenol. Acetone is a co-product of the cleavage reaction, and α-methylstyrene (AMS) and/or acetophenone can also be isolated as a desirable by-product from this process [5, Weber et al. 2010], [8, Weber et al 2005], [10, Zakoshansky 2009], [11, Zakoshansky 2007].

From a business perspective, process routes that avoid the generation of an acetone co-product are desirable in order to avoid cyclic acetone price sensitivities. There are a number of such processes, including

- the oxidation of toluene in two steps via benzoic acid to phenyl benzoate with subsequent hydrolysis which accounts for less than 5 % of production in Europe and is no longer a commercial route;
- the direct oxidation of benzene to phenol which has not yet been exploited commercially;
- previously exploited processes for the production of phenol via either sodium benzene sulphonate or the hydrolysis of chlorobenzene which are no longer employed in Europe;
- the recovery of phenol from coal tar.

Shell has developed a process that co-produces both acetone and methyl ethyl ketone [298, Liu 2013].

8.2.2 Cumene oxidation process

[5, Weber et al. 2010], [123, Weber et al. 2014].

Cumene is produced by the alkylation of benzene with propylene, using either an acid-based or zeolite-based catalyst (see cumene thumbnail description).

Cumene is oxidised to cumene hydroperoxide (CHP) in an exothermic reaction taking several hours:

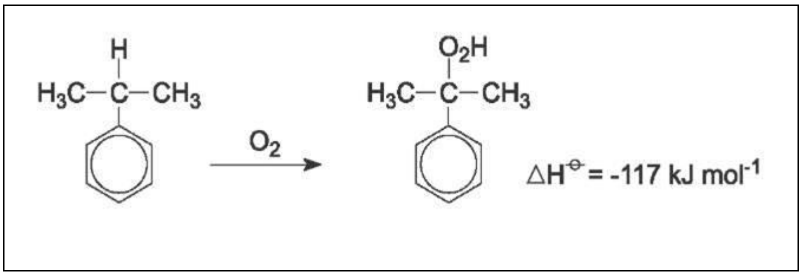


Figure 8.1: Oxidation of cumene to cumene hydroperoxide

CHP then undergoes catalysed cleavage to phenol and acetone, again in an exothermic but very fast reaction:

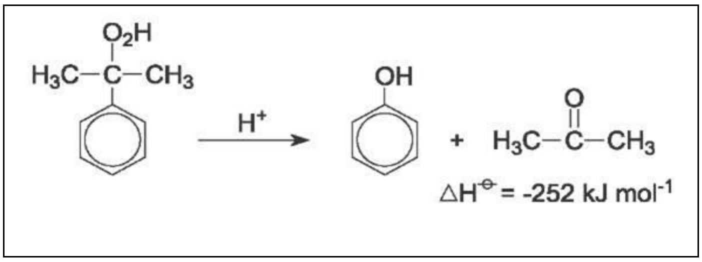


Figure 8.2: Cleavage of cumene hydroperoxide to phenol and acetone

Phenol production plants employing the cumene oxidation route generally include the following main process elements.

8.2.2.1 Oxidation section

For the liquid-phase oxidation of cumene with air to cumene hydroperoxide (CHP), as many as two to six or more reactors (usually bubble column reactors) can be used in multiple reaction trains depending on the capacity of the unit, location, processing objectives, and the capability to stagger the investment over time as capacity increases are needed. Recycled cumene streams from other sections of the plant are combined with fresh cumene feed. The cumene oxidisers operate in series with respect to liquid flow but in parallel with respect to airflow. The oxygen requirement for the oxidisers is supplied from atmospheric air. The air is first filtered and then compressed before going into the oxidisers through a sparger.

The autocatalysed complex reaction is carried out at temperatures of 80–120 °C and at pressures ranging from atmospheric pressure to about 700 kPa, with residence times between 4 and 20 hours. Temperature is controlled by internal or external heat exchangers.

The main side-products are dimethylbenzyl alcohol (DMBA) and acetophenone (ACP), besides the formation of methanol and organic acids.

The oxidation step used to be carried out as a three-phase reaction (‘wet oxidation’), adding aqueous sodium carbonate to control the content of organic acids by extraction and neutralisation. Nowadays, the oxidation is operated more efficiently as ‘dry oxidation’, without adding any caustic.

Cumene is not only used as feed, but also for various utility-like purposes throughout the plant. For example, cumene is sent from the day tank to the phenol recovery section on a batch basis as make-up solvent. It can also be used to flush pump seals in various sections of the plant.

The process off-gas from the oxidiser is monitored to ensure, for safety reasons, a low oxygen concentration. It is routed to a recovery and abatement system consisting of a combination of the following elements:

- two-step condensation (cooling water, chilled water or refrigerant);
- adsorption on activated carbon;
- final treatment, e.g. with thermal oxidisers.

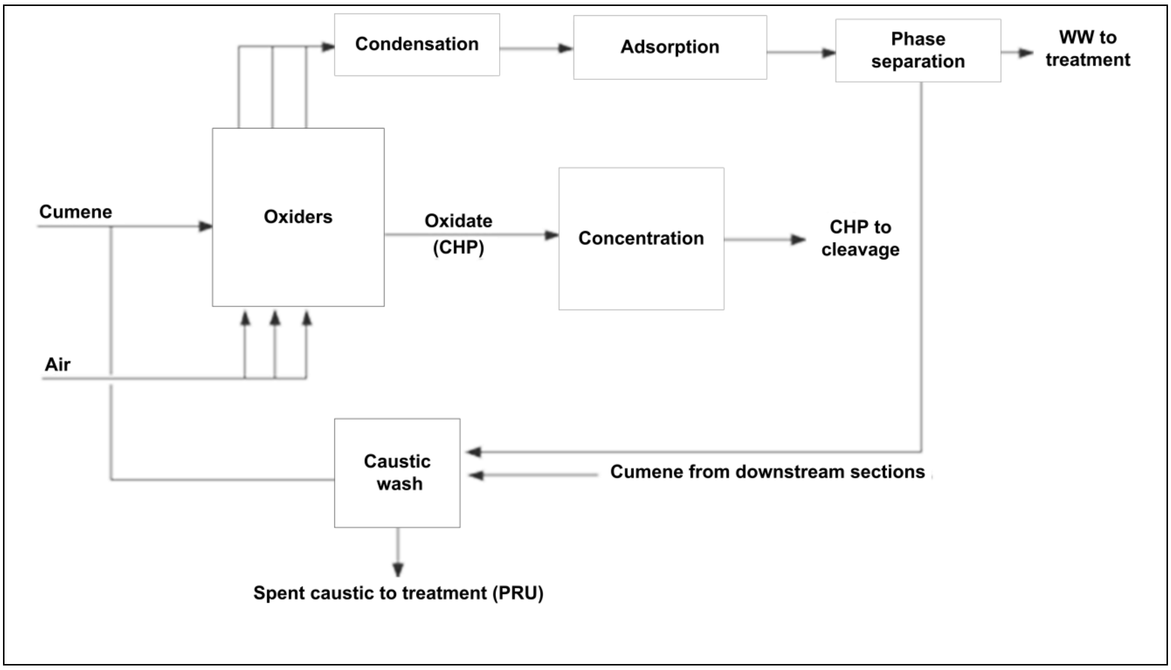


Figure 8.3: Cumene oxidation process

8.2.2.2 Concentration section

This section increases the CHP concentration from 17–30 % at the oxidation outlet to 65–85 % at the cleavage inlet. Conceptual designs seek low hold-up. This can be achieved with thin film evaporators or flash columns. The oxidate from the last oxidiser flows to the concentration section to recover unreacted cumene. For large phenol units, it is economical to use a two-column concentration system, in which the heat of reaction from the last oxidiser and very low-pressure steam are used to vaporise cumene in the first (pre-flash) column, reducing the size of the main flash column. The pre-flash drum and flash column operate under vacuum to minimise the temperature needed to concentrate the CHP. The vacuum is typically generated by an ejector system. Under vacuum in the pre-flash drum, cumene vaporises in the upper vaporiser. Additional cumene vaporises in the lower vaporiser with heat supplied by very low-pressure steam. The final CHP concentration is achieved in the flash column vaporiser and flash column, both of which operate under deeper vacuum than the pre-flash drum. The pre-flash drum bottom stream flows through the flash column vaporiser, where additional cumene vaporises using heat from low-pressure steam [10, Zakoshansky 2009], [11, Zakoshansky 2007].

8.2.2.3 Cleavage section and neutralisation

The decomposition of the concentrated cumene hydroperoxide (CHP) to produce phenol and acetone is catalysed by an acid (usually sulphuric acid) and typically carried out as a two-step reaction. Two-phase heterogeneous systems (with a ratio of about 1:4 of CHP to diluted

sulphuric acid (concentration around 40 wt-%) and recycling of the aqueous phase) and homogeneous systems with only small amounts of acid added are used.
Besides the main reaction, DMBA dehydrates to α-methylstyrene (AMS).

The acid added in the cleavage section needs to be neutralised to prevent yield loss, due to side reactions, and to protect against corrosion in the fractionation section. The most common neutralisation techniques used are with sodium phenate (to phenol and natrium sulphate) or ion exchange resins (e.g. caustic-exchanged sulphonic resins) (which need regeneration cycles).

8.2.2.4 Fractionation/purification section; hydrogenation of AMS

Distillation operations are performed to isolate the different reaction products: phenol, acetone, unreacted cumene and other by-products. Techniques like filtration and ion exchange resins or further reactions are required in some designs to deliver high-purity products. The AMS generated will require either purification (distillation) or hydrogenation to recover cumene.

Hydrogenation is carried out in fixed-bed reactors under pressure with an excess of hydrogen, with recycling of excess hydrogen.

8.2.3 Other than normal operating conditions

8.2.3.1 Specific other than normal operating conditions

The following operations deviate from the stable and normal operating procedures.

Some frequencies reported in the BREF review data collection, via questionnaires, are included below (in days per year).

Operations with potentially higher emissions to air of VOCs:

- malfunction or failure of spent air oxidiser post-condensers (0 to 15 days/yr);
- charcoal absorbers' end of run and malfunction (0 to 40 days/yr);

Operations with potentially higher emissions to water:

- charcoal decanter malfunction;
- neutralisation decanter malfunction;
- malfunction of phenol recovery treatment;
- higher emissions to water from fractionation upon azeotrope equilibrium changes (complex azeotrope with water, phenol, 2MBF, etc.)

8.2.3.2 Generic other than normal operating conditions

The following operations can arise and deviate from the standard operating procedures in phenol manufacturing plants:

- Routine start-up.
- Shutdown for maintenance preparation: equipment flushing, higher load to WWT, potential emission to surface water (rainwater) header.
- Low plant rate due to force majeure in final product consumption or in raw material supply.

- Containment losses greater than normal in systems that operate under vacuum (CHP concentration, fractionation or AMS distillation). This will increase ejector water/steam usage, and net emissions to water or air.
- Plant being idle due to loss of containment.
- Service or utility failure: malfunction of cooling water and/or chilled water; power, DCS, instrument air.

Reported frequency of all these events: 15 to 35 days per year (not taking into account lower plant rate events). There are outlier/exceptional values of 57 and 167 days per year for shutdowns.

8.2.4 Equipment important for environmental protection

The following assets perform important operations for the protection of the environment and should have as high a level of reliability and availability as possible:

- air: charcoal adsorber outlet periodic sampling; chilled water TIC (oxidiser condensers); charcoal adsorber regeneration programme;
- water: phenol recovery unit (PRU) interphase level instruments; PRU aqueous stream periodic sampling;
- by-products: O_2 concentration monitoring at oxidiser outlet; cleavage TIC control loop.

8.3 Current emission and consumption levels

The main emission to air from the process is from the spent air downstream of the cumene oxidisers. Cumene and other VOCs are present in this stream. There are numerous sources of emissions to water. The aqueous emissions are normally treated collectively to recover phenol, cumene and acetone. The largest by-product is a stream of tars, which are separated in a fractionation section but are generated in reaction sections upstream. Reaction selectivity is a key parameter to minimise tar production at source. Salts (e.g. sodium sulphate) formed in the neutralisation section and other sections also need to be addressed. Fugitive emissions and emissions from storage are also important.

Figure 8.4 shows the main emission streams from the phenol manufacturing process. The diagram corresponds to one of the design options for the cumene oxidation process.

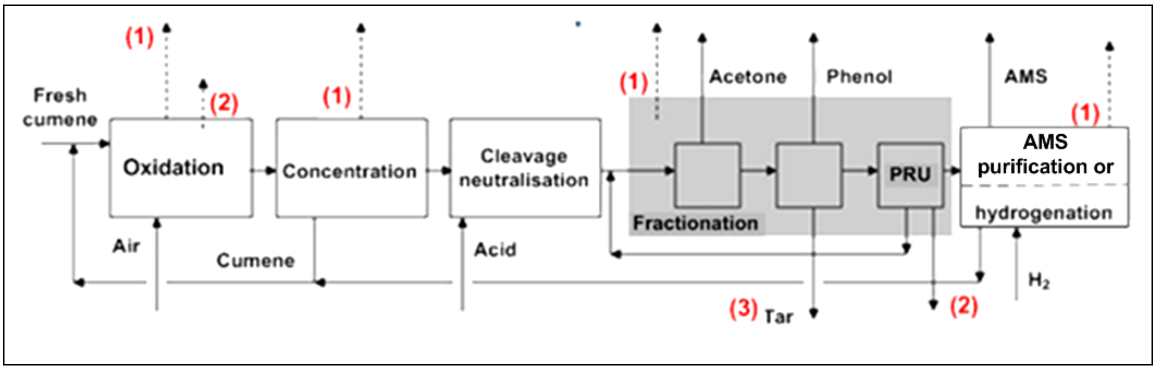


Figure 8.4: Phenol production process: (1) waste gas to treatment (2) waste water to treatment, (3) residues

8.3.1 Emissions to air

8.3.1.1 VOC and benzene emissions from oxidiser spent air

The spent air stream from the oxidation reactors comprises warm, wet air with a depleted oxygen level and containing a range of VOCs. Entrainment separators or knock-out drums, condensers and chilled water post-condensers are used to reduce the load and recover material. Operating at lower O_2 levels in the spent air will reduce the volumetric airflow and so the level of entrainment.

The organic load consists mainly of cumene; however, other pollutants present are cumene hydroperoxide, benzene, methyl hydroperoxide, methanol, and acetone.

Benzene: as an estimate, with a benzene content of 0.001 wt-% in the cumene feed (maximum content according to standard specifications), about 14 g benzene/t of phenol produced or 13 mg/Nm^3 could be present in the oxidiser vent before treatment. Benzene is expected to be removed very efficiently by adsorption (where it then would leave the process via the light-boiling fractions of the distillation section) and/or thermal oxidisers. For either technique, it can be expected that the achieved benzene concentration will be constantly < 1 mg/Nm^3.

Methane: methane is present too, in ranges between 100 mg/Nm^3 and 400 mg/Nm^3 after oxidation and before treatment (data from five plants).

VOC levels after oxidation will depend on the pressure applied during the reaction, with higher concentrations for low-pressure reactions.

Monitoring format: the emission pattern in the outlet of an adsorber is normally ‘sawtoothed’. The combined vent from several adsorbers will show a smaller spread. Some plants have continuous monitoring of TVOC or NMVOC.

Data downstream of adsorbers that are used as an end-of-pipe treatment without further downstream VOC abatement:

- flow rate: ~ 1 000–1 500 Nm^3/t of phenol (the stoichiometric flow rate for spent air would be about 1 100 Nm^3/t of phenol for complete reaction of oxygen and using air without additional oxygen);
- total organic compounds: 35 mg C/Nm^3 (NMVOC) maximum monthly average;
- methanol: < 100 mg/Nm^3 maximum;
- benzene: 3 mg/Nm^3 maximum.

Further reduction is often achieved using thermal or catalytic oxidisers as an end-of-pipe treatment (see Section 8.3.1.5). Then, the optimisation of the performance of the abatement system may lead to higher concentrations in the outlet of the adsorbers.

8.3.1.2 VOC emissions from CHP concentration

The gas flow rates from the vacuum system in the CHP concentration step are small compared to the gas flow rates coming from the oxidisers. The streams can be combined with the oxidiser's vent upstream of the adsorber or of the thermal oxidiser or routed to other shared devices to incinerate VOCs.

To reduce the organic load, condensers are used on the top cuts of process distillation and concentration equipment. Pollutants are cumene mainly and others such as acetone.

8.3.1.3 VOC emissions from fractionation

The fractionation processes involve multiple distillations, some of which are conducted under vacuum in order to reduce product degradation and colour.

To reduce the organic load, condensers are used in distillation columns and vacuum systems.

The flow rate is in the range of 10–15 Nm^3/t of phenol (one plant, including vents from storage).

Pollutants are methanol, acetone, cumene and phenol.

For VOC abatement, the waste gas is routed to a thermal oxidiser or a combustion unit.

Other than normal operating conditions: vacuum leaks may lead to a larger condenser workload (flow of non-condensables plus air intake) and thus lower the condensing efficiency, resulting in a larger load being sent to the final abatement device.

8.3.1.4 VOC emissions from hydrogenation of AMS

Most installations have a hydrogenation unit to enable the reconversion of the α-methylstyrene (AMS) by-product to cumene. Downstream of the hydrogenation reactor there will be a flash separator or flash drum to split the product (cumene, AMS, etc.) from the gas stream. Excess hydrogen is recycled, but a small vent occurs from the depressurisation of the product (figures from two plants: 0.8 Nm^3/t, 1.2 Nm^3/t and < 10 Nm^3/t of phenol).

Pollutants are cumene and AMS.
The TVOC concentration before abatement was reported to be about 2 000 mg/Nm^3 (corresponding to a specific TVOC load of 2.4 g/t of phenol) (one plant).

For VOC abatement, the preferred option is to route the waste gas to a dedicated activated carbon adsorber, to achieve TVOC concentrations < 50 mg C/Nm^3.

Other than normal operating conditions: according to information from CEFIC, the abatement systems in place at the plants in the EU also cover the hydrogen stream from hydrogenation during start-ups, with no emission values higher than during normal operation.

8.3.1.5 Emissions after end-of-pipe abatement

Typically, regenerative thermal oxidisers (RTOs) are used as final abatement for the waste gas from the oxidisers. They could be used for the common treatment of various waste gas streams. However, in most cases the RTO treats mainly or only the waste gas from the phenol plant, e.g. from the oxidiser and the concentration unit. For emissions of organic pollutants, see Section 8.3.1.1. Flow rates are typically about 1 200 Nm^3/t of phenol. Data from two plants with addition of air for the RTO: 1 320 Nm^3/t and 1 180 Nm^3/t of phenol including 260 Nm^3/t and 275 Nm^3 of air/t of phenol to carry out thermal oxidation.

- VOCs: 3– ~ 35 mg C/Nm^3 average for thermal oxidisers, ~ 110 mg/Nm^3 for one catalytic oxidiser;
- benzene: < 0.007 (three plants) – 0.4 mg/Nm^3 (one plant) average (or typical concentration);
- methane: < 1–5 mg/Nm^3 for thermal oxidisers, 50–60 mg/Nm^3 for one catalytic oxidiser.

For further details, see Table 8.6 in Section 8.4.1.

US EPA reported 2 g of benzene emitted per tonne of phenol downstream of condensers and 0.058 g per tonne downstream of the thermal oxidiser. [12, US EPA 1998].

Referring to a specific flow of about 1 200 Nm^3/t of product, this would correspond to estimated average benzene concentrations of 1.7 mg/Nm^3 and 0.05 mg/Nm^3.

Alternatively to the combined treatment together with the off-gas from the oxidiser unit, vents from the vacuum systems (concentration, fractionation) are incinerated separately and are reported to achieve similar VOC concentrations (TVOC < 50 mg/Nm^3). The flow rate is reported to be around 100 Nm^3/t of phenol, most of it (75 Nm^3/t of phenol) from the added air that is needed for the waste gas oxidation.

No data have been collected for emissions of CO and NO_X from thermal oxidisers at phenol plants. NO_X concentrations are expected to be low since RTOs can be run with low NO_X emissions and temperatures above 1 000 °C are not expected to be required.

8.3.1.6 VOC emissions from fugitive emissions

Many assets operate under pressure which increases the potential for fugitive emissions.

Pollutants are cumene, acetone, phenol, etc.

Other than normal operating conditions: maintenance turnarounds lead to equipment opening and higher emission values.

Information from the data collection:

- Monitoring methods: LDAR, sniffing; SF6 or UNE EN 15446.
- Frequency: dependent on site and/or permit requirements, e.g. once per year, full plant survey every five years, up to 3 600 samples/year. Other units perform periodic emission measurements in the surroundings; gas detectors at specific locations with the highest risk (e.g. for acetone).
- Fugitive VOC emissions: 0.02–0.06 kg/t of phenol produced, 0.5–200 t/yr.

8.3.1.7 VOC emissions from storage

Tanks, spheres and other storage assets are used for raw materials, consumable end-products and intermediates. These may be geographically too far apart in the plant layout to share abatement techniques with the main process streams. See the EFS BREF.

Pollutants are cumene (potentially with some benzene), acetone and phenol.

8.3.1.8 Emissions to air from combustion processes

Steam boilers or hot oil furnaces that supply heating fluid utilities can be dedicated to a phenol plant or shared with nearby installations. These emissions will also include the combustion of non-conventional (non-commercial) fuel, such as the tar stream generated in the fractionation section.

Pollutants are VOCs, NO_X, CO and dust.

8.3.2 Emissions to water

The main organic load from phenol production can be categorised as:

- process waste water from the oxidation section (reaction and concentration) containing organic hydroperoxides (followed by pretreatment to reduce organic hydroperoxides); and
- process water from the fractionation containing phenol and other organic compounds such as acetone (followed by pretreatment to remove/recover phenol and other organic compounds).

8.3.2.1 Waste water from the oxidation section

The waste water may comprise the following sources.

Source	Description
Aqueous caustic used in the oxidation section	If the 'wet' oxidation route is used, water will be introduced at the beginning of the process in the form of caustic solution and will need to be removed at a later stage.
Wet scrubbing of the oxidation feed	The low-pressure oxidation route generates an aqueous stream from the scrubbing of the oxidation feed (air and cumene). This stream contains cumene, organic salts and organic acids. Analytical control (of washing performance) should reduce this flow.
Condensers	Condensation of the off-gas from the oxidation results in an aqueous phase, after phase separation.
Regeneration of the adsorbers	The steam desorption of VOCs from the activated carbon adsorbers will result in an aqueous stream from a decanter.

Typical pollutants are organic hydroperoxides (CHP, MHP), methanol and organic acids.

At most sites, the waste water from the oxidation section is pretreated to decompose organic peroxides. Industry carried out a data collection on the peroxide concentration with (five plants) or without (two plants) pretreatment. The findings are summarised in Table 8.2 below.

Total peroxide concentrations (sum of CHP and MHP) are expressed as mg CHP/l.

Table 8.2: Organic peroxide concentration in waste water from cumene oxidation

Plant	Waste water from (1)	Pre-treatment (2)	Organic peroxides as CHP (mg/l)	Method	Detection limit (mg/l)	Frequency
1	A	TT	< 100	Iodometric titration	50	Once a day
2	A, B	TT	< 50	Spectro-photometric	50	Not regularly
3	A, B	None	8 370	Iodometric titration	50	Once a day
4	A, B	TT	< 100	CHP: extraction (chloroform) and gas chromatography MHP: titration	50	NI
5	A, B	None	3 500–8 200	Iodometric titration	100	Regularly
6	A	TT	< 100	Iodometric titration	50	Once a day
7	A	CT	< 100	HPLC	50	Twice a day

(1) A: Oxidation and concentration section only (emission sources for organic peroxides).
B: Other units of the phenol process (where waste wate streams do not contain organic peroxides).
(2) Hydrolysis: TT: Thermal treatment; CT: Catalytic treatment.
NB: NI: No information.

All operators used in-house methods for analysis, without reference to standard methods. Most operators used iodometric titration to determine the total peroxide content, although other methods such as high-performance liquid chromatography (HPLC) can be used to determine the content of the different peroxide species, at lower detection limits.

8.3.2.2 Waste water from the fractionation section

The waste water may comprise the following sources/streams.

Source	**Description**
Cleavage section	Water or steam may be introduced in the second cleavage step to improve selectivity towards phenol, acetone and AMS. Some water is formed by the dehydration of DMBA. This stream will be withdrawn in fractionation.
Neutralisation	Sodium phenate option: Water will be introduced into the process in the form of the caustic solution that is used to neutralise the acid catalyst and/or remove phenol from the recycled cumene. The aqueous phase from the neutralisation decanter will contain salts (sodium sulphate from the neutralisation of sulphuric acid) and phenol from the neutralisation of sodium phenate. Ion exchange option: the regeneration of the ion exchange resin used for neutralisation will give rise to a discontinuous effluent.
Crude acetone column	Water is injected into the crude acetone column to increase the volatility of the acetone and maintain the bottom temperature. The overhead of the column (acetone, water and cumene) flows to the finished acetone column.
Acetone finishing column	An aqueous stream results from the final pure acetone distillation column as a result of caustic scrubbing to remove aldehydes.
Phenol purification	Aqueous stream(s) may contain impurities such as 2-methylbenzofuran.
Vacuum systems	The use of steam ejectors will give rise to more waste water and emissions to water than the use of liquid-ring or dry-running pumps.
Phenol recovery unit (PRU) (see Section 8.4.2.3)	The PRU's extraction column bottom stream will contain solvent (cumene), phenol, acetophenone, acetone and salts (sodium sulphate).

Most of these waste water streams contain relevant concentrations of phenol (e.g. 1–2 % in the neutralisation effluent [8, Weber et al 2005]) and other organic compounds. Phenol is typically removed by extraction with cumene or other appropriate solvents under acid conditions (pH < 7), followed by the removal of solvent and other light boilers, e.g. by stripping (alternative adsorption).

The total process effluent sent to the final waste water treatment could contain the below pollutants and quantities at the WWT unit inlet.

Table 8.3: Collective effluent composition upstream of the final waste water treatment

Parameter	**Unit**	**Average (1)**	**Min.–max.**	**Method**
Phenol	(mg/l)	135	18–425	ASTM-D1783; DIN38409-16
Acetone	(mg/l)	314	15–1 000	NI
Cumene	(mg/l)	20	0.6–50	NI
SO_4^{2-}	(mg/l)	14 676	34–29 319	NI
COD	(mg/l)	5 550	2 000–15 000	DIN 38409-41

(1) Average value obtained from all the raw data sets received by the EIPPCB.
NB: NI: No information.
Source: Data collection

- Phenol: Phenol is partially soluble in water and it may be present as a discrete organic phase. Phenol in high concentrations in waste water could have harmful consequences for any downstream biological effluent treatment plants, and may even cause a sufficient toxic shock to render the effluent treatment plant ineffective for days. Phenol in low concentrations may become feedstock for the bacteria.
- Phenolates: Phenolates are highly soluble in water and will form free phenol when reducing the pH of the effluent (pKs ~ 10).
- Cumene: Cumene is nearly insoluble in water. It is toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. Cumene is readily biodegradable [5, Weber et al. 2010].
- Acetone: Acetone is miscible with water.
- Sodium sulphate: The neutralisation of the sulphuric acid with sodium hydroxide/phenolate will result in the formation of sodium sulphate.
- Depending on the pretreatment, COD levels can be high at the phenol plant outlet.

8.3.3 Raw material consumption

a) Consumption of cumene

Cumene consumption is dependent on the quantity of waste and/or by-product generated and is a key parameter that influences profitability. Some producers hydrogenate AMS to recover cumene feedstock but others recover and purify AMS. Cumene consumption is expressed per total production of acetone, phenol and AMS. Cumene consumption is typically in the range 1.31–1.38 tonnes per tonne of phenol [10, Zakoshansky 2009], [9, Schmidt 2005], [11, Zakoshansky 2007], [13, Eni-polimeri 2009], [14, IPP 2009].

Table 8.4 shows how some parameters impact on feedstock usage.

Table 8.4: Parameters that affect feedstock usage

Aspects	Impact on feedstock usage	Applicablility	Cross-media effects
Raw material quality	Small reduction	Fully applicable	None
High reaction volume oxidation	Medium reduction	New plants	None
Low reaction volume oxidation	Medium increase	New plants	None
Oxidation control at low temp. and low CHP %	Medium reduction	Fully applicable	Lower conversion. Higher energy usage
Cleavage two-step design	Large reduction	New plants	None
Calorimeters in cleavage control	Medium reduction	Fully applicable	None
PRU recovery efficiency	Small reduction	New plants	None
Fractionation recovery efficiency	Small reduction	New plants	None

b) Consumption of sulphuric acid

For the cleavage reaction, an acid catalyst is used, normally sulphuric acid. New techniques now employ a second modifier. The required concentration of acid in the process mixture is very low. Acid is also used to separate at source any phenol carried over into the main aqueous emission stream.

c) Consumption of caustic

Caustic can be used at various points in the process, including the below:

- Oxidation: Caustic is used in every process design alternative to remove phenol from the recycled cumene stream, and to possibly neutralise the acids in that stream.
- Caustic is also used in the neutralisation of cleavage product when exchange resins are not used.
- Fractionation: In some designs, caustic is injected into the acetone purification column (FAC) to catalyse the condensation of trace aldehydes. The heavier condensation products are less volatile and leave with the column bottoms. High-purity acetone flows by gravity from the acetone purification column side cut, near the top of the column, to the acetone product day tank.
- The AMS stream is recovered from the fractionation section with some cumene content. Caustic scrubbing is applied to avoid phenol content.
- Effluent treatment at source: Use in the phenol recovery unit (PRU).

d) Hydrogen consumption

If AMS is hydrogenated to cumene, the process will consume hydrogen. Any hydrogen that might be consumed can be offset against reduced cumene consumption, as not hydrogenating the AMS would necessitate a higher make-up of cumene, all other things being equal. However, AMS can be a valuable product.

Hydrogenation is carried out under pressure and excess hydrogen is recycled to the hydrogenation reactor. Only small hydrogen losses occur from the downstream depressurisation of the cumene phase.

e) Hydrogenation catalyst consumption

Where a process incorporates the hydrogenation of AMS, it will be necessary to periodically replenish the catalyst (normally palladium-based). However, it is believed that this will be an infrequent operation.

f) Ammonia consumption

Ammonia will be consumed only if it is fed to the oxidation reactors in an effort to reduce by-product formation.

g) Spent ion exchange resins

The use of resin guard beds is a design option for both the neutralisation step and the phenol purification step: Spent resin is typically ~ 80 kg/t of phenol. (*Source*: Data collection).

8.3.4 Energy consumption

Data availability and confidentiality limit the analysis of energy consumption versus techniques. Data from literature are as follows.

Table 8.5: Energy usage in phenol plants

Steam (t/t)	Electrical (kWh/t)
1.9 (18 bar) 0.4–0.9 (5 bar)	190
6.32	326
Source: [13, Eni-polimeri 2009] [14, IPP 2009]	

a) Concentration and fractionation

The concentration of CHP and the separation and purification of the various co-products (and possible by-products) are achieved by distillation. The number of columns involved, and the nature of the separations required, mean that the energy consumed for the fractionation processes is likely to be a major influence on energy use. The fractionation energy will be reduced by applying those techniques that reduce the generation of by-products.

b) Oxidation reactor air compressors

The oxidation reactors are supplied with compressed ambient air. The energy consumed by the compressors will therefore be significant.

c) Vacuum systems

In order to prevent the decomposition of CHP (which, as a safety issue, is the main driver) and to reduce by-product formation (and therefore possibly reduce cumene consumption, fractionation energy consumption, etc.), the temperature of the CHP concentration step is reduced by operating under vacuum. The energy consumption will depend upon the degree of vacuum desired.

8.3.5 Water usage

Total water usage is typically 1–4 tonnes of water per tonne of phenol including cooling water make-up. Water is introduced into the process as part of some raw materials (e.g. sodium hydroxide solution, sulphuric acid). See Section 8.3.2.

Process water may also be added at the fractionation and purification units in order to modify a column's composition and temperature profile. Water may also be needed for the washing of process streams (e.g. to remove salts) and the regeneration of ion exchange columns (used for neutralisation after the cleavage reaction). Water that is used in the operation of vacuum pumps could be reused as process water.

8.3.6 By-products and waste generation

a) Tar

The crude phenol isolation step results in a high-boiling distillation residue including degradation products (also called tar). The tar can be used in the furnace to recover heat. The tar used can also be cracked to recover feedstock. Tar generated: 20–200 kg per tonne of phenol. [10, Zakoshansky 2009], [11, Zakoshansky 2007].

Data from questionnaires fall inside the range mentioned above.

b) Methanol and MHP

Methanol and methylhydroperoxide (MHP) are generated in the oxidation reaction.

c) Acetophenone

Acetophenone (ACP) is either recovered as a commercial product or used as a fuel in furnaces or steam boilers.

d) Spent catalyst from the hydrogenation reactor

If AMS is hydrogenated back to cumene, this will involve the use of a catalyst, which will need to be replaced from time to time.

f) Spent activated carbon

The adsorbent used to recover VOCs from the oxidation off-gases will need to be replaced periodically due to a loss of efficiency. The lifetime of the charcoal used depends strongly on the amount of charcoal used in the adsorbers and the amount of off-gas cleaned by it and by the set-up of the process (i.e. depending on whether adsorption is the end-of-pipe technique or whether it is followed by a thermal oxidiser). The reported amount of charcoal generated is 0.1 kg per tonne of phenol.

g) Ion exchange resins

Ion exchange resin beds are used both in the neutralisation unit and in the phenol purification steps. The amount generated is approximately 0.5 kg/t.

8.4 Techniques to consider in the determination of BAT

This section describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this chapter. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations). Cross references to other chapters are used, where relevant to avoid repetition.

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 2.6 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

8.4.1 Techniques to reduce emissions to air

8.4.1.1 Techniques to reduce the VOC load sent from the oxidation section to final treatment

The following table is an extract of the information gathered by the BREF review data collection, via questionnaires, regarding treatment strategies and final emissions.

Table 8.6: Emissions from the phenol plant oxidation section after treatment

Plant	**Emission values**				**Monitoring**		**Techniques applied**		
	TVOC (mg C/Nm^3)		Benzene (mg C/Nm^3)		Frequency	Averaging period	Condensers	Adsorber	Thermal oxidiser
	Average	Max.	Average	Max.					
1	34.6 (1)(2)	112 (1)(2)	ND	ND	Continuous	1 month (max.)	ND	Yes	No (3)
2	6	ND	ND	ND	Individual samples	3 years	ND	No	Yes
3	ND	57 (4) (5)	ND	3	Continuous (6)	ND	Yes	Yes	No
4 (7)	24.2. (1)	33.6 (1)	1.7	3.8	4 samples/yr	8 hours	ND	Yes	Yes
5	ND	ND	ND	ND	ND	ND	Yes (8)	Yes	No
6	15.8 (1)	ND	ND	ND	Continuous	1 year	ND	Yes	Yes
7	~ 110 (9)	< 120	< LOD	< LOD	Continuous	1 year	Yes (8)	No	Cat. ox.

(1) NMVOC.
(2) Average and maximum from measurements over 1 year; maximum of half-hourly averages.
(3) RTO installed after data collection.
(4) Mainly methanol (maximum concentration 100 mg/Nm^3).
(5) Calculated NMVOC as C from total of individual organic compounds reported in questionnaire; number of measurements not available.
(6) For benzene.
(7) From questionnaire (2010–2012 data); later on, data of quarterly periodic measurements (averages over 8 hours) for 2010–2015 were provided as a graph, with NMVOC concentrations in the range of 18–72 mg/Nm^3; according to the operator, the concentration mainly depends on the age of the ceramic in the RTO unit, the age of the activated carbon in the adsorption unit and the plant activity.
(8) Combination of condensers with cooling water and chilled water.
(9) Methane concentration 50–60 mg/Nm^3 corresponding to 38–45 mg C.
NB: ND = No data available. LOD = Limit of detection.
Source: Data collection and supplementary information from industry.

8.4.1.1.1 Reduction of liquid entrainment

Description
Reduction of liquid entrainment

Technical description
This involves the use of techniques that reduce the carry-over of droplets in gaseous streams (e.g. from chemical processes, condensers, distillation columns) by mechanical devices such as settling chambers, mist filters, cyclones and knock-out drums.

It is used for example in the oxidation section for the off-gas leaving the condensation unit (see Section 8.4.1.1.2 below).

8.4.1.1.2 Condensation

Description
Condensation is used to recover organic material from the off-gas of the oxidation reactor and to reduce the workload for the downstream treatment.

Technical description
Two-stage condensation uses cooling water for the pre-condensation and chilled water or other refrigerants for post-condensation. The main components are cumene and methanol, besides some water. Cumene is returned to the process, and the aqueous phase is discharged as waste water.

To improve the condensation efficiency, temperatures < 0 °C can be reached when substances which lower the freezing temperature are present or added to the reactor off-gas [121, Weber 2003].

To avoid an increase in emissions due to other than normal operating conditions, the following techniques can be used:

- redundant cooling water pumps;
- condensers' duties are designed with an additional safety factor;
- high level of process control and alarms on the cooling utility systems (CW and chilled water), e.g. with process interlock to avoid oxidation operation in the case of lower condensing capacity.

Achieved environmental benefits
- Recovery of organic feedstock (cumene).
- Reduction of VOC emissions to air.

Environmental performance and operational data
The temperature in the condensers can be lowered to < 0 °C, normally to -2 °C.

An increase of the lowest temperature from -2 °C to +2 °C would increase the cumene load by around +40 %.

Cross-media effects
Energy is required for cooling.

Technical considerations relevant to applicability
Generally applicable.

Economics
Condensation is expected to be more economically efficient for recovery than using only adsorption.

Driving force for implementation
Economics: Better yield due to feedstock recovery.

Example plants
Although only two operators reported using condensation (both with cooling water and chilled water), two-step condensation is used more often and is a standard feature of the production process [8, Weber et al 2005].

Reference literature
[10, Zakoshansky 2009], [11, Zakoshansky 2007].

8.4.1.1.3 Regenerative adsorption

Description
Use of adsorption to recover organics and reduce the VOC load sent to final abatement.

Technical description

In phenol production, adsorption (which is described in the CWW BREF) can be applied to the spent air stream from the cumene oxidation unit, typically after reducing the workload by condensation, in order to reduce the organic content of this gaseous stream and recover cumene for reuse.

The VOC removal efficiency and cumene recovery efficiency from the spent air stream will depend on:

- size of chambers per volumetric flow and VOC load;
- type of material selected;
- regeneration sequence;
- whether or not cooling is carried out prior to realigning the regenerated chamber.

At European plants, activated carbon is used for adsorption. Adsorption capacity and removal efficiency can be improved significantly by a combination of different types of activated carbon optimised to remove both cumene and methanol [121, Weber 2003].

If cumene oxidation is carried out under pressure, the adsorption will be too.

Adsorption efficiency decreases with higher temperatures, which can usually be compensated by elevated regeneration frequency. Regeneration is normally done with steam. This raises the bed temperature. Therefore, the bed needs to cool down after regeneration and prior to alignment to avoid bad performance / peak emissions in the initial adsorption stage.

Continuous VOC monitoring can be used to optimise the performance of the adsorption unit, i.e. the timing and frequency of regeneration.

The operation of the adsorption unit may differ to some extent depending on whether it is used as the final abatement step or whether there is an additional abatement step (usually an oxidiser) installed downstream, although the emissions from (regenerative) thermal oxidisers also depend on the level and fluctuation of the TVOC input.

The adsorption unit may also be used to abate emissions from other parts of the phenol process, e.g. from concentration.

If the adsorption is carried out under pressure, the purified off-gas may be used as technical-grade nitrogen, e.g. for blanketing or venting of process equipment [123, Weber et al. 2014].

Achieved environmental benefits

- Recovery of some organic feedstock (cumene).
- Reduced VOC emissions (including pollutants such as benzene).

Environmental performance and operational data

For removal efficiency, see Table 8.6 and specifically Plants 1 and 3 for adsorbers that perform the final abatement; concentration levels may be higher if the waste gas is routed to a thermal oxidiser for final abatement.

The optimal flow velocity is 0.1–0.2 m/s [121, Weber 2003].

Cross-media effects

- Consumption of energy (steam) for regeneration (about 5 kg steam/kg of VOCs adsorbed).
- Waste water from regeneration.

Technical considerations relevant to applicability
Generally applicable for the individual waste gas streams of the phenol plant or as shared treatment (the latter without waste gas from hydrogenation for safety reasons).
This technique is considered generally applicable and retrofitting is possible. This will result in more efficient use of raw materials and lower VOC emissions.

Economics
Benefits from the recovery of educt are reduced by the costs for work-up and steam.

Driving force for implementation

- Economics, regarding optimised recovery.
- Environmental legislation, regarding minimisation of emissions to air.

Example plants
Most phenol plants in Europe use adsorption for the off-gas from the oxidation reactor (see Table 8.6).

Reference literature
[121, Weber 2003], [10, Zakoshansky 2009], [11, Zakoshansky 2007].

8.4.1.2 Techniques for final VOC abatement

According to the data collection, every phenol plant has a dedicated treatment for the main waste gas stream, the off-gas from the oxidation reactor which may also be used for the waste gas from other units but which typically is not shared with other production processes. The smaller streams from other units (concentration, fractionation, hydrogenation) are treated at the plant or routed to shared systems.

The data collection shows that one plant uses a catalytic oxidiser as the final abatement step. Because of the high emission levels reported for VOCs, this technique has not been considered as a BAT candidate.

Regenerative thermal oxidiser (RTO)
See the description and technical description in the CWW BREF.

Achieved environmental benefits

- Reduction of VOC emissions to air.
- In comparison to other thermal oxidisers, reduction of combustion-related consumption (support fuel) and emissions (NO_X) to air.

Environmental performance and operational data
See data on emissions of VOCs and benzene in Table 8.6.

The concentration achieved is dependent on the input concentration (which itself depends on the performance of pretreatment), and may depend on the age of the ceramic bed.

Technical considerations relevant to applicability
Generally applicable.

Example plants
RTOs are used in most of the phenol plants in the EU, e.g. Ineos Phenol, Gladbeck (DE); Ineos Phenol, Antwerp (BE); Novapex S.A.S., Roussillon (FR); Borealis (SF), Porvoo (FI) (see Table 8.6).

Shared thermal oxidiser
See the description and technical description for thermal oxidisers in the CWW BREF.

Shared thermal oxidisers are used for the abatement of VOCs from streams other than the waste gas from the oxidation reactor.

For the waste gas from hydrogenation, the applicability may depend on safety considerations.

Combustion
This technique involves sending the waste gas stream to a combustion unit (boiler or furnace). For the description of combustion processes, see the LCP BREF.

Combustion is used for the abatement of VOCs from streams with calorific value, other than the waste gas from the oxidation reactor, combining VOC abatement and energy recovery.

For the waste gas from hydrogenation, the applicability may depend on safety considerations and the assessment of the benefits in comparison to the need for recompression.

Adsorption
See the description and technical description for adsorption in Section 8.4.1.1.1 and in the CWW BREF. Adsorption is used at three sites as dedicated treatment for the waste gas from hydrogenation, from the depressurisation after the reaction. Because of the much smaller load in comparison to the waste gas from the oxidation section, the adsorber unit may have a much smaller capacity or desorption frequency. For the same reason and due to the reduced potential for recovery of organic material, non-regenerative adsorption may be used.

8.4.2 Techniques to reduce emissions to water

8.4.2.1 Techniques at source: Optimised phase separation

In phenol production, several waste water streams arise from phase separation of aqueous and organic streams. Appropriate design and operation are needed to avoid any entrainment of undissolved organic material. For many effluents from the phenol process, phase separation has to be carried out at an optimum pH to reduce the solubility of organic material (e.g. phenol, organic acids). Acid conditions ($pH < 7$) are needed to covert phenolate to phenol. The recovery efficiency can be increased by cooling the effluent, as this will reduce the solubility for example of phenol in the aqueous phase.

8.4.2.2 Pretreatment of waste water from the oxidation section

8.4.2.2.1 Hydrolysis to decompose organic peroxides

Description
In order to reduce emissions to water of organic peroxides from the oxidation unit and, if necessary, to protect the downstream biological waste water treatment plant, waste water (mainly from the condensers and the adsorber regeneration, after phase separation) is treated thermally (at temperatures above 100 °C and a high pH) or using a solid catalyst to decompose organic peroxides to non-ecotoxic and more readily biodegradable compounds (such as methanol and formic acid).

The decomposition reaction may lead to the formation of gas (hydrogen).

Technical description
No information provided.

Achieved environmental benefits

- Prevention of increased emissions to water due to malfunctions of the biological treatment which can be caused by high levels of organic peroxides.
- Reduced emissions of peroxides to water (although the effect may be low, depending on the removal efficiency in the biological treatment).

Environmental performance and operational data
For information on environmental performance, see Table 8.2 in Section 8.3.2.1.

No data were provided for the concentration of peroxides at the outlet of the final treatment but it is expected to be far beyond the detection limits reported in Table 8.2 (50–100 mg CHP/l).

Cross-media effects

- Consumption of energy (heat).
- Potentially a small waste gas stream (mainly hydrogen).

Technical considerations relevant to applicability
No information provided.

Economics
Operational costs are estimated to be low (mainly supply of heat and, if needed, caustic).

Driving force for implementation
Environmental protection.

Example plants
Of the seven plants in the EU, four use thermal treatment (Borealis (SF), Porvoo (FI); Ineos Phenol, Gladbeck (DE); Ineos Phenol, Antwerp (BE); Novapex S.A.S., Roussillon (FR)) and one catalytical treatment (DOMO Caproleuna, Leuna (DE)) (see Table 8.2 in Section 8.3.2.1).

Reference literature
[5, Weber et al. 2010]. The reaction mechanism for the decomposition of MHP is discussed in [122, Rieche 1930].

8.4.2.2.2 Removal of methanol

Methanol, which is present in the waste water from the off-gas condensation and adsorber regeneration and additionally formed by the decomposition of MHP (see above), can be removed by stripping or distillation. Since methanol is readily biodegradable, the need to do so will depend on the assessment as part of the waste water management of the site.

Before applying distillation, MHP must be completely decomposed under controlled conditions. Otherwise explosions from spontaneous MHP decomposition may occur in the distillation column due to local accumulation of MHP.

8.4.2.3 Techniques to recover/remove phenol and other organics

In order to reduce the organic load discharged from the cleavage unit and the distillation unit to further waste water treatment, phenol and other organic compounds (e.g. acetone) are recovered using extraction followed by stripping.

8.4.2.3.1 Extraction

Solvents (such as cumene or MIBK) can be employed to extract phenol from aqueous effluents. The solvent and phenol are then separated, e.g. by distillation, and the solvent recycled. The waste water is stripped to remove the remaining solvent.

This allows the recovery of phenol but requires energy to both separate the phenol and solvent and to strip residual solvent from the effluent before discharge. See the CWW BREF.

8.4.2.3.2 Stripping

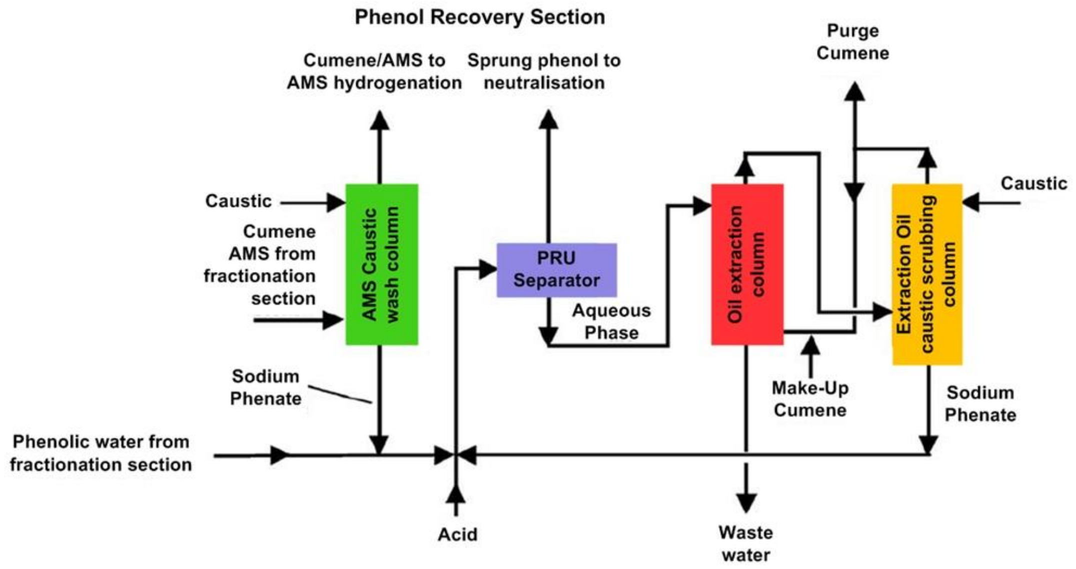
Stripping is used to remove purgeable organic compounds (e.g. acetone and cumene) from aqueous streams (process streams or waste water), e.g. from the PRU waste water effluent. See the CWW BREF.

8.4.2.3.3 Phenol recovery unit (PRU)

Description
A combination of generic techniques (phase separation, different extraction steps) is used to recover phenol from aqueous streams.

Technical description
At different stages of the phenol process, phenol is separated from organic phases (e.g. cumene-AMS mixture prior to AMS hydrogenation or AMS purification) as sodium phenate by caustic washing. If not used to neutralise the output from the cleavage reaction, these caustic streams are combined with other aqueous streams containing phenol and acidified with sulphuric acid (‘springing’) to convert dissolved phenate to phenol which forms an organic phase and is recovered by phase separation (decantation).

The aqueous phase is then treated by extraction with a solvent (typically cumene) to remove and recover the remaining phenol before discharge to further waste water treatment. The solvent is regenerated, e.g. by removing phenol as phenate with caustic which will then be returned to the PRU feed or to the cleavage/neutralisation section.



Source: [9, Schmidt 2005]

Figure 8.5: Example of phenol recovery set-up

Achieved environmental benefits

- Reduction of the phenol load in the waste water.
- Recovery of final products.
- Reduction and recovery of salts from the aqueous stream generated in the neutralisation section.

Environmental performance and operational data

Five out of seven plants reported average phenol concentrations < 100 mg/l (18–85 mg/l) for the total process effluent after pretreatment.

Cross-media effects

- Requires use of cumene as a solvent, and also caustic and acid consumption.
- Emission of sodium sulphate to water.

Technical considerations relevant to applicability

Fully applicable to all types of phenol plants.

The technique requires a small investment.

Economics

This treatment (at source) unit is expected to be paid back in a few years due to the recovery of raw materials and final goods.

Driving force for implementation

Mainly economics: benefits from recovery of feedstocks (cumene and phenol).

Example plants

No information provided.

Reference literature

[8, Weber et al 2005], [9, Schmidt 2005].

8.4.3 Techniques to reduce raw material consumption

See techniques to recover feedstock and product in Sections 8.4.1, 8.4.2 and 8.4.5.

8.4.4 Techniques to reduce energy consumption

The main consumption of energy as heat is connected to the distillation systems (concentration and fractionation). Therefore, the energy consumption depends to a large extent on the optimisation of the distillation systems in terms of energy consumption and heat recovery. One of the factors to be considered is the reduction of heat consumption by the use of vacuum distillation (which in turn will increase the consumption of electric power).

Both the oxidation of cumene and the cleavage of cumene hydroperoxide are highly exothermic. Therefore, heat recovery from these reactions is crucial to optimise the energy balance.

Improvement of the performance of compressors and pumps will be the main factor to reduce the consumption of electric power.

Table 8.7 summarises an assessment of techniques to reduce the energy consumption at phenol plants.

Table 8.7: Techniques to reduce energy consumption at phenol plants

Technique	Impact	Applicability	Cross-media effects
Heat of reaction from last oxidiser can be used to separate cumene in concentration	Medium reduction	Retrofit	None
Use heat from fractionation condensers for fractionation reboilers	High reduction	Retrofit	None
Use highly efficient packing trays instead of classic design	Small reduction	New fractionation unit	None
Use high vacuum instead of medium or low vacuum	Low reduction	New vacuum system	Higher energy for vacuum
Replace crude azeotropic phenol column with ion exchange technology	Medium reduction	New fractionation unit	Spent resin as waste
Reduce excess air (or the O_2 content in oxidation spent air)	Small reduction	Fully applicable	Selectivity issues

Reference literature
[9, Schmidt 2005].

8.4.5 Techniques to reduce waste generation

8.4.5.1 Techniques to reduce tar formation

Two-step cleavage process
There are numerous articles on how installations have incorporated improvements into their reaction systems, leading to higher yields in phenol, acetone and AMS.

Reference literature
[8, Weber et al 2005], [9, Schmidt 2005], [10, Zakoshansky 2009], [11, Zakoshansky 2007].

8.4.5.2 Techniques regarding reuse of tar

8.4.5.2.1 Tar cracking and distillation

Description
Recovery of valuable products (cumene, AMS and phenol) from tar by cracking with steam and distillation.

Technical description
The tar is fed to the middle part of a continuous operation column-type reactor (i.e. a thermocracker), heated and treated with steam. Upon heating, the phenol tar is refluxed, and the vapour which does not condense in the reactor is led into a phase separation stage to condense and recover organic compounds or reuse. The waste tar residue is removed from the bottom of the reactor.

Achieved environmental benefits
The amount of tar waste to be managed is reduced and the usage of feedstock is improved.

Environmental performance and operational data
No information provided.

Cross-media effects
Use of energy (steam).

Technical considerations relevant to applicability
No information provided.

Economics
Improved cumene feedstock yield.

Driving force for implementation
Improved cumene feedstock yield.

Example plants
No information provided.

Reference literature
No reference literature provided.

8.4.5.2.2 Use tar as a fuel

Description
Routing of the tar stream to a furnace to recover heat (typically for steam generation).

Technical description
The bottom cut from the phenol purification column is sent to an appropriate combustion unit. Phenol tar is a complex mixture which comprises phenol, acetophenone, dimethylbenzyl alcohol, α-methylstyrene dimers, p-cumylphenol, and small amounts of salts (mainly Na_2SO_4).

Achieved environmental benefits

- Reduction of waste.
- Recovery of energy.

Environmental performance and operational data
No information provided.

Cross-media effects

- Emissions to air from combustion.
- Potential for dust emissions due to salt content.

Technical considerations relevant to applicability
No information provided.

Economics
Benefits from saving fuel.

Driving force for implementation
Lower operating costs due to fuel savings.

Example plants
No information provided.

Reference literature
[8, Weber et al 2005], [9, Schmidt 2005].

8.5 Emerging techniques

8.5.1 Direct catalysed oxidation of benzene

Description
The direct catalysed oxidation of benzene to phenol is carried out using nitrous oxide, oxygen or air as the oxidant.

In the AlphOx process that was developed by Solutia and the Boreskov Institute of Catalysis in Moscow, nitrous oxide (N_2O) from other processes (e.g. production of adipic acid) is used as the oxidising agent, which reacts with benzene in the vapour phase to give phenol and nitrogen. The process uses metal-modified zeolite catalysts, such as V_2O_5 / MoO_5 / ZSM-5 and Fe_2O_3 / MoO_3 / ZSM-5, which transfer atomic oxygen, from the decomposition of the N_2O on their surface, to benzene. The active catalyst appears to be the metal species occupying the pores in the zeolite structure.

Another alternative could be the use of microreactor technology. One potential microreactor to produce phenol involves the use of a small diameter (2 mm), porous tube of alumina coated with a layer of palladium metal. A mixture of benzene and oxygen is fed through the tube. The tube is heated to 150–250 °C. Hydrogen gas is passed over the aluminium tube, permeates through it and is converted to atomic hydrogen by the palladium catalyst. The hydrogen atoms react with oxygen gas, releasing oxygen atoms, which in turn react with the benzene to form benzene epoxide. This isomerises to phenol. The boiling points of phenol (182 °C) and benzene (80 °C) mean that phenol is easily separated from unreacted benzene, and the final liquid phenol is in a very pure form. The reactor could easily be scaled up by adding more tubes, effectively using a modular approach. One single microreactor could produce up to 100 000 tonnes per year. The technology can also be applied to the manufacture of other materials.

Commercial development
The techniques are considered to be still far from being economically viable.

The AlphOx process has been run in a pilot plant since 1996.

Level of environmental protection
No information provided to allow an assessment of the environmental impact compared to the cumene oxidation route.

Cost savings compared to existing BAT
The direct oxidation of benzene can be achieved using several different oxidising agents, but none of these have yet proved economically viable on a large scale. Direct oxidation does not produce co-products, which may be the most important economic advantage in comparison to the cumene process, depending on the market for acetone.

Chance of becoming BAT in the future
Considerable research into finding catalysts which might allow the direct oxidation of benzene to phenol is ongoing.

When it might become commercially available
This technique may become commercially available in up to 20 years or more.

References
Information on the AlphOx process and the use of microreactors taken from [125, Greener Industry 2015].

9 ETHANOLAMINES

9.1 General information

Ethanolamines (EAs) is a collective term that refers to monoethanolamine (MEA; 2-aminoethanol), diethanolamine (DEA; 2,2'-iminodiethanol) and triethanolamine (TEA; 2,2',2''-nitrilotriethanol). Under some circumstances, polyethanolamines (PEAs) may also be produced as a by-product, a brownish black viscous liquid containing high-boiling alkanolamines and other compounds.

Ethanolamines have a wide range of potential uses:

- MEA is used primarily in the manufacture of ethylene amines, but it can also be used to make wood preservatives, detergents and metalworking fluids. It is also used as a gas purification medium.
- DEA is used mainly in surfactant applications, for the production of optical brighteners and agrochemicals, and for gas sweetening.
- The production of fabric softeners is the most important use of TEA, although it is also used in cosmetic applications, lubricants and as a cement additive.
- PEAs are produced in small volumes and can, for example, be used in the cement industry as a cement grinding aid, or as an asphalt chemical [20,Frauenkron et al. 2012], [21, CEFIC 2011], [24, Fässler et al. 2008].

MEA, DEA and TEA are produced by the continuous reaction of ethylene oxide with ammonia. There are two process routes: an aqueous route and an anhydrous route.

In 2011, the production capacity of ethanolamines in Europe was 415 000 tonnes. European production of ethanolamines is summarised in Table 9.1 below.

Table 9.1: European producers of ethanolamines

Country	**City**	**Operator**	**Process**	**Capacity (kt/yr)**
Belgium	Antwerp	BASF	Aqueous	230
Germany	Ludwigshafen	BASF	Aqueous	
France	Lavera	INEOS	Aqueous	53
Germany	Marl	Sasol	Aqueous	27
Sweden	Stenungsund	AkzoNobel	Anhydrous	105
Source: [21, CEFIC 2011]				

As can be seen from the table above, in 2011 there were four plants producing ethanolamines using the aqueous route and only one plant using the anhydrous route.

Producers of ethanolamines in the European Union (EU) are listed in Table 9.1. Besides these companies, DOW (320 kt/yr), Huntsman (198 kt/yr) and INEOS (164 kt/yr), with production sites located in the US, are other big producers of ethanolamines. There are also some ethanolamine producers (with more regional importance) in the Middle East and Asia, for example Arak Petrochemicals (Iran), Optimal (Malaysia), Nippon Shokubai (Japan), OUCC (Taiwan), Jiangsu Yinyan Chemical (China) and Fushun Beifang Chemical (China). All these companies have smaller design capacities than the market leaders like DOW and BASF; however, the market for ethanolamines is mainly growing in Asia [21, CEFIC 2011].

No global production figures have been provided. According to industry, new plants outside the EU (including those that belong to EU companies) result in reduced profitability of production in the EU.

Key environmental issues

The key environmental issues for the production of ethanolamines are:

- emissions to air of ammonia;
- emissions to air and water of organic substances like ethylene oxides, ethanolamines and ethylene glycol;
- diffuse and fugitive emissions of volatile organic compounds.

Emissions tend to be low (i.e. compared to most of the other illustrative processes) due to the high degree of recovery and the minimal venting.

9.2 Applied processes and techniques

9.2.1 Process options

Ethanolamines are produced by the continuous reaction of ethylene oxide with ammonia. This reaction produces MEA, DEA and TEA concurrently:

$$C_2H_4O + NH_3 \rightarrow NH_2\text{-}C_2H_4\text{-}OH \quad \text{(MEA)}$$
$$C_2H_4O + NH_2\text{-}C_2H_4\text{-}OH \rightarrow NH\text{-}(C_2H_4\text{-}OH)_2 \quad \text{(DEA)}$$
$$C_2H_4O + NH\text{-}(C_2H_4\text{-}OH)_2 \rightarrow N\text{-}(C_2H_4\text{-}OH)_3 \quad \text{(TEA)}$$

Further reaction with ethylene oxide leads to chain prolongation, e.g. $N\text{-}(C_2H_4\text{-}OH)_2$ $(C_2H_4\text{-}O\text{-}C_2H_4\text{-}OH)_{3,}$ and results in a mixture known as polyethanolamines (PEAs).

The ammonia is present in significant excess, primarily in order to promote the complete reaction of the ethylene oxide, which could present a safety risk if it were not fully reacted.

The amount of ammonia excess affects the relative proportions of the individual ethanolamines that are produced - a greater excess of ammonia favours MEA, whereas a lower excess favours DEA, TEA and PEAs. However, the relative proportions of DEA and TEA can be increased by recycling MEA and/or DEA, or by reacting MEA and/or DEA with ethylene oxide in a separate reactor [39, Edens et al. 2009].

The reaction is conducted either in the presence of water (which acts as an accelerator) or using a fixed-bed catalyst. These routes are referred to as the aqueous and anhydrous processes respectively. In the case of the anhydrous process, a catalyst that selectively favours the production of one or more particular ethanolamines can be used.

9.2.2 Aqueous process

The main process steps in the aqueous route are summarised in Figure 9.1 below. The streams are numbered for cross-referencing in Section 9.3.

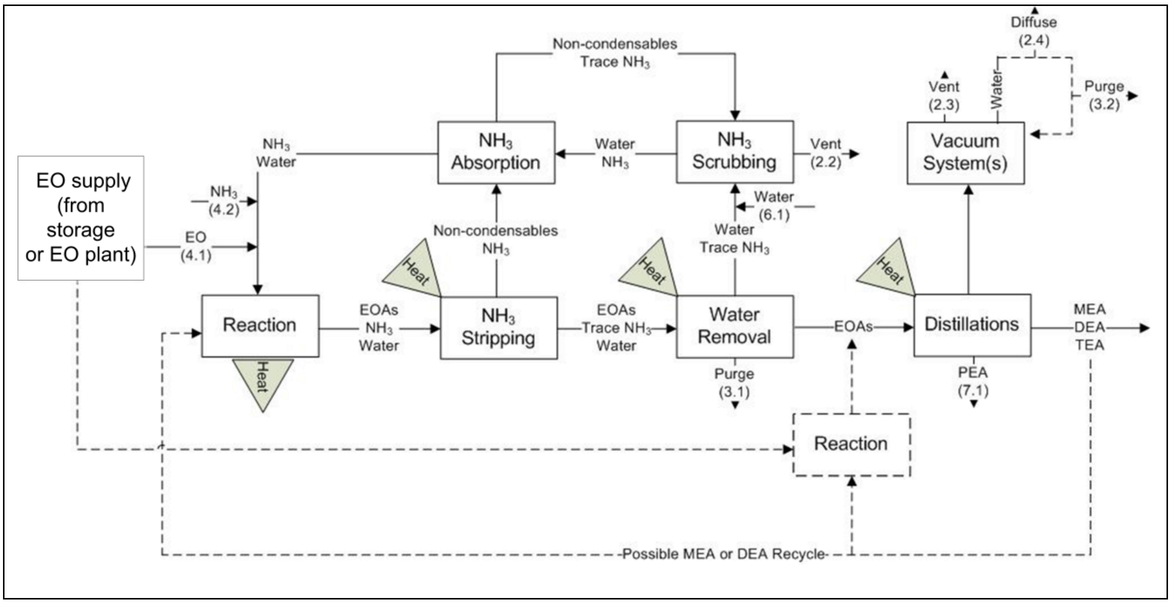


Figure 9.1: **Flow chart showing the process steps in the production of ethanolamines by the aqueous route**

The aqueous route involves the following sequence of process steps:

- Reaction of ethylene oxide with excess ammonia at a temperature of up to 150 °C and a pressure typically above 20 bar. Given the exothermic nature of the reaction, multiple reactors in series with intermediate cooling and multiple ethylene oxide additions may be used.
- Stripping of unreacted ammonia from the reaction mixture with steam. The stripped ammonia is recovered by wet scrubbing and recycled to the process.
- Removal of water and residual ammonia from the reaction mixture by evaporation. Both water and ammonia are recycled to the process.
- Fractionation of the individual ethanolamines by distillation under vacuum, either in a sequence of separate columns or in a single column featuring multiple product streams, that results in separate MEA, DEA and TEA fractions.
- Optionally, recycling of MEA and/or DEA to the earlier reaction step, or routing of MEA and/or TEA to a separate reactor after the addition of ethylene oxide.

[20, Frauenkron et al. 2012], [22, Zahedi et al. 2009], [87, Maxwell 2004].

9.2.3 Anhydrous process

The main process steps in the anhydrous route are summarised in Figure 9.2 below. The numbering of the streams is used for cross-referencing in Section 9.3.

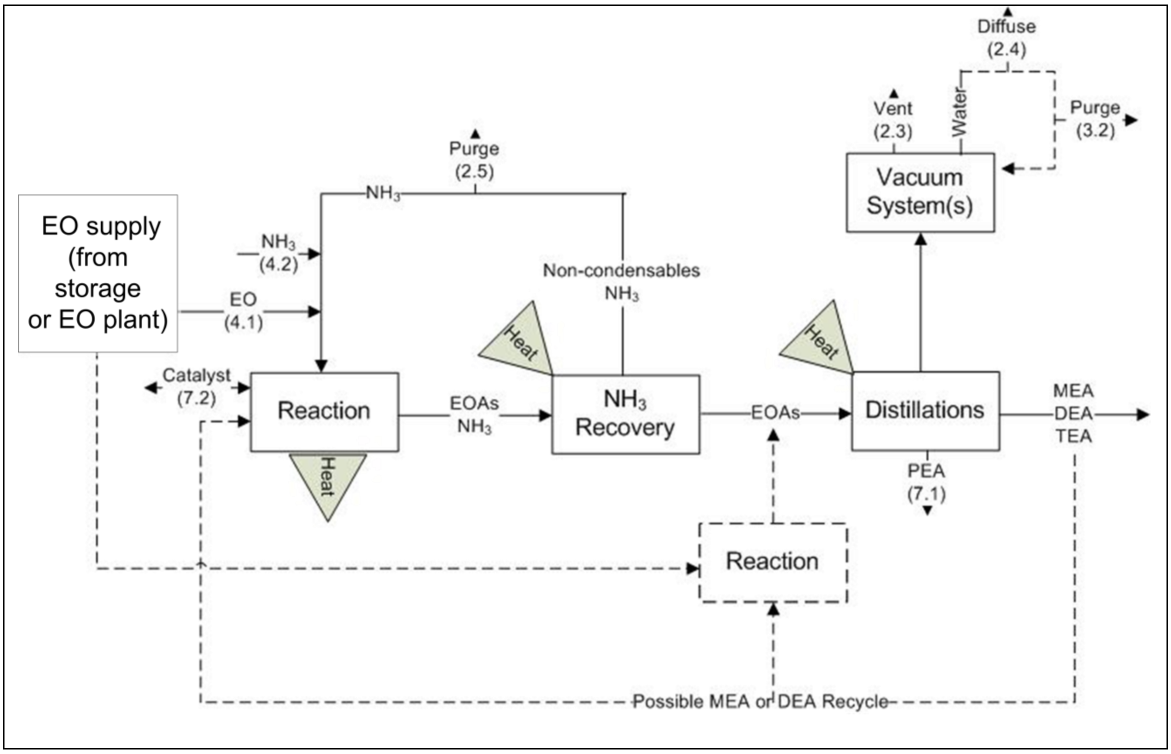


Figure 9.2: Flow chart showing the process steps in the production of ethanolamines by the anhydrous route

The anhydrous route involves the following sequence of process steps:

- Reaction of ethylene oxide with excess anhydrous ammonia at a temperature of up to 150 °C and a pressure of up to 160 bar in the presence of a catalyst. The high temperature is designed to ensure the complete reaction of ethylene oxide, and the high pressure is required in order to maintain the ammonia in the liquid state during the reaction.

- Stripping of unreacted ammonia from the reaction mixture, initially under pressure with the direct recycling of the recovered ammonia, and then under vacuum with the subsequent recompression and recycling of the recovered ammonia.
- Fractionation of the individual ethanolamines by distillation under vacuum, either in a sequence of separate columns, or in a single column featuring multiple product streams. MEA and DEA are normally obtained as essentially pure products, whereas TEA is normally obtained as a DEA/TEA mixture due to the separation challenge that would be involved in attempting its isolation.
- Optionally, recycling of MEA and/or DEA to the earlier reaction step, or routing of MEA and/or TEA to a separate reactor after the addition of ethylene oxide. [20, Frauenkron et al. 2012], [23, Tsuneki 2010].

9.2.4 Other than normal operating conditions

9.2.4.1 Specific other than normal operating conditions

For both the aqueous and anhydrous processes, the start-up and shutdown require the gradual introduction of raw materials with recirculation until conditions are appropriate. Raw materials and reaction products are not released during the operation.

The following operations deviate from the stable and normal operating procedures:

Reactors

- Reaction: A problem with the reaction (e.g. low temperature or water level) may result in some unreacted ethylene oxide, which would leave the reactor with the process gases. In view of the potential safety issues that might arise from the recirculation of ethylene oxide, it is anticipated that a high level of monitoring and intervention measures will have been incorporated into both the plant's design and its control strategy, particularly given likely additional regulation under the Seveso Directive. A control system is also needed to avoid the backflow of ethylene oxide to the ammonia stream.
- Heat removal: The reaction is exothermic and this heat is normally removed by vaporising water to produce steam (or by heating oil). If the supply of water (or oil) were to be interrupted or reduced to a problematic level, this could result in the overheating of the reactor, which could in turn result in the runaway decomposition of ethylene oxide, and therefore a need for the pressure relief system to operate. It is reported that plants employ a control system that would detect such a temperature rise and take appropriate action to trip the plant into a safe state, particularly given requirements that may be needed under the Seveso Directive.
- Malfunction in ammonia scrubbing: A partial or total failure of the ammonia scrubbing systems could result in significantly elevated ammonia emissions to air. The techniques that can be employed to prevent/minimise a problem in this respect would involve a control system that monitored key parameters, and which incorporated appropriate responses in order to shut the process down. Three incidents of this type have been reported in the last five years.
- Operating rate: Absorber performance is highly dependent upon flow rate, so a significant change in plant throughput could detrimentally affect a scrubber's performance. The primary way of avoiding such an occurrence would be for the plant operator to use a robust management of change procedure.
- Runaway reaction: A polymerisation incident involving ethylene oxide during the reaction, due to its build-up resulting from incomplete reaction, could result in a plant over-pressurisation, and consequent emission of ammonia (which is normally present in

excess) through emergency pressure relief systems. It is anticipated that the plant would include appropriate detection and intervention measures to address this issue under the Seveso Directive.

- Catalyst performance failure in the anhydrous process: A problem with the catalyst might result in unreacted ethylene oxide passing forward to the ammonia recovery section, which would mean that ethylene oxide would be present in the recycled ammonia, and therefore the purge stream – see below for more details.

Fractionation

- Failure to properly recover ammonia: If the recovery of ammonia in both processes, but in particular the anhydrous one, is not conducted properly, some ammonia could pass forward into the fractionation column(s), and this would be evacuated to air via the vacuum system's vent. However, this would probably result in difficulties in achieving the desired vacuum in the fractionation columns, and the plant's control system would therefore be expected to detect this and intervene to shut down the process.

Conditions with potentially high emissions to water

- Reaction conditions: If there is a problem with the reaction (i.e. temperature, water level), there may be some (more) ethylene oxide present in the process gases, and this may result in the formation of (more) ethylene glycols, which would be recycled for dilution instead of increasing the water purge.

Conditions with a potentially larger impact on material consumption

- Over-pressurisation: Such an incident will result in the loss of ethylene oxide.
- Reaction conditions: A lack of water or inactive catalyst could interfere with the reaction, thereby adversely affecting the ethylene-oxide-specific consumption rate. However, due to safety considerations, it is expected that the plant would be shut down automatically in such circumstances.
- Reaction temperature: Too high a temperature could result in the formation of ethylene glycols, which would increase the specific consumption of ethylene oxide, and may result in the need for additional separation efforts. The advanced control systems in all plants prevent this from occurring.
- Leak: The reactions are carried out under pressure. In the event of a leak, there could be losses of ethylene oxide from the reaction stage, so measures that are adopted to minimise fugitive emissions will also help to reduce ethylene oxide consumption.
- A malfunction or failure in the ammonia recovery process would result in a reduction of the ammonia that is recycled (and may result in an increase in ammonia and/or NO_X emissions to air). The advanced control systems in all plants prevent this and related material losses from occuring.

9.2.4.2 Generic other than normal operating conditions

- Start-up: Start-up is achieved by gradually introducing the reagents, which are recycled until the desired reaction conditions are obtained. There should therefore normally be no emissions to air during start-up.
- Shutdown: When the plant is shut down, its inventory will need to be removed and a process of purging may be employed in order to eliminate hazardous substances, particularly where maintenance activities are anticipated. Under normal shutdown scenarios, the main potential issue would be ammonia emissions.
- Loss of containment and excess leakages in the system.

9.2.5 Equipment important for environmental protection

The following assets perform important operations for the protection of the environment and should have as high a level of reliability and availability as possible:

- reactors;
- cooling system components;
- safety system regarding runaway reactions, etc.;
- ammonia scrubbers;
- hydrocarbon detectors;
- purges, vents;
- online process control.

Because of its hazardous properties (flammability, explosion limits, toxicity), safe transport, storage and handling of ethylene oxide are of special importance.

9.3 Current emission and consumption levels

9.3.1 Emissions to air

In this chapter the various potential emissions to air from the processes under normal operating conditions are considered in turn in order to provide an assessment of their possible significance, and the techniques that might be employed to avoid or, where that is not feasible, reduce them.

9.3.1.1 Aqueous process inerts vent

Inert substances introduced into the process along with the ammonia and ethylene oxide raw materials (e.g. nitrogen) will become associated with the excess ammonia that is vaporised from the reaction mixture. As these inert substances are not captured to any material extent in the water used in the subsequent ammonia absorption steps, they are vented to air. The origin within the process of this vent stream is shown as vent 2.2 in Figure 9.1.

According to the data collection, reported specific ammonia emissions are in the range of 0.01–0.03 kg/t of EAs. Industry commented that the upper value would need to be corrected to 0.13 kg/t (see CEFIC comment 1317 on Draft 1 of this BREF [182, TWG 2014]).

The vent is either released to atmosphere or routed to a shared VOC abatement system (thermal oxidiser).

9.3.1.2 Fractionation of ethanolamines

In both the anhydrous and aqueous processes, the separation of the individual ethanolamine co-products is achieved by multiple distillations conducted in series under vacuum, or possibly in a single vacuum distillation column with multiple side-streams. The evacuated gases from the vacuum system(s) are therefore a source of channelled emissions to air, and this is shown as vent 2.3 in Figure 9.1 and Figure 9.2 for both the aqueous and anhydrous process routes.

The substances present in the gases evacuated during the separation of ethanolamines could conceivably include MEA, DEA and TEA, as these are vaporised during the distillations. However, they have low (and progressively lower) vapour pressures. Consequently, although the use of a vacuum means that they could possibly be pulled into the vacuum system in material quantities, they should be quickly condensed under normal operating conditions, and therefore should not present a material emissions issue.

In the aqueous process, the fact that water is removed after the bulk of ammonia has been recovered should mean that the amount of ammonia passing forward into the fractionation column(s) should be low, and therefore the presence of ammonia in the evacuated gases from the column(s) associated with the aqueous process should be negligible under normal operating conditions. There is arguably more chance of ammonia passing into the fractionation column(s) in the anhydrous process, but the recovery step incorporated into this process is likely to be carried out in two stages, including a final vacuum distillation. It is therefore credible to assume that the feed forward of ammonia in the anhydrous process is also likely to be low under normal operating conditions. In any case, any excessive ammonia slippage past the recovery step may result in difficulties in establishing the desired vacuum levels in the fractionation column(s).

As it is assumed that there should be no ethylene oxide present at this stage under normal operating conditions, there should be little or no ethylene oxide in the evacuated gases.

9.3.1.2.1 Direct emissions of VOCs from the fractionation of ethanolamines

The direct emissions to air under normal operating conditions from the fractionation of ethanolamines will be restricted to non-condensable gases that are vented from the vacuum system(s).

VOC emissions are reported to be approximately 0.003–0.005 kg/t of EAs produced (calculated, expressed as TOC). There are only few data since these streams are combined with others and sent to shared abatement units (in most cases, thermal oxidisers).

9.3.1.2.2 Indirect (diffuse) emissions of VOCs from the fractionation of ethanolamines

Source and nature of emissions under normal operating conditions: Any water that is used in the vacuum systems will absorb VOCs that might be present in the evacuated gases. The handling of this water could result in diffuse emissions to air if the water were to be cooled in an open, direct-contact system. The emissions from the aqueous and anhydrous processes are shown as vent 2.4 in Figure 9.1 and Figure 9.2 for both the aqueous and anhydrous process routes.

According to the data collection, the VOC emission levels reported are calculated values between 0.003 kg/t and 0.005 kg/t of EAs produced (with a comment from industry that, from their data, the VOC range would be 0.0017–0.05 kg/t of EAs produced) (see CEFIC comment 1320 on Draft 1 of this BREF [182, TWG 2014]).

9.3.1.3 Anhydrous process' inerts vent

In order to limit the build-up of inert compounds introduced along with the ethylene oxide and ammonia raw materials (e.g. nitrogen) in the recycled ammonia, it is necessary to purge a proportion of the recirculating ammonia gas, which is generally done as shown by purge 2.5 in Figure 9.2.

As the vent rate will ordinarily be determined by the quantity of inert substances that are introduced to the process, it should normally be expected to be relatively low, with a limited load. However, unlike in the aqueous process, the ammonia concentration in the purge from the anhydrous process is very high.

The vent gas stream is routed to a shared thermal oxidiser.

9.3.2 Emissions to water

9.3.2.1 Emissions to water from the aqueous process' water recycling loop

The water that is used in the reaction is recovered by distillation and returned to the process feed. However, a portion of the water is purged from the process in order to control the build-up of impurities and by-products. This purge is shown as vent 3.1 in Figure 9.1.

This purge stream contains some residual ammonia and low levels of ethanolamines, and possibly also even smaller amounts of ethylene glycols. As the stream is a purge, the volume involved should be relatively low.

Data collected show a TOC-specific emission in the range of 0.3 kg/t to 0.7 kg/t of EAs (one plant, yearly averages of weekly grab samples) measured before combination with other streams being sent to the downstream CWWTP. Data also show specific emissions of total nitrogen (TNb) (by standard method EN 12260) of 0.1–0.41 kg/t of EAs (yearly averages of daily composite samples) measured after combination with the waste water of another production process, before the downstream treatment.

In the comments on Draft 1 of this BREF, industry commented that only limited data are available and no plant performs continuous sampling. On the basis of spot or composite samples and calculations, the aggregated information shows:

- NH_3 typically up to 76 kg/t of EAs as a yearly average;
- TOC would be 0.3–3.8 kg/t of EAs;
- COD up to 5.80 kg/t of EAs.

Also, some plants measure total nitrogen (TN). Levels of 8.6 mg/l for NH_3 and 430 mg/l for TNb would be realistic.

9.3.2.2 Emissions to water from vacuum systems

The separation of the individual ethanolamines is achieved by multiple distillations that are conducted under vacuum, and the recovery of ammonia in the anhydrous process can involve an element of processing under vacuum conditions. The systems employed for generating the vacuum comprise, besides positive displacement pumps, steam ejectors and/or liquid ring pumps, in which case an aqueous effluent with an organic load may arise from the steam condensate or the purge of the sealing water circuit.

9.3.3 Raw material consumption

Ammonia is used in significant excess relative to ethylene oxide (for safety and co-product profile management reasons). Therefore, the consumption will mainly be determined by the recovery rate. However, both the aqueous and anhydrous processes should feature the essentially full recycling of ammonia under normal operating conditions.

9.3.4 Energy consumption

For the manufacture of ethanolamines, the net energy consumption will be influenced by the process configuration, the extent of heat interchange, and any energy that might be recovered from the combustion of process residues.

In comparison, the overall energy consumption of the processes will largely depend on the energy required for a number of key energy-intensive operations, and the techniques that might be employed to help reduce the overall energy consumption associated with these operations.
The overall energy consumption will also be variable, being dependent on factors such as co-product profile.

For the production of ethanolamines, energy is mainly consumed as:

- heat/steam, e.g. for distillation (fractionation units) and, for the aqueous process, evaporation and stripping processes; and
- electric power for pumps and compressors.

The net heat demand is reduced by the heat provided from the exothermic reaction. It will depend on the implementation of techniques such as:

- control of ammonia and water levels;

- distillation column design;
- recovery of exothermic heat through the generation of low-pressure steam;
- heat integration;
- application of pinch technology.

For the anhydrous process, the consumption of electric power will depend *inter alia* on the ammonia excess applied which has to be compressed and recycled.

9.3.5 Water usage

Water is used mainly:

- as an accelerator within the aqueous process to promote the reaction between ethylene oxide and ammonia;
- for vacuum systems, as sealing liquid for liquid pumps or steam for ejectors; and
- to produce steam.

In any event, water is recycled or reused, typically with a small purge, and the net water usage will depend on the size of the purge.

9.3.6 Waste generation

9.3.6.1 Polyethanolamine by-product (aqueous process)

The only relevant by-products are polyethanolamines (PEAs), which are formed in the aqueous process.

PEAs are higher-boiling than TEA, and result as a bottom product from the final column employed for the isolation of TEA. They are therefore obtained as a mixture with TEA.

PEAs or PEA/TEA mixtures can be marketed as a product.

If PEAs are not wanted as a product, the process is carried out in such a way as to minimise the formation of PEAs which otherwise would have to be disposed of as waste.

9.3.6.2 Catalyst (anhydrous process)

Catalyst from the anhydrous process will need to be periodically replaced. The spent catalyst will form a waste for disposal or recovery.

9.4 Techniques to consider in the determination of BAT

This section describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this chapter. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations). Cross references to other chapters are used, where relevant to avoid repetition.

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 2.6 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

9.4.1 Techniques to reduce emissions to air

9.4.1.1 Reduction of emissions from ethylene oxide storage

Ethylene oxide is extremely flammable and its mixtures with air are explosive. When heated, it may rapidly expand, causing fire and explosion. It is a named dangerous substance in the Seveso Directive (2012/18/EU) with a lower tier threshold of 5 tonnes and an upper tier threshold of 50 tonnes. Ethylene oxide can burn in inert atmospheres and in water solutions due to the bound oxygen present.

In most cases, ethylene oxide is fed to the ethanolamine plant by pipeline and stored in a common tank field. A common practice is to place the ethanolamine plant in the proximity of an ethylene oxide production facility and directly pipe in ethylene oxide to the reactors [25, Ruehl et al. 2010]. The techniques that are generally considered to have the potential for achieving a high level of environmental protection for the storage, transfer and handling of liquefied gases, liquids and solids are those described in the EFS BREF.

9.4.1.2 Reduction of ammonia emissions to air from the aqueous process

The aqueous process operates with an excess of ammonia, which is recovered from the product mix and recycled back to the reaction stage. The ammonia recovery process is shown in Figure 9.1. The process involves the use of two-stage countercurrent wet gas scrubbing. The use of wet gas scrubbers is described in Section 2.4.3 and in the CWW BREF.

Scrubber liquor is recycled. Depending on the VOC content, scrubbing is followed by end-of-pipe abatement devices for VOC removal, like thermal or catalytic oxidisers, mostly shared with other waste gas streams present at the sites (see Section 9.4.1.4.2).

9.4.1.2.1 Wet scrubbing to recover ammonia

The ethanolamine production process is carried out using high excess levels of ammonia; therefore, the unreacted ammonia (mainly from the ammonia stripper, but also from the water evaporation unit) is recovered by the scrubber system and fed back into the process. Whilst providing higher efficiency to the process, this also reduces the amount sent to treatment. Due to the high reactivity of ammonia in aqueous solution, wet scrubbers are used for this purpose. Wet gas scrubbing is a generic technique used in the chemical sector and is described in more detail in Section 2.4.3 and in the related section of the CWW BREF.

To maximise recovery and reduce the ammonia concentration in the outlet, the main absorption column (‘NH_3 absorption’ in Figure 9.1) that is used to recover the bulk ammonia is supplemented by separate countercurrent water scrubber stages (‘NH_3 scrubbing’ in Figure 9.1) to recover ammonia from other gaseous streams, mainly from the evaporation unit. The resulting scrubber liquor is fed to the main absorption stage.

9.4.1.2.2 End-of-pipe abatement techniques to reduce ammonia emissions

As a generic technique (which according to information from CEFIC is not applied in the ethanolamine plants in Europe), scrubbing with diluted acids (e.g. sulphuric acid) can be applied where there is a need to further reduce ammonia emissions.

As a common technique to reduce VOCs, waste gases can be routed to a shared thermal oxidiser. This will also reduce the ammonia concentration but, due to the effect on the resulting NO_X emissions, the technique is not regarded as a suitable dedicated treatment for ammonia abatement.

9.4.1.3 Reduction of ammonia emissions to air from the anhydrous process

The following techniques have been identified as options to further reduce ammonia emissions from the small purge stream from the anhydrous process which is sent to VOC abatement. However, there are no data to quantify the environmental benefits, which may be small, and wet scrubbing is not used for normal operating conditions.

9.4.1.3.1 Maintenance of a low content of inerts in the feedstock

Description
Maintenance of a low content of inerts in the feedstock.

Technical description
This technique involves controlling the raw material quality to keep the content of uncondensable components as low as possible, and applying raw material specifications with limited inert content.

However, where there is realistically only a limited choice of raw materials, this could be more of a contextual factor rather than a technique, as the opportunities to change may be limited.

Achieved environmental benefits

- Reduction of ammonia emissions.
- Reduction, to a small extent, of the consumption of ammonia.

Example plants
One plant reported implementation of this technique.

9.4.1.3.2 Minimisation of the inerts' purge rate

Description
Minimisation of the inerts' purge rate by control of the pressure.

Technical description
The purge rate is optimised by use of a pressure control set-up that keeps the pressure in the ammonia recovery system at a predefined level. There are two control valves, to add nitrogen or to purge out, depending on the pressure in the system, and to ensure a very small purge during normal operating conditions.

Achieved environmental benefits
Reduction of ammonia emissions.

Example plants
One plant reported implementation of this technique.

9.4.1.3.3 Wet scrubbing as final abatement to reduce ammonia emissions

- A scrubber column with diluted sulphuric acid as the scrubbing solution and with an achieved removal efficiency of more than 98 % could be used. See the CWW BREF.
- Wet scrubbers are reported to be used as mobile back-up systems during maintenance operations.

9.4.1.4 Reduction of VOC emissions

9.4.1.4.1 Integrated techniques for distillation systems

Integrity of vacuum systems
As the ethanolamine separation is carried out under vacuum, reducing leaks (which are not viewed as an other than normal operating condition in this context) will reduce the quantity of non-condensable gases that enter the distillation plant, thereby reducing the gas volumes handled by the associated vacuum systems, and consequently the likely emissions from them. However, a significant amount of air ingress might affect the level of vacuum that is achieved, which could affect the nature of the process vapours, and may result in a plant shutdown.

Condensation of organic compounds (amines) upstream of vacuum systems
Condensers are placed on the vacuum lines to reduce ethanolamine entrainment to the vacuum system.

The incorporation of suitably designed condensers with appropriate cooling media at appropriate points before and within the vacuum systems reduces VOCs in the waste gas and in the liquid effluents from the vacuum system and allows the recovery of material for recycling to the process. The data collection confirmed the use of water-cooled condensers.

See also Section 2.4.3.5.2 and the CWW BREF.

9.4.1.4.2 Thermal oxidisers

Waste gas streams that contain VOCs are routed to a shared thermal oxidiser for final abatement. For VOC abatement with thermal oxidisers, see Section 2.4.3.5.6 and the CWW BREF. Some ethanolamine plants reported using the technique.

9.4.2 Techniques to reduce emissions to water

9.4.2.1 Reduction of emissions from vacuum systems

In order to reduce emissions to water from vacuum systems, priority is given to water-free vacuum systems, followed by vacuum systems with only small waste water arisings, followed by vacuum systems where the effluent is reused in the process. The following three techniques are listed in order of decreasing priority.

9.4.2.1.1 Water-free vacuum generation

This technique consists of the use of dry-running pumps, e.g. positive displacement pumps. Applicability to existing plants may be restricted by design and/or operational constraints. See the CWW BREF.

According to the comments on Draft 1 of this BREF, besides water ring pumps and ejectors, dry positive displacement pumps are also used for vacuum generation (see CEFIC comment 1325 in [182, TWG 2014].

9.4.2.1.2 Use of water ring pumps with recirculation of the ring water

The water used as the sealant liquid of the pump is recirculated to the pump casing via a closed loop with only small purges, so that the waste water generation is minimised.

According to the data collection and comments on Draft 1 of this BREF, water ring pumps with recirculation of the seal water are widely used.

9.4.2.1.3 Reuse of aqueous streams from vacuum systems in the process

Aqueous streams from water ring pumps or steam ejectors are returned to the process for recovery of organic material and reuse of the water.

For technical and economic reasons, steam ejectors are often used if higher vacuum levels need to be achieved. From the condensation of the used steam, steam ejectors usually generate a much higher effluent than the vacuum pump systems mentioned above (which would be even higher if, instead of indirect cooling, direct cooling were still to be used to condensate the steam). However, the generation of waste water can be reduced by first reducing the organic content by condensation of VOCs before entering the vacuum system (see Section 9.4.1.4.1) and consequently reusing the water stream in other parts of the process. The extent to which water can be reused in the process may be restricted by the water demand of the process.

For water ring pumps, if the seal water can be reused in other parts of the processes, this can also be an option to reduce the water consumption.

According to the data collection, steam ejectors are widely used (and may be difficult to replace) for the distillation of TEA.

9.4.3 Techniques to reduce raw material consumption

The following techniques are used to reduce the consumption of raw materials, mainly ethylene oxide.

9.4.3.1 Use of excess ammonia

Description
A high level of ammonia in the reaction mixture is maintained to ensure that all the ethylene oxide is converted into products.

Technical description
Ammonia is fed to the reaction in a large excess (a multiple of the stoichiometric ratio). The ammonia to ethylene oxide ratio depends on the ethanolamines product spectrum desired.

Achieved environmental benefits

- Reduction of waste.
- Minimisation of consumption of ethylene oxide.

Environmental performance and operational data
Depending on the product spectrum desired, ammonia to ethylene oxide molar ratios of 2:1 to 16:1 are used.

Cross-media effects
Energy consumption for the recycling of the excess ammonia.

Technical considerations relevant to applicability
Generally applicable.

Economics
No information provided.

Driving force for implementation
Economic and environmental efficiency.

Example plants
All ethanolamine production plants.

Reference literature
[22, Zahedi et al. 2009], [21, CEFIC 2011].

9.4.3.2 Optimisation of the water content in the reaction

Description
Water is used to accelerate the main reactions without changing the product distribution and without significant side reactions with ethylene oxide to glycols.

Technical description
In the aqueous process, water is used as a homogeneous catalyst for the reaction between ammonia and ethylene oxide. The extremely low reactivity of the added water with ethylene oxide, compared to the reactivity of ammonia and its resulting ethanolamines, allows the production of ethanolamines with a very high purity without the need to remove by-products. Water will remain in the ethanolamine mixture that results from the reaction and consequent ammonia removal. It can easily be removed by distillation, reused as an absorbent for ammonia and recirculated to the reaction.

The optimisation consists of balancing the advantages of a high water content with the cross-media effects (e.g. in terms of energy consumption) of the separation from the product and recirculation.

Achieved environmental benefits
Increased process efficiency.

Environmental performance and operational data
No information provided.

Cross-media effects
Energy consumption for water recovery and recirculation.

Technical considerations relevant to applicability
Generally applicable.

Economics
No information provided.

Driving force for implementation
Economic benefits from increased reactor throughput.

Example plants
All ethanolamine production plants.

Reference literature
[22, Zahedi et al. 2009], [21, CEFIC 2011].

9.4.3.3 Optimisation of the process operating conditions

Description
The optimum operating conditions (e.g. temperature, pressure, residence time) are determined and maintained to produce the desired mix of mono-, di- and triethanolamines.

Technical description
The reactions are carried out under pressure in order to ensure that the ammonia remains liquefied. A pressure control system is employed. The reactor pressure is maintained above the vapour pressure of the mixture. Low-pressure trip protection is incorporated, and pressure control and monitoring is done continuously by distributed control systems.

Achieved environmental benefits
Higher reaction yield and less waste or by-products generated.

Technical considerations relevant to applicability
Generally applicable.

10 TOLUENE DIISOCYANATE AND METHYLENE DIPHENYL DIISOCYANATE

10.1 General information

Toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) are high tonnage products, which together comprise about 90 % of the total diisocyanate market. The predominant use of TDI and MDI is in the manufacture of polyurethanes. Polyurethanes are produced by reacting diisocyanates with polyols and other chemicals.

TDI-based polyurethanes form the basic material for mattresses, furniture and automotive seating, coatings, fillers and adhesives whereas MDI-based polyurethanes are used for construction, insulation, appliances, etc.

One of the trends in polyurethanes is the gradual replacement of TDI with the less volatile MDI or polymeric MDI (PMDI) in many applications.

The term polymeric MDI is a misnomer as it is not a polymer. It is a liquid containing a mixture of monomeric MDI isomers and oligoisocyanates. Oligoisocyanates are similarly sometimes incorrectly referred to as oligomers. For some product applications it is necessary to refine the mixture by distillation and/or crystallisation to form pure MDI, which is a solid at ambient temperature. In 2013, the ratio of production levels of polymeric MDI to pure MDI that is manufactured was about 4:1. This ratio, and particularly the relative tonnages of modified MDI produced, will depend on the prevailing applications for which they are sold. MDI is used in reaction injection-moulding systems, coatings, adhesives and sealants, thermoplastic resins, elastomers and spandex fibres. PMDI is used primarily in the production of polyurethane resins for rigid polyurethane foams. In 2011, the total world production of MDI and PMDI was over 5 million tonnes [109, Wikipedia 2016].

Usually TDI or MDI plants are closely connected with an upstream phosgene plant. The process for phosgene production, which is a large volume inorganic process, is an exothermic gas phase catalytic reaction between chlorine and high-purity carbon monoxide. In 2013, about 75–80 % of global phosgene was consumed for isocyanates, 18 % for polycarbonates and about 5 % for other fine chemicals

The European production of TDI and MDI is summarised in Table 10.1 below.

Table 10.1: European producers of TDI and MDI (March 2014)

Country	City	Operator	Capacity (kt/yr)	
			TDI	MDI
Belgium	Antwerp	BASF	0	560
France	Pont de Claix	Vencorex	120	0
Germany	Brunsbuttel	Bayer	135 (1)	200
	Dormagen	Bayer	90 (2)	0
	Krefeld	Bayer	0	200
	Ludwigshafen	BASF	0 (2)	0
	Schwarzheide	BASF	80 (3)	0
	Stade	Dow	0	230
Hungary	Kazincbarcika	Wanhua	250	240
Netherlands	Rotterdam	Huntsman	0	400
Portugal	Estarreja	Dow	0	160
Spain	Tarragona	Bayer	0	160

(1) Planned expansion to 150 kt.
(2) New/expanded capacity to 300 kt under construction.
(3) Planned closure.

In 2013, the number of global TDI enterprises was over 30 with more than 40 sets of TDI production lines. The total production capacity was 2.1 million tonnes per year and mainly located in Asia, Europe and the United States. With most of the TDI output going into the furniture and automotive sectors, demand is sensitive to economic activity. Due to the economic downturn, demand for flexible polyurethane foams fell in 2009 by between 5 % and 20 % in the United States and western Europe. In stronger economies, the fall was more limited, i.e. less than 5 %. In 2014, the total economic value of the polyurethane (PU) industry in Europe was EUR 207.3 billion and it was responsible for around 1 million jobs both directly in its manufacture and also more so indirectly through the industries using PU products.

In Europe, the most competitive operators are building more efficient and larger TDI plants (up to 300 kt/yr) and this is leading to the closure of smaller plants which are becoming less profitable.

Key environmental issues

The key environmental issues for the production of TDI and MDI are as follows:

- The potential emissions from MDI and TDI plants are among the most harmful to human health and the environment, i.e. phosgene, Cl_2, HCl and other halogenated compounds, and PCDD/F from waste gas incinerators. These substances are mainly related to the phosgene generation and the phosgenation reactions. There is normally a shared vent system and end-of-pipe treatment unit to abate these emissions. There are also potential emissions to air from storage and from fugitive emissions of the same nature: VOCs and halogenated compounds.
- One of the main health and safety issues in phosgenation plants is the prevention of phosgene emissions due to other than normal operating conditions.
- For both the MDI and TDI production processes, the final phosgenation is preceded by the production of intermediate products that generate specific effluents. The aqueous effluents generated by these process units are normally pretreated at the source then managed collectively and sent to a common waste water treatment unit. The waste water may contain halogenated compounds (from the phosgenation, e.g. solvent), aromatic nitrogen compounds from nitration (TDI only), amines from hydrogenation (TDI only) or downstream processing, nitrate from nitration (TDI) and large quantities of chloride from phosgenation (TDI, MDI) and condensation (MDI).
- The processes generate organic liquid residue streams which are normally incinerated.

10.2 Applied processes and techniques

10.2.1 Process options

TDI and MDI/PMDI are produced by different processes which have in common the phosgenation of a primary amine isomer mixture, TDA or MDA.

The basic steps in a TDI production plant are the nitration of toluene, followed by hydrogenation to produce toluenediamine (TDA). TDA is then reacted with phosgene to produce TDI, with HCl as a by-product.

The basic steps in a MDI production plant are a condensation reaction between aniline and formaldehyde to produce MDA and oligomers (PMDA), followed by neutralisation, washing, MDA purification and phosgenation stages. The resultant MDI/PMDI mixture is then fractionated.

The process steps for the production of TDI and MDI are described in more detail in Section 10.2.2, including alternative options for the individual process steps (e.g. alternative phosgenation routes to produce TDI).

Both processes use other LVOC as feed. In Figure 10.1, the green shaded areas show the scope of this chapter.

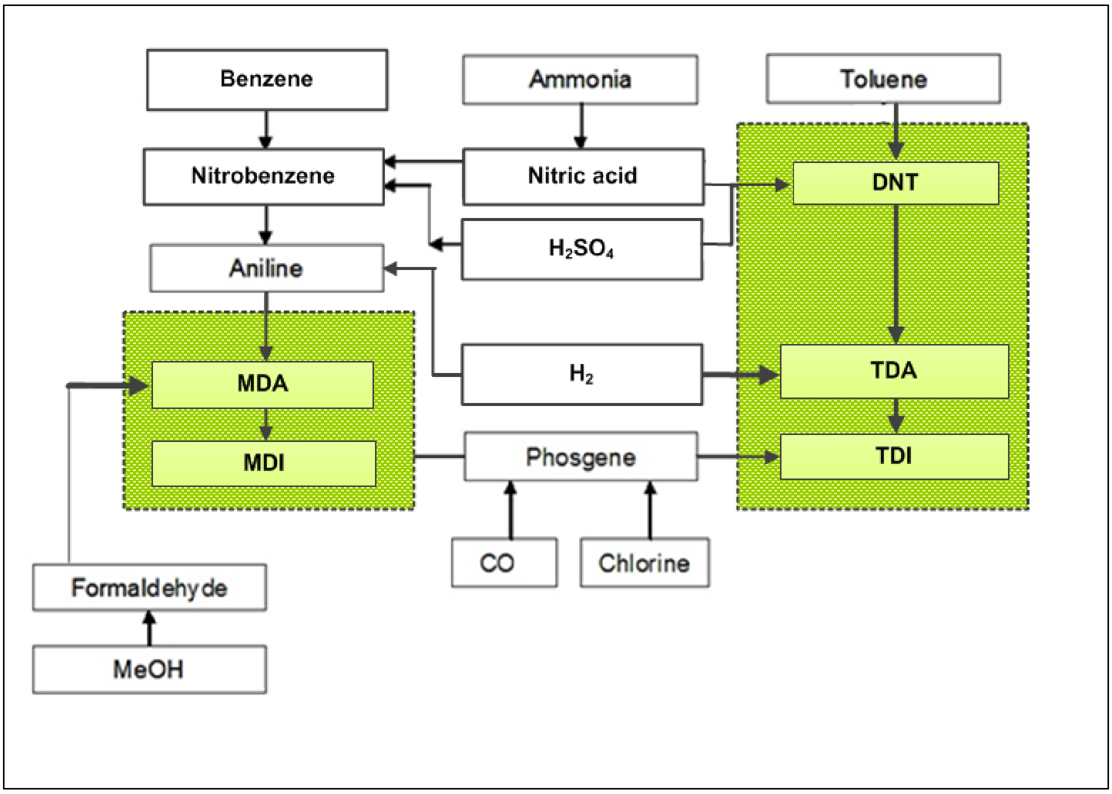


Figure 10.1: MDI and TDI routes with respect to other large volume chemical processes

10.2.2 Basic process steps

10.2.2.1 TDI process

10.2.2.1.1 Nitration of toluene to DNT

Nitration of toluene is a liquid organic/aqueous phase reaction carried out under strong agitation. On a large scale, it is a continuous two-step process. First, toluene is nitrated at 45–70 °C to produce mononitrotoluene (MNT), which is then nitrated to produce dinitrotoluene (DNT):

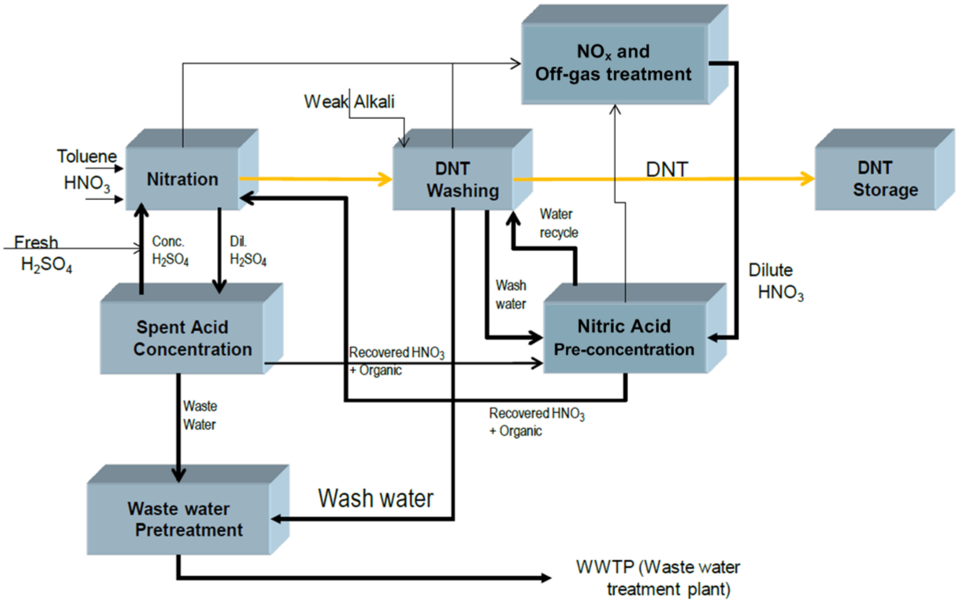
$$C_7H_8 + 2\ HNO_3 \rightarrow C_7H_6N_2O_4 + 2\ H_2O$$

The nitration is carried out using nitrating acid (a mixture of sulphuric acid (usually 85–98 wt-%) and nitric acid (approximately 65 wt-% or 98 wt-%)), which is mixed with MNT for the second reaction, then separated and used in a slightly diluted form for the first reaction step to produce MNT.

The reaction produces a mixture of 2,4-dinitrotoluene and 2,6-dinitrotoluene, along with other by-products such as the 2,3 and 3,4 isomers. After each nitration step, the product is separated from the used acid in phase separators and is then further processed. The used acid is routed to a recovery unit (see below).

As well as being a nitrating agent, HNO_3 also reacts as an oxidant, mainly in the first reaction step, to form phenols and cresols for example which then are nitrated during the second reaction step to other nitrogen-containing aromatic compounds (e.g. nitrophenols and nitrocresols).

The raw product therefore has to be purified by a sequence of washing steps, for example using water, alkaline solution (e.g. with carbonate) and water again to remove by-products and the remaining acid.



Source: [196, ISOPA 2014]

Figure 10.2: Flow chart of the DNT process

One of the typical layouts of the DNT process is shown in Figure 10.2 which also illustrates both the strong interconnection of the DNT process with the recovery of the used acid and the main emission sources.

Recovery of spent acid

The used sulphuric acid is diluted by the water produced in the reactions (approximately 0.2 t H_2O/t of DNT, disregarding side reactions) to concentrations of 72 wt-% for example. It contains organics from the process and some HNO_2 and unreacted HNO_3 which can be removed as a first step by extraction/reaction with toluene feed.

The spent acid which may still contain 0.4–1.5 % HNO_2, 0.1–0.5 % unreacted HNO_3 and 0.2–0.45 % MNT for example is then routed to an integrated multistep acid recovery/concentration unit.

There, the acid is first purified by distillation or stripping, with work-up of the overhead to recover nitric acid or HNO_3 and MNT/DNT.

Then, the purified acid is concentrated in a multistage evaporation step under vacuum to achieve a maximum H_2SO_4 concentration of 96 wt-% and returned to the reaction feed.

[110, Dugal 2005],[112, Booth 2012], [50, Meissner 2014], [133, patent US 7988942 B2 2011], [134, patent DE 102004005913 A1 2004].

10.2.2.1.2 Hydrogenation of DNT to TDA

Hydrogenation is a catalytic exothermic (1 100 kJ/mole) gas/liquid/solid phase reaction. Dinitrotoluene is reduced to toluenediamine (TDA) by a continuous hydrogenation process using a metal catalyst. Hydrogenation can be single- or multi-stage, with or without organic solvents (e.g. lower alcohols, ethers, esters or toluene) present and takes place at reaction temperatures of up to 200 °C and pressures of up to 8 000 kPa:

$$C_7H_6N_2O_4 + 6\ H_2 \rightarrow C_7H_6N_2H_4 + 4\ H_2O$$

If a two-stage hydrogenation process is applied, then the second hydrogenation stage may take place at a lower pressure, without any solvent present and using metal catalysts (e.g. nickel or palladium). Selectivity is high (up to 98–99 %). A side reaction may lead to the formation of trace amounts of ammonia and toluidines. Isopropanol, when used in the reaction mixture, reacts with the ammonia to form isopropylamine.

The reaction product is separated into a TDA-rich product stream. The residual catalyst is removed by filtration. (If a solvent is used, this is recovered by distillation.) In the subsequent distillation units, the TDA is dewatered and rectified to a mixture of 2,4-TDA and 2,6-TDA. Low-boiling-point compounds produced by side reactions (such as isopropylamine) and a higher-boiling-point residue are separated and sent for disposal.

[113, Cartolano 2005].

10.2.2.1.3 Phosgenation of TDA to TDI

[31, SIX et al. 2012].

All phosgenation processes include the same main reaction of TDA with an excess of phosgene, using an inert solvent like ortho-dichlorobenzene (ODB):

$$C_7H_6N_2H_4 + 2\ COCl_2 \rightarrow C_9H_6N_2O_2 + 4\ HCl$$

HCl is generated as a by-product in stoichiometric quantities (e.g. in a 70 kt/yr TDI plant, as much as 57 kt/yr of HCl can be generated). Hydrogen chloride and phosgene are recovered. The purified hydrogen chloride may be marketed or oxidised to chlorine, e.g. by electrolysis, for reuse in the phosgene production step.

TDI is purified by fractional distillation. The recovered solvent is recycled. The hot liquid residues from distillation may be treated for further TDI recovery and are then incinerated.

The phosgenation reaction is normally carried out in the liquid phase, which can be operated either at normal or high pressure. For TDI production, as a new process, phosgenation in the gas phase has been developed by one operator, with one production site in China and another in Europe. The different processes are described below:

- The typical **liquid phase phosgenation** process consists either of a semi-continuously operated cascade of agitated vessels or a continuously operated series of reaction towers at normal or slightly elevated pressures and temperatures between 20 °C and 180 °C with the use of an inert solvent. Generally a 25–50 % solution of phosgene or pure phosgene is added to a 10–20 % solution of TDA in an inert organic solvent (such as o-dichlorobenzene (DCB)). In the first reaction (‘cold’ phosgenation) stage, TDA reacts at low temperatures with phosgene. Efficient mixing is achieved by high turbulence and possibly by recirculation. The resulting slurry of carbamoyl chlorides and amine hydrochlorides is heated in the ‘hot’ reaction stage with excess phosgene until a clear solution of TDI is obtained. The overall reaction proceeds efficiently, without the need for any catalyst, if a large excess of phosgene (50–300 %), high dilution, and an intense and rapid mixing of the reactants are maintained in the process.

- The by-product hydrogen chloride and excess phosgene are stripped out with nitrogen at high temperatures to prevent recombination of hydrogen chloride with TDI. Hydrogen chloride, phosgene and solvent are recovered. The purified hydrogen chloride may be marketed or oxidised to chlorine for reuse in the phosgene production step.

- A variation of the liquid phase phosgenation is the **high-temperature / high-pressure phosgenation** process. In this continuous process, the high temperature (from 100 °C to 300 °C) and high pressure (from 5 bar to 100 bar) very significantly increase the kinetics of phosgenation compared to the lower temperature process. The amine hydrochlorides species are not produced, toluene dicarbamoyl chloride isomers (di and mono) are produced directly in less than 200 milliseconds, preferably in less than 15 milliseconds. This leads to a high yield of reaction, smaller size equipment and no reaction towers as in the cold process.

- Liquid raw materials are pumped at high pressure into a plug flow reactor through a specially designed nozzle which increases the velocity of the reactants to achieve good mixing inside it, without the use of any rotating device. The reaction is very quick and efficient due to the velocity of the reactants, the design of the nozzle and the shape of the reactor. In comparison to the low-pressure process, more efforts have to be made to prevent fugitive emissions of phosgene.

- With this process, the high liquid pressure conditions of the reaction drive the recovery of a mix of chlorinated solvent/TDI and gaseous HCl under pressure. HCl purification is thus easily performed by means of a distillation column since HCl is under pressure. This produces high-purity gaseous HCl, with less than 1 ppmv of organic solvent and less than 5 ppmv of phosgene, which can be used for many applications. Chlorinated solvent is separated from TDI and recycled in the reaction section. As the reaction is very efficient, there is no need to purify the solvent for reuse.

- In the **gas phase phosgenation** process, TDA, phosgene and a small amount of solvent are heated to temperatures > 300 °C. The amine and phosgene feeds are mixed in a reactor tube, with a high molar excess of phosgene to maintain a high reaction rate. Solvent, excess phosgene and HCl are separated as a vapour phase. After condensation, the TDI slurry is distilled to remove the remaining phosgene and solvent [106, Sonnenschein 2014].
-

  In comparison to the liquid phase processes, the much shorter residence time of TDA and phosgene in the reactor reduces the required phosgene process inventory considerably. Further benefits are significantly greater reactor throughput per unit time (space-time yield) and the ability to downsize key plant components. Process safety is improved by the reduction in both phosgene and solvent inventories within the process. A further safety enhancement is the ability to start up and shut down the gas phase process quickly. See also Section 10.4.3.2.

In recent years, some research has looked into producing the major aromatic diisocyanates TDI and MDI/PMDI by **non-phosgene processes** which are described in Chapter 10.5.

10.2.2.2 MDI process

The first basic step in a MDI plant is a condensation reaction between aniline and formaldehyde to produce MDA and oligomers (PMDA). This is followed by neutralisation and phosgenation stages. The product is then fractionated.

10.2.2.2.1 Condensation of aniline to MDA

MDA and oligomers (PMDA) are produced by the acid (typically HCl)-catalysed condensation of aniline (C_6H_7N) with formaldehyde (CH_2O):

$$2\ C_6H_7N + CH_2O \rightarrow NH_2\text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}NH_2 + H_2O$$

$$n+1\ C_6H_7N + n\ CH_2O \rightarrow [NH_2\text{-}C_6H_4\text{-}CH_2]_n\text{-}C_6H_4\text{-}NH_2 + n\ H_2O$$

The formaldehyde is normally fed as an aqueous solution with some methanol content.

The reaction of aniline with formaldehyde could be carried out in a single reactor as a batch process. However, commercial processes use reactor cascades, which provide greater control of the MDA isomer distribution and oligomeric content of the final product.

The reaction of aniline with formaldehyde does not lead to a single product, but to a mixture of 4,4'-, 2,4'-, and 2,2'-isomers and oligomeric MDA. The amounts of MDA isomers and oligomers formed depend on the ratios of aniline, formaldehyde and acid used, as well as the reaction temperature and time.

Neutralisation and product purification: Caustic soda is added to neutralise the acid catalyst which leads to the formation of two phases. The organic phase that contains PMDA (polymeric MDA) undergoes purification steps (washing, distillation/stripping and optionally nitrogen injection) to remove and recover unreacted aniline and other low-boiling compounds. The aqueous phase which is mainly sodium chloride solution (brine) will follow several steps to remove/recover aniline, MDA and methanol prior to discharge to waste water treatment.

10.2.2.2.2 Phosgenation of MDA to MDI

The MDA/PMDA mixtures are reacted with phosgene to produce the corresponding isocyanates and HCl by-product:

$$\underset{\text{MDA}}{NH_2\text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}NH_2} + 2\ COCl_2 \rightarrow \underset{\text{MDI}}{OCN\text{-}C_6H_4\text{-}CH_2\text{-}\ C_6H_4\text{-}NCO} + 4\ HCl$$

The process is analogous to the liquid phase phosgenation of TDA (Section 10.2.2.1.3).

The reaction is carried out in a solvent, e.g. monochlorobenzene (MCB). The reaction blend goes to the processing section where the phosgene and solvent are removed at a higher temperature and lower pressure to avoid thermal decomposition of the product.

Phosgene, solvent and HCl are separated from various process streams. Phosgene and solvent are returned to the process. HCl is generated as a by-product in stoichiometric quantities (146 kg HCl per 250 kg of MDI). This HCl can be used in other processes, e.g. in an EDC plant, or to produce hydrochloric acid, or to recover chlorine as a raw material using electrolysis or the Deacon process.

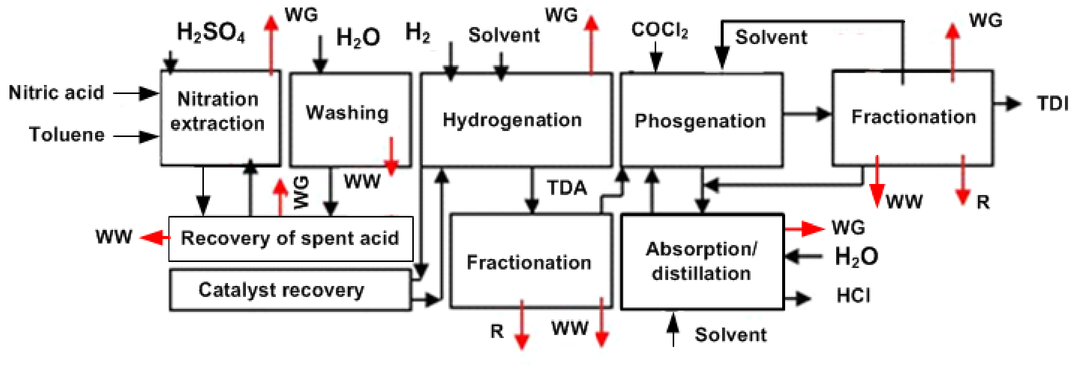
Fractionation: The isocyanate mixtures from the phosgenation reaction, commonly called crude polymeric MDI (PMDI), can be sold directly and may have varied chemical compositions.

Alternatively, the 4,4'-MDI can be separated from the PMDI products by distillation or crystallisation. The amount of 4,4'-MDI that is removed depends on market conditions. The fractionation takes place at low pressure. The bottom product has a relatively high content of polyfunctional isocyanate groups. It is stored in bulk as PMDI. The 4,4'-MDI (‘pure’ MDI) and the mother liquor, a mix of 4,4'-MDI and 2,4'-MDI, are produced from the top product. The pure MDI, mother liquor and polymeric MDI are stored in bulk for internal processing or transportation to customers. In MDI production, the oligomeric fraction is a viable commercial product., [31, SIX et al. 2012].

10.3 Current emission and consumption levels

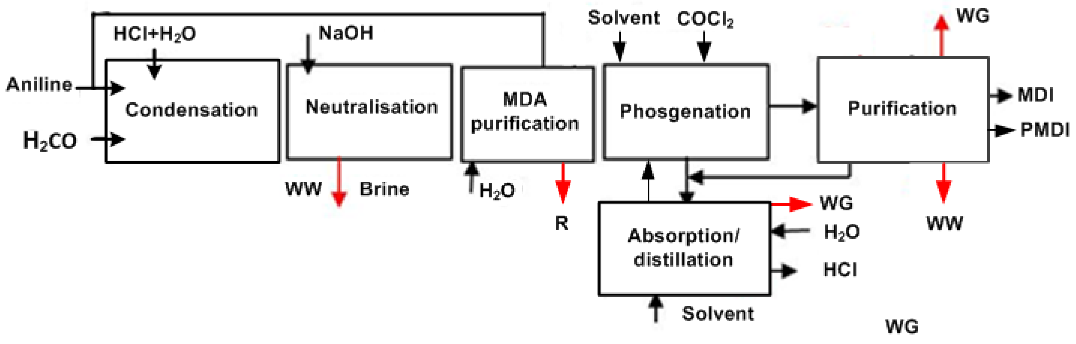
The production of TDI and MDI involves several process steps as described in the previous sections.

Figure 10.3 and Figure 10.4 are block flow diagrams that show the major emission streams of these industrial chemical processes.



NB: WG: Waste gas to treatment; WW: Waste water to treatment; W: Waste.

Figure 10.3: Block flow diagram of a TDI manufacturing process



NB: WG: Waste gas to treatment; WW: Waste water to treatment; W: Waste.

Figure 10.4: Block flow diagram of a MDI manufacturing process

There are several basic unit operations that are common to both TDI and MDI plants:

- Both phosgenation units generate a by-product stream of HCl gas that can be recovered. However, this first needs to be separated from other components of the waste gas such as unreacted phosgene and solvent.
- Both phosgenation units are operated with a solvent, normally monochlorobenzene (MCB), and therefore include a solvent recovery unit to recycle the solvent.
- Both plants may generate gums or oligomers when purifying intermediate or finished products.

10.3.1 Emissions to air

10.3.1.1 DNT plants

Sources of waste gas streams arising from the nitration unit are:

- the nitration reactor;
- the wash tank;
- the alkaline scrubber; and
- the acid purification and concentration unit

Monitoring is normally not applied to each individual emission but at the header of the shared vent. The composition of these vent streams includes VOCs (such as toluene and possibly also nitroaromatics (potential NO_X precursors) like MNT and DNT), SO_2 and NO_X.

10.3.1.2 TDA plants

Sources of waste gas streams arising from the hydrogenation section are:

- the hydrogen reactor;
- the hydrogen recycle compressor purge;
- the catalyst separator/recovery; and
- the TDA distillation/vacuum system.

Monitoring is normally not applied to each individual emission but at the header of the shared vent. An example of the composition of these vent streams after scrubbing is shown in Table 10.2.

Table 10.2: Emissions from hydrogenation to air after scrubbing

Compound	**Solvent**	**TDA**	**NH_3**	**Isopropanol**	**H_2**	**Ammonia**	**Toluidines**
Emission (mg/m^3)	12	4	7	ND	ND	ND	ND
NB: ND: No data available. *Source*: 2003 LVOC BREF [190, COM 2003]							

A side reaction may lead to the formation of traces of ammonia. Isopropanol, when used in the reaction mixture, reacts with the ammonia to form isopropylamine.

10.3.1.3 TDI/MDI plants: emissions from the phosgenation section

TDI process: Off-gases from phosgenation contain phosgene, hydrogen chloride, solvent vapours (e.g. dichlorobenzene) and traces of TDI product. Emissions to air arising from the phosgenation section are from:

- the reactor's vents;
- the phosgene removal/recycling system vent;
- HCl stream;
- TDI phosgene recovery column top cut;
- TDI purification bottom cut;

- oligomers stream; and
- TDI vacuum system vent.

Gaseous emissions from the first reaction stage are routed to treatment.

Waste gases that contain phosgene can be routed to scrubbers or wet activated carbon columns to destroy phosgene (e.g. hydrolysis in a scrubber with water or NaOH giving a 99.9 % removal efficiency). Scrubber vents may be sent to incineration / thermal oxidation to destroy any trace of organic solvents, or sent to activated carbon adsorbers to remove any traces of VOCs (mainly solvent)s.

Emissions of the solvents may occur from the vacuum jet vents from the solvens recovery, TDI purification and residue separation.

After the solvent is stripped out and recycled, the off-gases are likely to contain hydrogen chloride (which can be recovered), tetrachloromethane, carbon monoxide and, depending on the pretreatment, traces of phosgene.

MDI process: Both the reaction and the recovery of HCl, phosgene and solvent are similar to the TDI phosgenation process, producing similar pollutants in the waste gas streams that are sent to treatment: solvents (here typically MCB instead of o-DCB), CO, HCl, chlorine, CCl_4, etc.

As for TDI plants, the main final abatement consists of a combined treatment where the organic pollutants are incinerated.

10.3.1.4 MDA plants

In contrast to the process steps discussed above, the liquid phase condensation reaction to produce MDA does not involve gaseous educts or products. Therefore, waste gas flows from the MDA production steps (condensation, neutralisation, product purification) will be comparatively small and arise mainly from the distillation and stripping units. The waste gas may contain nitrogen, formaldehyde, aniline, methanol and ammonia.

10.3.1.5 MDI/TDI process: Emissions from shared end-of-pipe abatement systems

It is common for MDI and TDI plants to have shared vent treatment systems for end-of-pipe treatment. Generally, the waste gas streams from all processes (production of intermediates and final products) are treated to remove organic and acidic compounds. The treatment usually includes a thermal treatment (incinerator or oxidiser) that may be shared with other processes, and therefore final emissions may be dependent on the inputs from other processes.

There are a number of other vents from diverse sources, including process vessels, loading facilities, process analysers, sampling connections, safety valves and maintenance vents. These vents usually contain valuable products (e.g. TDI, hydrogen chloride) diluted by non-condensable gases (i.e. carbon dioxide, nitrogen, air).

As explained in the sections above, the waste gas will contain a wide variety of pollutants. These include a number of toxic and corrosive chemicals, and adequate controls are necessary.

The shared vent treatment may also receive vent streams from the phosgene plant that contain phosgene, CO and other organic pollutants such as tetrachloromethane (TCM); TCM results from a side reaction of methane in the phosgene production, but possibly also from the phosgene itself during phosgenation.

10.3.1.5.1 Data from Member States

One Member State provided emissions data from two MDI units which are summarised in Section 10.4.1.5.

From other Member States, emission limit values from permits give an idea of the main pollutants of concern and achievable emissions although real emissions may be much lower.

Table 10.3: ELVs for shared waste gas treatment (mg/Nm^3)

Pollutant	**Member State**			
	DE1	**DE2**	**PT**	
TVOC	50	ND	10	20
NO_X	ND	100*/300**	180	350
HCl	ND	10	8	50
DCB	20	ND	No ELV	No ELV
CO	ND	ND	30	100
TDI	20	ND	No ELV	No ELV
Phosgene	ND	1	No ELV	No ELV
Isocyanates expressed as NCO	0.1	ND	No ELV	No ELV
SOx	ND	20	40	150
Reference conditions	ND	Reference conditions for achievable levels are 273 K, 101.3 kPa	Daily average	Average 30 min
			Values are expressed in 11 % O_2, 273 K and 101.3 KPa	
Comments	TDI process	TDI process * from nitration ** from combustion	MDI process Incinerator of organochlorine residues from the MDI process and other LVOC processes	

NB: ND: No data available.
Source: 2003 LVOC BREF [190, COM 2003]; [38, PT 2012]

10.3.1.5.2 Data from Industry for TDI and MDI plants

Industry (ISOPA) organised a data collection on emissions to air from TDI and MDI plants in 2015. The data collection did not differentiate between TDI and MDI plants. It covered emissions from thermal treatment and from wet scrubbers.

The definitions used for the survey were the following:

- The plants covered by the TDI/MDI process are defined according to Figure 10.1.
- Normal operating conditions (NOC): The composition of the 18 reported streams are typical for normal operating conditions and represent the largest sources of emissions to air of TDI/MDI plants. For OTNOC (other than normal operating conditions), there are normally existing additional abatement units with separate waste gas streams, which are not included in this survey. Only NOC data were collected.
- Main abatement techniques: The technique mentioned is the one predominantly used for waste gas streams of this composition (and may be used in combination with other techniques).

- Combined waste gas streams: Most of the reported streams are combinations of waste gases from different parts of the TDI/MDI plants and different parts of production units in the vicinity of the abatement unit.

- The averaging periods associated with the BAT-AELs for emissions to air are defined as follows: For periodic measurements: the average of three spot samples of at least 30 minutes each. For the monthly average of continuous measurements: the average over a period of one month based on valid hourly averages. For the daily average of continuous measurement: the average over a period of one day based on valid hourly averages.

- Concentration of the emission (mg/Nm^3) to air (end of pipe). The emission values are standardised at 11 % oxygen in waste gas for the thermal oxidisers.

When performed, results from monitoring required by the permit, i.e. data that are available for the public, have been reported (unlike data from self-monitoring which may be performed more frequently for some parameters).

Data from five companies with 18 combined waste gas streams were collected.

Data on streams for thermal abatement (or thermal treatment when it is the main step of a combined treatment often including a wet post-scrubber or a post-scrubber system where, in a first stage, HCl is absorbed in water and the remaining HCl is then removed by caustic scrubbing) are shown in the tables below.

Table 10.4: MDI/TDI waste gas survey: Technical information

Stream No.	**Ox 1**	**Ox 2**	**Ox 3**	**Ox 5**	**Ox 6**	**Ox 8**	**Ox 11**	**Ox 12**	**Ox 13**	**Ox 16**
Technique										
Thermal oxidiser	X	X	X	X	X	X	X	X	-	-
Regenerative oxidiser	-	-	-	-	-	-	-	-	X	X
With SCR	-	-	-	-	-	-	X	-	-	-
With SNCR	X	X	-	-	-	-	-	-	-	-
Wet gas scrubber	X	-	X	X	ND	X	X	X	ND	ND
Multiple scrubber system	ND	ND	ND	ND	ND	ND	X	X	ND	ND
Flow rate (Nm^3/h)										
1 000–10 000	X	X	X	X	-	X	-	X	X	X
> 10 000	-	-	-	-	X	-	X	-	-	-

NB:
Other information on waste gas origin/characteristics:
Ox 3: Nitrogen-containing compounds used as liquid fuel substitute (NO_X precursors).
Ox 6: Combined stream of two production units (including concentration/recovery of sulphuric acid from DNT).
Ox 8: No nitrogen-containing compounds in raw gas.
ND: No data available.

Table 10.5: MDI/TDI waste gas survey: Average emissions (mg/Nm^3, 11 vol-% O_2) from oxidisers

Parameter	**Ox 1**	**Ox 2**	**Ox 3**	**Ox 5**	**Ox 6**	**Ox 8**	**Ox 11**	**Ox 12**	**Ox 13**	**Ox 16**
NH_3 ^{C}	4.7	NE	NE	NM	50	NE	NM	NM	NE	NE
NO_X	218	202	464	203	70	23	92	120	4	< 2
CO	1.4	7.0	NE	< 6.6	3	2.8	10	0.2	NM	NM
SO_2	NM	1.5	NE	NE	20	NE	0	0	NE	NE
TOC	< 1.4	3.4	2.4	< 2.6	35	1	2.1	0.1	NM	NM
HCX (1)	NM	NM	NM	< 1.45	NM	0	NM	NM	< 2	2.6
Cl_2	NM	NE	NM	< 0.03	NM	0.03	NE	NE	< 0.5	< 0.5
Phosgene	< LOD	NE	NM	< 0.05	NM	NE	NE	NE	NE	NE
HCl	33	NE	6	< 0.11	10	1.2	0.12	0.3	3	1.5
PCDD/F (2)	0.03	NE	NE	NM	NM	0	0.03	NM	0.06	< 0.01

(1) Chlorinated hydrocarbons.
(2) ng iTEQ/Nm^3.
NB: NM: Not measured; NE: Not expected therefore not measured; LOD: Limit of detection.

The survey shows that:

- the average emission of many parameters, if present at all, can be reduced to low concentration levels (CO, SO_2, TVOC, hydrocarbons, chlorine, phosgene and PCDD/F); and
- some parameters show higher emissions for one or a few waste gas streams (NH_3, NO_X, HCl).

When wet scrubbers were used as the main abatement technique, fewer parameters were measured.

Table 10.6: MDI/TDI waste gas survey: Average emissions (mg/Nm^3) from scrubbers

Stream No.	**WGS 4**	**WGS 7**	**WGS9**	**WGS10**	**WGS14**	**WGS15**	**WGS17**	**WGS18**
Flow rate (Nm^3/h)								
< 100	X	-	-	-	-	-	-	-
100–1 000	-	-	-	-	-	X	X	X
1 000–10 000	-	-	X	-	X	-	-	-
> 10 000	-	X	-	X	-	-	-	-
Emissions (mg/Nm^3)								
TOC	29	90	13	8.8	NM	NM	NM	NM
Chlorinated hydrocarbons	NE	NM	6.3	4.3	NM	NM	NM	NM
Cl_2	NE	< 1	NE	NE	< LOD	< 0.5	< LOD	< 0.5
Phosgene	NE	< 0.5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HCl	< 0.3	< 1	NM	NM	< LOD	2.1	< LOD	2.8

NB: NM: Not measured; NE: Not expected therefore not measured; LOD: Limit of detection.

Companies mostly reported using internal analytical methods which may differ in some detail from the available standard methods.

There was a wide variation in the monitoring frequency depending on the parameters and possibly permit conditions.

Table 10.7: MDI/TDI waste gas survey: Monitoring frequencies for oxidisers

Parameter	**Ox 1**	**Ox 2**	**Ox 3**	**Ox 5**	**Ox 6**	**Ox 8**	**Ox 11**	**Ox 12**	**Ox 13**	**Ox 16**
NH_3	1/3	NA	NA	NA	4	NA	NA	Cont.	NA	NA
NO_X	1	1/3	1/3	1/2	4	4	Cont.	Cont.	1	1
CO	Cont.	1/3	NA	1/2	4	4	Cont.	Cont.	NA	NA
SO_2	NA	1/3	NA	NA	4	NA	1	Cont.	NA	NA
TOC	NA	1/3	1/3	1/2	12	4	Cont.	Cont.	NA	NA
HCX (^{1})	NA	NA	NA	1/2	NA	4	NA	NA	1/3	1/3
Cl_2	NA	NA	NA	1/2	NA	4	NA	NA	Cont.	Cont.
Phosgene	NI	NA	NA	1/2	NA	NA	NA	NA	NA	NA
HCl	NI	NA	1/3	1/2	Daily	4	Cont.	Cont.	Cont.	Cont.
PCDD/F	1/3	NA	NA	1/2	NA	NI	1	NA	1/2	NI

(^{1}) Chlorinated hydrocarbons.
NB: Cont.: continuous; number: frequency per year (e.g. 4 = 4 measurements per year, 1/3 = 1 measurement every 3 years); NA: Not applicable (not monitored); NI: No information provided.

Table 10.8: MDI/TDI waste gas survey: Monitoring frequencies for scrubbers

Parameter	WGS 4	WGS 7	WGS 9	WGS 10	WGS 14	WGS 15	WGS 17	WGS 18
TOC	1/3	12	4	4	NA	NA	NA	NA
HCX (1)	NA	NA	4	4	NA	NA	NA	NA
Cl_2	NA	1	NA	NA	1/3	Cont.	1/3	Cont.
Phosgene	NA	1	NI	NI	1/3	NI	1/3	NI
HCl	1/3	1	NA	NA	1/3	Cont.	1/3	Cont.

(1) Chlorinated hydrocarbons.
NB: Cont.: continuous; number: frequency per year (e.g. 4 = 4 measurements per year, 1/3 = 1 measurement every 3 years). NA: Not applicable (not monitored).

For most plants, the measurements cover several years (three to five). The frequency of the reported measurements showed wide variations. For CO, TOC, NO_X, ammonia, SO_2, HCl and chlorine, the frequency ranged from once every three years to continuous measurement. For chlorinated hydrocarbons, the maximum frequency was four times a year, and for PCDD/F twice a year.

10.3.1.5.3 Data from the E-PRTR

For chemical sites, the European Pollutant Release and Transfer Register (E-PRTR) contains data on emissions to air and water from facilities as reported by the operators. Since a facility as defined for the E-PRTR may include several different installations, the data are only of limited use for the estimation of emissions from specific production processes but in some cases they may give an indication. The E-PRTR data may include emissions from OTNOC events and estimates of diffuse emissions.

For tetrachloromethane (TCM), which may be relevant as a pollutant from the phosgenation process, the following E-PRTR data were reported for 2013 for sites with TDI/MDI installations.

Table 10.9: TCM emissions in 2013 from E-PRTR facilities with TDI/MDI production

Country	Operator	Capacity (kt/yr)		TCM	TCM
		TDI	MDI	kg/yr (1)	g/t
France	Vencorex	120	NA	206 (2) (3)	(3)
Germany	Dow	NA	230	1005 (3)	(3)
Netherlands	Huntsman	NA	400	1270	3.2

(1) Tentative estimate from load and capacities; only valid if the MDI/TDI process is the only source; emissions may also occur from the production of chlorine or from aliphatic chlorination processes, etc.
(2) TCM emissions to water (15 kg) also reported.
(3) TCM emissions result mainly or only from other processes.
NB: NA: Not applicable.

The E-PRTR threshold value to report emissions of TCM is 100 kg/yr which would correspond to a maximum specific emission below 1 g/t for a 100 kt production or 0.25 g/t for a 400 kt production for facilities that do not report TCM emissions.

10.3.1.6 Incineration of residues

TDI and MDI plants may have facilities to incinerate process residues. The incineration facilities will generate waste gases. As there will be chlorinated compounds, *ex novo* formation of PCDD/F is possible and should be monitored.

10.3.1.7 Emissions to air with low VOC content

In TDI and MDI plants, the plant design details will change depending on many factors. In some cases, the plant will generate vent streams that contain acid gases but with a very low or negligible VOC content. Examples of these streams are:

- the vent from the HCl absorption column, which will contain HCl, but only traces of VOCs, if any;
- the net vent from a distillation operation.

The normal abatement method for these vents would be a scrubber system that could operate without a thermal treatment downstream if samples prove that the concentration/load of VOCs is acceptably low.

10.3.1.8 VOC emissions from fugitive emissions

Fugitive emissions to air are important since there are many parts of the process that operate under pressure.

Fugitive emissions will mainly consist of TDI, hydrogen chloride and volatile organic compounds, e.g. solvents.

Due to the toxic nature of phosgene, hydrogen chloride and other fugitive chemicals, sensitive detection systems are installed for continuous monitoring inside the plant and of ambient air quality. Containment systems or other secondary mitigation measures are employed to collect and treat fugitive emissions in case of an accidental release. This is for occupational health reasons but has consequential environmental benefits; extensive measures have been taken to prevent releases.

See the CWW BREF for more information on fugitive emissions. Further information on phosgene safety can also be found in the OFC BREF [205, COM 2006] and the publications of the International Isocyanate Institute Inc. (www.phosgenesafety.info).

10.3.1.9 VOC emissions from storage

Storage tanks used for raw materials, consumables, end-products and intermediates are typically operated at atmospheric pressure. If not geographically too far apart in the plant layout, the abatement of emissions can be shared with the main process streams. Tank vent gases are, in some cases, partially recovered by condensation (chilled water), and the non-condensable gases are routed for incineration. Other processes use storage tanks blanketed with nitrogen, where vent gases are sent to the atmosphere or to an adsorption column to remove hydrocarbons. Gas equilibrium lines can be used for unloading/loading to reduce emissions to the atmosphere.

For more information on VOC emissions from storage, see the EFS BREF.

10.3.2 Emissions to water

Emissions after biotreatment (including nitrification/denitrification) for the whole TDI process (including production of DNT and TDA) are TOC < 0.4 kg/t of TDI and TNb (total nitrogen) < 0.2 kg/t of TDI.

10.3.2.1 Emissions to water from waste gas treatment

Throughout the plant there are numerous waste gas streams that need treatment by scrubbing using an appropriate scrubbing agent (e.g. dilute caustic, dilute HCl or water). Therefore, one of the largest contributions to the quantity of waste water could arise from the waste gas treatment.

According to the information provided by one MDI installation, the waste gases from the preparation of the phosgene and MDI are neutralised in a caustic soda scrubber or hydrolysed, during which sodium chloride, carbonate and sometimes hypochlorite are formed. This is taken to the water purification plant (WPP) with other waste water after the solvent MCB is removed in a steam stripper.

10.3.2.2 DNT plants

Waste water from the nitration unit arises from washing the product and as condensates from steam stripping the spent acid to remove nitroaromatics or nitric acid, any steam stripping of aqueous streams inside the nitration unit, from the reaction (0.2 m^3/t of DNT) and from the nitric acid used (0.37 m^3/t of DNT using 65 % HNO_3, < 0.01 m^3/t of DNT using 99 % HNO_3). Waste water is released at the concentration/recovery of the sulphuric acid and at the washers. The total amount of waste water depends on reuse/recycling and operation of the strippers and washers. The main components are the organic products and by-products, namely di- and trinitrocresols, nitrate/nitrite and sulphates. The organic load is toxic and poorly biodegradable.

The waste water from the nitration reaction will contain a number of organic and inorganic components.

The inorganic components will include sulphates and nitrites/nitrates. Optimisation of the process can give emissions of < 10 kg of nitrate per tonne of DNT and much lower emissions of nitrites (before possible further removal by the biological treatment). Re-engineering of the process may increase the process efficiency and lead to an almost complete reduction of nitrite and a certain reduction of sulphate and nitrate. If highly concentrated nitric acid is used and the concentration of the nitric acid does not take place on site, the amount of waste water per product may be reduced accordingly.

The organic components will include products and by-products, namely di- and trinitrocresols. The organic load is toxic and poorly biodegradable. At a German plant, this results in an effluent stream of 1.3 m^3/t and 4 kg COD/t of DNT produced. The measured toxicity (luminescent bacteria) was in the range of LID = 600–800. At another, older, German plant, the effluent stream after pretreatment (extraction) is 1 m^3/t, with, per tonne of DNT, 4 kg COD, 1 kg TOC, 14 kg nitrate, 10 kg nitrite and 23 kg sulphate.

Further data are given in Table 10.10 below.

Data on the composition of another example plant are given in Table 10.14 with 2,4-dinitro-6-amino o-cresol, 2,4,6-trinitrohydroximethyl-benzene, 2,6-dinitro-o-cresol and 4-nitrobenzoic acid identified as the main pollutants. The poor biodegradability is reflected by a BOD to COD ratio of 0.04.

10.3.2.3 TDA plants

In the hydrogenation unit, the waste water results from any steam stripping of the waste water inside the hydrogenation unit, and from the reaction (0.6 m^3/t of TDA) and also from product purification. One of the common plant configurations includes a distillation train downstream of the hydrogenation and also after the catalyst recovery. These distillation columns will generate several streams such as recycling gas to the reactor, purified TDA to phosgenation and an aqueous stream to be treated before being sent to the shared WWT installation. These streams may include:

- ammonia;
- low-boiling hydrocarbons;
- TDA;
- COD;
- solvents like isopropanol.

For emissions data, see Table 10.10 below.

10.3.2.4 TDI and MDI plants (phosgenation)

The phosgenation reaction is carried out without water but water is used downstream, for example to absorb HCl and for wet scrubbing of waste gas (see Section 10.3.2.1), e.g. in decomposition towers to remove phosgene. Depending on the options for reuse, part of the water may end up as waste water.

The waste water may contain hydrochloric acid or chloride and, as an organic pollutant, some solvent. Unlike DNT and TDA, TDI in waste water hydrolyses and decomposes to insoluble ureas and carbon dioxide.

For one German TDI plant, the waste water from the phosgenation unit contained less than 0.4 kg TOC per tonne of TDI (prior to biological treatment) (2003 LVOC BREF).

Specific emission values for waste water from a German site are given in Table 10.10.

Table 10.10: Emissions to water from a TDI production site

		Total process (1)	**Manufacture of:**		
			TDI only (2)(3)	TDA	DNT
		Per tonne of TDI	Per tonne of TDI	Per tonne of TDA	Per tonne of DNT
Amount of waste water	m^3/t	NI	NI	0.7	0.9
COD	kg/t	6	1.3	1.0	4.6
TOC	kg/t	2	0.4	0.3	1.2
Nitrate	kg/t	15	NI	NI	20
Nitrite (4)	kg/t	10	NI	NI	14
Sulphate	kg/t	24	NI	NI	33

(1) At other sites, waste water emissions are reduced by replacing wet waste gas treatment with incineration.
(2) At other sites, waste water emissions approach zero by replacing wet waste gas treatment with incineration.
(3) Including waste water from storage tanks.
(4) Nitrite emissions are avoided at other sites by in-process measures.
NB: NI: No information provided.

Referring to measurements at one German site, the emission of o-dichlorobenzene after biological treatment was less than 1 g per tonne of TDI (2003 LVOC BREF [190, COM 2003]).

10.3.2.5 MDA plants

After completion of the condensation reaction, the acidic MDA is treated with aqueous sodium hydroxide to neutralise the excess acid. A large amount of sodium chloride is formed during this step, thus the plants must be located near an outlet capable of handling the saltwater generated (normally by the coast). Processes that recycle the acid and eliminate the salt disposal problem have been patented but are not known to be used on an industrial scale.

After phase separation, the aqueous stream (with brine) will normally follow several steps to remove/recover MDA, aniline and methanol prior to its release to a final waste water treatment unit.

10.3.3 Raw material consumption

An example of the raw materials used in a MDI plant is given in Table 10.11.

Table 10.11: Usages of a MDI plant

Raw material	(kg/kg of MDI)
Chlorine	0.56
Phosgene	0.78

Other materials that are used in this type of plant are solvents, process water, sodium hydroxide, etc.

10.3.4 Energy consumption

Steam is used for energy, mainly for distillation in each of the processes (production of DNT, TDA, TDI, MDA and MDI). This can be partly compensated by heat recovery, mainly from exothermic reactions (e.g. hydrogenation of DNT).

Electric power is mainly needed for pumps (e.g. for the distillation systems) and also for compressors (e.g. for hydrogenation) and the reactors (e.g. production of DNT).

10.3.5 Water usage

The TDI/MDI production process does not consume water as a main raw material but as a utility, mainly to wash the raw product (DNT, MDA) and for wet scrubbing of waste gases and for HCl absorbers. Water is also introduced into the process via acids (e.g. sulphuric and nitric acid for DNT) and caustic solutions for neutralisation. The water consumption is, to a great extent, reduced by internal reuse of aqueous streams.

10.3.6 By-products and waste generation

TDI and MDI plants generate a number of by-product and waste streams.

HCl is generated as a by-product and normally isolated after phosgenation.

Spent catalyst: Catalysts are used in nitration, hydrogenation and phosgenation. When catalysts reach the end of their useful life, these materials need to be analysed prior to determining the disposal route.

Spent adsorbent: Activated carbon or similar materials used in adsorption units are dedicated to treating phosgenation off-gases. According to the permit of a German TDI plant (2014), the spent adsorbent material (waste for incineration) may reach 0.17 kg per tonne of TDI produced.

Liquid streams from TDA purification: TDA purification is normally carried out with a distillation train where low-boiling compounds are removed as a residue. The hydrogenation unit produces 0.03 tonnes of liquid residue per tonne of TDA. In addition the distillation separates about 0.03–0.06 tonnes of TDA isomers per tonne of TDA which cannot be used for TDI manufacture and have to be disposed of. These residues are incinerated or, if possible, exploited.

Dimers and oligomer residues from phosgenation: These are produced in the TDI and MDI purification.

The crude TDI still contains some of the chlorobenzene solvent in which it was reacted. In an exemplary distillation process for TDI purification and solvent recovery, this mixture (TDI and solvent) is transferred to a vacuum distillation column where the solvent is recovered and recycled; the remaining crude TDI is vaporised by vacuum flash distillation to separate the TDI from any polymeric isocyanates that may have formed. The phosgenation unit produces 0.05 tonnes of distillation residue per tonne of TDI. The distillation residue may contain *inter alia* 0–80 wt-% TDI, urea compounds, TDI oligomers, urethanes and isocyanurates.

The distillation residue is incinerated, after solidification by polymerisation or reaction with water, and may be treated beforehand to recover TDI or TDA (see Section 10.4.5).

According to the permit of a German TDI plant (2014), the TDI residue/tar (waste for incineration) may reach 36 kg/t of TDI produced and the small fraction of mid-boiling residues (waste for incineration) may reach 0.33 kg/t of TDI produced.

In MDI production, these oligomers present a valuable product although there may still be some residues from the product purification containing oligomers and solvent (see Table 10.12).

Contaminated solvents: These include o-DCB and MCB.

Others: The use of concentrated sulphuric acid may generate corrosion products based on iron sulphate. For aromatic amines, the urea by-products can be dehydrated by phosgene to form carbodiimides, which then react with excess phosgene to give N-chloroformyl chloroformamidines; cycloadducts of carbodiimides with isocyanates are also formed.

Waste for incineration from a MDI plant: For one MDI plant, the following waste streams have been reported to be routed to an incinerator which is shared with an EDC/VCM plant for the treatment of both liquid wastes and gaseous organic emissions (Table 10.12).

Table 10.12: MDI streams that are treated in a shared incinerator

Stream	Description/composition	Amount (t/yr)
Solvents and streams from halogenated organics washing	Liquid stream with MCB	35
Solvents and organic stream washing	Organic solvents	0.65
Reaction and purification by-products/residues	Isocyanate oligomers with MCB	85.7

(1) Gaseous vents are also sent here; those contain VOCs, CO and HCl.

(2) Composition: monochlorobenzene, dichlorobenzene, dichloromethane, MDI, TDI, phosgene, trichloromethane, solvents.

10.3.7 Emissions from other than normal operating conditions

Emissions from other than normal operating conditions (OTNOC) depend on the available treatment options. Often, the treatment in place can also cope with emissions from routine OTNOC production events, e.g. emissions from start-up and shutdown. Sometimes, back-up systems are used that are not always as efficient.

Example from a MDI permit:
During start-up and shutdown, the waste gas cannot be treated by the regenerative thermal oxidiser due to its high CO content and is treated by caustic scrubbing only, which leads to higher emissions of VOCs and chlorinated hydrocarbons. In comparison with the normal emissions, these emissions during other than normal operating conditions make up a large share of the total emissions, e.g. more than 80 % of the emissions of tetrachloromethane.

10.4 Techniques to consider in the determination of BAT

This section describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this chapter. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations). Cross references to other chapters are used, where relevant to avoid repetition.

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 2.6 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation. Specific techniques will contain a description in this chapter and generic techniques will either have a description in the generic chapter of this BREF (Section 2.4) or in other relevant BREFs, e.g. the CWW, REF or LCP BREFs.

10.4.1 Techniques to reduce emissions to air

10.4.1.1 DNT plants

Emissions from the nitration and acid recovery unit depend on the control of the reaction and the generic retention techniques in place and are controlled by the treatment of the off-gases from the reaction unit and the acid recovery unit. The following techniques are used before routing the waste gases to a combined treatment for final abatement (see Section 10.4.1.5).

10.4.1.1.1 Caustic scrubbing

For wet scrubbing, see Section 2.4.

Description
Caustic scrubbing is used to remove inorganic acid compounds. It may be used for NO_2 removal for low waste gas flows when recovery systems (scrubbing with oxidation) cannot be used. It may also be used for the removal of SO_X.

Reference literature
2003 LVOC BREF [190, COM 2003])

10.4.1.1.2 Wet gas scrubbing and partial oxidation

Description

Absorption with partial oxidation is used to oxidise nitrogen oxides and VOCs from the reaction and from the acid recovery unit and to recover nitric acid.

Technical description

Wet scrubbing with water is used in combination with the addition of an oxidant which can be a chemical or a chemical-air combination (low-pressure systems) or air (medium- or high-pressure systems). Low-pressure systems are used at low NO_X input concentrations, higher pressures at high NOx levels.

Oxidation of NO_X and dissolving it in water give nitric acid which can be reused.

Achieved environmental benefits

- Reduction of emissions of NO_X and VOCs.
- Reduction of consumption of HNO_3.

Environmental performance and operational data

VOC emissions can be reduced by 99.8 %.

Cross-media effects

- Consumption of water and oxidant.
- Potential for emissions of nitrate and nitrite to water.

Technical considerations relevant to applicability

The applicability of the technique may be restricted at very low flows for economic reasons.

Economics

No information provided.

Driving force for implementation

Economics, and protection of the environment.

Example plants

See, for example, the reference list in [107, Chemetics 2013].

Reference literature

[108, PLINKE 2012], [107, Chemetics 2013].

10.4.1.1.3 Condensation

See the CWW BREF on condensers.

Condensation is used to remove and recover VOCs (educt and product) and nitrous vapours.

To improve efficiency, condensers with cooling water are supplemented by condensers with chilled water or refrigerants. Since vent streams from the DNT process and the acid recovery will contain water, post-condensation with temperatures below the freezing point cannot be applied.

10.4.1.1.4 Thermal reduction

Technical description
NOx is reduced at elevated temperatures in the presence of a reducing gas in an additional combustion chamber, where an oxidation process takes place but under low oxygen conditions/deficit of oxygen. Unlike SNCR, no ammonia and/or urea are added.

The thermal reduction of nitrogen oxides with natural gas is known as the fuel staging process. In this process, natural gas is generally added to a flue-gas that has significant concentrations of NO_X. The nitrogen oxides obtained during combustion are converted to molecular nitrogen and intermediate components (HCN and NH_3) by adding a fuel (e.g. natural gas) under reducing conditions. Burnout then takes place by a further addition of combustion air.

Alternatively to hydrocarbons, hydrogen or hydrogen-containing gas streams may be used as reducing gas.

Technical considerations relevant to applicability
Applicability to existing units may be restricted by space availability.

Reference literature
[111, patent WO 2015189235 A1 2015].

10.4.1.1.5 Catalytic reduction (NSCR)

NO_X is reduced in the presence of a catalyst and a reducing gas. Unlike SCR, no ammonia and/or urea are added. See the CWW BREF and the LVIC-AAF BREF.

10.4.1.2 TDA plants

Depending on the waste gas composition, one or both of the following techniques are applied before routing the waste gases to a combined treatment for final abatement (see Section 10.4.1.5).

10.4.1.2.1 Wet scrubbing

See Section 2.4.

Description
Wet scrubbers are used to remove organic amines or ammonia.

10.4.1.2.2 Condensation

See the CWW BREF on condensers.

Condensation is used to remove and recover VOCs, e.g. from the reactor vent and vents from depressurisation and distillation.

To improve efficiency, condensers with cooling water are supplemented by condensers with chilled water or refrigerants. Since vent streams from the hydrogenation will contain water, post-condensation with temperatures below the freezing point cannot be applied.

10.4.1.3 MDA plants

Depending on the waste gas composition, one or both of the following techniques are applied before routing the waste gases to a combined treatment for final abatement (see Section 10.4.1.5).

10.4.1.3.1 Wet scrubbing

See Section 2.4.

Description
Wet scrubbers are used to remove organic amines, formaldehyde, methanol and/or ammonia. Removal of aniline may be improved by reaction with formaldehyde in the scrubbing solution. Removal of ammonia and amines may be enhanced, if needed, by adding acids. However, this has potential negative effects on the options for recovery/reuse.

10.4.1.3.2 Condensation

See the CWW BREF on condensers.

Condensation is used to remove and recover VOCs.

To improve efficiency, condensers with cooling water are supplemented by condensers with chilled water or refrigerants. Since vent streams from the condensation unit will contain water, post-condensation with temperatures below the freezing point cannot be applied.

10.4.1.4 TDI/MDI process: Phosgenation

The following techniques are applied before routing the waste gases to a combined treatment for final abatement (see Section 10.4.1.5).

10.4.1.4.1 Decomposition of phosgene

Description
Unrecovered phosgene is decomposed with alkaline scrubbing agents in packed towers or activated carbon towers where the activated carbon catalyses decomposition.

Reference literature
[31, SIX et al. 2012].

10.4.1.4.2 Recovery of HCl and phosgene

Description
Phosgene is recovered from the process by distillation or absorption (see Section 10.4.3) and HCl is recovered by absorption (wet scrubbing) and/or purification (see Section 10.4.3).

Technical description
Phosgene from process gas streams, e.g. from distillation units or the HCl gas from the reaction, is recovered by condensation or scrubbing with organic solvent and returned to the process.
HCl from process gas streams is recovered by wet scrubbing or, from vapours, by condensation.

Condensation (condensers and post-condensers) is carried out in such a way as to also retain VOCs (solvent vapours and traces of TDI). To improve efficiency, condensers with cooling water are supplemented by condensers with chilled water or refrigerants. A sufficient condensing duty will reduce VOC emissions in the vent gas.

Achieved environmental benefits

- Reduction of the load to further waste gas treatment (phosgene and HCl).
- Reduction of the consumption of phosgene.
- Reuse of HCl.

10.4.1.5 TDI/MDI process: Combined waste gas treatment

10.4.1.5.1 Multi-component waste gas treatment system

Description

The individual waste gas streams from DNT, TDA, TDI, MDA and MDI plants are combined and treated with a thermal oxidiser, followed by caustic scrubbing. If needed, the treatment may include further treatment steps, e.g. the use of SCR or SNCR to abate NO_X emissions or injection of activated carbon to remove PCDD/F.

Technical description

Following the application of specific process-integrated prevention, recovery and pretreatment steps (see Sections 6.4.1.1 to 6.4.1.3), the waste gas streams are combined and routed to an appropriate combined treatment to remove VOCs. This typically consists of a thermal oxidiser to destroy VOCs, a post-scrubber system to remove HCl and, if needed, a post-treatment (SCR, SNCR) to reduce NO_X emissions. Instead of the thermal oxidiser, an incinerator for the combined treatment of liquid waste and the waste gas may be used.

For thermal oxidisers, see Section 2.4.3.5.6. The temperature and residence time have to be sufficient to destroy the organic pollutants. High temperatures are needed to destroy some of the pollutants, especially tetrachloromethane from the phosgenation unit.

Scrubbing to reduce HCl is needed when the raw gas contains HCl or HCl precursors (chlorinated organic compounds) which mainly occurs in waste gas from the phosgenation step and downstream processing. Depending on the HCl content, a caustic scrubber is used or a two-stage system where HCl is recovered in the first stage (absorption in water or diluted acid), followed by a caustic scrubber to minimise emissions of HCl and chlorine (which can be present in the raw gas or formed from HCl). Due to the significant amount of CO_2 in the gas, the composition of the circulating liquid and the amount of caustic added is chosen to capture HCl, but prevent CO_2 absorption. See also Section 10.3.1.5.2.

To prevent or reduce emissions of thermal NO_X from the combustion, regenerative thermal oxidisers (RTOs) with electrical heating have proven to be efficient if the potential for NO_X formation from NO_X precursors (chemical NO_X) is low. However, if the raw gas contains relevant concentrations of NO_X or NO_X precursors (nitrogen-containing organic compounds, ammonia), a dedicated post-treatment is needed. Generic options are the use of SCR or, if it is equally efficient or if SCR cannot be used, SNCR. See also Section 2.4.

To prevent or reduce emissions of PCDD/F, where relevant, rapid quenching and activated carbon injection can be applied (see Section 2.4.3.5.6).

Combined waste gas treatment may be shared for the whole TDI or MDI process or shared to also treat waste gas from other units. Another option is to use more than one treatment unit to treat waste gas streams from different parts of the TDI/MDI process separately.

Achieved environmental benefits

Reduction of emissions of organic compounds (including chlorinated hydrocarbons), HCl, chlorine and NO_X to air.

Environmental performance and operational data

Thermal oxidisers

Except for one outlier, industry reported oxidisers to achieve average TVOC concentrations of 0.1–3.4 mg/Nm^3 (11 % O_2). Concentrations of TCM are generally claimed to be below the limit of detection.

RTOs

Regenerative thermal oxidisers are only used at one site. They are reported to treat waste gases from MDI phosgenation and work-up sections at temperatures between 800 °C and 1 000 °C to achieve removal efficiencies of 95–98 % for MCB and 95–97 % for TCM. The reported outlet concentrations of the caustic post-scrubber (from a quartals measurement in the first year after installation) of TCM are in the range of 2–9 mg/Nm^3, corresponding to a specific TCM load of 0.5 g/t of MDI produced (which would correspond, from the ratio of molecular weights, to 0.7 g/t of TDI produced for TDI plants).

RTOs use electric heating. They have been reported to achieve very low NO_X emissions (< 2–4 mg/Nm^3).

Further data from RTOs are listed in Table 10.13. The measurements refer to averages from three samples over half an hour each. Flows are in the range of 1 800–2 400 Nm^3/h and the oxygen content is in the range of 16–18 vol-%.

Table 10.13: Emissions from MDI production after combined treatment (RTO and caustic scrubber)

		RTO1			RTO2			Standard
		Q1	Q2	Q3	Q1	Q2	Q3	
TCM	mg/Nm^3	3.2	8.8	8.8	2.2	3.5	4	EN 13649
MCB	mg/Nm^3	3.5	3.9	3.9	3.4	4.4	6.1	EN 13649
HCl	mg/Nm^3	16.6	3	3	1.5	< 0.5	< 0.5	EN 1911
Chlorine	mg/Nm^3	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	EPA 26a
PCDD/F	ng TEQ /Nm^3	0.05	0.03	0.03	0.015	0.02	0.02	EN 1948
NO_X	mg/Nm^3	4	< 2	< 2	< 2	< 2	< 2	EN 14792
TVOC	mg/Nm^3	< 2	< 2	< 2	< 2.6	< 2	< 2.5	EN 13526

SCR

The nitrogen oxide emissions of a DNT plant can be reduced by 99.5 % and the VOC emissions reduced by 99.8 % (2003 LVOC BREF, [190, COM 2003]).

Industry reported that one oxidiser with SCR achieves an average concentration of 92 mg/Nm^3 (11 % O_2), with a maximum concentration (daily average from continuous measurement) of 150 mg/Nm^3.

SNCR

Industry reported that two oxidisers with SNCR achieve average concentrations of 202 mg/Nm^3 and 218 mg/Nm^3 (11 % O_2), with maximum concentrations (for 30-minute samples) of 280–320 mg/Nm^3.

Wet scrubbing

- HCl: From the air emission survey (Section 10.3.1.5.2), reported maximum HCl emissions were typically (all but two plants) below 10 mg/Nm^3 both for combined treatment and for scrubbers without a thermal oxidiser. Average emissions were in the range of < 0.11–3 mg/Nm^3, with three oxidisers reporting higher emissions. See also Table 10.13. HCl emissions will depend on the content of HCl and chlorinated hydrocarbons in the raw gas and are mainly expected from the phosgenation units.
- Chlorine: Chlorine is not expected to be in the raw waste gas from the MDI/TDI process but may be present if the combined treatment also treats waste gas from the upstream or integrated chlorine production. Chlorine may also be formed in small quantities from the oxidation of HCl. In the air emission survey (see Section 10.3.1.5.2), all average emissions of chlorine reported were < 1 mg/Nm^3 which is near the limit of quantification (typically about 0.5 mg/Nm^3). See also Table 10.13.

Cross-media effects
Ammonia emissions from SCR/SNCR.

Technical considerations relevant to applicability
Depending on the nature of the organic pollutants, it may not be efficient to route waste gas streams with a very low TVOC content to the combined treatment; in this case, other techniques (e.g. adsorption, scrubbing) may be more efficient.

SCR
Retrofitting to an existing unit may be constrained by space limitations and the requirements for an optimal reactant injection.

SNCR
Retrofitting to an existing unit may be constrained by the residence time needed for the reactant injection.

Economics
No information provided.

Driving force for implementation
Environmental legislation.

Example plants
The following techniques are used in the EU in different combinations (see Section 10.3.1.5.2):

- thermal oxidiser (most sites) or RTO or incinerator;
- one- or two-stage wet scrubbers (most sites);
- SCR or SNCR (a few sites).

TDI plants: Covestro (ex Bayer MaterialScience) in Brunsbuttel and Dormagen (both DE); Vencorex, Pont de Claix (FR); Wanhua, Kazinbaricka (HU).

MDI plants: Covestro (ex Bayer MaterialScience) in Krefeld and Brunsbuttel (both DE) and Tarragona (ES); Huntsman, Rotterdam (NL).

Reference literature
No reference literature provided.

10.4.1.5.2 Monitoring of emissions from combined waste gas treatment

Description
Monitoring of pollutants is used as a tool to optimise the performance of the abatement techniques.

Technical description
Pollutants are regularly measured. Monitoring results are related to upstream conditions (regarding sources and waste gas parameters) and the process parameters of the abatement devices in order to identify measures to prevent peak emissions and optimise waste gas management and abatement. A procedure or internal process ensures and defines which actions are taken (after monitoring results are obtained) in order to optimise abatement techniques.
Monitoring should be done for any parameter for which a BAT-AEL has been defined, and for other compounds that may be relevant in terms of emissions (e.g. chlorinated compounds) or for the control of the abatement processes.

Continuous monitoring is applied if helpful for process control (e.g. CO for thermal oxidation or NO_X for SCR/SNCR) or if the maximum emission levels are high (e.g. near or beyond the upper end of the BAT-AEL range).

Achieved environmental benefits
Lower emissions to air.

Environmental performance and operational data
No information provided.

Cross-media effects
Not relevant.

Technical considerations relevant to applicability
Generally applicable.

Economics
No information provided.

Driving force for implementation
No information provided.

Example plants
According to the survey of industry (see Section 10.3.1.5.2), continuous monitoring in the outlet of the combined treatment is used at some TDI or MDI plants for the following parameters: NH_3, NO_X, CO, TVOC, SO_2, HCl and Cl_2.

Reference literature
No reference literature provided.

10.4.1.6 Fugitive emissions to air

See the CWW BREF.

There have been strenuous efforts in recent years to minimise workplace exposure and environmental releases, especially from fugitive sources.

Primary technical measures are aimed at preventing phosgene emission from closed equipment and include the selection of construction materials, the process control system, redundancy for particularly important equipment and automatic safety systems.

Secondary technical measures are used to detect leaks as early as possible and to combat escaped phosgene. They include systems for preventing unwanted releases of phosgene (e.g. steam ammonia curtains in the case of gaseous emissions) and complete containment for phosgene-processing plant units.

10.4.1.7 Emissions to air from storage

For more detailed information, see the EFS BREF.

When the volume and the breathing vent flows are not significant, techniques such as activated carbon adsorption and scrubbing can be used. For large-volume storage (such as raw materials and TDI or MDI storage), the tank volume and the flow generated will be relevant. In these cases, the most efficient treatment is to route these streams to the combined treatment.

A German TDI installation is routing lower emission flows (< 300 Nm^3/h) to an activated carbon adsorber and the larger ones (such as DCB tanks) to the central shared incinerator. The permit from the competent authority requests the following performance downstream of the activated carbon adsorber: < 20 mg/Nm^3 for TDI and DCB, and < 50 mg/Nm^3 for TVOC.

Vapour recovery systems or incineration are usually used for vents of organic liquids. Nitric acid storage tank vent emissions should be recovered with wet scrubbers and recycled; organic liquid storage tank vent emissions should be recovered or incinerated.

10.4.2 Techniques to reduce emissions to water

10.4.2.1 DNT plants: Integrated techniques to reduce emissions to water

10.4.2.1.1 Use of highly concentrated nitric acid

Description
Use of highly concentrated nitric acid for the nitration reaction.

Technical description
The nitric acid feed to the nitration reaction is concentrated upstream from an azeotropic (65–68 wt-%) or lower concentration to about 99 wt-% using extractive rectification with sulphuric acid (which then has to be reconcentrated itself). See also the LVIC-AAF BREF.

Re-engineering of the process including the use of concentrated nitric acid may increase the process efficiency and lead to almost complete reduction of nitrite and a certain reduction of sulphate and nitrate emission. Organic emissions can be reduced by using nitric acid in the second reaction step (MNT to DNT) to oxidise the compounds formed by side reactions in the first reaction step to less toxic and/or more biodegradable compounds.

Instead of using common mixtures of concentrated sulphuric acid (98 wt-%) and azeotropic nitric acid (65–68 wt-%) as feed, concentrated nitric acid can also be used in combination with less concentrated sulphuric acid (about 90 wt-%). This avoids the last and most demanding concentration step for the spent sulphuric acid, thus compensating the cross-media energy demand (see below) (although with a certain reduction in the benefits in terms of waste water generation).

Achieved environmental benefits
Lower specific emissions of organic pollutants and nitrite/nitrate to water from the nitration reaction.

Environmental performance and operational data

Waste water arisings from the nitration unit derive from steam stripping the spent acid to remove nitroaromatics or nitric acid, any steam stripping of the waste water inside the nitration unit and from the reaction (0.2 m^3/t of DNT), from the nitric acid used (0.37 m^3/t of DNT using 65 % HNO_3, < 0.01 m^3/t of DNT using 99 % HNO_3) and from washing the product.

Accordingly, the use of concentrated HNO_3 can reduce waste water arisings by up to 0.37 m^3/t of DNT (and possibly improve the efficiency of pretreatment), provided waste water from the upstream concentration of HNO_3 is collected separately or condensates from upstream concentration are more efficiently reused than condensates from the acid recovery section.

Cross-media effects

- Use of energy for the reconcentration of sulphuric acid from the upstream concentration of nitric acid is compensated to a large extent by the respective reduced energy consumption for the recovery of the spent sulphuric acid.
- Emissions of HNO_3 vapours which can be controlled by wet scrubbing.
- Waste water from wet scrubbing and nitrate loads to the final treatment if the scrubber liquor is not returned to the process.

Technical considerations relevant to applicability

Appropriate measures have to be taken (e.g. use of resistant, high-grade materials for equipment) to limit risks with regard to the hazardous properties of concentrated nitric acid as a strong oxidant (CLP classification H272, H314).

As with the concentration of spent sulphuric acid, there are several plant manufacturers that offer units that produce highly concentrated nitric acid from fresh or spent acids, including features such as the destruction of organic impurities and the recovery of nitric acid from nitrous gases.

This technique is applicable to new DNT plants or major retrofits.

Economics

No information provided.

Driving force for implementation

No information provided.

Example plants

No information provided.

Reference literature

No reference literature provided.

10.4.2.1.2 Reuse of water from the first washing step in the process

Description

Return of water from the first acidic washing step to the process.

Technical description

The raw DNT product is washed with water to remove the remaining acid and organic by-products.

Nitric and sulphuric acid are extracted from the organic phase. The acidified water is returned to the process (the nitration unit or the acid recovery unit), for direct reuse or further processing to recover materials (e.g. recovery of 24–40 % HNO_3).

Achieved environmental benefits
Reduction of emissions to water (nitrate/nitrite, sulphate, TOC).

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Several plant manufacturers offer technical options to recover the acids and organic content of the spent wash water and enable reuse of the water.

This technique is applicable to new plants or major retrofits.

Economics

- Processing to recover nitric acid may increase the energy consumption/costs of the plant.
- Reduction of the waste water volume and load may decrease costs for treatment.

Driving force for implementation
Environmental legislation.

Example plants
No information provided.

Reference literature
[50, Meissner 2014], [107, Chemetics 2013], [134, patent DE 102004005913 A1 2004].

10.4.2.1.3 Reuse of process water to wash DNT

Description
Reuse of process water to wash the product.

Technical description
Reuse of process water from the spent acid recovery unit and the nitration unit to wash DNT. Further potentially suitable process water streams include condensates from the downstream hydrogenation of DNT.

Achieved environmental benefits
Reduced generation of waste water.

Technical considerations relevant to applicability
The technique is applicable to new plants or major retrofits. Applicability to existing units may be restricted by design and/or operational constraints.

10.4.2.1.4 Optimised regeneration and recovery of spent acid

Description
Optimised regeneration and recovery of spent acid.

Technical description
The regeneration of the spent acid from the nitration reaction is carried out in such a way that water and the organic content are also recovered for reuse, by using an appropriate combination of evaporation/distillation, stripping and condensation.

Furthermore, inorganic nitrogen (nitrite, nitrate) in aqueous streams (from the purification of the spent acid and the respective off-gas treatment) is recovered and reused as nitric acid.

Water, i.e. condensates from the concentration of sulphuric acid and nitric acid, is reused, e.g. for washing the organic raw product (see Section 10.4.2.1.3).

Achieved environmental benefits

- Reduced loads of organic compounds and nitrite/nitrate to the waste water system and consequently reduced emissions to water.
- Reduced consumption of water per tonne of product.

Technical considerations relevant to applicability
The technique is offered by several plant manufacturers. The adaption of older plants is considered a major retrofit. Applicability to existing units may be restricted by design and/or operational constraints.

Reference literature
[50, Meissner 2014], [107, Chemetics 2013], [134, patent DE 102004005913 A1 2004].

10.4.2.1.5 Multiple use and recirculation of water

Description
Reuse of water from washing, rinsing and equipment cleaning, e.g. in the countercurrent multistep washing of the organic phase.

Technical description
Besides water from production processes (see Section 10.4.2.1.3), other water streams, e.g. from washing, rinsing and equipment cleaning, can be used for the product washing steps as long as they are compatible with product quality requirements.

For washing with soda or caustic, washing water may be recirculated with a purge to limit the content of organic pollutants and salts according to the technical requirements.

10.4.2.2 DNT plants: Pretreatment of waste water

Many of the nitro-organic components in the waste water from DNT production are toxic and poorly biodegradable. Figures for biodegradation of the whole effluent depend on the ratio of poorly biodegradable compounds to readily biodegradable compounds such as unreacted toluene.

Techniques to reduce the toxicity and improve the biodegradability of the effluent are:

- oxidation with ozone or H_2O_2: advanced oxidation processes with hydrogen peroxide (see Section 10.4.2.2.1) and oxidation with ozone (see Section 10.4.2.2.2) are used to convert toxic to less toxic and poorly biodegradable to biodegradable compounds;
- extraction (see Section 10.4.2.2.3).

For any of the techniques, pretreatment will be followed by a final biological treatment, for further abatement of COD/TOC and nitrate.

Achieved environmental benefits
Removal of nitroaromatic compounds (e.g. DNT, di/trinitrocresols) to reduce the organic load (< 1 kg TOC per tonne of DNT after pretreatment), to ensure biodegradability (> 80 % elimination by the Zahn-Wellens test) and consequently reduce emissions to water.

10.4.2.2.1 Chemical oxidation

Description
Organic compounds are oxidised with ozone or hydrogen peroxide, optionally supported by catalysts or UV radiation, to convert them into less harmful and more easily biodegradable compounds.

Technical description
In advanced chemical oxidation processes (AOP), OH• (hydroxy) radicals are formed from ozone or hydrogen peroxide by catalysts or UV radiation. These radicals oxidise the organic compounds in the effluent.

For the treatment with hydrogen peroxide, metal salts can be used as catalysts, e.g. the Fenton process using iron salts. The oxidation is performed efficiently at moderate pressures and temperatures (between 1 barg and 1.5 barg and between 110 °C and 130 °C). The treatment includes the following steps: homogenisation and pH adjustment, addition of H_2O_2 and catalyst, reaction, neutralisation and precipitation of metallic compounds, and filtration.

For the oxidation with ozone, see Section 10.4.2.2.2.

The waste water pretreatment is used to reduce the toxicity and/or to increase the biodegradability of the pollutants by partial oxidation.

Achieved environmental benefits
Lower emissions of organic pollutants to water.

Environmental performance and operational data
At the example plant, the process was used to reduce the organic load and to remove toxic and recalcitrant nitroaromatics. The biodegradability (in terms of the BOD to COD ratio) was increased by 600 % (see Table 10.14) to 1:4.

Table 10.14: Waste water from DNT production - performance of chemical oxidation

Parameter	Without oxidation (ppm)	With oxidation (ppm)
TOC	1 560	378
COD	3 840	710
BOD	157	179
BOD/COD	0.04	0.25
4-nitrobenzoic acid	110	< LOD
2,4-dinitro-6-amino-o-cresol	490	< LOD
2,6-dinitro o-cresol	140	< LOD
2,4,6-trinitrohydroximethyl-benzene	215	< LOD
2,4-dinitrotoluene	25	< LOD
NB: LOD limit of detection		

As the process aims at the conversion of organic compounds (to biodegradable ones) rather than the achievement of complete oxidation, the dosage of oxidant can be kept low (substoichiometric).

Cross-media effects
Sludge (iron(III) hydroxide) for disposal.

Technical considerations relevant to applicability
This process is applicable to waste water streams that are recalcitrant and have low biodegradability.

Economics
In the example, the operational costs are reported to be below EUR 3/m^3.

Driving force for implementation
Environmental protection and legislation.

Example plants
These data were obtained through several tests at a pilot waste water treatment plant treating the waste water of a DNT plant in Germany.

Reference literature
FMC Foret technical bulletins [36, FMC-foret 2009], [37, FMC-foret 2009].

10.4.2.2.2 Combined pretreatment including chemical oxidation with ozone

Information from the 2003 LVOC BREF [190, COM 2003] is provided below:

In a German plant, waste water from the nitration unit is pretreated together with a stream from the polyol plant (2.5 m^3/h) in a three-stage plant (see below), mainly to eliminate the highly persistent and toxic part of the COD. The overall COD elimination efficiency is 98 % and the elimination efficiency of the nitroaromatic compounds is > 99 %. The three stages of the pretreatment are as follows:

- Stage 1: In the adsorption/sedimentation unit, organic substances are adsorbed by sludge from a biological treatment plant, and the sludge is separated by sedimentation and incinerated. The COD elimination is 22 %.
- Stage 2: Biological pretreatment includes denitrification of nitrite/nitrate and adsorption of nitroaromatic compounds, and further reduces COD by 59 % (COD elimination 80 %). The sludge is incinerated.
- Stage 3: In the ozonation step, the non-degradable COD (i.e. nitroaromatic substances) is converted to degradable COD to make it amenable to further treatment in the central biological plant. This further reduces COD by only 4 % (COD elimination of 21 % in the ozonation step using only 1.5 kg ozone/kg reduction of COD) but the biodegradability of the remaining organic load is improved and is measured to be 88 % (Zahn-Wellens test).

For the description of the generic techniques mentioned, see the CWW BREF.

10.4.2.2.3 Extraction

Instead of oxidation, recovery techniques can be used to remove toxic and/or poorly biodegradable compounds and so reduce the organic load of the effluents from the nitration process. The recovered organic material is returned to the process or sent to disposal (incineration). Of the techniques listed in Section 10.4.2.3, extraction (e.g. with toluene) is commonly used, resulting in an almost complete removal of DNT and a reduction of nitrocresols emissions to < 0.5 kg/t of DNT in the outlet of the pretreatment.

When using extraction, dissolved pollutants are transferred from the waste water phase to an organic solvent, e.g. in countercurrent columns or mixer-settler systems. After phase separation, most of the solvent is separated and purified, e.g. by distillation, and returned to the extraction. The remaining distillation residue with the pollutants is disposed of or returned to the process.

Losses of solvent to the waste water are controlled downstream by appropriate further treatment (e.g. stripping).

10.4.2.3 Generic pretreatment techniques

This section presents pretreatment techniques that are used, usually separately, for several production steps (production of DNT, TDA and MDA). Specific combinations for the MDA process are further discussed in Section 10.4.2.4.

For MDI and TDI phosgenation units, no waste water pretreatment is usually needed, although the listed unit processes are widely used within the process for recovery and purification of material. As described in Section 10.3.2.4, waste water may arise from operations downstream of the reaction section. The amount of waste water will mainly depend on the techniques implemented for reuse and may be very low. The organic load will mainly consist of solvent.

10.4.2.3.1 Stripping

See Section 17.16.2 of the CWW BREF for a description of the technique.

Stripping is used to remove amines, solvent and/or ammonia at TDA and MDA units. It is also used to remove the remaining extractant after waste water extraction (DNT, TDA and MDA units). And it is used to remove solvents from process and waste water streams at phosgenation units (TDI/MDI).

Ammonia can be separated by stripping. Low-boiling components can be separated by distillation and/or stripping with steam and destroyed by incineration. Achievable elimination rates are: amino toluene > 99 %, TDA > 90 % and COD > 70 %.

In a German plant, the pretreatment and reuse of waste water (by removal of ammonia and low-boiling organic compounds) reduced the waste water from hydrogenation by 50 % (remaining waste water volume of 0.7 m^3/t of TDA). Besides TDA, the waste water contained ammonia, aminotoluene and hexahydrotoluidene.

10.4.2.3.2 Evaporation

See the CWW BREF for a description of the technique.

Key steps normally involve concentrating the contaminant in the water stream using evaporation (either single or multiple stages). The concentrated contaminated stream is handled in different ways depending on the design of the plant, e.g. incineration of the stream or routing to other parts of the process in order to maximise the recovery of saleable products before incineration.

This technique is used at TDA and MDA units.

10.4.2.3.3 Distillation

See the CWW BREF for a description of the technique.

Distillation is used to remove low-boiling compounds at TDA and MDA units.

Example and performance from the 2003 LVOC BREF: See under Stripping above.

10.4.2.3.4 Extraction

See the CWW BREF for a description of the technique.

Extraction is used to remove/recover organic compounds from process and waste water by means of a solvent, typically followed, after phase separation, by stripping of the waste water to remove the remaining solvent.

The technique is used at DNT, TDA and MDA plants.

At DNT plants, extraction with toluene is commonly used, resulting in an almost complete removal of DNT and a reduction of nitrocresols emissions to < 0.5 kg/t of DNT in the outlet of the pretreatment.

10.4.2.4 MDA plants

The aqueous stream from the condensation unit of MDI process undergoes several steps to remove/recover MDA, aniline and methanol prior to it being sent to final waste water treatment. Technical options include extraction (which may be combined with evaporation), steam stripping and distillation.

Achieved environmental benefits

- Recovery of organic material for reuse.
- Reduction of cross-media effects (energy consumption, sludge generation) at the final treatment.
- Lower emissions of pollutants to water.

10.4.2.4.1 Recovery of MDA

Technical description

MDA is removed first by extraction with aniline or another appropriate solvent and subsequently the solvent is removed by steam stripping. The current direct-contact extraction process requires the brine to be denser than the solvent. If the brine is not dense enough, water needs to be evaporated to increase the density and enable the phase separation after extraction.

Alternatively, pertraction with aniline has been investigated as a technique to remove/recover MDA. Pertraction does not require a density difference and therefore the energy-consuming evaporation of water can be omitted. However, the technique is not known to be used.

See the CWW BREF for a description of the techniques.

Reference literature (for pertraction)

[131, Medevoort1 et al. 2012].

10.4.2.4.2 Recovery of aniline

Aniline is recovered for reuse in the process using steam stripping, distillation or extraction with a solvent, e.g. toluene.

See the CWW BREF for a description of the technique.

10.4.2.4.3 Recovery of methanol

Methanol is removed from the aqueous phase by stripping or distillation and reused, e.g. by returning it to the provider of formaldehyde, or, if this is not possible, used as a fuel.

See the CWW BREF for a description of the techniques.

The environmental benefits of methanol removal may be low if there is a demand for easily biodegradable compounds to run the final waste water treatment, especially if a high methanol content in the waste water is needed to carry out the anaerobic denitrification process.

10.4.2.5 Techniques to reduce the organic load from phosgenation units

As described in Section 10.3.2.4, waste water may arise from operations downstream of the reaction section. The amount of waste water will mainly depend on the techniques implemented for reuse of water and recovery of organic material and can be very low. The organic load will mainly consist of solvent.

For MDI and TDI phosgenation units, solvent emissions can be controlled, e.g. by steam stripping, but often no waste water pretreatment is needed.

10.4.3 Techniques to reduce raw material consumption

10.4.3.1 Process optimisation

- Optimisation of the use and recovery of HCl (see Section 10.4.1.4.2).
- Optimisation of the use and recovery of solvents.
- Optimisation of the use and recovery of phosgene.
- Optimisation of the use and recovery of solid catalyst (for hydrogenation).

10.4.3.2 Use of gas phase phosgenation

Description
Both TDA and phosgene are heated above 300 °C before mixing. The reaction takes place in the gas phase.

Technical description
The vaporised reactants are brought together and mixed in the reactor. A nozzle designed specifically for the purpose ensures proper mixing. Then, solvent is added. After reaction, the solvent, excess phosgene and HCl are separated as a vapour phase. After condensation, the TDI slurry is distilled to remove the remaining phosgene and solvent.

The speed of the reaction is dramatically increased: while the residence time for the conventional process is 50 minutes, for the gas phase phosgenation (GPP) process it is a mere 20 seconds. The benefits include greater selectivity and a higher yield (about 99 %).

The process results in significant savings on solvents in comparison to liquid phosgenation, leading to operating cost savings due to a reduction in the energy consumption required to process the much smaller volume of solvent during distillate recovery. The much shorter residence time of TDA and phosgene in the reactor reduces the required phosgene process inventory considerably. Further benefits are a significantly greater reactor throughput per unit time (space-time yield) and the ability to downsize key plant components. These size reductions lead to additional investment cost savings. The gas phase technology also provides improved reaction selectivity, generating fewer by-products.

Process safety is improved by the reduction in both phosgene and solvent inventories within the process. A further safety enhancement is the ability to start up and shut down the gas phase process quickly. Because the reaction does not take place under pressure, the risk of phosgene leakages is significantly reduced.

Achieved environmental benefits
According to the operator, the GPP process features several advantages over the conventional approach:

- solvent consumption is reduced by 80 %;
- energy consumption is reduced by 40–60 %;
- wastes from side reactions are reduced.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Gas phase phosgenation has been used only in new plants (which may have replaced existing plants) and will not be feasible for a modification/major retrofit of existing liquid-phase reactors.

Although patents have been published by more companies, according to industry the applicability is restricted due to proprietary knowledge of the operator of the existing plants.

Economics
According to the operator, the initial investment required is lowered by 20 % in comparison to liquid phase phosgenation.

Savings in operation result from the lower consumption of energy and solvent and lower formation of by-products.

Driving force for implementation
Economics.

Example plants
One world-scale plant in China is in operation and one recently started in Germany (Dormagen), both of which are developed and run by the same company.

Reference literature
Dormagen TDI plant in Germany, press release [33, Bayer 2012], [106, Sonnenschein 2014].

10.4.3.3 Recovery and reuse of solvents

Description
Organic solvents are separated from the raw product, purified and reused, typically in the same process.

Technical description
In the phosgenation process, after the separation of phosgene and HCl, the solvent (e.g. DCB or MCB) is separated from the raw product, usually by distillation. If necessary, stripping may be used to remove traces of phosgene and/or HCl. Furthermore, the solvent may need drying. The solvent is then returned to the phosgenation feed. See also the description in Section 10.4.3.5.

At TDA plants, in the event that hydrogenation is carried out with solvents, the solvent is recovered from the organic phase after reaction, typically by distillation, purified if necessary (e.g. by distillation or stripping) and returned to the process.

Driving force for implementation
Economic reasons and environmental legislation.

Example plants
All TDI/MDI plants in Europe recover solvent for reuse.

10.4.3.4 Recovery and reuse of phosgene

Description
Unreacted phosgene from phosgenation is separated from the phosgenation raw product and reused in the phosgenation process.

Technical description
For phosgenation, phosgene is used in excess. Unreacted phosgene is recovered for reuse.

Crude TDI/MDI is sent to a rectification column for the removal of residual phosgene. The recovered phosgene is recycled to the phosgenation reactor.

Furthermore, phosgene can be recovered from process gas streams (see Section 10.4.1.4.2).

Reference documents
[30, US EPA 1994], [32, WorldBank-icf 2007], MDI plant in Portugal, [38, PT 2012].

10.4.3.5 Recovery of HCl from phosgenation for reuse

Description
The by-product HCl from the phosgenation reaction is absorbed in water and/or, if needed, purified in order to be reused.

Technical description
The techniques involves the absorption of HCl in water by scrubbing the process off-gas in a countercurrent absorber to produce hydrochloric acid, which, depending on the purity, may be marketed, reused or further processed.

Achieved environmental benefits
- Reduction of consumption of chlorine.
- Reduction of HCl emissions (to air or water).
- Reduction of waste from HCl.

Environmental performance and operational data
The typical HCl concentration of the hydrochloric acid is about 30 wt-%.

If the specifications for reuse or marketing are not met, the recovered hydrochloric acid is purified (typically by distillation or stripping).

Options for reuse of the hydrochloric acid include the following:

- Oxidation to chlorine by electrolysis. The chlorine may then be used again to produce phosgene.
- Oxidation to chlorine by the Deacon process.
- Use as feed for the oxychlorination process to produce 1,2-dichloroethane (EDC) (see Chapter 11).
- Hydrochloric acid is used as such in many other processes.

For electrolysis for example, the content of aromatic solvent needs to be minimised for several reasons including to prevent the formation of toxic hexachlorobenzene.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Generally applicable.

Economics
No information provided.

Driving force for implementation
Economic reasons and environmental legislation.

Example plants
Most TDI and MDI plants.

Reference literature
[31, SIX et al. 2012].

10.4.4 Techniques to reduce energy consumption

10.4.4.1 Gas phase phosgenation

See Section 10.4.3.2.

10.4.4.2 MDI plants

Methanol is normally fed as an impurity with the feedstock (formalin).

Methanol can be recovered downstream of the neutralisation section (from the aqueous stream or the organic stream purification operations). This methanol can be used as an alternative fuel for the steam boiler or hot oil furnace or in a thermal oxidiser.

10.4.5 Techniques to reduce waste generation

In addition to the techniques discussed in this section, all of the recovery techniques in Section 10.4.3 will also prevent or reduce the generation of waste.

10.4.5.1 Organic residues

The distillation residue from the TDI purification may still contain significant amounts of TDI.

The tar can be processed to recover TDA or TDI before being incinerated.

10.4.5.1.1 Recovery of TDA from oligomer residues

Description
Tars from distillation are additionally processed to recover the maximum amount of feedstock contained in them.

Technical description
The tar is hydrolysed to recover part of the amines.The tar is reacted with water in a continuous or semi-continuous process at temperatures preferably in the range of 120–250 °C, pressures in the range of 1–50 bar and an optimum mass ratio of water to tar of 1:1–3:1. The reaction of water with TDI and oligomers leads to the formation of TDA and carbon dioxide. Backmixing with the product solution is crucial to prevent solidification. The reaction can be enhanced by the addition of caustic or metal salt catalysts. The further processing may be facilitated by the addition of solvent. Water and possibly solvent are separated by distillation for reuse. TDA is recovered by distillation and may be routed to the upstream TDA plant for further purification.

Achieved environmental benefits
Higher yields, reduced material usage and lower waste generation.

Environmental performance and operational data
The recovery of TDA depends on the content of TDI and TDI oligomers in the tar.

Cross-media effects
Consumption of energy by several distillation steps.

Technical considerations relevant to applicability
According to industry, the TDA yield from tar may be low and therefore not justify the required consumption of energy.

Economics
Net benefits depend on the potential benefits derived from the material recovery rate (which depends on the composition of the tar) and the costs for energy, and may be very low. According to industry, TDA recovery from tars is not used commercially.

Driving force for implementation
No information provided.

Example plants
No information provided.

Reference literature
[111, patent WO 2015189235 A1 2015].

10.4.5.1.2 Recovery of TDI from oligomer residues

Description
Increased recovery of TDI by evaporation, further distillation and drying.

Technical description
Liquid residues from distillation are additionally processed to recover the maximum amount of TDI contained therein, e.g. using a thin film evaporator or other short-path distillation units, followed by a vacuum dryer. At the end of the process, a polymeric solid residue granulate is formed.

Achieved environmental benefits
Higher yields, reduced material usage and lower waste generation.

Cross-media effects
Higher energy usage.

Economics
Net benefits depend on the potential benefits derived from the material recovery (which depends on the composition of the residue) and the costs for energy, and may be very low.

10.5 Emerging techniques

In recent years, some research has been done into producing the major aromatic diisocyanates TDI and MDI/PMDI by non-phosgene processes, to avoid the safety issues related to the highly reactive, poisonous, and corrosive nature of phosgene gas, the environmental and safety issues concerning phosgene production and the formation of large volumes of HCl. Alternative phosgene-free production routes have been successfully introduced for the manufacture of non-aromatic isocyanates and polycarbonates (with a market share of 20 % for polycarbonates in 2007) [35, Centi et al. 2009].

Several novel processes have been developed that do not use phosgene and that are often not based on amines as starting materials. However, none of the processes developed so far have been commercialised due to technical and economic reasons. In many cases, the efficiency and stability, as well as the operating life of the homogeneous or heterogeneous catalysts, are a significant issue.

As a substitute for phosgene, dimethyl carbonate (DMC) is considered a prototype example of a green reagent, as it is non-toxic, can be made by a comparatively clean process (e.g. catalytic oxidative carbonylation of methanol with oxygen), is biodegradable and it reacts in the presence of a catalytic amount of base, thereby avoiding the formation of undesirable inorganic salts as by-products [35, Centi et al. 2009].

10.5.1 Phosgene-free process for MDI

For the phosgene-free manufacture of MDI, the most viable route has been considered to be a three-step process:

- synthesis of methyl phenyl carbamate (MPC) from aniline and DMC;
- condensation of MPC with formaldehyde to dimethyl methylene diphenyl carbamate (MDC);
- thermal decomposition of MDC to MDI (with methanol as a co-product).

The process has been assessed to still involve some technological uncertainties and, in its current state, it is not (yet) economically feasible [34, Vetter 2010].

10.5.2 Phosgene-free process for TDI

Description

TDI can be produced directly from dinitrotoluene by liquid phase carbonylation with o-dichlorobenzene, avoiding the use of phosgene and the recovery problems associated with hydrogen chloride. One-step processes based on the reaction between dinitrotoluene and carbon monoxide have been developed but not commercialised [135, ICIS 2008].

In 2012, Enichem announced that a pilot plant was planned for the phosgene-free two-step manufacture of TDI from TDA using dimethyl carbonate (DMC) to catalytically produce the urethane at 160–170 °C (100 % conversion of TDA, 95 % selectivity for urethane), followed by cracking of the urethane in the gas phase at 400–450 °C [31, SIX et al. 2012].

ICI disclosed a process in which organic isocyanates (e.g. TDI) were prepared via the corresponding carbamates with a high yield and selectivity by treating an amine (e.g. TDA) with DMC in the presence of a catalyst [31, SIX et al. 2012].

A patent (US 6,992,214 B2, Jan. 31, 2006) assigned to Dow Global Technologies discloses an integrated process for producing TDI from TDA and DMC. The process chemistry is not new, involving the intermediate production of the toluene diurethane (TDU) via reaction of TDA with DMC in the presence of a zinc catalyst followed by thermal decomposition of the TDU to TDI and methanol. The process has been estimated to be potentially economically viable [29, Gelbein 2006].

Level of environmental protection
This technique avoids the use of phosgene and the emissions associated with hydrogen chloride handling and recovery. It reduces emissions of chlorinated compounds to air and water, and it reduces the potential for PCDD/F emissions to air.

Cost savings compared to existing BAT
Not known.

Chance of becoming BAT in the future
Not known.

When it might become commercially available
Not known.

References
[31, SIX et al. 2012], [135, ICIS 2008], [29, Gelbein 2006].

11 ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER

11.1 General information

Ethylene dichloride (EDC) is mainly used for the production of vinyl chloride monomer (VCM), which in turn is used almost exclusively for the manufacture of polyvinyl chloride (PVC) and associated co-polymers. EDC and VCM are therefore considered together in this chapter. In the EU, stand-alone EDC production accounts for around just 5 % of the EDC plants. A small amount of EDC is used for ethylenediamine production.

The EDC/VCM production process is often integrated with chlorine production because of the issues associated with the transportation of chlorine, and because the EDC/VCM/PVC production chain represents the largest overall use of chlorine. EDC is synthesised either by the direct chlorination of ethylene or by chlorination using HCl and oxygen (oxychlorination). VCM is then produced through the thermal cracking of dry, pure EDC.

In 2013, the production capacity of ethylene dichloride in Europe was 10.8 million tonnes, representing 13 % of global capacity. For vinyl chloride monomer, the production capacity in Europe was 7.7 million tonnes, representing 13 % of global capacity. There are 23 vinyl chloride monomer (VCM) manufacturing plants in Europe. European production of EDC and VCM is summarised in Table 11.1 below.

Table 11.1: European producers of ethylene dichloride and vinyl chloride monomer

Country	City	Operator	Capacity (1) (kt/year)
Belgium	Tessenderlo	Ineos ChlorVinyls	550
Belgium	Zandvliet	Solvin (no VCM)	390 (2)
Belgium	Jemeppe-sur-Sambre	SolVin	500
Czech Rep.	Neratovice	Spolana	143
France	Jarrie	KEM ONE	0 (3)
France	Lavera	KEM ONE	525
France	Fos sur mer	KEM ONE	375
France	Tavaux	SolVin	300
Germany	Stade	Dow (no VCM)	260 (2)
Germany	Schkopau	Dow	330
Germany	Wilhelmshaven	Ineos ChlorVinyls	400
Germany	Rheinberg	SolVin	320
Germany	Marl	VESTOLIT	400
Germany	Gendorf	Vinnolit	300
Germany	Knapsack (Hurth)	Vinnolit	365
Greece	Thessalonica	Eko	0 (3)
Hungary	Kazincbarcika	Borsodchem	350
The Netherlands	Botlek	Shin-Etsu	620
Norway	Rafnes	Ineos ChlorVinyls	520
Poland	Wloclawek	Anwil	300
Romania	Ramnicu Valcea	Oltchim	170
Slovakia	Novaky	Novacke	90 (4)
Spain	Vila-Seca	Ercros	200
Spain	Martorell	SolVin	300
Sweden	Stenungsund	Ineos ChlorVinyls	150
United Kingdom	Runcorn	Ineos Vinyls (no VCM)	435 (2)

(1) Unless otherwise mentioned, capacity relates to VCM.
(2) Capacity of EDC production.
(3) Closed.
(4) Partly by acetylene process.

The majority of the European producers of EDC/VCM are members of the European Council of Vinyl Manufacturers (ECVM). The main licensors for these processes are: OxyVinyls, Ineos, ICI, Solvay, KEM ONE, PPG, Mitsui and Tosoh. Ineos is the leading provider (formerly EVC and ICI) with over 125 licensed facilities in the world producing over 21 million tonnes, with a further 3 million tonnes of capacity at the design stage or under construction. Thyssen-Krupp (Uhde)/Vinnolit also offers an EDC/VCM/PVC process [16, Uhde.ThyssenKrupp 2011], Aker Solutions (now part of Jacobs) offers Oxyvinyls EDC/VCM technologies and Arkema (now KEM ONE) PVC.

EDC/VCM plants generally have large capacities and are highly automated. The total costs of EDC/VCM production vary with both ethylene and chlorine costs and so are partially decoupled from the petrochemical business cycle. However, EDC, VCM and PVC are commodity products in a very competitive market. From a global perspective, production capacities have increased in recent years, mainly in the Middle East and China [101, Khoo 2013].

Key environmental issues

The principal environmental emissions from the EDC and VCM processes are to air. They are generated in the direct chlorination and oxychlorination reactions, purification stages and EDC cracker furnaces. These waste gases are of concern as they include halogenated compounds (including dioxins (PCDD/F)), HCl and, in some cases, Cl_2. There are also emissions to air from storage and fugitive releases of VOCs and halogenated compounds. There is normally a shared end-of-pipe vent treatment unit to abate emissions.

The aqueous effluents generated in different process units are normally pretreated at the EDC/VCM plant, prior to discharge to a shared biological treatment. This stream normally contains chlorinated hydrocarbons such as EDC, VCM and, for many EDC plants, suspended solids with copper compounds and PCDD/F. Coke, catalyst and sludge are generated as solid waste. Other liquid streams generated by the process are seldom of commercial value and so are normally incinerated.

11.2 Applied processes and techniques

11.2.1 Process options

The principal options for the production of EDC are:

- direct chlorination of ethylene in the liquid phase;
- oxychlorination of ethylene in the gas phase.

In practice, both of these options are commonly applied in tandem as part of an integrated balanced process, and are described in detail in the subsequent sections of this chapter. The main choices within these processes are whether to carry out:

- direct chlorination as a low- or high-temperature process;
- oxychlorination with air or oxygen and using a fluidised-bed or a fixed-bed reactor.

The principal options for the production of VCM are:

- thermal cracking of EDC;
- catalytic cracking of EDC.

I.

Of these, the most commonly applied process is thermal cracking and this is the only process described in detail in this chapter. Catalytic cracking of EDC is currently not used in Europe. A brief description and assessment can be found in Section 11.4.1.2.3.

A process that was used previously in Europe is the hydrochlorination of acetylene. This is an energy-intensive process with possible mercury emissions from its use as a catalyst. It is still used in Chinese plants because of the availability of cheap coal.

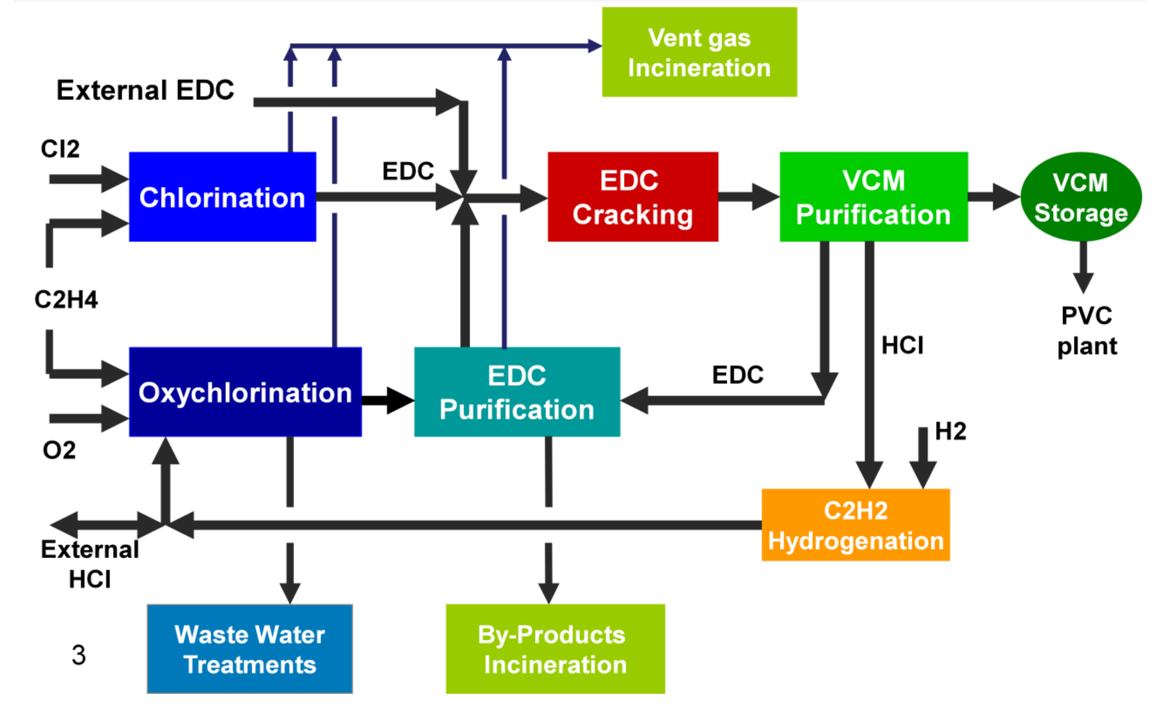
There are other processing routes that have the potential to offer certain benefits compared to the above, but none of these are currently operated on a large scale because of their drawbacks: e.g. direct chlorination of ethane, chlorohydrin/oxirane by-products; laser-induced EDC cracking; hydrochlorination of ethylene; hydrochlorination of cracked gases; or single-step production of VCM from ethylene. The most promising development, the direct oxidation of HCl to recover chlorine in order to balance the EDC/VCM process without using oxychlorination, is described in Section 11.5 on emerging techniques.

11.2.2 Key process steps

In the ethylene-based process, EDC is synthesised by the chlorination of ethylene (known as direct chlorination (DC)) and by the chlorination of ethylene with HCl and O_2 (known as oxychlorination (OC)). After purification of the EDC, thermal cracking of the dry, pure EDC produces VCM and HCl. The HCl resulting from the cracker process is recycled to the oxychlorination plant. When all the HCl generated in the EDC cracking process is reused in this way, and no EDC or HCl is imported or exported, then the EDC/VCM plant is called a 'balanced unit'. Approximately 90 % of the plants in the world operate in this manner. The reactions are represented by the chemical formulae below:

chlorination:	$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$ (EDC)	(-180 kJ/mol);
cracking:	$C_2H_4Cl_2 \rightarrow CH_2CHCl$ (VCM) + HCl	(+71 kJ/mol);
oxychlorination:	$C_2H_4 + 1/2O_2 + 2HCl \rightarrow C_2H_4Cl_2$ (EDC) + H_2O	(-239 kJ/mol).

The EDC/VCM manufacturing plant involves several steps. Figure 11.1 is a block flow diagram of one of several possible layouts (the balanced process) showing the main steps and emissions (waste gas and waste water).



Source: [194, ECVM 2014]

Figure 11.1: Block flow diagram of a VCM manufacturing process

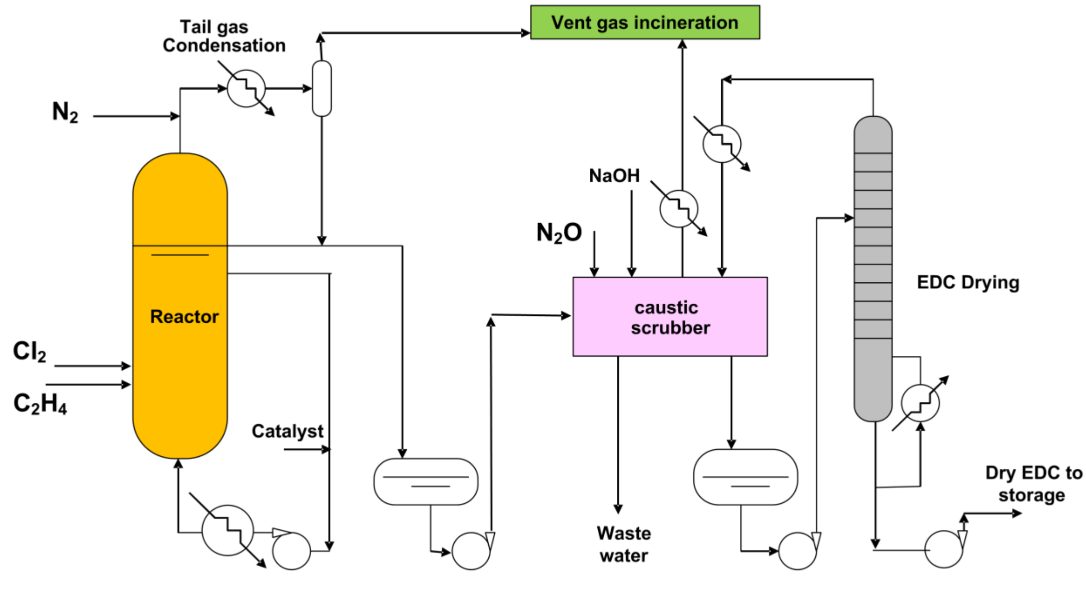
11.2.2.1 Direct chlorination

In direct chlorination, EDC is synthesised by the exothermic reaction of ethylene and chlorine, generally in the liquid phase using the EDC product as the reaction medium. Dry, compressed chlorine is required and, depending on site-specific factors, this may derive from cell-room tail gas (containing O_2, H_2, N_2, and CO_2 inerts) from a chlor-alkali plant or may be revaporised from liquid chlorine (see the CAK BREF). Purified liquid chlorine can be used to avoid brominated by-products from impurities which may be present in cell-room tail gas. The operating temperatures are normally 35–120 °C and the pressure ranges from atmospheric to 5 bar. The reaction may be run with a slight excess of ethylene or chlorine depending on the variant of the direct chlorination reaction process. The reaction is catalysed by metal chlorides, typically ferric chloride, but aluminium, copper and antimony chlorides may also be used. The catalyst concentration in the reactor may vary in a wide range (between around 0.01 wt-% and 0.5 wt-%). Some processes use iron filler bodies in the reactor to improve mass and heat transfer or use iron as a construction material. This equipment generates sufficient $FeCl_3$ *in situ* to catalyse the reaction.

The reaction product consists of more than 99 % EDC and less than 1 % other chlorinated hydrocarbons (predominantly 1,1,2-trichloroethane and ethyl chloride). An oxygen inhibitor may be added to reduce the formation of chlorinated by-products (especially 1,1,2-trichloroethane) by substitution reactions. Two variants of the direct chlorination reaction are currently used:

- low-temperature chlorination (LTC);
- high-temperature chlorination (HTC).

These processes tend to be characterised by their design rather than by the temperature ranges applied, which overlap. In the EU, approximately half the plants operate with a low-temperature DC design and the rest operate with a high-temperature design.

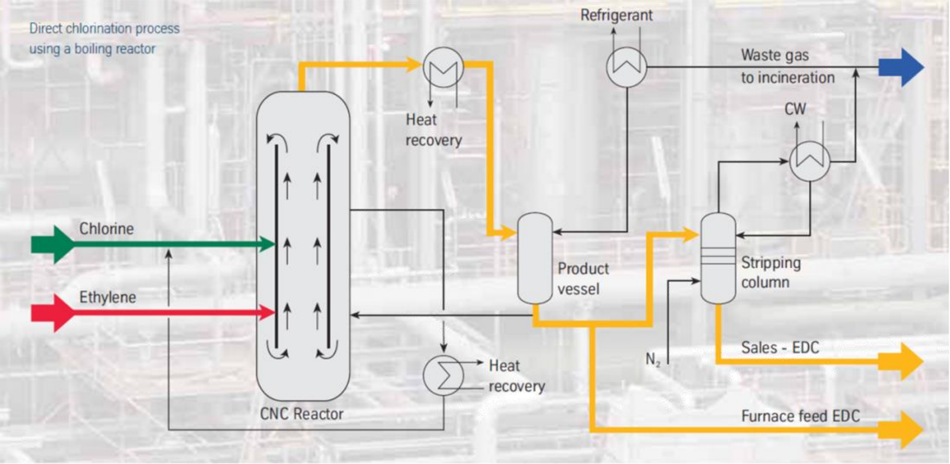


Source: [194, ECVM 2014]

Figure 11.2: Block flow diagram of a low-temperature direct chlorination process

In the LTC process, ethylene and chlorine react in 1,2-dichloroethane as a solvent at temperatures below the boiling point of 1,2-dichloroethane (at about 20–70 °C). The heat of reaction is transferred by external cooling either by means of heat exchangers inside the reactor or by circulation through exterior heat exchangers.

The liquid EDC leaving the reactor must generally be washed to eliminate the catalyst, thus leading to wet EDC (which requires drying and distillation before cracking) and to a liquid effluent (which requires treatment). This route produces slightly less by-product than high-temperature chlorination and allows the use of lower-grade construction materials, but it has higher energy requirements because of the EDC distillation.



Source: [192, TK - Vinnolith 2013]

Figure 11.3: Block flow diagram of a high-temperature direct chlorination process

In the HTC process, the chlorination reaction is carried out at a temperature between 50 °C and 200 °C, mostly at about 100 °C. Gaseous chlorine and ethylene are thoroughly mixed and fed into a reaction tower which is also supplied with dry EDC from oxychlorination or recycled

EDC from the VCM section. The reaction takes place in the liquid phase. The heat of reaction is used to distil the EDC. The light ends are drawn off from the head section, and the unreacted ethylene is condensed and recycled. The catalyst remains in the reactor.

In the following condensation section, EDC is separated and can then be processed with the EDC from EDC cracking. The remaining vent gas is sent to treatment. For optimal heat recovery, cross exchange can be used for chlorine feed evaporation. Due to the relatively low temperatures and anhydrous conditions, carbon steel equipment can be used.

Since EDC leaves the reaction section as a vapour, it may be possible to send it, after condensation, directly to the EDC cracking unit, thus obviating the need for washing. Energy may also be recovered from the hot vapour stream. By sophisticated reactor design and thorough mixing conversion, yields comparable to the LTC process can be obtained with considerably lower energy consumption for an integrated EDC/VCM process.

[99, Dreher et al. 2011].

11.2.2.2 Oxychlorination

Compared with direct chlorination, the oxychlorination process has higher capital investment costs and produces less pure EDC, but it provides the HCl sink that realises the balanced process.

In oxychlorination, EDC and water are formed by the gaseous phase reaction of HCl, ethylene and oxygen over a copper-salt catalyst (usually on an aluminium support) at 220–300 °C and usually 0.4–0.6 MPa. The oxychlorination of ethylene in the liquid phase is now considered obsolete. The reactor technology can either be a fixed or fluidised catalyst bed. Fluidised-bed reactors are more widely used. Both options are described in more detail in Section 11.2.2.

The HCl input is recycled from the EDC cracking unit and from VCM purification, but external sources of gaseous, dry HCl with a suitable purity can also be used. The oxygen source can be ambient air, or oxygen, or a mixture of both (for the technical impacts and differences in environmental performance see Section 11.4.1.1.2). Both ethylene and oxygen/air are fed in stoichiometric excess to ensure complete conversion of HCl.

The reaction is highly exothermic and temperature control by surface cooling is important to minimise the formation of undesirable by-products. The heat of reaction is recovered to generate steam.

This reaction has lower selectivity than direct chlorination. Conversions of 98–99 % are achieved at contact times of between around 0.5 and 40 seconds with selectivities to EDC of 93–98 %.

The reaction products are separated from the inert gas flow by cooling/quenching and condensing at decreasing temperature levels. Further separation of residual EDC from the inert gas mixture may be appropriate using adsorption or absorption, and this captured EDC can be recovered by stripping.

After quenching and condensation, water and EDC (with other organic chlorinated hydrocarbons) separate naturally into two phases as EDC and most of the other chlorinated hydrocarbons have a low solubility in water. Typical exceptions are chloral and chloroethanol, which accumulate in the water phase. The organic and the acidic aqueous phases require washing with dilute NaOH in order to remove residual chloral and chloroethanol.

The oxychlorination stage generates a number of waste streams:

- impurities (e.g. tri- and tetrachloromethane and 1,1,2-trichloroethane) removed from the
- oxychlorinator raw product at the EDC distillation section;
- a process vent that requires treatment prior to release to atmosphere;
- an aqueous effluent stream from reactor outlet quenching containing dissolved chlorinated organic compounds, and, for fluidised-bed reactors, copper (dissolved and as suspended matter) from entrained fines of the catalyst;
- an aqueous effluent stream from the reactor outlet condensation and phase separation, also containing small quantities of dissolved chlorinated organic compounds;
- spent catalyst on a periodic basis (fixed-bed reactors only);
- oxychlorination leads to the formation of dioxins (PCDD/F) (mainly hepta- and octa-PCDF) that will partly adsorb to the catalyst and partly end up in the heavy ends of the EDC purification.

11.2.2.3 EDC purification

EDC product may arise from direct chlorination (‘dry crude’), oxychlorination (‘wet crude’), recycling of unreacted EDC from VCM production or from external sources. All EDC must be purified as EDC cracking may be susceptible to inhibition and fouling by trace quantities of impurities.

Purification may entail the following:

- Washing with water and caustic to remove traces of HCl, chlorine, entrained catalyst and some water-soluble organics (e.g. chloral, 2-chloroethanol). This is often integrated with the direct chlorination, especially if low-temperature chlorination is used.
- Azeotropic drying / light ends distillation in one or two columns, to remove water and chlorinated organic by-products with a boiling point lower than EDC (e.g. trichloromethane, ethyl chloride, tetrachloromethane, chlorobutadiene). Some EDC is lost with the light ends due to the presence of azeotropes.
- Heavy ends distillation, to remove chlorinated organic by-products and tars with a boiling point higher than EDC (primarily highly chlorinated chlorocarbons such as tetrachloroethane, trichloroethylene, 1,1,2-trichloroethane, chlorinated butanes and other relatively high-boiling liquids). These heavy end streams may also be distilled to recover high-boiling chlorinated solvents. Pure, dry EDC is taken overhead from the distillation column. Some EDC will be purged with the tars to ensure their mobility.
- Further light ends and heavy ends processing (by distillation or reaction stages) to recover more EDC, to remove water from the light ends, or to separate the fractions useful as feedstock for other chlorination processes.
- A chlorination reaction to convert, into heavies, those light products that would be difficult to separate from EDC using distillation. Chloro-1,3-butadiene (chloroprene) can form tarry polymerisation products, which plug the equipment when separated from 1,2-dichloroethane together with other light products. In some plants, this substance is nearly entirely chlorinated (in a separate chlorination reactor for recycled EDC or in the main DC reactor).

11.2.2.4 EDC cracking

EDC is converted into VCM in large cabin-type furnaces. A catalyst is not used in the EU, but initiators can be used. EDC dehydrochlorination to form VCM and HCl takes place in the vapour phase at temperatures of around 500 °C, with mean residence times of about 10–20 seconds and pressures of 1–4 MPa, with conversion rates of 50–65 % per pass. At these conversion rates, vinyl chloride yields of 95–99 % are obtainable. The cracking reaction is followed by quenching of the process gas stream. Rapid cooling of the pyrolysis gases is of major importance for reducing the formation of tars and heavy by-products in the gas phase. Cold recycled EDC condensate is often used as the quench medium. Quenching may be preceded by indirect cooling. Heat is recovered for reuse, e.g. at downstream distillation stages.

Coke and tars which are formed in the EDC boilers and in the gas phase and on the inner surface of the cracking reactor affect process efficiency as:

- the build-up in the reactor both reduces the heat transfer from the furnace and increases the pressure drop (and therefore coke has to be removed periodically by decoking, see Section 11.2.3, for disposal as hazardous waste); and
- entrained coke has to be removed downstream from the liquid EDC and VCM.

The purity of feed has to be greater than 99.5 wt-% to reduce coke formation and fouling of the pyrolysis reactor. The EDC feed must also be dry to prevent the corrosion of equipment by hydrogen chloride. The content of inhibitors (such as propane and ethane) should be minimised. Initiators and promoters may be present in the feed or added to enhance reaction conditions.

Most vinyl chloride producers have developed their own furnace technology for optimal yield and a low shutdown frequency for pipe decoking. Most plants in the EU use natural gas as fuel although a few supplement this with hydrogen-rich fuel gas using hydrogen from on-site chlor-alkali plants. Flue-gases are released directly to atmosphere. What makes an EDC cracker different from a large combustion plant (LCP) is that the EDC cracker furnace is operated to ensure an optimal temperature/heat supply for the cracking reaction. According to the outcome of the data collection, the nominal thermal capacity of an EDC cracker furnace is typically in the range of 10–20 MW. Some installations require several furnaces (mostly two or three).

11.2.2.5 VCM purification

At the downstream distillation unit, first HCl, then VCM and then EDC are separated.

HCl (together with low-boiling side products) is recycled to the oxychlorination process (after an optional hydrogenation stage to remove any traces of acetylene) or marketed. The second distillation train separates VCM. Traces of HCl present in VCM are neutralised with NaOH or separated by distillation or adsorption. The bottoms of the vinyl chloride columns are purified in two more distillation stages. First, the low-boiling impurities are removed in the light ends column, followed by EDC separation from the heavy ends in the last tower. EDC is recycled to the VCM cracker, after purification.

Liquid VCM product is transferred to storage after an optional step to remove the last traces of HCl. No gaseous emissions are generated in this section and there are only minor quantities of waste (e.g. spent hydrogenation catalyst, and spent alkaline agent for VCM neutralisation).

11.2.2.6 Incineration of residues

Many sites have an integrated incineration unit to dispose of liquid organic residues (mainly from the EDC purification unit) that cannot be marketed, and to recover the chlorine content as HCl which can be reused in the oxychlorination process. The incineration temperature has to be high enough to ensure complete destruction of the chlorinated compounds (including pollutants like PCDD/F which may be present in the heavy ends from the oxychlorination process). The incinerator may also serve as a liquid/gas incinerator to treat the combined waste gas streams of the EDC/VCM process. The incineration is described as a BAT candidate in Section 11.4.3.5.

Alternatively, catalytic systems are in place to oxidise liquid residues under milder conditions. Under appropriate conditions, the resulting gaseous product stream (containing CO_2, HCl and water) can be routed directly to fluidised-bed oxychlorination. However, in most cases, HCl is recovered from the waste gas by aqueous scrubbers (absorbers) before further waste gas treatment.

11.2.2.7 Auxiliary systems

Abatement systems such as oxidisers, incinerators, scrubbers and strippers are key assets used to reduce the environmental impact of the process.

EDC/VCM plants route the waste gas streams to combined end-of-pipe treatment that may be shared with other installations (typically PVC production installations).

Strippers are needed to pretreat waste water to remove volatile chlorinated compounds. The waste water from fluidised-bed oxychlorination is treated to remove suspended solids. After pretreatment, the waste water is routed to a (shared) biological treatment.

No EU plant operates its own oxychlorination catalyst regeneration system.

The storage of EDC is typically in atmospheric storage tanks using blanketing with nitrogen. VCM may be stored instead with low pressure (i.e. undercooled) or under pressure. Vents are routed to treatment before release. Tank vent gases are, in some cases, partially recovered by condensation (chilled water), and non-condensable gases are oxidised or incinerated.

11.2.3 Other than normal operating conditions

OTNOC operations cover planned and unforeseen events. They may result in higher or lower emissions and affect one or more environmental media. Emissions to the environment will depend on the systems in place to prevent an increase of emissions (e.g. redundancy or back-up systems for key abatement devices) and to prevent unforeseen events (see Section 2.4.11).

11.2.3.1 Specific other than normal operating conditions

The following operations deviate from stable and normal operating conditions:

- shared vent treatment unit or systems (e.g. oxidisers and incinerators) are out of operation;
- catalyst end of life / loss of fluidisation;
- decoking of furnace;
- coke filter cleaning;
- leak due to corrosion: in an EDC/VCM plant there are several important equipment items (e.g. reactor, columns and pipes) that operate under a combination of humidity and high acidity;
- leak to vacuum in purification;
- equipment fouling.

Decoking is described in more detail in the lower olefins chapter (Section 3.2.3.1, with discussion of related BAT candidates in Section 3.4.1.6). However, contrary to LO crackers, mainly in order to avoid potential emissions of chlorinated compounds, the waste gas from decoking is not routed to the furnace for further treatment. Periodic furnace decoking is still normally accomplished thermally by controlled air/steam oxidation. Alternatively or in addition, pigging and sand jetting with non-abrasive particles are used. Shot peening and catalytic decoking are two more recent alternative methods aimed at faster turnaround times and less thermal stress on the cracker furnaces [18, Cowfer et al. 2006]. According to industry, these techniques are not used in Europe.

Usually, the waste gas from decoking is treated to remove dust before release to atmosphere.

Due to lower reaction temperatures, the decoking frequency is lower than for lower olefins; frequencies as low as once every one or even two years are achieved.

11.2.3.2 Generic other than normal operating conditions

The following operations deviate from standard operating procedures in EDC/VCM plants:

- Routine start-up: this operating condition may last from a few hours to several days. The plant may be in start-up mode for between 1 and 20 days per year.
- Shutdown for maintenance: equipment flushing, higher load to WWT, potential emission to surface water (rainwater) header. Plants may be in this mode from 1 to 30 days per year.
- Idle. Unplanned partial stoppage.
- Malfunction/shortage of cooling water and/or chilled water and/or other utilities.
- Low plant rate due to force majeure. (These are problems with the final product consumption or raw material supply.)

11.2.4 Equipment important for environmental protection

The following systems perform operations which are important for environmental protection (for many process designs) and should have the longest uptime possible:

- combined vent gas treatment unit;
- gaseous HCl emergency scrubber;
- waste water pretreatment plant: waste water stripper, solids removal;
- liquid residues incinerator.

For the treatment of waste gas and waste water streams that cannot be stored for later treatment, provisions for the shutdown of abatement devices are important to maintain the control of emissions. Typically these include redundancy of equipment (e.g. strippers) or routing the waste streams to other appropriate facilities that are available within the EDC/VCM plant (e.g. running the liquid incinerator as a replacement for a thermal oxidiser) or at the chemical site (sharing/using abatement facilities from other processes).

11.3 Current emission and consumption levels

The EDC/VCM manufacturing plant involves several steps (see Figure 11.1). The main emissions to air for normal operating conditions are caused by the combustion used to heat the EDC cracker furnaces (see Section 11.3.1.1) and from the oxychlorination step and the incineration of chlorinated liquids (see Section 11.3.1.3). The main emissions to water are caused by the oxychlorination step (see Section 11.3.2).

11.3.1 Emissions to air

11.3.1.1 Emissions from cracker furnaces

This section refers to emissions from the combustion side of the EDC cracking unit. Flue-gas arises from the combustion of natural gas (or from fuel gas, which may contain some hydrogen). Emissions from the EDC cracker furnace contain no chlorinated compounds. The principal emissions are NO_X, and CO. SO_2 emissions are only relevant when burning sulphur-containing fuels, e.g. some liquid fuels, or sulphur-containing fuel gas. Only five plants report data on SO_2 emissions, the highest of these is 9 mg/Nm^3. Therefore, emissions of SO_2 are not a significant environmental issue for EDC crackers. Dust emissions are only relevant when burning non-gaseous fuels. Only five plants report data on dust emissions, the highest of these is 4.4 mg/Nm^3. Therefore emissions of dust are also not a significant environmental issue for EDC crackers.

Table 11.2: Average emissions to air from EDC crackers

Compound	Emission range (mg/Nm^3, dry, 3 % oxygen)	Median value	Analytical method
NO_X	30–181	70	Chemiluminescence; EN 14792
CO	0.3–396	8	EN 15058
SO_2	0.3–9 (1)	(2)	EN 14791
Dust	0.3–3 (3)	(2)	EN 13284
VOCs	0.2–1 (4)	(2)	EN 12619; EN 13526

(1) Data only cover part of the crackers. Generally, SO_2 emissions are expected to be very low because of the use of sulphur-free fuels.
(2) No median value because of low number of data sets.
(3) Data only cover part of the crackers. Generally, dust emissions are expected to be very low because of the use of only gaseous fuels.
(4) Data only cover a small part of the crackers. One plant reported an outlier: 181 mg/Nm^3.
NB: Sampling: ISO 10396; NO and NO_2: ISO 10849.
Source: Data collection

NO_X emissions are mainly related to the flame temperatures of the burners. Furnaces have many burners, hence it may be difficult or even impossible to control the air to fuel ratio precisely on each of them. This can result in temperature variations across burners, with some emitting more NO_X. Other factors that influence NO_X emissions are discussed in Section 11.4.1.2.

Monitoring is typically periodic. The questionnaires revealed the monitoring frequencies shown in Table 11.3.

Table 11.3: Monitoring frequencies

Pollutant	Frequency		Sampling time		Avg. period	
	Max.	Min.	Min.	Max.	Min.	Max.
NO_X	4/yr	1/4yr	30 min	24 h	3*30 min	360 min
O_2	Cont.	4/yr	NI	NI	NI	NI
Dust	1/yr	None	30 min	120 min	30 min	60 min
SO_2	2/yr	None	30 min	120 min	30 min	120 min
NB: NI: No information.						

11.3.1.2 Emissions from decoking

Periodic thermal decoking with air/steam results in a process emission of dust and possibly of carbon monoxide. No monitoring is in place to determine the amount or the composition of this emission stream. The CO level will depend on the relative airflow rate. As this has to be restricted/optimised during the early part of the decoking process (in order to avoid generating too much heat and damaging the tubes), the CO level is likely to be highest at the start of the decoking. The ability to allow more air into the process as the decoking progresses means that CO levels could be very low by the end of the cycle. In addition to these emissions from the process side (flow inside the tubes), there are the emissions from the furnace which will be operating at reduced duty to heat the tubes.

Alternatively or as a primary step before thermal decoking, mechanical decoking (pigging, sand jetting, shot peening) may be used which prevents (or, in combination with thermal decoking, reduces) CO emissions and emissions from the furnace (however, it will increase the dust load to be abated and the resulting hazardous waste to be disposed of).

11.3.1.3 Emissions from the combined end-of-pipe abatement of process vents

Normally, a combined waste gas treatment is in place for the waste gas streams from the process that contain organic pollutants. As listed below, there are various sources; some of the streams may have undergone a pretreatment at source to reduce the workload of the abatement system. As the overall stream will have a wide range of pollutants, a multistage system will normally be applied. Typically, an incinerator or oxidiser is combined with scrubbers. The abatement system may be shared with other production processes, most often to also treat vents from PVC production.

The sources of those streams sent to the combined abatement systems include the following:

Waste gas from the DC processes: The vent contains inert gases (from the chlorine feed or from their intentional addition for safety purposes and to suppress by-product formation) that are partly saturated with EDC and contain traces of ethylene and chlorine from the reaction, along with some unreacted impurities from the ethylene and chlorine feed and traces of other halogenated hydrocarbons.

Waste gas from the OC process: The reaction vent post-wash stream from the OC section, which may be large if air is used as the source of oxygen, mainly consists of the process vent gas (N_2, CO_2 and CO, O_2) as well as unreacted ethylene; pollutants include 1,1,2-trichloroethane, trichloromethane and carbon tetrachloride. Because oxygen is present, oxidation products such as acetaldehyde and its chlorinated derivatives, primarily trichloroacetaldehyde (chloral), are found in the process gas. Oxirane (ethylene oxide) and glycols may also be formed in oxychlorination. Oxidation products are partly removed from the process gas by scrubbing/quenching to end up in the waste water. The volume flow mainly depends on whether air or oxygen is used (factor 10–30 or more) [98, Centi et al. 2009].

Waste gas from the incineration of liquid residues when it is sent to the combined treatment as a second line of abatement or if the incinerator is used directly for combined treatment.

Waste gas from EDC and VCM purification: EDC (as well as 1,2- and 1,1-dichloroethylene, 1,1-dichloroethane) is expected in the overheads since distillation columns will not have 100 % separation efficiency. As well as EDC and VCM, a number of by-products from EDC pyrolysis will also be present (acetylene, benzene, 1-3 butadiene, vinyl aetylene, chloroprene, trichloromethane, tetrachloromethane). Impurities may include ethylene, acetylene, vinylacetylene, 1,3-butadiene, 2-chloro-1,3-butadiene, benzene, 1,1,1- and 1,1,2-trichloroethane, methyl and methylene chloride, trichloromethane, and tetrachloromethane.

Other vents (e.g. from low-pressure storage, waste water systems, product recovery, rotary kilns for sludge treatment [15, ECVM 2000], back-pressure-sensitive analysers).

Note that halogenated and chlorinated compounds are sent to the oxidiser or incinerator, and this has the potential for *de novo* generation of PCDD/F. For further information, see the WI BREF.

The reported emissions after abatement in terms of concentrations vary significantly. The ranges and median values are summarised in Table 11.4. Section 11.4.1.3 provides further details regarding emissions from individual plants and respective abatement techniques (incinerator or oxidiser).

Table 11.4: Emission values from combined end-of-pipe treatment

Pollutant	**Min.**	**Median** (1)	**Max.**	**Unit**
VCM	0	< LOD	3.7	(mg/Nm^3)
EDC	0.0015	< LOD	3.5	(mg/Nm^3)
Ethylene	0	< LOD	23	(mg/Nm^3)
HCl	0.075	3	29	(mg/Nm^3)
PCDD/F	0.0002	0.008	0.12	(ng TEQ/Nm^3)
Cl_2	0.0069	1.2	18	(mg/Nm^3)
CH_4	0.1	NI	6.5 (2)	(mg/Nm^3)
NO_X	0.2	36	98	(mg/Nm^3)
CO	0.048	1.7	68 (3)	(mg/Nm^3)
SO_X	< LOD	0.01	7	(mg/Nm^3)
Total VOCs	0.09	0.2	66	(mg/Nm^3)

(1) Median of reported average emissions; values < limit of detection (LOD) classified as being below the median value. More than 50 % of the plants report emissions < LOD.
(2) One installation with a catalytic oxidiser reported annual averages of 39–58 mg/Nm^3.
(3) Some installations included CO_2, which generated outliers: e.g. 333.786 mg/Nm^3
NB: Measurements standardised at: 273 K, 101.3 KPa and 11 % oxygen dry gas.
LOD: Limit of detection.
NI: No information.
Source: Data collection

Monitoring of stack emissions includes:

- continuous online instrumental monitoring of O_2 and partially CO;
- periodic monitoring for C_2H_4, VCM, EDC, Cl_2, HCl and PCDD/F.

Table 11.5: Monitoring frequencies at end-of-pipe device

Pollutant	Higher	Lower	Normal
VCM	Cont.	1/year	Monthly
EDC	Cont.	1/year	Monthly
Ethylene	Cont.	1/year	Monthly
HCl	Cont.	1/year	Monthly
PCDD/F	2/year	1/year	1/year
Cl_2	Cont.	1/year	Monthly
CH_4	Cont.	Not measured	Monthly
NO_X	Cont.	1/year	Monthly
CO	Cont.	1/year	Monthly
SO_X	Cont.	1/year	Monthly
VOCs	Cont.	1/year	Monthly

Source: Data collection

Table 11.6: Analytical methods

VCM	EN13649:2001 Sampling, GC-FID analysis
EDC	EN13649:2001 Sampling, GC-FID analysis
Ethylene	EN13649:2001 Sampling, GC-FID analysis
HCl	EN 1911:2010
PCDD/F (TEQ)	EN 1948 parts 1 to 3:2006
Cl_2	No EN standard but mentioned in EN 1911
CH_4	EN 13526:2001 EN 12619:1999 EN 12619:2013
NO_X	EN 14792:2005
CO	EN 15058:2006
SO_X	EN 14791:2005
Total VOCs	EN 13526:2001

Source: Data collection

11.3.1.4 Fugitive emissions of organic compounds

Fugitive emissions to air are relevant because there are many assets and process pipes that work under pressure. Methods to monitor fugitive emissions and related BAT are described in the CWW BREF. The European industry has developed a specific measurement methodology and implemented a monitoring programme.

Current monitoring practices in the VCM plants on fugitive emission concentrations include the following:

- Continuous, online instrumental monitoring of VCM and EDC at numerous (e.g. 10 or 20) points in the plant ambient airspace (GC). Up to 50 points per plant (safety detectors).
- Spot checks of VCM and EDC, with hand-held instruments, to detect leaks. Up to 5 000 checks per year (depending on the LDAR programme).
- Personal monitors (e.g. activated carbon buttons) for VCM and EDC. Up to 150 per year.

This type of monitoring is primarily for safety reasons, but these measurements, reference values and calculation models can give a useful indication of the level of emissions for comparison with emissions from other sources. Volatile chlorinated hydrocarbons from fugitive sources are < 5 kg/h.

Table 11.7: **Estimated fugitive EDC and VCM emissions**

Pollutant	Min. (g/t of VCM produced)	Median (g/t of VCM produced)	Max. (g/t of VCM produced)
EDC	0.01	8	93
VCM	0.01	7	93
NB: Monitoring methods in place: EPA-453/R-95-017; HRGC-HRMS/GC-FID; ECVM 2004 method on sniffing; photo ionisation. *Source:* Data collection			

Besides from the chemical process, fugitive emissions arise from the use of refrigerants in the cooling systems. Significant improvements have been achieved by replacing hydrochlorofluorocarbons as refrigerants with non-substituted compounds (propylene or ammonia) (which is required by EC/1005/2009 to reduce the ozone depletion potential and by EC/842/2006 to reduce emissions of greenhouse gases). For example, one site reported for the PRTR a decrease of HCFC emissions from 1 800 kg in 2009 to 200 kg in 2012.

11.3.2 Emissions to water

Integrated EDC/VCM plants may have the following sources of waste water:

- **OC reaction** section: Water is a product of that reaction, and water effluent is also a result of the post-reaction quench. Two streams result: one richer in HCl and the other in NaOH. The caustic stream can be used in the quench column.
- **DC reaction** section: Water effluent is a result of the post-reaction washing (when existing). The OC stream may be used for the acid washing, hence only alkali wash water is adding to the stream.
- **Incinerator and oxidisers**: Wet scrubbing is used to recover HCl, caustic scrubbing is used to remove HCl and chlorine. Both can generate aqueous effluents.
- **EDC purification**: Drying columns.

Expected pollutants are EDC, VCM, HCl, Cl_2, VOCs, other volatile chlorinated hydrocarbons and non-volatile chlorinated material (chloral hydrate or chloroethanol), NaOH, organic compounds (such as sodium formate, glycol and trichloromethane), copper catalyst (mainly when oxychlorination uses fluidised-bed technology), and PCDD/F (mainly PCDF) components with a strong affinity to catalyst particulates, in the case of fluidised-bed technology.

The effluents are collected and pretreated at the EDC/VCM plant, to remove volatile chlorinated hydrocarbons by stripping and to remove solid copper catalyst typically by flocculation and solids separation.

Table 11.8 and Table 11.9 give the ranges and the median values of the average effluent composition after pretreatment as reported by the operators in the BREF questionnaires. The median is the numerical value separating the lower half of the data from the upper half, i.e. the value that half of the values (here average emissions) comply with, and therefore gives an indication of the typical order of magnitude to be expected. By default, concentration values below the detection limit have been allocated to the lower half of the data set.

Additionally, Table 11.8 includes the ranges and median values of the specific emissions (loads per tonne of product) which have been calculated on the basis of the average concentration values, the corresponding waste water flows and the production capacities. Depending on the pollutant, the production capacity refers to different products:

- For EDC, the EDC purification capacity has been chosen as a reference which has already been established, e.g. in the ECVM charter for the production of VCM and PVC from 1995 and OSPAR Decision 98/4 [19, OSPAR 1998], the latter sets an emission limit for chlorinated hydrocarbons of 0.7 g/t of EDC purification capacity.
- For VCM, the emissions are related to the VCM production capacity.

Table 11.8: Composition after stripper

	Unit	EDC	VCM
Range (1)	mg/l	0.02–1.47	0.001–0.2
Median	mg/l	0.2	< LOD (4)
Range	g/t product	0.003–1.8 (2)	0.007–0.12 (3)
Median	g/t product	0.075 (2)	< LOD (4)

(1) Monitoring ISO10.301 (GC).
(2) Related to EDC purification capacity.
(3) Related to VCM production capacity.
(4) < LOD: more than half of the values are below the limit of detection (i.e. < 0.01 to < 0.1 mg/l).
Source: Data collection (excluding outliers); specific loads calculated by EIPPCB.

Table 11.9: Composition after pretreatment

	Unit	Cu	PCDD/F	TSS	COD
Range	mg/l	0.2–0.6	0.2–1.5 (1)	7–75	425–3 130
Median	mg/l	0.4	0.6 (1)	27	1 030

(1) PCDD/F: ng TEQ/l.
Source: Data collection

The amount of waste water effluent from EDC/VCM production typically is 0.5–1 m^3 per tonne of VCM produced. Stripper effluents reported ranged from 10 m^3/h to 90 m^3/h. The waste water is alkaline; pH values reported range from 8.0 to 10.4.

PCDD/F are adsorbed to the suspended particles; this is confirmed by the correlation of reported TSS and PCDD/F averages after pretreatment (Figure 11.4).

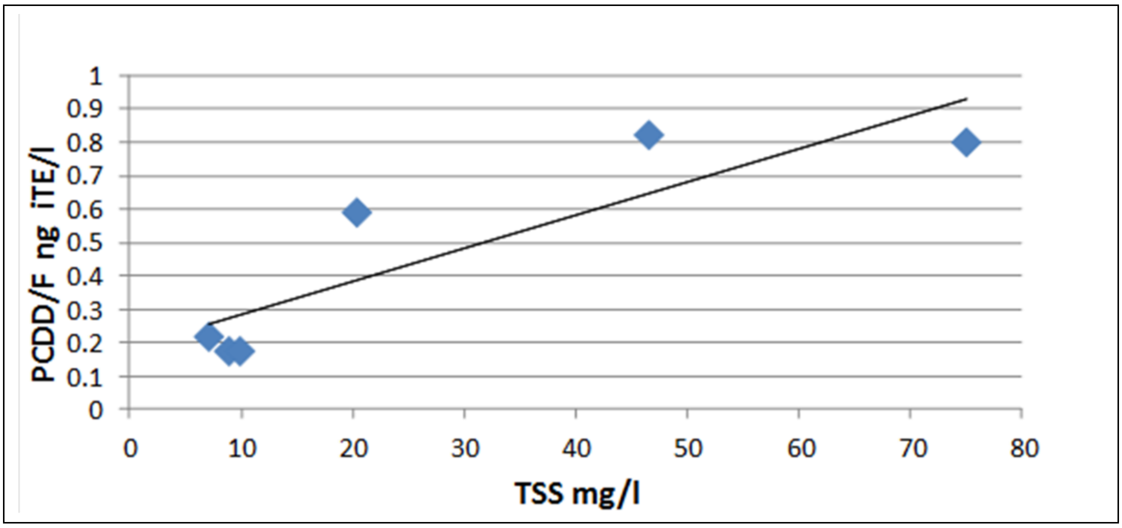


Figure 11.4: Correlation of average concentrations of PCDD/F and TSS after waste water pretreatment (solid removal)

EDC and VCM from the stripper effluent have been reported by virtually all operators, whereas the other parameters have often been reported either for the outlet of the pretreatment or for the outlet of the final biological treatment (see Table 11.10). The pretreated waste water from EDC/VCM production is usually treated together with waste water from other processes on site, ranging from shared treatment with only PVC manufacture to numerous processes at large sites. Therefore, the magnitude of the concentration in the final effluent will depend on the dilution or pollutant loads from these other processes.

Table 11.10: Composition after final biological treatment (annual averages)

Pollutant	**EDC**	**VCM**	**Cu**	**PCDD/F**	**TSS**	**COD**
Unit	µg/l	µg/l	µg/l	ng TEQ/l	mg/l	mg/l
Range	0.1–200	(< 0.5)–30	1.0–80	0.0002–0.25	5.0–62	50–167
Median	20	< LOD (1)	20	0.02	25	80
Method	GC	GC	ISO 8288	EN1948		ISO 6060

(1) < LOD: most VCM values are below the limit of detection (LOD) (i.e. < 0.5–100 µg/l).
Source: Data collection

For more details regarding the results from the BREF questionnaires, see Section 11.4.2.

In this section, all ranges and averages are based on monitoring data from the data collection for one to five years. With the exception of PCDD/F which has typically been monitored only once or twice per year, the pollutants have been monitored at least weekly at most of the reporting plants. The distribution of the monitoring frequency for the different sites and parameters is given in Table 11.11 for the stripper effluent (EDC/VCM) / outlet of the pretreatment and for the outlet of the biological treatment, referring to the total number of plants that have reported for each. It cannot be excluded that in some cases the reported monitoring frequency may refer to the minimum requirements of the permit rather than to the higher monitoring frequency in place.

Table 11.11: Monitoring frequency – distribution of plants per monitoring category

	EDC	**VCM**	**PCDD/F**	**Cu**	**TSS**	**pH**	**COD**
Frequency	%	%	%	%	%	%	%
After pretreatment							
Continuous	6	0	0	0	0	33	0
1–3/day	33	31	0	0	33	17	0
1–4/week	39	31	0	63	50	33	50
1–3/month	17	19	14	25	0	17	17
1–4/year	6	6	86	13	0	0	17
Not measured	0	13	0	0	17	0	17
After biological treatment							
Continuous	0	0	0	0	0	17	0
1–3/day	30	22	0	10	18	25	36
1–4/week	40	56	0	40	45	33	36
1–3/month	10	0	0	40	9	8	18
1–4/year	20	22	70	10	9	8	0
Not measured	0	0	30	0	18	8	9

11.3.3 Raw material consumption

In a balanced unit, the only raw material requirements for the reactions are ethylene, air (or oxygen) and chlorine. These are generally supplied by pipeline from nearby production facilities. Other units will have the same ethylene and chlorine requirements, but may also need to import or export gaseous hydrochloric acid and EDC. This is shown in the table below.

Table 11.12: Usages of a VCM plant (with air-based oxychlorination)

Raw material	**(kg/kg of VCM)**
Ethylene	0.46–0.47
Chlorine	0.59
Air	0.73
Oxygen	0.13–0.14
Source: [99, Dreher et al. 2011] [192, TK - Vinnolith 2013]	

Reducing by-product formation is then the key for more efficient raw material use. Some examples of these by-products in ethylene oxychlorination are: monochloroethane formed by direct HCl addition to ethylene; 1,1,2-trichloroethane formed by chlorination of EDC or chlorine addition to VCM; 1,1-dichloroethane formed by the addition of HCl to VCM; and other cracked or substitution products such as tri- and tetrachloromethane, 1,1-dichloroethylene, cis- and trans-1,2-dichloroethylene, trichloroethylene and tetrachloroethanes.

At the oxychlorination process, the ethylene feed is partially consumed, especially at higher temperatures, by deep oxidation to yield carbon oxides (CO, CO_2). Major by-products such as chloroethane and 1,1,2-trichloroethane are sometimes recovered and sold, or used as feedstock for other chlorinated hydrocarbon processes, such as 1,1-dichloroethylene production.

Other materials that are used in this type of plant are given below:

- Sodium hydroxide, to wash the crude EDC from direct chlorination (low-temperature only), to scrub the oxychlorination reactor off-gas, and to remove the trace acidity from the distilled VCM.
- Anhydrous ferric chloride catalyst, in the direct chlorination reactor.
- Oxychlorination catalyst (e.g. based on copper chloride), to replace the continuous catalyst lost in the fluidised-bed process, and as a complete replacement of the catalyst charge in the fixed-bed process. Catalyst usage for OC reaction: catalyst particulates will be entrained in the reaction outlet stream.
- Organic solvent, to remove EDC from the oxychlorination off-gas after condensation.
- Hydrogen and hydrogenation catalyst to hydrogenate trace acetylene.
- Hydrochloric acid solution in certain low-temperature chlorination processes to remove ferric chloride from crude EDC.
- Anti-fouling agents for some boilers.
- Nitrogen, for inerting.
- Oxygen for oxychlorination.
- Air, or air/steam mixtures, for EDC cracker furnace decoking.
- Steam or air, for direct injection into the waste water stripper.

11.3.4 Water usage

The process does not consume water as a main raw material, but as a consumable, in the following activities:

- DC: overhead vent scrubber (if present);
- DC: EDC decanter caustic wash;
- EDC purification washing in the LTC process;
- OC post-reaction washing;
- VCM final products scrubbing;
- safety water, to scrub the hydrochloric acid from cracking when the oxychlorination section is not fully operational or is shut down.

There are several auxiliary uses for process water, mainly in caustic solution to remove HCl.

Furthermore, water is needed for steam production and for indirect cooling.

11.3.5 Energy consumption

The rate and type of energy usage of the plant will largely depend on the process design. Regional or local variations in energy costs may lead to process changes in order to improve the margins of the operating costs. Energy consumption also depends on operational parameters (such as EDC conversion and column reflux ratios).

Data ranges from the questionnaires are summarised in Table 11.13.

Table 11.13: Energy usage in a VCM plant

Energy (unit)	**Min.**	**Max.**
Steam (GJ/t)	0.3	1.7
Fuel (GJ/t)	3.4	4.2
Total electrical (MWH/t) (1)	0.11	0.21

(1) Oxygen-based OC has lower electrical energy consumption.
Source: Data collection

Fuel is mainly needed for the cracker furnaces. Electrical energy is mainly needed for the compressors, to feed raw materials to the oxychlorination reactions, to recycle gas from the oxychlorination reactors and for cooling. Steam is mainly used for several distillation operations used to purify EDC and VCM and for the waste water strippers.

In the oxychlorination reaction, heat can be recovered to the hot oil system. An alternative recovery is steam generation at the oxychlorination reactor. From the data collection, reported energy recovery/savings are in the range of 0.43–3.5 GJ/t.

According to the data collection, the reported heat energy recovery/savings from the liquid incinerators are in the range of 180–540 GJ/yr.

11.3.6 Residues

VCM plants generate the following waste streams:

Spent oxychlorination catalyst containing PCDD/F: the values reported in the BREF review questionnaires were 12–170 g/t of VCM. Spent oxychlorination catalyst (copper) is removed either continuously (by the entrainment of fines in fluidised-bed reactors) or periodically (when replacing exhausted fixed-bed reactors). Small quantities of highly chlorinated organics (e.g. PCDD/F) are adsorbed onto the waste catalyst and this determines the disposal route.

Coke from EDC cracking: the values reported in the BREF review questionnaires were 20–300 g/t of VCM. Coke is formed by the thermal cracking of EDC and may contain residual chlorinated hydrocarbons (in the range of a few wt-%) (but is free of PCDD/F). Coke is removed from the cracked gas with liquid EDC in a quench column; the coke-containing stream may then be filtered. Coke also arises from the decoking of the cracking section. The total amount arising is in the range of 100–200 g/t of VCM. The previous BREF mentioned one outlier plant which reported a coke generation rate from the cracker alone (i.e. excluding the quench) of 6 g/t of VCM.

Sludge from waste water pretreatment: the values reported in the BREF review questionnaires were 0.07–2.1 kg/t of VCM.

Light and heavy residues from fractionation/purification processes: the values reported in the BREF review questionnaires were 20–62 kg/t of VCM (the majority below 30 kg/t of VCM). Typically three times more heavies than lights were reported: e.g. for a lights production of 6 kg/t of VCM one would expect a heavies production of around 18 kg/t of VCM, and total by-products of around 17 kg/t of VCM. However, some plants produce significantly more by-products, especially heavy ones.

Other waste streams:

- Direct chlorination residues such as spent catalyst.
- VCM purification: spent alkaline agent from the VCM neutralisation.
- Generic wastes from waste water treatment sludge, tank/vessel sludge and maintenance activities.
- Occasional wastes when organic by-products cannot be recovered or the hydrochloric acid solutions cannot be reused or sold.

11.4 Techniques to consider in the determination of BAT

This section describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this chapter. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations). Cross references to other chapters are used, where relevant to avoid repetition.

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 2.6 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

Among the techniques, some consider the choice between different process options that may concern several environmental aspects. These options are described under the respective major environmental aspect:

Technique	Section	Major aspect
Use of a boiling reactor for direct chlorination	11.4.4.1	Energy
Use of oxygen instead of air for oxychlorination	11.4.1.1.2	Air
Fixed/fluidised-bed reactor for oxychlorination	11.4.2.2.1	Water
Combined incineration of liquid residues and waste gas with recovery of HCl	11.4.3.5	Consumption/Wastes

11.4.1 Techniques to reduce emissions to air

11.4.1.1 Direct chlorination and oxychlorination

11.4.1.1.1 Control of purity of fresh and recycled feedstock

Description
The quality of the feed (ethylene, chlorine, hydrogen chloride) is controlled to minimise the formation of halogenated by-products and pollutants, e.g. use of hydrogenation to reduce the acetylene content in hydrogen chloride.

Technical description
The propane and propene content in the ethylene feed need to be controlled to minimise the formation of chloropropanes and chloropropenes, which are difficult to separate from 1,2-dichloroethane by distillation. The purity of EDC and HCl from external sources (in the case of non-balanced plants) are also important.

Direct chlorination: A slight excess of chlorine (or ethylene) is preferred in order to ensure complete ethylene (or chlorine) conversion.

The use of high-purity chlorine will minimise the formation of brominated by-products. However, the bromine content of the feed chlorine is directly affected by the source of the salt used in its manufacture (see the CAK BREF). The formation of impurities involves the occurrence of radicals. For this reason small amounts of oxygen, often present in the chlorine produced by electrolysis, may increase the selectivity to EDC, by inhibiting the secondary reactions.

Oxychlorination

Purity of HCl (fresh and recycled): In most cases, HCl from the EDC cracking section is used as a source of chlorine, and the organic content has to be controlled to prevent the formation of more highly chlorinated side products. For example, the VCM content in the recycled HCl needs to be reduced to about 100 ppm.

The acetylene content (from VCM cracking) in the recycled HCl may be critical and should be controlled (below 0.1 %), as acetylene tends to form highly chlorinated side products (such as dichloroethylenes, trichloroethylenes, tetrachloroethane and pentachloroethylene) and tars, which can lead to catalyst deactivation by coking (pore plugging) and may also influence downstream operations (trichloroethylene hinders the distillation of the light ends in order to recover EDC). Selective hydrogenation to ethylene is often used to remove acetylene from this HCl stream. Hydrogenation is carried out to achieve acetylene concentrations typically below 50 ppm.

Achieved environmental benefits

Reduced emissions to air.

Technical considerations relevant to applicability

The techniques are widely used and established.

11.4.1.1.2 Use of oxygen instead of air for oxychlorination

Description

For oxychlorination, oxygen is used instead of air.

Technical description

The oxychlorination process requires air or pure oxygen as a reactant. Changing from air to oxygen implies the following issues:

- Possible increase in throughput depending on installed technology.
- The reaction is typically run with a larger excess of ethylene to ensure a good heat transfer and to avoid the explosive range. Most of the excess ethylene is compressed and recycled.
- Careful design (avoid ignition sources; safety valves/membranes) is needed to ensure process safety and to avoid the formation of flammable mixtures.
- No compression or filtration of air is required (but compression of the recycled ethylene is).
- Only a small purge vent is required which may be incinerated, oxidised or routed to a HTC unit for chlorination of ethylene and removal of chlorinated by-products. (Meanwhile oxychlorination with air produces a large process vent for abatement and efficient recovery is hindered by the dilution with inerts.)

Achieved environmental benefits

- Increase in selectivity and therefore decrease in consumption of ethylene and emissions to air.
- Improved recovery of organics from process gas streams.
- Reduced waste gas flow and emissions to air.
- Energy savings due to the higher calorific value of the waste gas.

Environmental performance and operational data

By using oxygen, the vent flow from oxychlorination is reduced to 1–5 % [100, Gunardson 1997] or < 1 000 m^3/h (compared to 10 000–30 000 m^3/h using air) [98, Centi et al. 2009]. The reduction of flow and inerts content (nitrogen) allows for better recovery of ethylene by compression.

For the shared waste gas abatement, the data collection showed no correlation between the pollutant concentration and the choice of oxidant air / pure oxygen. This means that, when using air, the emissions in terms of loads are significantly higher due to the higher total waste gas flow of the EDC/VCM unit.

Cross-media effects

- Reduced consumption of electricity in the process.
- Energy consumption for upstream production of oxygen.

Technical considerations relevant to applicability

Replacing air with oxygen means a major retrofit of the whole oxychlorination unit.

Economics

For new plants, savings in investment costs (due to reduced waste gas abatement) and operation (reduced consumption of energy and ethylene) are typically higher than additional costs (mainly for the supply of oxygen).

Driving force for implementation

Economics (costs for production and abatement).

Example plants

In the data collection, about two thirds of the installations reported using pure oxygen. Nearly all oxychlorination processes built since 1990 are oxygen-based, and many existing air-based units have been retrofitted for a pure oxygen feed [18, Cowfer et al. 2006].

11.4.1.1.3 Condensation and other techniques to reduce the pollutant load from individual streams prior to final abatement

Description

Techniques applied to gas streams in order to recover liquids and reduce the workload of the waste gas treatment system.

Technical description

A combination of different techniques is used for the waste gas streams at the different units (DC, OC, EDC purification, VCM purification) to reduce the workload and possibly recover organics before being routed to the end-of-pipe treatment.

KO drums or demisters are widely used mechanical devices for performing vapour-liquid phase separation and reducing the entrainment of liquid droplets. Demisters may be a mesh-type coalescer, vane pack or other structure intended to aggregate the mist into droplets that are heavy enough to separate from the vapour stream.

Condensation is used to recover organic vapours from waste gas streams by reducing the temperature below the dew point. A larger condensing duty will reduce VOC emissions in the vent gas. A second condenser with chilled water or refrigerants, after the first cooling water one, improves the efficiency. Heat exchangers with refrigerant fluids such as propylene or ammonia can reach lower temperatures (-20 °C to -40 °C) and minimise emissions to the shared vent treatment system. See the CWW BREF on condensers.

Achieved environmental benefits

- Lower emissions to air (although, depending on the design and capacity of the downstream final treatment, the reduction may be small).
- Reduction of PCDD/F emissions by the reduction of PCDD/F precursors upstream of the thermal treatment.
- Recovery of educts and/or organochlorine compounds.

Cross-media effects

Condensation: Energy consumption for use of refrigerants and chilled water.

Technical considerations relevant to applicability

For wet gas, the temperature should be kept above the freezing temperature to avoid icing problems. Temperatures < 0 °C can be reached when substances which lower the freezing temperature are present or added. For example, the water-saturated process gas from oxychlorination is usually cooled to temperatures as low as -20 °C (CZ, Comment 4044 to D1 [182, TWG 2014].

Driving force for implementation

Economic considerations and environmental legislation.

Example plants

The following tables summarise the information gathered in the data collection.

Table 11.14: Techniques applied in direct chlorination plants to reduce the load in waste gas streams

Technique	Number of installations	
	Apply	Do not apply
Entrainment avoidance	15	3
CW condensers	17	4
Chilled water/refrig. condensers	20	1

Table 11.15: Techniques applied in oxychlorination plants to reduce the load in waste gas streams

Technique	Number of installations	
	Apply	Do not apply
Entrainment avoidance	19	1
CW condensers	21	0
Chilled water/refrig. condensers	18	2
NB: For some plants, not all items have been answered, which explains the differences in totals for the techniques in Tables 11.14 and 11.15.		

11.4.1.2 EDC cracker furnaces

What makes an EDC cracker different from a large combustion plant (LCP) is that the goal of the EDC cracker furnace is to convert EDC into VCM safely and with a high conversion rate and selectivity. The techniques that are used on the energy supply side in these furnaces are not specific to the EDC cracking process. Therefore, cross references to the LCP BREF and the generic chapter of the LVOC BREF will be used in order to avoid repetition. However, there are specific techniques on the demand side of the furnace that may reduce the required energy input and related emissions.

11.4.1.2.1 Primary measures to prevent or reduce emissions

Description
Design and operation of furnaces in such a way as to reduce emissions of CO, NO_X and TVOC and prevent emissions of SO_2 and dust.

Technical description
Emissions from EDC crackers depend on the fuel, the design and the combustion control of the furnaces.

a) Fuels
EDC crackers typically use natural gas or fuel gas as fuel. Where fuel gas is used, it tends to have a high hydrogen content since hydrogen is available at many sites from the upstream chlorine production (chlor-alkali process). The replacement of natural gas by hydrogen leads to a higher flame temperature and therefore higher potential for the formation of NO_X which can be prevented/compensated by primary measures. The sulphur content of the fuel is typically low. In the EU, no plants use liquid fuels.

b) Furnace design
EDC crackers are cabin-type furnaces. EDC passes through one or several coils located inside the ‘cabin’. The heat is delivered by burners fixed to the lateral walls of the cabin in horizontal furnaces or at several different height levels in vertical ones. In order to achieve good distribution of the heat to the coil, without local overheating of tubes, it is important to distribute burners along the vertical surface of the cabin and to use flat flame or terrace wall burners (as already included in the 2003 LVOC BAT conclusions). Local overheating of tubes can lead to metallurgical degradation of the tube material and to increased formation of by-products and coke inside the coil.

To reduce NO_X emissions from process furnaces, there is a selection of measures available (for more details see the description in the generic section, Section 2.4.4.4):

- low-NO_X burners;
- staged combustion burners;
- internal recirculation;
- external recirculation.

However, not all of them are applicable for EDC crackers (see technical considerations relevant to applicability below).

The lower operating temperatures of EDC cracking furnaces in comparison with lower olefin crackers or large combustion plants mean that there may be more potential to reduce combustion temperatures to minimise the production of thermal NO_X. However, the potential may be very limited, when the resulting flame temperatures are still similar to olefin crackers (especially when hydrogen is burnt).

c) Combustion control

See the LCP BREF (gas-fired furnaces). To control the combustion process in order to ensure complete combustion, monitoring of the excess oxygen concentration and the temperature profile within the furnace is required.

Achieved environmental benefits

- Prevention of emissions of dust and SO_2 by using gaseous fuels with a low sulphur content.
- Reduction of emissions of CO and TVOC by combustion control.
- Reduction of NO_X emissions.

Environmental performance and operational data

Table 11.16 lists the average emissions of furnaces (average per EDC/VCM site) from the data collection (all furnaces except outliers for NO_X and CO (see below)). The data are from periodic measurements from one to five years with low monitoring frequencies (see Table 11.3).

Table 11.16: Average emissions (mg/Nm^3, dry, 3 % O_2) from EDC cracker furnaces in the EU

Installation (site)	NO_X	CO	SO_2	Dust	VOCs
#1	96	ND	1.9	2.01	ND
#2	84	15	ND	ND	ND
#3 (1)	89	6	0.3	0.7	ND
#4 (2)	63	25	0.65	0.7	0.6
#5	42	27	0.8	4.4	181
#6 (2)	70	1.4	ND	ND	ND
#7	52	5	9	ND	ND
#8 (1)	75	< 12	ND	ND	ND
#12	54	2	ND	ND	ND
#13a	48	29	ND	ND	ND
#13b (1)	58	6	ND	ND	ND
#14 (1)	43	15	ND	ND	ND
#16 (1)	86	ND	ND	ND	ND
#18 (1)	78	35 (3)	ND	ND	ND
#19 (1)	48	0.7	ND	ND	ND
#20	53	2.7	ND	ND	ND
#22	35	7	ND	ND	ND
#22-MS (4)(5)	50	5	ND	ND	ND

(1) Hydrogen used as fuel (typically in combination with natural gas).
(2) Average from data for 2–3 furnaces.
(3) Estimate from reported range 20–50 mg/Nm^3.
(4) Additional data from one Member State; NO_X 1 single measurement, CO continuous measurement.
(5) Emissions correspond to 38 g NO_X and 4 g CO per t of product (VCM).
NB: All values in mg/Nm^3 at 3 % O_2. Averages for 1–5 years.
ND: No data (not measured).

NO_X: Most furnaces show average NO_X emissions in the range of 50–100 mg/Nm^3, with reported maximum emissions (not included in the table) of up to 119 mg/Nm^3. Five sites reported average emissions even slightly below 50 mg/Nm^3 (35–48 mg/Nm^3). Only two sites (#17 and #9) reported average emissions (far) above 100 mg/Nm^3, with 164 mg/Nm^3 and 181 mg/Nm^3.

NO_X emissions depend on the flame temperatures which depend on many technical parameters such as the burner type, use of hydrogen as a fuel, air excess and air preheating. The data revealed no correlation between NO_X emissions and the use of hydrogen as a fuel.

Air preheating which is used to reduce the consumption of fuel and related emissions to air may lead to increased NO_X emissions, due to higher flame temperatures. According to the data collection, less than half of the EDC crackers in the EU apply air preheating (some of them partially) (sites #1, #4, #9, #17, #18 and #19). Some of them show low NO_X emissions, but more furnaces are in the upper range, amongst them the two with the highest NO_X emissions (sites #9 and #17, site #9 also using hydrogen as fuel).

CO: Average CO emission show a wide spread between the different furnaces. Most sites achieve average emissions < 20 mg/Nm^3 (14 out of 20) or ≤ 35 mg/Nm^3 (18 out of 20). Only 2 out of 20 (#10 and #15) report average emissions (far) above 35 mg/Nm^3. As expected, CO emissions from crackers using (also) hydrogen as fuel are at the lower end of the range.

Data from the continuous monitoring of CO from one EDC cracker over one year with an average emission of 4.4 mg/Nm^3 show the following distribution.

Table 11.17: Distribution of CO emissions from an EDC cracker

Concentration	Corresponding percentile	Corresponding percentile
(mg/Nm^3) (3 % O_2)	Daily average	2-hour average
5	78.7	–
10	97.4	83.4
15	99.0	–
20	99.7	98.2

Technical considerations relevant to applicability

Primary measures to reduce NO_X:

- It may be possible to change the burners in flat wall EDC cracker furnaces to low-NO_X burners without any other major modifications.
- Staged combustion burners are well adapted for vertical burners. For EDC cracker furnaces, the use of staged combustion burners is applicable only if compatible with the flat flame concept.
- Also, the use of internal recirculation is applicable only if compatible with the flat flame concept.
- External recirculation is not used for large EDC crackers. For existing furnaces, addition of external recirculation is not applicable because the significant increase of flue-gases would lead to a complete redesign of the furnace and because of space constraints.

Driving force for implementation

Environmental legislation.

Example plants

Combustion control: Continuous monitoring of oxygen generally applied with very few exceptions.

Some example plants that took part in the data collection of emissions as reported above are: SolVin, Jemeppe-sur-Sambre (BE); Vinnolit, Gendorf (DE); Vinnolit, Knapsack (Hurth) (DE); Ineos Vinyls, Strenungsund (SE); Kem One, Lavera (FR).

11.4.1.2.2 Secondary measures to prevent or reduce emissions

Description
Treatment of waste gas from EDC crackers to reduce emissions.

Technical description
Generally, emissions can be controlled sufficiently by primary measures (see Section 11.4.1.2.1 above). If required, generic flue-gas treatment techniques to abate NO_X, SO_2 or dust can be applied (see Section 2.4.2), taking into account the technical considerations relevant to applicability below.

Achieved environmental benefits
Reduction of emissions to air (NO_X, SO_2, dust).

Environmental performance and operational data
See the LCP BREF.

Cross-media effects
See Section 2.4.2 and the LCP BREF.

Technical considerations relevant to applicability
Reduction of NO_X by SCR (selective catalytic reduction) requires the addition of a catalytic bed and injection of ammonia. This bed introduces a pressure drop into the system that is not compatible with the existing draft in the furnaces. Additional power would be required for the gas handling equipment. Ammonia must be properly injected into the flue-gases, in the proper temperature window, in the proper amount to achieve the expected NO_X reduction and to avoid unreacted ammonia slipping through. These constraints are difficult to combine with the process constraints of the operation of the EDC furnace (control of process temperature, of tube wall temperature, of oxygen excess, etc. at variable EDC loads). SCR systems are not very tolerant to changing conditions. Other operating issues are the progressive fouling of the catalytic bed and regular regeneration (or replacement) of the catalyst.

Reduction of NO_X by SNCR (selective non-catalytic reduction) requires temperatures between 900 °C and 1 050 °C. This range is outside the range of the flue-gases in EDC crackers. Implementation of SNCR would lead to a significant increase of specific fuel consumption and of CO_2 emissions.

Economics
No information provided.

Driving force for implementation
Environmental legislation.

Example plants
No plant in the EU is known to apply waste gas treatment of the EDC cracker flue-gas.

11.4.1.2.3 Techniques on the energy demand side

Any measures on the reaction side that lead to lower reaction temperatures or improved heat transfer will reduce the energy demand and therefore the required furnace duty (see also Section 11.4.4.2).

a) Use of initiators or promoters

Description
Initiators and promoters are used to enhance the cracking reaction and reduce the reaction temperature.

Technical description
The addition of initiators and promoters reduces the reaction temperature and increases overall energy efficiency by an increased conversion of EDC to VCM.

It is possible to use initiators, such as chlorine and tetrachloromethane, and promoters: as chlorine or other radical species are important for the chain propagation, chlorine or chlorine-delivering compounds such as hexachloroethane, as well as other radicals, can be added as promoters and will suppress methyl chloride formation. Although according to the literature there are several promotors that do not contain chlorine (bromine and iodine compounds, nitromethane), the use of these may technically not be feasible because of the formation of further unwanted by-products.

Good results can be achieved when chlorine is fed into the reaction zone at different points, though this may be difficult to implement.

The initiators/promoters may be present in the EDC feed (e.g. tetrachloromethane from oxychlorination) or added. (Note: Because of its high ozone-depleting potential, emissions from addition of tetrachloromethane would contravene Regulation EC/1005/2009.)

Achieved environmental benefits
Lower net emissions to air due to lower energy consumption, and moderate lowering effect on furnace duty. Improved environmental performance due to increased conversion rate.

Environmental performance and operational data
The presence of nitromethane was reported to increase EDC conversion to 92.5 % [17, Rossberg 2006]. Promoter concentrations (mg/kg) in the 1,2-dichloroethane feed may vary between a few hundred ppm up to 5 %.

Technical considerations relevant to applicability
Generally applicable.

Driving force for implementation
Economics.

Reference literature
[17, Rossberg 2006].

b) Use of catalysts

Description
The use of a catalyst leads to a similar conversion of EDC to VCM at lower duties in the furnace.

Technical description
The gas phase dehydrochlorination is performed with catalysts at lower temperatures (200–450 °C) which reduce side reactions and the formation of coke. In addition to activated carbon, which can be doped with ammonium salt promoters, a variety of other materials have been patented as catalysts, e.g. silicates, metal-promoted alumina, sodium chloride and zeolites.

Achieved environmental benefits
Lower net emissions to air from combustion processes.

Environmental performance and operational data
1,2-Dichloroethane conversions are not much improved compared to the non-catalytic process. On average a 50–70 %, but mostly a 55–60 %, conversion per pass is obtained.

Technical considerations relevant to applicability
Generally applicable.

Economics

The higher costs of catalytic processes (extended shutdown periods) are considered to no longer compensate the slightly higher energy requirements of modern yield- and energy-optimised non-catalytic processes.

Example plants

The catalytic gas phase dehydrochlorination is only used by a minority of vinyl chloride producers, and is not currently used in the EU.

Reference literature

[99, Dreher et al. 2011]

11.4.1.3 Combined treatment of the waste gas from the EDC/VCM units by thermal treatment (thermal oxidiser or incinerator) and scrubbing

After all recovery options for individual streams have been exhausted, the concentrations of chlorinated compounds and ethylene in the off-gas are further reduced by applying treatment techniques such as those described below.

The 2003 LVOC BREF [190, COM 2003] contained a BAT to connect the vents from normal operations (that contain chlorinated hydrocarbons and/or ethylene or other organics) to a recovery system or to vent gas treatment if their concentrations exceed the following:

VCM	5 mg/Nm^3
EDC	5 mg/Nm^3
Ethylene	150 mg/Nm^3
HCl calculated as total chloride	30 mg/Nm^3
Chlorine	5 mg/Nm^3
Dioxin iTEQ	0.1 ng/Nm^3

It was considered that where the mass emission of chlorinated hydrocarbons was below 0.025 kg/h and below 2 kg/h for ethylene, the environmental benefits of connection may not be justified by the costs.

The data collection confirmed that EDC/VCM plants usually route the vents to an oxidiser or incinerator for final abatement and that this may be shared, e.g. to also treat streams from a PVC plant. As explained below (see Environmental performance and operational data), according to the data, catalytic oxidisers are not considered a BAT candidate.

Description

The combined waste gas streams from EDC and/or VCM production are treated by using a thermal oxidiser followed by two-stage wet scrubbing. Instead of using a dedicated thermal oxidiser, the thermal oxidation can also be carried out in a liquid waste incineration plant (see Section 11.4.3.5).

To reduce emissions of PCDD/F, rapid quenching and, if necessary, injection of activated carbon is applied.

All waste gas streams that contain organic compounds are treated with a combined treatment consisting of a thermal oxidiser or a liquid/waste gas incinerator, an HCl absorber and a caustic scrubber, possibly combined with a pre-scrubber and/or a final activated carbon adsorber, in order to minimise emissions of TVOC, organochlorine pollutants including PCDD/F, HCl and Cl_2. And combustion is controlled in order to control emissions of NO_X and CO.

Technical description
All waste gas streams from the EDC/VCM installations that contain organic compounds are combined (following measures to reduce the load as described in Section 11.4.1.1.2). This includes:

- the process vents from direct chlorination and oxychlorination;
- the overhead vents and possibly light ends from product purification and recovery (washing, distillation);
- vents from the waste water pretreatment;
- waste gas from the incineration of liquid residues when it is sent to the combined treatment as a second line of abatement;
- vents from low-pressure storage tanks, depending on the tank location.
-

The combined waste gas generally contains HCl, several chlorinated hydrocarbons (mainly EDC, carbon tetrachloride, $CHCl_3$, dichloromethane, C_2HCl_3, C_2H_2, VCM, C_2HCl_3O, vinyl acetylene, chloroethane) and unreacted ethylene. Depending on the HCl concentration, the first step of the combined treatment is a wet pre-scrubber to reduce the HCl content before incineration/oxidation, in order to recover HCl and reduce the potential for PCDD/F formation. The following incineration/oxidation is performed in such a way as to almost completely destroy the chlorinated hydrocarbons from the waste gas and, for gas/liquid incineration, the liquids (including contaminants like PCDD/F) and to avoid *de novo* formation of PCDD/F (optimised design including turbulent burners, sufficient minimum residence time and temperature, rapid quenching). The combustion is controlled in order to control emissions of NO_X and CO. For further details, see Section 2.4.3.5.6 for thermal oxidisers and the WI BREF for incinerators.

Following the oxidation/incineration, the waste gas is scrubbed in two steps to remove HCl and chlorine, where first most of the HCl is recovered by an absorber which is run with water or diluted HCl, followed by a caustic scrubber for final abatement of HCl and chlorine emissions. An activated carbon adsorber may follow, if necessary, to further reduce PCDD/F emissions.

Achieved environmental benefits
Reduction of emissions of TVOC, organochlorine hydrocarbons, PCDD/F, HCl and Cl_2.

Environmental performance and operational data
All plants use a combination of techniques for the treatment of the combined waste gas stream prior to its release. Nearly all plants are based on a four-stage treatment process:

- Step 1: physical separation – KO drum or demister.
- Step 2: thermal treatment, either:
    - an incineration plant for the thermal treatment of liquid residues, which also acts as a thermal oxidiser for gaseous streams; or
    - a thermal oxidiser which treats only gaseous streams.
- Step 3: wet scrubber to recover HCl.
- Step 4: caustic scrubber to remove any residual HCl.

The data on the design of the combined treatment collected from the questionnaires are summarised in the tables below.

Table 11.18: Techniques applied in the shared vent treatment unit

Techniques		Number of plants (1)			
		Rapid quench	**Entrainment abatement**	**HCl absorption**	**Final caustic scrubber**
Incinerator	17	9/3/5	13/0/4	14/3/0	15/0/2
Thermal oxidiser	5	1/3/1	5/0/0	3/2/0	3/0/2
Catalytic oxidiser	2	0/2/0	1/0/1	0/1/1	2/0/0

(1) In sequence for the following cases: Technique applied/not applied/no information.

Most plants have devices to reduce entrainment (KO drums, demisters). Most plants use caustic scrubbing after thermal treatment. Some of the higher HCl values are related to plants which, according to the questionnaires, seem not to use demisters or caustic scrubbing.

Two plants use catalytic oxidisers, one in combination with an activated carbon adsorber. These plants show low emissions of NO_X, but high emissions of organic compounds (compared to thermal oxidisers and incinerators) (see Table 11.19 and Table 11.20 below). They are therefore not considered BAT candidates.

Table 11.19 summarises the emission data received for the pollutants that are related to the combustion process. Table 11.20 summarises the emission data for the process-related pollutants.

Table 11.19: Emissions from EDC/VCM end-of-pipe treatment – TVOC and combustion parameters

Plant	Average emission (mg/Nm^3) (1)					Monitoring (2)		
	NO_X	CO	SO_X	TVOC	No of years	NO_X	CO	TVOC
Catalytic oxidisers								
#6	1	0.1	ND	15 (3)	5	M	M	
#11	5		ND	51 (4)	5	S	C	C
Thermal oxidisers								
#4	36	10	ND	9	2	S	M	M
#5	16	4.9	0.2	0.6	1	S	S	S
#13b	9	1.1	ND	< 2.4 (5)	2			
#15	33	27	ND	ND	1	M	M	
#16	44	8.1	ND	ND	2	W	C	ND
#21	32	1.3	< 2.0	3.7	2	C	C	C
#22	83	6	ND	0.5	1	S	S	C
#22 (6)	ND	ND	ND	0.3	1			C
Incinerators								
#1	101	1.7	7.1	0.1	1	S	S	C
#2	42	3.3	ND	ND	4	S	C	
#3	78	1	ND	9 (7)	1	S		S
#7	54	1.7	0	0.1	3	C	C	C
#8	65	< 12	< 3.2	2.2	5	C	C	
#9	70	7.4	ND	< 1	5	S	S	M
#10	29	3.2	ND	< 1 (8)	4	S	S	S
#12a	29	0.2	ND	ND	1	ND	ND	ND
#12b	20	0.2	ND	ND	1	ND	ND	ND
#13a	8.1	1.7	ND	< 2.4 (5)	1	ND	ND	ND
#14a	82	0.7	3.5	0.2	2	C	C	C
#14b	16	0.2	1.2	0.2	2	S	ND	C
#17	58	2.1	2	1.6	4	ND	ND	ND
#18	91	5	ND	1	3	S	S	S

(1) All data in mg/Nm^3 (except for PCDD/F in ng/Nm^3) and at 11 % O_2. Average for 1–5 years.
(2) C: Continuous. W: Weekly. M: Monthly. S: Single measurements, typically 1–4/yr.
(3) From yearly measurements 2013–2016, range 10–18 mg/Nm^3.
(4) Mainly methane.
(5) Methane 0.1–0.2 mg/Nm^3.
(6) Additional data from the Member State; emissions from end-of-pipe treatment (incinerator, aqueous and caustic scrubber, adsorption activated carbon).
(7) Methane 4 mg/Nm^3.
(8) Without methane which is about 5 mg/Nm^3.
NB: ND: No data.

Table 11.20: Emissions from EDC/VCM end-of-pipe treatment – pollutants from process

Plant	Average emission (mg/Nm^3) (1)						ng TEQ/ Nm^3	No of years	Monitoring (2)	
	VCM	EDC	Ethene	TVOC	HCl	Cl$_2$	PCDD/F		EDC/ VCM/ Ethene	HCl
Catalytic oxidisers										
#6	2	2.3	13	15. (3)	6.7	4.4	0.023	5	M	M
#11	0.45	0.66	13.1	51 (4)	0.4	3	0.01	5	C	M
Thermal oxidisers										
#4	0.32	0.65	0.32	9	0.6	0.6	0.003	2	M	M
#5	0.02	0	5.53	0.6	12.7	7.2	0.053	1	S	S
#13b	< 0.01	< 0.01	< 0.01	< 2.4 (5)	4.2	0.4	0.019	2	S	S
#15	< LOD	< LOD	< LOD	ND	1.9	2.1	0.061	1	S	M
#16	0	0.03	0	ND	0.8	0.1	0.042	2	W	W
#21	ND	ND	ND	3.7	2.9	< 0.2	0.09	2		C
#22	ND	ND	ND	0.5	4	ND	< 0.05	1		C
#22 (6) (7)				0.3	3 (8)		0.04	1		C
Incinerators										
#1	ND	ND	ND	0.1	5.4	ND	0.002	1		
#2	< 0.2	< 0.2	ND	ND	3.2	ND	0.02	4	S	C
#3	< 0.1	< 0.1	< 0.1	9 (9)	< 5	ND	< 0.1	1	S	C
#7	< 1	< 1	< 1	0.1	5.7	1	0.006	3	S	C
#8	< 1	< 1	< 1	2.2	2.1	< 5	0.018	5	M	M
#9	< 1	< 1	< 1	< 1	5.7	< 5	0.121	5	M	M
#10	< 2	< 1	< 5	< 1 (10)	12.4	4.4	0.002	4	S	S
#12a	< 0.01	0.02	< 0.43	ND	28.8	n/a	0.003	1	S	S
#12b	0.002	0.01	< 0.48	ND	2.4	n/a	0.008	1	S	S
#13a	< 0.01	< 0.01	< 0.01	< 2.4 (5)	1.9	0.7	0.008	1	S	S
#14a	ND	ND	ND	0.2	2.4	ND	0.006	2		C
#14b	ND	ND	ND	0.2	3	ND	ND	2		C
#17	< 0.11	< 0.17	ND	1.6	13.5	2.5	0.041	4	S	C
#18	< 0.1	< 0.1	< 0.1	1	0.7	0.8	0.003	3	S	S

(1) All data in mg/Nm^3 (except for PCDD/F in ng/Nm^3) and at 11 % O$_2$. Averages for 1–5 years.
(2) C: Continuous. W: Weekly. M: Monthly. S: Single measurements, typically 1-4/ yr.
(3) From yearly measurements 2013–2016, range 10–18 mg/Nm^3.
(4) Mainly methane.
(5) Methane 0.1–0.2 mg/Nm^3.
(6) Additional data from one Member State for one EDC/VCM plant; emissions from end-of-pipe treatment (incinerator, aqueous and caustic scrubber, adsorption activated carbon).
(7) Corresponds to 0.18 g TOC, 1.9 g HCl and 25 ng TEQ PCDD/F per t of product (VCM + EDC sold).
(8) Total chlorine expressed as HCl.
(9) Methane 4 mg/Nm^3.
(10) Without methane which is about 5 mg/Nm^3.
NB: < LOD: below limit of detection.
ND: No data.

TVOC: Most of the plants with thermal oxidisers or incinerators reported average emissions below 5 mg/Nm^3. Only a few reported emissions above 5 mg/Nm^3 which did not exceed 10 mg/Nm^3.

EDC/VCM: For both EDC and VCM, the reported monitoring results were mostly below the detection limit or the limit of quantification which differed considerably in the questionnaires (< 0.01 mg/Nm^3 to < 2 mg/Nm^3). The reported averages above the detection limit were in the range of 0.002–0.3 mg/Nm^3 for VCM and 0.01–0.7 mg/Nm^3 for EDC. Catalytic oxidisers reported higher emissions, and for ethene and TVOC too.

HCl: Most plants reported average concentrations in the range of 1–10 mg/Nm^3. Three plants reported values below 1 mg/Nm^3 and four above (three of them in the range of 12–14 mg/Nm^3).

Chlorine: Chlorine concentrations were typically in the range of 0.5–5 mg/Nm^3, with three plants below and one above this range.

NO_X: High temperatures are needed to destroy some of the chlorinated compounds, and NO_X emissions are to be expected. The reported average emissions were in the range of 9–36 mg/Nm^3 for thermal oxidisers and 8–101 mg/Nm^3 for incinerators.

CO: Although some incinerators reported CO emissions below 1 mg/Nm^3, the average CO emissions for thermal oxidisers and incinerators were typically in the range of 1–10 mg/Nm^3.

Continuous monitoring of VOCs was in place at the plants using an activated carbon adsorber (one combined with a catalytic oxidiser, one with an incinerator) and at six of the other incinerators.

The monitoring frequencies for EDC/VCM and ethane are typically the same (if monitored at all), ranging from weekly monitoring to a singular measurement. The monitoring frequency for chlorine, if performed, is generally similar to that of HCl, ranging from continuous monitoring to a single measurement. The monitoring of PCDD/F is typically carried out once or twice a year.

For HCl, data from the continuous monitoring over one year from two EDC/VCM incinerators that use caustic scrubbers for final abatement showed the following distributions for HCl, with average emissions of 4.4 mg/Nm^3 and below 2 mg/Nm^3.

Table 11.21: Distribution of HCl emissions from EDC/VCM incinerators

Concentration (mg/Nm^3) (3 % O_2)	Corresponding percentile of	
	Daily average	**2-hour average**
Plant 1		
2	8	81
5	58	99.5
10	99.7	99.94
Plant 2		
2	86	99.3
5	99.7	99.98
10	100	100

Cross-media effects

- Emissions from the combustion of fuels (CO, NO_X).
- Waste water from the caustic scrubber.
- If an activated carbon adsorber is used, waste from the spent adsorbent.

Technical considerations relevant to applicability
Generally applicable.

Thermal oxidisers will be preferred if liquid residues are not incinerated on site.

Economics
For an existing plant operated with a catalytic oxidiser, it will be much more cost-efficient, if technically feasible, to upgrade the catalytic oxidiser to achieve a similar VOC abatement performance (whilst maintaining low NO_X and PCDD/F emissions) than to replace it with a new thermal oxidiser.

Driving force for implementation
Legislation.

Example plants
Some of the plants from the data collection as indicated above: SolVin, Jemeppe-sur-Sambre (BE); Vinnolit, Gendorf (DE); Vinnolit, Knapsack (Hurth) (DE); Ineos Vinyls, Strenungsund (SE); Shin-Etsu, Botlek (NL); Kem One, Lavera (FR).

11.4.1.4 Decoking

Decoking, which is considered an operation related to other than normal operating conditions (OTNOC), is carried out regularly but with a very low frequency.

Emissions from decoking are reduced by:

- optimisation of thermal/mechanical decoking to reduce the required frequency of decoking; and
- appropriate wet or dry dust abatement.

11.4.1.4.1 Optimisation of decoking

Description
Optimisation of thermal/mechanical decoking to reduce the required frequency of decoking.

Technical description
Coke formation in cracker tubes depends on several factors, and there are several techniques to reduce coke formation and the decoking frequency (see Section 11.4.3.4) that accordingly will contribute to reduce the emissions from decoking.

Thermal decoking
As an integrated technique, the dust load and decoking frequency can be reduced by optimisation of operating conditions, i.e. airflow, temperature and steam content across the decoking cycle, to maximise the coke removal (see Section 3.4.1.5).

Mechanical decoking
Optimisation of mechanical decoking (e.g. sand jetting) to maximise the coke removal as dust: Thermal decoking may be replaced (or the need for thermal decoking reduced) by mechanical decoking (sand jetting or shot peening) using a turbulent stream of impact-resistant particles in a carrier gas. The performance (to maximise coke removal) will focus on operating conditions (flow velocity) and the selection of the material used: non-angular, non-abrasive particles are entrained at a concentration of about 0.1 kg to about 10 kg per kg of gas (e.g. nitrogen), and the gas is introduced into the inlet of the furnace tubes at a gas flow rate corresponding to an outlet gas velocity of 25 m/s up to the sonic velocity of said gas, preferably at an outlet gas velocity of about 70 m/s to 200 m/s, thereby avoiding the use of a water scrubber or spray tower. This

prevents (or, in combination with thermal decoking, reduces) CO emissions from the process side and emissions from the furnace (although it will increase the dust load for abatement and the resulting waste to be disposed of). The technique may require the strengthening of the tube bends and an arrangement to protect the thermal elements.

11.4.1.4.2 Dust abatement

In contrast to lower olefin crackers, the waste gas is not routed back to the furnace for abatement of CO and dust for the following reasons:

- the need for additional process safety equipment and control measures to prevent blocking of the pipes and ensure complete combustion of the coke;
- coke can contain chlorinated hydrocarbons in concentrations above 1 % which would lead to the formation of hydrogen chloride which may damage the firebox and convection coils of the furnace;
- the separate removal of solids would still be necessary.

Description
Use of wet dust scrubbing, cyclones and/or fabric filters to retain the dust from decoking.

Technical description
The decoking of the cracker tubes results in a carrier gas or a steam/air mixture laden with dust. Dry and wet abatement devices are used to remove dust (see also Section 3.4.1.5.4 in the lower olefins chapter). In the data collection, most operators did not specify the dry abatement technique used; fabric filters may be used for dry dust instead of or in combination with cyclones. According to the data collection, three operators reported using both wet and dry abatement (and three neither), nine use only dry abatement and five use wet abatement. The removed dust is disposed of as hazardous waste.

11.4.1.5 Fugitive emissions to air

The control of fugitive emissions to air and related BAT for monitoring and prevention/reduction are described in the CWW BREF.

As VCM is a known carcinogen there have been strenuous efforts over recent years to minimise environmental releases, especially from fugitive sources, primarily as a health and safety measure to minimise workplace exposure.

11.4.1.5.1 Leak detection and repair programmes

Strict LDAR (leak detection and repair) regimes have proven valuable in the prevention of fugitive emissions and have particular relevance to EDC/VCM plants.

Fugitive emissions are reduced by installing leak-safe technology and by frequent inspections to check the integrity of all relevant sealings. This can be supported by installing fixed monitoring systems for measuring VCM/EDC concentrations.

11.4.1.5.2 Closed waste water collection systems and removal of volatile organic compounds from waste water

The volatile components of contaminated process effluent may go to atmosphere, and therefore closed collection systems are used to prevent emission before treatment by stripping. If process effluent is stripped to less than 1 ppm of EDC (see Section 11.4.2), then this reduces emissions to air from any subsequent effluent treatment.

11.4.2 Techniques to reduce emissions to water

The LVOC BREF only addresses effluent treatment at source and specific pretreatments. Subsequent waste water treatment steps are described in the CWW BREF. The data collection process has shown that most installations use a combination of pretreatment techniques. All sites use alkaline stripping to remove volatile organochlorine compounds, and those with a fluidised-bed oxychlorination unit carry out pretreatment to remove copper and suspended solids.

Findings from the data collection are summarised in Table 11.24 regarding emissions at the outlet of the strippers, in Table 11.25 regarding the pretreatment including solids removal, and in Table 11.22 and Table 11.23 below regarding the outlet of the final biological WWTP. They include calculations for specific emissions, based on the reported flows, concentrations and production capacities.

Table 11.22: EDC and VCM content in waste water after final treatment

Plant	**EDC** (mg/l)	**VCM** (mg/l)	**EDC** (g/t of EDC purified) (1)	**VCM** (g/t of VCM produced)
#2	≤ 0.007	< 0.001	0.011 (2)	NA
#3	0.0001	< 0.0005	0.001	NA
#5	0.20	0.03	0.12	0.06
#12	0.08	< 0.1	0.03	NA
#13	0.01	< 0.001	0.02	NA
#15	0.03	< 0.0015	0.15	NA
#16	0.08	0.015	0.036	0.01
#17	0.05	< 0.001	0.26	NA
#21	0.02	< 0.1	0.008	NA
#22	0.01	0.01	0.03	0.06

(1) EDC purified: Total of EDC produced and EDC returned from the VCM production to purification.
(2) From 2015; ≤ 0.05 g/t reported to be generally achieved under normal operating conditions.
NB: Averages from 1–5 years.
NA: Not applicable.

For Plants #13 and #17, calculated specific EDC loads are above those at the outlet of the stripper (0.01 g/t and 0.05 g/t) instead of significantly below, indicating that there may be other EDC sources at the chemical site.

Table 11.23: Pollutant content after final biological treatment

Plant	**OC reactor**	**Cu**	**Mon. Cu (1)**	**PCDD/F**	**TSS**	**COD**	**Cu (2)**	**PCDD/F (2)**	**Pretreatment**	
	(3)	mg/l		ng TEQ/l	mg/l	mg/l	g/t EDC	µg TEQ/t EDC	Precip./Flocc.	Filtration
#2	FL	0.04	W	0.02 (4)	25	38	0.35 (5)	0.09 (6)	Yes	No
#3	FL	0.001	M	0.0002	ND	50	0.04	0.01	No	Yes
#5	FL	0.016	M	0.03	29	63	0.05	0.09	Yes	No
#13	FL	0.003	W	ND	20	122	0.03	ND	Yes	No
#15	FL	0.075	W	0.08	30	75	0.23	0.19	Yes	yes
#16	FL	0.04	D	0.02	ND	ND	0.07	0.04	Yes	No
#17	FX	0.013	M	< LOD	41	169	0.26	0.00	No	No
#21	FX	0.08	W	0.09	42	150	0.14	0.22	No	No
#22	FX	0.01	A	0.01	5	ND	0.06	0.08	No	No
#22 (7)	FX	0.0029	A	< 0.006	ND	ND	0.02	< 0.04	No	No

(1) Monitoring; reported monitoring frequency:
D: 1/day. W: 1–2/week. M: 1–2/month. A: 1–3/yr.
(2) Per tonne of EDC produced by oxychlorination.
(3) FL: Oxychlorination fluidised bed.
FX: Oxychlorination fixed bed.
(4) From 2011–2015 data for normal operating conditions; range 0.0002–0.038 ng i-TEQ/l.
(5) 0.14–0.28 g/t in 2012–2015; further reduction expected because of refurbishment of pretreatment.
(6) From 2011–2015 data for normal operating conditions; range 0.001–0.28 µg i-TEQ/t.
(7) Additional data from one Member State; averages based on daily flow-proportional samples (except PCDD/F).
NB: < LOD: Below detection limit.
ND: No data.

For the final effluent, the calculations do not take into account that other processes/sources besides the EDC/VCM production may contribute to the emissions. This means that in these cases the calculated specific loads will be higher than the real emissions from the EDC/VCM process.

For example, for EDC, for Plants #13 and #17 the loads derived from the reported concentrations are higher than those in the stripper effluent which may be taken as an indication of the existence of further sources. And for copper and PCDD/F, emissions are also reported at sites where EDC is produced by the fixed-bed process only, without specification of the sources in the questionnaires. For one site with fixed-bed oxychlorination, a Member State provided data from measurements that indicate that roughly half of the average concentration in the final effluent of about 8 µg/l (based on yearly measurements for several years) can be allocated to the EDC/VCM production process (including emissions caused by corrosion) which would correspond to an average emission of 0.025 g/t of oxychlorination capacity, the rest coming from other processes/sources (e.g. the PVC production and cooling water purges).

11.4.2.1 Techniques to reduce the organic load to the WWT unit

11.4.2.1.1 Stripping to remove VOCs

Description
Stripping of waste water streams containing volatile chlorinated hydrocarbons**.**

Technical description
Volatile chlorinated organic compounds such as EDC, VCM, trichloromethane and carbon tetrachloride can be effectively removed by steam or air stripping to effluent concentrations of less than 1 mg/l. EDC from the top of effluent strippers is condensed by a water condenser. The stripped compounds can be recycled to the process.

Depending on the plant arrangement, stripping can be performed at atmospheric pressure or under vacuum. Vacuum stripping is expected to give the best stripping efficiency but requires larger columns and vacuum pumps. The waste water enters the column at pH > 10 in order to avoid corrosion and to allow chloral destruction (see the following section). The column has two or three packing beds of stainless steel or plastic, or has trays.

A few plants also apply stripping to the sludge from solids removal (see Section 11.3.2) before it goes to the filter press, and to the effluent from the filter press. This refers mainly to plants where solids removal is performed before stripping the waste water.

The operation of strippers will usually be controlled by physical parameters. To ensure removal efficiency, the outlet of the stripper is monitored at short time intervals (e.g. every 20 minutes) for EDC/chlorinated hydrocarbons using headspace gas chromatography, which is connected to an online alarm system. Process control may be supplemented by additionally monitoring dissolved organic carbon (DOC).

The stripping of VOCs from effluents is described in more detail in the CWW BREF.

Achieved environmental benefits

- Reduction of fugitive emissions from waste water.
- Reduction of emissions of chlorinated organic hydrocarbons to water.

Environmental performance and operational data

Table 11.24: Pollutant content in EDC/VCM stripper effluent

Plant	EDC (mg/l)	VCM (mg/l) (1)	Monitoring (2)	EDC (g/t) (3)(4)	VCM (g/t) (1)(4)(5)
#1	0.09	0	S	0.003	0.000
#2	0.19	< 0.001	W	0.08	0.000
#3	0.03	0	M	0.007	0.000
#4	0.5	*	D	0.11	0.000
#7	0.36	0	W	0.11	0.000
#8	< 0.2	*	M	0.000	*
#9	< 0.2	< 0.1	M	0.000	0.000
#10	0.024	< 0.1	W	0.005	0.000
#11	0.14	*	C	0.09	*
#13	0.09	< 0.01	W	0.01	0.000
#16	0.08	0.014	W	0.05	0.012
#17	0.19	0.001	D	0.45	0.007
#18	0.23	*	W	0.07	*
#21	0.17	0.021	D	0.02	0.011
#22	0.13	0.011	D	0.04	0.07
#22 (6)	0.07	0.017	D	0.04	<0.009

(1) * : No data and/or no VCM production.
(2) Reported monitoring frequency:
C: Continuous. D: 1–3/day. W: 1–3/week. M: 1–2/month. S: Single measurement.
(3) g/t of purified EDC (total of EDC produced and EDC returned from the VCM production to purification).
(4) Data < detection limit interpreted as 0.000.
(5) g/t of VCM produced.
(6) Additional data from one Member State; annual average based on daily flow-proportional samples.
NB: Averages from 1–5 years.

The reported average concentration values at the outlet of the strippers show a wide variation (EDC: 0.024–9.5 mg/l; VCM: 0.001–0.23 mg/l). Of 20 plants, 12 reported average EDC emissions of < 0.2 mg/l, 14 plants of < 0.4 mg/l and 15 plants of ≤ 0.5 mg/l; only the latter are listed in Table 11.24. In terms of specific loads, these emissions correspond to a range of 0.005–0.45 g EDC/t of EDC purification capacity for plants with a stripper outlet EDC concentration below 0.5 mg/l. It may be concluded that most of these plants will usually comply with the ELV of OSPAR Decision 98/4 which is 0.7 g chlorinated hydrocarbons per tonne of EDC purification capacity (annual average). Typically, because of the higher volatility and probable lower concentration at the inlet, concentrations of VCM are significantly lower than those of EDC, typically below 0.05 mg/l.

Reported monitoring frequencies ranged from continuous to monthly; this may refer to the frequency actually applied to control the process efficiency or to (lower) frequencies prescribed by the authorities. For 5 out of the 15 plants listed in Table 11.24, the reported emissions are based on daily or continuous sampling; they tend to cover the upper part of the emission range (0.1–0.5 mg EDC/l) (whereas 5 plants that reported emissions below 0.1 mg/l performed weekly or monthly monitoring).

Stripping is typically performed under atmospheric pressure. Two plants reported using a vacuum. Stripping under pressure, which according to the data collection is used at only one site, shows a comparatively poor performance in terms of achieved outlet concentration.

Cross-media effects

- Energy for vacuum generation (pumps).
- Heat for steam generation (available from process).

The stripping steam consumption required to achieve an EDC concentration of 0.16 mg/l in the stripper outlet could be up to 25 % higher compared to the consumption required to achieve 0.32 mg/l.

Technical considerations relevant to applicability
According to the data collection, all EDC and EDC/VCM plants use strippers for pretreatment. For low concentrations at the stripper outlet, the stripping efficiency can be affected by the water hardness (in particular when recycling water collected from slabs).

Driving force for implementation
Legislation (e.g. OSPAR Decision 98/4).

Example plants
Anwil, Wloclawek (PL); Ineos ChlorVinilys, Wilhelmshaven (DE); Kem One, Lavera (FR); Solvin, Jemeppe-sur-Sambre (BE); Vinnolit, Gendorf (DE); Ineos ChlorVinilys, Rafnes (NO); Spolana, Neratovice (CZ)

11.4.2.1.2 Hydrolysis to remove non-volatile organics (chloral)

Description
Decomposition of chloral hydrate by alkaline treatment (hydrolysis).

Technical description
Trichloroacetaldehyde (chloral) is present as chloral hydrate in the waste water from oxychlorination. Hydrolysis is carried out at alkaline pH to decompose chloral hydrate from the oxychlorination process: under alkaline conditions, chloral hydrate decomposes in an exothermic reaction to trichloromethane (which then is removed by stripping) and formate (which is easily biodegradable).

Caustic (e.g. sodium hydroxide solution) is added to the waste water before stripping in order to ensure alkaline conditions (pH > 10).

The same reaction is used to remove chloral from EDC by caustic washing.

Achieved environmental benefits
Reduction of emissions of chlorinated compounds to water.

Environmental performance and operational data
No information provided.

Cross-media effects
Increase of trichloromethane fraction in stripper output to the process.

Technical considerations relevant to applicability
Generally applicable.

Economics
Costs are expected to be low. Addition of caustic would be needed downstream anyway to remove solids (see Section 11.4.2.2.3).

Driving force for implementation
Legislation.

Example plants
Widely used.

11.4.2.2 Techniques to reduce copper, TSS and PCDD/F emissions to the WWT unit

The losses of catalyst are the main cause of copper emissions to water. PCDD/F generated during oxychlorination have a strong affinity to particulate surfaces such as the oxychlorination catalyst.

The emissions of copper and PCDD/F to water therefore depend on the process selection and the applied waste water treatment. Fixed-bed oxychlorination has virtually no carry-over of copper catalyst. Fluidised-bed technology allows some catalyst fines to transfer to process waste water. After stripping, treatment of waste water (by chemical precipitation, flocculation and filtration) is required to ensure efficient removal of PCDD/F and copper.

11.4.2.2.1 Process selection: Use of fixed-bed reactors for oxychlorination

The presence of dioxin-related compounds in the effluent from EDC production is influenced by the technology used in the oxychlorination process.

- Fixed-bed oxychlorination has virtually no carry-over of copper catalyst, which potentially could have been contaminated with PCDD/F, but the spent catalyst must be removed regularly from reactors.
- Fluidised-bed technology allows some catalyst fines to transfer to process waste water. The waste water needs to be pretreated by an appropriate combination of chemical precipitation, flocculation and filtration to remove these fines which than have to be disposed of as hazardous waste. Very low emissions to water of PCDD/F and Cu can be achieved.

Whilst the use of a fluidised catalyst bed leads to a greater catalyst entrainment to the process gas treatment system, it affords better temperature control (no hot spots) and thereby reduces the formation of by-products.

Description
Use of fixed-bed reactors for oxychlorination (if benefits are not outweighed by differences in process efficiency in favour of the fluidised-bed process).

Technical description
Fixed-bed oxychlorination is performed in one or a cascade of plugged flow tube reactors at 230–300 °C with the catalyst (cupric chloride on alumina) packed in the tubes while cooling water flows on the shell side for temperature control. The catalyst bed typically consists of cupric chloride on alumina and additives such as graphite (as diluents) to vary catalyst activity. The size of the tubular reactors varies from 2 m to 5 m in diameter and 4 m to > 10 m in length. They may comprise several thousand tubes for the catalyst.

Due to the highly exothermic oxychlorination reaction, special care is needed to ensure temperature control which is achieved by having different levels of catalyst activity at different stages of the reactor and split addition of oxygen. To achieve different activity levels, diluents (typically graphite) or staged catalysts (e.g. with $CuCl_2$ and KCl) are used. Thus, catalyst activity at the reactor inlet is normally low and increases to its maximum at the outlet. Catalyst dilution requires exact mixing techniques and appropriate charging procedures in order to avoid demixing, i.e. segregation of diluent from active catalyst when different materials are used. In reactor cascades, split addition of oxygen can be used and may also serve to avoid more easily explosive mixtures at the reactor inlet and possibly to reduce oxidation by-products.

To improve heat transfer and selectivity, ethylene may be fed in excess; unreacted ethylene in the reactor effluent gas is sent to a direct chlorination reactor for conversion to EDC.

Fluidised-bed oxychlorination reactors are typically vertical cylindrical vessels equipped with a support grid and feed sparger system designed to provide good fluidisation and feed distribution. The reaction is carried out on a slightly lower temperature bed (typically at around 220–260 °C). Fluidised-bed reactors offer the advantages of improved heat transfer and almost isothermal operation, and that the reaction can be carried out within the explosive limit, which makes feed control less critical. However, backmixing, which influences conversion and selectivity, cannot be avoided. Heat from the reaction is used to generate steam or is transferred to a hot oil system by internal cooling coils positioned in the fluidised bed.

Unlike fixed-bed reactors, fluidised-bed reactors suffer a constant loss of entrained catalyst. This is partly recovered from the process gas by cyclones and/or filtration systems; the rest will mainly find itself in the waste water from the quench system and then is almost completely removed by a waste water pretreatment to reduce emissions of copper and PCDD/F, with disposal of the produced sludge as hazardous waste.

Table 11.25 shows a comparison of the processes. However, many of the problems of either process can be minimised by skilful operation and appropriate measures:

- For example, the catalyst change in a fixed bed does not necessarily require a long shutdown as catalyst may be charged in a spare reactor, making a swift change possible.
- Good heat transfer can also be achieved in a fixed bed, and even close to isothermal operation is possible when a combination of catalyst loading pattern and proper reactor control is employed.
- For the fluidised-bed reactor, emissions to water from the catalyst entrainment can be minimised by partial recovery from the process gas (cyclone or filtration), followed by solids removal from the waste water and appropriate handling of the sludge.

Table 11.25: Comparison of fluidised-bed and fixed-bed oxychlorination systems

Technical issue	Fluidised bed	Fixed bed
Heat transfer	Good heat transfer	Temperature control problems because of generally poor heat transfer
	Near isothermal operation	Temperature distribution in catalyst bed is not uniform
	Good temperature control	Non-uniform temperature may affect product selectivity
	Always good mixing of catalyst particles	Static catalyst particles lead to occurrences of pore plugging or coking, with increased risk that unreacted substances may break through
Performance		
EDC purity	Higher	Lower
Ethylene yield	No information	More by-products but compensated by lower ethylene oxidation
Pressure drop	Lower and more stable	Higher – pressure drop increases because of coke formation and degradation of mechanical properties of the fixed bed
Catalyst performance	Stable performance	Faster catalyst deactivation
Maintenance		
Catalyst change	Only quick catalyst make-up	Longer shutdown for changing – each a complete catalyst change
Safety		
Flammable mixtures	Oxygen is usually introduced separately from ethylene and hence the reactants are usually only mixed in the bed. The fluidised bed then acts as a flame arrestor, which excludes or reduces explosion risk depending on the design of the distribution grid and sparger	All reactants (HCl, ethylene and oxygen) are mixed before introduction into the reactors, hence more risk of build-up of flammable mixtures
Emissions		
Oxychlorination generates PCDD/F irrespective of the type of bed. PCDD/F are partly adsorbed on catalyst particles	Some entrainment of catalyst particles	No entrainment during normal operation. However, special attention is required when the catalyst has to be changed (every one to three years). This operation is often followed by a washing operation. This technology generates waste catalyst loaded with PCDD/F, which must be handled accordingly
Source: [126, ECVM 2013].		

Some companies (outside Europe) combine both processes by first reacting the gases in an isothermal fluidised bed and then passing them across a fixed bed for optimal yields and conversion.

Achieved environmental benefits
There is low potential for waste water emissions of copper and PCDD/F. Therefore, there is no waste (sludge) from copper and PCDD removal.

Environmental performance and operational data
Data from one Member State for copper in the effluent of an EDC/VCM unit with fixed-bed oxychlorination, before combined final treatment (annual measurements over seven years): range: 31–222 µg/l, and average: 126 µg/l, corresponding to a specific load of around 0.09 g/t of oxychlorination capacity. These copper emissions are supposed to be partly from copper alloys used in the piping material.

Cross-media effects
In comparison to the fluidised-bed process, higher consumption of catalyst and more waste from the used catalyst.

Technical considerations relevant to applicability
Since the selection of the process (fixed bed versus fluidised bed) will determine the basic layout of the entire oxychlorination unit, the technique is only applicable for new plants.

As described, the process selection will have impacts on the environmental performance in terms of several aspects. Depending on the technical developments, the benefits of the fixed-bed process in terms of prevention of emissions to waste water may be outweighed by the benefits of the fluidised-bed process in terms of overall process efficiency.

Economics
No information provided.

Driving force for implementation
Economic considerations.

Example plants
Fixed-bed technology is used and licensed by different companies, e.g. INEOS.

Example plants in data collection: Spolana, Neratovice (CZ); Ineos Vinyls, Stenungsund (SE).

11.4.2.2.2 Recovery of catalyst fines from the gas phase

Description
A cyclone or a dry catalyst filtration system is used to reduce catalyst losses from the fluidised-bed reactor and therefore also their transfer to waste water.

Technical description
Cyclones or filtration are applied to retain catalyst fines before the process gas is contacted with water.

Achieved environmental benefits

- Reduction of hazardous waste from waste water pretreatment.
- Reduction of potential for emissions of copper and PCDD/F to water.

Technical considerations relevant to applicability
Cyclones are widely used to retain catalyst from the fluidised-bed reactor, and the technique is to maximise the recovery by appropriate design. Filtration is available as a feature of licensed oxychlorination processes.

Driving force for implementation
Economic and environmental considerations.

Reference literature
For filtration: [16, Uhde.ThyssenKrupp 2011].

11.4.2.2.3 Pretreatment to remove catalyst fines (TSS), copper and PCDD/F from waste water

Description
Removal of catalyst fines (total suspended solids (TSS)), copper and PCDD/F by an appropriate combination of chemical precipitation, coagulation and flocculation and membrane filtration.

Technical description
Copper from the entrained copper catalyst from the oxychlorination process may be partly dissolved in the acid process effluent. The dissolved copper can be removed by alkaline precipitation at pH 8–9 or above. The suspended catalyst and the precipitated copper can then be separated by flocculation and solids removal, typically by sedimentation and filtration. Filtration is typically carried out as membrane filtration (micro- or ultrafiltration), treating the suspension after decantation or the total effluent from solids removal. The sludge is dewatered, normally by means of a chamber filter press, before disposal as hazardous waste.

In most cases, the pretreatment for solids removal is carried out with the stripper effluent from the oxychlorination plant. However, in some cases it takes place before stripping. Then, care has to be taken to avoid fugitive emissions, and the sludge will have to be treated accordingly. The techniques that reduce TSS will also reduce the PCDD/F content.

Besides the measurement of pH for the operation of the treatment, monitoring of the solids content in the outlet is required to ensure good performance.

Chemical precipitation, flocculation and membrane filtration are all described in more detail in the CWW BREF.

Achieved environmental benefits
Reduction of pollutant emissions to water (copper and PCDD/F) and in waste (sewage sludge from biological treatment).

Environmental performance and operational data
Table 11.26 lists the average concentrations from the data collection and the corresponding specific loads for copper, TSS and PCDD/F after pretreatment. Table 11.27 gives the ranges of annual averages for these parameters.

Table 11.26: Average pollutant content in EDC/VCM effluent after pretreatment

Plant	**Copper** (mg/l)	**PCDD/F** (ng TEQ/l)	**pH**	**TSS** (mg/l)	**COD** (mg/l)	**Copper** (g/t of EDC) (1)	**PCDD/F** (μg TEQ/t of EDC) (1)
#1	0.6	ND	ND	17	ND	0.05	ND
#6	0.4	0.8	8.6	47	763	0.2	2.8
#7	0.6	0.6	8.8	20	1296	0.5	0.5
#8	0.4	ND	8.2	33 (2)	529	0.3	ND
#9	0.3	0.2	7.5	7	ND	0.2	0.1
#10	0.2	0.2	10.4	10	2978	0.1	0.1
#11	0.4	1.5	10.4	ND	3129	0.2	0.7
#15	0.5	0.8	8.7	75	425	0.9	1.3

(1) Load per tonne of EDC oxychlorination capacity.
(2) Trend: TSS 37–64 mg/l for first three years, 9 mg/l for last two years.
NB:
All plants use a fluidised bed for the oxychlorination process.
All plants combine flocculation/precipitation and filtration for pretreatment.
ND: No data.

Table 11.27: Pollutant content in EDC/VCM effluent after pretreatment – ranges of yearly averages

		Concentration			**Monitoring (1)**	
Plant	**No of years**	**Cu**	**PCDD/F**	**TSS**	**Cu**	**TSS**
		mg/l	**ng TEQ/l**	**mg/l**		
#1	< 1	0.6	ND	17	S	ND
#6	5	0.34–0.53	0.28–1.8	40–52	W	W
#7	3	0.58–0.6	0.04–1.58	16–26	W	W
#8	5	0.3–0.6	ND	9–64 (2)	W	W
#9	5	0.27–0.71	0.04–0.61	6–9	M	M
#10	5	0.12–0.36	0.05–0.42	8–15	W	D
#11	5	0.16–0.61	0.34–4.17	ND	M	ND
#15	1	0.54	0.8	75	W	D

(1) D: 1–2/day. W: 1–3/week. M: 1/month. S: Single measurement.
(2) Trend: TSS 37–64 mg/l for first three years, 9 mg/l for last two years .
NB:
All plants use a fluidised bed for the oxychlorination process.
All plants combine flocculation/precipitation and filtration for pretreatment.
ND: No data.

All plants reported using flocculation/precipitation and filtration. Membrane filtration of the waste water is expected to result in very low levels of TSS and PCDD/F, which is confirmed by the PCDD/F data for Plant #3 (Table 11.23). Higher values reported for pretreatment indicate that in those cases filtration is not fully applied.

The average emissions of suspended solids (TSS) vary from 7 mg/l to 75 mg/l which mainly reflect differences in the operation of the treatment since they deal with similar waste water from the same process. The data show a correlation of TSS and PCDD/F concentrations.

For TSS, two out of seven sites reported average TSS concentrations (average of one to five years) of ≤ 10 mg/l (with 15 mg/l as the maximum annual average), a third site (Plant #8) reported having improved from concentrations of about 60 mg/l (first three years) to 9 mg/l (last two years). Two other sites reported average concentrations ≤ 20 mg/l (with 26 mg/l as the maximum annual average).

For PCDD/F, these plants are in the range of 0.2–0.6 ng TEQ/l (or 0.2–1.6 ng TEQ/l regarding maximum annual averages), corresponding to a specific load of 0.1–0.5 µg TEQ/t of oxychlorination capacity (or 0.2–2.1 µg/t regarding maximum annual averages) which for most sites/years is less than the ELV of 1 µg/t for the final effluent given in OSPAR Decision 98/4.

The average concentration for copper is in the narrow range of 0.2–0.6 mg/l for all plants. Discarding the worst performer for solids removal (Plant #15), all plants are in the range of 0.05–0.5 g/t of oxychlorination capacity (or 0.1–0.6 g/t regarding maximum annual averages) which is less than the ELV of 1 g/t for the final effluent given in OSPAR Decision 98/4.

For the pollutant content after combined final biological treatment (see Table 11.23), if related to the oxychlorination (fluidised bed) as the hypothetical only source, the corresponding specific loads would range from 0.03 g/t to 0.08 g/t of oxychlorination capacity for copper (discarding Plant #2 and, again, Plant #15) and 0.01–0.19 µg TEQ/t of oxychlorination capacity for PCDD/F which compares favourably with the ELVs from OSPAR Decision 98/4 mentioned above.

Cross-media effects
Sludge from solids removal (hazardous waste).

Technical considerations relevant to applicability
Generally applicable.

Driving force for implementation
Environmental legislation (e.g. OSPAR Decision 98/4).

Example plants
Anwil, Wloclawek (PL); Ercros, Vila-Seca (ES); SolVin, Jemeppe-sur-Sambre (BE); Innovyn, Martorell (ES); SolVin, Rheinberg (DE); SolVin, Tavaux (FR); SolVin, Zandvliet (Antwerp) (BE); Ineos ChlorVinyls, Tessenderlo (BE)

11.4.3 Techniques to reduce raw material consumption and waste generation

Raw material consumption and waste generation are reduced by measures to:

- improve selectivity and therefore reduce the formation of unwanted compounds from side reactions;
- recover material for reuse;
- treat material to enable reuse;
- reduce the need for abatement measures that consume raw materials and produce waste.

The reuse of the by-product HCl via oxychlorination is at the very heart of the balanced process but it may also be marketed to be used for other purposes. Recycling, too, is inherent to the process. This mainly refers to unreacted ethylene from the VCM unit and often also the oxychlorination process, but also to several other process streams.

11.4.3.1 Direct chlorination

Yields and selectivity are high (> 99 %) and are ensured by the use of feed of a high purity and appropriate reaction conditions. Improvements in catalysts (e.g. replacing ferric chloride with other inorganic salts) are claimed to further reduce the formation of by-products in high-temperature chlorination (see Uhde/Vinnolit brochure [16, Uhde.ThyssenKrupp 2011]).

Contrary to the HTC process, in the LTC process, the catalyst has to be removed from the product by washing, implying a loss of catalyst and leading to the generation of sludge as waste (see Sections 11.2.2.1 and 11.4.2.2).

11.4.3.2 Oxychlorination

Process optimisation in order to reduce consumption of feedstock, improve process efficiency and reduce wastes will *inter alia* consider the following:

- Reaction temperature control: above 325 °C, the catalyst is deactivated and by-product production will increase, leading to CO and CO_2 generation. Operating at higher temperature leads to increased by-product formation.
- Optimal catalyst system design (dilution, particle size, preparation, etc.) can prevent overheating and the formation of impurities.
- Fluidised-bed reactors lead to less by-products because of the more homogeneous temperature. Fluidised-bed reactors produce a continuous hazardous waste from waste water pretreatment (sludge with contaminated catalyst and flocculation agents), whereas fixed-bed reactors show higher rates of spent catalyst which arise during periodic catalyst replacements. See Section 11.4.2.2.
- Oxychlorination feed: oxygen leads to higher yields than air. See Section 11.4.1.1.2.
- Measures to minimise EDC vent losses (like condensers or EDC absorption or chilled cooling) significantly improve yields.
- Purity of HCl (fresh and recycled): In most cases, HCl from the EDC cracking section is used as a source of chlorine. The organic content has to be controlled (e.g. VCM, acetylene) to avoid side reactions which will decrease the process efficiency in terms of raw material consumption. See also Section 11.4.1.1.1. Selective hydrogenation to ethylene is often used to remove acetylene from recycled HCl.

11.4.3.3 EDC cracking and VCM purification

Process optimisation in order to reduce consumption of feedstock, improve process efficiency and reduce wastes will *inter alia* consider the following:

- EDC feed purity is important because trace species in feed inhibit the cracking reaction. More stringent control of EDC feed purity can reduce fouling and by-product formation.
- Improved furnace design: countercurrent flow, avoiding hot spots, etc.
- Use of promoters or initiators: See Section 11.4.1.2.3.
- Quenching: Rapid cooling of the pyrolysis off-gas at the furnace outlet is done to avoid/stop side reactions and the formation of coke/tars at high temperatures. See Section 11.4.3.4.2.
- Use of burners with a flat flame in the EDC cracker furnaces. The use of these burners can reduce the hot spots on the walls of the process tubes and consequently the production of by-products due to the high temperatures. Alternatively, terrace wall crackers (e.g. Foster Wheeler design) can achieve homogeneous heat flux profiles without using flat flame burners. See also Section 11.4.3.4.4.

- EDC from VCM purification is recycled back to EDC purification.
- In order to reuse HCl for oxychlorination, the acetylene content needs to be controlled (see oxychlorination above).

11.4.3.4 Reduction of coke from EDC cracking

Preventing coke formation is a major issue in operating the furnace for EDC cracking, mainly because of the negative impacts of coke build-up on the selectivity of the reaction. The formation of coke is increased by high wall temperatures (including hot spots) and by the presence of highly chlorinated hydrocarbons, e.g. trichloroethylene.

During normal operation, coke is removed from the VCM, e.g. by filtration or by sedimentation. It also leaves the process by entrainment in the heavy ends. Coke that remains in the cracking reactor is removed from time to time by decoking (see Section 11.2.3.1). From any source, coke ends up as solid waste and is normally incinerated.

Additional to the required high purity of the feed (> 99.5 wt-%), there are a number of techniques to reduce coke formation. All the techniques listed below have as common achieved environmental benefits (although the effects in some cases may be low):

- improved selectivity of EDC cracking;
- lower coke generation/waste per tonne of product;
- lower energy consumption due to lower insulation by coke build-up;
- lower energy consumption for decoking.

Economic benefits will arise from a reduced decoking frequency and the resultant extended production cycles and better process performance, and are the main driving force for the implementation of the techniques.

11.4.3.4.1 Use of promoters

Keeping the reaction temperature below 500 °C prevents coke formation but decreases the reaction rate. High reaction rates at lower temperatures can be achieved by the use of promoters (see Section 11.4.1.2.3). But this will be only one of several factors (such as pressure and heat-load distribution) determining the optimal pyrolysis temperature profile.

11.4.3.4.2 Reduction of coke by rapid quenching

The rapid cooling of the process gas from cracking reduces side product formation. Substantial yield losses to heavy ends and tars can occur if cooling is done too slowly. Therefore, the hot process gas is normally quenched and partially condensed by direct contact with cold EDC in a quench tower. Alternatively, the process gas can first be cooled by heat exchange with cold liquid EDC furnace feed in a transfer line exchanger (TLE) prior to quenching in the quench tower. In this case, the application of a TLE to preheat and vaporise incoming EDC furnace feed saves energy by decreasing the amount of fuel gas required to fire the cracker furnace and/or steam needed to vaporise the feed.

11.4.3.4.3 Reduction of coke by pre-evaporation

Description
Coke formation is reduced by evaporating EDC upstream of the reactor to remove high-boiling coke precursors.

Technical description
Upstream EDC pre-evaporation reduces the formation of coke in the furnace, because high-boiling impurities in the feed EDC (which are the precursors for coke formation) are mostly retained in the evaporator and prevented from entering the furnace. Some coke will however be formed in the evaporator and must consequently be removed from there.

Reference literature
[16, Uhde.ThyssenKrupp 2011].

11.4.3.4.4 Use of flat flame burners

This consists of the use of burners with a flat flame or terrace wall burners in the cracker furnaces. The use of these burners can reduce the hot spots on the walls of the process tubes and the related side reactions at high temperatures.

The use of burners with a flat flame in the EDC cracker furnaces will deliver a lower coke formation rate. Alternatively, terrace wall crackers (e.g. Foster Wheeler design) can achieve homogeneous heat flux profiles without using flat flame burners.

The use of flat flame burners is essential to protect the tubes against damage by the burner flames / flame temperature (the flame temperature is > 1 000 °C, but the tube wall design temperature is approximately 650 °C).

Changes in the burner configuration will change the layout of the whole furnace and are therefore only applicable to new furnaces or major plant upgrades.

11.4.3.4.5 Reduction of coke formation by the use of appropriate construction materials

Description
Selection of tube construction materials that retard coke formation.

Technical description
Any nickel (including any nickel oxide sites) in the materials used for the construction of the cracker tubes has the potential to catalyse the formation of coke. This technique therefore relates to the use of materials with low nickel levels, or with an appropriate surface coating that blocks access to available nickel (oxide) sites.

Environmental performance and operational data
For EDC crackers, it has been reported that several metals act similarly and, from practical experience, there are no indications of different levels of coke formation. Effects may be low in comparison to those from process conditions.

Technical considerations relevant to applicability
The use of less resistant metals in cracker tubes may increase the risk of leakages and compromise safety.

11.4.3.5 Use of an incinerator to dispose of liquid residues and to recover chlorine as hydrogen chloride

Description

Use of an incinerator to dispose of liquid residues and to recover chlorine as hydrogen chloride. HCl is recovered from the incinerator off-gas (by wet scrubbing with water or diluted HCl) and reused (e.g. in the oxychlorination plant).

Technical description

Liquid residues that cannot be reused or marketed as by-products (mainly from the EDC purification unit) are incinerated (usually with air) and converted completely to CO_2, HCl and water. The incinerator may be shared with other installations that generate organochlorine wastes.

Often, the incinerator is designed as a combined waste gas/liquid incinerator to receive vent gases as part of the feed and treat the combined waste gas streams from the EDC/VCM process and possibly vents from other installations that produce organochlorine compounds (see Section 11.4.1.3).

The incineration temperature has to be high enough to ensure complete destruction of the chlorinated compounds (including pollutants such as PCDD/F which may be present in the heavy ends from the oxychlorination process). It has to be run in such a way as to avoid the *de novo* formation of PCDD/F which typically includes a quench directly after the incineration chamber (performed as a circuit with a certain purge as waste water). Heat is recovered as steam. For more information, see the WI BREF.

When run under pressure, the resulting process stream can be routed directly to fluidised-bed oxychlorination. However, in most cases HCl is recovered from the waste gas by aqueous scrubbers (absorbers), leading to a commercial-grade 25–35 % hydrochloric acid solution for internal use (e.g. for effluent neutralisation, water demineralisation) or for external sale; residual HCl and Cl_2 are further abated by caustic scrubbing.

Achieved environmental benefits

- Disposal/destruction of hazardous residues.
- Recovery of chlorine as HCl.
- Reduction of emissions to air (when used for combined waste gas treatment).

Environmental performance and operational data

In accordance with Chapter IV of the IED, to ensure complete destruction of the organochlorine compounds, a temperature of > 1 100 °C is required in the last combustion stage for at least two seconds.

For emissions to air, see Section 11.4.1.3.

Heat recovery from the incinerators: According to the data collection, reported energy recovery/savings are in the range 180 GJ/yr to 540 GJ/yr.

Cross-media effects

NO_X emission from the combustion process.

Driving force for implementation

Environmental legislation. The requirements of Chapter IV of Directive 2010/75 EU will apply to these plants. This sets emission limit values for a wider range of substances and requires their continuous monitoring.

Example plants
According to the data collection, most EDC/VCM plants in the EU have a liquid incinerator on site which is typically also used for the end-of-pipe treatment of the combined EDC/VCM waste gas streams.

The data collection shows that, in the EU:

- eight installations use *in situ* liquid incineration to recover HCl;
- two installations have *ex situ* liquid incineration;
- four of them reported that the vents from this liquid incinerator are channelled to the shared vent treatment unit;
- one installation reported that the liquid incinerator is integrated into the shared vent treatment unit;
- other plants reported that the vents are channelled to the OC reactor.

Reference literature
No reference literature provided.

11.4.3.6 Recovery of chlorinated organic by-products

Description
Isolation and purification of chlorinated compounds for further use.

Technical description
In some plants, major by-products such as chloroethane and 1,1,2-trichloroethane are recovered and reused (or marketed for use) as feedstock for other chlorinated hydrocarbon processes. For example, 1,1,2-trichlororethane may be used to produce 1,1-dichloroethylene, and monochloroethane can be recycled to the oxychlorination section or used as a feedstock for ethyl cellulose manufacture.

Some of the light and heavy fractions can be used as feedstock for other chlorination processes, but this option is declining due to the reduced production of chlorinated solvents.

The application of the technique depends on the sufficiently reliable demand or availability of downstream users.

Achieved environmental benefits
This technique reduces waste generation and emissions to air from waste incineration.

Technical considerations relevant to applicability
The technique may imply major changes in the distillation unit.

Economics
The economic balance contains lower operational costs for waste disposal/treatment, and benefits from sales or internal reuse versus the investment in additional distillation facilities and the related operational costs (mainly energy).

11.4.4 Techniques to reduce energy consumption

Techniques to reduce energy cover process options (e.g. HTC) to reduce the energy demand or to enhance recovery, and to make use of the several opportunities for heat recovery in the EDC/VCM process.

The direct chlorination and oxychlorination reactions are highly exothermic. However, the EDC cracking process is an endothermic reaction, and the EDC and VCM separations are energy (steam) consumers. This provides opportunities for energy recovery and reuse. Though dependent on the unit design and on the process integration inside the overall chemical facility, some common practices in EDC/VCM units are:

- heat recovery from the furnace combustion gases;
- heat recovery from the process gas leaving the cracker furnace;
- steam generation or recovery of heat to the hot oil system in the oxychlorination reactor;
- in the case of high-temperature chlorination, use of the low level heat of reaction to vaporise/distil the EDC and/or to boil some distillation columns;
- heat recovery from the off-gas from incinerators and oxidisers.

Electric energy is mainly needed for compression. For oxychlorination, the consumption is reduced by using pure oxygen (instead of air) as the oxidant (see Section 11.4.1.1.2).

11.4.4.1 Use of a boiling reactor for direct chlorination

Description
Direct chlorination of ethylene is carried out using boiling reactors.

Technical description
The use of a boiling reactor which allows the distillation of EDC from the liquid reaction mixture is the core element of the HTC process (see Section 11.2.2.1) to achieve the environmental benefits listed below (compared to the LTC process).

Achieved environmental benefits

- Reduced energy consumption regarding the direct chlorination and the integrated EDC/VCM process.
- Reduced consumption of catalyst.
- Prevention/reduction of water consumption and waste water generation.
- No waste from catalyst separation.

Technical considerations relevant to applicability
Because of the basic differences in the layout and interface to the integrated process, replacement of a LTC unit with a HTC unit means building a new direct chlorination plant, with additional measures to adjust the process stream and energy interconnections with the other units of the EDC/VCM process.

Economics
The investment is higher compared to LTC but there are benefits in terms of operational costs (energy, catalyst, waste disposal).

Building a new DC unit is a major investment.

Driving force for implementation
Economics.

Example plants
In the data collection, about half of the installations reported using boiling reactors.

Reference literature
[17, Rossberg 2006], [18, Cowfer et al. 2006].

11.4.4.2 Techniques to reduce energy consumption for EDC cracking

Process optimisation in order to reduce the energy consumption at the EDC crackers will *inter alia* consider the following:

- Heat recovered from the process gas leaving the cracker furnace could be used to vaporise the EDC feed to the furnace or to generate steam, depending on the energy situation of the plant. According to the data collection, the majority of plants recover heat from the process gas exiting the furnace
- EDC cracking process selection: Higher pressure processes (2.0–3.0 MPa) are often used because the high pressure reduces the furnace size, improves heat transfer, and makes the downstream separation easier. Medium pressure (1.0–2.0 MPa) leads to less by-product formation while downstream separation is still possible. However, in new installations low-pressure cracking is normally used as this reduces the by-product formation significantly.
- For vapour-fed crackers, a feed purge upstream of the EDC cracking is used to avoid iron build-up (and a decrease of heat transfer).
- Use of promoters in EDC cracking (see Section 11.4.3.4.1) will reduce the energy demand.
- More severe cracking conditions will lead to higher EDC conversion to VCM (compared to the typical 50–65 % conversion). The higher the cracking conversion, the lower the EDC recycling and thus the lower the energy usage for EDC purification. However, higher temperatures and higher cracking conversions tend to increase side product and coke formation.

11.5 Emerging techniques

11.5.1 Ethane-based VCM production

Description
New catalytic process technology based on ethane rather than ethylene feedstock has been at the testing stage at a 1 000 t/yr pilot plant at Wilhelmshaven, Germany, since May 1998.

Commercially developed
To date, no commercial industrial manufacture has been undertaken.

Level of environmental protection
No information provided.

Cost savings compared to existing BAT
A 20–30 % reduction in production costs across the PVC chain.

Chance of becoming BAT in the future
No information provided.

When it might become commercially available
No information provided.

References
[101, Khoo 2013].

11.5.2 Direct oxidation of HCl to replace oxychlorination

Description
Oxychlorination is avoided by direct oxidation of HCl to Cl_2 (Sumitomo process).

The concept underpinning the OC reaction is achieving a balanced process, by reusing the HCl generated in the EDC cracking directly for EDC production.

Alternatively, HCl could be converted directly into Cl_2, which would avoid the drawbacks of the OC reaction (e.g. the generation of more by-products in comparison to direct chlorination). This would be possible by the means of the classical Deacon reaction:

$$2\ HCl + 0.5\ O_2 \rightarrow Cl_2 + H_2O\ (+\ 14\ kcal/mol)$$

One alternative would be the electrolytic oxidation of HCl as applied, for example, in the context of the manufacture of TDI (see Chapter 10 of this BREF).

Another approach would be to use a cyclic oxidation process. Probably the best-known application was proposed by Kellogg (A.G. Oblad (1969) 'The Kel-Clor process' Ind. Eng. Chem. 16 (7) pp. 23–26): A cyclic oxidation process using nitrosyl sulphuric acid ($HNSO_5$) for the oxidation of HCl at 4 bar and 260–320 °C. However, this process has been used on a large scale for only a few years and has not yet proven to be economically viable.

To use the Deacon reaction, improved catalysts have been developed that show higher activity and allow for lower reaction temperatures, thus shifting the equilibrium towards a higher yield in chlorine.

Sumitomo has developed the following process: Hydrogen chloride and oxygen react in a gas-phase reaction in a fixed-bed reactor containing a Ru/Ti catalyst. Reaction heat is removed using heat transfer salt and recovered as steam. The process gas is quenched, and water and unreacted HCl are removed by absorption. HCl is recycled. The process gas is dried using concentrated sulphuric acid. Chlorine is separated by compression and condensation.

Commercially developed

A plant with a chlorine capacity of 100 000 t/yr started in 2003.

Level of environmental protection

The process is reported to consume 1.05 tonnes of HCl, 163 Nm^3 of O_2 and 165 kWh per tonne of chlorine. The energy consumption would be much less compared to using electrolysis (1 100 kWh/t).

Regarding the production of EDC, the benefits of using direct HCl oxidation instead of oxychlorination are that it:

- raises the overall yield for EDC to over 99 % (see direct chlorination);
- avoids emissions to air and water related to the OC process (i.e. avoids the majority of emissions of chlorinated compounds of a balanced EDC/VCM unit) (including processing of by-products);
- avoids wastes related to the OC process.

Cost savings compared to existing BAT

Costs for the Sumitomo process will have to be compared to the OC process plus the related downstream facility minus the costs related to the DC capacity needed to replace OC.

Costs savings related to BAT are mainly the costs of the replaced OC process regarding:

- waste gas treatment;
- waste water treatment: stripper and, for fluidised-bed reactors, solids removal including sludge disposal;
- waste incineration;
- waste disposal (fixed-bed OC: spent catalyst).

Chance of becoming BAT in the future

High. The process itself seems to only generate low levels of emissions and is expected to also be of commercial interest for other processes that use chlorine and produce HCl as a by-product, e.g. the manufacture of TDI/MDI.

When it might become commercially available

Available for licensing.

References

[102, Iwanaga et al. 2004].

12 HYDROGEN PEROXIDE

12.1 General information

Hydrogen peroxide (H_2O_2) is widely used in many industrial areas, particularly in the chemical industry and environmental protection. The only degradation product from its use is water, and thus it has played a significant role in environmentally friendly production methods in the chemical industry.

In Europe, 50 % of hydrogen peroxide is used in chemical synthesis. Sodium percarbonate, used in detergents, is the largest single outlet for hydrogen peroxide in western Europe. Hydrogen peroxide is also used to manufacture other bleaching compounds, e.g. sodium percarbonate. Other important products produced in western Europe that use hydrogen peroxide include propylene oxide, epoxidised oils (speciality plasticisers), catechol/hydroquinone (photographic industry, polymerisation inhibitors, antioxidants, chemical intermediates), hydrazine, organic and inorganic peroxides, peracetic acid and caprolactone. Hydrogen peroxide is also widely used in the manufacture of pharmaceutical compounds.

The next most significant application in Europe is paper bleaching; 41 % of hydrogen peroxide is used in this way. It is used for the bleaching of chemical pulp, mechanical pulp and for the de-inking of recycled paper. This latter use in particular is consuming increasing volumes of hydrogen peroxide.

With 8 % of hydrogen peroxide being used in the textile industry, it is currently the dominant bleach in the industry, although the market for all textile bleaching agents in western Europe is stagnant to declining.

Other uses of hydrogen peroxide include the treatment of industrial effluent and of municipal water. It is also used for disinfection, hair bleaching, cosmetics, food processing, aseptic packaging, rocket fuel, wood bleaching and cleaning of etched microchips, etc.

Although hydrogen peroxide is not an organic chemical, it is included in this BREF because it is produced using predominantly organic substances. It is produced on an industrial scale by the alkylanthraquinone oxidation (AO) process. This process involves the sequential hydrogenation and oxidation of an alkylanthraquinone dissolved in a mixture of organic solvents followed by liquid-liquid extraction to recover the oxidation product, H_2O_2.

In 2010, the production capacity of hydrogen peroxide in Europe was 1.4 million tonnes, which was 35 % of global capacity. European production of hydrogen peroxide is summarised in Table 12.1 below.

Table 12.1: European producers of hydrogen peroxide

Country	City	Operator	Capacity (kt/year)
Austria	Weissenstein	Evonik	50
Belgium	Zandvliet (Antwerp)	Solvay	230
Belgium	Jemeppe-sur-Sambre	Solvay	70
Belgium	Antwerp	Evonik	110
Finland	Oulu	Kemira	75
Finland	Voikkaa	Solvay	65
France	Jarrie	Arkema	115
Germany	Bernburg	Solvay	70
Germany	Rheinfelden	Evonik	50
Germany	Leuna	Arkema	40
Italy	Rosignano	Solvay	35
The Netherlands	Delfzijl	Peroxychem (now Evonik)	60
The Netherlands	Europoort	Kemira	46
Norway	Rjukan	Akzo Nobel	21
Poland	Pulawy	Zaklady Azotowe Pulawy	10
Portugal	Povoa de Santa Iria	Solvay	14
Slovenia	Ljubljana	Belinka Perkemija	18
Spain	Sabinanigo	ERCROS	12
Spain	La Zaida	Peroxychem	52
Sweden	Helsingborg	Kemira	60
Sweden	Alby	Akzo Nobel	100
Sweden	Bohus	Akzo Nobel	70
United Kingdom	Warrington	Solvay	50

Key environmental issues

The key environmental issues for the production of hydrogen peroxide are as follows:

The AO process' main VOC emissions to air (mainly solvents such as alkylated benzene) are generated in the oxidation section. There are several effluents to water from different process sections. Residues and waste are generated in the working solution reversion and catalyst regeneration. The process may generate a waste stream of quinone-derived by-products that requires environmentally acceptable disposal.

Although the process reactions are exothermic, the process requires significant energy input.

12.2 Applied processes and techniques

12.2.1 Process options

Industrial production of hydrogen peroxide has moved from wet chemical processes, through electrochemical processes, to organic autoxidation processes.

Large-scale plants came with the organic autoxidation processes, especially the alkylanthraquinone process. In 2002, the global production capacity excluding China was estimated to be 2 800 kt/yr (calculated as 100 % H_2O_2), and it has further increased since then.

An organic autoxidation process with only a limited contribution to total production was the 2-propanol process (Shell), where the oxidation of 2-propanol with oxygen led to the formation of hydrogen peroxide and acetone, the latter being hydrogenated back to 2-propanol. Another autoxidation process based on the oxidation of methylbenzyl alcohol to hydrogen peroxide and acetophenone was developed by ARCO (Lyondell) but has not been commercialised.

Today, virtually all hydrogen peroxide is produced by the alkylanthraquinone process (the so-called autoxidation or AO process).

The trend in hydrogen peroxide production is towards large-scale plants that generate savings in capital and fixed operating costs. Some of these plants are directly connected to downstream production processes such as the manufacture of propylene oxide by the HPPO process.

This document covers solely H_2O_2 production and does not cover downstream derivatives.

[2, Goor et al. 2007], [3, Fierro et al. 2006].

12.2.2 The autoxidation process

[2, Goor et al. 2007], [3, Fierro et al. 2006].

12.2.2.1 Autoxidation chemistry and choice of working solution

The predominant industrial method for manufacturing hydrogen peroxide is the autoxidation (AO) of alkylanthraquinone. The process consists of cyclic hydrogenation and oxidation steps. Reactions are performed in a solution of solvents and quinones/hydroquinones (working solution (WS)).

Choice of solvent: The solvent is always a mixture because alkylanthraquinones dissolve readily in non-polar aromatic solvents, such as alkylated benzenes, whereas hydroquinones dissolve well in polar solvents, such as alcohols and esters. As with the quinone system, which is described below, the solvent mixture is also required to satisfy a number of criteria; namely good solubility of both quinone and hydroquinone, good resistance to both hydrogenation and oxidation, low solubility in water and aqueous hydrogen peroxide solutions, lower density than water to ensure separation of the two phases during extraction, low volatility, high distribution coefficient for hydrogen peroxide in water relative to the solvent water system, and low toxicity. Besides the solvent and the alkylanthraquinone, the WS may contain additives (e.g. organic amines) to improve selectivity.

Hydrogenation: An alkylanthraquinone derivative is hydrogenated to the corresponding anthrahydroquinone (AHQ) using a palladium catalyst.

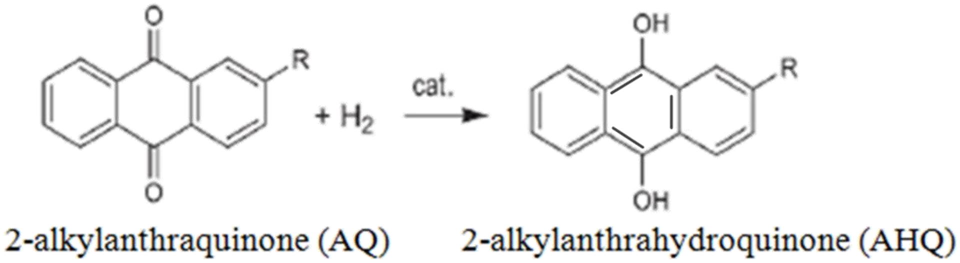
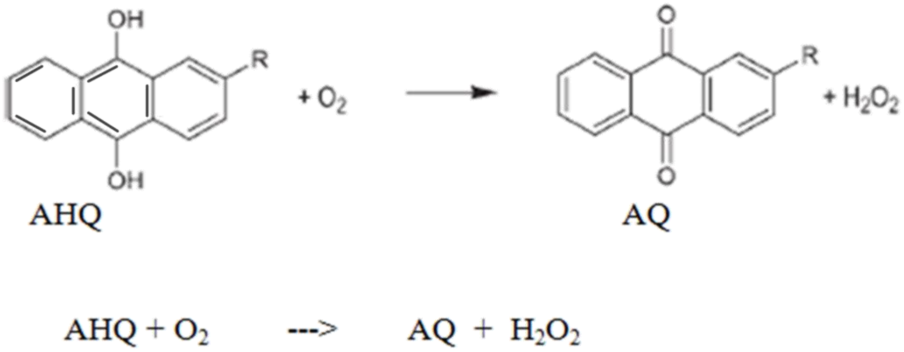


Figure 12.1: Reduction of AQ to AHQ

Oxidation: H_2O_2 is formed when the AHQ solution is oxidised back to AQ by bubbling air or oxygen through the solution. In the next step, H_2O_2 is extracted with water from the organic solution, which is then returned to the first hydrogenation step, resulting in a cyclic process. The extracted crude aqueous solution contains 20–50 % H_2O_2 and is purified, e.g. by washing with an organic solvent. Finally, the aqueous solution is concentrated to give a 50–70 % H_2O_2 solution.



$AHQ + O_2$ ---> $AQ + H_2O_2$

Figure 12.2: Oxidation of AHQ to AQ and hydrogen peroxide

Choice of working components: The choice of quinone depends mainly on its properties, especially the solubility of the products formed in the AO process. Examples of commonly used quinone compounds are: 2-ethylanthraquinone, 2-tert-butylanthraquinone, 2-neopentylanthraquinone, 2-isohexenylanthraquinone, diethylanthraquinones, mixtures of 2-amylanthraquinones, and mixtures of different alkylanthraquinones. The quinone or quinone mixture that is used as the working compound in the working solution must fulfil some essential criteria such as:

- good solubility of the quinone form to prevent precipitation in the oxidised working solution;
- good solubility of the hydroquinone form to maximise the capacity of the working solution; the productivity of the working solution is defined as the quantity of hydrogen peroxide that can be produced per m^3 of recycled working solution;
- ability of hydrogenation and oxidation degradation products to be regenerated to active quinones;

- availability and price.

As mentioned above, the formation of degradation products and their ability to be regenerated to active quinones play a role in the choice of quinone. In addition to hydroquinone formation, a number of secondary reactions occur during the hydrogenation step. By ring hydrogenation, 2-alkyl-5,6,7,8-tetrahydro-9,10-dihydroxyanthracene (THAHQ) is formed, which is also oxidised by oxygen to regenerate 2-alkyl-5,6,7,8-tetrahydroanthraquinone (THAQ, known as ‘tetra’), with simultaneous quantitative formation of hydrogen peroxide. Although ‘tetra’ is more readily hydrogenated than a 2-alkylanthraquinone, the resulting ‘tetra’ hydroquinone is much more difficult to oxidise.

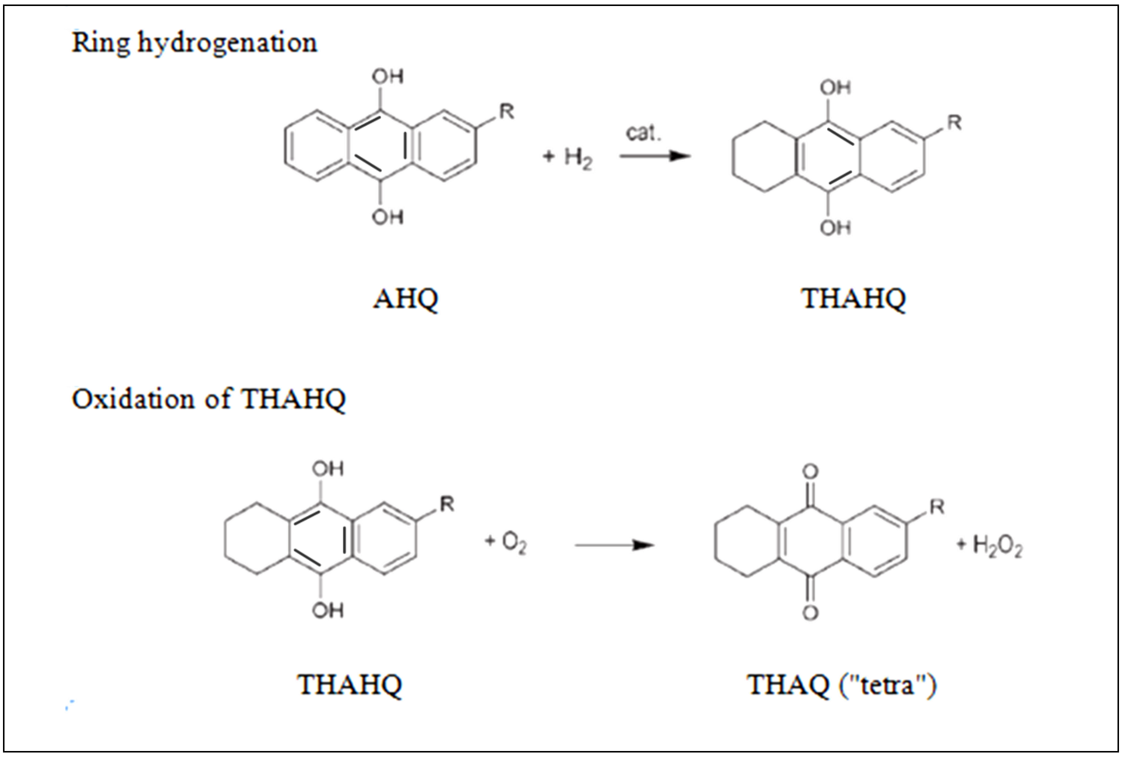


Figure 12.3: Side reactions during hydrogenation and oxidation

The formation of ‘tetra’ in the synthesis loop depends on the process conditions and has led to two methods for carrying out this process.

a) The ‘anthra’ system

When the ‘tetra’ content of the working solution is kept low (i.e. if AHQ is formed almost exclusively during hydrogenation), the process is referred to as the ‘anthra’ system. ‘Tetra’ formation is suppressed by using different techniques, including selective catalysts, special solvents, special working compounds, and mild hydrogenation conditions (e.g. the use of olefins has been recommended for the steady dehydrogenation of ‘tetra’).

Specific drawbacks of this route: when the ‘anthra’ system is used, tautomeric 2-alkyl-10-hydroxy-9-anthrone (oxanthrone) is also formed during hydrogenation and the subsequent oxidative dimerisation of anthrone may lead to dianthrones, which represent a loss of quinone.

Specific techniques of this route: the build-up of anthrones and oxanthrones can be minimised by adding an aromatic tertiary amine to the working solution or by pretreatment of the hydrogenation catalyst with halide.

b) ‘All-tetra’ system

If ‘tetra’ formation is not suppressed during hydrogenation or ‘tetra’ is not dehydrogenated, an equilibrium is reached in which the hydroquinone charged to the oxidiser consists solely of THAHQ. Such a system is called an ‘all-tetra’ system. This means that the hydroquinone leaving the hydrogenation step is always the ‘tetra’ hydroquinone THAHQ.

Specific drawbacks of this route: dianthrone formation does not occur in the ‘all-tetra’ system, but oxidation of THAHQ leads to a by-product, the ‘epoxide’. The epoxide does not participate in the formation of hydrogen peroxide and must be reconverted to ‘tetra’ in the reversion sector.

Different measures have been suggested for regenerating ‘tetra’ from the epoxide.

12.2.2.2 Process steps: Hydrogenation

The working solution (WS) is usually hydrogenated in the presence of a palladium catalyst (which, in comparison to the nickel catalyst formerly used, offers benefits in terms of the conversion rate of hydrogen, catalyst exchange and regeneration, and being non-pyrophoric). The hydrogenation reactor is operated at a slightly elevated pressure (up to 5 bar) and at a temperature usually below 100 °C. The heat of reaction released can be removed before, during or after hydrogenation. To minimise by-product formation, conversion of anthraquinone is normally kept below 60 % of the total quinone.

The palladium catalyst can be used as suspended palladium black or supported on a carrier for slurry or fixed-bed operation. Unless fixed bed, the hydrogenation step includes a primary filtration stage, which retains the catalyst and allows it to be returned to the hydrogenation reactor by periodical back-flushing. The design of the hydrogenation reactor depends on the type of catalyst used. Suspended palladium black is preferentially used in loop reactors made of tubes. Maintaining constant catalyst productivity is easily achieved by withdrawing used catalyst and adding fresh catalyst; catalyst regeneration can be done on site. Supported catalysts have a particle size of 0.05–0.2 mm; these large particles are much more easily filtered than the fine palladium black. To keep the catalyst fluidised, the reactor is agitated either mechanically or with gas. In the case of gas agitation, excess hydrogen is sparged at the bottom, and unreacted hydrogen at the top of the reactor is recycled.

In fluidised-bed hydrogenation reactors, good contact between the three reacting phases is obtained and thus the productivity and selectivity are generally high. However, the catalyst particles can be broken down by abrasion and can block the filters needed to separate the suspended catalyst and the hydrogenated working solution. This kind of reactor is also subject to back-mixing. Therefore, the use of suspended catalyst frequently requires the use of a larger hydrogenation reactor and an expensive filtration section to obtain a fully hydrogenated form.

Fixed-bed reactors (see below), with a catalyst particle size of 0.5–10 mm, do not need catalyst filtration.

Catalyst is regenerated by means of steam or acid wash for example. At most sites, used catalyst is not regenerated on site but is returned to the off-site provider and regenerated there.

There are several hydrogenation reactor configurations differing *inter alia* in the choice of catalyst. Examples are as follows [2, Goor et al. 2007]:

- Using palladium black: Working solution and hydrogen are fed to a loop reactor cascade, the hydrogen is almost completely converted using palladium black, with the remaining hydrogen vented from a separator after the reaction; a part of the hydrogenated working solution is returned to the reactor feed. Developed by Degussa.

- Using supported catalyst: Various reactor designs may be used (tube reactor, column reactor, continuously stirred reactor). Hydrogen is fed in excess to the working solution as reagent and also for agitation. The reaction is carried out with supported palladium catalyst. The excess hydrogen is compressed and returned to the reactor. A hydrogen off-gas stream can result from the depressurisation of the working solution (if not recycled). Developed by Laporte.

- A variation is based on the concept of the foam regime developed by Solvay. The hydrogenation reaction is conducted at a moderate temperature (50–70 °C) with a surface velocity of the hydrogenating gas in the range of 3–10 cm s^{-1} and a liquid surface velocity in the range of 0.5–1.0 cm s^{-1}, while the liquid to gas ratio is kept below 0.15. Under these conditions, no degradation of the working solution by over-hydrogenation is observed despite the high hydrogenation rates achieved [3, Fierro et al. 2006].

- Using fixed-bed catalyst: Hydrogen and working solution are fed co-currently to the reactor. This achieves virtually complete conversion of hydrogen. A part of the hydrogenated working solution is returned via a heat exchanger to the reactor feed. First developed by FMC. See also Solvay patent EP 1.051.352.B1 [9, Vandenberg 2003].

- Instead of particles, honeycomb monoliths can be used as support. The monoliths contain parallel channels with an open diameter of 1–2 mm. The monolith combines a large geometrical surface area with a low pressure drop and a high degree of uniformity which makes it suitable for a process characterised by high flow rates and a need for high selectivity. Hydrogen and working solution are distributed through parallel small channels, forming a Taylor flow. The improved mass transfer characteristics of a Taylor flow make it an attractive flow pattern for carrying out gas-liquid operations in small channels. Although the catalyst structure is fixed, the reaction conditions are closer to a fluidised-bed reactor than a fixed-bed reactor using catalyst particles. Developed by AkzoNobel.

12.2.2.3 Process steps: Oxidation

Before the hydrogenated working solution can be fed to the oxidation step, it must pass through a safety filtration step to prevent any palladium entering the oxidiser and extractor, which would result in the decomposition of hydrogen peroxide.

Catalyst-free hydrogenated working solution is usually oxidised with slightly pressurised air, which is sometimes enriched with oxygen. The stoichiometric oxygen consumption is 659 Nm^3 per tonne of hydrogen peroxide, but an excess of 20–40 % is normally used. Oxidation with air proceeds at 40–70 °C and pressures ranging from atmospheric up to 10 bar. The reaction is exothermic and not catalysed (autoxidation) and the overall rate depends on temperature, oxygen partial pressure and liquid-gas interfacial area. The temperature of the working solution will increase over the reactor. A higher operating temperature means a higher reaction rate, or an increased production rate per unit reactor volume, but also more by-products.

Several types of oxidisers are currently used: working solution and air may flow either co-currently or countercurrently in a single- or multiple-column system with or without internals. The reactors are normally bubble columns, either with packing or sieve plates.

The off-gas from the oxidation with air is routed via condensers to an adsorber unit where solvent is recovered by adsorption on activated carbon and then released to atmosphere.

12.2.2.4 Process steps: Product extraction and purification

Hydrogen peroxide is recovered from the oxidised working solution by water extraction. The most common extraction technique is a sieve-tray extraction column, but a number of other extractors such as packed columns, pulsed packed columns, spray columns and mechanical extractors have been described.

The working solution leaving the extraction unit contains dispersed water droplets and is fed into coalescers to separate the free water. Before the working solution is recycled to the hydrogenation reactor, the moisture content in the solution may be adjusted. Further details on working solution drying are given in Section 12.3.1.5. The extractor is operated at a relatively low temperature. The extracted working solution is heat exchanged with hydrogenated working solution; this also helps to lower the free moisture content.

The crude aqueous hydrogen peroxide from the extractor has a H_2O_2 concentration of 20–50 wt-%. The amount of dissolved organic impurities can be lowered by washing with solvents (e.g. the quinone solvent) and/or treatment with adsorber resins. Inorganic impurities can be removed with ion exchange resins or reverse osmosis. The resulting purified crude product is stored in the crude product storage tank.

12.2.2.5 Regeneration of the working solution (reversion)

During the cyclic reduction and oxidation of the working solution, degradation products are formed (from both the quinone and the solvents) that may deteriorate the crude hydrogen peroxide quality or negatively affect the working solution characteristics such as solubility of active quinone, density, viscosity and interfacial tension. In addition, these degradation products also decrease the activity and lifetime of the hydrogenation catalyst.

Two different processes are used to remove these degradation products or convert them into active quinone:

- treatment with an aqueous caustic solution;
- treatment with solids (sodium aluminium silicates or activated alumina).

Treatment is done with either hydrogenated or oxidised working solution or a mixture of both.
Sodium aluminium silicate and activated alumina lose their activity while regenerating the degraded working solution and therefore have to be replaced from time to time. Solvents adsorbed on the solids are recovered with steam.

12.2.2.6 Product concentration

As an option, the purified crude product can be further concentrated by vacuum distillation to commercial grade up to 70 wt-%, or even higher concentrations if required. Water and hydrogen peroxide do not form an azeotrope; their boiling point difference at atmospheric pressure is 50.2 °C. The final product is stabilised and stored. Water vapour, produced during concentration, is condensed and can be recycled into the water storage tank.

12.2.3 Other than normal operating conditions

12.2.3.1 Specific other than normal operating conditions

The following operations deviate from the stable and normal operating procedures:

- malfunction or failure of off-gas treatment;
- exhaustion of activated carbon absorbers: this normally occurs every three to five years;
- adsorber malfunction;
- hydrogenation start-up: the frequency of this event ranges from 1 to 20 times per year;
- activated carbon decanter malfunction;
- events in which hydrogenation catalyst enters the oxidation section, as a consequence of failure of safety filtration, resulting in H_2O_2 decomposition and consequent plant shutdown.

The operations listed below are addressed in this document as normal operating conditions:

- catalyst regeneration;
- washing of solid regeneration agent: the frequency of this event ranges from 26 to 355 days per year.
-
-

12.2.4 Equipment important for environmental protection

The following systems perform important operations for environmental protection and should have the longest uptime possible:

- activated carbon adsorbers: adsorption, outlet monitoring and regeneration programme;
- cooling water temperature control (oxidiser condensers);
- phase separation (performance and control);
- working solution reversion operation efficiency.

12.2.4.1 Generic other than normal operating conditions

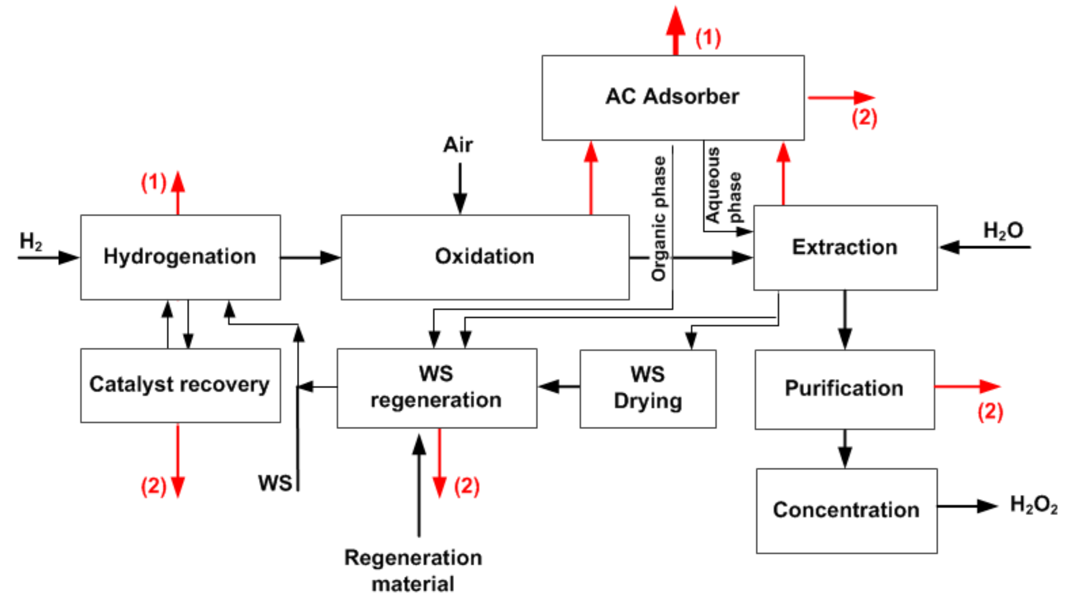
The following operations deviate from standard operating procedures in H_2O_2 plants:

- Routine start-up: the frequency of this event ranges from 1 to 13 days per year.
- Shutdown for maintenance preparation: equipment flushing, higher load to WWT, potential emission to surface water (rainwater) header. The frequency of this event ranges from 1 to 10 days per year.
- Low plant rate due to force majeure, e.g. interruption in final product consumption or raw material supply.
- Hydrogen or oxygen supply issues. The frequency of this event ranges from 1 to 7 times per year.

12.3 Current emission and consumption levels

The AO process' main environmental emissions to air are generated in the oxidation, working solution drying and hydrogenation sections. These emissions are VOCs (solvents such as alkylated benzene). There are several aqueous streams from different process sections which are treated and/or reused. Residues and waste are generated in auxiliary systems like the working solution reversion and catalyst regeneration.

The autoxidation process for the production of hydrogen peroxide involves several steps. The block flow diagram in Figure 12.4 shows the main emissions.



NB: WS: Working Solution. (1) Waste gas. (2) Waste water.

Figure 12.4: Block flow diagram of a hydrogen peroxide manufacturing process

12.3.1 Emissions to air

12.3.1.1 Emissions to air from the oxidation section

The reaction is carried out in a mixture of solvents, so the off-gas from the oxidation reaction will contain one or more of these solvents. However, the organic load is limited by the moderate reaction temperatures.

After oxidation, the process off-gas and working solution are separated. The process off-gas will be saturated with solvent and water; it usually passes through a condenser(s) where a large part of the solvents and water are condensed and recycled to the process. Upstream of the condenser, a demister can be used to reduce liquid entrainment. The gas stream is purified with activated carbon, which is periodically regenerated, normally with steam, to recover the adsorbed solvent. Any steam condensing in the activated carbon beds is drained and is normally an aqueous effluent.

Composition of the treated waste gas: Besides nitrogen and excess oxygen, the waste gas will still contain some VOCs; these can be solvents or working compounds. Most working compounds such as quinones have a very low vapour pressure and therefore are not relevant for emissions to air.

Using air with the stoichiometric amount of oxygen, the specific volume of spent air would be approximately 2 600 Nm^3/t. Using a 20-40 % excess of oxygen, the corresponding specific volume of spent air would be in the range of 3 300–4 000 Nm^3/t.

Methane can sometimes be present from the hydrogen source. It dissolves in the working solution at the hydrogenation stage and is stripped out by the process air in the oxidation unit.

Emissions in the outlet of the adsorber: See Section 12.4.1.1.4.

Averaging periods: Different plants may have different emission profiles due to their different adsorption/ regeneration cycles, and averaging periods should be chosen in such a way as to allow the assessment of the whole cycle.

Analytical method: Normal FID, often in compliance with standard EN-12619. More than half of the installations that reported data had a continuous measurement system in place (optionally shared in sequence by several adsorbers, switching from one adsorber to the next to monitor the end of the adsorption cycle).

12.3.1.2 Emissions to air from the hydrogenation section

Process design: Although some of the installations reported having no release at all from the hydrogenation unit, most units have a process vent (for degassing or pressure control/release) that is rarely channelled to a vent header or abatement device and mainly consists of inerts (e.g. nitrogen) and hydrogen. It cannot be routed to the shared activated carbon adsorber for safety reasons. Most of the installations currently send to atmosphere (in some cases via water locks) a stream whose flow depends on several factors and the data collection shows similar ranges for installations with and without recycling of hydrogen:

- 0–75 Nm^3/h for those that recycle excess hydrogen;
- 2–100 Nm^3/h (except one unit with a purge of 250–300 Nm^3/h) for those operators that do not recycle H_2 to the feed.

Data from the data collection (2012) are summarised in Table 12.2; some of the reported VOC emissions are not based on monitoring but on calculations based on the theoretical vapour pressure.

Table 12.2: VOC emissions from hydrogenation

Recycling of hydrogen	Flow (Nm^3/h)	VOCs (mg C/Nm^3)	VOC load (g C/h)
Yes	0–75	450–5 100	0–330
No	2–300	7–3 500	0.02–210

Composition: The reactions are conducted in a mixture of solvents, so the off-gases from the hydrogenation reactions will contain one or more of these solvents. Methane may be present in the H_2 vent stream, from the hydrogen source.

12.3.1.3 Emissions to air from extraction units

The extractor is operated at a relatively low temperature and has a small breathing connection to the atmosphere which may be channelled to the activated carbon adsorption unit.

Composition: The emissions are likely to be solvent vapours of relatively high concentrations. Nevertheless, the volume is very low (breathing level) except in very large plants where the breathing emissions from extraction can be significant. The VOC content can be around 250 mg C/Nm^3.

- This stream is seldom measured. Data from the data collection show specific emissions of 0.5–10 g/t of product.

12.3.1.4 Emissions to air from the purification and concentration sections

The purification section removes dissolved organics from the crude hydrogen peroxide. Concentration then increases the aqueous H_2O_2 concentration prior to storage and distribution (from 20–50 % to 50–70 %). These downstream sections involve multiple operations, some of which are conducted under vacuum in order to reduce temperature and minimise product decomposition.

Process-integrated techniques: condensers and decanters are included in vacuum systems but all of them will have a net vent stream which is typically either routed to the adsorber for abatement or released directly to atmosphere.

12.3.1.5 Emissions of VOCs to air from auxiliary systems

There are at least three auxiliary systems that may generate emissions to air. The emission rate from these sources is generally low (as a total from all three sources, according to the data collection, VOC values ranged from < 0.1 g to 30 g per tonne of product). They are described below.

- WS drying: there are various options for drying the working solution.
    - The working solution leaving the extraction unit contains dispersed water droplets and is led into coalescers to separate free water. Before the working solution is recycled to the hydrogenation reactor, the moisture content in the solution may be adjusted in a dryer.
    - A vacuum is used to eliminate water, followed by condensers and decanters to separate VOCs from the vent gas for reuse and recycling, leaving only a very small net vent gas stream.
    - The drying tower (not used in Europe) performs a countercurrent wash (scrubber) with K_2CO_3 on the crude working solution from the extraction tower.

  According to the data collection, VOCs are mainly related to the vacuum systems and are typically routed to the activated carbon adsorber.

- Working solution regeneration: there are also design options here.
    - With the use of solids (sodium aluminium silicates or activated alumina). This regeneration will generate VOC emissions to air when reloading an adsorber.
    - Alkaline solution. This can also generate VOC emissions to air (can be channelled to the adsorber for VOC abatement).

- Catalyst regeneration. Some operators regenerate the catalyst on site. For example, fixed-bed catalysts may be regenerated using steam and hydrogen peroxide or acid wash [2, Goor et al. 2007]. Pollutants mentioned in the data collection are VOCs (polar solvents such as acetone) and HCl. A reported gaseous HCl emission after scrubbing was 0.05 g/t of product based on spot samples.

12.3.1.6 VOC and H_2O_2 emissions to air from fugitive emissions

The reaction steps need to be operated under pressure. Fugitive emissions (particularly of solvents) are therefore possible. Although the process might be operated at low pressure, the possibility of fugitive emissions to air will still remain, and this will depend on plant age, operation pressure, nature of the solvents, maintenance attention, etc., and these emissions could still be high relative to point source emissions. Small leaks may also occur. Leaks may be detected visually as solvent evaporation may leave working solution crystals.

Hydrogen peroxide has a significant vapour pressure (1.2 kPa at 50 °C) and exposure to the vapour is potentially hazardous.

12.3.1.7 VOC emissions to air from storage

Tanks and other storage assets are used for raw materials, solvents and product. The working solution storage, hydrogenation feed tank, working solution regeneration tank, working solution metering tank, solvent storage tank, etc. are typically atmospheric storage tanks. These tanks may share abatement techniques (e.g. adsorption) with the main process streams. Vapours are, in some cases, partially recovered by condensation (with cooling water). Other processes use storage tanks blanketed with nitrogen where vent gases are sent to the atmosphere or to an adsorber to remove hydrocarbons.

12.3.2 Emissions to water

Most of the process effluents comprise an aqueous phase and an organic phase. The organic phase is separated and recycled to the process. However, low concentrations of soluble substances and some solids may remain in the aqueous phase. Some of these aqueous streams are typically recycled back to the process, e.g. from the adsorber regeneration, the concentration section and vacuum systems. Others, e.g. from alkaline reversion, are routed to the final biological treatment, sometimes after pretreatment to remove poorly bioeliminable compounds.

The combined effluent from the hydrogen peroxide plant has the following characteristics upstream of the final biological waste water treatment.

Table 12.3: Waste water from the hydrogen peroxide process (1)

Parameter	Unit	Average	Median	Min.	Max.	Number of sites
Flow	(m^3/t of H_2O_2)	1.5	1.5	0.1	3.0	17 (2)
TSS	(mg/l)	61	56	6	126	4
TOC	(mg/l)	279	217	2	900	18
	(kg/t of H_2O_2)	0.6	0.6	0.01	1.4	13 (2)
COD	(mg/l)	1277	1112	215	2425	11
	(kg/t of H_2O_2)	2.0	1.8	0.06	5.4	10 (2)

(1) Average flows and concentrations, from the data collection; total process effluent before final treatment.
(2) One outlier discarded (high specific waste water volume flow from a small plant).

a) Alkaline reversion of the working solution

There are a number of alternative processes to treat the working solution to remove impurities from both the working compound and the solvent. Most of these processes include treatment with alkaline compounds followed by washing with water. This generates the main process effluent.

The wash liquor from reversion is saturated with solvents and solvent degradation products (plus a very small amount of quinone and quinone derivatives).

According to the data collection, the organic load prior to final treatment of the total process effluent from hydrogen peroxide plants using alkaline reversion was in the range of 0.5–1.4 kg TOC or 1.6–5.4 kg COD per tonne of H_2O_2 produced.

b) Reversion of the working solution with solids

When using solids for WS reversion, the solid agent has to be changed periodically. Before removal, it is treated with steam to recover solvent. The phase separation produces an aqueous effluent.

According to the data collection, the organic load prior to final treatment of the total process effluent from hydrogen peroxide plants using reversion with solids was in the range of 0.01–0.8 kg TOC or 0.06–2.9 kg COD per tonne of H_2O_2 produced.

c) Adsorber regeneration

The desorption of the activated carbon adsorber used to treat the off-gas from the oxidation unit generates some water effluent from the steam condensate, which will contain dissolved solvents. The design should ideally include condensers before the adsorbers to reduce the amount of solvent arriving to the adsorbers and thus reduce the steam needed for regeneration and recovery. When steam is first introduced to the loaded activated carbon at the beginning of the regeneration step, there is a limited amount of steam condensate produced as the carbon warms up to steam temperature. This condensate runs out from drains at the bottom of the bed. It may be contaminated with carbon fines, and so cannot be returned to the process because of its potential to disrupt the phase interfaces in the product extraction step. The quantity of steam used is normally in the range of 4–6 kg/kg of solvent adsorbed. The steam from desorption is condensed; the condensed aqueous phase is separated from the condensed organic phase (mainly solvent) in a separator or decanter. Both phases are normally recycled to the process.

d) Aqueous streams from extraction

Working solution leaving the extraction unit contains dispersed water droplets and flows through coalescers to separate the aqueous phase, which may be reused or end up as effluent.

e) Vacuum systems

The purification and concentration of H_2O_2 may be carried out under a vacuum generated by steam ejectors and/or liquid ring pumps, which will generate an aqueous effluent.

f) Condensates from the concentration section

At some installations, distillation of dilute solutions is used to produce commercial 50–70 wt-% hydrogen peroxide solutions. The distilled water is condensed and normally recycled to the AO process.

g) Waste water from catalyst regeneration

The hydrogenation step is catalysed by palladium, which slowly loses its activity and needs to be periodically regenerated. Regeneration and recycling steps are carried out in separate units, which in some cases may be linked to the production process but these steps are often carried out by external companies.

If regeneration is carried out on site, small volumes of effluent containing inorganic salts and complexing agents are generated.

12.3.3 Raw material consumption

The table below shows the overall raw material use of these plants. In this section, the usages of key feedstocks are discussed.

Table 12.4: Input of a hydrogen peroxide plant

Raw material	kg/t of H_2O_2 produced (100 %)
Hydrogen	60–70
Oxygen	1 000–1 300 (1)
Quinone	0.5–2.5 (2)
Solvents	2–5
Reversion agent	4–20
Sodium hydroxide	1.5–4
Nitric acid	2.5–7
Stabilisers	
Demineralised water	1–2 m^3/t
Cooling water, once-through	45–350 m^3/t
Cooling water, evaporative cooling tower	3–15 m^3/t

(1) Corresponding to 3 300–4 600 Nm^3 of air.
(2) The data collection (2013) reveals values in the 0.7–1.6 kg/t range.

a) Solvents usage

The solvents that are used in the working solution to dissolve alkylanthraquinones and hydroquinones are selected with respect to several criteria (see Section 12.2.2.1):

Alkylanthraquinone solvents:

- xylene;
- tert-butylbenzene;
- trimethylbenzene;
- tetramethylbenzene (isodurene);
- mixtures of polyalkylated benzenes, e.g. C_9-C_{11} aromatic solvents;
- methylnaphthalene.

Hydroquinone solvents:

- alkyl phosphates, e.g. tris-(2-ethylhexyl)-phosphate;
- nonyl alcohols, e.g. diisobutylcarbinol;
- alkylcyclohexanol esters, e.g. 2-methyl-cyclohexylacetate;
- tetraalkyl ureas, e.g. tetra-n-butylurea;
- cycloalkyl ureas, e.g. dihexyl propyleneurea or octyl caprolactam.

Solvent mixtures:

- polyalkylated benzenes and any of the hydroquinone solvents or mixtures of the hydroquinone solvents.

- Solvents can also be used for final product purification.

b) Hydrogenation catalyst

The hydrogenation step is catalysed by palladium, which slowly loses its activity and so is regularly recycled to the catalyst manufacturer for regeneration, or is regenerated on site. To maintain hydrogenation activity, part of the catalyst is removed, regenerated in the catalyst regeneration area and returned to the hydrogenation reactor. Every hydrogenation set-up, except for the fixed-bed reactor, has a downstream catalyst filtration (capture) step, a regeneration step and a recycling step.

For some plants, losses of palladium have been reported to be in the order of 0.1–0.3 g/t for fixed-bed processes and around 1 g/t for slurry processes.

12.3.4 Energy consumption

Energy is consumed as heat/steam and electric energy.

Steam is used for indirect heating (e.g. distillation), steam ejectors, the regeneration of the activated carbon adsorbers and the regeneration of the solid reversion agent. Since both oxidation and hydrogenation are exothermic reactions, the net consumption is reduced to a great extent by heat recovery. The energy balance will also depend on whether the recovered heat is used in the process or externally, e.g. for other chemical processes or for heating of buildings.

Electrical energy is required for driving the process air compressors, the hydrogenation gas recycle compressors, the working solution circulation pumps and numerous small drives. The total electrical energy consumption depends mainly on the pressure of oxidation, the excess air and the productivity of the working solution.

Table 12.5 below summarises the data reported from three hydrogen peroxide plants and gives an idea of the extent to which the total net consumption may depend on the energy demand for the product distillation (purification/concentration) and for the compressors, and of the benefits from heat recovery.

Table 12.5: Energy data from the data collection (2012)

	Energy (GJ/t of H_2O_2)
Total net consumption	2.9–5.7
Distillation net consumption	0.3–1.5 (1)
Compression of air	1.4 (2)
Heat recovery from process (mainly vapour recompression and heat exchangers)	1.7–4.2

(1) Referring to a hydrogen peroxide product concentration of 50 wt-%.
(2) If oxygen or oxygen-enriched air is used, the consumption is lower.

Energy and hydrogen costs represent three quarters of the variable cost of production.

a) Energy consumed in fractionation operations

Concentration of H_2O_2 to produce a commercial-grade 50–70 wt-% solution by vacuum distillation is a significant consumer of energy.

b) Energy usage on compressors

The energy consumption for compression increases with the required pressure for reaction (< 1–10 bar for oxidation, < 1–5 bar for hydrogenation). This is partially counterbalanced by the improved options for heat recovery at higher pressure.

d) Energy recovery in oxidation

The oxidation of hydroanthraquinones is exothermic with a heat of reaction of 75–80 kJ/mol, or 2.20–2.35 GJ/t of H_2O_2.

The possibilities for energy recovery from off-gas are larger when the pressure is higher. The technology offers few possibilities for energy recovery and demands large process vessels and pipes. A low pressure also means that more working solution is needed. By using a medium- or high-pressure process (1–10 barg), smaller equipment and less working solution can be used. On the other hand, the multistage turbocompressors that are needed demand larger investments. Of the increase in the operating costs of air compression for higher pressure oxidation, 75–80 % can be recovered, at increased capital investment, by passing the off-gas from the oxidation reactor through a turbo-expander, which drives one of the compressor stages, or an independent electrical generator. The higher the pressure in the process, the more important it is to recover the energy contained in the gas.

e) Energy recovery in distillation

Both the feed concentration and the concentration of the final product are important for energy consumption in distillation. Crude peroxide, which will feed the distillation, normally has a concentration that can vary from 20 wt-% to 50 wt-% hydrogen peroxide. The crude concentration depends on which type of solvent mixture is used in the process, and on the peroxide concentration in the working solution.

There are several heat recovery options to reduce energy consumption (see Section 12.4.3.1).

12.3.5 Water usage

The H_2O_2 production process has, at least, the following water usage:

- demineralised water used in the extraction of H_2O_2 from the working solution (approximately 1–2 m^3/t of hydrogen peroxide);
- boiler feed water to generate steam that is then used in activated carbon regeneration and concentration;
- cooling water: losses from evaporation using closed cooling water circuits for indirect cooling are in the range of 3–15 m^3/t of hydrogen peroxide.

12.3.6 Waste generation

Data from the data collection are summarised in Table 12.6.

Table 12.6: Wastes/residues generated in hydrogen peroxide plants

Residue	Amount (kg/t of H_2O_2)
Liquid residue (caustic tar)	0.78–2.4 (1)
Spent reversion agent	0.5–16 (typically 7–10)
Spent adsorbent	0.01–0.34
Spent ion exchange resins	0.005–0.027 (1)
(1) Only limited data (5 plants).	

The regeneration of reversion agent generates a stream depending on the plant design.

a) Spent reversion agent

When activated alumina is used in the working solution reversion process, the spent material may be supplied as raw material to cement manufacture to avoid waste disposal. In certain situations, it may be practicable to thermally regenerate the alumina in an off-site facility serving the oil-refining industry.

b) Working compound

The selectivity of the process is 99.99 % on anthraquinone (molar basis), which means that less than 1 kg of degraded quinone is rejected per tonne of H_2O_2 (100 % basis) manufactured. This degraded quinone is discharged via the reversion treatment, either as part of the liquid residue (caustic tar) or the spent reversion agent. Quinone consumption directly influences the quantity of degraded quinone waste that must be disposed of by incineration.

c) Spent hydrogenation catalyst

Spent catalyst will need to be periodically replaced and sent back to the supplier for recycling.

d) Spent adsorbent

The activated carbon used in the off-gas treatment of the oxidation unit slowly degrades and has to be exchanged. The replacement frequencies reported range from one year to more than 10 years.

Spent adsorbent may also result from solvent recovery.

e) Ion exchange resins

Ion exchange resins can be used to purify hydrogen peroxide. They require replacement at least every five years. Essentially, ion exchangers are organic polyelectrolytes (based on polystyrene or polyacrylate).

f) Filter and coalescer cartridges

Filter and coalescer cartridges are used in the production of hydrogen peroxide principally to separate catalyst from the working solution, as well as to separate organic and water solutions. Cartridges are used to filter the working solution at the exit of the hydrogenation section and to physically separate entrained water from the working solution at the exit of the extraction section. After being used, they usually contain traces of organic matter or solid inorganic materials. The elements are made from glass fibres with a load-bearing core of perforated stainless steel plate or polypropylene.

12.4 Techniques to consider in the determination of BAT

This section describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this chapter. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations). Cross references to other chapters are used, where relevant, to avoid repetition.

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 2.6 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

12.4.1 Techniques to reduce VOC emissions to air

12.4.1.1 Emissions from the oxidation section

The gas stream from the oxidation unit is treated to recover hydrocarbons. Common treatment/recovery techniques are the use of devices to avoid or reduce entrainment, and the use of condensation and adsorption. Other minor streams may also be channelled to the adsorber system.

12.4.1.1.1 Optimisation of the oxidation process

Description
Optimisation of the process in order to reduce the solvent vapour concentration in the process off-gas.

Process optimisation includes elevated oxidation pressure and reduced oxidation temperature.

Technical description
The concentration of the solvent vapour leaving the oxidation process is inversely proportional to the oxidation pressure and is lowered by the reduction of the oxidation temperature.

Achieved environmental benefits

- Reduced emissions of VOCs to air.
- Lower energy consumption for regeneration (benefits may be reduced by higher energy consumption for process air compression).

Cross-media effects
Energy consumption for increase of process pressure.

Environmental performance and operational data
No information provided.

Technical considerations relevant to applicability
For existing plants, changes in the process (pressure, temperature) will be restricted to major plant upgrades.

Economics
Benefits are derived from the recovery of material and the reduction in the adsorber capacity or regeneration frequency required.

Driving force for implementation
Economics.

Example plants
Widely used.

Reference literature
No information provided.

12.4.1.1.2 Techniques to reduce solids and/or liquids entrainment

Technical description
The most frequent measures are meshes, knock-out (KO) drums, and pipe enlargement to reduce the gas stream velocity. The majority of installations use entrainment avoidance devices (KO drum or demister) and condensers upstream of the solvent recovery adsorbers.
The air and the working solution leaving the top of the oxidation column are fed together into a separator. Entrainment of the liquid phase to the overheads system is reduced, e.g. by KO drums or meshes.

Achieved environmental benefits

- Reduced emissions of VOCs to air.
- Recovery of working solution.

Technical considerations relevant to applicability
Techniques for the reduction of entrainment are generally available.

12.4.1.1.3 Condensation

See the CWW BREF on condensers.

Technical description
After oxidation, the waste gas and working solution are separated. The waste gas, saturated with solvent and water, usually passes through condenser(s) where part of the solvents and water are condensed and recycled to the process.

A larger condensing duty will reduce the VOC load on the activated carbon adsorbers and, therefore, steam consumption for their regeneration. A second condenser with chilled water (chilled to 2–12 °C according to the data collection), after the one with cooling water, can be used to further reduce the solvent load.

Achieved environmental benefits

- Reduction of emissions to air.
- Recovery of organic material for reuse.

Environmental performance and operational data
Emissions from oxygen-based plants where condensation is used as final abatement are listed in Table 12.7 (based on periodic monitoring).

Table 12.7: VOC emissions to air from oxygen-based plants downstream of the oxidation section

Plant	Questionnaire	Flow (Nm^3/h)	VOC range (mg C/Nm^3)
14	S	100–150	800–1 200
18	X	38–44	0.4–34

For the air-based plants, as the load reduction by condensation is only one of many factors which determine the performance of the adsorber unit in terms of VOC concentrations, no correlation has been found between the use of chilled water condensers and emissions from the adsorber unit.

Cross-media effects
Energy consumption for chilling.

Technical considerations relevant to applicability
Generally applicable.

Economics
Benefits are derived from the recovery of material and the reduction in the adsorber capacity or regeneration frequency required.

Costs are associated with the consumption of energy (mainly for chilling).

Driving force for implementation
Economics and protection of the environment.

Example plants
According to the data collection, the vast majority of plants use condensation with cooling water, e.g. Evonik, Antwerp (BE); Evonik, Weissenstein (AT); Evonik, Rheinfelden (DE); Solvay, Voikkaa (FI), Solvay, Warrington (UK), Kemira, Oulu (FI).

Five plants confirmed also using condensation with chilled water: Arkema, Jarrie (FR); Arkema, Leuna (DE); Kemira, Helsingborg (SE); Kemira, Oulu (FI); Kemira, Rozenburg (NL).

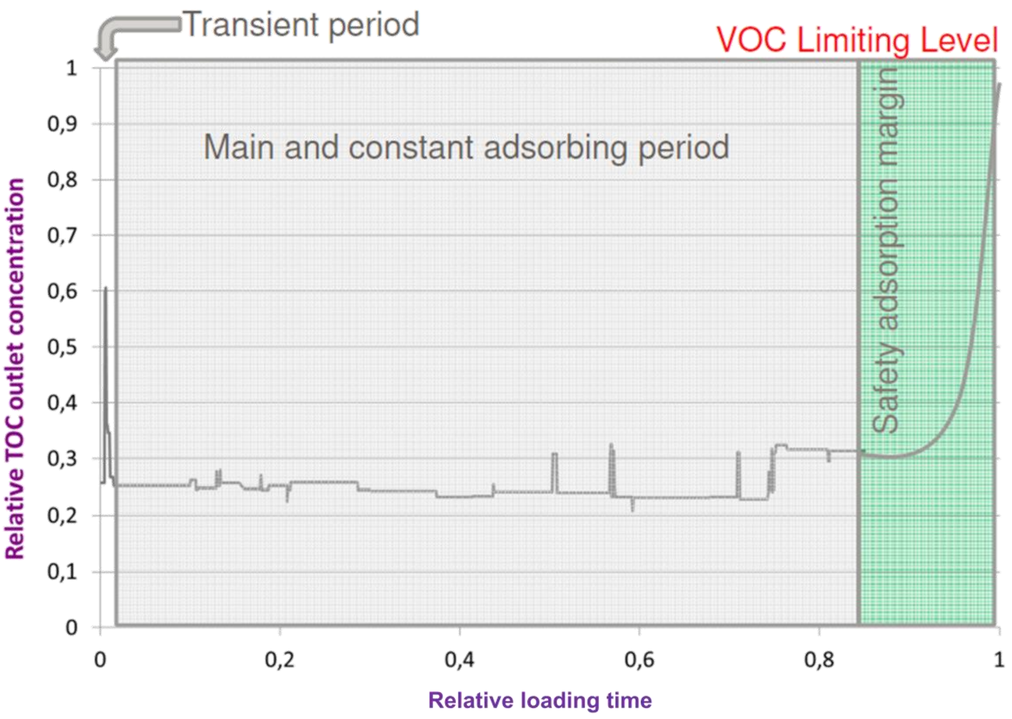
Reference literature
[2, Goor et al. 2007],

12.4.1.1.4 Regenerative adsorption

Technical description
A number of adsorber beds are connected in parallel to remove the organic content for recovery and to abate organic emissions to air as final treatment. The adsorbers also treat gaseous streams from other sections of the hydrogen peroxide process. The removal efficiency is dependent on parameters such as:

- properties of the adsorbent used (usually activated carbon, but zeolites may also be efficient);
- bed volume compared to organic load;
- contact time;
- temperature of the adsorbent;
- ageing of the adsorbent.

The TVOC concentration in the outlet of the adsorber is low in the first part of the adsorption cycle and then rises increasingly while the adsorber is being loaded. The peak emission depends on when the adsorber is taken off-line for desorption. Desorption may be triggered by a concentration threshold value when using continuous monitoring. Alternatively, adsorption is carried out in adsorption cycles with a constant length which has been determined (and is periodically adjusted) to include a safety margin to ensure low emissions (see Figure 12.5). Desorption is usually performed with low- or medium-pressure steam to regenerate the adsorbent and recover solvent for reuse. Steam condensing in the activated carbon bed is drained as aqueous effluent. During desorption, the input load to the other adsorbers is increased, the difference depending on the total number of adsorber beds.



Source: [193, Evonik 2015]

Figure 12.5: Adsorber VOC emission profile

Activated carbon has proved to be efficient for the organic compounds from the manufacture of hydrogen peroxide but may be less efficient for the removal of methane which, depending on the hydrogen source, may be introduced to the process via the hydrogenation step and may still be present in the off-gas from the oxidation.

In order to maintain low emission levels, factors that have a negative impact on the capacity of the adsorber can be largely compensated by increasing the desorption frequency (although this implies an increase in energy consumption in the form of steam). One of these factors is the ageing of the activated carbon which needs to be replaced from time to time by fresh material.

The design and the operation of the adsorbers can be optimised in terms of recovery or abatement. When used for final abatement, measures are taken to keep emissions low and to avoid peak emissions. These measures include the following:

- Design: An increase of the number of adsorber beds will reduce the increase in inlet concentration when taking adsorbers off-line (e.g. for desorption); the related reduction of the single adsorber bed volume may facilitate cooling after desorption (see below).
- Adsorption management: This feature involves all actions taken by the operator to optimise adsorption performance. They include: intensive (quasi-continuous) monitoring of adsorption performance to optimise on-stream life or regeneration time; procedures that include measures (such as plant shutdown) to be taken in the event that the emission threshold value is reached; ensuring sufficient fresh adsorbent is available (in place) for unplanned end-of-life events; process optimisation system for continuous improvement of adsorption performance (such as process models or six sigma methodology).
- Cooling feature prior to alignment: When going back online after regeneration, because of the hot/wet activated carbon bed, there could be a short period when VOCs are not adsorbed optimally: the VOC concentration would then be high but only for a few minutes in an adsorption step of hours. An option to reduce the peak emissions at the beginning of the adsorption is to cool down the AC bed with air recycled from the outlet but additional equipment and electric power is needed.

See the CWW BREF on recovery for end-of-pipe abatement devices.

Achieved environmental benefits

- Reduction of emissions to air.
- Recovery of organic material for reuse.

Environmental performance and operational data

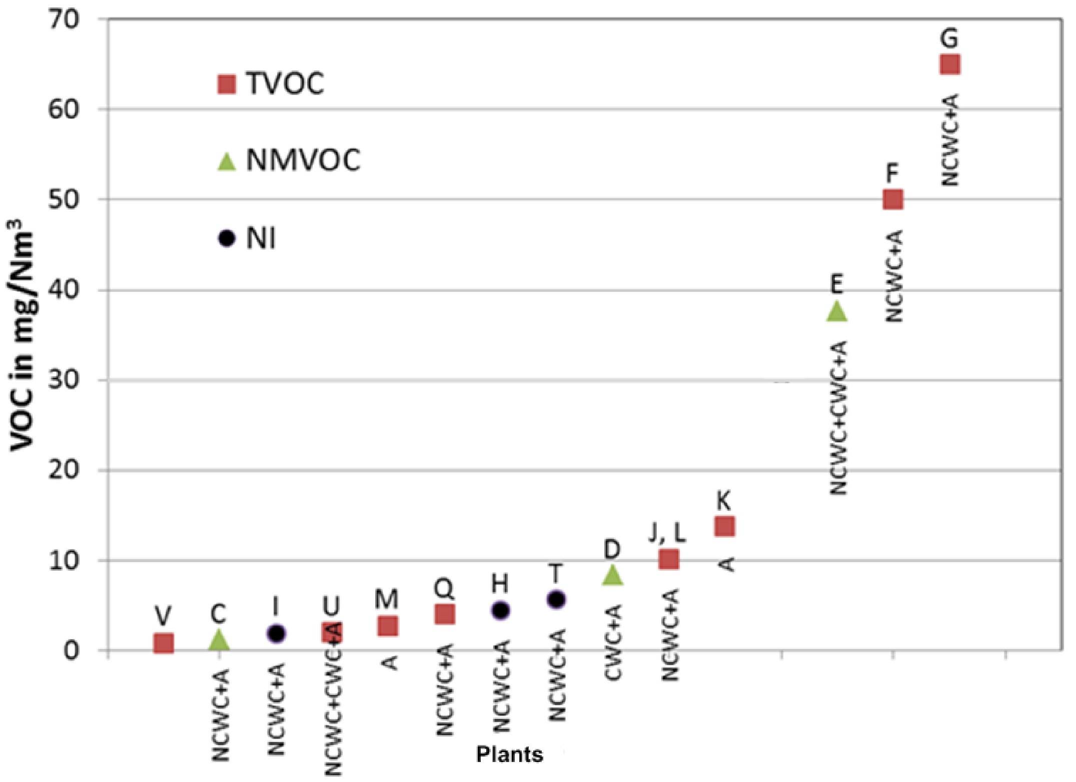
Table 12.8 summarises the questionnaires' findings from the outlet of the adsorber unit which may also be used to treat other vents from the hydrogen peroxide installation, in addition to the vents from the oxidation section. Depending on the data provided, averages refer to averages of periodic measurements (typically for one year) or averages from continuous measurements (which have been reported as an annual average or a series of average emissions for shorter periods, e.g. per month or quarter). Continuous monitoring may refer to the common outlet of the adsorber unit or to sequential monitoring of individual adsorbers at the end of the adsorption period.

Table 12.8: VOC emissions to air from the adsorber unit downstream of the oxidation section

Plant	**Questionnaire**	**Air/O_2**	**Cont. monitoring (yes/no)**	**Flow (Nm^3/h)**	**VOC Average/range (mg C/Nm^3)**	**VOC Max. (mg C/Nm^3)**	**Limit of det. (LOD) (mg C/Nm^3)**
1	D	Air	No	20 691	8.42	14	5 ppm
2	E	Air	No	19 700	37.7	ND	0.1 ppm
3	F	Air	Yes	36 000	50	ND	0.05
4	G	Air	Yes	22 000	65	100	20 ppm
5	K	Air	Yes	28 100	12.05	13.8	0.1
6	L	Air	Yes	6500	9.76	24	1
7	M	Air	Yes	23 700	2.15	ND	0.1
8	N	Air	No	6480	7.1	ND	ND
9	O	Air + O_2	No	10 631	< 0.34–37.1	37.1	< 0.18
10	P	Air	Yes	ND	1.9–2.8	< 20	0.1
11	Q	Air	Yes	22 774	4.0–4.1	< 20	1
12	R	Air	Yes	66 450	17.5–35.6	< 50	4
13	U	Air	Yes	23 000	2	> 160	ND
15	H	Air	Yes	34 900	0.1–2.3 ppm	ND	0.1 ppm
16	T	Air	No	28 000	< 1–2.9 ppm	2.9	1 ppm
17	I	Air + O_2	No	3800	< 1 ppm	ND	1 ppm
19	V	Air/O_2	Yes	9000–10 500	0.8–1.0	1.0	0.8
20	A	Air	Yes	24 000	4.1–5.7	ND	ND
21	B	Air	No	25 000	4.6	ND	ND
22	C	Air	Yes	49 000	0.6–1.2	ND	ND
NB: ND: No data.							

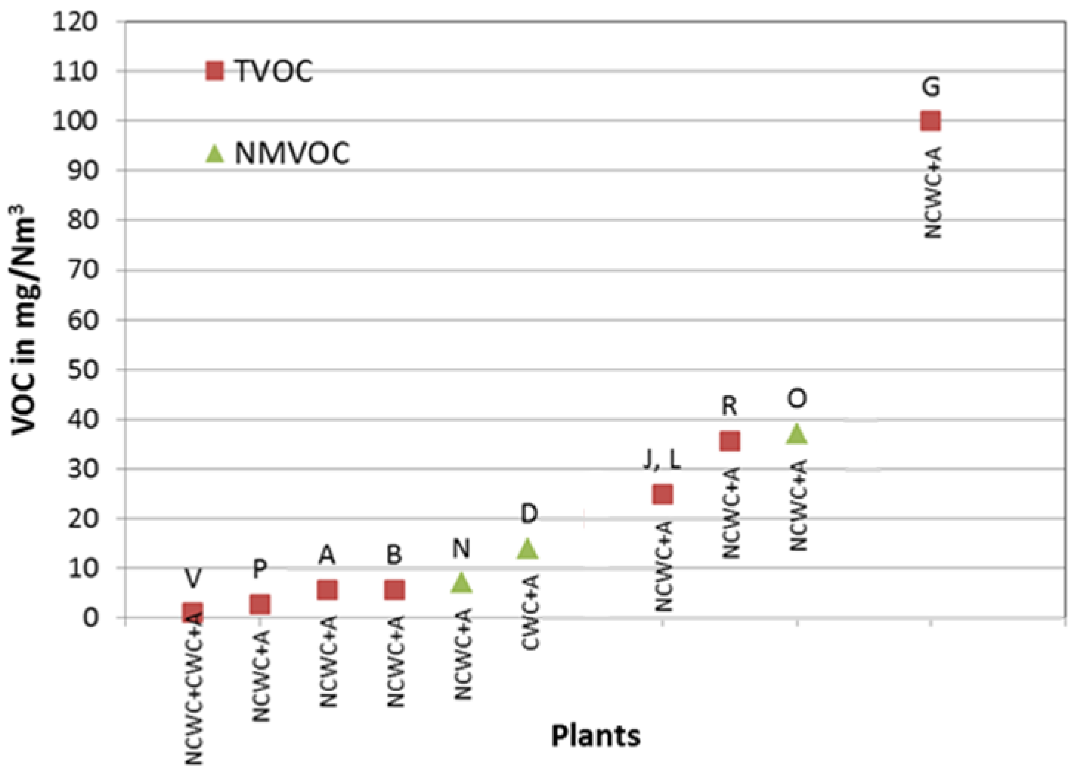
According to the data collection, the replacement frequency for the spent activated carbon ranges from one to two years to more than 10 years.

Data for long-term emissions and short-term emissions are shown in Figure 12.6 and Figure 12.7.



NB: NCWC: Condensation with non-chilled water; CWC: Condensation with chilled water; A: Adsorption.

Figure 12.6: Long-term VOC emissions (maximum averages) at the outlet of the adsorber unit



NB: NCWC: Condensation with non-chilled water; CWC: Condensation with chilled water;
A: Adsorption.

Figure 12.7: Short-term VOC emissions at the outlet of the adsorber unit

Long-term VOC averages are typically below 15 mg C/Nm^3. Plants with higher concentration values were both comparatively low in terms of the number of adsorber chambers (two to three) and the adsorber volume per production capacity (0.1–0.5 m^3 per yr/kt). Other important factors that influence the emissions include the desorption frequency and the control of the organic load routed to the adsorber.

Cross-media effects
Consumption of steam for desorption.

Technical considerations relevant to applicability
Because of the high oxygen content of the process off-gas, adsorption cannot be used for safety reasons when the oxidation is carried out with oxygen instead of air.

Economics
No information provided.

Driving force for implementation
Environmental legislation and economic benefits from material recovery.

Example plants
According to the data collection, all plants using air for oxidation use adsorbers with activated carbon for final abatement, e.g. Kemira, Oulu (FI); Solvay, Voikkaa (FI); Evonik, Rheinfelden (DE); Evonik, Weissenstein (AT); Solvay, Póvoa de Santa Iria (PT); Evonik, Antwerp (BE); AkzoNobel, Rjukan (NO); Solvay, Jemeppe-sur-Sambre (BE); Kemira, Helsingborg (SE).

Reference literature
[2, Goor et al. 2007]

12.4.1.1.5 Use of oxygen instead of air for the oxidation reaction

Description
Use of oxygen instead of air or enrich air with oxygen to carry out the autoxidation.

Technical description
Oxygen is used instead of air for the oxidation reaction. If needed, e.g. for safety reasons, nitrogen may be added. Both unreacted oxygen and nitrogen can be recycled.

Since there are only very small amounts of inerts from the oxidant that need to be purged, the process off-gas stream can be much smaller. This means that the reactor and reactor inventory (working solution) and the gas treatment equipment can also be smaller, and recovery more efficient.

By analogy, for air-based installations, a certain reduction in waste gas flows and loads can be achieved by enriching the air with oxygen.

Achieved environmental benefits
Lower net emission of VOCs to air in terms of loads.

Environmental performance and operational data
Emissions to air are reduced because oxidation with oxygen leads to a smaller waste gas flow (e.g. about 10 Nm^3/t of H_2O_2 produced, compared to 3 000–4 000 Nm^3/t of H_2O_2 produced for oxidation with air).

According to the data collection, the plants using oxygen instead of air do not apply adsorption.

The average VOC concentration after condensation with cooling water is reported to be about 1 000 mg/Nm^3; for condensation with chilled water, the reported outlet concentrations are in the range of 0.4–34 mg/Nm^3.See Table 12.7.

Cross-media effects
With respect to the life cycle of oxygen, the overall consumption of energy is increased because oxygen production by liquefaction and distillation of air requires more energy than the compression of atmospheric air. The balance is improved when the nitrogen obtained from air distillation is also used.

Technical considerations relevant to applicability
The technique is generally applicable for new installations (for oxidation with oxygen) or major retrofits (for enrichment of air with oxygen). According to the data collection, oxidation with oxygen is only used at smaller plants (< 40 kt/yr).

Economics
Operational costs may be similar to air-based processes (higher costs for oxygen versus benefits with respect to energy consumption and off-gas treatment) but investment costs can be reduced (smaller reactor, no adsorber unit).

Driving force for implementation
Economic: Lower investments costs for new plants (pure oxygen) and debottlenecking (air enrichment).

Example plants
Plant 14 and Plant 18.

Reference literature
No reference literature provided.

12.4.1.2 Emissions from the hydrogenation section

Hydrogenation can be carried out with a significant excess of hydrogen, which is recycled (see Section 12.4.1.2.1 below). Other designs do not recycle hydrogen and minimise the use of hydrogen instead (use of no or low excess of hydrogen with almost complete conversion).

Usually, small waste gas streams arise from the depressurisation of the hydrogenated working solution and from purges and may require treatment, depending on the VOC content (see Section 12.4.1.2.2 below).

12.4.1.2.1 Recirculation of hydrogen

Description
Recycling of excess hydrogen to the feed stream.

Technical description
This is a normal design feature for hydrogenation reactors working with excess hydrogen. A recycle compressor is required. The recirculation of hydrogen also recycles VOCs to the working solution.

Achieved environmental benefits

- Reduced consumption of hydrogen.
- Reduced emissions of VOCs to air.

Environmental performance and operational data
For emission ranges, see Table 12.2.

Cross-media effects
Energy consumption for compression.

Technical considerations relevant to applicability
Applicable to hydrogenation units using hydrogen in excess.

Economics
Lower raw material costs due to lower hydrogen usage.

Driving force for implementation
Lower feedstock costs.

Example plants
According to the data collection, the majority of installations use this technique.

Reference literature
[2, Goor et al. 2007].

12.4.1.2.2 VOC abatement: Combustion or adsorption

Even if no excess hydrogen is used, small vents arise from depressurisation and, in very few cases using hydrogen from other processes with a lower purity, from purges. These vents are usually not recycled or combusted due to the low hydrogen content and calorific value but are released to air.

However, depending on the volume flow and VOC content, the waste gas can be routed to a combustion unit or treated in a dedicated small activated carbon adsorber for VOC abatement.

Routing of the hydrogenation off-gas to a combustion unit

This technique consists of injecting the generated waste stream into the fuel gas manifold to recover energy.

The applicability of combustion of the gas stream from depressurisation may be limited when comparing the benefits with the energy needed for compression. The applicability may be restricted by safety considerations.

Adsorption

- VOCs can be abated in a dedicated activated carbon adsorber which, due to the lower load, will be much smaller than the adsorber unit for the oxidation unit (see also treatment of waste gas from hydrogenation in the production of phenol).
- See Section 2.4 and the CWW BREF.

12.4.1.3 Condensation during start-up operations

During start-up of the hydrogenation reactor, off-gas streams with a higher VOC content may arise. These streams are routed to a condensation unit (with appropriate design in terms of condensation temperature and condenser duty) in order to recover the condensable organic content (mainly solvent). Alternatively, adsorption is used (see Section 12.4.1.2.2 above).

12.4.1.4 Emissions from other sections

Vent gas streams from other sections (extraction, purification, drying, reversion, product concentration) that contain VOCs are routed to the adsorber unit and treated together with the process off-gas from the oxidation section.

12.4.2 Techniques to reduce emissions to water

12.4.2.1 Optimised liquid phase separation

Description
Separation of organic and aqueous phases with appropriate design and operation (e.g. sufficient residence time, phase boundary detection and control) to prevent any entrainment of undissolved organic material.

Technical description
In the hydrogen peroxide process, most aqueous streams arise from liquid phase separation of aqueous and organic phases. Entrainment of undissolved organic material is prevented by proper design and operation including:

- optimum pH to reduce the content of dissolved organic compounds and facilitate phase separation;
- proper design to minimise turbulence;
- sufficient residence time for phase separation;
- phase boundary detection and control to ensure that outlets are at a sufficient distance from the phase boundary.

Proper phase separation typically facilitates both the further processing of the organic phase and the reuse of the aqueous phase. In the event that the aqueous phase cannot be reused, optimised phase separation reduces the organic load discharged to the downstream waste water treatment.

Achieved environmental benefits
Reduction of emissions to water.

12.4.2.2 Reuse of water

Description
Reuse of water, e.g. from cleaning or liquid phase separation. The extent to which water can be reused in the process depends on product quality considerations.

Technical description
In the hydrogen peroxide process, which is a net consumer of water, many aqueous streams can be reused because their organic content is low and/or compatible with the process. Examples are the reuse of:

- the aqueous phase from the regeneration of the adsorbers;
- condensates from the product concentration;
- water from cleaning operations.

Achieved environmental benefits

- Reduction of emissions to water.
- Reduction of usage of water.

Technical considerations relevant to applicability

Water streams cannot be returned to the process if they induce product decomposition or are not compatible with product quality. This typically applies for the alkali effluents from the regeneration of the working solution.

12.4.2.3 Waste water treatment to remove poorly bioeliminable organic compounds

Description

Waste water streams that contain poorly bioeliminable organic compounds and carry the main organic load from the hydrogen peroxide plant are incinerated or pretreated using activated carbon adsorption.

Technical description

In the event that a significant part of the organic load discharged from hydrogen peroxide production (e.g. from the regeneration of the working solution) is not efficiently reduced by the final biological treatment, either waste water incineration or adsorption is applied to reduce the total load or selectively the load of poorly biodegradable compounds discharged to the final treatment.

In the BREF review data collection, several plants reported using activated carbon adsorption and considered it a critical asset for protecting the environment. This mainly (but not only) concerned plants with effluents from alkaline reversion systems for the regeneration of the working solution. For the technique description, see the CWW BREF.

Waste water incineration has been reported as being used for the concentrated effluent from alkaline reversion (containing the main recalcitrant load from the hydrogen peroxide plant). Waste water incineration will be preceded by evaporation to increase the concentration of the waste water.

Information related to the categorisation of waste water streams in terms of bioeliminability can be found in the CWW BREF and the OFC BREF [205, COM 2006].

BAT 11 of the CWW BAT conclusions stipulates that it is BAT to pretreat waste water that contains pollutants that cannot be dealt with adequately during final waste water treatment. This generally includes compounds that are insufficiently abated during final treatment (e.g. poorly / non-biodegradable organic compounds. Section 5.2.4.2.1 of the OFC BREF states that it is BAT to segregate and pretreat waste water streams containing relevant refractory organic loadings. Refractory organic loading is not relevant if the waste water stream shows a bioeliminability greater than around 80–90 % or if it is lower than around 7.5–40 kg TOC per batch or per day.

Achieved environmental benefits

Reduced emissions of organic pollutants (TOC) to water.

Environmental performance and operational data

No information provided.

Cross-media effects

- Waste from used activated carbon.
- In the case of waste water incineration, energy consumption for the concentration and possibly transportation of the waste water.

Technical considerations relevant to applicability
The technique is considered applicable to waste water streams carrying the main organic load from the hydrogen peroxide plant and when the reduction of the TOC load from the hydrogen peroxide plant by means of biological treatment is lower than 90 %.

Waste water incineration plants will typically be off site or shared with other processes and not dedicated to the hydrogen peroxide plant. Therefore, the use of the technique will be dependent on the available options for transporting the waste water concentrate to a waste water incineration plant.

Economics
For continuous effluents, costs for treatment by adsorption are supposed to be lower than the costs for waste water incineration.

Driving force for implementation
Environmental legislation.

Example plants
From the data collection, waste water incineration is used at one plant and adsorption at several plants.

Reference Literature
[1, Chematur 2008].

12.4.2.4 Solvent selection: Replacement of benzene in the working solution

Hydroquinones and anthraquinones have different solubility, so mixtures of solvents are often required. Some candidate solvents will be more environmentally problematic than others, and might result in more harmful emissions to air and water as a result (due to toxicity, solubility, relative density, etc.).

Benzene was used by BASF as a solvent but, because of its carcinogenic properties, it has been replaced by other solvents. According to industry, benzene is no longer used in the hydrogen peroxide process in the EU although it is still mentioned as a potential solvent in the literature [2, Goor et al. 2007].

A large variety of other, less toxic, solvents are available which are also better suited with regard to safety aspects (flammability).

Environmental benefits
Prevention of emissions of benzene to air and water.

12.4.3 Techniques to reduce energy consumption

Energy consumption is reduced by heat recovery from the reaction and distillation.

The consumption of electric energy for compression (air/oxygen, hydrogen) depends on the design of the compressors. Energy consumption for compression is reduced by using oxygen instead of air as the oxidant (see Section 12.4.1.1.4).

See also Section 2.4 for generic techniques to reduce energy consumption.

12.4.3.1 Energy recovery in distillation

Description

Recovery of heat from the distillation product, the evaporated steam and the condenser in the hydrogen peroxide concentration unit.

Technical description

There are several heat recovery options to consider:

- Heat exchange between distillation feed and product: heat may be exchanged from the product flow to the feed flow in order to save energy in the distillation.
- Vapour recompression: in order to reduce energy, it is possible to use the steam, which is evaporated and separated from the peroxide through the column, as a heating source for the evaporator. To be able to do so, it is necessary to increase the temperature and pressure of the steam by compression. In some large plants mechanical thermo-compressors are used. They are normally electrically driven and the distillation does not need any external steam to heat the evaporator. The compressor recompresses low-pressure steam from the distillation column and feeds it to the evaporator. At low feed concentrations, a compressor can reduce the energy needed by up to 90 %. These machines are big because they have to operate under vacuum and require a large investment, but they can be used where high steam prices allow large investments.
- Energy recovery from condenser: a large amount of low-energy heat is removed in the distillation condenser (if no thermo-compressor is used). Normally, the cooling water leaving the condenser is at temperatures below 40 °C but its enthalpy could be transferred, by means of a heat pump, to other processes where low-temperature energy could be used (e.g. heating of buildings).

Achieved environmental benefits

Lower energy consumption.

Environmental performance and operational data

No information provided.

Cross-media effects

Vapour recompression uses more electricity but saves steam.

Technical considerations relevant to applicability

Generally applicable for major retrofits or new plants.

Economics

No information provided.

Driving force for implementation

Reduction of costs related to energy consumption.

Example plants

Most H_2O_2 plants.

Reference literature

No reference literature provided.

12.5 Emerging techniques

12.5.1 Direct synthesis process to produce H_2O_2

Description
The direct synthesis of hydrogen peroxide (DSHP) from oxygen and hydrogen is the subject of intense research. The main challenges are:

- selectivity, since in terms of thermodynamics the formation of other products (water) is favoured; and
- safety, to control the mixture of oxygen and hydrogen.

Selectivity mainly depends on the choice of catalyst and solvent (which may be organic, CO_2 or water). Strategies to control the safety include dilution of the reactants, staged feed of reactants or the use of membranes or microreactors.

A pilot plant for the direct synthesis of hydrogen peroxide in the production of propylene oxide (DSHP/HPPO process) was built in Germany by Degussa-Evonik and Headwaters Nanokinetix. The process uses a palladium-platinum catalyst and methanol as a solvent. The plant was expected to start operating in 2009. No further reports about plants using the technology have been released [117, Pérez Ferrández 2015].

Commercial development
Various processes for the direct combination of H_2 and O_2 have been patented but, until now (2015), none have been implemented on an industrial scale.

This technique is considered ready for larger scale demonstration [118,García-Serna et al.2014], and technologies are available (e.g. KIT offering a microstructured reactor [119, KIT 2015]).

Level of environmental protection
The process avoids all the hazardous reaction conditions and chemicals of the existing process, along with its undesirable by-products. It produces H_2O_2 more efficiently, cutting both energy use and costs.

Direct synthesis is expected to be more resource-efficient than the existing process. Depending on the design, it has the potential to use less energy and to reduce waste and emissions to air and water. It prevents the emissions that are related to the use and processing of the working solution in the existing process.

Cost savings compared to existing BAT
It is estimated that direct synthesis can be competitive compared to the established process when on-site production is required and capacities of less than 10 kt per year are demanded. The total investment cost should be approximately USD 40.3 million ± USD 12.1 million (in 2012) for a 10 kt per year process to be comparable to the traditional process in terms of costs [118, García-Serna et al. 2014].

Chance of becoming BAT in the future
High, for smaller units.

When it might become commercially available
No information provided.

References
[118, García-Serna et al. 2014].

12.5.2 Electrochemical route to produce hydrogen peroxide using fuel cells

Description

As one of the older process routes, hydrogen peroxide can be produced by cathodic reduction of oxygen. The DOW process uses a monopolar cell in a dilute sodium hydroxide solution. A unit with a capacity of around 3 000 t/yr has been operated since 1992 in the US. [3, Goor et al. 2007]. This technique implies a high consumption of electrical energy and the hydrogen peroxide produced is unstable (in alkaline conditions) and therefore is only suitable for immediate consumption.

The energy consumption could be reduced by using fuel cells instead of electrical power. A suitable product concentration (e.g. 6 %) can be achieved by using porous membrane electrodes for example.

Commercially developed

No.

References

[3, Fierro et al. 2006].

13 BEST AVAILABLE TECHNIQUES (BAT) CONCLUSIONS FOR THE PRODUCTION OF LARGE VOLUME ORGANIC CHEMICALS

Scope

These BAT conclusions concern the production of the following organic chemicals, as specified in Section 4.1 of Annex I to Directive 2010/75/EU:

a) simple hydrocarbons (linear or cyclic, saturated or unsaturated, aliphatic or aromatic);
b) oxygen-containing hydrocarbons such as alcohols, aldehydes, ketones, carboxylic acids, esters and mixtures of esters, acetates, ethers, peroxides and epoxy resins;
c) sulphurous hydrocarbons;
d) nitrogenous hydrocarbons such as amines, amides, nitrous compounds, nitro compounds or nitrate compounds, nitriles, cyanates, isocyanates;
e) phosphorus-containing hydrocarbons;
f) halogenic hydrocarbons;
g) organometallic compounds;
k) surface-active agents and surfactants.

These BAT conclusions also cover the production of hydrogen peroxide as specified in Section 4.2 (e) of Annex I to Directive 2010/75/EU.

These BAT conclusions cover combustion of fuels in process furnaces/heaters, where this is part of the abovementioned activities.

These BAT conclusions cover production of the aforementioned chemicals in continuous processes where the total production capacity of those chemicals exceeds 20 kt/year.

These BAT conclusions do not address the following:

- combustion of fuels other than in a process furnace/heater or a thermal/catalytic oxidiser; this may be covered by the BAT conclusions for Large Combustion Plants (LCP);
- incineration of waste; this may be covered by the BAT conclusions for Waste Incineration (WI);
- ethanol production taking place on an installation covered by the activity description in Section 6.4 (b) (ii) of Annex I to Directive 2010/75/EU or covered as a directly associated activity to such an installation; this may be covered by the BAT conclusions for Food, Drink and Milk Industries (FDM).

Other BAT conclusions which are complementary for the activities covered by these BAT conclusions include:

- Common Waste Water/Waste Gas Treatment/Management Systems in the Chemical Sector (CWW);
- Common Waste Gas Treatment in the Chemical Sector (WGC).

Other BAT conclusions and reference documents which may be of relevance for the activities covered by these BAT conclusions are the following:

- Economics and Cross-media Effects (ECM);
- Emissions from Storage (EFS);

- Energy Efficiency (ENE);
- Industrial Cooling Systems (ICS);
- Large Combustion Plants (LCP);
- Refining of Mineral Oil and Gas (REF);
- Monitoring of Emissions to Air and Water from IED installations (ROM);
- Waste Incineration (WI);
- Waste Treatment (WT).

General considerations

Best Available Techniques

The techniques listed and described in these BAT conclusions are neither prescriptive nor exhaustive. Other techniques may be used that ensure at least an equivalent level of environmental protection.

Unless otherwise stated, the BAT conclusions are generally applicable.

Averaging periods and reference conditions for emissions to air

Unless stated otherwise, the emission levels associated with the best available techniques (BAT-AELs) for emissions to air given in these BAT conclusions refer to values of concentration, expressed as mass of emitted substance per volume of waste gas under standard conditions (dry gas at a temperature of 273,15 K, and a pressure of 101,3 kPa), and expressed in the unit mg/Nm^3.

Unless stated otherwise, the averaging periods associated with the BAT-AELs for emissions to air are defined as follows.

Type of measurement	Averaging period	Definition
Continuous	Daily average	Average over a period of one day based on valid hourly or half-hourly averages
Periodic	Average over the sampling period	Average of three consecutive measurements of at least 30 minutes each (1) (2)

(1) For any parameter where, due to sampling or analytical limitations, 30-minute sampling is inappropriate, a suitable sampling period is employed.
(2) For PCDD/F, a sampling period of 6 to 8 hours is used.

Where BAT-AELs refer to specific emission loads, expressed as load of emitted substance per unit of production output, the average specific emission loads l_s are calculated using Equation 1:

Equation 1:

$$l_s = \frac{1}{n}\sum_{i=1}^{n} \frac{c_i q_i}{p_i}$$

where

n = number of measurement periods;
c_i = average concentration of the substance during ith measurement period;
q_i = average flow rate during ith measurement period;
p_i = production output during ith measurement period.

Reference oxygen level
For process furnaces/heaters, the reference oxygen level of the waste gases **(O_R)** is 3 vol-%.

Conversion to reference oxygen level
The emission concentration at the reference oxygen level is calculated using Equation 2:

Equation 2:

$$E_R = \frac{21 - O_R}{21 - O_M} \times E_M$$

where

E_R = emission concentration at the reference oxygen level O_R;
O_R = reference oxygen level in vol-%;
E_M = measured emission concentration;
O_M = measured oxygen level in vol-%.

Averaging periods for emissions to water

Unless stated otherwise, the averaging periods associated with the environmental performance levels associated with the best available techniques (BAT-AEPLs) for emissions to water expressed in concentrations are defined as follows.

Averaging period	Definition
Average of values obtained during one month	Flow-weighted average value from 24-hour flow-proportional composite samples obtained during one month under normal operating conditions (1)
Average of values obtained during one year	Flow-weighted average value from 24-hour flow-proportional composite samples obtained during one year under normal operating conditions (1)
(1) Time-proportional composite samples can be used provided that sufficient flow stability can be demonstrated.	

Flow-weighted average concentrations of the parameter (c_w) are calculated using Equation 3:

Equation 3:

$$c_w = \sum_{i=1}^{n} c_i q_i \Big/ \sum_{i=1}^{n} q_i$$

where

n = number of measurement periods;
c_i = average concentration of the parameter during ith measurement period;
q_i = average flow rate during ith measurement period.

Where BAT-AEPLs refer to specific emission loads, expressed as load of emitted substance per unit of production output, the average specific emission loads are calculated using Equation 1.

Acronyms and definitions

For the purposes of these BAT conclusions, the following acronyms and definitions apply.

Term used	Definition
BAT-AEPL	Environmental performance level associated with BAT, as described in Commission Implementing Decision 2012/119/EU. BAT-AEPLs include emission levels associated with the best available techniques (BAT-AELs) as defined in Article 3(13) of Directive 2010/75/EU
BTX	Collective term for benzene, toluene and ortho-/meta-/para-xylene or mixtures thereof
CO	Carbon monoxide
Combustion unit	Any technical apparatus in which fuels are oxidised in order to use the heat thus generated. Combustion units include boilers, engines, turbines and process furnaces/heaters, but do not include waste gas treatment units (e.g. a thermal/catalytic oxidiser used for the abatement of organic compounds)
Continuous measurement	Measurement using an 'automated measuring system' permanently installed on site
Continuous process	A process in which the raw materials are fed continuously into the reactor with the reaction products then fed into connected downstream separation and/or recovery units
Copper	The sum of copper and its compounds, in dissolved or particulate form, expressed as Cu
DNT	Dinitrotoluene
EB	Ethylbenzene
EDC	Ethylene dichloride
EG	Ethylene glycols
EO	Ethylene oxide
Ethanolamines	Collective term for monoethanolamine, diethanolamine and triethanolamine, or mixtures thereof
Ethylene glycols	Collective term for monoethylene glycol, diethylene glycol and triethylene glycol, or mixtures thereof
Existing plant	A plant that is not a new plant
Existing unit	A unit that is not a new unit
Flue-gas	The exhaust gas exiting a combustion unit
I-TEQ	International toxic equivalent – derived by using the international toxic equivalence factors, as defined in Annex VI, part 2 of Directive 2010/75/EU
Lower olefins	Collective term for ethylene, propylene, butylene and butadiene, or mixtures thereof
Major plant upgrade	A major change in the design or technology of a plant with major adjustments or replacements of the process and/or abatement units and associated equipment
MDA	Methylene diphenyl diamine
MDI	Methylene diphenyl diisocyanate
MDI plant	Plant for the production of MDI from MDA via phosgenation
New plant	A plant first permitted on the site of the installation following the publication of these BAT conclusions or a complete replacement of a plant following the publication of these BAT conclusions
New unit	A unit first permitted following the publication of these BAT conclusions or a complete replacement of a unit following the publication of these BAT conclusions
NO_X precursors	Nitrogen-containing compounds (e.g. ammonia, nitrous gases and nitrogen-containing organic compounds) in the input to a thermal treatment that lead to NO_X emissions. Elementary nitrogen is not included
PCDD/F	Polychlorinated dibenzo-dioxins and -furans
Periodic measurement	Measurement at specified time intervals using manual or automated methods

Term used	Definition
Process furnace/heater	Process furnaces or heaters are: • combustion units whose flue-gases are used for the thermal treatment of objects or feed material through direct contact, e.g. in drying processes or chemical reactors; or • combustion units whose radiant and/or conductive heat is transferred to objects or feed material through a solid wall without using an intermediary heat transfer fluid, e.g. furnaces or reactors heating a process stream used in the (petro-)chemical industry such as steam cracker furnaces. It should be noted that, as a consequence of the application of good energy recovery practices, some of the process furnaces/heaters may have an associated steam/electricity generation system. This is considered to be an integral design feature of the process furnace/heater that cannot be considered in isolation.
Process off-gas	The gas leaving a process which is further treated for recovery and/or abatement
NO_X	The sum of nitrogen monoxide (NO) and nitrogen dioxide (NO_2), expressed as NO_2
Residues	Substances or objects generated by the activities covered by the scope of this document, as waste or by-products
RTO	Regenerative thermal oxidiser
SCR	Selective catalytic reduction
SMPO	Styrene monomer and propylene oxide
SNCR	Selective non-catalytic reduction
SRU	Sulphur recovery unit
TDA	Toluene diamine
TDI	Toluene diisocyanate
TDI plant	Plant for the production of TDI from TDA via phosgenation
TOC	Total organic carbon, expressed as C; includes all organic compounds (in water)
Total suspended solids (TSS)	Mass concentration of all suspended solids, measured via filtration through glass fibre filters and gravimetry
TVOC	Total volatile organic carbon; total volatile organic compounds which are measured by a flame ionisation detector (FID) and expressed as total carbon
Unit	A segment/subpart of a plant in which a specific process or operation is carried out (e.g. reactor, scrubber, distillation column). Units can be new units or existing units
Valid hourly or half-hourly average	An hourly (or half-hourly) average is considered valid when there is no maintenance or malfunction of the automated measuring system
VCM	Vinyl chloride monomer
VOCs	Volatile organic compounds as defined in Article 3(45) of Directive 2010/75/EU

13.1 General BAT conclusions

The sector-specific BAT conclusions included in Sections 13.2 to 13.11 apply in addition to the general BAT conclusions given in this section.

13.1.1 Monitoring of emissions to air

BAT 1. BAT is to monitor channelled emissions to air from process furnaces/heaters in accordance with EN standards and with at least the minimum frequency given in the table below. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality.

Substance/ Parameter	**Standard(s) (1)**	**Total rated thermal input (MW_{th}) (2)**	**Minimum monitoring frequency (3)**	**Monitoring associated with**
CO	Generic EN standards	≥ 50	Continuous	Table 13.1 Table 13.10
	EN 15058	10 to < 50	Once every three months (4)	
Dust (5)	Generic EN standards and EN 13284-2	≥ 50	Continuous	BAT 5
	EN 13284-1	10 to < 50	Once every three months (4)	
NH_3 (6)	Generic EN standards	≥ 50	Continuous	BAT 7 Table 13.1
	No EN standard available	10 to < 50	Once every three months (4)	
NO_X	Generic EN standards	≥ 50	Continuous	BAT 4 Table 13.1, Table 13.10
	EN 14792	10 to < 50	Once every three months (4)	
SO_2 (7)	Generic EN standards	≥ 50	Continuous	BAT 6
	EN 14791	10 to < 50	Once every three months (4)	

(1) Generic EN standards for continuous measurements are EN 15267-1, -2, and -3, and EN 14181. EN standards for periodic measurements are given in the table.

(2) Refers to the total rated thermal input of all process furnaces/heaters connected to the stack where emissions occur.

(3) In the case of process furnaces/heaters with a total rated thermal input of less than 100 MW_{th} operated less than 500 hours per year, the monitoring frequency may be reduced to at least once every year.

(4) The minimum monitoring frequency for periodic measurements may be reduced to once every six months, if the emission levels are proven to be sufficiently stable.

(5) Monitoring of dust does not apply when combusting exclusively gaseous fuels.

(6) Monitoring of NH_3 only applies when SCR or SNCR is used.

(7) In the case of process furnaces/heaters combusting gaseous fuels and/or oil with a known sulphur content and where no flue-gas desulphurisation is carried out, continuous monitoring can be replaced either by periodic monitoring with a minimum frequency of once every three months or by calculation ensuring the provision of data of an equivalent scientific quality.

BAT 2. BAT is to monitor channelled emissions to air other than from process furnaces/heaters in accordance with EN standards and with at least the minimum frequency given in the table below. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality.

Substance/ Parameter	**Processes/Sources**	**Standard (s)**	**Minimum monitoring frequency**	**Monitoring associated with**
Benzene	Waste gas from the cumene oxidation unit in phenol production (1)	No EN standard available	Once every month (2)	BAT 57
	All other processes/sources (3)			BAT 10
Cl_2	TDI/MDI (1)	No EN standard available	Once every month (2)	BAT 66
	EDC/VCM			BAT 76
CO	Thermal oxidiser	EN 15058	Once every month (2)	BAT 13
	Lower olefins (decoking)	No EN standard available (4)	Once every year or once during decoking, if decoking is less frequent	BAT 20
	EDC/VCM (decoking)			BAT 78
Dust	Lower olefins (decoking)	No EN standard available (5)	Once every year or once during decoking, if decoking is less frequent	BAT 20
	EDC/VCM (decoking)			BAT 78
	All other processes/sources (3)	EN 13284 -1	Once every month (2)	BAT 11
EDC	EDC/VCM	No EN standard available	Once every month (2)	BAT 76
Ethylene oxide	Ethylene oxide and ethylene glycols	No EN standard available	Once every month (2)	BAT 52
Formaldehyde	Formaldehyde	No EN standard available	Once every month (2)	BAT 45
Gaseous chlorides, expressed as HCl	TDI/MDI (1)	EN 1911	Once every month (2)	BAT 66
	EDC/VCM			BAT 76
	All other processes/sources (3)			BAT 12
NH_3	Use of SCR or SNCR	No EN standard available	Once every month (2)	BAT 7
NO_X	Thermal oxidiser	EN 14792	Once every month (2)	BAT 13
PCDD/F	TDI/MDI (6)	EN 1948-1, -2, and -3	Once every six months (2)	BAT 67
PCDD/F	EDC/VCM			BAT 77
SO_2	All processes/sources (3)	EN 14791	Once every month (2)	BAT 12
Tetrachloromethane	TDI/MDI (1)	No EN standard available	Once every month (2)	BAT 66
TVOC	TDI/MDI	EN 12619	Once every month (2)	BAT 66
	EO (desorption of CO_2 from scrubbing medium)		Once every six months (2)	BAT 51

	Formaldehyde		Once every month (2)	BAT 45
	Waste gas from the cumene oxidation unit in phenol production	EN 12619	Once every month (2)	BAT 57
	Waste gas from other sources in phenol production when not combined with other waste gas streams		Once every year (2)	
	Waste gas from the oxidation unit in hydrogen peroxide production		Once every month (2)	BAT 86
	EDC/VCM		Once every month (2)	BAT 76
	All other processes/sources (3)		Once every month (2)	BAT 10
VCM	EDC/VCM	No EN standard available	Once every month (2)	BAT 76

(1) The monitoring applies where the pollutant is present in the waste gas based on the inventory of waste gas streams specified by the CWW BAT conclusions.

(2) The minimum monitoring frequency for periodic measurements may be reduced to once every year, if the emission levels are proven to be sufficiently stable.

(3) All (other) processes/sources where the pollutant is present in the waste gas based on the inventory of waste gas streams specified by the CWW BAT conclusions.

(4) EN 15058 and the sampling period need adaptation so that the measured values are representative of the whole decoking cycle.

(5) EN 13284-1 and the sampling period need adaptation so that the measured values are representative of the whole decoking cycle.

(6) The monitoring applies where the chlorine and/or chlorinated compounds are present in the waste gas and thermal treatment is applied

13.1.2 Emissions to air

13.1.2.1 Emissions to air from process furnaces/heaters

BAT 3. In order to reduce emissions to air of CO and unburnt substances from process furnaces/heaters, BAT is to ensure an optimised combustion.

Optimised combustion is achieved by good design and operation of the equipment which includes optimisation of the temperature and residence time in the combustion zone, efficient mixing of the fuel and combustion air, and combustion control. Combustion control is based on the continuous monitoring and automated control of appropriate combustion parameters (e.g. O_2, CO, fuel to air ratio, and unburnt substances).

BAT 4. In order to reduce NO_X emissions to air from process furnaces/heaters, BAT is to use one or a combination of the techniques given below.

	Technique	Description	Applicability
a	Choice of fuel	See Section 13.12.3. This includes switching from liquid to gaseous fuels, taking into account the overall hydrocarbon balance	The switch from liquid to gaseous fuels may be restricted by the design of the burners in the case of existing plants
b	Staged combustion	Staged combustion burners achieve lower NO_X emissions by staging the injection of either air or fuel in the near burner region. The division of fuel or air reduces the oxygen concentration in the primary burner combustion zone, thereby lowering the peak flame temperature and reducing thermal NO_X formation	Applicability may be restricted by space availability when upgrading small process furnaces, limiting the retrofit of fuel/air staging without reducing capacity For existing EDC crackers, the applicability may be restricted by the design of the process furnace
c	Flue-gas recirculation (external)	Recirculation of part of the flue-gas to the combustion chamber to replace part of the fresh combustion air, with the effect of reducing the oxygen content and therefore cooling the temperature of the flame	For existing process furnaces/heaters, the applicability may be restricted by their design. Not applicable to existing EDC crackers
d	Flue-gas recirculation (internal)	Recirculation of part of the flue-gas within the combustion chamber to replace part of the fresh combustion air, with the effect of reducing the oxygen content and therefore reducing the temperature of the flame	For existing process furnaces/heaters, the applicability may be restricted by their design
e	Low-NO_X burner (LNB) or ultra-low-NO_X burner (ULNB)	See Section 13.12.3	For existing process furnaces/heaters, the applicability may be restricted by their design
f	Use of inert diluents	'Inert' diluents, e.g. steam, water, nitrogen, are used (either by being premixed with the fuel prior to its combustion or directly injected into the combustion chamber) to reduce the temperature of the flame. Steam injection may increase CO emissions	Generally applicable
g	Selective catalytic reduction (SCR)	See Section 13.12.1	Applicability to existing process furnaces/heaters may be restricted by space availability
h	Selective non-catalytic reduction (SNCR)	See Section 13.12.1	Applicability to existing process furnaces/heaters may be restricted by the temperature window (900–1 050°C) and the residence time needed for the reaction. Not applicable to EDC crackers

BAT-associated emission levels (BAT-AELs): See Table 13.1 and Table 13.10.

BAT 5. In order to prevent or reduce dust emissions to air from process furnaces/heaters, BAT is to use one or a combination of the techniques given below.

Technique		Description	Applicability
a	Choice of fuel	See Section 13.12.3. This includes switching from liquid to gaseous fuels, taking into account the overall hydrocarbon balance	The switch from liquid to gaseous fuels may be restricted by the design of the burners in the case of existing plants
b	Atomisation of liquid fuels	Use of high pressure to reduce the droplet size of liquid fuel. Current optimal burner design generally includes steam atomisation	Generally applicable
c	Fabric, ceramic or metal filter	See Section 13.12.1	Not applicable when only combusting gaseous fuels

BAT 6. In order to prevent or reduce SO_2 emissions to air from process furnaces/heaters, BAT is to use one or both of the techniques given below.

Technique		Description	Applicability
a	Choice of fuel	See Section 13.12.3. This includes switching from liquid to gaseous fuels, taking into account the overall hydrocarbon balance	The switch from liquid to gaseous fuels may be restricted by the design of the burners in the case of existing plants
b	Caustic scrubbing	See Section 13.12.1	Applicability may be restricted by space availability

13.1.2.2 Emissions to air from the use of SCR or SNCR

BAT 7. In order to reduce emissions to air of ammonia which is used in selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) for the abatement of NO_X emissions, BAT is to optimise the design and/or operation of SCR or SNCR (e.g. optimised reagent to NO_X ratio, homogeneous reagent distribution and optimum size of the reagent drops).

BAT-associated emission levels (BAT-AELs) for emissions from a lower olefins cracker furnace when SCR or SNCR is used: See Table 13.1.

13.1.2.3 Emissions to air from other processes/sources

13.1.2.3.1 Techniques to reduce emissions from other processes/sources

BAT 8. In order to reduce the load of pollutants sent to the final waste gas treatment, and to increase resource efficiency, BAT is to use an appropriate combination of the techniques given below for process off-gas streams.

Technique		Description	Applicability
a	Recovery and use of excess or generated hydrogen	Recovery and use of excess hydrogen or hydrogen generated from chemical reactions (e.g. for hydrogenation reactions). Recovery techniques such as pressure swing adsorption or membrane separation may be used to increase the hydrogen content	Applicability may be restricted where the energy demand for recovery is excessive due to the low hydrogen content or when there is no demand for hydrogen
b	Recovery and use of organic solvents and unreacted organic raw materials	Recovery techniques such as compression, condensation, cryogenic condensation, membrane separation and adsorption may be used. The choice of technique may be influenced by safety considerations, e.g. presence of other substances or contaminants	Applicability may be restricted where the energy demand for recovery is excessive due to the low organic content
c	Use of spent air	The large volume of spent air from oxidation reactions is treated and used as low-purity nitrogen	Only applicable where there are available uses for low-purity nitrogen which do not compromise process safety
d	Recovery of HCl by wet scrubbing for subsequent use	Gaseous HCl is absorbed in water using a wet scrubber, which may be followed by purification (e.g. using adsorption) and/or concentration (e.g. using distillation) (see Section 13.12.1 for the technique descriptions). The recovered HCl is then used (e.g. as acid or to produce chlorine)	Applicability may be restricted in the case of low HCl loads
e	Recovery of H_2S by regenerative amine scrubbing for subsequent use	Regenerative amine scrubbing is used for recovering H_2S from process off-gas streams and from the acid off-gases of sour water stripping units. H_2S is then typically converted to elemental sulphur in a sulphur recovery unit in a refinery (Claus process).	Only applicable if a refinery is located nearby
f	Techniques to reduce solids and/or liquids entrainment	See Section 13.12.1	Generally applicable

BAT 9. In order to reduce the load of pollutants sent to the final waste gas treatment, and to increase energy efficiency, BAT is to send process off-gas streams with a sufficient calorific value to a combustion unit. BAT 8a. and BAT 8b. have priority over sending process off-gas streams to a combustion unit.

Applicability

Sending process off-gas streams to a combustion unit may be restricted due to the presence of contaminants or due to safety considerations.

BAT 10. In order to reduce channelled emissions of organic compounds to air, BAT is to use one or a combination of the techniques given below.

Technique		Description	Applicability
a	Condensation	See Section 13.12.1. The technique is generally used in combination with further abatement techniques	Generally applicable
b	Adsorption	See Section 13.12.1	Generally applicable
c	Wet scrubbing	See Section 13.12.1	Only applicable to VOCs that can be absorbed in aqueous solutions
d	Catalytic oxidiser	See Section 13.12.1	Applicability may be restricted by the presence of catalyst poisons
e	Thermal oxidiser	See Section 13.12.1. Instead of a thermal oxidiser, an incinerator for the combined treatment of liquid waste and waste gas may be used	Generally applicable

BAT 11. In order to reduce channelled dust emissions to air, BAT is to use one or a combination of the techniques given below.

Technique		Description	Applicability
a	Cyclone	See Section 13.12.1. The technique is used in combination with further abatement techniques	Generally applicable
b	Electrostatic precipitator	See Section 13.12.1	For existing units, the applicability may be restricted by space availability or safety considerations
c	Fabric filter	See Section 13.12.1	Generally applicable
d	Two-stage dust filter	See Section 13.12.1	
e	Ceramic/metal filter	See Section 13.12.1	
f	Wet dust scrubbing	See Section 13.12.1	

BAT 12. In order to reduce emissions to air of sulphur dioxide and other acid gases (e.g. HCl), BAT is to use wet scrubbing.

Description
For the description of wet scrubbing, see Section 13.12.1.

13.1.2.3.2 Techniques to reduce emissions from a thermal oxidiser

BAT 13. In order to reduce emissions to air of NO_X, CO, and SO_2 from a thermal oxidiser, BAT is to use an appropriate combination of the techniques given below.

	Technique	Description	Main pollutant targeted	Applicability
a	Removal of high levels of NO_X precursors from the process off-gas streams	Remove (if possible, for reuse) high levels of NO_X precursors prior to thermal treatment, e.g. by scrubbing, condensation or adsorption	NO_X	Generally applicable
b	Choice of support fuel	See Section 13.12.3	NO_X, SO_2	Generally applicable
c	Low-NO_X burner (LNB)	See Section 13.12.1	NO_X	Applicability to existing units may be restricted by design and/or operational constraints
d	Regenerative thermal oxidiser (RTO)	See Section 13.12.1	NO_X	Applicability to existing units may be restricted by design and/or operational constraints
e	Combustion optimisation	Design and operational techniques used to maximise the removal of organic compounds, while minimising emissions to air of CO and NO_X (e.g. by controlling combustion parameters such as temperature and residence time)	CO, NO_X	Generally applicable
f	Selective catalytic reduction (SCR)	See Section 13.12.1	NO_X	Applicability to existing units may be restricted by space availability
g	Selective non-catalytic reduction (SNCR)	See Section 13.12.1	NO_X	Applicability to existing units may be restricted by the residence time needed for the reaction

13.1.3 Emissions to water

BAT 14. In order to reduce the waste water volume, the pollutant loads discharged to a suitable final treatment (typically biological treatment), and emissions to water, BAT is to use an integrated waste water management and treatment strategy that includes an appropriate combination of process-integrated techniques, techniques to recover pollutants at source, and pretreatment techniques, based on the information provided by the inventory of waste water streams specified in the CWW BAT conclusions.

13.1.4 Resource efficiency

BAT 15. In order to increase resource efficiency when using catalysts, BAT is to use a combination of the techniques given below.

Technique		Description
a	Catalyst selection	Select the catalyst to achieve the optimal balance between the following factors: - catalyst activity; - catalyst selectivity; - catalyst lifetime (e.g. vulnerability to catalyst poisons); - use of less toxic metals.
b	Catalyst protection	Techniques used upstream of the catalyst to protect it from poisons (e.g. raw material pretreatment)
c	Process optimisation	Control of reactor conditions (e.g. temperature, pressure) to achieve the optimal balance between conversion efficiency and catalyst lifetime
d	Monitoring of catalyst performance	Monitoring of the conversion efficiency to detect the onset of catalyst decay using suitable parameters (e.g. the heat of reaction and the CO_2 formation in the case of partial oxidation reactions)

BAT 16. In order to increase resource efficiency, BAT is to recover and reuse organic solvents.

Description

Organic solvents used in processes (e.g. chemical reactions) or operations (e.g. extraction) are recovered using appropriate techniques (e.g. distillation or liquid phase separation), purified if necessary (e.g. using distillation, adsorption, stripping or filtration) and returned to the process or operation. The amount recovered and reused is process-specific.

13.1.5 Residues

BAT 17. In order to prevent or, where that is not practicable, to reduce the amount of waste being sent for disposal, BAT is to use an appropriate combination of the techniques given below.

Technique		Description	Applicability
Techniques to prevent or reduce the generation of waste			
a	Addition of inhibitors to distillation systems	Selection (and optimisation of dosage) of polymerisation inhibitors that prevent or reduce the generation of residues (e.g. gums or tars). The optimisation of dosage may need to take into account that it can lead to higher nitrogen and/or sulphur content in the residues which could interfere with their use as a fuel	Generally applicable
b	Minimisation of high-boiling residue formation in distillation systems	Techniques that reduce temperatures and residence times (e.g. packing instead of trays to reduce the pressure drop and thus the temperature; vacuum instead of atmospheric pressure to reduce the temperature)	Only applicable to new distillation units or major plant upgrades
Techniques to recover materials for reuse or recycling			
c	Material recovery (e.g. by distillation, cracking)	Materials (i.e. raw materials, products, and by-products) are recovered from residues by isolation (e.g. distillation) or conversion (e.g. thermal/catalytic cracking, gasification, hydrogenation)	Only applicable where there are available uses for these recovered materials
d	Catalyst and adsorbent regeneration	Regeneration of catalysts and adsorbents, e.g. using thermal or chemical treatment	Applicability may be restricted where regeneration results in significant cross-media effects.
Techniques to recover energy			
e	Use of residues as a fuel	Some organic residues, e.g. tar, can be used as fuels in a combustion unit	Applicability may be restricted by the presence of certain substances in the residues, making them unsuitable to use in a combustion unit and requiring disposal

13.1.6 Other than normal operating conditions

BAT 18. In order to prevent or reduce emissions from equipment malfunctions, BAT is to use all of the techniques given below.

Technique		Description	Applicability
a	Identification of critical equipment	Equipment critical to the protection of the environment ('critical equipment') is identified on the basis of a risk assessment (e.g. using a Failure Mode and Effects Analysis)	Generally applicable
b	Asset reliability programme for critical equipment	A structured programme to maximise equipment availability and performance which includes standard operating procedures, preventive maintenance (e.g. against corrosion), monitoring, recording of incidents, and continuous improvements	Generally applicable
c	Back-up systems for critical equipment	Build and maintain back-up systems, e.g. vent gas systems, abatement units	Not applicable if appropriate equipment availability can be demonstrated using technique b.

BAT 19. In order to prevent or reduce emissions to air and water occurring during other than normal operating conditions, BAT is to implement measures commensurate with the relevance of potential pollutant releases for:

(i) start-up and shutdown operations;
(ii) other circumstances (e.g. regular and extraordinary maintenance work and cleaning operations of the units and/or of the waste gas treatment system) including those that could affect the proper functioning of the installation.

13.2 BAT conclusions for lower olefins production

The BAT conclusions in this section apply to the production of lower olefins using the steam cracking process, and apply in addition to the general BAT conclusions given in section 13.1

13.2.1 Emissions to air

13.2.1.1 BAT-AELs for emissions to air from a lower olefins cracker furnace

Table 13.1: BAT-AELs for emissions to air of NO_X and NH_3 from a lower olefins cracker furnace

Parameter	**BAT-AELs (1) (2) (3) (daily average or average over the sampling period) (mg/Nm^3, at 3 vol-% O_2)**	
	New furnace	Existing furnace
NO_X	60–100	70–200
NH_3	< 5–15 (4)	

(1) Where the flue gases of two or more furnaces are discharged through a common stack, the BAT-AEL applies to the combined discharge from the stack.
(2) The BAT-AELs do not apply during decoking operations.
(3) No BAT-AEL applies for CO. As an indication, the CO emission level will generally be 10–50 mg/Nm^3 expressed as a daily average or an average over the sampling period.
(4) The BAT-AEL only applies when SCR or SNCR are used.

The associated monitoring is in BAT 1

13.2.1.2 Techniques to reduce emissions from decoking

BAT 20. In order to reduce emissions to air of dust and CO from the decoking of the cracker tubes, BAT is to use an appropriate combination of the techniques to reduce the frequency of decoking given below and one or a combination of the abatement techniques given below.

Technique		**Description**	**Applicability**
Techniques to reduce the frequency of decoking			
a	Tube materials that retard coke formation	Nickel present at the surface of the tubes catalyses coke formation. Employing materials that have lower nickel levels, or coating the interior tube surface with an inert material, can therefore retard the rate of coke build-up	Only applicable to new units or major plant upgrades
b	Doping of the raw material feed with sulphur compounds	As nickel sulphides do not catalyse coke formation, doping the feed with sulphur compounds when they are not already present at the desired level can also help retard the build-up of coke, as this will promote the passivation of the tube surface	Generally applicable
c	Optimisation of thermal decoking	Optimisation of operating conditions, i.e. airflow, temperature and steam content across the decoking cycle, to maximise coke removal	Generally applicable
Abatement techniques			
d	Wet dust scrubbing	See Section 13.12.1	Generally applicable
e	Dry cyclone	See Section 13.12.1	Generally applicable
f	Combustion of decoking waste gas in process furnace/heater	The decoking waste gas stream is passed through the process furnace/heater during decoking where the coke particles (and CO) are further combusted	Applicability for existing plants may be restricted by the design of the pipework systems or fire-duty restrictions

13.2.2 Emissions to water

BAT 21. In order to prevent or reduce the amount of organic compounds and waste water discharged to waste water treatment, BAT is to maximise the recovery of hydrocarbons from the quench water of the primary fractionation stage and reuse the quench water in the dilution steam generation system.

Description

The technique consists of ensuring an effective separation of organic and aqueous phases. The recovered hydrocarbons are recycled to the cracker or used as raw materials in other chemical processes. Organic recovery can be enhanced, e.g. through the use of steam or gas stripping, or the use of a reboiler. Treated quench water is reused within the dilution steam generation system. A quench water purge stream is discharged to downstream final waste water treatment to prevent the build-up of salts in the system.

BAT 22. In order to reduce the organic load discharged to waste water treatment from the spent caustic scrubber liquor originating from the removal of H2S from the cracked gases, BAT is to use stripping.

Description

For the description of stripping, see Section 13.12.2. The stripping of scrubber liquors is carried out using a gaseous stream, which is then combusted (e.g. in the cracker furnace).

BAT 23. In order to prevent or reduce the amount of sulphides discharged to waste water treatment from the spent caustic scrubber liquor originating from the removal of acid gases from the cracked gases, BAT is to use one or a combination of the techniques given below.

Technique		Description	Applicability
a	Use of low-sulphur raw materials in the cracker feed	Use raw materials that have a low sulphur content or have been desulphurised	Applicability may be restricted by a need for sulphur doping to reduce coke build-up
b	Maximisation of the use of amine scrubbing for the removal of acid gases	The scrubbing of the cracked gases with a regenerative (amine) solvent to remove acid gases, mainly H_2S, to reduce the load on the downstream caustic scrubber	Not applicable if the lower olefin cracker is located far away from an SRU. Applicability for existing plants may be restricted by the capacity of the SRU
c	Oxidation	Oxidation of sulphides present in the spent scrubbing liquor to sulphates, e.g. using air at elevated pressure and temperature (i.e. wet air oxidation) or an oxidising agent such as hydrogen peroxide	Generally applicable

13.3 BAT conclusions for aromatics production

The BAT conclusions in this section apply to the production of benzene, toluene, ortho-, meta- and para-xylene (commonly known as BTX aromatics) and cyclohexane from the pygas by-product of steam crackers and from reformate/naphtha produced in catalytic reformers; and apply in addition to the general BAT conclusions given in Section 13.1.

13.3.1 Emissions to air

BAT 24. In order to reduce the organic load from process off-gases sent to the final waste gas treatment and to increase resource efficiency, BAT is to recover organic materials by using BAT 8b. or, where that is not practicable, to recover energy from these process off-gases (see also BAT 9).

BAT 25. In order to reduce emissions to air of dust and organic compounds from the regeneration of hydrogenation catalyst, BAT is to send the process off-gas from catalyst regeneration to a suitable treatment system.

Description
The process off-gas is sent to wet or dry dust abatement devices to remove dust and then to a combustion unit or a thermal oxidiser to remove organic compounds in order to avoid direct emissions to air or flaring. The use of decoking drums alone is not sufficient.

13.3.2 Emissions to water

BAT 26. In order to reduce the amount of organic compounds and waste water discharged from aromatic extraction units to waste water treatment, BAT is either to use dry solvents or to use a closed system for the recovery and reuse of water when wet solvents are used.

BAT 27. In order to reduce the waste water volume and the organic load discharged to waste water treatment, BAT is to use an appropriate combination of the techniques given below.

	Technique	Description	Applicability
a	Water-free vacuum generation	Use mechanical pumping systems in a closed circuit procedure, discharging only a small amount of water as blowdown, or use dry-running pumps. In some cases, waste-water-free vacuum generation can be achieved by use of the product as a barrier liquid in a mechanical vacuum pump, or by use of a gas stream from the production process	Generally applicable
b	Source segregation of aqueous effluents	Aqueous effluents from aromatics plants are segregated from waste water from other sources in order to facilitate the recovery of raw materials or products	For existing plants, the applicability may be restricted by site-specific drainage systems
c	Liquid phase separation with recovery of hydrocarbons	Separation of organic and aqueous phases with appropriate design and operation (e.g. sufficient residence time, phase boundary detection and control) to prevent any entrainment of undissolved organic material	Generally applicable
d	Stripping with recovery of hydrocarbons	See Section 13.12.2. Stripping can be used on individual or combined streams	Applicability may be restricted when the concentration of hydrocarbons is low
e	Reuse of water	With further treatment of some waste water streams, water from stripping can be used as process water or as boiler feed water, replacing other sources of water	Generally applicable

13.3.3 Resource efficiency

BAT 28. In order to use resources efficiently, BAT is to maximise the use of co-produced hydrogen, e.g. from dealkylation reactions, as a chemical reagent or fuel by using BAT 8a. or, where that is not practicable, to recover energy from these process vents (see BAT 9).

13.3.4 Energy efficiency

BAT 29. In order to use energy efficiently when using distillation, BAT is to use one or a combination of the techniques given below.

Technique		Description	Applicability
a	Distillation optimisation	For each distillation column, the number of trays, reflux ratio, feed location and, for extractive distillations, the solvents to feed ratio are optimised	Applicability to existing units may be restricted by design, space availability and/or operational constraints
b	Recovery of heat from column overhead gaseous stream	Reuse condensation heat from the toluene and the xylene distillation column to supply heat elsewhere in the installation	
c	Single extractive distillation column	In a conventional extractive distillation system, the separation would require a sequence of two separation steps (i.e. main distillation column with side column or stripper). In a single extractive distillation column, the separation of the solvent is carried out in a smaller distillation column that is incorporated into the column shell of the first column	Only applicable to new plants or major plant upgrades. Applicability may be restricted for smaller capacity units as operability may be constrained by combining a number of operations into one piece of equipment
d	Distillation column with a dividing wall	In a conventional distillation system, the separation of a three-component mixture into its pure fractions requires a direct sequence of at least two distillation columns (or main columns with side columns). With a dividing wall column, separation can be carried out in just one piece of apparatus	
e	Thermaly coupled distillation	If distillation is carried out in two columns, energy flows in both columns can be coupled. The steam from the top of the first column is fed to a heat exchanger at the base of the second column	Only applicable to new plants or major plant upgrades. Applicability depends on the set-up of the distillation columns and process conditions, e.g. working pressure

13.3.5 Residues

BAT 30. In order to prevent or reduce the amount of spent clay being sent for disposal, BAT is to use one or both of the techniques given below.

Technique		Description	Applicability
a	Selective hydrogenation of reformate or pygas	Reduce the olefin content of reformate or pygas by hydrogenation. With fully hydrogenated raw materials, clay treaters have longer operating cycles	Only applicable to plants using raw materials with a high olefin content
b	Clay material selection	Use a clay that lasts as long as possible for its given conditions (i.e. having surface/structural properties that increase the operating cycle length), or use a synthetic material that has the same function as the clay but that can be regenerated	Generally applicable

13.4 BAT conclusions for ethylbenzene and styrene monomer production

The BAT conclusions in this section apply to the production of ethlybenzene using either the zeolite- or $AlCl_3$-catalysed alkylation process; and the production of styrene monomer either by ethylbenzene dehydrogenation or co-production with propylene oxide; and apply in addition to the general BAT conclusions given in Section 13.1.

13.4.1 Process selection

BAT 31. In order to prevent or reduce emissions to air of organic compounds and acid gases, the generation of waste water and the amount of waste being sent for disposal from the alkylation of benzene with ethylene, BAT for new plants and major plant upgrades is to use the zeolite catalyst process.

13.4.2 Emissions to air

BAT 32. In order to reduce the load of HCl sent to the final waste gas treatment from the alkylation unit in the $AlCl_3$-catalysed ethylbenzene production process, BAT is to use caustic scrubbing.

Description
For the description of caustic scrubbing, see Section 13.12.1.

Applicability
Only applicable to existing plants using the $AlCl_3$-catalysed ethylbenzene production process.

BAT 33. In order to reduce the load of dust and HCl sent to the final waste gas treatment from catalyst replacement operations in the $AlCl_3$-catalysed ethylbenzene production process, BAT is to use wet scrubbing and then use the spent scrubbing liquor as wash water in the post-alkylation reactor wash section.

Description
For the description of wet scrubbing, see Section 13.12.1.

BAT 34. In order to reduce the organic load sent to the final waste gas treatment from the oxidation unit in the SMPO production process, BAT is to use one or a combination of the techniques given below.

Technique		Description	Applicability
a	Techniques to reduce liquids entrainment	See Section 13.12.1	Generally applicable
b	Condensation	See Section 13.12.1	Generally applicable
c	Adsorption	See Section 13.12.1	Generally applicable
d	Scrubbing	See Section 13.12.1. Scrubbing is carried out with a suitable solvent (e.g. the cool, recirculated ethylbenzene) to absorb ethylbenzene, which is recycled to the reactor	For existing plants, the use of the recirculated ethylbenzene stream may be restricted by the plant design

BAT 35. In order to reduce emissions of organic compounds to air from the acetophenone hydrogenation unit in the SMPO production process, during other than normal operating conditions (such as start-up events), BAT is to send the process off-gas to a suitable treatment system.

13.4.3 Emissions to water

BAT 36. In order to reduce waste water generation from ethylbenzene dehydrogenation and to maximise the recovery of organic compounds, BAT is to use an appropriate combination of the techniques given below.

	Technique	Description	Applicability
a	Optimised liquid phase separation	Separation of organic and aqueous phases with appropriate design and operation (e.g. sufficient residence time, phase boundary detection and control) to prevent any entrainment of undissolved organic material	Generally applicable
b	Steam stripping	See Section 13.12.2	Generally applicable
c	Adsorption	See Section 13.12.2	Generally applicable
d	Reuse of water	Condensates from the reaction can be used as process water or as boiler feed after steam stripping (see technique b.) and adsorption (see technique c.)	Generally applicable

BAT 37. In order to reduce emissions to water of organic peroxides from the oxidation unit in the SMPO production process and to protect the downstream biological waste water treatment plant, BAT is to pretreat waste water containing organic peroxides using hydrolysis before it is combined with other waste water streams and discharged to the final biological treatment.

Description

For description of hydrolysis, see Section 13.12.2.

13.4.4 Resource efficiency

BAT 38. In order to recover organic compounds from ethylbenzene dehydrogenation prior to the recovery of hydrogen (see BAT 39), BAT is to use one or both of the techniques given below.

	Technique	Description	Applicability
a	Condensation	See Section 13.12.1	Generally applicable
b	Scrubbing	See Section 13.12.1. The absorbent consists of commercial organic solvents (or tar from ethylbenzene plants) (see BAT 42b.). VOCs are recovered by stripping of the scrubber liquor	

BAT 39. In order to increase resource efficiency, BAT is to recover the co-produced hydrogen from ethylbenzene dehydrogenation, and to use it either as a chemical reagent or to combust the dehydrogenation off-gas as a fuel (e.g. in the steam superheater).

BAT 40. In order to increase the resource efficiency of the acetophenone hydrogenation unit in the SMPO production process, BAT is to minimise excess hydrogen or recycle hydrogen by using BAT 8a. If BAT 8a. is not applicable, BAT is to recover energy (see BAT 9).

13.4.5 Residues

BAT 41. In order to reduce the amount of waste being sent for disposal from spent catalyst neutralisation in the $AlCl_3$-catalysed ethylbenzene production process, BAT is to recover residual organic compounds by stripping and then concentrate the aqueous phase to give a usable $AlCl_3$ by-product.

Description
Steam stripping is first used to remove VOCs, then the spent catalyst solution is concentrated by evaporation to give a usable $AlCl_3$ by-product. The vapour phase is condensed to give a HCl solution that is recycled into the process.

BAT 42. In order to prevent or reduce the amount of waste tar being sent for disposal from the distillation unit of ethylbenzene production, BAT is to use one or a combination of the techniques given below.

	Technique	Description	Applicability
a	Material recovery (e.g. by distillation, cracking)	See BAT 17c.	Only applicable where there are available uses for these recovered materials
b	Use of tar as an absorbent for scrubbing	See 13.12.1. Use the tar as an absorbent in the scrubbers used in styrene monomer production by ethylbenzene dehydrogenation, instead of commercial organic solvents (see BAT 38b.). The extent to which tar can be used depends on the scrubber capacity	Generally applicable
c	Use of tar as a fuel	BAT 17e.	Generally applicable

BAT 43. In order to reduce the generation of coke (which is both a catalyst poison and a waste) from units producing styrene by ethylbenzene dehydrogenation, BAT is to operate at the lowest possible pressure that is safe and practicable.

BAT 44. In order to reduce the amount of organic residues being sent for disposal from styrene monomer production including its co-production with propylene oxide, BAT is to use one or a combination of the techniques given below.

	Technique	Description	Applicability
a	Addition of inhibitors to distillation systems	BAT 17a.	Generally applicable
b	Minimisation of high-boiling residue formation in distillation systems	See BAT 17 b.	Only applicable to new distillation units or major plant upgrades
c	Use of residues as a fuel	See BAT 17e.	Generally applicable

13.5 BAT conclusions for formaldehyde production

The BAT conclusions in this section apply in addition to the general BAT conclusions given in Section 13.1.

13.5.1 Emissions to air

BAT 45. In order to reduce emissions of organic compounds to air from formaldehyde production and to use energy efficiently, BAT is to use one of the techniques given below.

	Technique	Description	Applicability
a	Send the waste gas stream to a combustion unit	BAT 9	Only applicable to the silver process
b	Catalytic oxidiser with energy recovery	See Section 13.12.1. Energy is recovered as steam	Only applicable to the metal oxide process. The ability to recover energy may be restricted in small stand-alone plants
c	Thermal oxidiser with energy recovery	See Section 13.12.1. Energy is recovered as steam	Only applicable to the silver process

Table 13.2: BAT-AELs for emissions of TVOC and formaldehyde to air from formaldehyde production

Parameter	BAT-AEL (daily average or average over the sampling period) (mg/Nm^3, no correction for oxygen content)
TVOC	< 5–30 (1)
Formaldehyde	2–5

(1) The lower end of the range is achieved when using a thermal oxidiser in the silver process.

The associated monitoring is in BAT 2

13.5.2 Emissions to water

BAT 46. In order to prevent or reduce waste water generation (e.g. from cleaning, spills and condensates) and the organic load discharged to further waste water treatment, BAT is to use one or both of the techniques given below.

	Technique	Description	Applicability
a	Reuse of water	Aqueous streams (e.g. from cleaning, spills and condensates) are recirculated into the process mainly to adjust the formaldehyde product concentration. The extent to which water can be reused depends on the desired formaldehyde concentration	Generally applicable
b	Chemical pretreatment	Conversion of formaldehyde, into other substances which are less toxic, e.g. by addition of sodium sulphite or by oxidation	Only applicable to effluents which, due to their formaldehyde content, could have a negative effect on the downstream biological waste water treatment

13.5.3 Residues

BAT 47. In order to reduce the amount of paraformaldehyde-containing waste being sent for disposal, BAT is to use one or a combination of the techniques given below.

	Technique	Description	Applicability
a	Minimisation of paraformaldehyde generation	The formation of paraformaldehyde is minimised by improved heating, insulation and flow circulation	Generally applicable
b	Material recovery	Paraformaldehyde is recovered by dissolution in hot water where it undergoes hydrolysis and depolymerisation to give a formaldehyde solution, or reused directly in other processes.	Not applicable when the recovered paraformaldehyde cannot be used due to its contamination
c	Use of residues as a fuel	Paraformaldehyde is recovered and used as a fuel	Only applicable when technique b. cannot be applied

13.6 BAT conclusions for ethylene oxide and ethylene glycols production

The BAT conclusions in this section apply in addition to the general BAT conclusions given in Section 13.1.

13.6.1 Process selection

BAT 48. In order to reduce the consumption of ethylene and emissions to air of organic compounds and CO_2, BAT for new plants and major plant upgrades is to use oxygen instead of air for the direct oxidation of ethylene to ethylene oxide.

13.6.2 Emissions to air

BAT 49. In order to recover ethylene and energy and to reduce emissions of organic compounds to air from the EO plant, BAT is to use both of the techniques given below.

	Technique	Description	Applicability
Techniques to recover organic material for reuse or recycling			
a	Use of pressure swing adsorption or membrane separation to recover ethylene from the inerts purge	With the pressure swing adsorption technique, the target gas (in this case ethylene) molecules are adsorbed on a solid (e.g. molecular sieve) at high pressure, and subsequently desorbed in more concentrated form at lower pressure for reuse or recycling. For membrane separation, see Section 13.12.1	Applicability may be restricted when the energy demand is excessive due to a low ethylene mass flow
Energy recovery techniques			
b	Send the inerts purge stream to a combustion unit	See BAT 9	Generally applicable

BAT 50. In order to reduce the consumption of ethylene and oxygen and to reduce CO_2 emissions to air from the EO unit, BAT is to use a combination of the techniques in BAT 15 and to use inhibitors.

Description

The addition of small amounts of an organochlorine inhibitor (such as ethylchloride or dichloroethane) to the reactor feed in order to reduce the proportion of ethylene that is fully oxidised to carbon dioxide. Suitable parameters for the monitoring of catalyst performance include the heat of reaction and the CO_2 formation per tonne of ethylene feed.

BAT 51. In order to reduce emissions of organic compounds to air from the desorption of CO_2 from the scrubbing medium used in the EO plant, BAT is to use a combination of the techniques given below.

	Technique	Description	Applicability
Process-integrated techniques			
a	Staged CO_2 desorption	The technique consists of conducting the depressurisation necessary to liberate the carbon dioxide from the absorption medium in two steps rather than one. This allows an initial hydrocarbon-rich stream to be isolated for potential recirculation, leaving a relatively clean carbon dioxide stream for further treatment	Only applicable to new plants or major plant upgrades
Abatement techniques			
b	Catalytic oxidiser	See Section 13.12.1	Generally applicable
c	Thermal oxidiser	See Section 13.12.1	Generally applicable

Table 13.3: BAT-AEL for emissions of organic compounds to air from the desorption of CO_2 from the scrubbing medium used in the EO plant

Parameter	**BAT-AEL**
TVOC	1–10 g/t of EO produced (1) (2) (3)

(1) The BAT-AEL is expressed as an average of values obtained during one year.
(2) In the case of significant methane content in the emission, methane monitored according to EN ISO 25140 or EN ISO 25139 is subtracted from the result.
(3) EO produced is defined as the sum of EO produced for sale and as an intermediate.

The associated monitoring is in BAT 2

BAT 52. In order to reduce EO emissions to air, BAT is to use wet scrubbing for waste gas streams containing EO.

Description

For the description of web scrubbing, see Section 13.12.1. Scrubbing with water to remove EO from waste gas streams before direct release or before further abatement of organic compounds.

BAT 53. In order to prevent or reduce emissions of organic compounds to air from cooling of the EO absorbent in the EO recovery unit, BAT is to use one of the techniques given below.

	Technique	Description	Applicability
a	Indirect cooling	Use indirect cooling systems (with heat exchangers) instead of open cooling systems	Only applicable to new plants or major plant upgrades
b	Complete EO removal by stripping	Maintain appropriate operating conditions and use online monitoring of the EO stripper operation to ensure that all EO is stripped out; and provide adequate protection systems to avoid EO emissions during other than normal operating conditions	Only applicable when technique a. cannot be applied

13.6.3 Emissions to water

BAT 54. In order to reduce the waste water volume and to reduce the organic load discharged from the product purification to final waste water treatment, BAT is to use one or both of the techniques given below.

	Technique	Description	Applicability
a	Use of the purge from the EO plant in the EG plant	The purge streams from the EO plant are sent to the EG process and not discharged as waste water. The extent to which the purge can be reused in the EG process depends on EG product quality considerations	Generally applicable
b	Distillation	Distillation is a technique used to separate compounds with different boiling points by partial evaporation and recondensation. The technique is used in EO and EG plants to concentrate aqueous streams to recover glycols or enable their disposal (e.g. by incineration, instead of their discharge as waste water) and to enable the partial reuse/recycling of water	Only applicable to new plants or major plant upgrades

13.6.4 Residues

BAT 55. In order to reduce the amount of organic waste being sent for disposal from the EO and EG plant, BAT is to use a combination of the techniques given below.

Technique		Description	Applicability
a	Hydrolysis reaction optimisation	Optimisation of the water to EO ratio to both achieve lower co-production of heavier glycols and avoid excessive energy demand for the dewatering of glycols. The optimum ratio depends on the target output of di- and triethylene glycols	Generally applicable
b	Isolation of by-products at EO plants for use	For EO plants, the concentrated organic fraction obtained after the dewatering of the liquid effluent from EO recovery is distilled to give valuable short-chain glycols and a heavier residue	Only applicable to new plants or major plant upgrades
c	Isolation of by-products at EG plants for use	For EG plants, the longer chain glycols fraction can either be used as such or further fractionated to yield valuable glycols	Generally applicable

13.7 BAT conclusions for phenol production

The BAT conclusions in this section apply to the production of phenol from cumene, and apply in addition to the general BAT conclusions given in Section 13.1.

13.7.1 Emissions to air

BAT 56. In order to recover raw materials and to reduce the organic load sent from the cumene oxidation unit to the final waste gas treatment, BAT is to use a combination of the techniques given below.

	Technique	Description	Applicability
Process-integrated techniques			
a	Techniques to reduce liquids entrainment	See Section 13.12.1	Generally applicable
Techniques to recover organic material for reuse			
b	Condensation	See Section 13.12.1	Generally applicable
c	Adsorption (regenerative)	See Section 13.12.1	Generally applicable

BAT 57. In order to reduce emissions of organic compounds to air, BAT is to use technique d. given below for waste gas from the cumene oxidation unit. For any other individual or combined waste gas streams, BAT is to use one or a combination of the techniques given below.

	Technique	Description	Applicability
a	Send the waste gas stream to a combustion unit	See BAT 9	Only applicable where there are available uses for the waste gas as gaseous fuel
b	Adsorption	See Section 13.12.1	Generally applicable
c	Thermal oxidiser	See Section 13.12.1	Generally applicable
d	Regenerative thermal oxidiser (RTO)	See Section 13.12.1	Generally applicable

Table 13.4: BAT-AELs for emissions of TVOC and benzene to air from the production of phenol

Parameter	**Source**	**BAT-AEL (daily average or average over the sampling period) (mg/Nm^3, no correction for oxygen content)**	**Conditions**
Benzene	Cumene oxidation unit	< 1	The BAT-AEL applies if the emission exceeds 1 g/h
TVOC		5–30	–

The associated monitoring is in BAT 2.

13.7.2 Emissions to water

BAT 58. In order to reduce emissions to water of organic peroxides from the oxidation unit and, if necessary, to protect the downstream biological waste water treatment plant, BAT is to pretreat waste water containing organic peroxides using hydrolysis before it is combined with other waste water streams and discharged to the final biological treatment.

Description
For the description of hydrolysis, see Section 13.12.2. Waste water (mainly from the condensers and the adsorber regeneration, after phase separation) is treated thermally (at temperatures above 100 °C and a high pH) or catalytically to decompose organic peroxides to non-ecotoxic and more readily biodegradable compounds.

Table 13.5: BAT-AEPL for organic peroxides at the outlet of the peroxides decomposition unit

Parameter	**BAT-AEPL (average value from at least three spot samples taken at intervals of at least half an hour)**	**Associated monitoring**
Total organic peroxides, expressed as cumene hydroperoxide	< 100 mg/l	No EN standard available. The minimum monitoring frequency is once every day and may be reduced to four times per year if adequate performance of the hydrolysis is demonstrated by controlling the process parameters (e.g. pH, temperature and residence time)

BAT 59. In order to reduce the organic load discharged from the cleavage unit and the distillation unit to further waste water treatment, BAT is to recover phenol and other organic compounds (e.g. acetone) using extraction followed by stripping.

Description
Recovery of phenol from phenol-containing waste water streams by adjustment of the pH to < 7, followed by extraction with a suitable solvent and stripping of the waste water to remove residual solvent and other low-boiling compounds (e.g. acetone). For the description of the treatment techniques, see Section 13.12.2.

13.7.3 Residues

BAT 60. In order to prevent or reduce the amount of tar being sent for disposal from phenol purification, BAT is to use one or both of the techniques given below.

	Technique	**Description**	**Applicability**
a	Material recovery (e.g. by distillation, cracking)	See BAT 17c. Use distillation to recover cumene, α-methylstyrene phenol, etc.	Generally applicable
b	Use of tar as a fuel	See BAT 17e.	Generally applicable

13.8 BAT conclusions for ethanolamines production

The BAT conclusions in this section apply in addition to the general BAT conclusions given in Section 13.1.

13.8.1 Emissions to air

BAT 61. In order to reduce ammonia emissions to air and to reduce the consumption of ammonia from the aqueous ethanolamines production process, BAT is to use a multistage wet scrubbing system.

Description
For the description of wet scrubbing, see Section 13.12.1. Unreacted ammonia is recovered from the off-gas of the ammonia stripper and also from the evaporation unit by wet scrubbing in at least two stages followed by ammonia recycling into the process.

13.8.2 Emissions to water

BAT 62. In order to prevent or reduce emissions of organic compounds to air and emissions to water of organic substances from the vacuum systems, BAT is to use one or a combination of the techniques given below.

Technique		Description	Applicability
a	Water-free vacuum generation	Use of dry-running pumps, e.g. positive displacement pumps	Applicability to existing plants may be restricted by design and/or operational constraints
b	Use of water ring vacuum pumps with recirculation of the ring water	The water used as the sealant liquid of the pump is recirculated to the pump casing via a closed loop with only small purges, so that waste water generation is minimised	Only applicable when technique a. cannot be applied. Not applicable for triethanolamine distillation
c	Reuse of aqueous streams from vacuum systems in the process	Return aqueous streams from water ring pumps or steam ejectors to the process for recovery of organic material and reuse of the water. The extent to which water can be reused in the process is restricted by the water demand of the process	Only applicable when technique a. cannot be applied
d	Condensation of organic compounds (amines) upstream of vacuum systems	See Section 13.12.1	Generally applicable.

13.8.3 Raw material consumption

BAT 63. In order to use ethylene oxide efficiently, BAT is to use a combination of the techniques given below.

	Technique	Description	Applicability
a	Use of excess ammonia	Maintaining a high level of ammonia in the reaction mixture is an effective way of ensuring that all the ethylene oxide is converted into products	Generally applicable
b	Optimisation of the water content in the reaction	Water is used to accelerate the main reactions without changing the product distribution and without significant side reactions with ethylene oxide to glycols	Only applicable for the aqueous process
c	Optimise the process operating conditions	Determine and maintain the optimum operating conditions (e.g. temperature, pressure, residence time) to maximise the conversion of ethylene oxide to the desired mix of mono-, di-, triethanolamines	Generally applicable

13.9 BAT conclusions for toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) production

The BAT conclusions in this section cover the production of:

- dinitrotoluene (DNT) from toluene;
- toluene diamine (TDA) from DNT;
- TDI from TDA;
- methylene diphenyl diamine (MDA) from aniline;
- MDI from MDA;

and apply in addition to the general BAT conclusions given in Section 13.1.

13.9.1 Emissions to air

BAT 64. In order to reduce the load of organic compounds, NO_X, NO_X precursors and SO_X sent to the final waste gas treatment (see BAT 66) from DNT, TDA and MDA plants, BAT is to use a combination of the techniques given below.

	Technique	Description	Applicability
a	Condensation	See Section 13.12.1	Generally applicable
b	Wet scrubbing	See Section 13.12.1. In many cases, scrubbing efficiency is enhanced by the chemical reaction of the absorbed pollutant (partial oxidation of NO_X with recovery of nitric acid, removal of acids with caustic solution, removal of amines with acidic solutions, reaction of aniline with formaldehyde in caustic solution)	
c	Thermal reduction	See Section 13.12.1	Applicability to existing units may be restricted by space availability
d	Catalytic reduction	See Section 13.12.1	

BAT 65. In order to reduce the load of HCl and phosgene sent to the final waste gas treatment and to increase resource efficiency, BAT is to recover HCl and phosgene from the process off-gas streams of TDI and/or MDI plants by using an appropriate combination of the techniques given below.

	Technique	Description	Applicability
a	Absorption of HCl by wet scrubbing	See BAT 8d.	Generally applicable
b	Absorption of phosgene by scrubbing	See Section 13.12.1. The excess phosgene is absorbed using an organic solvent and returned to the process	Generally applicable
c	HCl/phosgene condensation	See Section 13.12.1	Generally applicable

BAT 66. In order to reduce emissions to air of organic compounds (including chlorinated hydrocarbons), HCl and chlorine, BAT is to treat combined waste gas streams using a thermal oxidiser followed by caustic scrubbing.

Description

The individual waste gas streams from DNT, TDA, TDI, MDA and MDI plants are combined to one or several waste gas streams for treatment. (See Section 13.12.1 for the descriptions of thermal oxidiser and scrubbing.) Instead of a thermal oxidiser, an incinerator may be used for the combined treatment of liquid waste and the waste gas. Caustic scrubbing is wet scrubbing with caustic added to improve the HCl and chlorine removal efficiency.

Table 13.6: BAT-AELs for emissions of TVOC, tetrachloromethane, Cl_2, HCl and PCDD/F to air from the TDI/MDI process

Parameter	**BAT-AEL (mg/Nm^3, no correction for oxygen content)**
TVOC	1–5 (1) (2)
Tetrachloromethane	$\leq$ 0.5 g/t MDI produced (3) $\leq$ 0.7 g/t TDI produced (3)
Cl_2	< 1 (2) (4)
HCl	2–10 (2)
PCDD/F	0.025–0.08 ng I-TEQ/Nm^3 (2)

(1) The BAT-AEL only applies to combined waste gas streams with flow rates of > 1 000 Nm^3/h.
(2) The BAT-AEL is expressed as a daily average or an average over the sampling period.
(3) The BAT-AEL is expressed as an average of values obtained during one year. TDI and/or MDI produced refers to the product without residues, in the sense used to define the capacity of the plant.
(4) In the case of NO_X values above 100 mg/Nm^3 in the sample, the BAT-AEL may be higher and up to 3 mg/Nm^3 due to analytical interferences.

The associated monitoring is in BAT 2.

BAT 67. In order to reduce emissions to air of PCDD/F from a thermal oxidiser (see Section 13.12.1) treating process off-gas streams containing chlorine and/or chlorinated compounds, BAT is to use technique a., if necessary followed by technique b., given below.

Technique		**Description**	**Applicability**
a	Rapid quenching	Rapid cooling of exhaust gases to prevent the *de novo* synthesis of PCDD/F	Generally applicable
b	Activated carbon injection	Removal of PCDD/F by adsorption onto activated carbon that is injected into the exhaust gas, followed by dust abatement	

BAT-associated emission levels (BAT-AELs): See Table 13.6.

13.9.2 Emissions to water

BAT 68. BAT is to monitor emissions to water with at least the frequency given below and in accordance with EN standards. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality.

Substance/ Parameter	Plant	Sampling point	Standard(s)	Minimum monitoring frequency	Monitoring associated with
TOC	DNT plant	Outlet of the pretreatment unit	EN 1484	Once every week (1)	BAT 70
	MDI and/or TDI plant	Outlet of the plant		Once every month	BAT 72
Aniline	MDA plant	Outlet of the final waste water treatment	No EN standard available	Once every month	BAT 14
Chlorinated solvents	MDI and/or TDI plant		Various EN standards available (e.g. EN ISO 15680)		BAT 14

(1) In the case of discontinuous waste water discharges, the minimum monitoring frequency is once per discharge.

BAT 69. In order to reduce the load of nitrite, nitrate and organic compounds discharged from the DNT plant to waste water treatment, BAT is to recover raw materials, to reduce the waste water volume and to reuse water by using an appropriate combination of the techniques given below.

	Technique	Description	Applicability
a	Use of highly concentrated nitric acid	Use highly concentrated HNO_3 (e.g. about 99 %) to increase the process efficiency and to reduce the waste water volume and the load of pollutants	Applicability to existing units may be restricted by design and/or operational constraints
b	Optimised regeneration and recovery of spent acid	Perform the regeneration of the spent acid from the nitration reaction in such a way that water and the organic content are also recovered for reuse, by using an appropriate combination of evaporation/distillation, stripping and condensation	Applicability to existing units may be restricted by design and/or operational constraints
c	Reuse of process water to wash DNT	Reuse process water from the spent acid recovery unit and the nitration unit to wash DNT	Applicability to existing units may be restricted by design and/or operational constraints
d	Reuse of water from the first washing step in the process	Nitric and sulphuric acid are extracted from the organic phase using water. The acidified water is returned to the process, for direct reuse or further processing to recover materials	Generally applicable
e	Multiple use and recirculation of water	Reuse water from washing, rinsing and equipment cleaning e.g. in the counter-currrent multistep washing of the organic phase	Generally applicable

BAT-associated waste water volume: See Table 13.7.

BAT 70. In order to reduce the load of poorly biodegradable organic compounds discharged from the DNT plant to further waste water treatment, BAT is to pretreat the waste water using one or both of the techniques given below.

Technique		Description	Applicability
a	Extraction	See Section 13.12.2	Generally applicable
b	Chemical oxidation	See Section 13.12.2	

Table 13.7: BAT-AEPLs for discharge from the DNT plant at the outlet of the pretreatment unit to further waste water treatment

Parameter	BAT-AEPL (average of values obtained during one month)
TOC	< 1 kg/t DNT produced
Specific waste water volume	< 1 m^3/t DNT produced

The associated monitoring for TOC is in BAT 68.

BAT 71. In order to reduce waste water generation and the organic load discharged from the TDA plant to waste water treatment, BAT is to use a combination of techniques a., b. and c. and then to use technique d. as given below.

Technique		Description	Applicability
a	Evaporation	See Section 13.12.2	Generally applicable
b	Stripping	See Section 13.12.2	
c	Extraction	See Section 13.12.2	
d	Reuse of water	Reuse of water (e.g. from condensates or from scrubbing) in the process or in other processes (e.g. in a DNT plant). The extent to which water can be reused at existing plants may be restricted by technical constraints	Generally applicable

Table 13.8: BAT-AEPL for discharge from the TDA plant to waste water treatment

Parameter	BAT-AEPL (average of values obtained during one month)
Specific waste water volume	< 1 m^3/t TDA produced

BAT 72. In order to prevent or reduce the organic load discharged from MDI and/or TDI plants to final waste water treatment, BAT is to recover solvents and reuse water by optimising the design and operation of the plant.

Table 13.9: BAT-AEPL for discharge to waste water treatment from a TDI or MDI plant

Parameter	BAT-AEPL (average of values obtained during one year)
TOC	< 0.5 kg/t product (TDI or MDI) (^{1})
(^{1}) The BAT-AEPL refers to the product without residues, in the sense used to define the capacity of the plant.	

The associated monitoring is in BAT 68.

BAT 73. In order to reduce the organic load discharged from a MDA plant to further waste water treatment, BAT is to recover organic material using one or a combination of the techniques given below.

Technique		Description	Applicability
a	Evaporation	See Section 13.12.2. Used to facilitate extraction (see technique b.)	Generally applicable
b	Extraction	See Section 13.12.2. Used to recover/remove MDA	Generally applicable
c	Steam stripping	See Section 13.12.2. Used to recover/remove aniline and methanol	For methanol, the applicability depends on the assessment of alternative options as part of the waste water management and treatment strategy
d	Distillation	See Section 13.12.2. Used to recover/remove aniline and methanol	

13.9.3 Residues

BAT 74. In order to reduce the amount of organic residues being sent for disposal from the TDI plant, BAT is to use a combination of the techniques given below.

Technique		Description	Applicability
Techniques to prevent or reduce the generation of waste			
a	Minimisation of high-boiling residue formation in distillation systems	BAT 17b.	Only applicable to new distillation units or major plant upgrades.
Techniques to recover organic material for reuse or recycling			
b	Increased recovery of TDI by evaporation or further distillation	Residues from distillation are additionally processed to recover the maximum amount of TDI contained therein, e.g. using a thin film evaporator or other short-path distillation units followed by a dryer	Only applicable to new distillation units or major plant upgrades
c	Recovery of TDA by chemical reaction	Tars are processed to recover TDA by chemical reaction (e.g. hydrolysis)	Only applicable to new plants or major plant upgrades

13.10 BAT conclusions for ethylene dichloride and vinyl chloride monomer production

The BAT conclusions in this section apply in addition to the general BAT conclusions given in Section 13.1.

13.10.1 Emissions to air

13.10.1.1 BAT-AEL for emissions to air from an EDC cracker furnace

Table 13.10: BAT-AELs for emissions to air of NO_X from an EDC cracker furnace

Parameter	**BAT-AELs (1) (2) (3)** **(daily average or average over the sampling period)** **(mg/Nm^3, at 3 vol-% O_2)**
NOx	50–100

(1) Where the flue-gases of two or more furnaces are discharged through a common stack, the BAT-AEL applies to the combined discharge from the stack.
(2) The BAT-AELs do not apply during decoking operations.
(3) No BAT-AEL applies for CO. As an indication, the CO emission level will generally be 5–35 mg/Nm^3 expressed as a daily average or an average over the sampling period.

The associated monitoring is in BAT 1.

13.10.1.2 Techniques and BAT-AEL for emissions to air from other sources

BAT 75. In order to reduce the organic load sent to the final waste gas treatment and to reduce raw material consumption, BAT is to use all of the techniques given below.

	Technique	**Description**	**Applicability**
Process-integrated techniques			
a	Control of feed quality	Control the quality of the feed to minimise the formation of residues (e.g. propane and acetylene content of ethylene; bromine content of chlorine; acetylene content of hydrogen chloride)	Generally applicable
b	Use of oxygen instead of air for oxychlorination		Only applicable to new oxychlorination plants or major oxychlorination plant upgrades
Techniques to recover organic material			
c	Condensation using chilled water or refrigerants	Use condensation (see Section 13.12.1) with chilled water or refrigerants such as ammonia or propylene to recover organic compounds from individual vent gas streams before sending them to final treatment	Generally applicable

BAT 76. In order to reduce emissions to air of organic compounds (including halogenated compounds), HCl and Cl_2 , BAT is to treat the combined waste gas streams from EDC and/or VCM production by using a thermal oxidiser followed by two-stage wet scrubbing.

Description
For the description of thermal oxidiser, wet and caustic scrubbing, see Section 13.12.1. Thermal oxidation can be carried out in a liquid waste incineration plant. In this case, the oxidation temperature exceeds 1 100 °C with a minimum residence time of two seconds, with subsequent rapid cooling of exhaust gases to prevent the *de novo* synthesis of PCDD/F.

Scrubbing is carried out in two stages: Wet scrubbing with water and, typically, recovery of hydrochloric acid, followed by wet scrubbing with caustic.

Table 13.11: BAT-AELs for emissions of TVOC, the sum of EDC and VCM, Cl_2, HCl and PCDD/F to air from the production of EDC/VCM

Parameter	**BAT-AEL (daily average or average over the sampling period) (mg/Nm^3, at 11 vol-% O_2)**
TVOC	0.5–5
Sum of EDC and VCM	< 1
Cl_2	< 1–4
HCl	2-10
PCDD/F	0.025–0.08 ng I-TEQ/Nm^3

The associated monitoring is in BAT 2.

BAT 77. In order to reduce emissions to air of PCDD/F from a thermal oxidiser (see Section 13.12.1) treating process off-gas streams containing chlorine and/or chlorinated compounds, BAT is to use technique a., if necessary followed by technique b., given below.

	Technique	**Description**	**Applicability**
a	Rapid quenching	Rapid cooling of exhaust gases to prevent the *de novo* synthesis of PCDD/F	Generally applicable
b	Activated carbon injection	Removal of PCDD/F by adsorption onto activated carbon that is injected into the exhaust gas, followed by dust abatement	

BAT-associated emission levels (BAT-AELs): See Table 13.11.

BAT 78. In order to reduce emissions to air of dust and CO from the decoking of the cracker tubes, BAT is to use one of the techniques to reduce the frequency of decoking given below and one or a combination of the abatement techniques given below.

	Technique	Description	Applicability
Techniques to reduce the frequency of decoking			
a	Optimisation of thermal decoking	Optimisation of operating conditions, i.e. airflow, temperature and steam content across the decoking cycle, to maximise coke removal	Generally applicable
b	Optimisation of mechanical decoking	Optimise mechanical decoking (e.g. sand jetting) to maximise coke removal as dust	Generally applicable
Abatement techniques			
c	Wet dust scrubbing	See Section 13.12.1	Only applicable to thermal decoking
d	Cyclone	See Section 13.12.1	Generally applicable
e	Fabric filter	See Section 13.12.1	Generally applicable

13.10.2 Emissions to water

BAT 79. BAT is to monitor emissions to water with at least the frequency given below and in accordance with EN standards. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality.

Substance/ Parameter	Plant	Sampling point	Standard(s)	Minimum monitoring frequency	Monitoring associated with
EDC	All plants	Outlet of the waste water stripper	EN ISO 10301	Once every day	BAT 80
VCM					
Copper	Oxy-chlorination plant using the fluidised-bed design	Outlet of the pretreatment for solids removal	Various EN standards available, e.g. EN ISO 11885, EN ISO 15586, EN ISO 17294-2	Once every day (1)	BAT 81
PCDD/F			No EN standard available	Once every three months	
Total suspended solids (TSS)			EN 872	Once every day (1)	
Copper	Oxy-chlorination plant using the fluidised-bed design	Outlet of the final waste water treatment	Various EN standards available, e.g. EN ISO 11885, EN ISO 15586, EN ISO 17294-2	Once every month	BAT 14 and BAT 81
EDC	All plants		EN ISO 10301	Once every month	BAT 14 and BAT 80
PCDD/F			No EN standard available	Once every three months	BAT 14 and BAT 81

(1) The minimum monitoring frequency may be reduced to once every month if adequate performance of the solids and copper removal is controlled by frequent monitoring of other parameters (e.g. by continuous measurement of turbidity).

BAT 80. In order to reduce the load of chlorinated compounds discharged to further waste water treatment and to reduce emissions to air from the waste water collection and treatment system, BAT is to use hydrolysis and stripping as close as possible to the source.

Description
For the description of hydrolysis and stripping, see Section 13.12.2. Hydrolysis is carried out at alkaline pH to decompose chloral hydrate from the oxychlorination process. This results in the formation of chloroform which is then removed by stripping, together with EDC and VCM.

BAT-associated environmental performance levels (BAT-AEPLs): See Table 13.12.

BAT-associated emission levels (BAT-AELs) for direct emissions to a receiving water body at the outlet of the final treatment: See Table 13.14.

Table 13.12: BAT-AEPLs for chlorinated hydrocarbons in waste water at the outlet of a waste water stripper

Parameter	**BAT-AEPL (average of values obtained during one month)** (1)
EDC	0.1–0.4 mg/l
VCM	< 0.05 mg/l

(1) The average of values obtained during one month is calculated from the averages of values obtained during each day (at least three spot samples taken at intervals of at least half an hour).

The associated monitoring is in BAT 79.

BAT 81. In order to reduce emissions to water of PCDD/F and copper from the oxychlorination process, BAT is to use technique a. or, alternatively, technique b. together with an appropriate combination of techniques c., d. and e. given below.

	Technique	**Description**	**Applicability**
Process-integrated techniques			
a	Fixed-bed design for oxychlorination	Oxychlorination reaction design: in the fixed-bed reactor, catalyst particulates entrained in the overhead gaseous stream are reduced	Not applicable to existing plants using the fluidised-bed design
b	Cyclone or dry catalyst filtration system	A cyclone or a dry catalyst filtration system reduces catalyst losses from the reactor and therefore also their transfer to waste water	Only applicable to plants using the fluidised-bed design
Waste water pretreatment			
c	Chemical precipitation	See Section 13.12.2. Chemical precipitation is used to remove dissolved copper	Only applicable to plants using the fluidised-bed design
d	Coagulation and flocculation	See Section 13.12.2	Only applicable to plants using the fluidised-bed design
e	Membrane filtration (micro- or ultrafiltration)	See Section 13.12.2	Only applicable to plants using the fluidised-bed design

Table 13.13: BAT-AEPLs for emissions to water from EDC production via oxychlorination at the outlet of the pretreatment for solids removal at plants using the fluidised-bed design

Parameter	BAT-AEPL (average of values obtained during one year)
Copper	0.4–0.6 mg/l
PCDD/F	< 0.8 ng I-TEQ/l
Total suspended solids (TSS)	10–30 mg/l

The associated monitoring is in BAT 79.

Table 13.14: BAT-AELs for direct emissions of copper, EDC and PCDD/F to a receiving water body from EDC production

Parameter	BAT-AEL (average of values obtained during one year)
Copper	0.04–0.2 g/t EDC produced by oxychlorination (1)
EDC	0.01–0.05 g/t EDC purified (2) (3)
PCDD/F	0.1– 0.3 µg I-TEQ/t EDC produced by oxychlorination

(1) The lower end of the range is typically achieved when the fixed-bed design is used.
(2) The average of values obtained during one year is calculated from the averages of values obtained during each day (at least three spot samples taken at intervals of at least half an hour).
(3) Purified EDC is the sum of EDC produced by oxychlorination and/or direct chlorination and of EDC returned from VCM production to purification.

The associated monitoring is in BAT 79.

13.10.3 Energy efficiency

BAT 82. In order to use energy efficiently, BAT is to use a boiling reactor for the direct chlorination of ethylene.

Description
The reaction in the boiling reactor system for the direct chlorination of ethylene is typically carried out at a temperature between below 85 °C and 200 °C. In contrast to the low-temperature process, it allows for the effective recovery and reuse of the heat of reaction (e.g. for the distillation of EDC).

Applicability
Only applicable to new direct chlorination plants.

BAT 83. In order to reduce the energy consumption of EDC cracker furnaces, BAT is to use promoters for the chemical conversion.

Description
Promoters, such as chlorine or other radical-generating species, are used to enhance the cracking reaction and reduce the reaction temperature and therefore the required heat input. Promoters may be generated by the process itself or added.

13.10.4 Residues

BAT 84. In order to reduce the amount of coke being sent for disposal from VCM plants, BAT is to use a combination of the techniques given below.

	Technique	Description	Applicability
a	Use of promoters in cracking	See BAT 83	Generally applicable
b	Rapid quenching of the gaseous stream from EDC cracking	The gaseous stream from EDC cracking is quenched by direct contact with cold EDC in a tower to reduce coke formation. In some cases, the stream is cooled by heat exchange with cold liquid EDC feed prior to quenching	Generally applicable
c	Pre-evaporation of EDC feed	Coke formation is reduced by evaporating EDC upstream of the reactor to remove high-boiling coke precursors	Only applicable to new plants or major plant upgrades
d	Flat flame burners	A type of burner in the furnace that reduces hot spots on the walls of the cracker tubes	Only applicable to new furnaces or major plant upgrades

BAT 85. In order to reduce the amount of hazardous waste being sent for disposal and to increase resource efficiency, BAT is to use all of the techniques given below.

	Technique	Description	Applicability
a	Hydrogenation of acetylene	HCl is generated in the EDC cracking reaction and recovered by distillation. Hydrogenation of the acetylene present in this HCl stream is carried out to reduce the generation of unwanted compounds during oxychlorination. Acetylene values below 50 ppmv at the outlet of the hydrogenation unit are advisable	Only applicable to new plants or major plant upgrades
b	Recovery and reuse of HCl from incineration of liquid waste	HCl is recovered from incinerator off-gas by wet scrubbing with water or diluted HCl (see Section 13.12.1) and reused (e.g. in the oxychlorination plant)	Generally applicable
c	Isolation of chlorinated compounds for use	Isolation and, if needed, purification of by-products for use (e.g. monochloroethane and/or 1,1,2-trichloroethane, the latter for the production of 1,1-dichloroethylene)	Only applicable to new distillation units or major plant upgrades. Applicability may be restricted by a lack of available uses for these compounds

13.11 BAT conclusions for hydrogen peroxide production

The BAT conclusions in this section apply in addition to the general BAT conclusions given in Section 13.1.

13.11.1 Emissions to air

BAT 86. In order to recover solvents and to reduce emissions of organic compounds to air from all units other than the hydrogenation unit, BAT is to use an appropriate combination of the techniques given below. In the case of using air in the oxidation unit, this includes at least technique d. In the case of using pure oxygen in the oxidation unit, this includes at least technique b. using chilled water.

	Technique	Description	Applicability
Process-integrated techniques			
a	Optimisation of the oxidation process	Process optimisation includes elevated oxidation pressure and reduced oxidation temperature in order to reduce the solvent vapour concentration in the process off-gas	Only applicable to new oxidation units or major plant upgrades
b	Techniques to reduce solids and/or liquids entrainment	See Section 13.12.1	Generally applicable
Techniques to recover solvent for reuse			
c	Condensation	See Section 13.12.1	Generally applicable
d	Adsorption (regenerative)	See Section 13.12.1	Not applicable to process off-gas from oxidation with pure oxygen

Table 13.15: BAT-AELs for emissions of TVOC to air from the oxidation unit

Parameter	**BAT-AEL** (1) **(daily average or average over the sampling period)** (2) **(no correction for oxygen content)**
TVOC	5–25 mg/Nm^3 (3)

(1) The BAT-AEL does not apply when the emission is below 150 g/h.
(2) When adsorption is used, the sampling period is representative of a complete adsorption cycle.
(3) In the case of significant methane content in the emission, methane monitored according to EN ISO 25140 or EN ISO 25139 is subtracted from the result.

The associated monitoring is in BAT 2.

BAT 87. In order to reduce emissions of organic compounds to air from the hydrogenation unit during start-up operations, BAT is to use condensation and/or adsorption.

Description
For the description of condensation and adsorption, see Section 13.12.1.

BAT 88. In order to prevent benzene emissions to air and water, BAT is not to use benzene in the working solution.

13.11.2 Emissions to water

BAT 89. In order to reduce the waste water volume and the organic load discharged to waste water treatment, BAT is to use both of the techniques given below.

	Technique	Description	Applicability
a	Optimised liquid phase separation	Separation of organic and aqueous phases with appropriate design and operation (e.g. sufficient residence time, phase boundary detection and control) to prevent any entrainment of undissolved organic material	Generally applicable
b.	Reuse of water	Reuse of water, e.g. from cleaning or liquid phase separation. The extent to which water can be reused in the process depends on product quality considerations	Generally applicable

BAT 90. In order to prevent or reduce emissions to water of poorly bioeliminable organic compounds, BAT is to use one of the techniques given below.

Technique		Description
a	Adsorption	See Section 13.12.2. Adsorption is carried out prior to sending waste water streams to the final biological treatment
b	Waste water incineration	See Section 13.12.2

Applicability

Only applicable to waste water streams carrying the main organic load from the hydrogen peroxide plant and when the reduction of the TOC load from the hydrogen peroxide plant by means of biological treatment is lower than 90 %.

13.12 Descriptions of techniques

13.12.1 Process off-gas and waste gas treatment techniques

Technique	Description
Adsorption	A technique for removing compounds from a process off-gas or waste gas stream by retention on a solid surface (typically activated carbon). Adsorption may be regenerative or non-regenerative (see below).
Adsorption (non-regenerative)	In non-regenerative adsorption, the spent adsorbent is not regenerated but disposed of.
Adsorption (regenerative)	Adsorption where the adsorbate is subsequently desorbed, e.g. with steam (often on site) for reuse or disposal and the adsorbent is reused. For continuous operation, typically more than two adsorbers are operated in parallel, one of them in desorption mode.
Catalytic oxidiser	Abatement equipment which oxidises combustible compounds in a process off-gas or waste gas stream with air or oxygen in a catalyst bed. The catalyst enables oxidation at lower temperatures and in smaller equipment compared to a thermal oxidiser.
Catalytic reduction	NOx is reduced in the presence of a catalyst and a reducing gas. In contrast to SCR, no ammonia and/or urea are added.
Caustic scrubbing	The removal of acidic pollutants from a gas stream by scrubbing using an alkaline solution.
Ceramic/metal filter	Ceramic filter material. In circumstances where acidic compounds such as HCl, NO_X, SO_X and dioxins are to be removed, the filter material is fitted with catalysts and the injection of reagents may be necessary. In metal filters, surface filtration is carried out by sintered porous metal filter elements.
Condensation	A technique for removing the vapours of organic and inorganic compounds from a process off-gas or waste gas stream by reducing its temperature below its dew point so that the vapours liquefy. Depending on the operating temperature range required, there are different methods of condensation, e.g. cooling water, chilled water (temperature typically around 5 °C) or refrigerants such as ammonia or propene.
Cyclone (dry or wet)	Equipment for removal of dust from a process off-gas or waste gas stream based on imparting centrifugal forces, usually within a conical chamber.
Electrostatic precipitator (dry or wet)	A particulate control device that uses electrical forces to move particles entrained within a process off-gas or waste gas stream onto collector plates. The entrained particles are given an electrical charge when they pass through a corona where gaseous ions flow. Electrodes in the centre of the flow lane are maintained at a high voltage and generate the electrical field that forces the particles to the collector walls.
Fabric filter	Porous woven or felted fabric through which gases flow to remove particles by use of a sieve or other mechanisms. Fabric filters can be in the form of sheets, cartridges or bags with a number of the individual fabric filter units housed together in a group.
Membrane separation	Waste gas is compressed and passed through a membrane which relies on the selective permeability of organic vapours. The enriched permeate can be recovered by methods such as condensation or adsorption, or can be abated, e.g. by catalytic oxidation. The process is most appropriate for higher vapour concentrations. Additional treatment is, in most cases, needed to achieve concentration levels low enough to discharge.
Mist filter	Commonly mesh pad filters (e.g. mist eliminators, demisters) which usually consist of woven or knitted metallic or synthetic monofilament material in either a random or specific configuration. A mist filter is operated as deep-bed filtration, which takes place over the entire depth of the filter. Solid dust particles remain in the filter until it is saturated and requires cleaning by flushing. When the mist filter is used to collect droplets and/or aerosols, they clean the filter as they drain out as a liquid. It works by mechanical impingement and is velocity-dependent. Baffle angle separators are also commonly used as mist filters.

Regenerative thermal oxidiser (RTO)	Specific type of thermal oxidiser (see below) where the incoming waste gas stream is heated a ceramic-packed bed by passing through it before entering the combustion chamber. The purified hot gases exit this chamber by passing through one (or more) ceramic-packed bed(s) (cooled by an incoming waste gas stream in an earlier combustion cycle). This reheated packed bed then begins a new combustion cycle by preheating a new incoming waste gas stream. The typical combustion temperature is 800–1 000 °C.
Scrubbing	Scrubbing or absorption is the removal of pollutants from a gas stream by contact with a liquid solvent, often water (see 'Wet scrubbing'). It may involve a chemical reaction (see 'Caustic scrubbing'). In some cases, the compounds may be recovered from the solvent.
Selective catalytic reduction (SCR)	The reduction of NO_X to nitrogen in a catalytic bed by reaction with ammonia (usually supplied as an aqueous solution) at an optimum operating temperature of around 300–450 °C. One or more layers of catalyst may be applied.
Selective non-catalytic reduction (SNCR)	The reduction of NO_X to nitrogen by reaction with ammonia or urea at a high temperature. The operating temperature window must be maintained between 900 °C and 1 050 °C.
Techniques to reduce solids and/or liquids entrainment	Techniques that reduce the carry-over of droplets or particles in gaseous streams (e.g. from chemical processes, condensers, distillation columns) by mechanical devices such as settling chambers, mist filters, cyclones and knock-out drums.
Thermal oxidiser	Abatement equipment which oxidises the combustible compounds in a process off-gas or waste gas stream by heating it with air or oxygen to above its auto-ignition point in a combustion chamber and maintaining it at a high temperature long enough to complete its combustion to carbon dioxide and water.
Thermal reduction	NO_X is reduced at elevated temperatures in the presence of a reducing gas in an additional combustion chamber, where an oxidation process takes place but under low oxygen conditions / deficit of oxygen. In contrast to SNCR, no ammonia and/or urea are added.
Two-stage dust filter	A device for filtering on a metal gauze. A filter cake builds up in the first filtration stage and the actual filtration takes place in the second stage. Depending on the pressure drop across the filter, the system switches between the two stages. A mechanism to remove the filtered dust is integrated into the system.
Wet scrubbing	See 'Scrubbing' above. Scrubbing where the solvent used is water or an aqueous solution, e.g. caustic scrubbing for abating HCl. See also 'Wet dust scrubbing'.
Wet dust scrubbing	See 'Wet scrubbing' above. Wet dust scrubbing entails separating the dust by intensively mixing the incoming gas with water, mostly combined with the removal of the coarse particles by the use of centrifugal force. In order to achieve this, the gas is released inside tangentially. The removed solid dust is collected at the bottom of the dust scrubber.

13.12.2 Waste water treatment techniques

All of the techniques listed below can also be used to purify water streams in order to enable reuse/recycling of water. Most of them are also used to recover organic compounds from process water streams.

Technique	Description
Adsorption	Separation method in which compounds (i.e. pollutants) in a fluid (i.e. waste water) are retained on a solid surface (typically activated carbon).
Chemical oxidation	Organic compounds are oxidised with ozone or hydrogen peroxide, optionally supported by catalysts or UV radiation, to convert them into less harmful and more easily biodegradable compounds
Coagulation and flocculation	Coagulation and flocculation are used to separate suspended solids from waste water and are often carried out in successive steps. Coagulation is carried out by adding coagulants with charges opposite to those of the suspended solids. Flocculation is carried out by adding polymers, so that collisions of microfloc particles cause them to bond to produce larger flocs.
Distillation	Distillation is a technique to separate compounds with different boiling points by partial evaporation and recondensation. Waste water distillation is the removal of low-boiling contaminants from waste water by transferring them into the vapour phase. Distillation is carried out in columns, equipped with plates or packing material, and a downstream condenser.
Extraction	Dissolved pollutants are transferred from the waste water phase to an organic solvent, e.g. in counter-current columns or mixer-settler systems. After phase separation, the solvent is purified, e.g. by distillation, and returned to the extraction. The extract containing the pollutants is disposed of or returned to the process. Losses of solvent to the waste water are controlled downstream by appropriate further treatment (e.g. stripping).
Evaporation	The use of distillation (see above) to concentrate aqueous solutions of high-boiling substances for further use, processing or disposal (e.g. waste water incineration) by transferring water to the vapour phase. Typically carried out in multistage units with increasing vacuum, to reduce the energy demand. The water vapours are condensed, to be reused or discharged as waste water.
Filtration	The separation of solids from a waste water carrier by passing it through a porous medium. It includes different types of techniques, e.g. sand filtration, microfiltration and ultrafiltration.
Flotation	A process in which solid or liquid particles are separated from the waste water phase by attaching to fine gas bubbles, usually air. The buoyant particles accumulate at the water surface and are collected with skimmers.
Hydrolysis	A chemical reaction in which organic or inorganic compounds react with water, typically in order to convert non-biodegradable to biodegradable or toxic to non-toxic compounds. To enable or enhance the reaction, hydrolysis is carried out at an elevated temperature and possibly pressure (thermolysis) or with the addition of strong alkalis or acids or using a catalyst.
Precipitation	The conversion of dissolved pollutants (e.g. metal ions) into insoluble compounds by reaction with added precipitants. The solid precipitates formed are subsequently separated by sedimentation, flotation or filtration.
Sedimentation	Separation of suspended particles and suspended material by gravitational settling.
Stripping	Volatile compounds are removed from the aqueous phase by a gaseous phase (e.g. steam, nitrogen or air) that is passed through the liquid, and are subsequently recovered (e.g. by condensation) for further use or disposal. The removal efficiency may be enhanced by increasing the temperature or reducing the pressure.
Waste water incineration	The oxidation of organic and inorganic pollutants with air and simultaneous evaporation of water at normal pressure and temperatures between 730 °C and 1 200 °C. Waste water incineration is typically self-sustaining at COD levels of more than 50 g/l. In the case of low organic loads, a support/auxiliary fuel is needed.

13.12.3 Techniques to reduce emissions to air from combustion

Technique	Description
Choice of (support) fuel	The use of fuel (including support/auxiliary fuel) with a low content of potential pollution-generating compounds (e.g. lower sulphur, ash, nitrogen, mercury, fluorine or chlorine content in the fuel).
Low-NO_X burner (LNB) and ultra-low-NO_X burner (ULNB)	The technique is based on the principles of reducing peak flame temperatures, delaying but completing the combustion and increasing the heat transfer (increased emissivity of the flame). It may be associated with a modified design of the furnace combustion chamber. The design of ultra-low-NO_X burners (ULNB) includes (air/)fuel staging and exhaust/flue-gas recirculation.

14 CONCLUDING REMARKS AND RECOMMENDATIONS FOR FUTURE WORK

Timing of the review process

The key milestones of the review process are summarised in the table below:

Table 14.1: Key milestones in the review of the BREF for the Production of Large Volume Organic Chemicals

Key milestone	Date
Re-activation of the TWG	12 February 2009
Call for wishes	27 January 2010
Kick-off meeting	13 to 16 December 2010
Drawing up of questionnaires	2011 to 2013
Collection of information (12 illustrative processes)	September 2012 to September 2013
Draft 1 of the revised LVOC BREF	30 April 2014
End of commenting period on Draft 1 (4073 comments received)	04 July 2014
End of targeted additional data collection	04 July 2014
Final TWG meeting	25 to 29 April 2016

During the BREF review process, a total of 10 LVOC plants were visited in four Member States (Belgium, Germany, the Netherlands and Spain), most of them during the Draft 1 (D1) comments assessment.

Sources of information and information gaps

The main sources of information for the review process were:

- scientific and technical literature (encyclopaedia such as Ullmann's or Kirk-Othmer; many other publications for specific processes and details);
- process descriptions and surveys on emissions from industry (CEFIC);
- filled-in questionnaires from operators of LVOC plants for the various illustrative processes;
- additional data from Member States (AT, CZ, IT, NL, PT, SE and UK);
- more than 4 000 comments on Draft 1;
- information gathered from site visits.

As a result, more than 350 documents have been uploaded or cited on BATIS, and about 200 of them are referenced in the revised LVOC BREF.

About 200 questionnaires containing plant-specific data have been received by the EIPPCB, typically directly from industry. Participation of plant operators differed regarding the individual chemical sectors or illustrative processes. Regarding data on emissions and consumption, the data provided were heterogeneous in quality and quantity. The data collection mainly focused on the illustrative processes. Questionnaires for the individual illustrative processes which had been set up separately by individual sector groups were not always harmonised with respect to the requested emission data, in terms of parameters, units and averaging periods. For smaller sources of emissions to air, sometimes only estimates or very few monitoring results were available.

Due to confidentiality concerns, no data on costs have been reported, and hardly any on raw material and energy consumption which are relevant environmental factors in the LVOC sector.

Degree of consensus reached during the information exchange

At the final TWG meeting in April 2016, a high degree of consensus was reached on most of the BAT conclusions. However, 10 dissenting views were expressed, 5 of which fulfil the conditions set out in Section 4.6.2.3.2 of Commission Implementing Decision 2012/119/EU. They are summarised in Table 14.2.

Table 14.2: Dissenting views

Reference in BAT conclusions	Subject	TWG member(s)	Split view
Table 13.14	BAT-AEL for emissions of NO_X from a lower olefins cracker furnace	DE, SE	Reduce the upper end of the BAT-AEL range for NO_X emissions to 180 mg/Nm^3 (as a daily average or average over the sampling period).
Table 13.14	BAT-AEL for emissions of NO_X from a lower olefins cracker furnace	EEB	Reduce the lower end of the BAT-AEL range for NO_X emissions to 65 mg/Nm^3 (as a daily average or average over the sampling period).
Table 13.1 and Table 13.10	Set BAT-AELs for emissions of CO from a lower olefins or EDC cracker furnace	BE, DE, SE, EEB	Set BAT-AELs for CO emissions to air instead of indicative levels.
Section 13.1	Generic: Not to use catalysts containing mercury	EEB	Add a BAT that the use of mercury-containing catalysts is not BAT. ([1])
Table 13.7	TDI/MDI: BAT-AEPL on waste water volume from DNT and TDA production	CEFIC	For DNT plants where BAT 69a is not applicable, increase the upper end of the BAT-AEPL range for the waste water volume to < 1.4 m^3/t of DNT.
([1]) Note that the use of amalgam for the production of sodium/potassium methylate/ethylate is not considered as use of mercury-containing catalysts.			

Consultation of the Forum and subsequent formal adoption procedure of the BAT Conclusions

In accordance with Article 13(3) of the Directive, the Forum gave its opinion on the draft Best Available Techniques (BAT) reference document for the production of Large Volume Organic Chemicals at its meeting of 5 April 2017:

1.The Forum welcomed the draft Best Available Techniques (BAT) reference document for the production of Large Volume Organic Chemicals as presented by the Commission.
2.The Forum acknowledged the discussions held at its meeting of 5 April 2017 and agreed that the changes to the draft Best Available Techniques (BAT) reference document for the production of Large Volume Organic Chemicals, as proposed in Annex A, should be included in the final document.
3.The Forum reaffirmed the comments in Annex B as representing the views of certain members of the Forum but on which no consensus existed within the Forum to include them in the final document.

Subsequently, the Commission took the opinion of the IED Article 13 Forum into account when preparing the draft Commission Implementing Decision establishing best available techniques (BAT) conclusions for the production of Large Volume Organic Chemicals. The IED Article 75

Committee, at its meeting of 28 June 2017, gave a positive opinion on this draft Commission Implementing Decision.

Subsequently, the Commission Implementing Decision (EU) 2017/2017 establishing best available techniques (BAT) conclusions for the production of Large Volume Organic Chemicals was adopted on 21 November 2017 and published in the Official Journal of the European Union (OJ L 323, 07.12.2017, p. 1).

Recommendations for future work
The information exchange revealed a number of issues that should be addressed during the next review of the LVOC BREF. Generic recommendations include:

- to consider techniques to reduce the consumption of material and energy or to reduce emissions at the most generic level, i.e. if appropriate for the whole LVOC sector;
- to assess the options to define BAT and derive BAT-AEPLs for unit operations and unit processes rather than for illustrative processes;
- to focus the data collection on issues that, based on an assessment, are relevant and not considered to be sufficiently covered by more generic BREFs (such as CWW, WGC, ENE).

More specific recommendations include:

- to collect information on the decommissioning of LVOC plants;
- related to process furnaces/heaters:
  - to collect more information on the applicability of the use of inert diluents for EDC crackers;
  - to collect more information on the correlation between NO_X emissions and the H_2 content in the fuel;
  - to collect more information on the use of SCR for lower olefin crackers and achieved emission levels;
  - to collect more information on integrated emissions management for lower olefin crackers;
- related to the production of lower olefins:
  - to collect information on the performance of dry cyclones during decoking, also to allow comparisons with wet scrubbing;
  - to collect more and better data on dust emissions from the decoking of lower olefin crackers, as a BAT-AEPL for dust emissions from lower olefin crackers during decoking was not set due to insufficient data in terms of quality and quantity; to monitor dust emissions from lower olefin decoking, calculation methods are used in some EU Member states;
- related to the production of TDI/MDI:
  - to collect information on the oxygen concentration in waste gases;
  - to collect information on the TOC discharges and waste water volumes from the DNT plants;
- related to the production of EO/EG:
  - to collect information on the levels of TVOC emissions to air, in particular when thermal oxidisers are used;
- related to the production of formaldehyde:
  - to collect information on the performance and the oxygen concentration when thermal or catalytic oxidisers are used;
- related to the production of phenol:

  - to collect information on the performance of catalytic oxidisers;
- related to the production of ethylbenzene and styrene:
  - to collect information on emissions to air and water;
- related to the production of EDC/VCM:
  - to collect information on the oxygen concentration and the TVOC/NMVOC emission levels in waste gases;
  - to collect information on dust emissions from the decoking of EDC/VCM crackers and on the performance of all decoking techniques used in EDC/VCM crackers, as a BAT-AEPL for dust emissions from EDC/VCM crackers during decoking was not set due to a lack of data.

The following recommendations were made for the drawing up of the Common Waste Gas Treatment in the Chemical Sector (WGC) BREF:

- to use the information on NO_X emissions from the use of thermal oxidisers that has been collected for the review of the LVOC BREF;
- to consider addressing emissions from storage specific to the LVOC and other chemical sectors in the Common Waste Gas Treatment in the Chemical Sector (WGC) BREF.

Suggested topics for future R&D work

The Commission is launching and supporting, through its Research and Technological Development programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially, these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the European IPPC Bureau of any research results which are relevant to the scope of this document (see also the fifth section of the Preface of this document).

GLOSSARY

This glossary is meant to facilitate the understanding of the information contained in this document. The definitions of terms in this glossary are not legal definitions (even if some of them may coincide with definitions given in European legislation), they are meant to help the reader understand some key terms in the context of their use in the specific sector covered by this document.

This glossary is divided up into the following sections:

I. ISO country codes
II. Monetary units
III. Unit prefixes, number separators and notations
IV. Units and measures
V. Chemical elements
VI. Chemical formulae commonly used in this document
VII. Acronyms

I. ISO country codes

ISO code	**Member State** (1)
Member States (*)	
AT	Austria
BE	Belgium
CZ	Czech Republic
DE	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
HU	Hungary
IE	Ireland
IT	Italy
NL	Netherlands
PL	Poland
PT	Portugal
RO	Romania
SE	Sweden
SK	Slovakia
UK	United Kingdom
Non-member countries	
NO	Norway
US	United States
(1) The protocol order of the Member States is based on the alphabetical order of their geographical names in the original language(s).	

II. Monetary units

Code(1)	Country/territory	Currency
Member State currencies		
EUR	Euro area (2)	euro (pl. euros)
GBP	United Kingdom	pound sterling (inv.)
Other currencies		
USD	United States	US dollar

(1) ISO 4217 codes.

(2) Includes Austria, Belgium, Cyprus, Estonia, Finland, France, Germany, Greece, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, the Netherlands, Portugal, Slovakia, Slovenia and Spain.

III. Unit prefixes, number separators and notations

Numbers in this document are written using the '.' character as the decimal separator and the space as the separator for thousands.

The symbol ~ (around; approximately) is the notation used to indicate approximation.

The following table contains the frequently used prefixes:

Symbol	Prefix	10^n	Word	Decimal Number
G	giga	10^9	Billion	1 000 000 000
M	mega	10^6	Million	1 000 000
k	kilo	10^3	Thousand	1 000
h	hecto	10^2	Hundred	100
da	deca	10^1	Ten	10
-------	-------	1	One	1
d	deci	10^{-1}	Tenth	0.1
c	centi	10^{-2}	Hundredth	0.01
m	milli	10^{-3}	Thousandth	0.001
µ	micro	10^{-6}	Millionth	0.000 001
n	nano	10^{-9}	Billionth	0.000 000 001

IV. Units and measures

Unit symbol	Unit name	Measure name (Measure symbol)	Conversion and comment
atm	normal atmosphere	Pressure (P)	1 atm = 101 325 N/m^2
bar	bar	Pressure (P)	1.013 bar = 100 kPa = 1 atm
barg	bar of gauge pressure	Pressure relative to current atmospheric pressure	
°C	degree Celsius, centigrade	Temperature (T)	
cm	centimetre	Length	
d	day	Time	
db(A) or dbA	a-weighted decibels	Sound pressure	
g	gram	Weight	
h	hour	Time	
ha	hectare	Area	1 ha = 10^4 m^2
J	joule	Energy	
K	kelvin	Temperature (T)	0 °C = 273.15 K
kcal	kilocalorie	Energy	1 kcal = 4.19 kj
kg	kilogram	Weight	1 kg = 1 000 g
kJ	kilojoule	Energy	1 kj = 0.24 kcal
kPa	kilopascal	Pressure	
kPag	kilopascal of gauge pressure	Pressure relative to current atmospheric pressure	
kWh	kilowatt-hour	Energy	1 kWh = 3 600 kJ
l	litre	Volume	
m	metre	Length	
m^2	square metre	Area	
m^3	cubic metre	Volume	
mbar	millibar	Pressure	
mg	milligram	Weight	1 mg = 10^{-3} g
min	minute	Time	
MJ	megajoule	Energy	1 MJ = 1 000 KJ
mm	millimetre	Length	1 mm = 10^{-3} m
MWh	megawatt hour	Energy	
Nm^3	normal cubic metre	Volume	at 101.325 kPa, 273.15 K
Pa	pascal	Pressure	1 Pa = 1 N/m^2
ppm	parts per million	Composition of mixtures	1 ppm = 10^{-6}
ppmv	parts per million by volume	Composition of mixtures	
psi	pounds per square inch	Pressure	1 psi = 6 894.76 Pa
psig	pounds per square inch gauge pressure	Pressure relative to current atmospheric pressure	
s	second	Time	
t	metric tonne	Weight	1 t = 1 000 kg or 10^6 g
t/yr	tonnes per year	Mass flow Materials consumption	
TEQ or I-TEQ	international toxicity equivalents (dioxins and furans)	Toxicity	
vol- % % v/v	percentage by volume	Composition of mixtures	
W	watt	Power	1 W = 1 J/s
Wh	watt-hour	Energy	1 wh = 3 600 J
wt-% % w/w	percentage by weight	Composition of mixtures	
yr	year	Time	

V. Chemical elements

Symbol	Name
Al	Aluminium
Bi	Bismuth
Ca	Calcium
Cl	Chlorine
Cu	Copper
F	Fluorine
Fe	Iron
I	Iodine
K	Potassium
N	Nitrogen
Na	Sodium
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
P	Phosphorus
S	Sulphur
Sb	Antimony
Se	Selenium
Sn	Tin
Te	Tellurium
Ti	Titanium
V	Vanadium
Zn	Zinc

VI Chemical formulae commonly used in this document

Chemical formula	Name
$AlCl_3$	Aluminium (tri)chloride
CH_4	Methane
$Ca(OH)_2$	Calcium hydroxide
CO_2	Carbon dioxide
CO	Carbon monoxide
H_2SO_4	Sulphuric acid
H_2S	Hydrogen sulphide
HCl	Hydrogen chloride
HNO_3	Nitric acid
H_3PO_4	Phosphoric acid
K_2O	Potassium oxide
KOH	Potassium hydroxide
MoO_5	Molybdenum oxide
NaOH	Sodium hydroxide. Also called caustic soda
NaCl	Natrium chloride
N_2	Nitrogen gas
N_2O	Nitrous oxide
NH_3	Ammonia
NH_4	Ammonium
NH_3-N	Ammonia (expressed as N)
NH_4-N	Ammonium (expressed as N)
NO_2^--N	Nitrite (expressed as N)
NO_3^-	Nitrate
NO_3^--N	Nitrate (expressed as N)
NO_X	The sum of nitrogen oxide (NO) and nitrogen dioxide (NO_2), expressed as NO_2
O_2	Oxygen gas
PCDD - PCFF	Polychlorinated dibenzodioxins - Polychlorinated dibenzofurans
SF_6	Sulphur hexafluoride
SO_X	The sum of sulphur dioxide (SO_2) and sulphur trioxide (SO_3), expressed as SO_2
V_2O_5	Vanadium(V) oxide

VII Acronyms

List of acronyms commonly used in this document.

Acronym	Definition
ABS	Acrylonitrile butadiene styrene
ACP	Acetophenone
AMS	Alpha-methylstyrene
AO	Alkylanthraquinone oxidation
AOP	Advanced oxidation process
AOX	Adsorbable organically bound halogens
AQ	Alkylanthraquinone
ASTM	
BAT	Best Available Techniques (as defined in Article 3(10) of the IED)
BAT-AEL	Emission levels associated with the BAT (as defined in Article 3 (13) of the IED)
BOD	Biochemical oxygen demand
BREF	Best Available Techniques Reference Document (as defined in Article 3(11) of the IED)
BTX	Collective term for mixtures of benzene, toluene and xylene aromatics
CEFIC	The European Chemical Industry Council (Trade Body)
CEN	Comité Européen de Normalisation (European Committee for standardisation)
CHP	Cumene hydroperoxide
COD	Chemical oxygen demand
CPI	Corrugated plate interceptor
o-DCB	Ortho dichlorobenzene
DC	Direct chlorination
DCS	Distributed control system
DEA	Diethanolamine (2,2'-iminodiethanol)
DEG	Diethylene glycol
DIN	Deutsches Institut für Normung (the German national organisation for standardisation)
DMC	Dimethyl carbonate
DMDS	Dimethyl disulphide
DNT	Dinitrotoluene
DPC	Diphenyl carbonate
EA	Ethanolamine(s)
EB	Ethylbenzene
EBD	Ethylbenzene dehydrogenation
EBHP	Ethylbenzene hydroperoxide
EC	European Commission
EDC	Ethylene dichloride
EIPPCB	European Integrated Pollution Prevention and Control Bureau
EN	European Norming or European Norming Standard adopted by CEN
EG	Ethylene glycol
ELV	Emission limit value
EMAS	European Eco-Management and Audit Scheme (Council Regulation (EC) No 1221/2009)
EMS	Environmental management system
EO	Ethylene oxide
E-PRTR	European Pollutant Release and Transfer Register
ETBE	Ethyl tert-butyl ether
EU	European Union
FA	Formaldehyde
FCC	Fluid catalytic cracking
FID	Flame ionisation detector
GC	Gas chromatography
HAD	Hydrodealkylation
HPU	Hydrogen purification unit
HTC	High temperature chlorination
IED	Directive 2010/75/EU of the European Parliament and the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control (Recast))

Acronym	**Definition**
IPA	Isopropyl alcohol
IPPC	Integrated Pollution Prevention And Control
IPPC Directive	Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 concerning integrated pollution prevention and control (IPPC Directive) that has been replaced by Directive 2010/75/EU on industrial emissions (IED)
ISO	International Organisation for Standardization. Also international standard adopted by this organisation
LDAR	Leak detection and repair
LO	Lower olefins
LPG	Liquefied petroleum gas
LTC	Low temperature chlorination
α-MBA	α-methylbenzyl alcohol
MCB	Monochlorobenzene
MDA	Methylene diphenyl diamine
MDI	Methylene diphenyl diisocyanate
MEA	Monoethanolamine (2-aminoethanol)
MEG	Mono ethylene glycol
MHP	Methyl hydroperoxide
MIBK	Methyl isobutyl ketone
MTBE	Methyl tert-butyl ether
NAFTA	North American Free Trade Area
NG	Natural gas
NIOSH	National Institute for Occupational Safety and Health (Federal agency US)
NMVOC	Non methane volatile organic compound(s)
OC	Oxychlorination
OTNOC	Other than normal operating conditions
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Poly chlorinated biphenyls
PEA	Poly-ethanolamine(s)
PEB	Polyethylbenzenes
PMDI	Polymeric MDI
PMPPI	Polymeric polyphenyl isocyanate
PO	Propylene oxide
PRU	Phenol recovery unit
PSA	Pressure swing absorber
SCR	Selective catalytic reduction
SM	Styrene monomer
SMPO	co-production of styrene monomere and propylene oxide
SNCR	Selective non catalytic reduction
SRU	Sulphur recovery unit
SSH	Steam superheater
TDA	Toluene diamine
TDI	Toluene diisocyanate
TDP	Toluene disproportionation
TEA	Triethanolamine (2,2',2"-nitrilotriethanol)
TEG	Triethylene glycol
TSS	Total suspended solids
TWG	Technical Working Group. Group of experts composed of representatives from Member States, the industries concerned, non-governmental organisations promoting environmental protection and the Commission for the drawing up and review of BREFs
VCM	Vinyl chloride monomer
VDI	Verein Deutscher Ingenieure (the association of German engineers)
VOC	Volatile organic compound(s)
WS	Working solution

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