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THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY**

EMISSION SCENARIO DOCUMENT ON THE CHEMICAL INDUSTRY

**OECD Environment, Health and Safety Publications
No. 30 Series on Emission Scenario Documents**

Mr. Hirofumi Aizawa
Tel: +33 (0) 1 45 24 79 07; Fax: +33 (0) 1 44 30 61 80; Email: hirofumi.aizawa@oecd.org

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**EMISSION SCENARIO DOCUMENT ON
THE CHEMICAL INDUSTRY**

IOMC

INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS

A cooperative agreement among **FAO, ILO, UNEP, UNIDO, UNITAR, WHO, World Bank and OECD**

Environment Directorate

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

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**OECD Environment Directorate,
Environment, Health and Safety Division
2 rue André-Pascal
75775 Paris Cedex 16
France**

Fax: (33-1) 44 30 61 80

E-mail: ehscont@oecd.org

FOREWORD

Purpose and background

An OECD Emission Scenario Document (ESD) is a document that describes the sources, production processes, pathways and use patterns with the aim of quantifying the emissions (or releases) of a chemical into water, air, soil and/or solid waste. Such documents are lacking for the chemical industry. For this complex branch of industry, sectors have been prioritised for which ESDs are most urgently needed. This document is intended to prioritize the sectors of the chemical industry for which ESDs are urgently needed and to provide key concepts and tools which are instrumental in the production of ESDs for the chemical industry such as life cycle stages, factors influencing emissions and release quantification methods. As such, this will be a starting point for the development of ESDs for the chemical industry.

This document should be seen as a 'living' document, which provides the most updated information available. As such, the document can be updated to take account of changes and new information that becomes available. Readers of the document are encouraged to submit comments, corrections, updates and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org). The comments received will be forwarded to the OECD Task Force on Exposure Assessment, which will review the comments so that the lead country can update the document. The comments will also be made available to users on the OECD web-site (www.oecd.org/env/riskassessment).

How this document was developed

This document is based on a report produced by P. van der Poel and J. Bakker of the National Institute for Public Health and the Environment (RIVM), the Netherlands, and overseen by the OECD Task Force on Environmental Exposure Assessment (TFEEA)¹. The first draft was submitted in June 2003. The TFEEA discussed the first draft at the 11th meeting September 2003 and the second draft at the 12th meeting in September 2004. The draft was developed by authors taking account of comments and information from members of the TFEEA. The TFEEA once adopted this document at the 13th meeting in October 2005. After the approval by the TFEEA, the document had further been developed t by taking into account recent progress or changes of approaches in European countries due to the enforcement of REACH as well as other editorial changes. The draft was finally confirmed by the TFEA in May 2011.

This document is published on the responsibility of the Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology of the OECD.

¹ The TFEEA was reformed to the Task Force on Exposure Assessment (TFEA) in late 2008.

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SUMMARY

Independent of the eventual application of a substance, the first place where emissions into the environment occur is chemical industry. A very large fraction of the substances produced is to serve the manufacture of other substances (intermediates). The chemical industry is therefore a very important industry for risk assessment of substances. The chemical industry is a very complex industry with a lot of specialised sectors. They produce thousands of different substances using a whole spectrum of different chemical reactions and involving usually a whole series of unit operations such as, e.g., extraction, distillation, and phase separation besides the actual reaction. Furthermore, many different processing aids – e.g., catalysts, solvents, and reagents – are used in the production in a range of process steps in all kinds of equipment. So, in the chemical industry we are dealing with emissions of certain substances at:

1. the manufacture of this substances, which is either an end product or an intermediate (life cycle stage Production)
2. the conversion of this substances (an intermediate) into another substance, which is either an end product or another intermediate (life cycle stage Industrial use)
3. the application of the substance as a processing aid in one or more unit operations in CPI (life cycle stage Industrial use)

The tools available at present for emission estimation for the chemical industry in the EU consist of the A-tables, which provide emission factors and B-tables for the size of the local source and duration of the emission (emissions to wastewater, air and soil during the synthesis of all kinds of chemicals and conversion of intermediates) and an emission scenario document (ESD) for intermediates (wastewater emissions). These tools have been described in the technical guidance document for risk assessment (EC, 2003). The emission factors of the A- and B-tables are based on expert judgement. The ESD contains emission factors derived from a cumulative series of emission factors for 29 intermediates (both synthesis and conversion). The value for the emission factor is set at the value within which 90 percent of the emission factors lie. The emission factors may be conservative enough (“worst case”) for most substances to avoid false negatives but probably also may lead to false positives. In some cases, however, emissions will be seriously underestimated (false negative).

This report identifies the sectors in chemical industry for which more refined ESDs should be developed. Therefore, the report firstly describes the chemical industry and its products, by discussing what is generally understood by the term chemical industry and which specific sectors belong to it. Next, priority in ESD development is given as a ranking for the various sectors according to the so-called NACE (Nomenclature générale des Activités économiques dans les Communautés Européennes) codes (see Table 3.1). The underlying reasoning for this prioritisation has been derived from Appendix 1, in which the various sectors have been described and the importance of a sector is considered in terms of size (volume) and number of products. Besides that, it is examined whether sectors can be characterised by specific production processes.

Based on the above criteria, the highest priority should be given to ESDs for the sectors concerning:

- the manufacture of dyes and pigments
- the manufacture of other organic basic chemicals
- the manufacture of plastics in primary forms
- the manufacture of synthetic rubber in primary forms
- the manufacture of basic pharmaceutical products

Other rather urgently needed ESDs to be developed concern:

- the manufacture of perfumes and toilet preparations
- the manufacture of petrochemicals (only for the application of processing aids, such as for instance catalysts)
- the manufacture of other inorganic basic chemicals (only for the application of processing aids, such as for instance catalysts, pH-regulators and oxidising agents)

For other life cycle stages than Production and Industrial use it may also be of importance to develop ESDs. This may be in case for the life cycle stages of Formulation and Service life of catalysts and the life cycle stage of recovery (“Waste treatment”) of solvents and catalysts.

Aspects and considerations for the development of ESDs and the importance of data are discussed. Many details are further elaborated: the aspects of the life cycle are discussed, as are the factors influencing emissions and chemical release estimation.

1 INTRODUCTION

Independent of the eventual application of a substance the first place where emissions into the environment occur is the chemical industry. A very large fraction of the substances produced is to serve the manufacture of other substances (intermediates). So, the chemical industry is a very important industry for risk assessment of substances. The chemical industry is a very complex industry with a lot of specialised sectors. They produce an enormous amount of different substances with a huge number of different chemical reactions. In the production many different processing aids – e.g., catalysts, solvents, and reagents – are used in a range of process steps in all kinds of equipment. So, in the chemical industry we are dealing with emissions from the manufacture of substances, the conversion of intermediates, and from the application of processing aids. The tools available at present for emission estimation in the EU consist of the A- and B-tables (emissions to wastewater, air and soil at the synthesis of all kinds of chemicals and conversion of intermediates) and an emission scenario document (ESD) for intermediates (wastewater emissions). The emission factors of the A- and B-tables are based on expert judgement, whereas the ESD has emission factors derived from the 90th percentile for 29 intermediates (both synthesis and conversion). The emission factors may be conservative enough (“worst case”) for most substances to avoid false negatives, but probably also may lead to false positives. In some cases, however, emissions will be seriously underestimated.

In order to identify the sectors of the chemical industry for which the development of ESDs is most urgently needed, the industry and its products are discussed together with all factors which have a potential influence on the emissions. Many of these factors are discussed in detail. Appendix 1 gives the final ranking of the priority for the individual chemical industry sectors. Furthermore, the relevant life cycle stages to be covered in ESDs – for end products, intermediates and processing aids – are determined on the basis of Chapter 5.

The second part of the report deals with the aspects and considerations for the development of ESDs and the importance of data. An overview of all the aspects and considerations is given in Chapter 4. Many details of this part are further elaborated in the following chapters. Chapter 5, as noted before, is discussing the aspects of the life cycle, Chapter 6 is dealing with factors influencing emissions, and chemical release estimation methods, are dealt with in Chapter 7.

2 CHEMICALS AND CHEMICAL INDUSTRY

The chemical industry consists of a complex of processes, operations, and organisations engaged in the manufacture of thousands of different chemicals and their derivatives. Several branch classifications and definitions for the chemical industry exist. This chapter deals with the various classification systems and definitions to define and describe the chemical industry.

2.1 Classification, branch

Although the chemical industry may be described simply as the industry that uses chemistry and manufactures chemicals, this definition, however, leaves open the question of what a chemical is (Enc. Britt., 2002). Because of statistical economic purposes most countries and organisations like the United

Nations have adopted certain definitions. The most widely used classification in the EU (European Union) is the so-called NACE (Nomenclature of economic activities in the European Union) coding. Presumably this classification corresponds almost – for the chemical industry – with economic classifications of individual Member States. The USA, Canada, and Mexico use the North American Industry Classification (NAICS), which replaces the former U.S. Standard Industrial Classification (SIC). As NACE and NAICS have conceptual differences a working group of the statistical agencies of Canada, the European Union and the United States have reported on their work on convergence of industrial classifications NAICS-NACE (UNSD, 2004). One of the hallmarks of NAICS is that it establishes the production process as the main determinant for grouping economic activities (UNSD, 2004). However, the classification structures of NAICS and NACE are quite similar and where they are different, a pragmatic approach could be adopted to make them converge (UNSD, 2004). In order to avoid complexity only the NACE code is considered in this report. Appendix 5 presents a comparison between the classifications for the manufacture of chemicals and chemical products. Table 2.1 presents the 4 digit NACE codes for the class ‘DG. Manufacture of chemicals, chemical products and man-made fibres’ of this classification system (EUROSTAT, 1996). In overviews of the chemical and related industries both the EEA (European Environment Agency) and OECD (Organisation for Economic Co-operation and Development) employ a comparable system. In the risk assessment of chemicals in the EU 16 industrial categories (IC) are applied to specify the branch of industry where emissions occur (EC, 2003). Below, some more attention has been given to the NACE codes in the classification of the chemical industry, as statistical data collected in this way will be of importance for the development of ESDs.

The scope of the chemical industry is in part shaped by custom rather than by logic. The petroleum industry is usually thought of as separate from chemical industry, for in the early days of the petroleum industry in the 19th century crude oil was merely subjected to a simple distillation treatment.

Table 2.1 Classification of the (petro)chemical industry in the EU with the NACE codes

NACE	Type of chemical process industry
<i>Manufacture of coke, refined petroleum products and nuclear fuel</i>	
2320	Manufacture of refined petroleum products ¹⁾
<i>Manufacture of basic chemicals</i>	
2411	Manufacture of industrial gases
2412	Manufacture of dyes and pigments
2413	Manufacture of other inorganic basic chemicals
2414	Manufacture of other organic basic chemicals
2415	Manufacture of fertilisers and nitrogen compounds
2416	Manufacture of plastics in primary forms
2417	Manufacture of synthetic rubber in primary forms
<i>Manufacture of pesticides and other agro-chemical products</i>	
2420	Manufacture of pesticides and other agro-chemical products
<i>Manufacture of paints, varnishes and similar coatings, printing ink and mastics</i>	
2430	Manufacture of paints, varnishes and similar coatings, printing ink and mastics
<i>Manufacture of pharmaceuticals, medicinal chemicals and botanical products</i>	
2441	Manufacture of basic pharmaceutical products
2442	Manufacture of pharmaceutical preparations
<i>Manufacture of soap and detergents, cleaning and polishing preparations, perfumes and toilet preparations (cosmetics)</i>	
2451	Manufacture of soap and detergents, cleaning and polishing preparations
2452	Manufacture of perfumes and toilet preparations (cosmetics)
<i>Manufacture of other chemical products</i>	
2461	Manufacture of explosives
2462	Manufacture of glues and gelatines
2463	Manufacture of essential oils
2464	Manufacture of photographic chemical material
2465	Manufacture of prepared unrecorded media
2466	Manufacture of other chemical products n.e.c.
<i>Manufacture of man-made fibres</i>	
2470	Manufacture of man-made fibres

¹⁾ Basic chemicals for chemical industry, viz. primary, secondary and tertiary building blocks in organic synthesis (see Table 2.2)

Modern petroleum industrial processes, however, bring about chemical changes, and some of the products of a modern refinery complex are chemicals by any definition. The term petrochemical is used to describe these chemical operations, but, because they are often carried out at the same plant as the primary distillation, the distinction between petroleum industry and chemical industry is difficult to maintain (Enc. Britt., 2002). The manufacture of refined petroleum products has NACE code 2320 and belongs – strictly

speaking – to Industrial Category 9 “Mineral oil and fuel industry” of the TGD (Technical Guidance Document) (EC, 1996; EC, 2003). So, only the manufacture of organic basic chemicals in petrochemical industry (these basic chemical are the so-called primary building blocks – and to some extent secondary and tertiary building blocks for organic chemicals, see Table 2.1) belong to the chemical industry.

Metals in a sense are chemicals because they are produced by chemical means, the ores sometimes requiring chemical methods of dressing before refining; the refining process also involves chemical reactions. Such metals as steel, lead, copper, and zinc are produced in reasonably pure form and are later fabricated into useful shapes. Yet the steel industry, for example, is not considered part of the chemical industry. In modern metallurgy, such metals as titanium, tantalum, and tungsten are produced by processes involving great chemical skill, yet they are still classified as primary metals (Enc. Britt., 2002). The manufacture of (primary production) metals – including ore benefaction – falls under Industrial Category 8 “Metal extraction, refining and processing industry”. Therefore, metal manufacture is not covered in this report.

The boundaries of chemical industry, then, are somewhat confusing. Its main raw materials are the fossil fuels (coal, natural gas, and petroleum), air, water, salt, limestone, sulphur or an equivalent, and some specialised raw materials for special products, such as phosphates and the mineral fluorspar. The chemical industry converts these raw materials into primary, secondary, and tertiary products, a distinction based on the remoteness of the product from the consumer, the primary being remotest. The products are most often end products only with regard to the chemical industry itself; a chief characteristic of the chemical industry is that its products nearly always require further processing before reaching the ultimate consumer (Enc. Britt., 2002). It should be noted that actual chemical processes only take place in a limited number of the categories of chemical industry of Table 2.1. In many industries the main activity is the formulation of chemical products. An example is the lacquers and varnishes industry (in the TGD classified as Industrial Category 14). In some cases industries may have both chemical processing and formulation, for example pharmaceutical industry (no separate industrial category in the TGD). In this industry branch companies are found with only formulation, only chemical processing, and both chemical processing and formulation. This reveals itself in the NACE codes 2441 and 2442 (see Table 2.1).

The TGD (EC, 2003) considers two ICs (Industrial Categories) for the chemical industry, viz.

IC 2 Chemical industry: basic chemicals (e.g. solvents, pH-regulating agents (acids, alkalis))

IC 3 Chemical industry: chemicals used in synthesis (e.g. intermediates (including monomers), process regulators)

In practice classification of a substance in IC 2 or 3 may be difficult. Many chemicals may be regarded as both a basic chemical and a chemical used in synthesis. A solvent may be widely used as a basic chemical for cleaning reactors, pipelines and accessories and for purification of chemicals by recrystallisation. The same chemical is probably also used as a reaction medium. Thus, the substance may also be regarded as a chemical used in synthesis regardless whether the solvent takes part in the reaction or not. Therefore, this report will consider chemical process industry (CPI) in its entirety. The focus is on the manufacture (life cycle stage production) of the substances and their application as a processing aid (life cycle stage industrial use) in the chemical industry. It should be noted that the use of chemicals in the manufacture of a chemical product, such as for example paint (NACE 2430), concerns mainly the life cycle stage formulation. Exception is the use in operations like cleaning of equipment where chemicals like detergents and solvents may be used as processing aids. Where such applications are identified the importance for developing Emission Scenario Documents (ESDs) should be judged at an ad-hoc basis. In some cases the activities in certain branches of chemical industry do not comprise chemical processing and/or formulation. The activities then consist of physical processes (unit operations) such as extraction

and distillation (e.g., the extraction of quinine from cinchona bark and the manufacture of essential oils). However, as these physical processes also take place extensively in the chemical industry these aspects are covered for a branch where, e.g., essential oils are produced.

Furthermore, the following points should be noted.

- Quite a lot of substances are produced as intermediates but many substances are used both as end products in all kinds of products and processes, and as intermediates.
- Some large chemical companies have complex factories consisting of many plants where a large spectrum of compounds is produced belonging to a number of NACE codes. This ESD focuses on the CPI, i.e., chemical factories where actual synthesis and typical chemical/physical unit operations take place.

2.2 Definitions, chemicals

In the chemical industry many terms are used for chemicals without official definitions. Some terms met frequently are raw materials, petrochemicals, base chemicals, commodities, performance chemicals, fine chemicals, active ingredients, agro-chemicals, pharmaceuticals, etc.

Most industrial branch organisations, chemical companies, and institutions like the EEA and the OECD employ a classification with raw materials, bulk chemicals, industrial chemicals, and specialities. Basic chemicals (often referred to as commodity chemicals) are divided in bulk inorganics and organics obtained from raw materials by chemical processing or refining, and fertilisers, industrial chemicals, plastics, resins, elastomers, fibres, dyestuffs, etc., obtained from bulk chemicals by chemical processing (EPA, 1995a; OECD, 2001). On the basis of the classification of EPA (1995a), OECD (2001), and an industrial source (ACFIS, 2002) the following definitions are used.

Raw materials are the base materials from which other materials are produced. In chemical industry raw materials are, e.g., oil, coal, gas, water, and minerals. The end products or semi-finished products of industries manufactured out of these raw materials are in their turn raw materials for another industry. In order to avoid confusion the term feedstock is used in this report.

Feedstocks are raw materials supplied to a processing plant (MW, 2002). This term is used in this report for chemicals manufactured out of the primary raw materials obtained from natural sources (ores from mines, petroleum from wells, water from groundwater layers, etc.).

Bulk chemicals (commodities) are used for the production of other basic chemicals, specialty chemicals, and other chemical products, as well as in other manufactured goods (textiles, motorcars, appliances, furniture, etc.) or in the processing applications (pulp and paper, oil refining, aluminium processing, etc.) (OECD, 2001).

Other basic chemicals include a large group of chemicals – such as, e.g., plastics, fibres, resins, and dyestuffs - and the industrial chemicals. Basic inorganic chemicals used for industrial processes are derived from chemicals, which are often of a mineral origin. Some examples are acids, alkalis, salts, oxidising agents, industrial gases, and halogens (EPA, 1995b). The largest use of basic inorganic chemicals is as processing aids and, therefore, often do not appear in final products (EPA, 1995b).

Next, the categories for chemicals manufactured for the product groups consumer care products, life science products, and specialty chemicals can be distinguished. Another classification – as used in chemical industry (ACFIS, 2002) – uses the main categories primary chemicals and secondary chemicals. Primary chemicals concern chemical products and base intermediates (commodities and bulk chemicals), which distinguish themselves by high manufacturing and sales volumes, low sales prices and price competition, manufacturing standardisation, low product innovation and process innovation. This almost matches the category basic (or base) chemicals. Secondary chemicals are chemicals characterised by low

manufacturing volumes, manufacturing flexibility, product diversification and innovation and a greater interest in service rather than in price. For the category secondary chemicals they employ the subcategories fine chemicals and special(i)ty chemicals.

Fine chemicals are synthesis products aimed at chemical uses as intermediates (or with the function of bulk chemicals), in the manufacturing of various chemical products such as pharmaceuticals, flavours and essences, agro-chemicals, detergents, etc. These products are characterised by medium to low sales volumes and higher prices compared to commodities. They are composition products, which are completely described by their chemical-physical properties.

Specialty chemicals are products that are manufactured with the specific aim of allowing the achievement of certain results. Therefore, they are called performance products and are highly differentiated among themselves, with a varying composition and are identifiable only by their performances and not by their chemical contents or their origin (ACFIS, 2002). These chemicals are derived from basic chemicals and more technologically advanced than their originators, for example adhesives and sealants, catalysts, coatings, electronic chemicals and plastic additives (OECD, 2001). It should be noted that adhesives, sealants, coatings, etc. are chemical products (formulations). The specialty chemicals in these products are, for example, antioxidants, viscosity index improvers, and antifoaming agents. Basic chemicals in these products may be bulk chemicals such as toluene and industrial chemicals such as coalescing solvents and resins. Specialty chemicals are manufactured in lower volumes than basic chemicals, give higher profit margins and have less cyclicity in their business cycle (OECD, 2001). Although dedicated and continuous operations are typical, there are also a growing number of plants that have general-purpose synthesis operations.

Industrial chemicals have not been defined in the literature studied. Only on one website searched on the Internet a definition for Australia was found: “chemicals that fall under the definition of *industrial chemicals* include dyes, solvents, plastics and photographic chemicals; industrial chemicals, however, can also be found in the home in paints, cleaning agents and cosmetics” (NOHSC, 1998). Outside the EU some chemical companies list many chemicals both under bulk chemicals and industrial chemicals. A good definition may be chemicals that are widely used either in chemical processing industry – either as a processing aid or as an intermediate – in considerable quantities or in chemical products industry in the manufacture of chemical products.

Life science products include pharmaceuticals, products for crop protection and products of modern biotechnology (OECD, 2001). Furthermore, biocidal products belong to this group of chemical products. Typical chemicals that are manufactured by chemical processing are the active ingredients for pharmaceuticals, pesticides, and biocides. Basic chemicals applied in the preparations (formulations) are, for example, solvents and dyestuffs. Plants where chemical processes take place generally use batch-oriented synthesis; plants where the products are formulated require good quality control and a clean environment (OECD, 2001).

Consumer care products comprise chemical products such as soap, detergents, bleaches, laundry aids, hair care products, skincare products, and perfumes (OECD). Consumer care products are formulated products, chemical processing does – very probably – not occur at all. Formulation is a typical batch type operation and some products, e.g. detergents, are manufactured in large dedicated plants.

Petrochemicals (or petroleum chemicals) are those chemicals, which are classified as such in order to indicate the source of the chemical compounds. As many common “petrochemicals” can be made from other feedstocks, the terminology therefore, is a matter of source identification. Generally, petrochemicals are considered to be chemical compounds, which are derived from petroleum either by direct manufacture (i.e., refining) or by indirect manufacture as a by-product from the variety of processes used during the refining of petroleum (chemical processing). Some sources consider also plastics as petrochemicals, besides a range of other common (industrial) chemicals, which are often used as building blocks (intermediates) in chemical industry (EPA, 1998a; SRI, 2002). Regardless of manufacture in oil refineries or chemical companies, most basic organic chemicals are considered to be petrochemicals in this report. These chemicals – primary, secondary and tertiary building blocks – are presented in Table 2.2. It should

be noted that for an emission scenario document a distinction between petrochemical (IC 8 “Mineral oil and fuel industry”) and IC 2/3 (“Chemical industry”) does not play a role.

The overview of the chemicals and related industries from OECD (2001) has been modified for this document and is presented in Figure 2.1. The main modification concerns the distinction between formulation and chemical processing. Red arrows present the flow of chemicals used as intermediates – i.e., chemically converted into another chemical. Green arrows present the flow of chemicals used in formulation processes. Blue arrows present the use and application (processing by industry or consumers). Dotted arrows present the flows of industrial chemicals directly to consumer care products, life science products, and specialty chemicals. Several possible direct uses – for example bulk chemicals used in consumer products and active ingredients used in consumer care products (formulation) - have been omitted in order to maintain transparency.

The following classes of substances are discussed in this report, related to the risk assessment under different legal frameworks:

- Industrial chemicals not covering pesticides and biocides:
 - High production volume chemicals (HPVCs)
 - Low production volume chemicals (LPVCs or Non-HPVCs)
- Pesticides
- Biocides (non-agricultural pesticides)

HPVCs are chemicals reported to be produced or imported (per producer or importer) at levels exceeding 1000 tonnes per year in at least one Member State or in the European Union region. LPVCs are placed on the EU market in volumes between 10 and 1000 tonnes per year per producer or importer. It should be noted that in the EU and in other jurisdictions, pesticides and biocides are regulated separately than ‘regular’ HPVCs and LPVCs’. Nevertheless, the same basic emission estimation may apply as for ‘regular’ LPVCs and HPVCs. Substances that are new to the market are usually produced in smaller quantities. If they are successful, production volumes may increase over the years, meaning that they may shift from LPVC to HPVC over the years. This implies that emissions may increase during scaling up. However, at a certain stage emissions may level off or even be reduced as a switch in production may be made from multipurpose equipment to dedicated equipment (with better and/or optimised abatement techniques).

In the part on definitions of chemical classes a rough idea on the quantities has been given already. Many basic chemicals, i.e., almost all bulk chemicals, many industrial chemicals, and some fine chemicals (intermediates) belong to the HPVCs. Quite often, industrial chemicals – and even fine chemicals – are shipped in bulk and so may be stated as “bulk chemicals” as well. It should be noted that in some cases a bulk chemical or industrial chemical may be used as, e.g., an active ingredient.

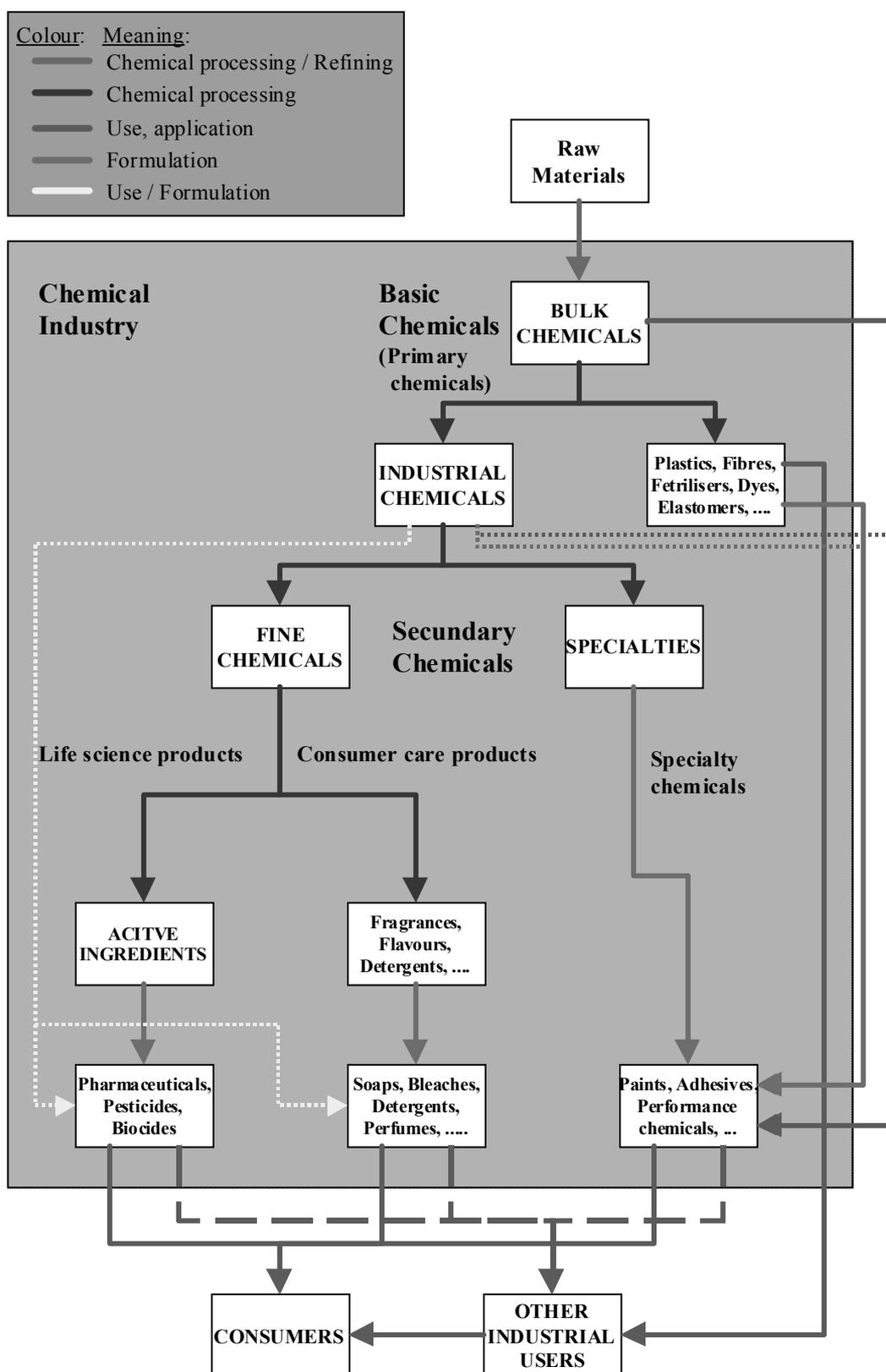


Figure 2.1 Overview of the chemicals and related industries (Modified, source: OECD, 2001)

An example is formaldehyde, an industrial chemical (often shipped in bulk) used extensively in industry, for example in chemical synthesis of many other chemicals and in adhesives for plywood and

chipboard. Formaldehyde is also used in pretty large quantities as an active ingredient in various biocidal products. In total there are some 400 substances of the EU list with over 2500 HPVCs, which are also used as a biocide in one or more product types of the 23 product types defined in the Biocides Directive (EC, 1998). For basic organic chemicals – belonging to the group of bulk chemicals – a subdivision may be used derived from the main components resulting from petrochemical plants (EPA, 1995a), see Table 2.2. Apparently, all chemicals of this table are HPVCs. Ten out of these 27 basic chemicals were on the Priority List of the EC, for which Risk Assessment Reports (RARs) have to be made (ECB, 2003). These substances are identified in Table 2.2.

Table 2.2 Basic chemicals derived from petrochemical industry (OECD, 1995)

Primary building blocks	Secondary building blocks	Tertiary building blocks
Ethylene	Ethylene dichloride	Vinyl chloride
	Ethylene oxide	Ethylene glycol
	Ethylbenzene	Vinyl acetate ¹⁾
Propylene	Propylene oxide ¹⁾	
	Acrylonitrile ¹⁾	
	Isopropyl alcohol	Acetone
Benzene ¹⁾	Ethylbenzene	Styrene ¹⁾
Toluene ¹⁾	Cumene ¹⁾	Phenol ¹⁾
		Acetone
Xylenes, p-isomer	Terephthalic acid	
Methanol	Acetic acid	
	Formaldehyde	
	Methyl t-butyl ether ¹⁾	
Butadiene ¹⁾		
Butylene		

¹⁾ Substance on EU priority lists. Risk assessments available from <http://ecb.jrc.ec.europa.eu/esis/>

It is important to bear in mind that this report focuses primarily on chemical processing, in other words on the chemical processing industry (CPI). CPI consists of a variety of small to very large factories where chemical compounds are produced. Furthermore, there is a large variety in the numbers of chemical products companies produce (OECD, 2001). By far the most chemical producers have less than 10 employees with a limited share in the sales. This is illustrated with the figures of Table 2.3. The manufacture of LPVCs and newly developed substances will mainly take place at large companies besides the manufacture of HPVCs. The manufacture of LPVCs which do not belong to specific chemical industry sectors like for example the manufacture of basic pharmaceutical products (NACE 2441), is not reflected in the classification by the NACE codes. Therefore, their manufacture is considered to belong to NACE code 2414 “Manufacture of other organic basic chemicals”. Also organic bulk chemicals – which are the building blocks for plastics, fibres, elastomers (synthetic rubber) and resins – do not fit into a chemical industry sector with a specific NACE code. So, they too are considered here to belong to NACE code 2414, together with industrial chemicals. It is notable that the manufacture of dyes and pigments has been classified in NACE and many classifications of chemicals (e.g., OECD, 2001) under basic chemicals. The majority of (organic) dyes and pigments will be produced in relative small amounts, and applied in specialty chemicals (e.g., chemical products such as paints) and consumer care products.

Table 2.3 Chemicals industry in the European Union (UNECE, 1999)

Number of employees at each site	1-9	10-99	100-249	250-499	=500
Sales (%)	3	10	10	14	63
Number (%)	70	22	4	2	2

In the continuation of this report the term ‘intermediate’ is used frequently. According to MW (2001) an intermediate is a) a chemical compound synthesised from simpler compounds and usually intended to be used in later syntheses of more complex products, and b) a usually short-lived chemical species formed in a reaction as an intermediate step between the starting material and the final product.

It should be noted that in risk assessment monomers and prepolymers are covered by use category (UC) 33 “Intermediates” in the TGD. However, crosslinking agents – usually the same as monomers – are counted as UC 43 “Process regulators” in the TGD. Monomers applied in CPI to manufacture macromolecular materials such as plastics are treated as intermediates in this report. Monomers, prepolymers and crosslinking agents are applied in a broad range of chemical products such as coatings and adhesives. These products are formulations and therefore not treated in this report.

3 POTENTIAL PRIORITY SECTORS FOR DEVELOPMENT OF ESDS

In this chapter sectors of chemical industry have been ranked for priority in the development of ESDs. The priority sectors are presented in Table 3.1. The sectors are according to the NACE list – including the petrochemical industry – despite the fact that this classification does not always reflect the chemical processes in the most appropriate way as mentioned in Chapter 2. However, ESDs do not just cover the establishment of emission factors for processes but also the size of the process as expressed by the fraction of the main source and the number of emission days (the so-called B-tables of the TGD). Statistical data on items, on product quantities, number of employees, etc. are available for each NACE code and thus are important in the development of ESDs.

The ranking is based on the discussions of Appendix 1.

There is a distinction between emissions of chemicals during their synthesis and conversion in case of an intermediate, and emissions of chemicals applied as a processing aid in CPI. As stated before, this report does not consider the application of chemicals either used as a component (life cycle stage of formulation) or as a processing aid (e.g. detergent or solvent) (life cycle stage of industrial use) in the manufacture of a chemical product (formulation or preparation). The aspects of the life cycle are discussed in Chapter 5. Summarising, the life cycle stages identified as relevant for end products, intermediates, and processing aids are presented in Table 3.2.

Table 3.1 Priority in the development of ESDs for [1] end products (EP), [2] intermediates (I), and [3] processing aids (PA): 0 = no need for development (EP) or not applicable (I), -- = very low priority, - = low priority, + = high priority, ++ very high priority

NACE	Chemical industry sector	Priority		
		EP	I	PA
2320	Manufacture of refined petroleum products	0	0	+
2411	Manufacture of industrial gases	--	--	-
2412	Manufacture of dyes and pigments	++	++	++/- ¹⁾
2413	Manufacture of other inorganic basic chemicals	-	-	+
2414	Manufacture of other organic basic chemicals	++	++	++
2415	Manufacture of fertilisers and nitrogen compounds	0	0	-
2416	Manufacture of plastics in primary forms	0	++	++
2417	Manufacture of synthetic rubber in primary forms	0	++	++
2420	Manufacture of pesticides and other agro-chemical products	-	-	-
2430	Manufacture of paints, varnishes and similar coatings, printing ink and mastics	0	0	--
2441	Manufacture of basic pharmaceutical products	++	++	++
2442	Manufacture of pharmaceutical preparations	0	0	--
2451	Manufacture of soap and detergents, cleaning and polishing preparations	-	-	-
2452	Manufacture of perfumes and toilet preparations (cosmetics)	+	+	+
2461	Manufacture of explosives	--	--	--
2462	Manufacture of glues and gelatines	-	-	-
2463	Manufacture of essential oils	-	-	-
2464	Manufacture of photographic chemical material	0	0	--
2465	Manufacture of prepared unrecorded media	0	0	--
2466	Manufacture of other chemical products n.e.c.	0	0	--
2470	Manufacture of man-made fibres	0	0	--

¹⁾ ++ for organic colourants, - for inorganic colourants

Table 3.2 Relevant life cycle stages to be covered in ESDs for the chemical industry

ESD on:	Life cycle stage				
	Production	Formulation	Industrial use	Service life	Recovery
End products	X	. ¹⁾	. ¹⁾	-	-
Intermediates	X	-	X	-	-
Processing aids	. ¹⁾	(X) ²⁾	X	(X) ²⁾	(X) ²⁾

¹⁾The relevant stage production should be covered in another ESD than the stage industrial use, and – if relevant – formulation as explained in Chapter 2.

²⁾If relevant (for example in the case of certain catalysts)

4 ASPECTS OF AND CONSIDERATIONS AT ESD DEVELOPMENT AND IMPORTANCE OF DATA

This chapter discusses the aspects to be considered for prioritising chemicals. The various aspects are further elaborated in the successive chapters, which treat the aspects of the life cycle (chapter 5) and factors influencing emissions (chapter 6).

For prioritising chemicals the following aspects should be considered:

- Annual volume
- Function
- Process
- Substance
- Number of substances
- Additional considerations
- Life cycle stages

Annual volume

The annual volume of a substance is not the most important factor. For HPVCs in most cases specific processes and dedicated equipment with provisions for optimal efficiency (also for the reduction of emissions) are used. Furthermore, for such HPVCs RARs (risk assessment reports) have to be made with site-specific assessments. Data on releases for chemicals used as processing aids, however, may be of importance in the development of emission scenarios.

Function

The first distinction which has to be made is between intermediates (production and conversion with their respective emissions) and processing aids. Processing aids may have many different functions with possibly very different emission factors. Two important functions met frequently are solvents and catalysts. Chapter 6 discusses this aspect extensively and presents a comprehensive list.

Process

For emission estimation the process steps (unit operations) and chemical reaction types involved with the accompanying process conditions and equipment used is most important. There is expected to be a strong relation between the physico-chemical properties and the emission factor. Chapter 6 discusses these aspects into depth.

It should be remembered that sectors with only formulation (operations like mixing, filling, and cleaning) are not important here as attention is focused on CPI.

Substance

The physico-chemical properties of a substance are also very important as stated above. The main properties are discussed also in Chapter 6.

It is evident that for the risk assessment of a substance the availability of data is of key importance. This is the reason that emission scenarios are used. However, in order to make an emission scenario, data on emissions of other substances have to be used. For specific unit operations and process conditions data are often available for a number of substances. In this way the emission scenarios can be made by analogy. Many of the aspects involved are discussed in Chapter 7 “Chemical release estimation”.

Number of substances

Sectors that develop a large number of new substances will have a higher priority than sectors that occasionally develop new substances. For the time being existing estimation tools such as the A- and B-tables of the TGD (EC, 2003) can be used.

Additional considerations

The A- and B-tables (EC, 2003) and the ESD for intermediates can be used to estimate (initial) emission factors. The A- and B-tables of the TGD (2003) are based on expert judgement and consider the type of equipment used the vapour pressure of the substance, and the scale of production/conversion. The ESD on intermediates only considers wet and dry processes. As notifiers – i.e., the producer and user of intermediates – know exactly about the equipment, unit operations, process conditions, etc., a refined emission estimate would be desirable.

The knowledge about the toxicity of a substance or a specific group of substances and the potential of high emissions does not necessarily imply a high priority for the development of an ESD as such, as many other factors play a role. This is illustrated with two examples. First, a very toxic chemical may have a high emission factor to wastewater. Yet the release to surface water may be extremely low if the degradability is extremely good. Second, a less toxic substance with a low emission factor may be accumulated in the environment and cause effects to organisms. So, only if such a substance falls into a sector that is prioritised, it is likely that a refined ESD might be developed in near future. Until that time, such chemicals hopefully will be detected as dangerous to the environment with the existing tools (assuming that the estimates are conservative enough).

Life cycle stages

In priority setting the relevant life cycle stages should be taken into account. Chapter 5 deals extensively with all aspects of the life cycle of chemicals.

A distinction has been made between ESDs for emission scenarios on [1] end products, [2] intermediates, and [3] processing aids. Every ESD might consist of separate sections for different types of chemicals or reactions. For end products there may be a section on dye manufacture for example. Dyes often belong to certain chemical classes for which specific types of reactions are carried out in particular equipment. For intermediates the whole spectrum of chemical reaction types may occur at synthesis and their conversion may – depending on the next chemicals (“end products”) – involve all kinds of reaction types. In some cases small-scale equipment (“laboratory glass-ware”) is used and in other cases large dedicated plants. So, many sections may have to be developed in due time. For processing aids some specific applications will be more important than others. Solvents used as a reaction medium, extraction solvent, cleaning agent, etc., are well known for environmental releases. By definition, a catalyst is a substance that increases the rate of a chemical reaction by reducing the activation energy, but which is left unchanged by the reaction. However, catalysts may be degraded or become inactive due to “poisoning”. At regeneration, emissions might occur. In the case of an alkylation reaction carried out with a Friedl-Craft catalyst suspended in the reaction mixture, recovery of the catalyst is normally impossible. During the removal of the spent catalyst emission are quite likely.

5 ASPECTS OF THE LIFE CYCLE

In this section the aspects of the life cycle are discussed to determine which life cycle stages should be covered in the three types of ESDs for the chemical industry.

The general scheme of the life cycle of a substance is shown in Figure 5.1. The individual stages of the life cycle are discussed in the following sections. It should be noted that this is done from the viewpoint of the CPI. For reasons of transparency the various stages of handling (filling and emptying of drums, containers, bags, tanks, etc.), storage, transfer, and transportation (with tank lorries, tank wagons, etc.) are not shown. These aspects are discussed briefly in section 5.7 “Handling, storage, transfer, and transport”.

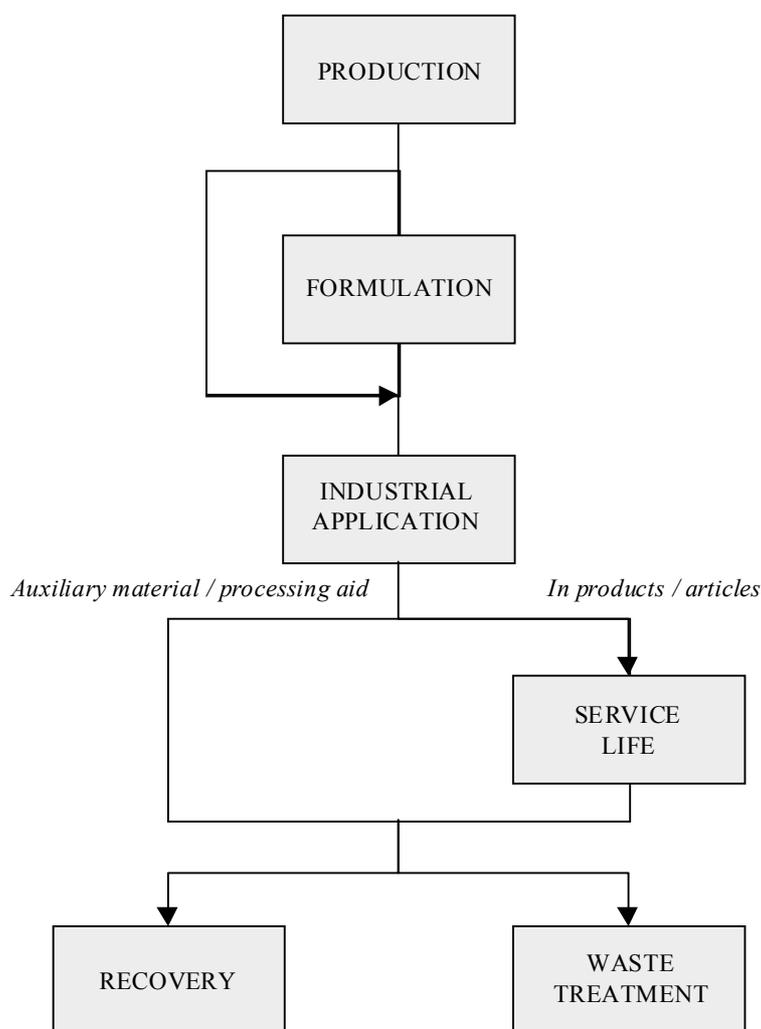


Figure 5.1 Simplified life cycle scheme for chemical compounds

5.1 Production

In the CPI we may distinguish the following types of substances:

1. Naturally occurring substance obtained from natural materials by unit operations such as extraction and distillation
2. Substances produced by chemical reactions to be used as processing aids or in products in all industrial categories (end products)
3. Intermediates, i.e. chemical compounds synthesised from simpler compounds and usually intended to be used in later syntheses of more complex products

This report considers the production of end products and intermediates, and the application of all kinds of compounds (basic chemicals, industrial chemicals and specialty chemicals such as catalysts) used as processing aids in unit operations in the CPI. It should be noted that in principle intermediates are the same as reactants; reactants may be characterised as simple molecules that take part in chemical reactions, e.g., sulphuric acid used in organic synthesis to prepare sulphonates and acetic acid to prepare esters (acetates).

The stage of production may consist of various steps as shown in Figure 5.2.

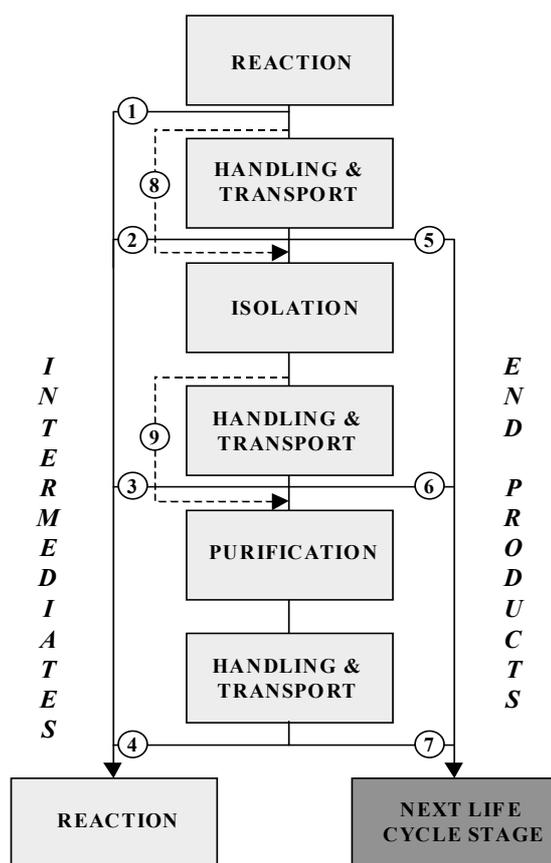


Figure 5.2 Possible steps during synthesis (stage of production) where emissions may occur

The production of a substance starts with the actual chemical reaction in which the substance is formed. Emissions during reaction may occur to air and wastewater. Also after the reaction emissions to air and wastewater will occur due to cleaning. Intermediates may be converted – life cycle stage processing –

into the next compound directly after synthesis in the same reactor (without isolation and purification) – pathway ① – or in another reactor after handling and transport of the reaction mixture (pathway ②). Intermediates may also be isolated and transported to another site without (pathway ③) or after (pathway ④) purification. Emissions may or occur during all these steps.

End products, i.e. substances to be applied in formulations, products or processes, may go without isolation (pathway ⑤) to the next stage of the life cycle. Normally substances will be isolated first (pathway ⑥) often after being purified (pathway ⑦). Pathways ⑧ and ⑨ reflect the situation that no handling and transport occur, i.e. isolation and/or purification take place in the same apparatus. The section “Handling, storage, transfer, and transport” examines the aspects of handling, storage, transfer, and transport. None of the next five stages of the life cycle depict these aspects.

Additional points in the scheme where emissions occur are during cleaning the equipment used for reaction, isolation and purification, and leakage of pipes, flanges and accessories used for transport. Furthermore, emissions occur due to cleaning drums and containers used for transport and storage and at waste treatment of empty packaging.

The level of emissions at application depends on many factors, which are discussed in Chapter 6.

5.2 Formulation

Formulation of a substance in the CPI is an exception. An example of a formulation in the CPI may be the formulation of certain catalysts. This specialised type of formulation is not considered in this report. Formulation of chemical products such as paints and adhesives occurs in specialised branches of the chemical industry (chemical products industry). As stated in Chapter 2, the sectors where chemical products are manufactured are not part of this report. These sectors of the chemical industry should be covered in separate ESDs as has been done already, for example, for industrial category 14 “Paints, lacquers and varnishes industry” of the TGD (Prats, 1992).

5.3 Industrial application

The application of substances in the CPI may concern intermediates, processing aids and auxiliary materials. Only in a few cases in the CPI are substances incorporated in products or articles that are also used in the CPI. This aspect has been considered in the section on “Service life”. The level of emissions during application depends on many factors, which are discussed in Chapter 6.

5.4 Service life

For the stage of service life one can think of a catalyst present on a catalyst support or a solid catalyst used in a reactor for a longer period (> 1 day, usually >> 1 day and often > 1 year). A special situation occurs when solvents are used as a reaction medium in chemical synthesis. After the reaction the solvent may be recovered (see also section “Recovery”) and reused. Usually, the solvent is distilled off and sometimes purified or dried prior to reuse. If the quality of the recovered solvent meets the prerequisites it is reused in the same chemical process. Otherwise, the solvent may either be used for less critical purposes or be processed as hazardous waste (see also section “Waste treatment”). Example 3 of the section on “Function of the substance” in Chapter 6 – where the relation between the function of a substance and the environmental releases are discussed – gives a visual presentation (Figure 6.3). In risk assessment for the local situation the total quantity of the solvent that is used in the processes over the whole year is considered (the so-called throughput) and related to the direct releases during the year with an overall emission factor.

5.5 Recovery

Recovery takes place when solvents used as a reaction medium are recycled or when the excess of one of the reactants is recovered. Also catalysts will be recovered and recycled in many cases. For recovery we may distinguish two basically different situations. Recovery may consist of the recovery of the substance assessed, as may be the case with a catalyst. Usually, however, it is a question of recovery of a material or component of a product. This can be illustrated by the following two examples.

Suppose that a substance is assessed, which is applied as an anti-halo additive in photographic baths. We have the situation then that most spent baths are collected and treated on-site or at a specialised firm for the recovery of silver. After silver recovery the remainder of the photographic baths is released into the sewer. The second example concerns an additive in printing ink. Most of the printing ink will remain on the paper until the waste stage where paper is recycled. In paper recycling much of the paper is de-inked. One part of the additive may be released with the wastewater and the other part will end up in the de-inking sludge (hazardous waste).

5.6 Waste treatment

This is the last stage of the life cycle. In the CPI this will be when auxiliary materials and processing aids remain after application and have to be disposed of. Final products and intermediates may end up in waste streams after synthesis and purification, as well as intermediates after reaction (processing). Also substances present in products and articles at the end of their service life have to be disposed of. If they are present in a material that is recovered they may be released into the environment. Then, however, this takes place at the stage of recovery (section "Recovery").

Waste materials in the CPI will be incinerated in the case of organic wastes or landfilled at special sites for hazardous waste in the case of inorganic compounds (and probably some organic wastes) that can not be transformed into harmless and/or usefully applicable materials.

5.7 Handling, storage, transfer, and transport

So far, releases of chemical compounds during handling, storage and transfer have been assumed to be included at the stage of production. Transport releases have been assumed to be negligible as actual losses are assumed only to occur due to accidents.

For volatile substances one should, however, consider the losses due to breathing and withdrawal. Many basic chemicals have high vapour pressures at ambient temperatures and are often stored in huge tank parks. It is suggested that a separate ESD should be produced for these releases. For the emission scenarios several useful documents are available (EPA, 1997; Mulder et al., 1993).

5.8 Relevant life cycle stages in ESDs

From the previous sections and Chapter 2 it follows which life cycle stages should be covered in the three types of ESDs for the chemical industry. An overview is presented in Table 5.1.

Table 5.1 Relevant life cycle stages to be covered in ESDs for the chemical industry

ESD on:	Life cycle stage				
	Production	Formulation	Industrial use	Service life	Recovery
End products	X	. ¹⁾	. ¹⁾	-	-
Intermediates	X	-	X	-	-
Processing aids	. ¹⁾	(X) ²⁾	X	(X) ²⁾	(X) ²⁾

¹⁾The relevant stage production should be covered in another ESD than the stage industrial use, and – if relevant – formulation as explained in Chapter 2.

²⁾If relevant (for example in the case of certain catalysts)

6 FACTORS INFLUENCING EMISSIONS

The substances occurring in the chemical process industry may have many functions and very different emission factors. Some important factors influencing the emission factors are:

1. Function of the substance
2. Physico-chemical properties
3. Process conditions
4. Type of equipment used
5. Type of process
6. Type of reaction
7. Series of subsequent process steps

In developing and ESD for the chemical processing industry these factors should always be considered. The following sections will discuss the factors stated above.

6.1 Function of the substance

For the function of a substance so-called use categories (UCs) have been established. The function or use categories of substances occurring in the CPI (IC 2 & 3) according to the TGD (EC, 2003), the classification of ChemUSES (EPA, 1980), and derived from Ullmann (2001) are listed in Table 6.1. This list is not exhaustive and, on the other hand, may contain use categories that are disputable. From this list it becomes clear that many more specific functions exist than appear from the list of 55 use categories of the TGD. Some functions will have the same emission level depending for example on the way they are used. Some examples are given here to illustrate the various characteristics of importance for the emissions. The examples are illustrated with a figure showing the relevant stages of the life cycle and block arrows that give a relative impression of the emission level (thin arrows low emissions, thick arrows high emissions).

For substances of UC 33 “Intermediates” the TGD contains a specific ESD. Default values for the emission factors for wastewater are presented for both the stages of production and industrial application (chemical conversion into the next compound). Emission factors for air are not presented and there is nothing known about abatement techniques which may have been applied for some of the substances investigated or on process conditions, equipment used, etc.

Next, three examples are presented for use categories that are quite common for the application of chemicals in the CPI, viz., IC 9 “cleaning agents”, IC 43 “Process regulators” – in this case catalysts – and IC 48 “solvents”. In the accompanying figures (Figure 6.1 – 6.4) the potential emissions are indicated by blue arrows, where the thickness of the arrows present the relative magnitude. The life cycle stages are presented as bright yellow rectangles for the cases where they are relevant for this report. Otherwise they are pale yellow. Storage has been incorporated for the example of solvents as well.

Table 6.1 Use categories (UCs) applicable to the chemical process industry

UC	Function	UC	Function
1	Absorbents and adsorbents	43	Process regulators (continued)
9	Cleaning/washing agents and additives	- retarders	
11	Complexing agents	- scavengers	
16	Dustbinding agents	- solubilising agents	
-	Emulsifiers	44	Reducing agents
29	Heat transferring agents	48	Solvents
33	Intermediates	50	Surface-active agents
37	Oxidising agents	55	Others
40	pH-regulating agents	- clarifiers	
43	Process regulators	- coupling agents	
-	accelerators	- deaerating agents	
-	activators	- dechlorinating agents	
-	catalyst supports	- dehydrating agents	
-	catalysts	- deionisers	
-	chain extenders ¹⁾	- demulsifiers	
-	chain terminators ¹⁾	- dewatering aids	
-	chain transfer agents ¹⁾	- eluting agents	
-	coagulants	- entraining agents	
-	coalescents	- evaporation control agents	
-	crosslinking agents ¹⁾	- extraction agents	
-	curing agents ¹⁾	- filtration aids	
-	defoamers	- functional fluids	
-	depolymerisation agents	- humidity indicators	
-	dispersants	- hydrotropic agents	
-	initiators	- indicators	
-	nucleating agents	- ion exchange agents	
-	polymerisation additive	- leaching agents	
-	polymerisation inhibitors	- poison gas decontaminants	
-	prevulcanisation inhibitors	- precipitating agents	
-	promoters	- reagents	
-	refining agents (non-petroleum)		

¹⁾ Substances used in polymerisation processes

Example 1

Use category 9: Cleaning/washing agents and additives

Substances of this type are used for the life cycle stage of industrial application in cleaning operations (“water and soap”) of vessels, pipes and auxiliaries. The emissions will be almost completely directed to wastewater (see Figure 6.1)

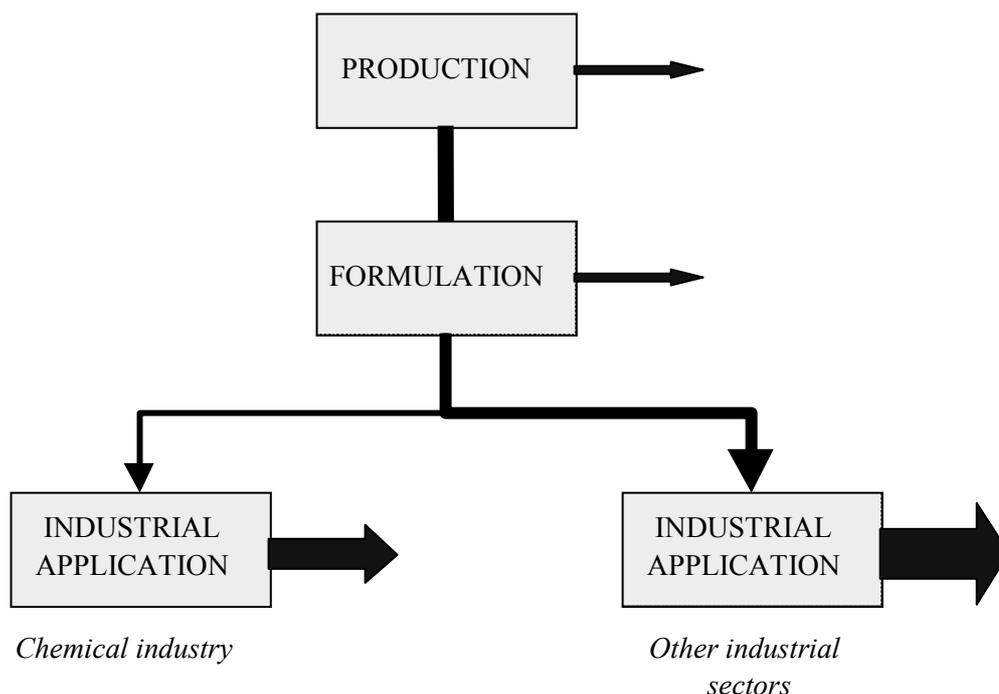


Figure 6.1 Life cycle stages and relative emissions for substances with use category 9 “Cleaning/washing agents and additives”

Example 2

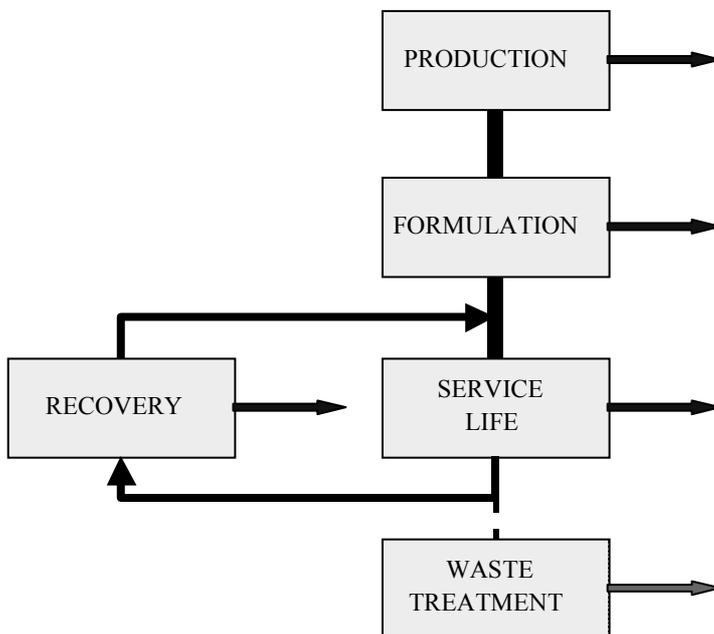
Use category 43: Process regulators, specific type: catalysts (see Figure 6.2)

In principle we have to distinguish between:

- A. Catalyst applied in *heterogeneous catalysis*; in this example a catalyst deposited on a catalyst support (e.g. clay or alumina-silica) is considered. Usually this type of catalyst is applied in continuous processes or over a prolonged period for a large number of batches.
- B. Catalyst dispersed in reactants (*homogeneous catalysis*).

It should be noted that a broken line represents the stage of waste treatment for situation B), because this stage will only occur in the case that a residue is generated at recovery. For situation A) also a recovery stage is shown, as after some time regeneration may be needed.

A)



B)

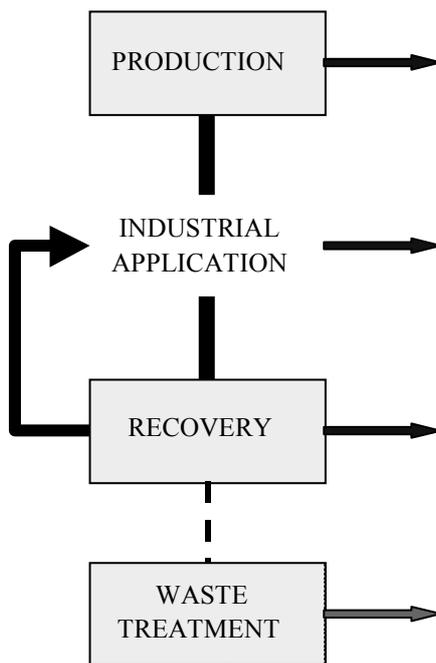


Figure 6.2 Life cycle stages and “Processregulators”, A) Catalyst

relative emissions for substances with use category 43 applied on a support and B) catalyst applied dissolved in reactants

Example 3

Use category 48: Solvents

Figures 6.3 and 6.4 present two possible situations:

- A. Application as a reaction medium with recycling (“throughput” is of interest for emission)
- B. Application “once-through”, where the solvent is not reusable and has to be disposed of.

A)

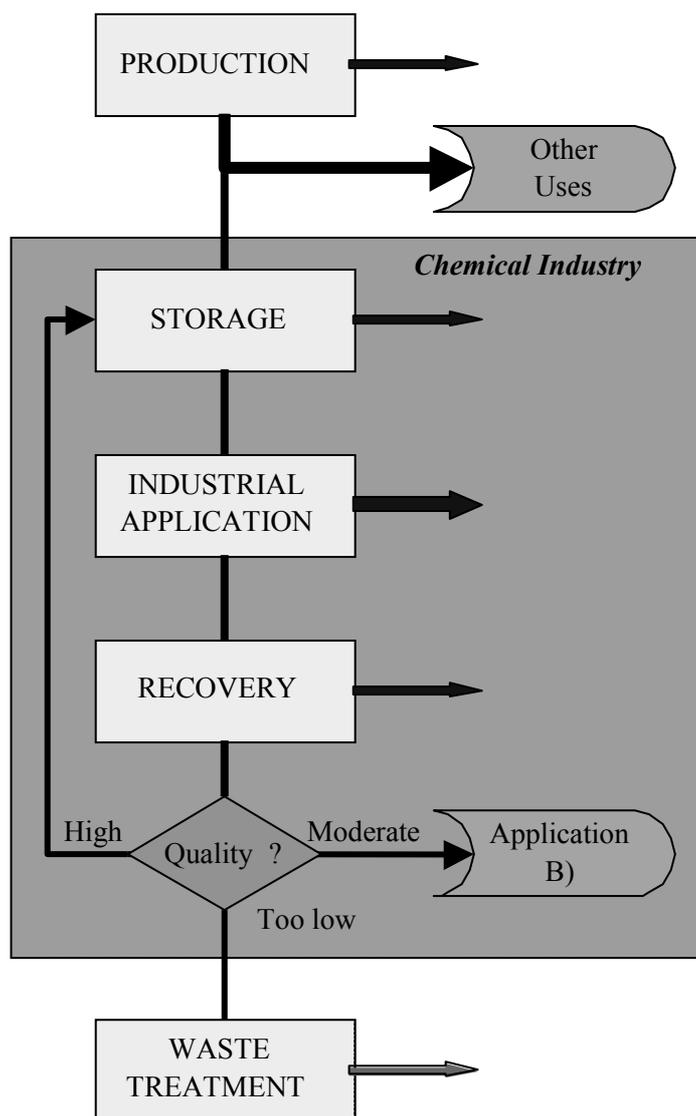


Figure 6.3 Life cycle stages and relative emissions for substances with use category 48 “Solvents”, A) for application as a reaction medium and B) (see next page) for “once-through” application

B)

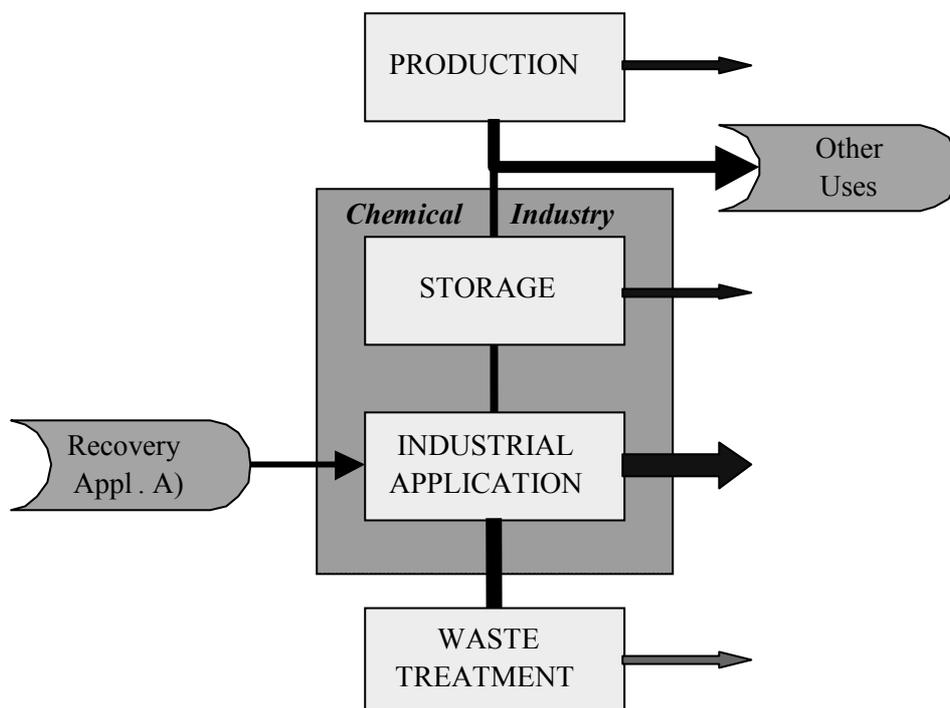


Figure 6.4 Life cycle stages and relative emissions for substances with use category 48 "Solvents", A) for application as a reaction medium (see previous page) and B) for "once-through" application

6.2 Physico-chemical properties

For environmental emissions vapour pressure and water solubility are the most prominent physico-chemical properties. For the distribution over air and water the Henry coefficient also plays an important role. This has been depicted in Figure 6.5.

Many – if not most – reactions in the CPI are carried out in the liquid phase. After reaction the product has to be separated from unreacted materials, by-products, and reaction medium (if appropriate). Quite often two phases occur, mostly a water phase and an organic phase. Assuming water and organic solvent the partitioning between the two phases can be calculated if the water solubility and solubility in the organic phase are known. Otherwise the octanol-water partition coefficient may be used as an approximation. Sometimes, reactions are carried out in emulsions or an emulsion layer is formed. After completion of the reaction the emulsion has to be broken.

However, not just vapour pressure and water solubility are important for the emission, a lot depends upon specific process conditions, type of process, and the equipment used (section "Process step, process conditions, and type of equipment").

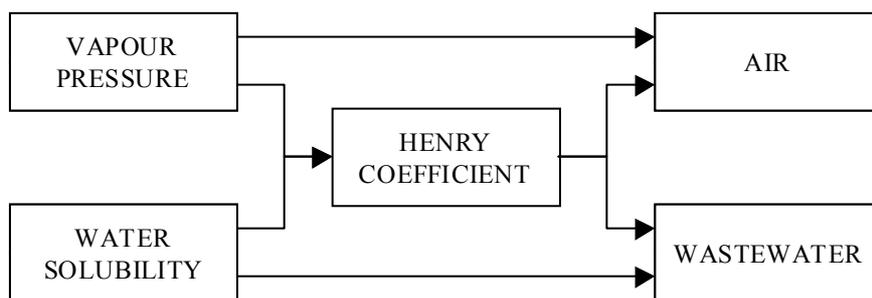


Figure 6.5 Overview of the main physico-chemical properties that (may) influence emission to air and wastewater

6.3 Process step, process conditions, and type of equipment

The reactor in which the chemical reaction is carried out occupies a central position in the chemical process. Additional process steps involve only physical treatment of the material streams such as separation (filtration, distillation) and conveyance.

The temperature at which reactions are carried out may strongly influence the air emissions for substances that have relatively high vapour pressures and if the vapour pressure increases sharply with the elevation of temperature. If one of the reactants and/or the desired reaction product is susceptible to oxidation a continuous nitrogen stream may be led through the reactor, giving rise to evaporation of substances involved. Also the duration of the process will have an influence.

After the reaction the way the synthesised compound is isolated and purified will strongly influence emissions to water and air. Water-solvent and solvent-water extractions have wastewater emissions. During distillation air emissions may occur, and if water-ring pumps are used for vacuum distillation transfer from air to the water may occur in the ring pump system.

The effects of process conditions are interrelated with the equipment used and the type of process. Also the resulting reaction mixture may constrain the next operation to be carried out and the equipment to be used. For example, two liquid layers may occur after reaction, usually a water layer and an organic layer, which have to be separated. Often a third layer – emulsion layer – remains between the water phase and the organic phase. The design of the apparatus and the accuracy of operation determine the losses at separation. Separation of solvent, the chemical synthesised, by-products, and other possible compounds may be achieved by distillation (under atmospheric conditions or under diminished pressure). The design of the condenser, vacuum pump, etc., influences the emissions. It is also possible that compounds are separated by filtration or centrifugation, where filtration may take place under reduced pressure.

Reactors operating at atmospheric pressure may have relatively large open surfaces during a certain period during the reaction time. Sometimes a nitrogen atmosphere is applied during the reaction so that the reactor is effectively closed; feeding of compounds to the reactor then takes place via sluices.

There are reactors of all kinds and sizes. The way they function and are operated will influence the emissions. Appendix 2 presents an overview of reactor types found in the CPI (Henkel, 2001). Henkel (2001) presents an extensive overview of all reactor types with their features and examples of important industrial applications. Also the equipment used for other process steps is of varied size and design.

6.4 Series of subsequent process steps

Depending on the type of reaction, the process steps needed, the reactants, processing aids used, reaction media, etc., a series of process steps may be needed in chemical synthesis. The process steps of interest are (Ros et al., 1990):

- chemical reaction
- extraction
- distillation
- filtration
- centrifugation
- drying
- storage

A production process of a substance usually includes a number of these process steps in a certain order. Figure 6.6 presents a fictitious example of a series of process steps in the production of a substance. The example contains five substances with specific functions and a series of process steps for the production of the chemical compound and the treatment of several side streams. A distinction has been made between the substance produced, two solvents applied, the intermediate used, a catalyst and a processing aid used. This has been done to show the possible differences in process steps of interest for emissions for different use categories of chemicals involved in the production process. It should be noted that depending on the function of the substances involved and the process steps considered also different stages of the life cycle might occur. For the substance produced the stage of the life cycle is production. For the substances applied the stage of the life cycle industrial application applies. Furthermore, for solvents and catalyst the stage recycling is also relevant in this example.

Below the substances involved in the fictitious example are specified with their description, use category and stages of the life cycle:

<u>Substance</u>	<u>Use category</u>	<u>Stage(s) of the life cycle</u>
Product P	<i>not applicable</i>	Production
Intermediate I	33 (intermediate)	Industrial application, Waste treatment
Reaction medium S1	48 (solvents)	Industrial application, Recycling, Waste treatment
Recrystallisation solvent S2	48 (solvents)	Industrial application, Waste treatment
Catalyst C	43 (process regulator)	Industrial application, Recycling
Initiator A	43 (process regulator)	Industrial application

The following assumptions have been made with regard to the physico-chemical properties of the substances:

- P** Low solubility in water, high solubility in S1, low solubility at low temperatures, and good solubility at elevated temperature in S2.
- I** Good solubility in S1 and good water solubility, rather high vapour pressure at elevated temperature
- S1** Low boiling point (high vapour pressure at ambient temperature)
- S2** High boiling point (low vapour pressure at ambient temperature)
- C** Solid (insoluble in water and solvents)
- A** Rather low solubility in S1 (but sufficient for the amount needed in the reaction mixture), very high water solubility

The process can be split in the following process steps:

1. Storage of the starting materials and processing aids (See remark 1)
2. Filling of reactor and reaction taking several hours
3. Filtering off C (C to step 9)
4. Extraction of the filtered mixture (present after reaction) with water and separation of the two liquid layers (to remove A and probably other water soluble contaminants such as by-products)
5. Distillation of the mixture to remove S1 (S1 to step 11)
6. Recrystallisation of raw P from S2
7. Filtration to obtain the purified P; S2 to step 12 (See remark 2)
8. Drying of P (P to next stage of the life cycle)
9. Washing of C
10. Drying of C
11. Fractionation (distillation) to purify S1 (removal of certain by-products and probably remains of D); S1 to storage and residue to step 10
12. Incineration of distillation residue and S2
13. Wastewater treatment in an STP (See remark 3)

The following remarks are made:

1. The emissions to air and water have not been depicted in the figure to avoid confusion; only the streams of the substances are presented (thick lines main flow, thin lines minor flow). For example, the minor flow of S2 to the drying process step of the purified product P is emitted completely to the air (unless an end-of-pipe technique is applied). Also the releases from storage (mainly for organic liquids) due to breathing and transfer have not been represented.
2. Normally, a solvent like S2 in the example will go to a distillation step to recover the solvent for recycling; this has not been done in this – arbitrary – example (e.g., because the by-products cannot be separated from the solvent). The flows of by-products from step 2 on have not been presented to maintain overview.
3. Wastewater treatment may take place in a POTW (Publicly Owned Treatment Works) or a STP (municipal sewage treatment plant). All wastewater streams from a chemical plant are sent there (including water used for cleaning apparatus and hence possibly containing the substances involved in the process).

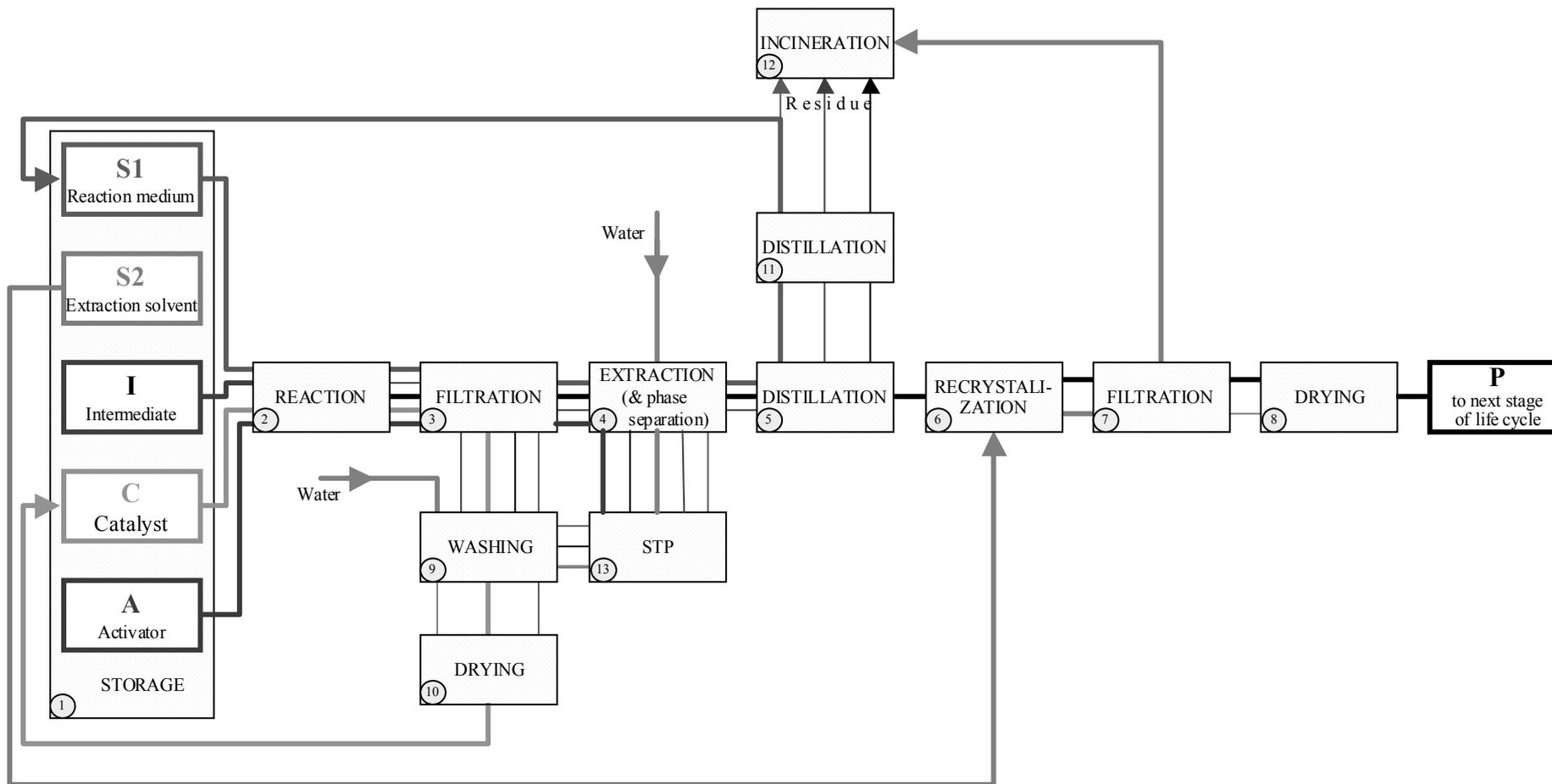


Figure 6.6 Example of a series of process steps in the chemical synthesis, isolation and purification of compound “P” and the flows of the substances involved in reaction and purification (Key of different line colours and thicknesses)

7 CHEMICAL RELEASE ESTIMATION

After identifying the important factors, which influence the release of a substance into the environment in Chapter 6, the application of release quantification methods will be discussed. These methods may provide useful information and data for the development of Emission Scenario Documents for the Chemical Process industry.

7.1 Emission sources

The chemical production process roughly consists of unit processes in which raw materials are converted into the desired products using chemical reactions and unit operations, bringing about physical changes to separate the product from other reaction components. Unit processes are carried out in reactors, of which there is a large range of different types and designs. Frequently applied unit processes (chemical reactions) in the CPI are: oxidation, halogenation, hydrogenation, esterification, sulphonation, hydrolysis, condensation etc. Unit operations (physical operations) in the CPI are for instance distillation, scrubbing, drying, filtration, extraction and absorption. Unit processes and unit operations together are categorised as process units. Within the CPI there is also a comprehensive infrastructure that interconnects the units. This infrastructure consists of pipelines and equipment like pumps, valves etc.

Releases include any spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment of any chemical or chemical mixture. The term “environment” includes water, air, and land, the three media to which release may occur (Allen and Shonnard, 2002).

As already discussed in Chapter 6 releases may be influenced by various factors, like the number and types of process steps and type of reaction, but also the processing aids and reaction media used. Process conditions and substance properties also play an important role in the way and to what extent a substance is released to the environment.

Some emission sources that can be identified within the CPI and these include:

- fugitive releases (including leaks)
- point sources (venting of equipment and through incomplete separation)
- residuals from (transport) containers (drums, tank trucks, rail cars)
- equipment cleaning

Fugitive emissions occur from sources in many places within the process. They include leaks from valves, compressors seals, pump seals, pressure relieve valves, flanges and other connections, open-ended lines and sampling connections, but also building ventilation systems and any other non-point sources.

Important point sources are those generally originating from unit operations like distillation columns, strippers, absorption columns, reactors, condensers and dryers. Point source releases also include air pollution control equipment and storage tanks. Emission occurs through vents, stacks, ducts and pipes. Material may also be lost through cleaning from various types of vessels containing remnants of chemicals including process equipment.

Chemical compounds can be discharged into air, water and soil. Emissions to air can be classified as direct (primary) and indirect (secondary) emissions. Primary emissions originate directly from the production process, like process unit emissions and fugitive equipment releases. Secondary emissions are not directly related to the production process of concern. In many processes for instance heating of process streams is required. Emissions resulting from these heating processes like combustion of fossil fuels in boilers are categorised under indirect emissions. Common pollutants released during combustion of fossil fuels are nitrogen oxides, sulphur dioxide, particulate matter and volatile organic carbons. Extensive sources of emission factors are available for a wide variety of combustion processes and fuels EPA (1995d), EA (2003) and EEA (2001). These emissions however are not relevant for the development of an ESD for the CPI and the focus is primarily on direct emissions.

There are also many potential sources for discharge into surface waters. This may be either the discharge of liquid (aqueous) process streams directly into surface water bodies or through treating waste streams in sewage water treatment plants. Emission to water can also be caused by storm-water run-off from hard surfaces. Common waste streams, which can be identified are those resulting from cleaning operations, liquid (aqueous) wastes from unit operations like scrubbers and decanters, reaction water, water as a reaction product, process water from washing (intermediate) products or even traces of water settled at the bottom of storage tanks. Recycling can be an alternative route to deal with process waste streams and may be beneficial from both an economical and environmental viewpoint. Process waste may also be removed through dumping into landfills. Chemicals may also be released to soil via spills or leaks. Other potential release sources to soil may be holding, settling and storage lagoons, pits and ponds depending on whether there is additional treatment of collected waste (temporary storage) or the reservoirs are intended as permanent waste depots.

7.2 Emission calculation

There are several approaches for estimating emissions. Release figures may be based on measurements or may be modelled based on engineering calculations or by applying average emission factors. The purpose of this document though is to identify possible sources and useful data. ESDs ought to be used when there are no measured or reported emission data available and should provide clear and straightforward emission calculation procedures. Therefore the attention is on modelling emissions based on average emission factors and engineering calculations.

The section “Emission factors” focuses on emission factors for mixtures of volatile compounds (VOCs) related to unit operations and specific equipment (e.g., valves, flanges). The section “Engineering calculations” describes modelling possibilities using engineering calculations – process units, process conditions, and physico-chemical properties – for mixtures of VOCs and solvents applied in the CPI. The emissions of other substances applied in the CPI and substances synthesised and/or converted are discussed in the sections “Other substances applied in the CPI” and “End products and intermediates”, respectively.

7.2.1 Emission factors

Air

The US-EPA (EPA, 1995c and EIIP, 1996) has compiled a set of average emission factors for equipment leaks to be used in combination with unit-specific data that are relatively easy to obtain. These emission factors (Table 7.2) were developed for refineries and gas and oil production, marketing terminals and process units in the synthetic organic chemical manufacturing industry (SOCMI), the latter being the most relevant. The emission factors refer to the atmospheric releases.

Data on emissions from a variety of process units in the CPI are available in several databases of which the most recent and comprehensive is the Factor Information Retrieval (FIRE) database. The FIRE database contains the emission factors for hazardous substances, which are documented in Locating and Estimating Air Emissions from Sources (L&E) reports. Emission factors are given for unit-operations like distillation and devices like scrubbers, decanters etc. In the L&E reports abated and unabated emission factors are distinguished where applicable.

Additional release estimation approaches for unit operations such as condensers, dust collectors, separators etc. can be found in EPA (1991), which contains standard methods and models for assessing workplace releases and exposures in the Chemical Engineering Branch.

The average emission factors for process units as presented in Table 7.1 are based on data from the L&E database (Allen and Shonnard, 2002). The emission factors can be used to estimate Total Organic Carbon releases to the atmosphere. The unit specific data, which are needed to calculate emissions include: number and type of components (reactors, stripper, valve, connector, etc.), the service each component is in (gas, light liquid or heavy liquid), TOC concentration of the stream (and VOC or substance concentration if speciation is needed), the time period each component was in that service or the throughput.

The average emission factors for estimating the TOC emissions from the CPI (SOCMI) equipment (both point and fugitive sources) are presented in Tables 7.1 and 7.2.

To estimate emissions using the average emission factor approach, the concentration of TOC within the stream is needed because equipment with higher TOC tends to have higher TOC emission rates. In the risk assessment of substances it is necessary to estimate emissions of a specific (volatile) organic compound (VOC) in the mixture being processed, this is also addressed below.

Table 7.1 Average emission factors for unit operations within the CPI

Process unit	Emission factor ($\text{kg}_{\text{TOC}} \cdot \text{tonne}_{\text{throughput}}^{-1}$)
Reactor vents	1.50
Distillation column vents	0.70
Absorber units	2.20
Strippers	0.20
Sumps/decanters	0.02
Dryers	0.70
Cooling towers	0.10

The emission rate for TOC from process units can be calculated using following equation:

$$E_{i,j} = Q_{\text{stream}_i} \cdot F_{\text{toc}_i} \cdot F_{\text{avg}_j} \quad (1)$$

where:

$E_{i,j}$ = emission rate for all equipment of type j in stream i ($\text{kg} \cdot \text{hr}^{-1}$)

Q_{stream_i} = mass flow rate of stream i ($\text{kg} \cdot \text{hr}^{-1}$)

F_{toc_i} = weight fraction of TOC in the stream or process unit (-)

F_{avg_j} = average emission factor for the process unit type j ($\text{kg}_{\text{TOC}} \cdot \text{tonne}_{\text{throughput}}^{-1}$)

The total emission rate ($\text{kg}\cdot\text{hr}^{-1}$) for all equipment in stream i can be calculated according to the equation:

$$E_i = \sum_j Q_{stream_i} \cdot Ftoc_i \cdot Favg_j \quad (2)$$

The total emission from process units ($\text{kg}\cdot\text{hr}^{-1}$) equals:

$$Estack = \sum_i E_i \cdot T_{emission} \quad (3)$$

where:

$Estack$ = total annual emissions from point sources (unit operations) ($\text{kg}\cdot\text{yr}^{-1}$)

$T_{emission}$ = Operation time of the facility ($\text{hr}\cdot\text{yr}^{-1}$)

Table 7.2 Average emission factors for estimating fugitive emissions

Source	Service	Emission factor ($\text{kg}_{\text{TOC}}\cdot\text{hr}^{-1}\cdot\text{source}^{-1}$)
Valves	Gas	0.00597
	Light liquid	0.00403
	Heavy liquid	0.00023
Pump seals	Light liquid	0.01990
	Heavy liquid	0.00862
Compressor seals	Gas	0.22800
Pressure-relief valves	Gas	0.10400
	Liquid	0.00700
Flanges and other connections	All	0.00183
Open-ended lines	All	0.00170
Sampling connections	All	0.01500

The following equations are used to calculate the fugitive emissions of TOC:

$$E_{i,j} = Favg_{i,j} \cdot Ftoc_i \cdot N_{i,j} \quad (4)$$

where:

$E_{i,j}$ = emission of TOC from all equipment in the stream i of a given equipment type j ($\text{kg}\cdot\text{hr}^{-1}$)

$Favg_{i,j}$ = average emission factor ($\text{kg}_{\text{TOC}}\cdot\text{hr}^{-1}\cdot\text{source}^{-1}$) for given equipment type j and stream i

$Ftoc_i$ = fraction of total organic carbon in the stream i (-)

$N_{i,j}$ = number of pieces of equipment of type j in stream i (source)

The total emission rate from all equipment in stream i is given through the next equation:

$$E_i = Ftoc_i \cdot \sum_j Favg_{i,j} \cdot N_{i,j} = \sum_j E_{i,j} \quad (5)$$

where:

E_i = emission rate from all equipment in the stream i ($\text{kg}\cdot\text{hr}^{-1}$)

The total amount of fugitive emissions (E_{fug}) is calculated with the following equation, which adds the fugitive emissions from the various streams with a different TOC composition and physical state and accounts for the operation time the equipment is in:

$$E_{fug} = \sum_i E_i \cdot T_{emission} \quad (6)$$

where:

E_{fug} = Annual fugitive emission of TOC ($\text{kg}\cdot\text{yr}^{-1}$)

$T_{emission}$ = Operation time of the facility ($\text{hr}\cdot\text{yr}^{-1}$)

The following equation is used to speciate emissions, i.e. release estimation for a specific compound:

$$E_{fug_{x,i}} \text{ or } E_{stack_{x,i}} = E_{fug_i} \text{ or } E_{stack_i} \cdot \frac{F_{x,i}}{FTOC_i} \quad (7)$$

where:

$E_{fug_{x,i}}$: Fugitive emission of compound x from all equipment in stream i

$E_{stack_{x,i}}$: Emission of organic compound x from unit operations in stream i

E_{fug_i} : Fugitive emission of TOC for all equipment in stream i

E_{stack_i} : Emissions of TOC from unit operations in stream i

$F_{x,i}$: Fraction of organic compound x in stream i

$FTOC_i$: TOC concentration in stream i

Applying equation (7) above assumes that the fraction of the chemicals in the mixture of a specific process stream equals the fraction of the chemicals in the leaking material. In general, this assumption should be accurate for single-phase gaseous or liquid streams containing constituents with a similar volatility. This assumption may not always be correct, for instance for a liquid mixture consisting of compounds with deviating volatilities. This depends on the physical mechanism of how the leakage occurs. The released vapour may contain relatively more of the more volatile constituents when it is “flashed” (vaporises) from the equipment. On the other hand, if the liquid leaks from the equipment and subsequently vaporises, the assumption is valid. For mixtures with constituents having varying vapour pressures the composition of the released vapour mixture can be based on the partial vapour pressure of each substance as will be elaborated next.

To be applicable for ESDs the emissions of specific compounds have to be calculated. Therefore the emission factors for TOC have to be converted to an emission factor for the specific compound of concern. There is a simple method proposed by EPA (1995c), which simply uses the weight fraction of the chemical in the process stream. A more realistic method is to deal with the composition and the temperature of the process stream and physical-chemical properties of the substance.

By applying the temperature corrected vapour pressure and the concentration in the stream, the partial vapour pressure can be calculated using Raoult’s Law. From this the vapour mass fraction of the substance of concern can be estimated.

The partial vapour pressure is calculated according to Raoult’s law:

$$VP_{part_x} = Fmol_x \cdot VP_x \quad (8)$$

where:

- VP_{part_x} = Partial vapour pressure of substance x (Pa)
 $Fmol_x$ = Mole fraction of substance x in solution or mixture (-)
 VP_x = Vapour pressure of substance x (Pa)

The mole fraction of substance x in a mixture is estimated from the next equation:

$$Fmol_x = \frac{Nmoles_x}{Nmoles_T} \quad (9)$$

where:

- $Fmol_x$ = Mole fraction of substance x (-)
 $Nmoles_x$ = Number of moles of substance x (-)
 $Nmoles_T$ = Total number of moles (-)

The vapour pressure of the solution or mixture is simply the sum of the partial vapour pressures (of y substances):

$$VP_T = \sum_y VP_y \quad (10)$$

where:

- VP_y = Partial vapour pressures of y individual substances (Pa)
 VP_T = Vapour pressure of the mixture (Pa)

The vapour fraction of substance x is calculated as follows:

$$Fvap_x = \frac{VP_x}{VP_T} \quad (11)$$

where:

- $Fvap_x$ = Vapour fraction of substance x (-)
 VP_x = Partial vapour pressure of substance x (Pa)
 VP_T = Vapour pressure of the mixture (Pa)

The overall molecular weight of the vapour is calculated from the next equation:

$$MOLW_{vap} = \sum Fvap_x \cdot MOLW_x \quad (12)$$

where:

- $MOLW_{vap}$ = Molecular weight of the vapour ($g \cdot mol^{-1}$)
 $Fvap_x$ = Vapour fraction of substance x (-)
 $MOLW_x$ = Molecular weight of substance x ($g \cdot mol^{-1}$)

The mass fraction of species x in the vapour is:

$$F_{mass-vap_x} = \frac{F_{vap_x} \cdot MOLW_x}{MOLW_{vap}} \quad (13)$$

where:

$F_{mass-vap_x}$ = Mass fraction of species x in the vapour (-)

$MOLW_{vap}$ = Molecular weight of the vapour ($g \cdot mol^{-1}$)

F_{vap_x} = Vapour fraction of substance x (-)

$MOLW_x$ = Molecular weight of substance x ($g \cdot mol^{-1}$)

Water

Release of a chemical through cleaning of drums, tanks and equipment depends on many factors. The potential loss is determined by the residual amount that remains in the equipment prior to cleaning. The quantity depends for instance on the type and capacity of the vessel and the method of unloading.

Other factors influencing the amount released through cleaning operations are the type and amount of solvent used, and chemical properties like the solubility in the solvent. Other variables, which are important, are the cleaning schedule and treatment of the waste stream, either disposal (wastewater treatment) or reworking into a new batch (recycling). Liquid waste streams from cleaning operations can be directed directly to surface water or a sewage treatment plant. Disposing of liquid wastes through landfilling or incineration is another possibility.

Table 7.3 presents factors for estimating residual amounts in vessels prior to cleaning. The factors are split according to the unloading method, vessel type and material properties (viscosity).

Table 7.3 Residual quantities in vessels as a weight percentage (Fresid•102) of the vessel capacity (Allen and Shonnard, 2002)¹⁾

Unloading method	Vessel type	Surfactant solution	Water	Kerosene	Motor oil	Viscosity > 200 cp
Pumping	Steel drum	3.060	2.290	2.480	2.060	3.0
Pumping	Plastic drum	NA	3.280	2.610	2.300	4.0
Pouring	Bung-top steel drum	0.485	0.403	0.404	0.737	1.0
Pouring	Open-top steel drum	0.089	0.034	0.054	0.350	0.5
Gravity drain	Slope-bottom steel tank	0.048	0.019	0.033	0.111	0.1
Gravity drain	Dish-bottom steel tank	0.058	0.034	0.038	0.161	0.2
Gravity drain	Dish-bottom glass-lined tank	0.040	0.033	0.040	0.127	0.2

¹⁾ original source PEI (1986)

Emission rates (E_{stp}/E_{disp}) can be calculated according to the following equation taking other important factors like cleaning frequency and recycling rate into account:

$$E_{stp} \text{ or } E_{disp} = Q_{vessel} \cdot RHOMaterial \cdot Fresid \cdot (1 - Frecycle) \cdot Nclean \quad (14)$$

where:

E_{stp} = Amount emitted to sewage treatment plant ($kg \cdot yr^{-1}$)

E_{disp} = Amount disposed off ($kg \cdot yr^{-1}$)

Q_{vessel} = Vessel capacity (m^3)

$RHOMaterial$ = Density of material contained in the vessel ($kg \cdot m^{-3}$)

- Fresid = Fraction of the vessel capacity remaining in the vessel after unloading
- Frecycle = Recycling rate (No reworking in next batch Frecycle = 0, otherwise Frecycle = 1)
- Nclean = Yearly number of cleaning events (yr⁻¹)

There is little quantitative information on releases from process operations to waste water. The information is generally available on the plant level. As mentioned before there are many potential sources of liquid effluents that can be identified, many of them are discussed in IPPC (2002).

Aqueous (liquid) waste streams originate from reactors as reaction water (e.g., reaction medium in chlorination with hydrochloric acid or inert diluent in steam cracking), water as a reaction product (condensation, hydrogenation, aldolysation and esterification reactions), water as a reactant (hydrolysis, decoking water in dehydrogenation). Aqueous waste streams are actually generated from physical separation processes (unit operations) after reaction or when water is used as washing liquid or solvent.

Table 7.4 lists sources of process water and other liquid effluents generated during unit operations. As discussed before, aqueous waste streams may also result from cleaning operations and surface run-off.

Table 7.4 Aqueous (waste) streams from unit operations

Process unit	Effluent specification
distillation	aqueous condensate aqueous bottom residues
extraction	water used as a solvent
reactor	reaction water (reaction medium) water as reaction product
absorption	water used as an absorbent
extraction	aqueous bottom residues or top condensates
solids-liquid separation: centrifuging filtration sedimentation, drying and crystallisation	water as an extraction solvent / intermediate layer water as separated liquid phase, wash water
adsorption	adsorbed water (removed)/ treated water (trace contamination)
condensation	water as condensed product

Crookes (2002) produced a document about the mineral oil and fuel industry as a first initiative for the development of an ESD for this industrial category. This document reports some emission factors for wastewater. These factors reflect the release of total organic carbon, which means that they are not suitable for the development of substance specific emission scenario documents in the first place. Additionally, no

specification is given with regard to release sources (unit operations) and the function of substances that end-up in the effluent.

7.2.2 Engineering calculations

The composition of process streams can be calculated with advanced software programs used in the design of chemical processes. These programs require very specific skills and are quite elaborate. As a consequence these methods are not very efficient estimation methods and go beyond the scope of developing emission scenario documents although they might provide very useful information. Also process design software often does not account for all of the releases from a process (Allen and Shonnard, 2002). Simple engineering calculations provide a way of calculating emissions from sources for which no average emission factors are available. Such releases occur at point sources like storage tanks (working and breathing losses) and during the loading of transport tanks. Fugitive sources are for example evaporative losses from static pools like open vats, solvent dip tanks, cleaning and maintenance activities or unintentional spills.

Storage tanks

In Chapter 6 it is suggested to develop a separate ESD for estimating the emissions from storage tanks and bulk transport loading operations. The emission models for these sources will therefore not be discussed in this section. Some references to these methods will be given though. Emission estimation models for the bulk transport loading operations of liquids are provided by the US EPA AP-42 documents (EPA, 1995e). Equations for estimating emissions from various types of storage tanks have been formulated by the US EPA. TANKS is the computerised software program developed by the US-EPA that performs all the calculations (EPA, 1999).

Process units, emission of solvents applied in the CPI

Chapter eight of Volume three of the emission inventory improvement program (EIIP, 2002) provides models for estimating air emissions from paint and ink manufacturing facilities. With these models releases of volatile organic compounds from spills and through surface evaporation and heat-up losses due to the expansion of gases during heat-up can be estimated. Many of these processes and calculations show similarities with the releases of solvents applied in the CPI (pharmaceutical industry), which will be elaborated next.

The RIVM carried out a target group study for the Dutch pharmaceutical industry (Ros and van der Poel, 1989; Ros et al., 1990). The report describes the releases from the pharmaceutical industry with emphasis on moderately and poorly water soluble solvents. The process losses in practice have been related to the throughput of the solvents. The throughput has been defined as the quantity of solvent that has been stocked (bought new product) + the quantity that becomes available after the processes carried out and is reused again directly + the quantity that is recycled after purification (distillation) of the polluted solvent coming from the processes carried out. This is elucidated in Figure 7.1. It appeared that losses varied from 1 up to more than 20%, which was caused to a great extent by the multipurpose character of the various plants.

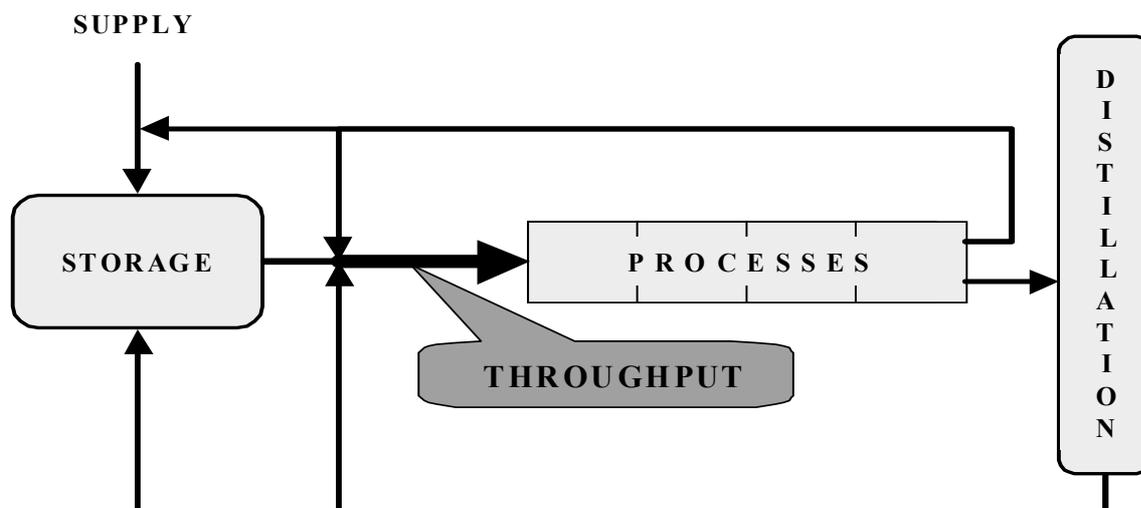


Figure 7.1 Scheme of solvent flows (emissions excluded) in the production processes of chemicals

A computer model has been developed to quantify the main causes of the process losses to both air and wastewater. For emissions to the air the main sources are distillations, displacements, evaporation from open systems or to a nitrogen atmosphere, and drying of the products. Discharges with wastewater occur at the let down of saturated water layers after extractions, filtration or centrifugation. Vacuum pumps can transfer solvent present in the gas phase largely to water (water ring pumps).

The main equations applied in the computer model, which may be of importance for an ESD describing process losses of solvents applied in the CPI are presented below for the various processes and causes of emission. It should be noted that the computer model distinguishes various “emission routes” with a certain inaccuracy, which results in a range for the outcome. Only at the start of the series of process steps solvent can be put in. The model calculates the losses per process step and remaining solvent quantity going to the next process step. During filtration or centrifugation the remaining quantity of the solvent is important.

If the volume is not put in explicitly the reactor characteristics are calculated. In the calculations the solvent input – if desired including water input – is employed as a starting point:

$$V_{reactor} = 4 \cdot (10 \cdot V_{solvent})^{1/3} \cdot (V_{solvent} + V_{water}) \quad (15)$$

$$AREAsolv/air = \left(\frac{V_{reactor}}{10} \right)^{1/3} \quad (16)$$

where:

$V_{reactor}$ = Reactor volume (m³)

$V_{solvent}$ = Volume of solvent per batch (m³)

V_{water} = Volume of water per batch (m³)

$AREAsolv/air$ = Surface solvent/air (m²)

The model distinguishes the following types of process emissions:

Displacement

The displacement loss is determined as the product of the volume of the liquid transferred and the vapour pressure of the solvent at the temperature in the reactor (or storage). It is assumed that the air displaced at the first time the liquid is pumped into the reactor is not saturated completely. The inaccuracy – expressed by the minimum-maximum – becomes less at an increasing number of batches.

minimum:

$$E_{rate_air} = (0.5 \cdot \frac{V_{solvent}}{V_{reactor}} + N_{batch} - 1) \cdot C_{solvent_sat-air} \cdot (V_{water} + V_{solvent}) \quad (17)$$

maximum:

$$E_{rate_air} = (0.9 \cdot \frac{(V_{water} + V_{solvent})}{V_{reactor}} + N_{batch} - 1) \cdot C_{solvent_sat-air} \cdot (V_{water} + V_{solvent}) \quad (18)$$

where:

- E_{rate_air} = Process emission per series of batch before opening (m³)
- $V_{reactor}$ = Reactor volume (m³)
- $V_{solvent}$ = Volume of solvent per batch (m³)
- V_{water} = Volume of water per batch (m³)
- N_{batch} = Number of batches before opening/cleaning of reactor (-)
- $C_{solvent_sat-air}$ = Concentration (saturated) of solvent in air/gas (kg.m⁻³) at the reactor temperature

Breathing

In case the temperature in a reactor is higher than in the previous reactor a breathing loss based on the difference of the vapour pressures at the two temperatures and the empty reactor volume is assumed:

minimum:

$$E_{rate_air} = 0.9 \cdot N_{batch} \cdot (V_{reactor} - V_{water} - V_{solvent}) \cdot \frac{VP_{T2}}{VP_{T1}} \cdot C_{solvent_sat-air} \quad (19)$$

maximum:

$$E_{rate_air} = 1.08 \cdot N_{batch} \cdot (V_{reactor} - V_{water} - V_{solvent}) \cdot \frac{VP_{T2}}{VP_{T1}} \cdot C_{solvent_sat-air} \quad (20)$$

where:

- E_{rate_air} = Process emission per series of batch before opening (m³)
- $V_{reactor}$ = Reactor volume (m³)
- $V_{solvent}$ = Volume of solvent per batch (m³)
- V_{water} = Volume of water per batch (m³)
- N_{batch} = Number of batches before opening/cleaning of reactor (-)
- $C_{solvent_sat-air}$ = Concentration (saturated) of solvent in air/gas (kg.m⁻³)
- VP_{T2} = Vapour pressure of solvent at the higher temperature (Pa)
- VP_{T1} = Vapour pressure of solvent at the lower temperature (Pa)

Remainders/Leaking/Spills

Remainders are firstly vapours in the reactor, which are released to the air at opening. The quantities are based on the reactor temperature and the reactor volume (with the reactor volume minus half the liquid input as a minimum):

minimum:

$$Erate_{air} = (V_{reactor} - 0.5 \cdot (V_{water} + V_{solvent})) \cdot C_{solvent_{sat-air}} \quad (21)$$

maximum:

$$Erate_{air} = V_{reactor} \cdot C_{solvent_{sat-air}} \quad (22)$$

where:

$Erate_{air}$ = Process emission per series of batch before opening (m^3)

$V_{reactor}$ = Reactor volume (m^3)

$V_{solvent}$ = Volume of solvent per batch (m^3)

V_{water} = Volume of water per batch (m^3)

$C_{solvent_{sat-air}}$ = Concentration (saturated) of solvent in air/gas ($kg \cdot m^{-3}$)

The remainder is assumed to be present in two reactors, using the distillation temperature in one reactor and ambient temperature in the other.

At the end of the process at opening the reactor also a remainder of liquid solvent is assumed. If also water was present it is determined – on account of the densities – which was the bottom layer. The remainder of solvent or water with solvent in it is calculated as:

minimum:

$$Vrem = 0.25 \cdot \left(\frac{Visc_{solvent}}{Visc_{water}} \right) \cdot V_{solvent}^{-1/3} \quad (23)$$

maximum:

$$Vrem = \left(\frac{Visc_{solvent}}{Visc_{water}} \right) \cdot V_{solvent}^{-1/3} \quad (24)$$

where:

$Vrem$ = Remainder of the solvent (m^3)

$V_{solvent}$ = Volume of solvent per batch (m^3)

$Visc_{solvent}$ = Viscosity of the solvent ($N \cdot s \cdot m^{-2}$)

$Visc_{water}$ = Viscosity of water ($N \cdot s \cdot m^{-2}$)

After cleaning with water the remainder is discharged to the wastewater (STP). After cleaning with solvent it is assumed that it is removed with other hazardous waste without any evaporation to the air. Leaking is included.

Cleaning with water:

$$Erate_{air} = Vrem \quad (25)$$

Cleaning with solvent:

$$E_{rate_air} = 0 \quad (26)$$

Evaporation

At (temporarily) open surfaces evaporation of the liquid to the gas phase is included. The losses are calculated with the following equations:

$$k l g_{solvent} = 2 \cdot \left(\frac{Kd_{if_air} \cdot WINDSPEED}{(\pi \cdot ARE_{Aliq-air})^{0.5}} \right)^{0.5} \quad (27)$$

minimum:

$$E_{rate_air} = 0.5 \cdot k l g_{solvent} \cdot C_{solvent_sat-air} \cdot ARE_{Aliq-air} \cdot T_{evap} \quad (28)$$

maximum:

$$E_{rate_air} = k l g_{solvent} \cdot C_{solvent_sat-air} \cdot ARE_{Aliq-air} \cdot T_{evap} \quad (29)$$

where:

$kl g_{solvent}$ = Mass transfer coefficient ($m \cdot s^{-1}$)

Kd_{if_air} = Diffusion coefficient in air ($m^2 \cdot s^{-1}$)

WINDSPEED = Gas speed ($m \cdot s^{-1}$)

$ARE_{Aliq-air}$ = Liquid/air surface (m^2)

$C_{solvent_sat-air}$ = Concentration (saturated) of solvent in air/gas ($kg \cdot m^{-3}$)

T_{evap} = Period that evaporation occurs (s)

The gas speed has been set at the air speed in the plant (set at $0.1 m \cdot s^{-1}$).

Process under a nitrogen atmosphere

If a process has to be carried out under a nitrogen atmosphere the vessel [1] may be flushed several times with nitrogen followed by applying an overpressure with the aid of a pump or [2] a stream of nitrogen is passed over the contents. The uptake of solvent in a nitrogen atmosphere should be approached as for evaporation. However, in practice the nitrogen flow rates usually result in near saturation with solvent. So, a saturated nitrogen stream has been assumed. A number of flushes of the empty reactor volume may be used to remove the solvent by suction under vacuum. Because of the distribution at the vacuum pump this has been spread out in time (a quarter of an hour). The nitrogen flow rate has to be entered as a replacement frequency of the empty reactor volume. The possibility of condensation is considered using the temperature for the gas stream.

Overpressure (pump)

minimum:

$$E_{rate_air} = 0.5 \cdot (2 + N_{batch}) \cdot N_{flush} \cdot (V_{reactor} - V_{solvent} - V_{water}) \cdot C_{solvent_sat-air} \quad (30)$$

maximum:

$$E_{rate_air} = (2 + N_{batch}) \cdot N_{flush} \cdot (V_{reactor} - V_{solvent} - V_{water}) \cdot C_{solvent_sat-air} \quad (31)$$

Passing over

minimum:

$$Erate_{air} = 0.9 \cdot Nbatch \cdot Nrepl \cdot (Treact + 1) \cdot (Vreactor - Vsolvent - Vwater) \cdot Csolvent_{sat-air} \quad (32)$$

maximum:

$$Erate_{air} = Nbatch \cdot Nrepl \cdot (Treact + 1) \cdot (Vreactor - Vsolvent - Vwater) \cdot Csolvent_{sat-air} \quad (33)$$

where:

Nbatch = Number of batches (-)

Nflush = Number of flushes (-)

Nrepl = Number of replacements (hr⁻¹)

Treact = Time the nitrogen is passed over (hr)

Vreactor = Reactor volume (m³)

Vsolvent = Volume of solvent per batch (m³)

Vwater = Volume of water per batch (m³)

Csolvent_{sat-air} = Concentration (saturated) of solvent in air/gas (kg.m⁻³) at condenser temperature (outlet)

Discharge after extraction

If the product ends up in the solvent layer discharge of the water layer is assumed. The discharge of any intermediate layers is considered as well. The thickness of the intermediate layer can be input. This leads to the following equations:

minimum:

$$Erate_{water} = 0.95 \cdot Nbatch \cdot Vwater \cdot SOLsolvent_{water} + 0.4 \cdot AREAint-layer \cdot THlayer \cdot RHOsolvent \quad (34)$$

maximum:

$$Erate_{water} = 1.05 \cdot Nbatch \cdot Vwater \cdot SOLsolvent_{water} + 0.6 \cdot AREAint-layer \cdot THlayer \cdot RHOsolvent \quad (35)$$

where:

Nbatch = Number of batches (-)

Vwater = Volume of water per batch (m³)

SOLsolvent = Solubility of solvent in water (kg.m⁻³)

AREAint-layer = Surface of the intermediate layer (m²)

THlayer = Thickness of the intermediate layer (m)

RHOsolvent = Density of the solvent (kg.m⁻³)

Distillation

Losses during distillation are very dependent on the capacity of the condenser, the flow of the vapour, and the difference in temperature. The model assumes a plate condenser with a fixed length and a free to choose width. The vapour flow supplied is determined by the speed of distillation, anticipating a possible irregular input. Therefore, an irregularity factor has been introduced in the model. This irregularity factor indicates the maximum of the vapour flow (maximum flow rate = [1 + irregularity factor] x average flow rate). The stream is then distributed over time as presented in Figure 7.2.

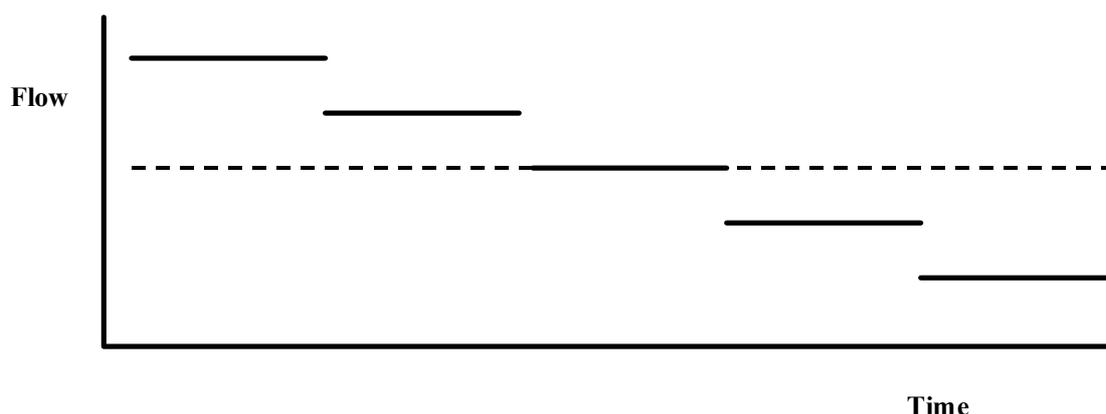


Figure 7.2 Distribution of the vapour flow at distillation over time at distillation (---- average flow rate)

An additional air flow of $1.7 \text{ m}^3 \cdot \text{hr}^{-1}$ (at 100 kPa) is taken into account (based on data of the plants considered in the study). For atmospheric distillation the approximate equations apply:

$$\text{Constant} = 1.2 \cdot 0.94 \cdot \left(\frac{L_{\text{vap}} \cdot \text{RHOSolvent}^2 \cdot \kappa^3 \cdot 9.98}{\text{LENGTH}_{\text{condenser}} \cdot \text{Visc}_{\text{solvent}} \cdot dT} \right)^{0.2} \cdot \text{WIDTH}_{\text{condenser}} \cdot \text{LENGTH}_{\text{condenser}}^{0.75} \cdot \frac{dT}{L_{\text{vap}}} \cdot V_{\text{air}}^{0.5} \quad (36)$$

minimum:

$$\text{Erate}_{\text{air}} = 0.9 \cdot \text{Nbatch} \cdot [\{(V_{\text{vapour}} + V_{\text{air}})^{0.5} - 2/3 \cdot \text{Constant}\}^2 - V_{\text{air}}] \quad (37)$$

maximum:

$$\text{Erate}_{\text{air}} = 1.1 \cdot \text{Nbatch} \cdot [\{(V_{\text{vapour}} + V_{\text{air}})^{0.5} - 2/3 \cdot \text{Constant}\}^2 - V_{\text{air}}] \quad (38)$$

where:

- L_{vap} = Heat of vaporisation ($\text{J} \cdot \text{kg}^{-1}$)
- RHOSolvent = Density of the solvent ($\text{kg} \cdot \text{m}^{-3}$)
- κ = Heat conduction of solvent ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)
- $\text{LENGTH}_{\text{condenser}}$ = Length of condenser (m)
- $\text{Visc}_{\text{solvent}}$ = Viscosity of solvent ($\text{N} \cdot \text{s} \cdot \text{m}^{-2}$)
- dT = Temperature difference in condenser (K)
- $\text{WIDTH}_{\text{condenser}}$ = Width of condenser (m)
- V_{air} = Volume of air (m^3)
- V_{vapour} = Volume of vapour (m^3)
- Nbatch = Number of batches (-)

The same equations are used for vacuum distillation but the outgoing flow is directed to the vacuum pumps. The vacuum pumps are discussed separately (water ring pumps).

Filtration under vacuum

First, the possible discharge of filtrate, if it consists of water (with solvent in it), is considered:

minimum:

$$Erate_{water} = 0.8 \cdot Nbatch \cdot 0.9 \cdot Vwater \cdot SOLsolvent \quad (39)$$

maximum:

$$Erate_{water} = Nbatch \cdot 0.9 \cdot Vwater \cdot SOLsolvent \quad (40)$$

where:

Nbatch = Number of batches (-)

Vwater = Volume of water (m³)

SOLsolvent = Solubility of the solvent in water (kg.m⁻³)

Evaporation from the liquid phase is also considered. A volume of 20 m³ of air leaking in is assumed for a batch size of 200 l at a filter, equalling about 50 m³.hr⁻¹ (at 100 kPa). A correction is carried out for the drop in temperature as a consequence of the heat of vaporisation by using an approximation of the concentration at the average temperature. The air goes to the vacuum pump.

Drying

It is assumed that the total amount of solvent will be released to the air (atmospheric conditions) or to the vacuum pump (under vacuum). So, this emission is dependent on the efficiency of the filtration/centrifugation.

Water ring pumps

For distillation, filtration, and drying vacuum may be chosen for process conditions, for which the use water ring pumps are assumed. It is assumed that the solvent reaching the vacuum pump will be distributed over the water phase and air phase according to the Henry coefficient. The temperature is corrected for the heat of condensation. The water flow rate can be chosen (default 0.6 m³.hr⁻¹). A correction for possible recirculation – resulting in a diminished amount of drain water – may be chosen. The airflow rate is determined by the previous process (e.g., at drying and filtration 50 m³.hr⁻¹, at vacuum distillation 1.7 m³.hr⁻¹). If supersaturation occurs discharge of solvent phase together with water is assumed unless the application of a separator has been chosen.

7.2.3 The role of the substance function in release estimation

For substances other than solvents the applicability of emission factors or engineering calculations based on process conditions and physico-chemical properties will depend on the function and form in which they are applied/used. The various situations that may be met in developing ESDs are described below in line with the use categories list of Table 6.1.

UC 1 Absorbents and adsorbents

Absorption and adsorption processes are applied extensively in the CPI and in petrochemical refineries. Absorption is the uptake of gases by a solvent and adsorption the accumulation of material – consisting of one or more components – on the surface of a solid adsorbent.

So, for absorption solvents, i.e., VOCs, are the absorbents. In ESDs dealing with absorption average emission factors as presented in Table 7.1 may be used. As can be seen from this table the emission factor is rather high at 2.20 kg.tonne⁻¹. It should be noted that absorption equipment generally consists of three vessels (“reactors”) with a pump, fittings and other accessories. Figure 7.3 presents the scheme of an absorption installation with desorption for regeneration (Kriebel, 2000). It should be considered, whether

the emission factor is related to the solvent (absorbent) only or also includes the components to be stripped. As the desorber is a kind of stripper it also should be considered whether the emission factor for absorber units includes the emission factor for strippers as well. It also has to be considered whether elaboration of emission estimation for absorbents has a high priority. The likelihood that newly developed substances will be notified as an absorbent is very low. Many well-known absorbents (e.g., methanol, and ethanolamines) will belong to HPVCs for which probably site-specific data on emissions will be available. The most important adsorbents are activated carbon, zeolites, silica gel, and aluminium oxide (Mersmann, 2000). Adsorption processes may be carried out batchwise or continuously and adsorbents are usually frequently regenerated by desorption (Mersmann, 2000). The priority for developing emission scenarios for adsorbents is low. New substances to be used as adsorbents are hardly to be expected and the relevance for risk assessment is expected to be low.

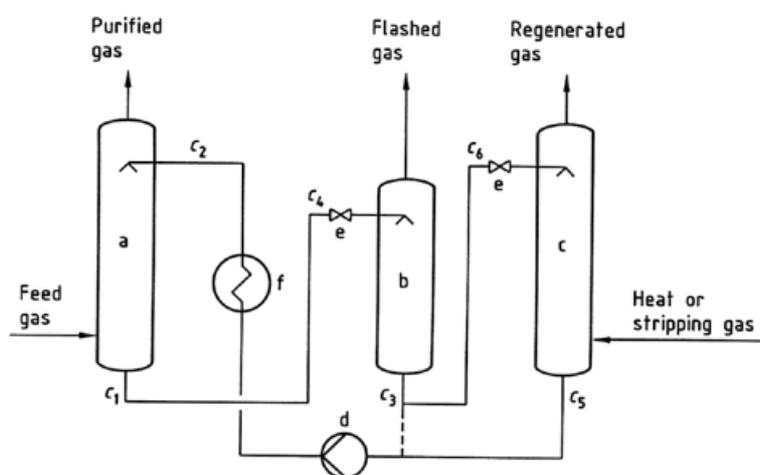


Figure 7.3 Schematic of absorption installation with desorption for regeneration (derived from Kriebel, 2000), where a) Absorber; b) Depressurisation (flash) stage; c) Desorber (regenerator); d) Pump; e) Reducing valve; f) Cooler

UC 9 Cleaning/washing agents and additives

It is not expected that substances will be used for cleaning of equipment in the chemical industry specifically. As in other ESDs the emission factor for substances with this use category will be 1 for wastewater. So, it is not necessary to develop an emission scenario for this use category.

UC 11 Complexing agents

Other function descriptions that meet more or less use category “complexing agents” are chelating agents, sequestering agents and antiprecipitants. The main purpose of the application of complexing agents is to immobilise unwanted chemicals (cations such as metal ions). Complexing agents are found in areas such as cleaning compounds, cosmetics/shampoos, detergent builders, food use, and water treatment. The four types of chelates utilised extensively in industry are (i) the family of ethylenediamine tetraacetic acid products, (ii) phosphonates, (iii) gluconates, and (iv) citric acid.

The application of complexing agents in boiler water is in principle the same as water treatment in other industries. Probably, the emission scenarios likely to be proposed in the ESD will harmonise with emission scenarios for biocides used as preservatives for liquid cooling and processing systems, which are

developed in the framework of EUBEES2 (EU project “Development of environmental emission scenarios for active substances used in biocidal products”, Groshart, 2003). Maybe some defaults used in that ESD could be changed to more representative values for the CPI.

Another application in the CPI that was found is reactive extraction. In reactive extraction the solvent (complexing agent) reacts with the extracted substance during the extraction. The active solvents are usually large, polyfunctional molecules, which are – in most cases – designed to extract specific cations (Blass, 2000). For the extraction of metal ions such as copper and nickel from the aqueous phase rather expensive substances (such as dioximes, hydroxyoximes, quinolines and β -diketones) are widely used (Blass, 2000). Phosphoric, sulfonic, and carboxylic acids are applied as cation exchangers in solution; their metal salts, which are formed, are soluble in most nonpolar solvents and, depending on the pH of the extraction and the pK_a of the acid, the cation will migrate to the organic phase or stay in the water phase (Blass, 2000). Most metal ions that are capable of forming anionic complexes (e.g., Fe, Au, In, and Ga) can be extracted with ethers and thioethers from an aqueous HCl solution (Blass, 2000). Ketones extract the same anionic complexes but in most cases at lower acid concentration. Both types of solvents are not completely insoluble in water. A distillation is needed to remove the dissolved solvent from the water phase (Blass, 2000). Trialkylphosphine oxides, -phosphinates, -phosphonates, and -phosphates most metals of group 3 to group 8 of the periodic system of elements can be extracted (Blass, 2000). Trialkylsulfonium, tetraalkylammonium, and -phosphonium salts are used in the production of Cr, V, Re, Tc, Mo, and W as a solution in a petroleum fraction (Blass, 2000).

In the emulsion polymerisation of styrene-butadiene rubber with the “cold” process the change in oxidation-reduction potential for metal ions on chelation using Fe(II)EDTA is employed commercially (Hart, 2000). Chelating agents are also added to chemical processes to remove traces of iron and other metal ions, which either interfere with the process or must be reduced to meet stringent specifications (Hart, 2000).

In many cases complexing agents are used in the production of metals. As such this process belongs to IC 8 “Metal extraction, refining and processing industry”. In the CPI the application of complexing agents will occur mostly in the water purification of effluents. It should be considered whether a specific ESD on complexing agents used in effluent treatment in the CPI is useful. That applies also to specific applications of complexing agents in combination with certain compounds as catalysts. This is, for example, the case when chelating agents are used in combination with alkylaluminium compounds as effective catalysts in the production of epichlorohydrin elastomers (Threadingham et al., 2000).

UC 16 Dustbinding agents

A search on the Internet did not reveal the application of dustbinding agents in the CPI so far. It is suggested to exclude this use category from the development of emission scenarios unless information on important applications and possible environmental releases become available.

UC 49 Emulsifiers and emulsion promoters

In the CPI emulsifiers are used in many emulsion polymerisations, e.g. for butadiene, chloroprene, styrene, vinyl polymers, ABS, and phenol formaldehyde (Heusch, 2000). Heusch (2000) also refers to the chemical industry for application reaction accelerators, extracting agent additives, and micellar catalysis. No specific data could be retrieved, however.

The application in emulsion polymerisation belongs to industrial category 11 “Polymers industry”. For the applications in the CPI it should be considered whether this use category is significant.

UC 29 Heat transferring agents

To this use category belong also substance with functions described like coolants, heating agents, and refrigerants. Substances used for these functions are applied in closed systems. Under normal operating conditions no releases into the environment occur. Furthermore, such substances are applied in many other industrial activities. It is suggested not to develop an ESD for the CPI for this use category.

UC 33 Intermediates

Intermediates are input in chemical processes in order to produce another substance. Intermediates are discussed together with end products in section “End products and intermediates”.

UC 37 Oxidising agents

Oxidising agents are substances that give up oxygen easily, remove hydrogen from other substances, or accept electrons in chemical reactions, and are used for such purposes (EC, 2003). Together with reducing agents such substances play an important role in the CPI. As they carry out their action – i.e., oxidising – they are transformed in another chemical. For an emission scenario it is important to get clear whether there is a complete conversion or (in some cases or always) just partial conversion. Furthermore, it is important to know in which cases regeneration of the oxidiser is possible and carried out in practice (with related environmental releases).

UC 40 pH-regulating agents

These are substances used to alter or stabilise the hydrogen ion concentration (pH): acids, alkalis, and buffers (EC, 2003). For this goal usually a certain range of – predominantly – high production volume chemicals are used. Alkalis and acids used to create a certain pH during a process in CPI have to be neutralised before discharge into wastewater according to legislation for the protection of the sewerage and STP (installation and micro-organisms). From neutralisation a salt will result, which is outside the scope of the risk assessment of the original acid or alkali. It is not likely that there will be a need for emission scenarios for this group of chemicals applied in the CPI.

UC 43 Process regulators

According to EC (2003) these are substances used to regulate the speed of a (chemical) process. As sub-categories, however, examples are given such as inhibitors, initiators, and cross-linking agents. An inhibitor regulates the speed of a reaction in such way that the reaction stops completely, e.g., a polymerisation process. An initiator is a substance that starts the reaction, which afterwards propagates by itself. An example is a peroxide, giving radicals to start the polymerisation of an unsaturated monomer (ethylene, propylene, styrene, etc.). Initiators and inhibitors usually are transformed in the process and will not be present anymore in the end product. Any remaining fractions may be included in a matrix (in the case of polymerisation processes). Cross-linking agents are used to interconnect (pre)polymers by chemical reaction. Styrene for example, is used as a reactive solvent in cross-linking unsaturated esters (polyester resins). These substances should be characterised as “monomers”. Table 6.1 of Chapter 6 lists a number of functions, which do not really fit the definition, but have some influence on the development of the process.

Within this use category the focus and priority should be catalysts (plus accelerators and activators if they are of importance for the CPI). Catalysts are used throughout the chemical industry in all kinds of processes at all imaginable scales. As stated in Chapter 4 emissions may occur, e.g., at regeneration of spent catalysts. In developing emission scenarios many widely distributed processes should be considered in order to evaluate (new) substances notified for use as catalyst in a certain processes (analogy principle).

UC 37 Reducing agents

Reducing agents are substances to remove oxygen, hydrogenate or, in general act as electron donors in chemical reactions (EC, 2003). As stated for UC 37 “Oxidising agents” such substances play an important role in the CPI and for an emission scenario it is important to get clear if there is a complete conversion or just partial conversion. Also, it is important to know in which cases regeneration of the reducing agent is possible and carried out in practice (with related environmental releases).

UC 50 Surfactants

For such substances the same applies as for UC 9 “Cleaning/washing agents” and additives.

UC 55 Others

This category comprises a lot of very different functions, which are difficult to catch in one ESD or even in a series of ESDs. Some effort should be made to clarify if and how this group could be tackled in a sensible way.

7.2.4 End products and intermediates

For the synthesis of chemicals – where the desired substance is supposed to be assessed – the approach used for VOCs (“solvents”) might be followed if the vapour pressures of the substances are comparable. Otherwise an approach should be investigated where the process description is taken as the basis. It should be possible to obtain data from the notifier as to the (i) type of reaction (e.g., Friedel-Craft) or the description of the reaction and its components and conditions (nitrogen atmosphere, temperature, etc.), (ii) the equipment/apparatus used (type and volume of reactor, reflux, etc.), (iii) way of purification (distillation, recrystallisation) with specifications on equipment (size of apparatus, number of washings/extractions, etc.), and any additional physico-chemical properties that are not present in the base set.

For intermediates also these data on the process where they are converted into another substance should be available. Furthermore data on the fraction that may be expected to remain in the end product should become available. If no remaining fraction is known comparison with data from similar reaction types may be used (derivation of realistic worst-case defaults). For quite a number of reactions rates of conversion are known. It should be noted that this is not just related to the conversion into the desired substance but also to the total conversion of the intermediate.

In a similar way as used for solvents, engineering calculations can be used for emission scenarios. For the elaboration of an ESD for end products and intermediates it will be an enormous amount of effort. An alternative approach might be followed as in the ESD for intermediates in the TGD (EC, 2003) for releases with wastewater. For intermediates and product the use of (conversion) the 90th percentile for some 30 substances is used as an overall emission factor for wastewater. An inquiry to chemical manufacturers on emission factors (releases related to the production volume) for wastewater, air, and hazardous waste should then be carried out. This should be for as many of the substances they produce as possible. Furthermore the manufacturers should supply the accompanying data on the type of reaction/process (reaction type, continuous/batch, multipurpose/dedicated equipment, extraction/purification, etc.), conversion rates, etc. Depending on the details a more specific realistic worst-case 90th percentile for certain classes of reactions/processes for both wastewater and air can be determined. Such a database on emission factors could also be used for another approach to emission estimation where a kind of checklist has to be filled in. A first idea for such a checklist is presented below together with some remarks. Any manufacturer will have a process description, which is usually supplied in a more or less detailed way with the notification. If a notifier does not supply information, worst case choices are made. Production in

dedicated equipment with batch processes or with a continuous process will only usually be carried out for HPVCs. For such production most of the information will be available on emissions because of permits granted by the authorities and, responsible care programs of the manufacturer. Furthermore, for quality requirements, process optimisation programs may be run. Indeed mass balances may even be drawn up for cost calculations. This is not necessarily to be restricted to HPVCs. If such data are supplied by chemical manufacturers a database could be set-up. This database should contain two values for each emission factor, the lower one for dedicated equipment and the higher one for multipurpose equipment. Table 7.5 presents a simplified checklist. Questions on process steps should also comprise specific data, e.g., volume of equipment, ratio solvent:water, solvent used at extraction and solubility of the substance in this solvent, etc. In Table 7.6 a more extended calculation schematic has been presented. It should be noted that for this report gas phase reactions have not been considered for batch production processes.

For intermediates the emissions during conversion have to be considered as well. If this processing takes place at the same site the emissions of production and processing (i.e., industrial use) have to be summed. For releases from conversion the process characteristics should be known preferably in order to perform emission estimation as for the production stage. How to cope with this problem has to be worked out in an ESD.

For industrial use of an intermediate and for each of the substances (“end products”) manufactured out of it consideration has to be given to the fraction of the intermediate that remains in the end product. Depending on the reaction (type and duration) a certain fraction will remain after isolation of the end product. The remains may be emitted – completely or partly – to air and wastewater or end up in the end product. It is well-known that polymers, for example, may contain a considerable amount of the monomer. For vinylchloride maximum contents have been set for PVC. This aspect should also be covered in the ESD to be developed.

Table 7.5 Checklist for emission estimation for the life cycle stage of production of end products and intermediates (Y = Yes, N = No/unknown)

	Remark (#)
Type of process: <input type="checkbox"/> Continuous <input type="checkbox"/> Batch process, dedicated equipment <input type="checkbox"/> Batch process, multipurpose equipment	
<input type="checkbox"/> Continuous process	
<i>Are emissions measured (per compartment) ?</i>	
Y: (1) Emission data directly to be used in risk assessment	1
N: (2) Database emission factors comparable processes (for direct process emissions)	
<i>Purification after production step?</i>	
N: (3) Emissions calculated with emission factors of (2) for risk assessment	
Y: (4) Type of process: As (5) Calculation of emissions at purification Risk assessment with sum of (2) + (4)	2
<input type="checkbox"/> Batch process, dedicated equipment	
<i>Are emissions measured (per compartment, for all process steps) ?</i>	
N: (5) Database applicable process steps (including purification steps)	2
Y: (6) Emission data directly to be used in risk assessment	3
<input type="checkbox"/> Batch process, multipurpose equipment	
N: (7) Database applicable process steps (including purification steps)	4
Y: Emission data directly to be used in risk assessment	3

Remarks:

1. From productions like this emission factors can be determined for the database as also the annual production (Qprod) related to the emissions (Qem_i) will be known: Emission factor for compartment *i*: $EF_i = Qem_i / (Qprod + \Sigma Qem_i)$.
2. The lower value of estimates.
3. If emissions are available per process step these data can be used to develop/update the database
4. The higher value of estimates

Table 7.6 Scheme for calculations of emission estimates for consecutive process steps

[A]	PROCESS	BATCH ? [B] ¹⁾ CONTINUOUS	? [C]		
[B]	- PRODUCT	BATCH SIZE No. BATCHES	+-----+ kg.batch ⁻¹ ²⁾ +-----+ d ⁻¹		
	- REACTION MEDIUM	WATER+-----+ l.batch ⁻¹ SOLVENT+-----+ l.batch ⁻¹	Q _{em,water,1} = ..., Q _{em,air,1} = ... ³⁾ ? [D] Q _{em,water,1} = ..., Q _{em,air,1} = ... ³⁾ ? [E]		
[D]	ISOLATION	DRYING ? [F] SOLVENT EXTRACTION FILTRATION DISTILLATION	? [G] ? [H] ? [I]		
[F]	DRYING	ATMOSPHERIC VACUUM ("dry" vacuum pumps) VACUUM (water ring pumps)	Q _{em,water,1} = 0, Q _{em,air,1} = ... ⁴⁾ Q _{em,water,1} = 0, Q _{em,air,1} = ... ⁴⁾ Q _{em,water,1} = ..., Q _{em,air,1} = ... ⁵⁾	? [J] ? [J] ? [J]	
[G]	SOLVENT EXTRACTION	SOLVENT+-----+ l.extraction ⁻¹ No. EXTRACTIONS SOLUBILITY (in solvent)	+-----+ d ⁻¹ +-----+ mg.l ⁻¹	} } }	Q _{em,water,2} = ..., Q _{em,air,2} = 0 ⁶⁾ ? [G2]
[G2]	ISOLATION	"EVAPORATION" (solvent) DITTO (partly)	→ [G3] → [G4]		
[G3]	DRYING/DISTILLING OFF SOLVENT		Q _{em,water,3} = 0, Q _{em,air,3} = ... ⁷⁾	? [J]	
[G4]	PARTIAL REMOVAL OF SOLVENT & FILTRATION		Q _{em,water,3} = 0, Q _{em,air,3} = ... ^{7) 8)}		<i>Emissions assumed to be zero for incineration of remaining mother liquor; for reprocessing calculation / estimation of emissions</i> → [J]
[H]	FILTRATION			Q _{em,water,4} = ..., Q _{em,air,4} = 0 ⁹⁾	? [J]

Table 7.6 Scheme for calculations of emission estimates for consecutive process steps (continued)

[I]	DISTILLATION	ATMOSPHERIC	$Q_{em_{water,5}} = 0, Q_{em_{air,5}} = \dots^{10)}$? [J]		
		VACUUM (“dry” vacuum pumps)	$Q_{em_{water,5}} = 0, Q_{em_{air,5}} = \dots^{10)}$? [J]		
		VACUUM (water ring pumps)	$Q_{em_{water,5}} = \dots, Q_{em_{air,5}} = \dots^{10)}$? [J]		
[E]	ISOLATION	As [G2]: calculations according to [G3], [G4] or [K] ⁸⁾				
		EXTRACTION	→ [K]			
[K]	EXTRACTION	WATER+-----+ l.extraction ⁻¹	} Emissions assumed to be zero for incineration of solvent; for recycling calculation/estimation of emissions → [F] / [H] ¹¹⁾ / [I]			
		No. EXTRACTIONS		+-----+ d ⁻¹		
		SOLUBILITY (in solvent)		+-----+ mg.l ⁻¹		
[C]	REACTION MEDIUM	WATER	$Q_{em_{water,6}} = \dots, Q_{em_{air,6}} = \dots^{12})?$	[J]		
		SOLVENT	$Q_{em_{water,6}} = \dots, Q_{em_{air,6}} = \dots^{12})?$	[J]		
		GAS PHASE REACTION				
[J]	PURIFICATION	DISTILLATION	Calculations as [I] for $Q_{em_{water,7}}$ and $Q_{em_{air,7}}$			
		RECRYSTALLISATION FROM SOLVENT	→ [L] [L]RECRYSTALLISATION FROM WATER		→[M]	
			→[N]			
[M]	RECRYSTALLISATION from water	WATER+-----+ l.extraction ⁻¹	} $Q_{em_{water,8}} = \dots, Q_{em_{air,8}} = 0$			
		No. EXTRACTIONS		+-----+ d ⁻¹		
		SOLUBILITY (in solvent)		+-----+ mg.l ⁻¹		
[N]	RECRYSTALLISATION	SOLVENT	+-----+ l.extraction ⁻¹	} Emissions assumed to be zero for incineration of remaining motherliquor; for reprocessing calculation / estimation of emissions		
		No. EXTRACTIONS	+-----+ d ⁻¹			
		SOLUBILITY (in solvent)	+-----+ mg.l ⁻¹			

Table 7.6 Scheme for calculations of emission estimates for consecutive process steps (continued)

-
- 1) Specification “dedicated equipment” or “multipurpose equipment”
 - 2) It should be noted that there are various interpretations for the batch size, i.e., the quantity of product synthesised. First, the theoretical maximum, which can be calculated on the basis of the quantity of the limiting reactant (raw material). Second, the quantity that is isolated from the reaction step before purification. Third, the quantity that is isolated from the reaction step after purification
 - 3) Emission factor for the compartment air from database (e.g., related to vapour pressure at reaction temperature, which both have to be stated; otherwise realistic worst case defaults) for relevant equipment (continuous, dedicated, multipurpose). For the emission factor to wastewater the possibility of cleaning with water and detergents should be considered as well. Also cleaning with solvent should be considered if recycling or reuse of the solvent – with the substance of interest in it – takes place
 - 4) A database for emission factors for air that have a relation with vapour pressure at operation temperature and time of operation (probably the quantity of water to be removed can be used as an estimate for duration of the process). At diminished pressure a correction has to be made
 - 5) The transfer from air to wastewater should be estimated (probably in analogy to the method mentioned at “water ring pumps” in the section “Engineering calculations”)
 - 6) A distribution based on the solubility of the substance in water and in solvent should be used in the calculation. It should also be considered which “extra” loss to wastewater should be taken because of discharge of an intermediate layer at phase separation in analogy to “extraction” as described in subsection “Engineering calculations” (e.g., 0 for dedicated equipment)
 - 7) A database for emission factors for air that have a relation with vapour pressure at operation temperature and time of operation (probably the quantity of solvent to be removed can be used as an estimate for duration of the process). At diminished pressure a correction has to be made
 - 8) At partial removal the quantity of solvent remaining must be specified (e.g., fraction of solvent remaining)
 - 9) Calculation with water solubility (base data set) and quantity of water per batch (input at [B])
 - 10) A database for emission factors for air that have a relation with vapour pressure at operation temperature and time of operation (probably the quantity of water to be removed can be used as an estimate for duration of the process). At diminished pressure a correction has to be made
 - 11) Probably the substance is precipitated by addition of chemicals to the aqueous solution
 - 12) For the database the emission factors are calculated in relation to the quantity of substance produced ($\text{kg}\cdot\text{d}^{-1}$); the other way round emission estimation with the database occurs using the emission factors from the database with the daily quantity of the substance produced. Finally the overall emissions for the site are calculated as $Q_{\text{em}_{\text{water},\text{total}}} = \sum Q_{\text{em}_{\text{water},i}}$

8 CONCLUDING REMARKS

The sectors of the chemical industry have been prioritised for which emission scenario documents are most urgently needed as describe in Chapters 2 and 3 and Appendix I. Many sectors of the chemical industry only comprise operations such as measuring and weighting, mixing of chemicals, filling and cleaning. Examples are the manufacture of photographic chemical materials and paints. The aim of the study is the chemical process industry (CPI) where actual chemical reactions are carried out, which are accompanied with series of operations like distillation, phase operations, etc.

The sectors for which the highest priority is expected are:

- the manufacture of dyes and pigments
- the manufacture of other organic basic chemicals
- the manufacture of plastics in primary forms
- the manufacture of synthetic rubber in primary forms
- the manufacture of pharmaceutical products

Other rather urgently needed EDSs to be developed concern:

- the manufacture of perfumes and toilet preparations
- the application of processing aids in the manufacture of petrochemicals
- the application of processing aids in the manufacture of other inorganic basic chemicals

Next to this prioritisation, key concepts and tools, which are instrumental in developing ESDs are discussed. All of this is meant to initiate the development of ESDs for the chemical processing industry.

REFERENCES

ACFIS (2002)

An introduction to Fine and Specialty Chemicals
 Italian Association of Fine and Specialty Chemicals
<http://www.acfis.com/english/inform/fineeng.pdf>

Allen, D.T. and Shoddard, D.R. (2002)

Green Engineering: environmentally conscious design of chemical processes
 Prentice Hall, Inc., ISBN 0-13-061908-6

Blass, E. (2000)

Liquid-Liquid Extraction: 5. Liquid-Liquid Extraction Processes
 In: Ullmann's Encyclopedia of Industrial Chemistry
 Wiley-VCH Verlag GmbH & Co. KGaA
<http://www.mrw.interscience.wiley.com/ueic/articles/b03-06/sect5.html>

Crookes, M., Quarterman P., Brooke, D. (2002)

Identification and Use of Databases for Release Estimation and Development of Emission Scenario Documents: A case study on the Mineral Oil and Fuel Industry. BRE Client report number 201100, Building Research Establishment Ltd (BRE)

EA (2003)

Emission Estimation Technique Manuals from the National Pollution Inventory Environment Australia (EA)
 URL: http://www.npi.gov.au/handbooks/approved_handbooks/eetmanuals.html

EC (1996)

Technical Guidance Documents in support of Directive 93/67/EEC on risk assessment of new notified substances and regulation (EC) No. 1488/94 on risk assessment of existing substances (Parts I, II, III and IV).
 EC catalogue numbers CR-48-96-001, 002, 003, 004-EN-C. Office for Official Publications of the European Community, Luxembourg

EC (1998)

Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market
 Office for Official Publications of the European Community, Luxembourg

EC (2003)

Technical Guidance Document (TGD) on Risk Assessment in support of the commission directive 93/67/EEC on risk assessment for new notified substances and the commission regulation (EC) 1488/94 on risk assessment for existing substances and the directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market, Part I,II,III,IV, Second Edition. European Chemicals Bureau (ECB), Ispra, Italy, 2003

ECB (2003)

Draft Risk Assessment Reports & Finalised Risk Assessment Reports
<http://ecb.jrc.it/existing-chemicals/>

EEA (2001)

EMEP/CORINAIR Emission Inventory Guidebook – 3rd edition. Technical report No 30. European Environment Agency (EEA)

EIIP (1996)

Preferred and Alternative Methods for Estimating Fugitive Emissions from Equipment Leaks. Volume II, Point Sources: Chapter 4 of the Emission Inventory Improvement Program.

EIIP (2002)

Preferred and Alternative Methods for estimating Air Emissions from Paint and Ink Manufacturing Facilities. Volume II, Point Sources: Chapter 8 of the Emission Inventory Improvement Program.

Enc. Britt. (2002)

Chemical industry
Encyclopedia Britannica 2002 DeLuxe (CD-ROM)

Endriß, H. (1997)

Aktuelle anorganische Bunt-Pigmente, Herausgegeben von Dr. Ulrich Zorll
Curt R. Vincentz Verlag, Hannover, ISBN: 3-87870-440-2

EPA (1980)

Chemical Use Standard Encoding System (ChemUSES). Volume 2: Function List and Function List Index
United States Environmental Protection Agency, Office of Toxic Substances, EPA 560/13-80-034b, Washington

EPA (1991)

Chemical engineering branch manual for the preparation of engineering assessments. IT Corporation for the USEPA/OPPT. Prepared for U.S. Environmental Protection Agency (US-EPA), Office of Toxic Substances, Chemical Engineering Branch. Washington, DC.

EPA (1995a)

Profile of the Organic Chemical Industry, SIC 286
EPA/310-R-95-012, EPA Office of Compliance Sector Notebook Project
Office of Compliance, Office of Enforcement and Compliance Assurance, Washington

EPA (1995b)

Profile of the Inorganic Chemical Industry, SIC 281
EPA/310-R-95-004, EPA Office of Compliance Sector Notebook Project
Office of Compliance, Office of Enforcement and Compliance Assurance, Washington

EPA (1995c)

Protocol for Equipment Leak Emission Estimates. EPA-453/R-95-017. United States Environmental Protection Agency (US-EPA), Office of Air and Radiation, Office of Air Quality Planning and Standards, North Carolina

EPA (1995d)

Compilation of Air Pollutant Emission Factors, AP-42, Fifth Edition, Volume I: Stationary Point and Area Sources. URL: <http://www.epa.gov/ttn/chief/ap42/>. United States Environmental Protection Agency (US-EPA), Research Triangle Park, NC.

EPA (1995e)

Emission Factor Documentation for AP-42, Section 5-2: Transportation and Marketing of Petroleum Liquids United States Environmental Protection Agency (US-EPA), Research Triangle Park, NC.

EPA (1997)

Emission Factor Documentation for AP-42, Section 7-1: Organic Liquid Storage Tanks
US-Environmental Protection Agency, Office of Air Quality Planning and Standards, Emission Factor and Inventory Group, MRI Project No. 4604-03

EPA (1998a)

A Word from the Bureau of Environmental Monitoring and Data Processing: Promoting Individual and Community Air Quality Monitoring Efforts
Environmental Policy Monthly, Volume I, Issue 8 February 1998
<http://www.epa.gov.tw/english/Epm/issue9802.htm>

EPA (1999)

USER'S GUIDE to TANKS, Storage Tank Emissions Calculation Software Version 4.0, September 30, 1999, Emission Factor and Inventory Group, Emissions, Monitoring, and Analysis Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. URL: <http://www.epa.gov/ttn/chief/software/tanks/>

EUROSTAT (1996)

NACE Rév. 1, Nomenclature statistique des Activités économiques dans la Communauté Européenne
Office Statistique des Communautés Européennes, EUROSTAT, Luxembourg, 1996, pp183, ISBN 92-826-9768-6

FAZ-Institut (2000)

Henkel announces withdrawal from chemicals business
Chemical Newsflash, News from 14 to 20 November, 2000
<http://www.chemicalnewsflash.de/en/news/310701/news2.htm>

Groshart, Ch. (2003)

Harmonisation of Environmental Emission Scenarios. Biocides: PT 11 – Preservatives for liquid cooling and processing systems
European Commission DG ENV, Royal Haskoning, 4L1784.A1/R0006/FBA/TL/Nijm (DRAFT)

Hart, J.R. (2000)

Ethylenediaminetetraacetic Acid and Related Chelating Agents: 7. Uses
In: Ullmann's Encyclopedia of Industrial Chemistry
Wiley-VCH Verlag GmbH & Co. KGaA
<http://www.mrw.interscience.wiley.com/ueic/articles/a10-095/sect7.html>

Henkel, K-D. (2002)

Reactor Types and Their Industrial Applications
In: Ullmann's Encyclopedia of Industrial Chemistry
Wiley-VCH Verlag GmbH & Co. KGaA
<http://www.mrw.interscience.wiley.com/ueic/articles/b04-087/>

Heusch, R. (2000)

Emulsions: Fields of Application

In: Ullmann's Encyclopedia of Industrial Chemistry

Wiley-VCH Verlag GmbH & Co. KGaA

<http://www.mrw.interscience.wiley.com/ueic/articles/a09-297/sect10.html>

IPPC (2002)

Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry.
Integrated Pollution Prevention and Control (IPPC)

IVC (2002)

Production of man-made fibres

Industrievereinigung Chemiefaser e.V., Frankfurt/Main, Germany

<http://www.ivc-ev.de/englisch/service/chemifaseng.htm>

Jolly, A.M., Willoughby, B., Karas, G.C., Hobbs, S.J. (1994)

Use Category Document: Plastic Additives

Building Research Establishment, Garston, UK

Kriebel, M (2000)

Absorption

In: Ullmann's Encyclopedia of Industrial Chemistry

Wiley-VCH Verlag GmbH & Co. KGaA

<http://www.mrw.interscience.wiley.com/ueic/articles/b03-08/sect3.html>

McEvoy, B. (2002)

Natural inorganic pigments

<http://www.handprint.com/HP/WCL/pigmt1a.html>

Synthetic inorganic compounds

<http://www.handprint.com/HP/WCL/pigmt1b.html>

Mersmann, A. (2000)

Adsorption

In: Ullmann's Encyclopedia of Industrial Chemistry

Wiley-VCH Verlag GmbH & Co. KGaA

<http://www.mrw.interscience.wiley.com/ueic/articles/b03-09/sect1.html>

Mulder, W., Verbeek, A., Eggels, P.G. (1993)

Emissiefactoren – Lekverliezen van apparaten en verliezen bij op- en overslag
Rapport Nr. 8, Publicatiereeks Emissieregistratie, VROM-DGM, Den Haag

MW (2002)

Merriam-Webster's Collegiate Dictionary

<http://www.m-w.com/cgi-bin/dictionary>

NOHSC (1998)

Ranking Priority Existing Chemicals

Media release, National Occupational Health and Safety Commission, Commonwealth of Australia

<http://www.nohsc.gov.au/NewsAndWhatsNew/MediaReleases/mr-151298.htm>

OECD (2001)

OECD Environmental Outlook for the Chemicals Industry (Environment)
<http://www.oecd.org/ehs>

PEI (1986)

Release during Cleaning of Equipment, Report prepared under Contract 68-02-428 to US-EPA, Office of Toxic Substances

Prats, A. (1992)

Etude sur l'identification et la quantification des principaux rejets dans l'environnement des additifs pour peintures et vernis
Contrat INERIS-Ministère Environnement DPPR/MCP/CR/VH lettre de commande 6n_122/92, France

Ros, J.P.M. (1985)

Beoordelingssysteem nieuwe stoffen. Onderdeel: Uitwerpv verwachting textielkleurstoffen
Report no. 851502001, National Institute for Public Health and the Environment (RIVM), Bilthoven, the Netherlands

Ros, J.P.M., Poel, van der, P. (1989)

Doelgroepstudie farmacie, deel 1: bronnen en emissies (Target group study Pharmaceutical Industry, part 1: Sources and Emissions)
Report no. 738509002, National Institute for Public Health and the Environment (RIVM), Bilthoven, the Netherlands

Ros, J.P.M., Poel, van der, P., Slootweg, J. (1990)

Target group study Pharmaceutical Industry
Report no. 736301002, National Institute for Public Health and the Environment (RIVM), Bilthoven, the Netherlands

Shonnard, D.R., Markey, J.M., Deshpande, P.A. (1995)

Evaluation of Unit Operation-specific Databases
Proceedings of the 1995 American Institute of Chemical Engineers Summer National Meeting, Boston, Mass.

Threadingham, D, Dunn, J., Meisenheimer, H., Marbach, A., Diedrich, K.M. (2000)

Rubber, 3. Synthetic: 4. Synthesis by Radical and Other Mechanisms
In: Ullmann's Encyclopedia of Industrial Chemistry
Wiley-VCH Verlag GmbH & Co. KGaA
<http://www.mrw.interscience.wiley.com/ueic/articles/a23-239/sect4.html>

Ullmann (2001)

Ullmann's Encyclopedia of Industrial Chemistry
<http://jws-edckinterscience.wiley.com:8087/>

UNECE (1999)

The Chemical Industry in 1999 - Annual Review
United Nations Economic Commission for Europe, Geneva, Sales No. E.00.II.E.16, ISBN 92-1-116712-4

ENV/JM/MONO(2011)49

UNSD (2004)

NACE-NAICS industrial classifications convergence project (with first – October 2000 – and second – October 2001, draft version – reports of the Working Group)

<http://www.unstats.un.org/unsd/class/intercop/convergence/default.htm>

APPENDIX 1 DISCUSSION OF THE CHEMICAL INDUSTRY SECTORS ACCORDING TO THEIR NACE CODES

Manufacture of coke, refined petroleum products and nuclear fuel

NACE 2320 Manufacture of refined petroleum products

According to the statement on the definition of petrochemicals made earlier in this report only the chemicals of Table 2.2 are concerned (primary, secondary and tertiary building blocks of organic chemicals). In a way the secondary and tertiary chemicals overlap with NACE 2414 “Manufacture of other organic basic chemicals”. Therefore, only the chemical synthesis of these chemicals is considered there. All primary building blocks belong to the group of HPVCs and thus are on the EU priority list and RARs have to be developed for them. These RARs should include site specific risk assessments for the life cycle stages production and industrial use (processing if used as an intermediate).

As stated earlier, these chemicals are produced at a very large scale with a limited number of well defined and described processes, which have been tuned to meet low production costs and provided often with specific abatement techniques for emission reduction. Probably data on emissions of processing aids used – for example as a catalyst or pH-regulating agent – in the manufacture of primary building blocks might be used for the development of an ESD on processing aids used in CPI. This, however, is only important for large scale, normally continuous, processes in dedicated equipment.

Manufacture of basic chemicals

NACE 2411 Manufacture of industrial gases

A distinction may be made between conventional industrial gases such as H₂, N₂, O₂, and special gases used in the manufacture of products, e.g. refrigerants such as CFCs and HCFCs, and toxic, explosive or etching gases such as SiH₄, AsH₃, PH₃, B₂H₆, HCl, Cl₂, CCl₄, SiCl₄, and CF₄. Industrial gases may be produced either by chemical or physical means. For HPVCs the same situation applies that they are on the EU priority lists and RARs have to be developed for them. The number of industrial gases being LPVCs is rather small and it is not likely that any new gases will be notified in near future. So, special attention for emission scenarios for gases is not needed.

Gases like N₂, O₂, He, Ar, and CO₂ may be produced by physical means from air. These processes fall outside the scope of this report. Gases like H₂ and Cl₂ may be produced by electrochemical means from brine. Such process are very specific and well documented with respect to releases of the products and processing aids such as mercury. Therefore, there is no urgency in developing emission scenario documents for such processing aids. Also the manufacture of CFCs, HCFCs and alike are well known processes, just like the manufacture of, e.g., acetylene (C₂H₂) and ammonia (NH₃). It is difficult to foretell whether emission data on chemicals used as processing aid will be important for the development of an ESD on chemicals used in CPI. The priority is estimated to be low.

For information from industry the European Industrial Gases Association (EIGA), a sector group of CEFIC (Conseil Européen de l'Industrie Chimique / European Chemical Industry Council), might be consulted.

NACE 2412 Manufacture of dyes and pigments

Probably due to the fact that organic dyes were produced as one of the first groups of chemicals from coal tar and that inorganic pigments have been produced since time immemorial, the manufacture of dyes and pigments is counted as basic chemicals. The main distinction between dyes and pigments is that dyes are soluble in the medium in which they are applied and pigments aren't. Dyes are mainly used for colouring textile, paper, inks, carpets, etc. Pigments are used for a variety of things, e.g., to lend colour to plastics and coatings. Both pigments and dyes – both use category 10 “colourants”- may be manufactured by physical or chemical processes. Organic colourants from living organisms have been used extensively in the past, for example indigo from plants of the genus *Indigofera* and Cochineal from the wing-case of a scale insect (*Dactylopius coccus*). The importance of chemically produced colourants is far more important nowadays and many new colourants are developed and brought to the market every year. The chemical processes in the manufacture of colourants are numerous. It is quite likely that some reactions are very specific for the synthesis of organic dyestuffs and used for hundreds if not thousands of dyestuffs. A section on organic colourants synthesis will be very useful for an ESD covering end products. So far, only information for textile dyes data on releases have been incorporated in a use category document (Ros, 1985).

Inorganic pigments may be divided in natural and synthetic pigments (Endriß, 1997). Natural pigments are obtained by grinding and washing clays or minerals, or by calcinating or roasting earths (Endriß, 1997; McEvoy, 2002). Synthetic pigments are made out of raw materials by chemical conversion of mineral compounds (McEvoy, 2002). For this report only the synthetic pigments are considered. Some pigments may be produced in enormous volumes, like zinc oxide, titanium dioxide and iron oxide. Such HPVCs are on the EU priority list and RARs have to be developed for each of them. In their manufacture specific chemical processes may be used. These processes are very specialised – for titanium dioxide two specific chemical processes exist – and information on emission of the processing aids involved is presumably not very helpful in the development of an ESD for processing aids in CPI. Development of emission scenarios for the production of inorganic pigments belonging to the group of LPVCs does not seem urgently needed at first sight.

By far most of the colourants produced are applied outside chemical industry. Small-scale applications of certain dyes – pH indicators – occur mainly in laboratories. Hence, these colourants will usually be considered as use category 34 “Laboratory chemicals”. So, the life cycle stage of industrial use should be covered in emission scenario documents for industrial categories. In the TGD (EC, 2003) dyes are considered in ESDs for IC 7 “Leather processing industry”, IC 12 “Pulp, paper and board industry”, IC 13 “Textile processing industry”, IC 14 “Paints, lacquers and varnishes industry”, and 0 “Others” for rubber industry.

Information from industry branch organisations is available from the Ecological and Toxicological Association of Dyes and organic pigments manufacturers (ETAD), EUROCOLOUR (part of CEFIC), and the European Council of the Paint, Printing Ink and Artists' Colours Industry (CEPE, part of CEFIC), amongst others.

NACE 2413 Manufacture of other inorganic basic chemicals

Many inorganic basic chemicals are manufactured in specifically developed chemical processes, for example the Haber-Bosch process for ammonia synthesis and the manufacture of nitric acid by catalytic oxidation of ammonia. The reactors and equipment used have been designed and optimised specifically for these processes. These processes and their environmental releases have been well documented. So, development of emission scenario documents for those basic inorganic chemicals is not useful or not needed in the case of HPVCs (RARs to be developed). However, for some inorganic LPVCs manufactured in multipurpose plants, emission scenarios might be desired in future. The urgency is estimated to be low, however. It should be noted that the manufacture of inorganic LPVCs is not completely covered by the

NACE codes. So, other inorganic chemicals that can not be allocated to a specific NACE code are classified here.

The application of inorganic basic chemicals in other industrial categories – for example as a filler in paint, IC 14 “Paints, lacquers and varnishes industry” – is not part of this report as this is a chemical product sector with only formulation and no chemical processing. The application of inorganic basic chemicals in chemical industry, however, is. Applications in the chemical industry may concern the application as an intermediate in the chemical industry of NACE 2413 itself (or e.g. in NACE 2412 in the manufacture of a pigment) or as a processing aid (both in NACE 2413 and any other sector with chemical processing). For the industrial use as an intermediate in this chemical industry sector itself the same low priority is expected as for its manufacture (see previous paragraph). Data on the industrial use as a processing aid may be useful for an ESD on the industrial use of processing aids in CPI.

NACE 2414 Manufacture of other organic basic chemicals

Here, a similar situation applies as for the inorganic basic chemicals. However, the number of substances produced in dedicated equipment and sometimes in a continuous way is much larger. Some chemicals may be produced in different ways (chemical processes, process circumstances, equipment used, abatement techniques, etc.) and from different feedstocks. This may lead to very different emission levels, i.e., emission factors.

There is no need to develop emission scenario documents for basic chemicals – including the secondary and tertiary building blocks – of the HPVCs group, as site specific assessments are carried out in RARs. Only, if no site-specific emission factors become available, generic emission scenarios for LPVCs should be used. As the NACE list does not cover specifically the manufacture of LPVCs, a generic ESD on organic chemical synthesis should be developed. Information may be obtained from sector groups of CEFIC such as the Aromatics Producers Association (APA), the oil companies' European organisation for environment, health and safety (CONCAWE), and many others. The other sector groups of CEFIC – and probably individual associations – are listed under the specific NACE codes in Appendix 4.

In the CPI many processing aids are used, e.g., as catalysts, solvents for cleaning or as a reaction medium, acids and alkalis, etc. Data collected on emissions of processing aids for specific reaction types, types of equipment used, reaction conditions, unit operations involved, etc., will be helpful in the development of an ESD on chemicals used as a processing aid in CPI.

2415 Manufacture of fertilisers and nitrogen compounds

This includes the manufacture of fertilisers such as phosphate and nitrogen fertilisers. These fertilisers are produced at a very large scale by processes, which are well known for their emissions. These chemicals will be HPVCs no doubt and thus will have to be provided with RARs. It is not likely that LPVCs will be notified as fertilisers. So, no specific emission scenarios are needed.

Information on emissions of processing aids used in the manufacturing processes of fertilisers do not seem to be of any help in the development of an ESD on processing aids at this moment.

2416 Manufacture of plastics in primary forms

Many plants manufacturing plastics in primary form, e.g. as granulates or pellets, are part of a company that also manufactures monomers, i.e. the building blocks for polymers. In the manufacture of plastics many processing aids may be used, for example, initiators, terminators, emulsifiers, etc. Sometimes polymers are delivered to customers as a ready to use product. This may be in the form of granules or pellets containing additives such as anti-oxidants or so-called master batches, which consist of pigment and additives incorporated in pellets of polymer. This supplies the customers who process polymers (i.e., shaping the pellets and granules into finished articles by moulding, extruding, etc.) with

feedstocks of a constant quality. This industrial use of polymer processing belongs to NACE codes 2521 up to and including 2524 (all kinds of manufacture of plastic products). According to the TGD both the production and processing of polymers falls under IC 11 “Polymers industry”. Data on emissions of intermediates (i.e., the building blocks for the polymers) and processing aids are of great importance and should be given urgent attention.

Information may be gathered from the Association of Plastics Manufacturers in Europe (APME) representing 90% of Western Europe’s polymer producing capability and the European Council of Vinyl Manufacturers (ECVM) representing over 98 per cent of Western Europe’s production of PVC resin. For processing – in other words industrial use – an ESD for polymer processing is beyond the scope of this report. The UK has already produced a draft ESD (Jolly et al., 1994), which has been finalised and circulated for approval in the OECD Task Force Environmental Exposure Assessment (4th quarter of 2003). It should be noted that emission scenarios worked out in such an ESD should be used for those kind of processes, which may be carried out in other industrial categories. Much polymer is processed in industrial category 4 “Electrical/electronic industry” and IC 16 “Engineering industries: civil and mechanical” (e.g. companies supplying parts to automobile industry). Thermosetting resins such as unsaturated polyesters and epoxies take a special place. Before processing into final products – for example as paints, adhesives, encapsulation for electronic components – a formulation stage usually takes place (formulation of paints, adhesives, etc.). Often these formulations consist of two components that are mixed prior to application.

2417 Manufacture of synthetic rubber in primary forms

For this particular sector the same situation occurs as for plastics. Information may be gathered from the European Synthetic Rubber Association (ESRA), which is part of CEFIC (see also Appendix 4). For the formulation/processing (industrial use) stage an ESD has been incorporated in the revised TGD (EC, 2003) for IC 0/15 “Others”.

Manufacture of pesticides and other agro-chemical products

2420 Manufacture of pesticides and other agro-chemical products

Pesticides are usually marketed in the form of formulations. Some manufacturers manufacture both the active ingredients and the formulated products. These formulated products may contain a variety of other chemicals, e.g., solvents, colourants, surface active ingredients, etc. Other specific active ingredients also belong to this group, for example fungicides and insecticides, and the complex group of biocides (non-agricultural pesticides), for example disinfectants and preservatives.

The manufacture of the active ingredients falls partly or completely under IC 2/3 “Chemical industry”. In some cases an active ingredient is also a basic chemical belonging to the group of HPVCs. In those cases no generic emission scenarios should be used but RARs for those chemicals should be developed. For the chemical synthesis (life cycle stage of production) of (new) pesticides that are LPVCs an ESD should be developed. The life cycle stage of formulation, i.e. the manufacture of finished pesticide and biocidal products falls outside the scope of this report. However, an ESD covering the emissions of other chemicals than the active ingredients would be very useful. Specific information on pesticide synthesis may be collected from the European Crop Protection Association (ECPA) and from the European Biocidal Product Forum (EBPF) at CEFIC.

As the importance of the chemical synthesis of active ingredients in this specific sector remains unclear at this moment, the priority for an ESD on end products is ranked as low. Therefore, data on emissions of intermediates and processing aids are estimated to be of little importance.

Manufacture of paints, varnishes and similar coatings, printing ink and mastics

2430 Manufacture of paints, varnishes and similar coatings, printing ink and mastics

The manufacture of these products is carried out in specialised factories and usually the processes carried out consist of mixing and blending (together with weighing, cleaning and packaging activities). These activities fall – with the exception of inks and mastics – under IC 14 “Paints, lacquers and varnishes industry” of the TGD, for which an ESD has been developed and incorporated (EC, 1996; EC, 2003) for the stages of formulation and industrial use (processing). The manufacture of the individual components (end products) belongs to IC 2/3 “Chemical industry“ where the same restrictions for HPVCs and LPVCs apply.

Manufacture of pharmaceuticals, medicinal chemicals and botanical products

2441 Manufacture of basic pharmaceutical products

This sector includes the manufacture of the active ingredients for all kinds of pharmaceutical preparations. This may range from small volumes, such as special hormones, to large volumes up to the scale of HPVCs. In many cases a lot of intermediates have to be synthesised before obtaining the final product. Some companies, which are counted as pharmaceutical firms, are specialists in the manufacture of such intermediates (“fine chemicals”). The same remarks for HPVCs and LPVCs apply as for pesticides and other agro-chemical products. Many processes in this chemical industry sector are very specific. So, the priority for the development of an ESD on end products is very high. Data on emissions of intermediate and processing aids are very important for ESDs on these chemicals. Information on pharmaceuticals may be collected from the Active Pharmaceutical Ingredients Committee (APIC), a sector group of CEFIC.

2442 Manufacture of pharmaceutical preparations

There are a lot of companies that do not manufacture active ingredients or other components of pharmaceutical products by chemical or physical means. They just mix the components and market them as finished preparations. These formulators in this sector are not the subject of this report.

Manufacture of soap and detergents, cleaning and polishing preparations, perfumes and toilet preparations (cosmetics)

2451 Manufacture of soap and detergents, cleaning and polishing preparations

The manufacture of these products consists mainly of the life cycle stage formulation, which is not part of this report. The ingredients for these products are manufactured in IC 2/3 “Chemical industry” – i.e., the life cycle stage production – as HPVCs or LPVCs. For the whole life cycle the TGD contains an ESD for soaps, fabric washing, dish cleaning and surface cleaning substances. The emission scenarios are based on HPVCs and may not necessarily apply to new chemicals (EC, 1996). The emission of chemicals that are used as end products in the formulation of these kinds of products will be considered under NACE 2414. So, the priority for an ESD on end products is ranked as low. Consequently, the importance of emission data on intermediates and processing aids is ranked low as well.

Specific information on the manufacture of detergents, surface active substances and the like may be obtained from AISE (Association Internationale de la Savonnerie, de la Détergence et des Produits d'Entretien) and CEFIC sector groups as the Comité Européen des agents de Surface et de leurs Intermediaires Organiques (CESIO) and the Conseil Européen des Phénols Alkylés et Dérivés (CEPAD). For other LPVCs one may also think of specific ingredients used such as colourants, fragrances and preservatives. For such chemicals associations mentioned in the specific industry sectors (NACE codes) may be consulted.

It still may occur that a company also has plants where chemical synthesis or certain unit operations of CPI – such as distillation – are carried out. Originally, the surfactants for detergents were soap. Soaps are produced out of raw materials such as plant and animal fats and oils. So, this manufacture might also be classified as NACE 2463 “Manufacture of essential oils”. A company like Henkel is hiving off its chemical production activities and will concentrate completely on the manufacture of chemical products (apart from detergents also adhesives for example) (FAZ, 2000).

2452 Manufacture of perfumes and toilet preparations (cosmetics)

This sector consists mainly of formulation processes. In some cases a manufacturer of perfumes has both production of fragrances (by chemical synthesis and extraction, distillation and similar physical processes) and formulation. The formulation stage means the manufacture of so-called perfume oil bases, which are sold to manufacturers of consumer products (e.g., perfumes, soaps, deodorants, etc.). The priority for end products is estimated to be high and the importance of emission data is also estimated to be high for ESDs on intermediates and processing aids.

Manufacture of other chemical products

2461 Manufacture of explosives

For the chemical synthesis of the ingredients of explosives again the same remarks for HPVCs and LPVCs apply. The number of chemicals is rather low and the process applied very specific. The introduction of new chemicals as a component of explosives is considered to be very rare. So, the priority for end products and importance for intermediates and processing aids is estimated to be very low. Specific information on the chemical synthesis of (ingredients for) explosives may be obtained from the CEFIC sector groups, viz., the Federation of European Explosives Manufacturers (FEEM) and (probably) the Association of European Manufacturers of Sporting Ammunition (AFEMS).

2462 Manufacture of glues and gelatines

This is another chemical industry sector with mainly formulation activities. For the chemical synthesis of substances the same remarks apply as for detergents and similar products. So, the rankings are low.

Specific information on the chemical synthesis of ingredients for adhesives may be obtained from the CEFIC sector groups the Aminoplast Glues Manufacturers Association and the Association of European Adhesives Manufacturers (FEICA).

2463 Manufacture of essential oils

This sector is related to vegetable and animal oils and fats and/or petrochemical feedstocks. The manufacture of the essential oils as such is carried out with physical means as far as vegetable and animal oils and fats are concerned. Petrochemical feedstocks fall under NACE 2320 or NACE 2414. The essential oils are feedstocks in the manufacture of a broad range of semifinished products such as fatty acids, glycerine, alcohols, metallic soaps, and fatty nitriles and their derivatives. So, if we count oleochemical companies in this sector, specific information on characteristic chemical processes in this sector should be collected for emission scenarios for LPVCs. It should be noted that many of the chemicals derived directly from the oils and fats (mainly glycerine, saturated and unsaturated fatty acids) are intermediates, which are converted into end products either in oleochemical industries or “general” organic chemicals industries, the priority is estimated to be low for this particular sector of chemical industry. The European Oleochemicals and Allied Products Group (APAG) might be consulted for this purpose. As the processes are very specific and well known the importance of emission data on intermediates and processing aids is estimated to be low.

2464 Manufacture of photographic chemical material

The manufacture of photographic materials consists of the formulation of films, paper and preparations for developing and fixation, etc. This is outside the scope of this report. Furthermore, the TGD contains a specific ESD on IC 10 “Photographic industry.”

The synthesis of photochemicals (both inorganics and organics) falls under other NACE codes, which should be treated as the “other” LPVCs to be covered in an ESD as it should be developed for “general” organic chemical industry (NACE 2414). Specific information on chemical synthesis of photochemicals might be obtained from European Photographic Chemical Industry (EPCI), a sector group of CEFIC.

2465 Manufacture of prepared unrecorded media

This manufacture does not involve chemical synthesis. All chemicals are obtained from other chemical companies. Out of basic chemicals, such as plastics in raw form, and industrial chemicals, such as iron and chromium compounds, they produce for example magnetic tapes. Such processes are not the subject of this report.

2466 Manufacture of other chemical products n.e.c.

The chemical synthesis of any substance used in the manufacture (life cycle stage of formulation) should be treated in a general ESD for LPVCs/ as stated before. The formulation of any chemical product in this sector falls outside the scope of this report.

2470 Manufacture of man-made fibres

In order to manufacture man-made fibres, viscous, stringy liquids are needed. The material resulting from dissolving or heating is called the spin mass. Today, three manufacturing processes are primarily used: polymerisation, polycondensation and poly-addition. The resulting spinnable matter from these processes is called a polymer. As a rule, a distinction is made between man-made fibres from synthetic polymers and those from cellulosic polymers. The acrylic-, polyamide-, polyester- and elastine fibres belong to the man-made fibres made from synthetic polymers. In the case of man-made fibres manufactured from cellulose polymers there is a distinction between the viscose- and the acetate fibres (IVC, 2002). The chemical manufacture of the polymer is considered here to occur in NACE 2416 "Manufacture of plastics in basic forms". In most cases the processes in NACE 2470 "Manufacture of man-made fibres" can be seen as formulation (manufacture of fibres by physical means out of polymers, including additives and colourants) and probably the industrial use of chemicals such as colourants in dyeing operations.

APPENDIX 2 OVERVIEW OF REACTOR TYPES APPLIED IN CHEMICAL PROCESSING INDUSTRY

- 1 Gas phase reactions
- 2 Liquid phase reactions
- 3 Gas-liquid reactions:
 - reactors with continuous liquid phase and fixed gas distribution devices (bubble columns)
 - reactors with continuous liquid phase and packed and tray reactors
 - reactors with mechanical gas dispersion (sparged stirred tanks)
 - reactors with a continuous gas phase and liquid dispersing devices (spray reactors, liquid ring pumps)
 - Thin-film reactors
- 4 Solid-catalysed reactions:
 - heterogeneous gas catalysis:
 - fixed-bed reactors: --- no special temperature control features (adiabatic operation)
 - stagewise temperature control (chiefly for equilibrium reactions)
 - continuous heat exchange along the flow path (polytropic operation)
 - moving bed and fluidised bed reactors
 - liquid phase & gas-liquid reactions over solid catalysts:
 - fixed bed reactors (trickle flow reactors and packed bubble columns)
 - suspension reactors (stirred tanks and bubble columns with suspended catalyst)
 - fluidised bed reactors
- 5 Non-Catalytic reactions involving solids:
 - gas-solid reactions:
 - reactors with gravity transport of solids (moving bed reactors)
 - reactors with mechanical transport of solids (rotary kilns, multiple-hearth furnaces)
 - reactors with pneumatic transport of solids (fluidised bed reactors, entrained flow reactors, dust roasters and suspension furnaces)
 - liquid-solid reactions
 - solid phase reactions
- 6 Electrothermal reactors:
 - plasma processes (high-temperature pyrolysis)
 - solid reactions (arc furnaces, resistance furnaces, metallurgical furnaces, and Acheson furnaces)
- 7 Electrochemical processes
- 8 Biochemical processes:
 - with dissolved or suspended biocatalysts (submerged processes)
 - with immobilised biocatalysts
- 9 Photochemical processes
- 10 Radiochemical processes

APPENDIX 3 CLASSIFICATION OF CATALYSTS

<u>Class</u>	<u>Type of catalysis/reaction</u>
Metals, alloys, and intermetallic compounds	Heterogeneous, redox
Oxides (insulator oxides, semiconductor oxides)	Heterogeneous, redox
Salts (including halides, sulphates, phosphate)	Redox, acid
Sulphides	Redox, acid
Acids (oxides)	Acid
Bases (oxides, hydroxides, carbonates, silicates of alkali or alkaline-earth metals, their hydrides or amides)	Base
Bifunctional catalysts	Redox + acid-base
Organic ion exchangers	Acid-base
Metal coordination complexes	Homogeneous/heterogeneous, redox
Miscellaneous compounds	Especially for polymerisation and oligomerisation
Enzymes	Heterogeneous (enzyme immobilisation)

APPENDIX 4 CHEMICAL INDUSTRY SECTORS OF CEFIC AND CORRESPONDING NACE CODES

Sector	Specific area sectors	NACE
Agriculture	European Crop Protection Association (ECPA)	2420
	European Fertilisers Manufacturers Association (EFMA)	2415
Biotechnology	European Association for Bioindustries (EuropaBio) ¹⁾	?
Catalysts	European Catalysts Manufacturers Association (ECMA)	2413/2466
	European Cracking Catalysts Producers Association (ECCPA)	2413/2466
	Zeolite Adsorbents (ZEAD)	2413/2466
Chlorine & Halogens	Comité Technique Européen du Fluor (CTEF)	2466
	Euro chlor	2466
	European Fluorocarbon technical committee (EFCTC)	2414
	European Methyl bromide association (EMBA)	2414
	Fluorspar	2413
	Sodium chlorate	2413
	Sodium chlorite	2413
Colourants and Fillers	Eurocolour	
	Asociacion Nacional de Fabricantes de Fritas, Esmaltes y Colores Ceramicos (ANFFECC) 1)	2412
	Association of Synthetic Amorphous Silica Producers (ASASP)	
	Associazione nazionale colorifici ceramici e produttori di ossidi metallici (Ceramicolor) 1)	
	British Colour Makers Association (BCMA) 1)	
	Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) 1)	
	European Manufacturers of Lead Chromate and Lead Molybdate Pigments (EMLC)	
	Industrievereinigung Farbstoffe und Organische Pigmente (IFOP) ¹⁾	
	Syndicat des Fabricants d'Emaux, Pigments, Sels et Oxydes Métalliques (EPSOM) ¹⁾	
	Verband der Mineralfarben industrie (VdMi) ¹⁾	
	European Lead Oxide Association (ELOA)	2412
	European Nitrators Association (ENA)	2414
	European Product Safety & Regulatory Committee for Carbon Black (EPSRC) 1)	-
	European Synthetic Colour Manufacturers Association (ESCMA) 1)	2412
	Natural Food Colours Association (NATCOL) 1)	-
	Titanium Dioxide Manufacturers Association (TDMA)	2412
Zinc Oxide Producers Association (ZOPA)	2413	

Sector	Specific area sectors	NACE
Detergents	Association of detergent zeolite producers (ZEODET)	2451
	Centre Européen d'Etudes des Polyphosphates (CEEP)	2451
	Centre Européen d'Etude des Silicates (CEES)	2451
	Comite Européen des agents de Surface et de leurs Intermediaires Organiques (CESIO)	2451
	Conseil Européen des Phenols Alkyles et Dérives (CEPAD)	2451
	Environmental Risk Assessment and Management (ERASM) 1)	2451
	European Centre of Studies on lab/las (ECOSOL)	2451
	Human and Environmental Risk Assessment on ingredients of household cleaning products (HERA) 1)	2451
	International Association for Soaps, Detergents and Maintenance Products (AISE) 1)	2451
	Food & feed	Acetic Acid Food Grade (AAFG)
Carbohydrates Sector Group (CSG)		2414
European Citric Acid Manufacturers Association (ECAMA)		2414
European Federation of the Animal Feed Additive Manufacturers (FEFANA)		?
European Food Emulsifiers Manufacturers Association (EFEMA) 1)		2414
European Food Phosphates Producers Association (EFPA)		2413
European Pure Phosphoric Acid Producers Association (EPPAA)		2413
Food Contact Additives sector group (FCA)		?
Food regulations panel (FRP)		?
Gelatin Manufacturers of Europe (GME)		-
Inorganic Feed phosphates		2413
Synthetic organic ion exchangers and adsorbents (SOIA)	2414	
Oleochemistry	European Oleochemicals and Allied Product Groups (APAG)	2414
Paints, Coatings & Adhesives	Aminoplast Glues Manufacturers Association	2462
	Association of European Adhesives Manufacturers (FEICA) 1)	2462
	European Aliphatic Isocyanates Producers Association (ALIPA)	24301/2462
	European Council of the Paint, Printing Ink and Artists' Colours Industry (CEPE)	2430
	European Melamine Producers Association (EMPA)	24301
	European Polymer Dispersion and Latex Association (EPDLA)	24301/2462
Paints, Coatings & Adhesives (continued)	Formaldehyde	2414
	Hydrocarbon Resins, Rosin Resins and Pine Chemicals Producers Association (HARRPA)	2414
	Polyols	2414/24301
Petrochemistry	Acetyls Sector Group (ASG)	23201/2414
	Acrylonitrile Producers Association	23201/2414
	Amines Sector Group	23201/2414

Sector	Specific area sectors	NACE
	Aromatics Producers Association (APA)	23201/2414
	Association for Emissions Control by Catalyst (AECC) 1)	-
	Association of Petrochemicals Producers in Europe (Appe)	23201
	Automotive Grade Urea (AGU)	?
	Coal Chemicals (CCSG)	2414
	Ethyl Alcohol Group (EAG)	23201/2414
	Ethylene Oxide & Derivatives Producers Association (EO & Glycols)	23201/2414
	European Basic Acrylic Monomer Group (EBAM)	23201/2414
	European Fuel Oxygenates Association (EFOA)	23201/2414
	European Phenolic Resins Association (EPRA)	23201/2414
	European Solvents Industry Group (ESIG)	23201/2414
	European Solvents VOC Co-ordination Group (ESVOCC)	23201/2414
	Hydrocarbon Solvent Producers Association (HSPA)	23201/2414
	Lower Olefins Sector Group (LOSG)	23201/2414
	Methacrylates Sector Group (MSG)	23201/2414
	Methanol Sector Group	23201/2414
	Methylamines and Derivatives Sector Group	23201/2414
	Oxygenated Solvent Producers Association (OSPA)	23201/2414
	Phenol Producers Association	23201/2414
	Propylene Oxide & Glycols Sector Group (PO & Glycols)	23201/2414
	Styrene Producers Association (SPA)	23201/2414
	Technical Committee of Petroleum Additive Manufacturers in Europe (ATC)	?
Plastics	ABS/SAN	2416
	Association of Plastics Manufacturers in Europe (APME)	2416
	Bisphenol A 2)	2414/2416
	Centre Europeen des Silicones (CES)	2416
	EB/UV Acrylate Resins	2416
	European brominated Flame retardant industry panel (EBFRIP)	2414
	European Council for Plasticisers and Intermediates (ECPI)	2414
	European Council of Vinyl Manufacturers (ECVM)	2416
	European Diisocyanate Producers Association (ISOPA)	2414/2416
Plastics (continued)	European Extruded Polystyrene Insulation Board Association (EXIBA)	2416
	European Flame retardants Association (EFRA)	2413/2414
	European Plastics Converters (EUPC)	2416
	European Rubber Chemicals Association (ERCA)	2417
	European Stabilisers Producers Associations (ESPA)	2414
	European Synthetic Rubber Association (ESRA)	2416
	Phosphate Ester Flame Retardants Consortium (PEFRC)	2414
	PUR Amines Catalysts (PUR)	2413/2414
	Unsaturated Polyester Resins (PES)	2416
	Vinyl2010	2416
Other	Activated Carbon Producers Association (ACPA)	2461/2466
	Active Pharmaceutical Ingredients Committee (APIC)	2441
	Association of European Manufacturers of Sporting Ammunition (AFEMS)	2466

Sector	Specific area sectors	NACE
	Cellulose ethers	2414
	Copperas	2413
	Cyanides	2413
	European Aminocarboxylates Committee (EAC)	2414
	European Biocidal Product Forum (EBPF)	2414
	European Industrial Gases Association (EIGA)	2411
	European Photographic Chemical Industry (EPCI)	2464
	European Producers of Electrofused Minerals (EPEM)	2413
	European Soda Ash Producers Association (ESAPA)	2413
	European Sulphuric Acid Association (ESA)	2413
	Federation of European Explosives Manufacturers (FEEM)	2461
	Inorganic Coagulants Producers Association (INCOPA)	2413
	Organoclays	2466
	Peracetic Acid Registration	2414
	Peroxygens	2414
	Persulphates Technical Group	2466
	Physical Sunscreen Manufacturers Association (PSMA)	2466
	Quaternisation of Starch Producers Association (QUAS)	2414
	Sodium Sulphate Producers Association (SSPA)	2413

¹⁾ Not connected to CEFIC

²⁾ A Global Industry Group of the American Plastics Council; the Association of Plastics Manufacturers in Europe (APME); and the Japan Chemical Industry Association.

According to <http://www.cefic.be/Templates/shwChemSectors.asp?NID=5&HID=18> (25 June 2004)

APPENDIX 5 COMPARISON OF CODES FOR CHEMICALS AND CHEMICAL PRODUCTS FOR NACE AND NAICS

NACE	Description	NAICS	Description
23201	Mineral oil refining	32411	Petroleum Refineries
		32511	Petrochemical Manufacturing
23202	Other treatment of petroleum products (excluding petrochemicals manufacture)	32412	Asphalt Paving, Roofing, and Saturated Materials Manufacturing
		32419	Other Petroleum and Coal Products Manufacturing
2411	Manufacture of industrial gases	32512	Industrial Gas Manufacturing
2412	Manufacture of dyes and pigments	32513	Synthetic Dye and Pigment Manufacturing
2413	Manufacture of other inorganic basic chemicals	32518	Other Basic Inorganic Chemical Manufacturing
2414	Manufacture of other organic basic chemicals	32519	Other Basic Organic Chemical Manufacturing
2415	Manufacture of fertilizers and nitrogen compounds	32531	Fertilizer Manufacturing
2416	Manufacture of plastics in primary forms	32521	Resin and Synthetic Rubber Manufacturing
2417	Manufacture of synthetic rubber in primary forms		
2420	Manufacture of pesticides and other agro-chemical products	32532	Pesticide and Other Agricultural Chemical Manufacturing
24301	Manufacture of paints, varnishes and similar coatings	32551	Paint and Coating Manufacturing
24302	Manufacture of printing ink	32591	Printing Ink Manufacturing
24303	Manufacture of mastics and sealants	?	
244	Manufacture of pharmaceuticals, medicinal chemicals and botanical products	3254	Pharmaceutical and Medicine Manufacturing
2451	Manufacture of soap and detergents, cleaning and polishing preparations	32561	Soap and Cleaning Compound Manufacturing
2452	Manufacture of perfumes and toilet preparations	32562	Toilet Preparation Manufacturing
2461	Manufacture of explosives	32592	Explosives Manufacturing
2462	Manufacture of glues and gelatines	32552	Adhesive Manufacturing
2463	Manufacture of essential oils	32599	All Other Chemical Product and Preparation Manufacturing
2464	Manufacture of photographic chemical material		
2465	Manufacture of prepared unrecorded media		
2466	Manufacture of other chemical products not elsewhere classified		
2470	Manufacture of man-made fibres	32522	Artificial and Synthetic Fibers and Filaments Manufacturing