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Energy efficiency and GHG emissions: Prospective scenarios for the Chemical and Petrochemical Industry

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Energy efficiency and GHG emissions: Prospective scenarios for the chemical and petrochemical industry

This study analyses the savings potential of energy consumption and GHG emissions from cost-effective technological improvements in the chemical and petrochemical industry up to 2050. The analysis follows a bottom-up approach; that is, it is based on information at facility level of existing plants with their production characteristics, best available and innovative technologies. The analysis includes 26 basic chemical compounds that cover 75 % of the total energy use (including energy used as feedstock) and more than 90 % of GHG emissions of the chemical sector in 2013. The bottom-up approach includes an annual cost-effectiveness analysis of the uptake of best available and innovative technologies in each facility up to 2050. The projections and assumptions used are in accordance with the reference scenario of the European Commission. In absolute terms, from 2013-2050 the total energy consumption increases by 39.2 % and the GHG emissions' decrease by 14.7 %; these values include the effect (and depend on) a demand increase of 45.6 %. In 2050, without any technological improvement, the GHG emissions and energy consumption would be 36 % and 4 % higher, respectively. The minor effect of technological improvements on energy savings can be partly explained by the fact that 73.5 % of the total energy consumed in the manufacturing of the products covered in this study is incorporated in the final products, and most of new technologies have an impact on the direct energy use, but not on the non-energy use.

Contents

Executive summary

In relation to climate action, there is an overall goal at global level to keep the average temperature increase caused by human activities below two degrees Celsius compared to pre-industrial levels. To achieve this goal, EU action alone is not enough, since the EU is responsible for only 11 % of global emissions (PBL, 2014). Nevertheless, there is a need for further progress in all areas if the EU is to achieve the 2050 goal (EC, 2011a) of reducing emissions to 80-95 % below 1990 levels. This document shows what potential contribution the European chemical and petrochemical industry could make to achieve this goal.

The first goal of this study consists of performing an in-depth analysis of the current technological status of the chemical and petrochemical industry and the second one the assessment of potential for energy efficiency and greenhouse gas (GHG) emissions reduction up to 2050. In order to achieve these objectives, a bottom-up model has been developed at facility level for the EU industry, with 2013 as starting year.

The chemical and petrochemical industry is very wide, complex and diverse. These characteristics, combined with a lack of publicly available data concerning energy use and efficiency, the variety of processes for producing even the same compound and the possibility of integration with refineries make the analysis of the industry as a whole quite challenging. As a result, the assessment had to be restricted to a selection of products that are expected to cover at least 70 % of the sector's final energy and non-energy use and GHG emissions.

In total, 26 basic chemical products were included in the analysis, covering chemical subsectors such as fertilisers, basic organic and inorganic substances, polymers and others. These products were found to cover 75 % of the total energy and non-energy use of the industry and the vast majority of the emissions in 2013. For these products, a detailed database was compiled, containing information such as the facilities producing the 26 chemical products, the production capacities, the processes used, inputs and outputs, as well as energy consumption of the processes, GHG emissions and production costs. It also includes a list of different technologies that can be applied in the processes used and can configure the current pathways so as to improve their performances, from the aspect of either energy efficiency or GHG emissions. These technologies can be already available or under development and are named best available techniques (BATs) or innovative technologies (ITs), respectively. It should be noted though, that this list cannot be comprehensive, as for some of them there is no information publicly available.

In addition, a model was developed in order to analyse the trend in energy consumption and GHG emissions to 2050. The model is based on the compiled database and future projections that are in accordance with the Reference Scenario of the European Commission (EC, 2013). At the core of this model is a cost-effectiveness analysis of the potential implementation of the best available and innovative technologies. Making these innovations take place can be the way to develop an ambitious policy that in the short-term aims for industrial production accounting for 20 % of the EU GDP by 2020, compared to around 15 % currently (EC, 2014a). A set of several scenarios was tested in order to determine the sensitivity of the chemical and petrochemical industry in key factors, such as fuel prices, GHG allowances and the maximum payback time of the technologies installed.

Key conclusions

The results obtained for the different scenarios are quite similar; meaning that already for the assumptions of the baseline scenario - that follows the Reference Scenario (EC, 2013) - practically all potential savings are materialized. The adoption of best available and innovative technologies would mean annual savings of 72.5 $Mt_{CO2.eq}$ and 225 PJ (5.4 Mtoe) by 2050. With these figures the total energy consumption of the products included in this study would increase from 2013-2050 by 39.2 % whereas the GHG emissions would decrease by 14.7 %, reaching in 2050 129 MtCO2 and 5515 PJ

(131.7 Mtoe); these values include the effect (and depend on) an increase by 45.6 % of the demand.

The savings in 2050 of 225 PJ (5.37 Mtoe) and 72.5 MtCO2 correspond to 4 % and 36 % of the energy consumption and GHG emissions that would be obtained without the contribution from the technological improvement. Regarding the small savings in energy consumption, it is worth noting that the chemical and petrochemical industry is unique among the energy-intensive industries in the fact that most of the energy consumed is stored in its products. For the period 2013-2050, the energy incorporated to the final products as raw material (that this, as feedstock), passes from 73 % of all energy consumed, to 77 %. The marginal improvement of 225 PJ is due to the fact that non-energy consumption is not much affected by the new technologies, while it represents 77 % of the total energy consumption. Most of the about 50 BATs and ITs considered in this study reduce the electricity, thermal energy or steam consumed in the processes, but not directly the feedstock needed. Out of the total savings of 225 PJ, 16 %can be attributed to savings of feedstock, while the rest 84 % (189 PJ in 2050) are savings in the electricity or fuels (used for thermal needs or steam). This reduction of 189 PJ corresponds to 13 % of the energy that would be consumed by 2050 as electricity, steam or heat without the effect of potential technological improvements. The only big changes in non-energy consumptions are expected from technologies that replace the fossil feedstock with some more sustainable alternative, such as production of hydrogen from electrolysis or for chemicals could be produced by biomass.

The chemical products that have already and will continue, to an extent, to contribute the most in savings of GHG emissions are nitric acid and adipic acid. The common characteristic of these sub-sectors is the production of nitrous oxide emissions, a pollutant with global warming potential(1) equal to 298 and they have a reduction potential of more than 75 % and 90 %, respectively. Some other chemical substances, such as ethylene, chlorine, ammonia and hydrogen have lower potentials (27 % for ethylene, 31 % for chlorine, 54 % for ammonia and 75% for hydrogen), but are playing an important role, as they cover about 33 % of the volume of all the 26 chemical products.

Regarding technologies resulting in energy or emission savings, the chemical and petrochemical industry is far too diverse and complex such as to include them in this summary. Nevertheless, there are two cross-cutting technologies worth mentioning: combined heat and power (CHP) and carbon capture and storage (CCS). CHP is already installed to a large extent in the chemical industry. According to our simulation there will be new CHP units installed with total electrical capacity 2750 MW. New CHP is foreseen in seven products: adipic acid, benzene, ethylbenzene, ethylene dichloride, vinyl chloride monomer, PVC-S and PVC-E. From the 9.4 TWh/y electricity produced via CHP, only 12 % is consumed inside the processes, while the excess is sold.

On the other hand, CCS is foreseen to be installed in all three subsectors that are sources of high purity CO_2. In the case of ammonia the technology becomes popular only in the part of the industry that is not integrated with urea production, but it is only expected, as CO_2 is usually consumed in producing urea. In the hydrogen industry, about 70 % of the facilities install CCS, while in the ethylene oxide subsector 80 %.

One of the main findings of this study is in line with the need for additional research priorities identified in the Energy Union Package (EC, 2015d), such as carbon capture and storage, so as to reach the 2050 climate objectives in a cost-effective way. Since a large part of the savings uncovered in this study comes from technologies that are not yet effectively implemented in the industry, it is clear that both an effective push and creating the right conditions are crucial factors for these potential savings to happen. In general, it is important that the European chemical and petrochemical industry remains competitive, as investments in new technologies depend mainly on this factor.

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[1] Global warming potential is a relative measure of the heat a greenhouse gas traps in the atmosphere. It is a comparative measure between each GHG and CO_2. Nitrious oxide is 298 times more intensive than CO_2.

The realisation of this work by the JRC, although an exhausting exercise, and the first of a kind for this industry, can always be extended. For example, most of the results of the model rely on factors that are exogenous and do not lack uncertainty. The treatment of that uncertainty might deserve some attention that cannot be encompassed within the scope of this work. Moreover, the analysis can be examined from additional points of view, for example, considering alternative scenarios varying the electricity price independently of the fuels prices. This latter scenario could throw additional insight about the prospects of the CHP in this industry. Also, additional information about the performance of current technologies or upcoming technologies could affect the results obtained.

1 Introduction

During the last few decades, there is increasing concern about climate change, which has created international policy responses. Since 2007, it has been agreed under the auspices of the United Framework Convention on Climate Change (UNFCCC) to limit global warming to 2°C (EC, 2007a).

Within this framework, the European Union (EU) endorsed an integrated approach to climate and energy policy, in order to mitigate climate change, increase the EU's energy security and to strengthen its competitiveness. To initialise this process, the EU adopted a series of targets, known as the "20-20-20" targets, that set three objectives for 2020: a 20 % reduction in EU greenhouse gas (GHG) emissions (from 1990 levels); raising the share of EU energy consumption produced from renewable resources to 20 %; and a 20 % improvement in the EU's energy efficiency (EC, 2016a). In a further effort, the European Council reconfirmed in February 2011 the objective of reducing GHG emissions by 80-95 % by 2050 (EC, 2011a).

Meeting the ambitions of the EU energy and climate change policy requires changes of the European energy system and has a profound effect on its technology mix. The core conviction of the EU is that Europe's industrial base should move towards a more sustainable future and focus on increased innovation and investment in clean technologies and low-carbon energy. The energy-intensive industries are playing an important role in this goal, as highlighted by the Industrial Emissions Directive (IED) (EC, 2010b). The chemical industry is one of these activities.

Chemical products and technologies are used in almost every area of the world economy. This characteristic makes the chemical industry complex. The wide range of products and technologies poses a challenge for modelling the whole industry. In addition, lack of publicly available detailed energy use and energy efficiency data, a large diversity of process routes for producing the same product and, in some cases, integration with refineries are factors that make the analysis even more challenging. This report is an effort to model the chemical industry of the EU.

The goal of this study consists of two parts: firstly, to perform an in-depth analysis of the current technological status of the chemical and petrochemical industry; and secondly, to assess the potential for energy efficiency and greenhouse gas emission reduction up to 2050. The year of base for our study is 2013, that corresponds to the latest data available at the time of writing and the boundary is the European Union's 28 Member States.

For the first goal of this study a detailed database is compiled, containing information at facility level for the European chemical industry. Specifically, the database includes information, such as an overview of the current plants capacities in the EU-28, the type of chemical product manufactured, the different processes used to produce these chemicals, inputs and outputs, as well as energy consumption of the processes, GHG emissions, production costs and technologies already installed in the facilities, for in total 26 basic chemical products. It also includes a list of technologies already available, as well as innovative, which have a potential of improving energy efficiency or reducing GHG emissions, with details such as a quantification of their potential, their investment costs and year of availability. The components of the database are collected, where possible, from both publicly available information and commercial databases. A first version of the database and model was provided by RINA VALUES S.R.I. (under contract no. 108530 to the European Commission, JRC-IET Petten).

The model is built up based on the data collected during the first part of the study. It estimates the trends in energy consumption and GHG emissions of the industry, depending only on a cost-effectiveness analysis of potential technological improvements. Other factors, such as potential policy development are incorporated into the analysis only to the extent at which they are already considered into the parameters of the reference scenario of energy and GHG trends in the European Union up to 2050 (EC, 2013).

Besides the basic scenario, which depends on the assumptions of the reference scenario, a series of six alternative scenarios are analysed, in order to evaluate the influence of some factors in the behaviour of the chemical industry. In three of them, the prices of fuels and feedstocks were simultaneously increased to several levels, while in another three the price of GHG allowances. All scenarios take for granted that cost-effective investments (those whose savings are able to recover the investment costs in less than 2 years –payback period lower than 2 years) are implemented by the industry.

This report is divided into eight chapters:

- Chapter 2 is devoted to providing an overview of the EU chemical and petrochemical sector including its energy consumption and its GHG emissions.
- Chapter 3 contains some of the main EU regulations affecting the chemical industry.
- Chapter 4 outlines the methodology followed to evaluate the EU chemical industry as a whole and demonstrates the state-of-art in the chemical industry in 2013, as this is concluded from the analysis of the individual products.
- In Chapter 5, the detailed analysis for each product considered is carried out.
- Chapter 6 outlines the model developed and used for the analysis and discusses the input variables.
- Chapter 7 summarises the different input scenarios that were considered for the sensitivity analysis.
- Chapter 8 demonstrates the results obtained by the simulation and includes the discussion of them.
- Chapter 9 outlines the major conclusions of this study.

2 Overview of the European chemical and petrochemical sector

The chemical industry is one of the largest in the world and a robust sector in Europe in terms of productivity and employment. It is also in the root of the several other industries. In 2013 its global sales were EUR 3.16 billion (Cefic, 2015) and employed over seven million people, while more than 95 % of all manufactured products rely on chemistry (IEA, 2013).

This chapter presents the current state of the chemical industry in the EU. Firstly, some general information concerning the industry's global position is provided, followed by information about energy consumption and GHG emissions.

2.1 Background of the EU chemical and petrochemical industry in the EU-28

In 2013, the global chemical industry showed marks of recovery compared to previous years, but the global sales were driven by China and in general by Asia. The chemical industry in the European Union represented 1.1 % of EU GDP (EC, 2014a) and in 2013 accounted for 16.7 % of the global sales (Cefic, 2015). This percentage increases to 20 % if we also include Switzerland, Norway, Turkey, Russia and Ukraine (Cefic, 2015). It is a mature and rather stable industry, which recovered relatively well from the economic crisis of 2008/2009, with a production level in 2013 9 % below the 2008 peak and a world market share 10 % lower than in 2001 (EC, 2014a). In the EU in 2013 chemical companies employed about 1.2 million (Cefic, 2015).

Figure 1. EU chemical industry sales in 2013 sorted by country (Cefic, 2015)

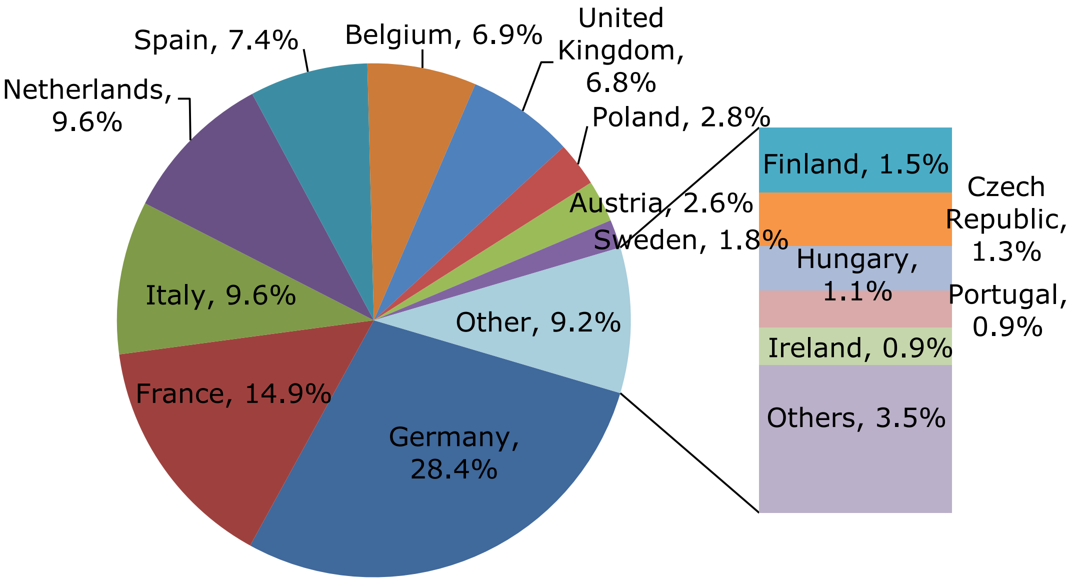

Figure 1 shows the distribution of the EU chemical industry in the 28 member states. Germany is the largest chemical producer, followed by France, Netherlands and Italy. Total EU chemicals sales were worth EUR 527 billion (2013), but only 26 % of these sales were exported out of the EU market (Cefic, 2015). If intra-EU trade is included, in 2013 the European Union was the leading exporter, responsible for 42.5 % of global exports, and the second strongest importer of chemicals in the world (after Asia), with a share of 35.3 % (Cefic, 2015).

Products from the chemical industry are present in the majority of everyday life. Chemistry is involved in different stages of multiple value added chains; it provides solutions in several areas, as alternative energy, transportation, buildings, pharmaceuticals and information technology. In the EU, about one third of all chemical production is consumed by big industrial users (rubber and plastics, construction, pulp and paper and the automotive industry), one third goes to the rest of the industrial sector (e.g. metal products, textiles, machinery, wood, mineral products etc.) and the last third goes to agriculture, health, trade, food, services and other business activities (Cefic, 2015).

According to (Cefic 2015), the position of the EU chemical industry has weakened during the last 20 years, especially in comparison with emerging Asian countries and the Middle East. Europe's market share nearly halved since 1992, from 35.2 % to 16.7 %, as already mentioned. In 2013, China's share increased to 33.2 % compared to 8.7 % in 2003 (Cefic, 2015). Asian countries have been advancing in sectors such as basic chemicals, while the Middle East is increasingly using its feedstock availability in petroleum so as to develop polymers and petrochemicals.

Concerning the future, projecting trends for the chemical industry forecast growth rates for the chemicals sales of about 3 % per year to 2050, but not distributed evenly geographically (UNEP, 2012). As has been seen from the last decade, countries such as Brazil, China, India, Russia and South Africa have higher growth rates than OECD countries. During the period 2012-2020, chemical production was predicted to change less than 30 % in Australia, Canada, Japan, Mexico, Western Europe (2) and the United States (UNEP, 2012). On the other hand, Latin America, Russia, Korea, Singapore and the Middle East had changes between 30 and 40 %, while India had 59 % and China 66 %.

2.2 Energy consumption and GHG emissions of the EU chemical and petrochemical industry

The chemical industry consumes energy and raw materials and transforms them into products. An important distinction in the use of the different types of energy carriers compared to other industries is that energy is used as raw material (or feedstock) and also consumed within the own chemical processes (in form of thermal energy or electricity consumption). GHG emissions are released when fuels are used for energy purposes. However, when fuels are used as feedstock, part of the carbon content may end up embedded in the product.

According to the most recent data (IEA, 2013), the global energy demand of the chemical industry was 15 EJ/y excluding feedstock and 42 EJ/y including feedstock, corresponding to approximately 10 % of the global energy demand or 28 % of the total industrial energy demand (IEA, 2014).

With the 2030 climate and energy framework, by 2030 the EU aims at increasing energy efficiency by at least 27 % (compared to 1990 levels) (EC, 2016b). The European chemical industry is already focused on decreasing its total energy consumption and is still continuing the efforts to improve its cost-efficient potential by investing in cost-effective efficiency measures, for instance by installing Combined Heat and Power (CHP) or setting up effective internal energy management systems (EMS). According to (Cefic, 2015), although production has increased by almost 60 % since 1990, the amount of energy consumed in 2012 was reduced by 16 %.

In 2013, the EU chemical industry consumed 53.952 million tonnes of oil equivalent (toe) (2 260 PJ) in the different processes, while the total final non-energy consumption attributed to the chemical/petrochemical industry and incorporated as feedstock, was 74.717 million toe (3 130 PJ) (Eurostat, 2016a). As shown in Figure 2, the profile of fuels used in each case is quite different. In the case of energy used as feedstock, 81.4 % is

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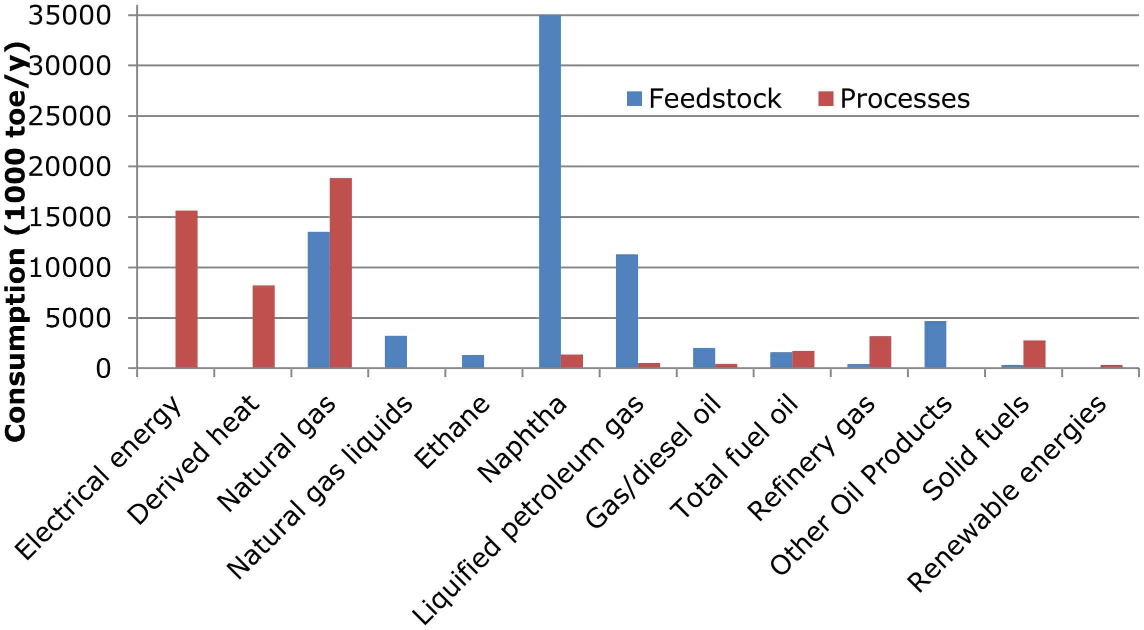
(2) Western Europe for the chemical studies usually included EU (at least EU15) and Norway or Switzerland.

petroleum products and mainly naphtha (46.9 %), while natural gas is covering 18.1 % of the total energy. On the other hand, natural gas (25.2 %), electrical energy (20.9 %) and petroleum products (14.2 %) are the main forms of energy used in the processes (Eurostat, 2016a).

Figure 2. Fuels consumed in the European chemical industry as feedstock and in the processes (Eurostat, 2016a)



As a major energy user, the chemical industry worldwide generates 5.5 % of carbon dioxide (CO_2) emissions (7 % of the global GHG emissions) and is responsible for 17 % of all industrial CO_2 emissions (IEA, 2013). According to the European Pollutant Release and Transfer Register (E-PRTR), the chemical industry in EU-27 emitted in total 145 Mt $CO_{2.eq}$ in 2013 (E-PRTR, 2016). In 1990 this value was 327.3 Mt $CO_{2.eq}$, which means that since 1990 there has been a decrease by 55.7 % of the total GHG emissions (Figure 3). If we consider the increase in production, which expanded by 60 % during the same period (Cefic, 2015), these results are even more relevant, demonstrating the commitment of the EU chemical industry in reducing its carbon footprint. It is interesting to note, though, that the application of abatement techniques has decreased N_2O emissions more than 90 %, while CO_2 emissions (3) have decreased only by 9 % (Figure 3).

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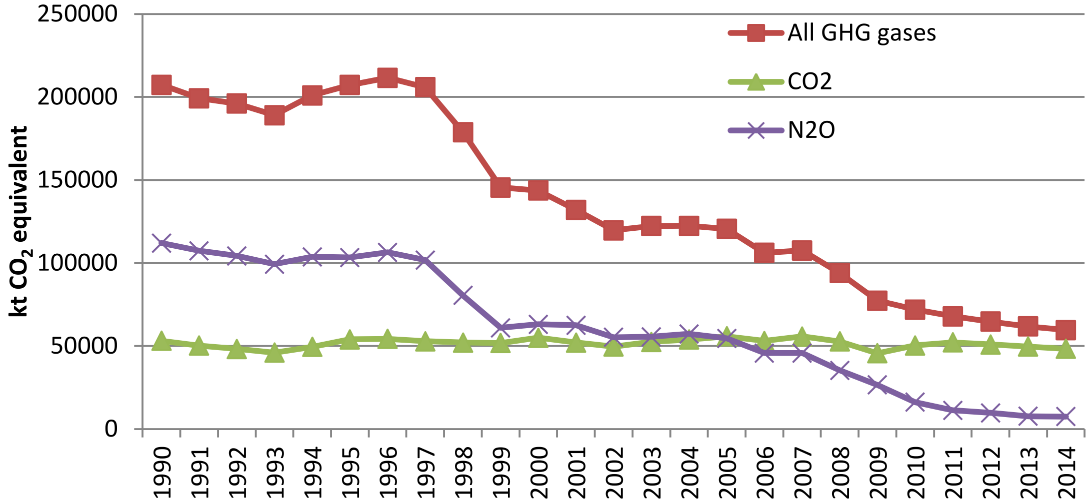
(3) These emissions are absolute CO_2 and not $CO_{2.eq}$, so N_2O emissions are not already included in them.

Figure 3. Comparative evolution of total GHG emissions and absolute CO_2 and N_2O emissions in the European chemical industry in the period 2007-2014 (UNFCCC, 2016)



More than 70 % of the total GHG emissions were CO_2 emissions. The second and third most important pollutants are methane and nitrous oxide with 15 201 t_{CH4} and 24 823 t_{N2O} respectively (E-PRTR, 2016). The global warming potential of the main GHG gases is shown in Table 1.

Table 1. Global warming potential for the main GHG gases

Greenhouse Gas	**Formula**	**100-year GWP**	
		IPCC[1]	**EC**[2]
Carbon dioxide	CO_2	1	1
Methane	CH_4	25	
Nitrous oxide	N_2O	298	298
Sulphur hexafluoride	SF_6	22 800	

[1] Source (IPCC, 2007a)
[2] Source (EC, 2014b)

3 Policy context

Different policies related to environment, climate, energy, product or consumer protection have originated legislation relevant for the chemical industry. This chapter summarises some basic EU legislation with high impact on the chemical industry, but is neither aiming to include all policies affecting the chemical industry, nor explaining them in detail; the interested reader can find a more detailed description on the CCA reports (EC, 2016c).

A cornerstone of the European legislation to minimise pollution arising from industrial activities is the directives on integrated pollution prevention and control (IPPC). The first one was adopted in 1996 (Directive 96/61/EC(4) was replaced in 2008 by Directive 2008/1/EC (5). Directive 2010/75/EU on industrial emissions (IED) (EC, 2010b), replaced the later IPPC Directive and brought together a total of seven directives. It applies to industrial installations including those producing organic and inorganic chemicals, fertilisers and biocides, pharmaceutical products and explosives on industrial scale by chemical or biological processing of substances; and installations refining mineral oil and gas. The detailed list of these installations can be found in Annex I of the Directive. These installations are obliged to:

- take all appropriate preventing measures against pollution;
- apply best available techniques (BATs);
- cause no significant pollution;
- reduce, recycle or dispose waste in a manner which creates least pollution;
- use energy efficiently;
- prevent accidents and limit their impact;
- remediate the sites when the activities are ceased.

In the framework of the IED and the previous IPPC Directive, reference documents on Best Available Techniques (BATs), dedicated to the different types of installations of Annex I of these directives, are regularly prepared and updated as a result of exchange of information between Member States and the industry. These documents are the main reference used by the authorities in the Member States so as to issue operating permits. The decision granting a permit must contain a number of specific requirements, including emission limit values (ELVs) for polluting substances, based on BATs. The reference documents do not propose ELVs, but help to determine the appropriate BAT-based conditions or to establish general binding rules under Article 17 of the IED.

Due to the diversity of the chemical industry, there are a several Reference documents encompassing all the chemical industry:

- large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers (EC, 2007b)
- large Volume Inorganic Chemicals – Solids and other Industry (EC, 2007c)
- production of Chlor-alkali (EC, 2014c)
- large Volume Organic Chemical Industry (EC, 2014d)
- refining of Mineral oil and gas (EC, 2015a)

Besides the IED, the legislation related to the EU Emissions Trading System (EU-ETS) is also important in the effort to combat climate change reducing industrial GHG emissions in a cost-effective way. Directive 2003/87/EC (6) and its amendments (Directives 2004/101/EC, 2008/101/EC and 2009/29/EC) establish a scheme for GHG emission

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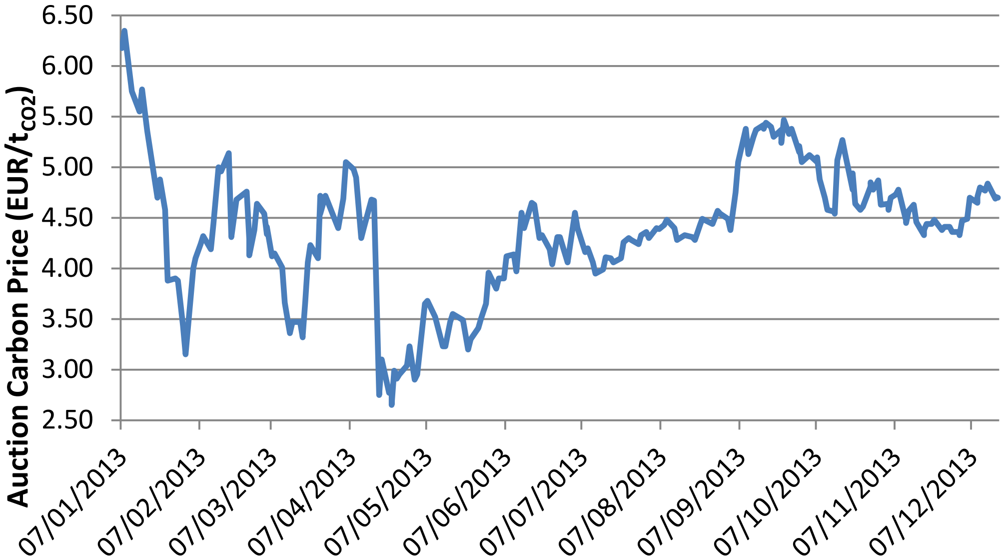
(4) Further information: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31996L0061:en:HTML

(5) Further information: http://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=URISERV:l28045&from=EN

(6) Further information: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32003L0087&from=EN

allowance trading that sets a cap in the total amount of greenhouse gases. This cap decreases according to the police objectives established. Companies in sectors covered by the EU-ETS have to render the allowances of CO_2 emitted. Within this limit, the companies receive or buy emission allowances that can be traded if needed. Every year each company has to cover all its emissions with enough allowances, otherwise heavy fines are imposed. Industrial installations that are exposed to a significant risk of carbon leakage receive higher share of free allowances, in order to ensure their competitiveness. The amount of free allocations of allowances is calculated based on the production of each installation multiplied by the benchmark value (7) for the particular product. Installations in sectors that are exposed in carbon leakage receive 100 % of this quantity for free (EC, 2016d). As a result of this legislation, a price is set on carbon, which fluctuates according to the market of trading emission allowances. In 2013 the average carbon price was EUR 4.38/t_{CO2} and its variation during the whole year is shown in Figure 4 (EEX, 2016).

Figure 4. Fluctuation of the carbon price is the EU ETS auctions during 2013 (EEX, 2016)



The sectors included in the EU-ETS are power and heat generation stations, commercial aviation and energy-intensive industry sectors (oil refineries, acids and bulk organic chemicals, steel and iron production, cement, aluminium and metals, lime, glass, pulp and paper etc.), accounting for the CO_2 they emit; installations producing nitric, adipic, glyoxal and glyoxlic acids, accounting for the N_2O they emit; and aluminium production sites, accounting for the perfluorocarbons (PFCs). For these sectors, participation in the scheme is mandatory with some exceptions (EC, 2015b).

Besides climate and environmental legislation, the chemical industry is also affected by the energy related directives. According to the Energy Efficiency Directive (EC, 2012a) a set of binding measures are established to ensure major energy savings for consumers and industry alike. Companies are encouraged to monitor their energy levels and make audits of their energy consumption to help them identify ways to reduce it. The Renewable Energy Directive (EC, 2009a), on the other hand, is promoting the production of energy from renewable sources, requiring that at least 20 % of the EU total energy needs are covered by renewable by 2020.

This study is focusing mainly on the energy efficiency and the GHG emissions of the chemical industry and therefore, the legislations presented up to this point are the most interesting. Nevertheless there is a series of other legislations that the chemical industry has to comply with. The Regulation on registration, evaluation, authorisation and

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(7) The product benchmarking values reflect the average GHG emissions of the 10% best performing installations in the EU

restriction of chemicals (REACH) (EC, 2006) is affecting directly the chemical industry and it renders industry responsible for assessing and managing risks posed by chemicals and providing safety information to the users. Other legislation affecting the chemical industry concerns restriction of hazardous materials (Directive 2002/95/EC (8)), waste treatment (Directive 2008/98/EC (9) and Directive 1999/31/EC (10)), chemical accident prevention (Directive 2012/18/EU (11)), water quality (Directive 2000/60/EC (12)) and waste water treatment (Directive 91/271/EEC (13)), as well as labelling and packaging (Regulation 1272/2008 (14)) and health and safety (Directive 2014/27/EU (15)).

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(8) Further information: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32002L0095&from=EN

(9) Further information: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0098&from=EN

(10) Further information: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31999L0031&from=EN

(11) Further information: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32012L0018&from=EN

(12) Further information: http://eur-lex.europa.eu/resource.html?uri=cellar:5c835afb-2ec6-4577-bdf8-756d3d694eeb.0004.02/DOC_1&format=PDF

(13) Further information: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31991L0271&from=EN

(14) Further information: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:353:0001:1355:en:PDF

(15) Further information: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32014L0027&from=EN

4 Methodology and current status of the EU chemical and petrochemical industry

This study aims to analyse the improvement margin of energy efficiency and GHG emissions of the sector up to 2050 for different scenarios. In order to achieve this ambitious goal, the first and not minor milestone is mapping the current technological status of the chemical and petrochemical industry in the 28 Member states of the European Union. The second milestone is the estimation of the future performance of the chemical industry up to 2050. The methodology for this second part of the study is presented in Chapter 6.

Two key challenges arise in attempting to fulfil the first milestone: firstly the uncountable number of chemical products and secondly the fact that many products are not produced by a single production process. Further difficulties are added, due to lack of publicly available detailed energy use and energy efficiency data, complex production sites with high level of heat integration, high levels of combined heat and power (CHP) potentials and in some cases integration with refineries. The heterogeneity of the industry expands further due to some characteristics of the industries, such as different levels of technological advancement for each process.

The chemical sector has a long tradition of energy analysis via benchmarking surveys (e.g. for ammonia by the International Fertiliser Industry Association and for steam cracking by the Solomon Associates) (UNIDO, 2010a), but they are usually confidential. Few studies have been found in the literature trying to map the chemical industry. Usually the sector is limited to a few large volume products (Phylipsen et al., 2002; Neelis et al., 2007), while others include more products and follow either a top-down or a bottom-up approach (Saygin et al., 2011; Serpec-cc, 2009).

In this study, in order to achieve our objective, a bottom-up model has been developed at facility level for the EU Chemical Industry. This chapter presents the methodology and the model followed. It includes a discussion of the boundaries of the study, a summary of the current technologies present in the industry and an explanation of the best available techniques (BATs) and innovative technologies (ITs) considered. The last two sections of this chapter refer to the methodology applied concerning cogeneration, a technology present in the majority of the industries and our approach about energy consumption and GHG emissions.

4.1 Definition of boundaries

Due to the challenges mentioned above, it would be unrealistic to analyse all chemical and petrochemical products. On the contrary, a more realistic approach is to construct specific energy consumptions and GHG emissions for key products. The first step of our analysis is, therefore, a literature screening within the variety of products, in order to select a group of the most important chemical and petrochemical key products that are expected to cover at least 70 % of the sector's final energy and non-energy use and GHG emissions.

Data for the total GHG emissions per product is not generally available. The benchmarking study by Ecofys on the chemical industry (Ecofys, 2009) includes a ranking of the most emission-intensive activities, but it is based on data from 2007/2008. The European Pollutant Release and Transfer Register (E-PRTR) includes much more detailed and up-to-date information (E-PRTR, 2016). The whole of the chemical industry in EU27 emitted in total 145 Mt $CO_{2.eq}$ in 2013, while if only selected NACE codes are considered (industrial gases, organic and inorganic basic chemicals, fertilisers and plastics in primary forms) the emissions add up to 138 Mt $CO_{2.eq}$ in 2013. The European Environmental Agency (EEA) reports GHG emissions for the chemical industry and some individual categories, as described by IPCC (Table 2) (EEA, 2015). In 2013, the EU-28 chemical industry reported in total 62 million tonnes CO_2 equivalent. Besides the chemical industry (as it is defined in the EEA inventory – category 2B in the reporting format), the boundaries of this study include also emissions from the fuel combustion in the chemical industry, which is included in category 1.A.2.c and amounted to 75.3 million tonnes CO_2 equivalent (EEA, 2015).

Table 2. Greenhouse gas emissions in the EU-28 chemical industry (EEA, 2015)

Emission sector (Category in EEA report)	Emissions (million tonnes $CO_{2.eq}$)	
	1990	2013
Ammonia production (2.B.1)	32.2	26.9
Nitric acid production (2.B.2)	49.5	5.0
Adipic acid production (2.B.3)	57.6	0.6
Caprolactam, glyoxal and glyoxylic acid production (2.B.4)	4.3	2.3
Carbide production (2.B.5)	1.7	0.3
Titanium dioxide production (2.B.6)	0.25	0.29
Soda ash production (2.B.7)	2.2	2.1
Petrochemical and carbon black production (2.B.8)	15.5	17.1
Fluorochemical production (2.B.9)	40.8	2.9
Other chemical industry (2.B.10)	2.0	4.5
Total chemical industry (2B)	206.1	62.0
Fuel combustion – Chemicals (1.A.2.c)	118.5	75.3
Total	324.6	137.3

In order to pre-select the key processes included in this study we estimate the cumulative percentage of total $CO_{2.eq}$ emissions of the chemical industry, using information from (Ecofys and EEA). Table 3 shows the key processes and their role in the total GHG emissions of the chemical industry, according to the literature (Ecofys, 2009; EEA, 2015).

Table 3. Ranking of the most emission intensive industries in the chemical industry according to (Ecofys, 2009; EEA, 2015)

Processes	GHG emissions	
	Share (%)	Cumulative (%)
Nitric acid	3.8	3.8
Steam cracking	25.5	29.1
Ammonia	19.6	48.7
Adipic acid	0.4	49.2
Hydrogen / Syngas (incl. Methanol)	9.2	58.3
Soda ash	1.5	59.9
Aromatics (BTX)	4.8	64.7
Carbon black	3.4	68.0
Ethylene chloride / Vinyl chloride / PVC	2.6	70.6
Ethylbenzene / Styrene	2.9	73.6
Ethylene oxide / Monoethylene glycol	2.6	76.2
Chlorine	10.6	86.8
Other	13.2	100.0

These key processes lead to a selection of 26 products. Some processes involve only one product (e.g. nitric acid, adipic acid, carbon black and soda ash), while other more than one. From the steam cracking process (SC), the products selected are ethylene, propylene, butadiene and butenes, while the main aromatics considered are benzene, toluene and xylene. Urea is included in the ammonia process. The detailed list of the products included in the scope is shown in Table 4.

Table 4. Products to be included in this study

Nr.	Product name	Molecular formula
1	Nitric acid	HNO_3
2	Ethylene	C_2H_4
3	Propylene	C_3H_6
4	Butadiene	C_4H_6
5	Butenes	C_4H_8
6	Acrylonitrile	C_3H_3N
7	Ammonia	NH_3
8	Urea	CH_4N_2O
9	Adipic acid	$C_6H_{10}O_4$
10	Hydrogen	H_2
11	Methanol	CH_4O
12	Soda ash	CN_2O_3
13	Benzene	C_6H_6
14	Toluene	C_7H_8
15	Xylene	C_8H_{10}
16	Carbon black	C
17	Ethylene oxide	C_2H_4O
18	Monoethylene glycol	$C_2H_6O_2$
19	Ethylene dichloride	$C_2H_4Cl_2$
20	Vinyl chloride monomer	C_2H_3Cl
21	PVC-S	$(C_2H_3Cl)_n$
22	PVC-E	$(C_2H_3Cl)_n$
23	PVC recycled	$(C_2H_3Cl)_n$
24	Ethylbenzene	C_8H_{10}
25	Styrene	C_8H_8
26	Chlorine	Cl_2

In order to simplify the calculations some basic assumptions have been made:

- The plants are operating 24 hours a day during 90 % of the year, unless stated differently in the data.
- The components in the systems behave as ideal gases or ideal solutions.
- In the environmental analysis, only GHG are considered.
- If the fuel used for producing thermal energy is not stated clearly in the description of each process, natural gas is assumed for the calculation of the emission factors.
- If in the information available for the different ITs, there is no clear indication about the year the investment costs refer to, the assumption will depend on the date of the corresponding reference.

4.2 Data sources for current technologies

The first milestone of this study is a description of the current technological status of the industry. In order to perform an in-depth analysis, a bottom-up approach at facility level is followed. The current technology pathways used in the industry were considered for each key process or products included in the analysis. As a result, a database was developed that includes data of 1004 small, medium and large scale chemical plants in the EU-28(16). The number of facilities in our study exceeds the ones used to determine the value of the benchmarking values used in the carbon leakage provision of the ETS.

According to the statistical classification of economic activities in the EU, the plants selected corresponded to NACE codes that associate with the products preselected. The NACE codes included in this study (Table 5) are subcategories of the C20 code "Manufacture of chemicals and chemical products" (EC, 2008).

Table 5. List of NACE codes considered in this study

NACE code	Activity description
C20.11	Manufacture of industrial gases
C20.13	Manufacture of other inorganic basic chemicals
C20.14	Manufacture of other organic basic chemicals
C20.15	Manufacture of fertilisers and nitrogen compounds
C20.16	Manufacture of plastics in primary forms

The information at facility level about the EU28 chemical industry has been gathered in a database that includes information on the production capacity and product manufactured, the production pathways, on the energy consumed and on the presence of cogeneration units. Most of the plant specific data were provided by (ICIS, 2012) and (IHS, 2015a), chemical/petrochemical market information providers, complemented by publicly accessible technical or scientific data. Due to confidentiality restrictions, the databases contain exclusively data on the processes in use at plant level and installed capacities. The information about energy consumptions and emission levels were collected from publicly available literature. Emission factors and lower heating (or net calorific) values (LHV) of each fuel type considered in this study are according to the 2006 IPCC Guidelines (IPCC, 2006a) and the relevant Commission Regulation (EC, 2012b) and are shown in Table 6.

Table 6. Fuel emission factors and lower heating values

Fuel type	Emission factor (t_{CO2}/ GJ)	Lower Heating value (MJ/kg)
Natural gas	0.0561	48.0
Naphtha	0.0733	44.5
Heavy fuel oil	0.0774	40.4
Gas/Diesel oil	0.0741	43.0
Electricity[1] (MWh)	0.465	
Steam[2]	0.072	

[1] Source (EC, 2012c)
[2] Source (Ecofys, 2009)

Data about the use of cogeneration units were provided by (ESAP, 2012). This database provides technical data on cogeneration systems at unit level, considering units above 100 kWe.

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(16) For some products (hydrogen and PVC) some fictitious plants were created to represent special cases of the industry and as a result the number of the facilities included in the study cannot be directly compared with the actual facilities of the whole chemical and petrochemical industry.

4.3 Energy consumption and GHG emissions

Due to the fact that neither of the databases (ICIS, 2012; IHS, 2015a) contain information about resources, energy consumptions and GHG emissions at facility level, the energy consumption per plant and the GHG emissions were calculated according to the data collected for each plant and process.

The energy use for each process can be measured by either the specific energy consumption (SEC) or the energy efficiency index -as developed by (Phylipsen et al., 2002) and (Neelis et al., 2007) (UNIDO, 2010a). Specific energy consumption is defined as the final energy use (fuels, steam or electricity) required to operate a process for the production per unit of product, since the fuels enters the factory gate to output of the product. On the other hand, the energy efficiency index is used when there is more than one product from the process and therefore the total energy use cannot be expressed as a function of their total physical output. In this study we use the first type of energy indicator; therefore, for each process the SEC is calculated based on the process performances according to literature.

For each plant, the total annual consumption of energy is calculated according to the generic formula:

*Total annual energy consumption = SEC * Installed capacity * Load factor*

For the total GHG emissions, we follow the definition used in the EU ETS (EC, 2011b). The benchmark values include all production-related direct emissions (the process direct emissions and the emissions due to fuel use for energy production). Emissions due to electricity used are usually considered outside the boundaries of the benchmark values, but are inside for processes where direct emissions and emissions from electricity are to a certain extent interchangeable (EC, 2011b). If electricity emissions are included in the total GHG emissions or not depends on the product and the distinction is included in Table 7.

In order to convert fuels that are consumed to emissions, emission factors are used. The fuel emission factors that are used in this study are the ones mentioned in (IPCC, 2006a) and (EC, 2012b) (Table 6).

Table 7. Benchmark values associated to the products considered in this study (EC, 2011b; 2012d)

Product	Benchmark value ($t_{CO2.eq}/t_{product}$)	Consideration of exchangeability of fuel and electricity
Nitric acid	0.302	Without
Ethylene	0.702	With
Propylene	0.702	With
Acrylonitrile	-	-
Ammonia	1.618	With
Urea	-	-
Adipic acid	2.790	Without
Hydrogen	8.850	With
Methanol	-	-
Soda ash	0.843	Without
Benzene [1]	0.155	With
Toluene [1]	0.155	With
Xylenes [1]	0.155	With
Carbon black	1.954	With
Ethylene oxide	0.512	With
Monoethylene glycol	0.512	With
Ethylene dichloride	-	-
Vinyl chloride monomer	0.204	Without

PVC-S	0.085	Without
PVC-E	0.238	Without
PVC recycled	-	-
Ethylbenzene	-	-
Styrene	0.527	With
Chlorine [2]	1.144	With

[1] For aromatics, the benchmark value is expressed in (EC, 2011b) per CO_2 weighted tonne of mix of aromatics (0.0295 $t_{CO2.eq}$/CWT) and the CWT function for aromatic solvent extraction is equal to 5.25. The multiplication of these two values results in the value displayed in Table 7.

[2] In the case of chlorine, the benchmark value in (EC, 2012d) is 2.461 MWh/$t_{product}$ and it is converted to 1.144 $t_{CO2.eq}/t_{product}$, by using the emission factor of electricity (Table 6).

As the energy consumption and GHG emissions calculations are based on literature, in the model all facilities producing the same product with the same manufacturing process have the same specific energy consumption and CO_2 emissions. However, benchmarking curves for the CO_2 emissions, according which the benchmarking values (17) were adopted by the European Commission (EC, 2011b) show that no two facilities are similar. This information at facility level is used to modify the initial values of CO_2 emissions in a manner, referred to as calibration that resembles the actual benchmarking curves.

Calibrated specific CO_2 emissions for each plant are estimated by the following equation:

$$CO_{2.p,c} = (Cap_p / Cap_{ref})^n * CO_{2.p,o}$$

where $CO_{2.p,c}$ is the calibrated specific CO_2 emissions at plant level, $CO_{2.p,o}$ the original specific CO_2 emissions of the plant, Cap_p is the plant capacity, Cap_{ref} is the plant reference capacity and n is a calculated scale coefficient.

The benchmark values, established by the European Commission for each cluster of facilities, relates to 10% of the best performers in terms of $CO_{2.eq}$ emissions. The values adopted for each product considered in this study (EC, 2011b; EC, 2012d) can be seen in Table 7.

Benchmarking curves for CO_2 emissions and energy consumptions in the chemical industry are available only for some of the products (Ecofys, 2009). Cap_{ref} and n are parameters obtained through the model and adopted to fit the given curves. With this calibration, each facility of the model is assigned one of the actual CO_2 emissions and energy consumptions recorded by the industry in 2007/08. This calibration enables the model to use values that are quite close to the real ones.

4.4 Best available techniques (BATs) and Innovative Technologies (ITs)

According to the bottom-up approach followed, the potential for energy efficiency improvement is the difference between the average current energy consumptions and the consumption if best available technologies (BATs) or innovative technologies (ITs) were implemented in the chemical processes.

Best Available Techniques (BATs) are different technologies that can be applied in the processes used and can configure the current chemical pathways in order to improve their performance. According to the Industrial Emissions Directive (IED) (EC, 2010b), BATs are the most effective and advanced stage in the development of activities and their methods of operation. They indicate the practical suitability of particular techniques for providing the basis for emission limit values and other permit conditions designed to

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(17) The benchmarking values are used in order to determine the free allocations of allowances under the EU-ETS legislation, which is explained briefly in Chapter 3. They reflect the average emissions of the 10% best performing installations in the EU.

prevent or reduce emissions and the impact on the environment as a whole. In the present study, BATs are considered to be deployed technologies that can be applied in multiple plants and whose integration will enable significant reductions in energy consumption or GHG emissions. It should be noted that we follow the term best available techniques that is used in the legislation, but we are neither limited nor bound by it in the technologies that are taken into consideration.

Innovative Technologies (ITs) are technologies either under development or applied in a small scale, but not yet implemented or well established in Europe. In the IED (EC, 2010b) they are named "emerging techniques" and are defined as novel techniques, not yet commercially developed, that could provide either a higher general level of protection of the environment or at least the same level of protection of the environment and higher cost savings than existing BATs. For this study, if there is no information about the years of expected availability of an IT, that time has been estimated based on the following assumptions:

- If the technology is close to be ready at industrial scale, it is assumed to be readily available. (TRL ≥9).
- If the technology is still under development, but close to scaling up, then 2020 is assumed to be its year of availability (TRL 7-8).
- If the technology is still under development, but far from technical implementation (3 < TRL ≤6), its year of availability is assumed to be 2030.
- If the technology is in the early stages of basic research (TRL ≤ 3), its year of availability would have to be after 2040. Nevertheless in most of the cases of so early technologies, there is not enough information concerning their performances and as a result they fall outside the scope of this study.

The BATs and ITs considered in this study are analysed per product in Chapter 5. The parameters that were taken into consideration for the advantage of using a BAT or an IT in a plant are heat and electricity consumptions, feedstock consumptions and GHG emissions, all per tonne of product. If a technology leads to reductions in electricity, thermal or feedstock consumptions, which will effectively lead to reduction of CO_2 emissions, no additional GHG reduction is taken into consideration, as this would be double counting. Technologies, whose improvement potential turned out to be lower than 3% of the total SEC of the process or have restrictions in their application in the industry, are disregarded(18). Concerning innovative technologies, if the availability of it is estimated to be further than 2040, they are not taken into consideration in this study.

As decision making criterion to decide whether an investment in a BAT or an IT is carried out we rely on the payback period. This criterion considers feasible investments when their investments costs are compensated (paid back) by the annual savings in a less than a given number of years (payback period). As a result, information concerning the economics of the technologies is also included in the database. This information is collected from publicly available sources. In order to compare the different technologies and use them in the scenarios, the investment costs should be referring to year 2013 and therefore, the historical data collected from the literature needs updating. Cost indices are available, so as to estimate the escalation costs over the years. The Chemical Engineering Plant Cost Index (CEPCI) is published monthly in the journal *Chemical Engineering* and is the index mostly widely used for the chemical industry. For this study, the updates are done using annual indices (Chemical Engineering 2009; 2014) and according to the following equation (Towler and Sinnott, 2013):

*Cost in year A = Cost in year B * (Index in year A / Index in year B)*

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(18) This restriction is applied in this study, as there are no actual data concerning the SEC of the individual plants, but only information about the theoretical processes. The SEC calculated for each plant in this study is based on this information and savings that are less than 3% are considered to be too close to the level of uncertainty of the calculation.

When applying this equation and the CEPCI indices, it is important to note that the indices refer to USD and therefore, the costs have to be expressed in this currency. In this study, if there is no clear indication for the year of reference of the investment costs found in the literature, the date of publishing the data is assumed to be the reference.

4.5 Cross-cutting BATs and ITs

4.5.1 Combined Heat and Power (CHP)

4.5.1.1 CHP in the European chemical and petrochemical industry

Combined Heat and Power (CHP) or cogeneration is a technology used to improve energy efficiency through the generation of both heat and power in the same plant. Heat is usually used for processes or space-heating purposes, while electricity can be sold out.

Since 2004 the European Commission is promoting cogeneration with the issuing of Directive 2004/8/EC (19) which have been facilitating the installation and operation of electrical cogeneration plants. This action was further strengthened under the energy efficiency directive, Directive 2012/27/EU (EC, 2012a), that advices the member states to carry out a comprehensive assessment of the potential for the application of high-efficiency cogeneration and adopt policies encouraging it.

In 2013, the total CHP electrical capacity installed in the EU-28 was 112.97 GW, 24.1% of which is located in Germany (Eurostat, 2015). In 2013, the share of CHP in the gross electricity generation in the EU-28 was 11.7%. Slovakia and Denmark have the highest power production share (77.0 and 50.6% respectively), while the lowest were in Greece, France and Cyprus (3.4%, 2.4% and 1.4% respectively). Malta is the only EU country that does not use CHP. The total CHP heat production was 2899.3 PJ and the total CHP electricity generation was 382.0 TWh (Eurostat, 2015). In 2013, the overall load factor of CHP units installed in Europe is 0.39 and this value is taken as reference for estimated the energy produced by each CHP unit. The load factor is calculated as following:

$$\textit{Load factor}_{CHP} = \textit{Total electricity production} \ / \ (\textit{Total CHP electrical capacity} * 8\ 760\ \mathrm{h})$$

A CHP unit has four basic elements: (1) a prime mover (engine or drive system), (2) an electricity generator, (3) a heat recovery system and (4) a control system. The prime mover, while driving the electricity generator, creates usable heat that can be recovered. CHP units are generally classified by the type of application, prime mover and fuel used. The amount of energy produced depends on the Overall Efficiency (OE) (20) of each technology. CHP plants generally convert 75-80% of the fuel source into useful energy, while the most modern plants reach efficiencies of 90% (IPCC, 2007b). The amount of electricity produced is compared to the amount of heat produced and is expressed as the power to heat ratio. If this ratio is less than 1, the amount of electricity produced is less than the amount of heat.

Optimal CHP systems are designed as a source of heat, with electricity as a by-product. If the electricity demands of the facility are not met with the presence of a CHP unit, the additional electricity needed is bought from the grid. Additional heat demand is typically supplied by stand-by boilers or boost heaters.

There are significant economic and environmental advantages to be gained from CHP use. Some of these advantages are the following (IEA, 2008; MNP, 2008):

- energy production exactly where it is needed;

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(19) Further information: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32004L0008&from=EN

(20) Overall efficiency is defined as the sum of electricity and mechanical energy production and useful heat output divided by the fuel input used for heat produced in a cogeneration process [EC, 2012a]

- reduction of transmission and distribution losses;
- overall cost savings (for the whole system) for energy use (it should be noted that a facility with CHP has to face the extra fuel cost that would not be necessary if all power is bought to the grid;
- lower CO_2 emissions of the system (but not for the facility with CHP unit);
- Reduced reliance on imported fossil fuels;
- reduced investment in energy system infrastructure, but again the investment avoided is in the power system at the partial expense of the cost of the CHP unit;
- enhanced electricity network stability.

Concerning emissions, it is important to note that integration of a CHP unit has a double effect. On one hand it leads to increased direct emissions due to the increase in fuel consumed to feed the CHP and produce heat and electricity. On the other hand it results in a reduction of indirect emissions, thanks to avoiding electricity bought from the grid.

Energy-intensive industrial sites have been traditional hosts for CHP facilities and represent more than 80% of the total global electric CHP capacities (IEA, 2007). In general, CHP units are applicable to plants with significant heat demands at temperatures within the range of medium or low pressure steam.

For the chemical industry, the general characteristics are high and medium temperature demands; typical system sizes 1-500 MWe, while the typical prime movers are steam turbines, gas turbines, reciprocating engines and combined cycles for the larger systems (IEA, 2008). In total, high temperature demands make up 43% of the total industry demand, while medium and low demands correspond to 30% and 27% respectively (Ecoheatcool, 2005-2006). Any liquid, gaseous or solid fuels, as well as industrial process waste gases are used as fuel sources and there is moderate to high ease of integration with renewables and waste energy.

Unfortunately, Eurostat has stopped publishing statistics on CHP generation and capacity by economic activity. The most recent publication (Eurostat, 2006) refers to data from 2002 and EU-25. According to those data, the chemical and petrochemical industry had in total 17.8 GW installed CHP capacity, when the total CHP capacity in EU-25 was 91.6 GW. By extrapolation of this correlation, the CHP installed capacity in chemical and petrochemical industry in 2013 would correspond to around 22 GW.

As mentioned earlier, there are four types of typical prime movers:

- *Steam turbines*: It is the simplest cogeneration power plant, where electricity is generated from the steam produced in a boiler. They can operate in a variety of fuels including oil products, natural gas, solid waste, coal, wood, wood waste and agricultural by-products. The capacity of commercially available steam turbines typically ranges between 50 kW to more than 250 MW (EPA, 2015). The power to heat ratio of these plants is normally 0.3-0.5 (EC, 2009b).
- *Gas turbines*: Gas turbines are typically available in sizes in the range 0.5 MW to more than 300 MW and can operate on a variety of fuels such as natural, synthetic or landfill gas and fuel oils (EPA, 2015). Usually they are used with heat recovery, where heat is generated with the hot flue-gases of the turbine. Temperatures can be as high as 430-480°C for smaller industrial turbines and up to 590°C for new large central station utility machines.
- *Internal combustion or reciprocating engines*: In these systems, heat can be recovered from lubrication oil and engine cooling water, as well as from exhaust gases. Chemically bound energy in fuel is converted to thermal energy by combustion. They have high single cycle efficiency and relatively high exhaust gas and cooling water temperatures.

- *Combined cycle*: These plants consist of one or more gas turbines connected to one or more steam turbines. The heat from the exhaust gases of the gas turbine is recovered for the steam turbine. The advantage of this system is a high power to heat ratio and a high efficiency.

These types of prime movers are further described and compared in the BREF for Energy Efficiency (EC, 2009b). Table 8 shows the default values for power to heat ratio suggested in Directive 2012/27/EU (EC, 2012a) and the overall efficiencies (IPCC, 2007b).

Table 8. Default power to heat ratios and overall efficiencies for CHP technologies

Type of CHP unit	Power to heat ratio (EC, 2012a)	Overall efficiency (IPCC, 2007b; EC, 2009b)
Combined cycle gas turbine with heat recovery	0.95	0.85
Steam backpressure turbine	0.45	0.80
Gas turbine with heat recovery	0.55	0.76
Internal combustion engine	0.75	0.875

Concerning installation costs, they can vary significantly and can depend on geographical factors, specific site requirements, whether the system is a new or retrofit application and if it includes emission control systems (EPA, 2015). There is definite economy of scale, with larger projects having lower costs per kW. The values available in the literature (EPA, 2015; Serpec-cc, 2009; IEA ETSAP, 2010) for representative CHP systems are summarised in Table 9. (EPA, 2015) includes a detailed breakdown of the estimated values and reports all assumptions. In (Serpec-cc, 2009) they assume that CHP investment costs will not decrease over time due to learning effects. The values from (Serpec-cc, 2009) and (IEA ETSAP, 2010) are rather in accordance, while the values reported by (EPA, 2015) are a bit higher.

In the current study, the CHP facilities considered are of industrial scale, therefore we assume that the investment costs will be rather at the lowest range of the values from literature, due to scale of size.

Table 9. Costs of typical CHP systems

Type of CHP unit	Size	Costs		Source
		Investment	Operation/ maintenance	
		(EUR$_{2013}$/kW)		
Combined cycle	>100 MW	750		(Serpec-cc, 2009)
	50-100 MW	1 000		(Serpec-cc, 2009)
		750-1 200	35	(IEA ETSAP, 2010)
Gas turbine	25-50 MW	815		(Serpec-cc, 2009)
	<25 MW	1250		(Serpec-cc, 2009)
	0.5-15 MW	2 500-940		(EPA, 2015)
		650-1 050	27	(IEA ETSAP, 2010)
Backpressure steam turbine	0.5-15 MW	830-490		(EPA, 2015)
Internal combustion engine	0.1-9 MW	2 180-1 070		(EPA, 2015)
		580-1350	170	(IEA ETSAP, 2010)

As mentioned earlier, the database developed for this study includes information on cogeneration at plant level. These data were provided by (ESAP, 2012). Based on these data, our database includes 495 chemical and petrochemical installations with a total CHP electrical capacity equal to 20027.85 MW gross and 19083.24 MW net.

ESAP includes information only on the CHP electrical capacity of the plants, but reports also the type of the units used. As a result, the CHP heat capacity of the plants can be calculated from the electrical capacity using the power to heat ratio of the unit used. In case more than one CHP technology is used in a plant, the average of power to heat ratios and overall efficiencies was considered.

Figure 5 and Figure 6 show the distribution of CHP units and net electrical capacity per country in the chemical and petrochemical sector of EU-28. More than 80% of these units use one of the four most typical prime movers or combination of them.

As already mentioned, for each process the SEC is being calculated, based on the process performances according to literature. The important factors in determining SEC per plant are the fuel requirements and the electricity bought from the grid. We assume that if the CHP unit does not cover the heat or electricity demand of the facility the share of energy missing is compensated through separate heat production, or electricity bought to the grid. On the contrary, if the CHP production is higher than the plant demands, the excess is sold. In each facility, when accounting for energy consumption and GHG emissions, we discount the fuel consumption and GHG emissions associated to the energy (heat and electricity) exported.

Figure 5. Number of CHP units installed per country in the European chemical industry in 2013

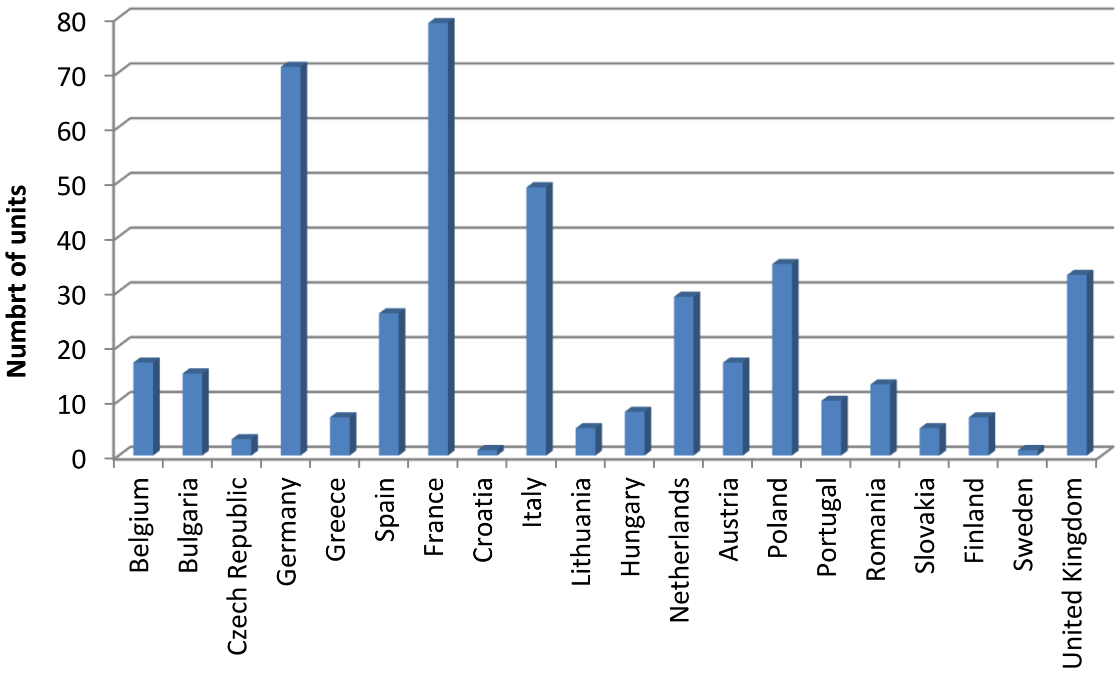
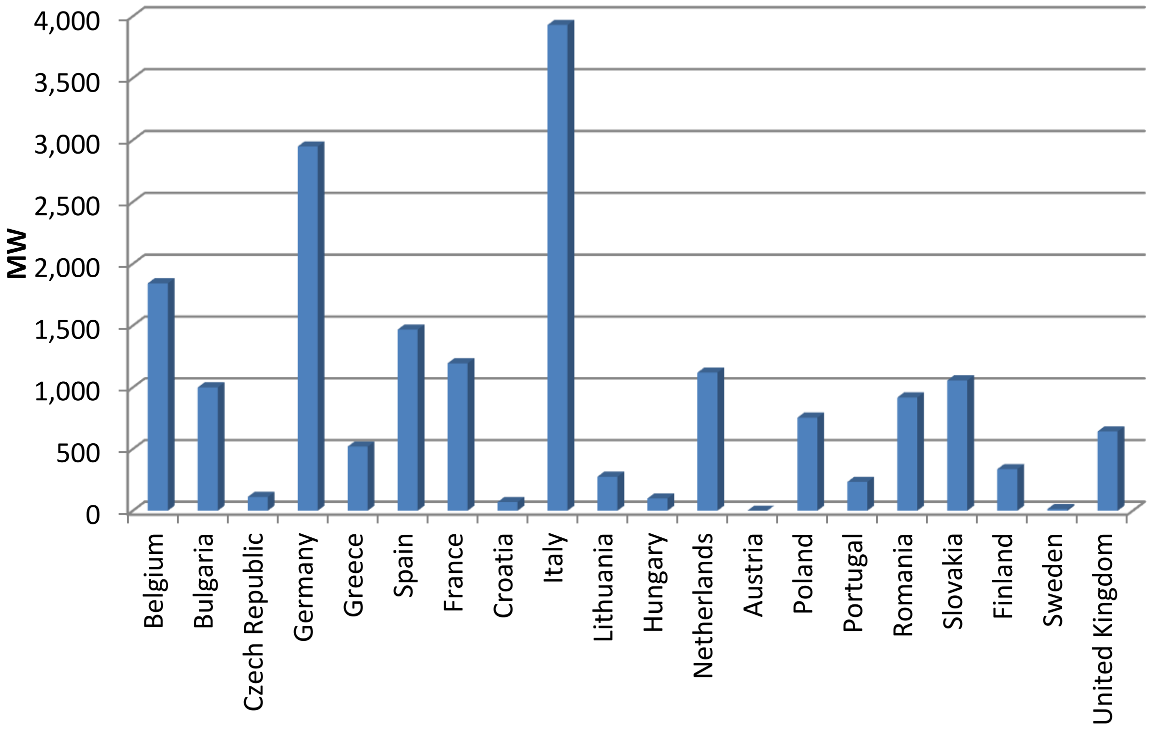


Figure 6. Net CHP electrical capacity installed per country in the European chemical industry



The methodology developed to calculate the overall energy balance, takes into account the energy produced at plant level by the CHP unit. If the plant has a cogeneration unit, we need to evaluate the potential deficits, that is, the difference between the plant's electricity and thermal energy requirements and the energy self-produced:

- *Delta Electricity*: $\Delta_{electr.}$ = *Plant Electrical Demand – CHP electrical production*

  If $\Delta_{electr}<0$ the plant self-produces more electricity than it needs, and it is assumed that it does not need to buy electricity from the grid. If $\Delta_{electr.}>0$ the electricity generated by the cogeneration does not cover the annual electricity requirements of the process, so the difference will have to be provided by the grid.

- *Delta Heat*: Δ_{heat} = *Plant Thermal Demand – CHP thermal production*

  Similarly, if $\Delta_{heat}<0$ there is a surplus of heat. If $\Delta_{heat}>0$ the heat generated by the cogeneration is not covering the annual thermal requirements of the process, so the difference will have to be produced in a different way.

4.5.1.2 Cogeneration as Best available technique

Cogeneration appears as a best available technique for most chemical products. As a result, it was decided to include it separately, as a cross-cutting technique.

In order for CHP to be included in this study as a BAT, we need to determine its energy-efficiency improvement potential, emission reduction potential and investment costs. The technologies already used in the plants were identified at plant level using the (ESAP, 2012) database. Table 10 shows the most common CHP technologies identified.

Table 10. Primary energy savings due to integration of cogeneration

Type of CHP technology	Ref H_η [1]	Ref E_η [2]	CHP H_η	CHP E_η	PES
Combined cycle	0.82	0.35-0.55	0.44	0.41	22.2-41.4%
Gas turbine	0.82	0.25-0.42	0.49	0.27	19.4-40.4%
Internal combustion engine with heat recovery	0.82	0.25-0.45	0.50	0.38	34.0-53.0%
Steam turbine	0.81	0.17-0.35	0.55	0.25	28.2-53.4%

[1] Source (EC, 2015c)
[2] Source (IPCC, 2007b)

Primary energy savings (PES) from integration of a CHP unit instead of separate electricity and heat production were calculated according to the following formula (EC, 2012a):

$$PES = \left(1 - \frac{1}{\frac{CHP\ H\eta}{Ref\ H\eta} + \frac{CHP\ E\eta}{Ref\ E\eta}}\right) \times 100\%$$

Where $CHP\ H_\eta$ is the heat efficiency of the cogeneration production (21)

- $Ref\ H_\eta$ the efficiency reference value for separate heat production
- $CHP\ E_\eta$ the electrical efficiency of the cogeneration production (22)
- $Ref\ E_\eta$ the efficiency reference value for separate electricity production.

The reference values for separate heat production were determined according to (EC, 2015c). They depend on the fuel that feeds the power or heat installation and on the construction year of the generation unit. For each CHP technology, the value chosen corresponds to the fuel most frequently used in the chemical industry to feed this technology and for year of construction before 2012. On the other hand, the reference values for separate electricity production were determined according to (IPCC, 2007b). We consider that the values in the regulations for heat are representative of the heat technologies considered in this study although they depend only on the fuel used, but in the case of electricity the differences among the CHP technologies are an important factor that has to be taken into consideration.

The heat and electricity efficiency of the cogeneration units was calculated from the overall efficiencies and the power to heat ratio for each technology (Table 8):

$$CHP\ H_\eta = OE\ /\ (Ratio+1)$$

$$CHP\ E_\eta = Ratio * CHP\ H_\eta$$

Table 10 summarises the estimations of efficiencies and primary energy savings.

Concerning emissions, the cogeneration increases direct emissions due to the fuel used to produce heat and electricity, but decreases the overall CO2 emissions (considering both, the power and chemical sector together), thanks to lower primary energy consumption than when producing the heat and power separately.

In practical terms, although this study estimates the primary energy savings due to CHP, it neither reports the extra CO2 emissions from the power self-generated that is exported, nor the primary energy savings. In the model and analysis presented in chapters 6-8, any investment in the CHP can only be justified if the revenue from the electricity sold (and savings from the electricity not bought) justifies the extra cost of the

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(21) Heat efficiency of cogeneration is defined as the useful heat output divided by the fuel input to produce the sum of heat and electricity from cogeneration

(22) Electrical efficiency of cogeneration is defined as the electricity produced divided by the fuel input to produce the sum of heat and electricity from cogeneration

additional fossil fuel consumption, additional CO2 emissions and investment cost of the CHP.

4.5.2 Carbon capture and storage as Innovative technology

Similarly to co-generation, CO_2 capture and storage (CCS) is a horizontal innovative technology for a number of chemical products. It is considered to be a significant abatement technique, as it has also the potential to reduce CO_2 emissions, and it is recognised as such by several intergovernmental scientific and environmental organisations (IPCC, 2013). In the European Union, there is a Directive on geological storage of CO_2 since 2009 (EC, 2009d), and the potential of CCS has been acknowledged in the 2030 Climate and Energy Policy Framework (EC, 2016e) and it has been included in the technology portfolio of the European Union Reference scenario (EC, 2013) as a central low-carbon technology to achieve the GHG emission reduction objectives.

CCS involves trapping CO_2 emitted from facilities, compressing it and transporting it to a suitable storage site via pipeline or ship or combination of the two, where it is injected in underground geological formations (EC, 2016e). It was initially aiming at capturing CO_2 produced in the power sector, but it can be applied in several industrial sectors (Global CCS Institute, 2016). According to the European Technology Platform for zero emission fossil fuel power plants (ZEP) 34 plants across the EU member states can be commercialised as of 2020 (ZEP, 2008) These facilities concern besides the power sector, also the steel and chemical industries.

In the chemical industry, CCS can be applied in the ammonia and urea production chain, the hydrogen production industry and the ethylene oxide industry, as well as some other applications, such as formic acid, polymers and inorganic carbons production. Several of the big chemical companies present in Europe (such as BASF, Bayern, Clariant, Lafarge, Haldor Topsoe, Linde, Repsol, Siemens, Solvay, ThussenKrupps, Total etc.) have been identified as even moving towards utilisation of captured CO_2 as raw material (SBC, 2012).

Several process of the chemical industry result in CO_2 streams of high purity and concentration (UNIDO, 2010b). In these cases, the energy-intensive CO_2 separation step is not necessary and the costs of CCS would be lower. Such processes include hydrogen production (mainly from refineries), ammonia and ammonia-based fertilisers production and a range of organic chemicals processes, such as ethylene oxide production. Examples of plants applying CCS are, in the case of hydrogen production the Pernis refinery in the Netherlands uses captured CO_2 to fertilise greenhouses and in the case of ammonia, all processes producing urea (UNIDO, 2010c).

Typical costs of CO_2 capture for industrial plants were estimated to range between 28 and EUR $42_{2004}/t_{CO2}$ (Ecofys & TNO, 2004). For ammonia plants and hydrogen production with pure CO_2 the costs can be as low as 3 EUR_{2004}/t_{CO2}, but if CO_2 is in flue gas it can be around EUR $36_{2004}/t_{CO2}$. In the case of petrochemical plants typical costs are EUR 32-36 $_{2004}/t_{CO2}$. These values exclude cost of compression, which would add EUR 6-10 $_{2004}/t_{CO2}$. (Ecofys & TNO, 2004).

Table 11 includes the performance of applying CCS in the chemical and petrochemical sector. The various types of application of this technology have been included in our database with the characteristics summarised in Table 11. The investment costs for the rest of the applications have been calculated as follow:

$$\textit{Investment cost} = \textit{GHG Reduction} \times \textit{Process emission factor} \times \textit{CCS cost} \times \textit{Reference capacity}$$

Table 11. CCS characteristics as innovative technology

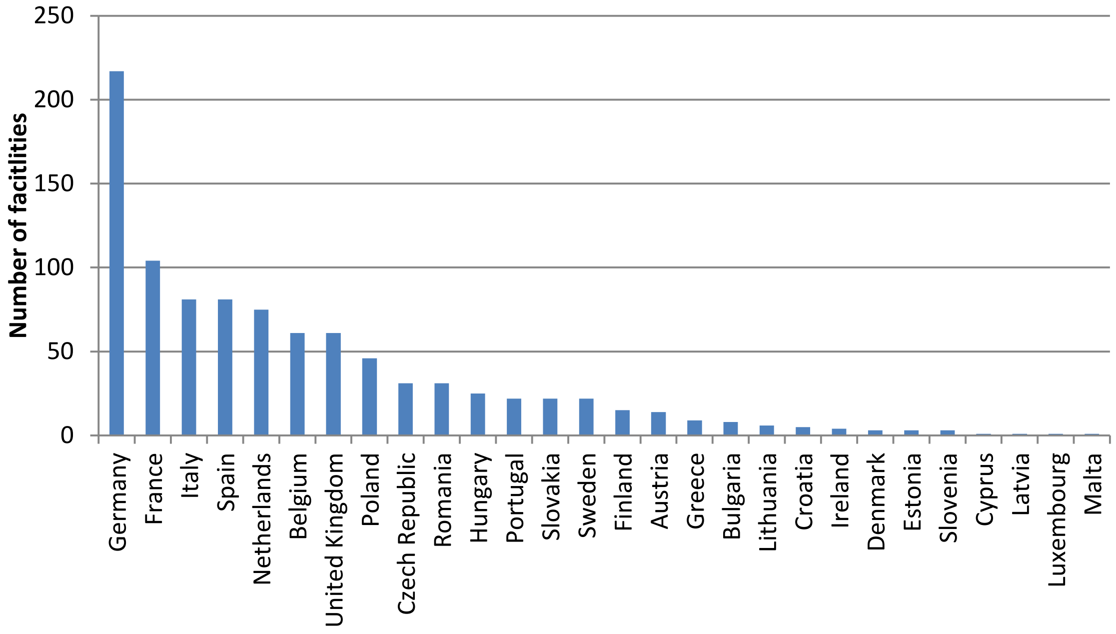
CCS in	Ammonia production	Hydrogen production	Ethylene oxide production
Process applicability	Ammonia	Hydrogen	Ethylene oxide
CO_2 reduction	81 % [1]	73-96 % [2]	50 % [3]
Year of availability	Currently mature	Currently mature	2020 [4]
Cost (EUR $_{2013}$/t_{CO2})	39	39	39
Energy requirement		CO_2 readily available	
Investment cost (EUR $_{2013}$)	25 572 100	6 700 000	500 000
Reference capacity (kt/y)	500	18.13	260

[1] Source (CE Delft, 2012)
[2] Source (IPCC, 2005)
[3] Due to lack of data, a conservative value of 50% has been assumed.
[4] Lack of information. According to (Carbon Counts, 2010) this industry shows low interest to implement CCS.

4.6 Current status of the EU chemical and petrochemical industry

The following chapter includes the detailed description of the technologies used in the chemical industry for producing the 26 chemical products considered in this study. In this paragraph, this information is summarised, in order to demonstrate the status of the EU chemical industry in 2013.

Figure 7. Distribution of chemical facilities included in the database in EU-28 by country

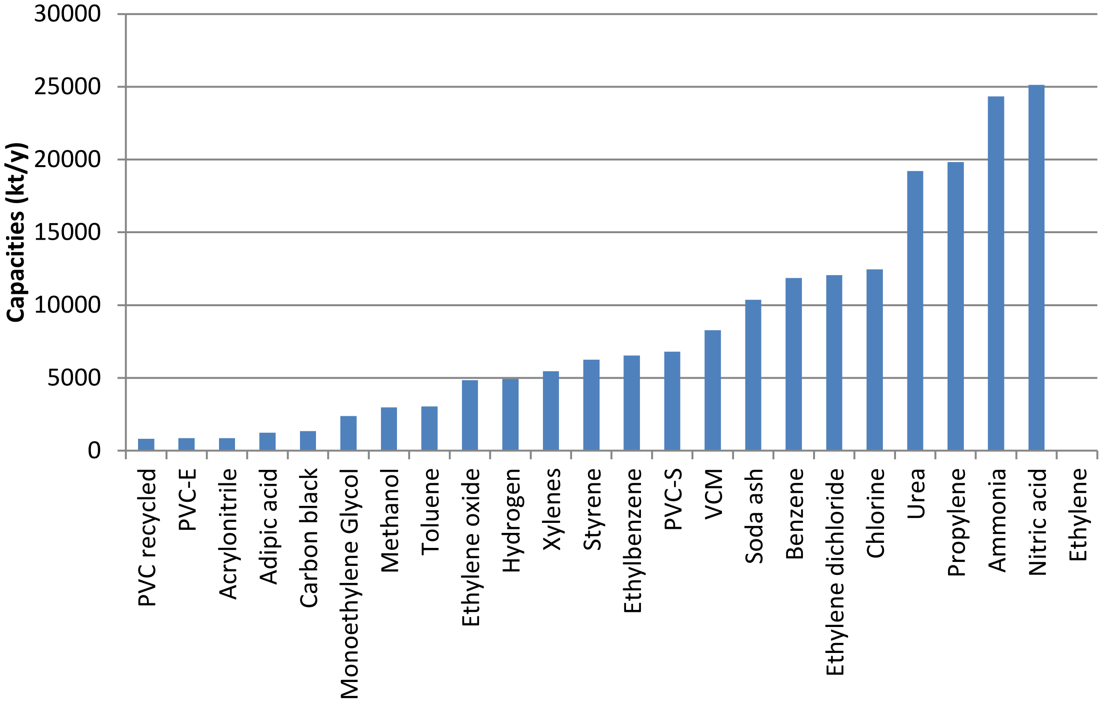


As it has been explained, we have followed a bottom-up analysis at facility level. The database, in which we have gathered all the related information, includes more than 1 000 facilities, 954 of which are still operating. This number includes the fictitious facilities, created in the case of hydrogen and PVC recycling, which summarise the several small facilities producing these products. This means that number of true facilities covered is much higher. Figure 7 shows the distribution of these facilities per country.

More than 70% of the total number of facilities are located in 7 Member States (Belgium, Germany, Spain, France, Italy, Netherland and United Kingdom), while in Cyprus, Latvia, Luxembourg and Malta only count with fictitious facilities. Regarding capacities, the same first 7 countries together with Poland cover more than 80% of the total.

More than 50% of the total installed capacity considered in the current study corresponds to five products: ethylene, nitric acid, ammonia, propylene and urea (Figure 8). This result confirms that high value chemicals and fertilisers are also large volume chemicals in the EU. Facilities producing nitric acid are mainly located in Germany, France, Netherlands, Poland, Belgium, Romania and Lithuania (this countries account for 69.3% of nitric acid installed capacity), while the same countries cover 72.7% of the total installed capacity of ammonia and 78.8% of urea. In the case of ethylene more than 80% is concentrated in Germany, Netherlands, France, United Kingdom, Belgium, Italy and Spain.

Figure 8. Distribution of chemical facilities' capacities included in the database in EU-28 by product



4.6.1 Technologies used and Production in 2013

Table 12 shows the current technology used in manufacturing the key products/processes included in this study. It includes also data on capacities and production volumes for each process/product. The typical load factor for each process can be determined by dividing the production volumes with the capacities. Installed capacities refer to year 2013, while for the production volumes there were not always available data. In the cases where data were not available, a typical load factor was assumed, which was the average of the load factors known (calculated at 0.77).

Table 12. Technology pathways in use for manufacturing each key product / process in the EU-28 and capacity, load factor and production in 2013

Key product or process	Technological pathway	Installed capacity (kt/y)	Load factor	Production volume (kt/y)	Fuel used
Nitric acid	Ostwald: Dual Pressure M/H	23 223.6	0.73 [1]	16 953.2	Natural gas
	Ostwald: Single Pressure M/M	1 105.0	0.73 [1]	806.7	Natural gas
Steam cracking (SC) – Fluid catalytic cracking (FCC) – Acrylonitrile	SC Ethane Based	4 075.0	0.83 [2]	3 382.3	Ethane
	SC Gas Oil Based	1 460.0	0.83 [2]	1 211.8	Gas oil
	SC Naphtha Based - Ethylene	19 590.0	0.83 [2]	16 259.7	Naphtha
	SC Naphtha Based - Propylene	13 748.0	0.83 [2]	11 410.8	Naphtha
	Fluid Catalytic Cracking	5 468.0	0.76 [3]	4 155.7	Refinery gas
	Ammoxidation (Sohio Process)	855.0	0.77	658.4	Natural gas
Ammonia	Natural Gas Based	18 647.0	0.79 [4]	14 731.1	Natural gas
	Heavy Residue Based	1179.0	0.89 [4]	1049.3	Heavy fuel oil
Urea	Urea Synthesis	12 455.0	0.81	10 088.6	Natural gas
Adipic acid	Cyclohexane KA Oxidation	680.0	0.65 [5]	442.0	Natural gas
	Phenol KA Oxidation	192.0	0.65 [5]	124.8	Natural gas
Hydrogen - Methanol	Steam Reforming	2 161.7	0.77	1 664.5	Natural gas
	Partial Oxidation	122.3	0.77	94.2	Heavy fuel oil
	Naphtha Reforming	289.8	0.77	223.1	Naphtha
	Average Reforming	186.9	0.77	143.9	Natural gas
	By-product Hydrogen	2 091.3	0.77	1 610.3	Natural gas
	Steam Reforming - Methanol	1 030.0	0.82 [6]	844.6	Natural gas
	Heavy Oil Partial Oxidation - Methanol	1 345.0	0.82 [6]	1 102.9	Heavy fuel oil
Aromatics	Pygas Based - Benzene	6 975.0	0.69 [7]	4 812.8	Naphtha
	Pygas Based - Toluene	934.0	0.71 [7]	663.1	Naphtha

	Pygas Based - Xylenes	570.0	0.63 [7]	359.1	Naphtha
	Naphtha Based - Benzene	3 396.0	0.69 [7]	2 343.2	Naphtha
	Naphtha Based - Toluene	2 033.0	0.71 [7]	1 443.4	Naphtha
	Naphtha Based - Xylenes	4360.0	0.63 [7]	2746.8	Naphtha
Soda ash	Solvay	8 285.0	0.85 [8]	7 042.3	Natural gas
Carbon black	Furnace Black	1 248.0	0.77	961.0	Heavy fuel oil
Ethylene Oxide	Direct Oxidation	3 045.0	0.87 [9]	2 649.2	Natural gas
Monoethylene Glycol	Hydration	1 340.0	0.83 [9]	1 112.2	Natural gas
Ethylene dichloride	Direct Chlorination	5 912.0	0.77	4 552.2	Natural gas
	Oxychlorination	5 947.0	0.77	4 579.2	Natural gas
Vinyl chloride monomer	EDC Cracking	6 810.0	0.77	5 243.7	Natural gas
PVC-S	Suspension Polymerisation	6 550.0	0.80 [10]	5240.0	Natural gas
PVC-E	Emulsion Polymerisation	814.0	0.80 [10]	651.2	Natural gas
PVC recycled	Mechanical Recycling	224.3	0.80 [10]	179.4	Natural gas
Ethylbenzene	Friedel Crafts	6 245	0.77	4 808.7	Natural gas
Styrene	EB Dehydrogenation	5 455.0	0.86 [9]	4 691.3	Natural gas
Chlorine	Chlor-alkali Mercury Cell	3 029.0	0.80 [11]	2 423.2	Natural gas
	Chlor-alkali Diaphragm Cell	1 679.0	0.80 [11]	1 343.2	Natural gas
	Chlor-alkali Membrane Cell	7 347.0	0.80 [11]	5 877.6	Natural gas

[1] Source (IHS, 2015a) – Load factors 0.71 and 0.78 for western and eastern Europe respectively, as IHS defines them.

[2] Source (Petrochemicals, 2016) and (IHS, 2015a)

[3] Source (IHS, 2014a) – Load factor 0.74 in western Europe, 0.79 in Poland, 0.80 in Hungary and 0.84 in Romania.

[4] Source (IHS, 2015a) – Load factors 0.89 and 0.69 for western and eastern Europe respectively, as IHS defines them.

[5] Source (IHS,2015a)

[6] Source (IHS, 2014a)

[7] Source (IHS, 2015a) – Load factors for western and eastern Europe respectively, as IHS defines them: 0.71 and 0.66 for benzene, 0.80 and 0.62 for toluene. For xylenes the value of mixed xylenes is used.

[8] Source (IHS, 2015a) – Load factors 0.82 and 0.90 for western and eastern Europe respectively, as IHS defines them.

[9] Source (Petrochemicals, 2016)

[10] Source (Ullmann's Encyclopaedia, 2014)

[11] Source (Euro Chlor, 2014)

Each production process is also associated with a typical fuel, based on the type of feedstock used (Table 12). In the cases where the type of feedstock did not allow the clear attribution of a typical fuel, natural gas has been used by default, since it is the fuel most used in the EU chemical industry.

4.6.2 Energy consumption and GHG emissions in 2013

Following the bottom-up analysis that is explained in the methodology and according to the performances of the processes that are described in detail in Chapter 5, the energy consumption and the energy incorporated as feedstock in the products can be calculated for the starting year of 2013.

The total energy consumption is calculated from the sum of the electricity and heat consumptions of each process, according to the following equation:

*Energy consumption = (Process electricity consumption * 3.6 * 3 + Process heat consumption) * Production*

It should be noted that in the above equation(23), the process electricity consumption is multiplied by a factor of 3. This is due to the fact that when estimating the total electricity consumptions of the chemical sector in a bottom-up analysis, the estimation does not cover more than a third of the total electricity used (IEA, 2009a). The part that cannot be quantified is attributed to pumping equipment, and auxiliary uses.

The total energy consumption for the EU chemical industry in 2013 is shown in Table 13. It is also compared with the value of total energy consumed in the chemical and petrochemical sector according to Eurostat (Eurostat, 2016a). As it can be seen with the products considered in the study and based on the theoretical values for energy consumptions of each process, which are explained in detail in Chapter 5, the present study covers close to 60% of the energy consumption of the chemical industry according to (Eurostat, 2016a).

Table 13. Thermal energy and electricity consumption of the chemical industry in 2013

Products	Energy consumptions				Cumulative thermal energy and electricity consumptions (%)
	Fossil fuel+Steam (PJ)	Electricity (PJ)	Total energy (thermal + electricity)		
			(PJ)	(%)	
Nitric acid	0.35	0.8	1.15	0.05	0.05
Steam cracking	273.1	6.0	279.1	12.4	12.5
Ammonia/ Urea	121.7	9.0	130.8	5.8	18.3
Adipic acid	17.8	0.4	18.2	0.8	19.1
Hydrogen/ Syngas	39.3	49.6	88.9	4.0	23.0
Soda ash	98.1	2.1	100.2	4.5	27.5
Aromatics	69.9	0.5	70.3	3.3	30.6
Carbon black	63.9	2.1	66.0	2.9	33.5
EO/MEG	15.5	3.3	18.7	0.8	34.7
EDC/VCM/PVC	113.3	23.9	137.2	6.1	40.5
PVC Recycled	0,00	8.6	8.6	0.4	40.9
EB/STY	50.8	3.7	54.5	2.4	43.3
Chlorine	37.9	241.4	279.4	12.4	**55.7**
Others	693.7	303.4	997.0	44.3	
Total	**1 595.3**	**654.5**	**2 250.0**	**100.0%**	

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(23) The factor 3.6 in the equation is the conversion factor from kWh to MJ.

Besides the energy consumption as thermal energy and electricity, the chemical industry is the main industry consuming energy as feedstock, that is, consuming energy as a raw material. The chemical industry accounted for more than 76% of the 4.1 PJ of final non-energy consumption in 2013 (Eurostat, 2016a).

The energy incorporated as feedstock is calculated according to the following equation:

$$\textit{Energy incorporated as feedstock} = \Sigma(E_{product} - E_{product\_reused})$$

where $E_{product}$ is the total energy incorporated as feedstock in the final product, calculated by multiplying the production of each product with its energy content; and $E_{product\_reused}$ is the amount of products used as feedstock in some other of the processes considered in this study. Such examples are ammonia, which is used in the production of nitric acid and urea, or ethylene that is used in the production of ethylene oxide, ethylene dichloride and ethyl benzene.

The total energy incorporated as feedstock in the products is shown in Table 14 and it is compared with the value for final non-energy consumption in the chemical and petrochemical sector in 2013 according to (Eurostat, 2016a). The present study covers almost 90% of this quantity.

Table 14. Final energy consumed as feedstock in the EU chemical industry in 2013

Products	Energy incorporated as feedstock		Cumulative energy incorporated as feedstock
	(PJ)	(%)	(%)
Nitric Acid	0.0	0.00	0.0
Steam cracking	1 365.9	43.7	43.7
Ammonia/Urea	299.5	9.6	53.2
Adipic Acid	0.0	0.0	53.2
Hydrogen/Syngas	487.4	15.6	68.8
Soda Ash	0.0	0.0	68.8
Aromatics	353.1	11.3	80.1
Carbon Black	31.5	1.0	81.1
EO/MEG	1.3	0.04	81.2
EDC/VCM/PVC	25.6	0.8	82.0
PVC Recycled	4.0	0.1	82.1
EB/STY	195.8	6.3	88.4
Chlorine	0.0	0.0	**88.0**
Others	364.1	11.6	
Total	**3 128.2**	**100.0**	

In total the products considered in the present study cover 75% of the total energy and non-energy use of the chemical industry in 2013, as it was reported in (Eurostat, 2016a).

Table 15 illustrates the total GHG emissions resulting from the bottom-up analysis in 2013 and the comparison with the total emissions of the chemical industry according to (EEA, 2015). The values for emission factors for the several processes in this study are in most cases in accordance with (IPCC, 2006b), a fact that might mean that the actual emissions in the industry might be improved since 2006. There has been an effort to be closer to the real situation in the chemical industry and in cases such as nitric and adipic acid the enormous improvements of the industry have been taken into consideration. With this remark in mind, the current study covers more than 99% of the emissions reported in (EEA, 2015).

Table 15. Total GHG emissions in the EU chemical industry in 2013

Products	**(Mt $_{CO2eq}$)**	**(%)**	**(%)**
Nitric Acid	16.9	12.0	12.0
Steam cracking	24.7	17.6	29.7
Ammonia/Urea	29.7	21.2	51.0
Adipic Acid	2.8	2.0	52.9
Hydrogen/Syngas	25.0	17.9	70.8
Soda Ash	7.6	5.4	76.2
Aromatics	6.0	4.3	80.4
Carbon Black	1.8	1.3	81.7
EO/MEG	3.4	2.4	84.1
EDC/VCM/PVC	5.8	4.1	88.2
PVC RECYCLED	0.4	0.3	88.5
EB/STY	4.4	3.1	91.6
Chlorine	11.3	8.0	**99.7**
Others	0.4	0.3	
Total	**140**	**100.0**	

5 European chemical and petrochemical industry per product

After describing the European chemical industry as a whole and explaining our methodology, this chapter presents the information included in our database concerning the 26 products included in our boundaries (Table 4).

The presentation is done either per product or per group of similar products and it follows the same pattern in all sections. Firstly, there is a short section describing each product, followed by four distinct parts:

1. The explanation of the main production processes,
2. The assessment of the consumption and emissions levels,
3. The identification of the possible Best Available Techniques (BATs) and
4. The identification of the Innovative Technologies (ITs).

The overview presented in this chapter, though, should not be considered neither exhaustive, nor including all details. The interested reader can find detailed descriptions of processes and R&D needs in the references provided.

5.1 Nitric acid

Nitric acid (HNO_3) is a strong highly corrosive acid, used primarily to produce synthetic commercial fertilisers. Other uses include the production of explosives and chemicals such as adipic acid and nitrobenzene. It can react explosively with compounds such as cyanides and carbides, as well as with most metals and as a result it is used in the extraction and purification of gold.

Table 16. Nitric acid plants in the EU-28 in 2013

Country	Number of plants	Capacity (kt/y)
Belgium	3	2 135
Bulgaria	2	843
Czech Republic	3	453
Germany	8	3 710
Greece	1	230
Spain	4	696
France	9	3 032.5
Croatia	1	415
Italy	2	480
Lithuania	1	1 410
Hungary	2	890
Netherlands	3	2 485
Austria	1	318
Poland	4	2276
Portugal	3	438
Romania	5	1 817
Slovakia	1	480
Finland	2	650
Sweden	1	270
United Kingdom	2	1 300
Total	58	24 328.5

In 2013, fertilisers accounted for almost 80 % of total nitric acid consumption, while non-fertiliser applications for 17.2 % (IHS, 2014b). Ammonium nitrate and calcium ammonium nitrate account for more than 96 % of the fertiliser applications, while nitrobenzene and adipic acid for about 40 % of the non-fertiliser applications.

The annual production of nitric acid worldwide in 2013 was about 60 million tonnes, one third of which is produced in Europe (CIEC, 2015). Europe, China and North America accounted for about 82% of capacity and 84% of production and consumption. Apparent world consumption increased annually by about 2% between 2008 and 2013, and is projected to grow at 2.3% annually until 2018 (IHS, 2014b).

In Europe 58 plants were in operation in 2013 with a total production capacity of 24.33 Mt/y, as shown in Table 16 (ICIS, 2012; Ecofys, 2009; ECHA, 2014).

5.1.1 Production processes

Nitric acid is commercially available in two concentrations: weak nitric acid (30-65% w/w) and strong nitric acid (up to 99% w/w). The world market is represented mainly by weak acid, while the strong acid market covers only 10% of the total production (Ecofys, 2009). Weak acid is used in the fertiliser industry, as well as in the production of adipic acid and concentrated nitric acid is used for the production of explosives, dyes and insecticides.

The two different grades are produced by different methods (EPA, 2010). The first method utilises oxidation, condensation and absorption to produce weak nitric acid. High-strength acid can be produced from dehydration, bleaching, condensation and absorption of weak acid.

Weak nitric acid is produced by the catalytic oxidation of ammonia, based on the Ostwald process and it involves three distinct chemical reactions:

$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$ (Oxidation) (reaction 1)

$2\ NO + O_2 \rightarrow 2\ NO_2$ (Condensation) (reaction 2)

$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$ (Absorption) (reaction 3)

The catalyst for oxidation is typically woven or knitted wire gauze pads with a composition of approximately 90% platinum, 5% rhodium (for increased mechanical strength) and 5% palladium (for reducing costs). A rhodium content of 5-10% is considered to be optimal, but pure platinum should be used in temperatures less than 800°C (EC, 2007b).

Table 17. Parameters of the catalyst used in ammonia oxidation related to applied pressures (EC, 2007b)

Pressure of NH_3 oxidation (bar)	1	3-7	8-12
Catalyst layer	3-5	6-10	20-50
Gas velocity (m/s)	0.4-10	1-3	2-4
Temperature (°C)	840-850	850-900	900-950
Catalyst loss (g/t_{HNO3})	0.04-0.06	0.10-0.16	0.25-0.32
Campaign length (months)	8-12	4-7	1.5-3

During the oxidation reaction, the gauze gradually deactivates, since platinum is lost as volatile platinum oxide and rhodium oxides accumulate on the surface of the catalyst (Lloyd, 2011). Regeneration does not occur in the conventional sense, but new layers are added to the gauzes once they are no longer effective, or the pad is sent for reformulation. Some of the platinum lost during operation can be recovered by using recovery gauzes that absorb platinum oxide vapours and form an alloy (Lloyd, 2011).

The recovery achieved is usually 60 - 80% of the total losses (EC, 2007b). Some typical characteristics of the catalysts are shown in Table 17.

An aqueous solution of nitric acid is collected at the bottom of the absorption tower, with concentrations varying from 50 to 65% w/w HNO_3, depending on the temperature, the pressure, the number of absorption stages and the concentration of NO entering the absorber (EC, 2007b). Concentration is limited to about 68% in water, which is the azeotrope. The gases that are not absorbed in the solution exit from the top of the tower at temperatures 20 - 30°C and are commonly referred as tail gas.

To create higher pressure in the absorption section, a compressor is installed between the cooler condenser and the absorption column. The heat of the compression is removed by heat exchange with the tail gas, or by heat recovery in a steam boiler. The absorption reaction is also exothermic and continuous cooling is needed (EC, 2007c; EPA, 2010).

Table 18. NO dependence on pressure and temperature (EC, 2007b)

Pressure (bar)	Temperature (°C)	NO yield (%)
Low (<1.7)	810-850	97
Medium (1.7-6.5)	850-900	96
High (>6.5)	900-940	95

Several process variations are available; the principal differences are operating temperatures and pressures, the concentrations of product acid, catalysts and spent catalyst recovery systems. The efficiency of the first step is favoured by low pressure (Table 18) whereas that of the second by high pressure and lower temperatures (EC, 2007c; EPA, 2010). This consideration explains the fact that there are mainly two types of nitric acid plants: single pressure plants and dual pressure plants, depending on the pressure where the oxidation and absorption take place. In single pressure plants, they take place in the same pressure, while in dual pressure plants absorption takes place at higher pressure than the oxidation stage. According to the pressure of the oxidation process, they can be classified to low, medium and high pressure plants. Medium pressure plants operate at pressures between 1.7 and 6.5 bar, while low pressure plants operate at pressures less than 1.7 bar and high pressure plants at pressures up to 13 bar. The majority of European plants are in the medium pressure range (Ecofys, 2009).

High-strength acid can be obtained either directly or indirectly. The direct process is used only in a few plants and is based on converting nitric oxide to nitric acid, according to the following reactions:

$$2\ NO_2 \leftrightarrow N_2O_4 \qquad \text{(reaction 4)}$$

$$N_2O_4 + H_2O + \tfrac{1}{2}\ O_2 \leftrightarrow 2\ HNO_3 \qquad \text{(reaction 5)}$$

Most production of concentrated acids is based on the indirect process, where weak acid is concentrated in additional extractive distillation units with the help of dehydrating agents, such as sulphuric acid or magnesium nitrate (EPA, 1998). Simple fractional distillation is not applicable, because of the azeotropic. Concentrated nitric acid is collected from the top of a packed dehydrating column as 99% vapour, containing small amounts of NO_2 and O_2, which are separated from the nitric acid in a bleacher. Dehydration agents are restored under vacuum.

5.1.2 Current consumption and emission levels

All of the plants included in our database are producing weak acid by the Ostwald process and as a result this is the only production process that will be considered in the study.

Starting materials for the production of nitric acid are ammonia, water and air. For the production of 1 tonne HNO_3 (100%) the requirements are 280 - 290 kg NH_3, 3600 - 3800 Nm^3 air, while about 1.93 t/t_N water is produced at the oxidation of ammonia. The typical consumptions for steam turbine-driven HNO_3 plants are shown in Table 19 (EC, 2007c; ThyssenKrupp, 2014).

As a typical nitric acid plant is a net producer of steam, the steam consumption of the process is considered to be negligible compared to the overall production.

Table 19. Typical consumption levels for steam turbine-driven HNO_3 plants and tail gas containing <50 ppm NO_x

	Single pressure plant		Dual pressure plant
	M/M	H/H	M/H
Operating Pressure (bar)	5.8	10	4.6/12
Ammonia (kg/t_{HNO3})	284	286	282
Electricity (kWh/t_{HNO3})	9	13	8.5
Platinum primary losses (g/t_{HNO3})	0.15	0.26	0.13
Steam 8 bar, saturated (t/t_{HNO3})	0.05	0.20	0.05
Excess steam 40 bar, 450 °C (t/t_{HNO3})	0.761	0.551	0.651
Cooling water ($\Delta T=10$ K) (t/t_{HNO3})	100	130	105

The by-products produced in the process are nitrogen oxides (NO_x), nitrous oxide (N_2O), oxygen and water. They are usually present in the tail gas streams in concentrations that depend on the applied process conditions and may vary within the limits shown in Table 20 during stable operation.

Table 20. Tail gas properties after absorption (EC, 2007c; EFMA, 2000a)

Parameter	Level
NO_x (mg NO_2/Nm^3)	200-4 000
N_2O (mg/Nm^3)	600-3 000
O_2 (% v/v)	1-4
H_2O (% v/v)	0.3-0.7
Flow ($Nm^3/t_{100\%\ HNO3}$)	3 100-3 400

The main environmental concern during nitric acid production is the acid forming oxides of nitrogen. Nitrous oxide has a 100-year greenhouse potential of 298 (Table 1). It is produced during the ammonia oxidation, according to three possible intermediate reactions in amounts that depend on combustion conditions, catalyst composition and age and burner design (IPCC, 2006b):

$$NH_3 + O_2 \rightarrow \tfrac{1}{2}\ N2O + 1.5\ H_2O \qquad \text{(reaction 6)}$$

$$NH_3 + 4\ NO \rightarrow 2.5\ N_2O + 1.5\ H_2O \qquad \text{(reaction 7)}$$

$$NH_3 + NO + 0.75\ O_2 \rightarrow N_2O + 1.5\ H_2O \qquad \text{(reaction 8)}$$

Reactions like these that lead to formation of N_2O are undesirable, as they decrease the conversion efficiency of ammonia and reduce the yield of NO. As a result abatement techniques are applied. The final amount of nitrous oxide emitted depends on the amount generated in the production process and the amount destroyed in any subsequent abatement process.

N_2O emissions from nitric acid production accounted for 0.1% of the total EU-28 GHG emissions in 2013 and amounted to 4950 $kt_{CO2.eq}$ in total, while in 2012 they amounted to 6578 $kt_{CO2.eq}$. Between 1990 and 2013 there has been a decrease by 90% in these emissions, while between 2012 and 2013 25% (EEA, 2015). Poland is responsible for 18% of the total emissions, while Greece (93%), Hungary (75%) and Croatia (63%) contributed the most in the decrease between 2012 and 2013. Some of the reasons for this remarkable improvement are implementations of new catalysts, or new and more advanced state-of-art production technologies (EEA, 2015).

IPCC suggests emission factors for N_2O including associated uncertainties and they are shown in Table 21 (IPPC, 2006b). The low and high values represent the uncertainty bound of the default factors. EPA is using the factor 9 $kg_{N2O}/t_{HNO3\ (100\%)}$ in calculating uncontrolled N_2O emissions (EPA, 2010).

Table 21. Default emission factors for nitric acid production (IPPC, 2006b; EPA, 2010)

Production process	Approximate pressure (atm)	N_2O Emission factor ($kg_{N2O}/t_{HNO3\ (100\%)}$)		
		Low	Average	High
Atmospheric pressure plants (low pressure)	1	4.5	5.0	5.5
Medium pressure combustion plants	4-8	5.6	7	8.4
High pressure plants	8-14	5.4	9	12.6
Plants with NSCR		1.9	2.0	2.1
Plants with process–Integrated or tail gas N_2O destruction		2.25	2.5	2.75

Nitric plants emit also CO_2 and methane, especially if they apply non-selective catalytic reduction (NSCR) processes (EC, 2007b). According to (Ecofys, 2009), the methane slip in these plants can have a significant impact, increasing N_2O emissions by 0.7 kg_{N2O}/t_{HNO3}. The values reported in Table 21 for plants with NSCR include already the effect of the abatement measures (IPPC, 2006b).

Another possibility of emitting CO_2 and methane is during start-up, if the plant is equipped with steam powered compressors (EPA, 2010). Natural gas is used at start-up, but once the plant operates normally, it generates enough steam to power the compressor.

Table 22. Consumption and emissions levels of the nitric acid production processes in the database

Process	Consumption	Emissions ($t_{CO2.eq}/t_{HNO3}$)		
	Electricity (kWh/t_{HNO3})	Direct	Electricity	Total
Ostwald single pressure M/M	9.0	1.5	0.004	1.504
Ostwald dual pressure M/H	8.5	1.6	0.004	1.604

Taking into consideration the consumptions shown in Table 19 and the emission factors of Table 21, the specific energy consumptions and the specific emissions of the nitric acid production used in the database can be summarised (Table 22). For direct process emissions, the lower N_2O emissions factors will be used instead of the average, as the performance of the industry has been improving during the last decade. As the majority of the European industry is medium pressure plants, although they are mainly applying the dual pressure M/H process, the average between atmospheric and medium pressure plants is used for the single pressure process and the average between medium and high pressure plants for the dual process.

Nitric acid is a benchmarked product with value 0.302 allowance/tonne (EC, 2011b), but since the industry's emissions have changed remarkably, no calibration is performed to the specific emissions from the industry.

5.1.3 Best available techniques (BATs)

As mentioned before, the main problem in the nitric acid production is emissions of nitrous oxide. There are three types of controls for N_2O at nitric acid plants based on the location of the control within the nitric acid production process (IPCC, 2006b):

- *Primary abatement measures* – prevent N_2O formed in the ammonia oxidation step. They involve modification of the ammonia oxidation process or catalyst.
- *Secondary abatement measures* – remove N_2O from the valuable intermediate stream.
- *Tertiary abatement measures* – involve treating the tail-gas downstream of the expansion.

The most commonly applied controls are secondary and tertiary. The technologies available are capable of achieving more than 80% N_2O emissions reduction (EPA, 2010). Table 23 lists an overview of the possible BATs available for the nitric acid industry and summarises their performance.

Table 23. Overview of the possible BATs in the nitric acid industry

BAT	Description	Investment cost (EUR)	Operating costs (EUR/t_{HNO3})	Energy savings (%)	GHG Reduction (%)
BAT	Primary measures: Suppression of N_2O formation	811 162 [1]	Unknown	None	30-85%
BAT	Secondary measures: Removal of N_2O in the reactor	811 162 [2]	at 0.76-0.94	None	70-90
BAT	Tertiary measures: N_2O reduction in the tail gas	1 561 613 [3]	at 0.76-0.94	None	> 80

[1] Investment costs are based on modifications of the catalysts, taking into consideration also the savings. The reference capacity is 465 kt/y, which is the average capacity of nitric plants in Europe, according to our database.

[2] There is no data available for the investment costs of the secondary measures, but since it involves catalysts, it is assumed to be the same as the investment costs of the primary measures and for the same reference capacity.

[3] Investment costs are based to Variant 1 of EnviNOx process and for reference capacity 328.5 kt/y.

Almost all the BATs included in the same type of abatement techniques have similar potentials in GHG reduction and as a result in our database representative technologies are included, one for each of the three different types.

Primary measures include optimisation of the oxidation process by modification of the process parameters or the catalyst. The process parameters that are important for optimisation of the oxidation are the ammonia/air ratio, pressure and temperature. The NO yield in the oxidation step is maximised at an optimum NH_3/air ratio of 9.5-10.5% ammonia (EC, 2007b). Higher ratios are avoided, in order to maintain a safety margin from the lower explosion level of ammonia. According to the laws of thermodynamics, lower pressure increases the conversion efficiency. On the contrary, high temperature, although it enhances ammonia combustion, it decreases the conversion efficiency, due to production of N_2 and N_2O (EC, 2007b).

There are several new catalysts available. Improved platinum catalysts, with modifications in composition and geometry, can lead to higher ammonia conversion efficiencies, reduced N_2O emissions and extended campaign length. Example plants achieved reductions of 30-50 %, but achieved N_2O emission levels were not lower than 3 $kg_{N2O}/t_{HNO3\ (100\ \%)}$ (EC, 2007b). Data from several European units with improved catalysts showed a range of 3.6-9.7 $kg_{N2O}/t_{HNO3\ (100\%)}$ (Entec, 2008). Alternatives could be Co_3O_4 based catalysts, or two-step catalysts, platinum gauzes in the first step and non-platinum oxide catalysts in the second steps. The former alternative results in ammonia conversion efficiencies from 88 to 95 %, when the efficiencies normally are 93-97 %, but longer catalyst lifetime and less plant shut-downs. The use of the latter reduces the amount of Pt used by 40-50 % and the Pt losses by 15-30 %. Retrofitting alternative catalysts in existing plants can have costs EUR 1 425 000-1 900 000 (in 2001), while the savings are EUR 0.50-2.00 per tonne HNO_3 (EC, 2007b).

Secondary measures aim at removing N_2O in the burner after the ammonia oxidation gauzes. There are two abatement techniques: homogeneous decomposition and catalytic decomposition.

The first technique involves expanding the volume of the process burner in order to achieve homogeneous decomposition of N_2O. Extending the reactor chamber results in increasing the residence time of the reacting mixture at high temperatures (850-950 ^oC), and therefore reduces N_2O production. According to a patented technology from Yara, the residence time is increased up to 3 seconds, achieving a reduction of 70-85 % (2-3 $kg_{N2O}/t_{HNO3\ (100\ \%)}$) (EC, 2007b). It is a technology applicable only to new plants, as long as they are not low pressure plants, but retrofitting in existing plants has much higher costs.

The second technique consists of installing a selective de–N_2O catalyst (secondary catalyst) under the ammonia oxidation gauzes. According to the BREF (EC, 2007b) there are three catalysts developed. The secondary catalyst is technically applicable to all types of plants, but for atmospheric pressure plants this technology is not favourable, as it ends in reduced plant capacity, due to additional pressure drop. No major modification of the reactor is needed, but depending on the case sufficient strength to withstand the extra weight and the additional load from the pressure drop is required (Entec, 2008). The use of secondary catalysts has the potential to reduce emissions over 80 % and below 2.5 $kg_{N2O}/t_{HNO3\ (100\ \%)}$ (Ecofys, 2009; EC, 2007b). The level of abatement efficiency depends on the design and operating conditions of the plant. The costs for the secondary catalysts do not show significant differences and are estimated at EUR 0.98-1.20/t_{HNO3} (EC, 2007b; Kuiper, 2001).

Tertiary measures are based on N_2O abatement in the tail-gas. The techniques can be either a combined NO_x and N_2O abatement in the tail-gas or Non-selective Catalytic Reduction (NSCR).

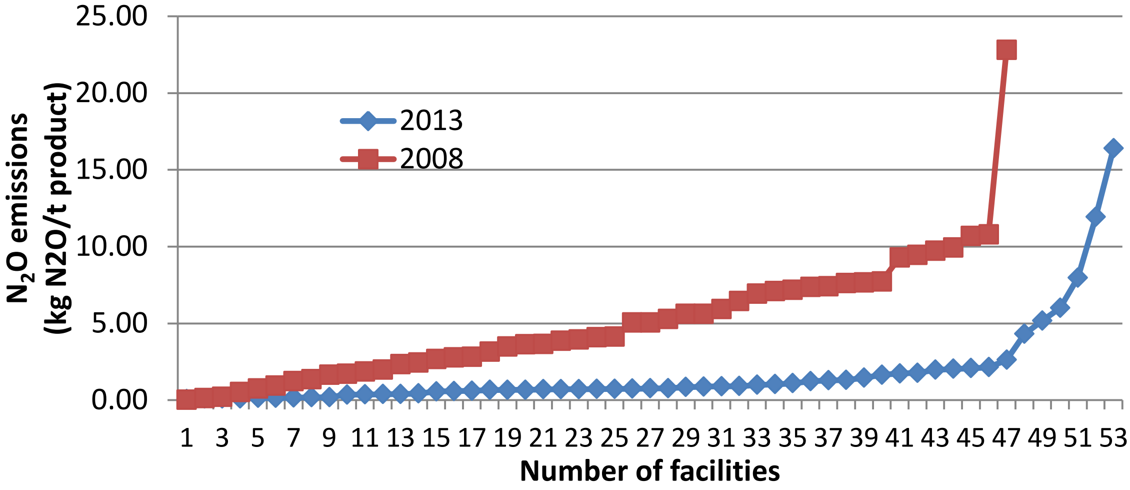
NSCR enables the reaction of a reducing agent (fuel) with nitrogen oxides, to produce N_2 and water. The most commonly used fuels are natural gas or CH_4, H_2 or ammonia purge gas (mainly H_2). The N_2O reduction efficiency of this technique is 80-95 %, while it also reduces NO_x emissions to 100-150 ppm (EC, 2007b). It is typically used in plants with the capability to preheat tail-gas to 200-450 ^oC and its application will demand major adjustments. It is not considered as a BAT, due to cross–media effects, namely the high energy consumption and additional emissions of CO_2 and methane slip (Ecofys, 2009).

The main tertiary technique involves the instalment of a combined NO_x and N_2O abatement in tail-gas between the final tail-gas heater and consists of a process called EnviNOx, proposed in two variants (ThyssenKrupp, 2009a). Variant 1 operates at tail gas temperatures of 420-480 ^oC (EC, 2007b) and as a result it is not appropriate for low pressure plants. Variant 2 is suitable for a much wider temperature range (300-520 ^oC) (EPA, 2010). Variant 1 consists of two catalyst layers (Fe zeolite) and an intermediate injection of NH_3, while in variant 2 N_2O is removed by catalytic reduction with a hydrocarbon such as natural gas or propane (EC, 2007b). Both variants can achieve emission levels as low as 0.12 $kg_{N2O}/t_{HNO3\ (100\ \%)}$ and NOx emission levels less than 5 ppm (EC, 2007b). The operational abatement efficiency is though slightly lower though, as increased tail gas temperatures decrease production levels and plants decide to operate at higher emissions (Entec, 2008). Variant 1 is very reliable and has no NH_3 slip, but variant 2 consumes hydrocarbons that tend to increase capital and operating costs, as well as emissions (EC, 2007b). Economics are available only for Variant 1, as for the example of the plant with a capacity of 1 000 t/d the investment costs were EUR 2 100 000, but due to experience gained reduction of the investment cost is expected to around EUR 1 700 000 (24) for nitric acid plants of the same capacity (EC, 2007b). Information concerning the operating costs is not generally available, but according to (EC, 2007b) they are estimated to be about EUR 0.98-1.20 $_{2001}/t_{HNO3}$.

Most of the EU nitric plants have one or more BATs concerning controlling N_2O emissions (Table 23) installed already. The most commonly applied controls are secondary and tertiary.

Many European nitric acid plants participated in joint implementation projects of the Clean Development Mechanism, aimed at reducing anthropogenic emissions (UNFCCC, 2015). As a result of the implementation of the abatement techniques, emissions of nitrous oxides in Europe have been considerably limited, as can be seen from Figure 9. It shows a comparison between 2008 and 2013 for the facilities reporting emissions, using information from the European Pollutant Release and Transfer Register (E-PRTR) (25) (PRTR, 2015).

Figure 9. N_2O emissions per facility level in 2008 and 2013 (PRTR, 2015)



5.1.4 Innovative technologies (ITs)

The only innovative technology according to the BREF is Variant 2 of the EnviNOx process (EC, 2007b), that should be considered as applied technique now and therefore is described in the previous paragraph.

5.2 Ammonia and Urea

Ammonia (NH_3) is a major industrial chemical and the principal source of nearly all synthetic nitrogen fertilisers. Its product chain is included in Annex 2. Almost all ammonia is produced in the anhydrous form, a colourless non-flammable gas at normal pressure and temperature, by combining nitrogen with hydrogen. It can readily dissolve

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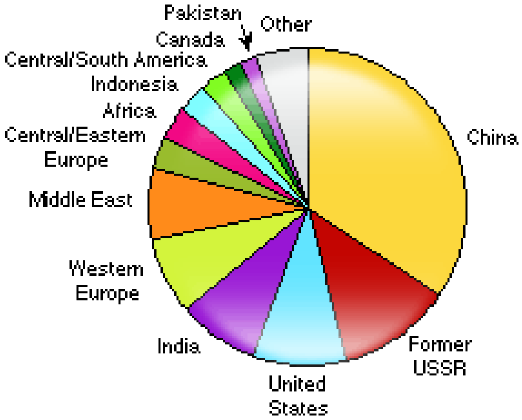
(24) Since the year of reference for this investment cost is not clearly stated, it is assumed that it is 2006, based on the year of publishing of the BREF.

(25) The total emissions per facility reported by [PRTR, 2015] are converted to emissions per facility using average load factors.

in water. Even in this form it can be used as fertiliser, either directly applied to the soil or as an aqueous solution with other nitrogenous fertilisers as ammonium nitrate or urea (Fertiliser Encyclopaedia, 2009). Commercial anhydrous ammonia has two grades of purity: minimum 99.7 wt% (about 0.2 wt% is water) and maximum 99.9 wt % (EC, 2007b).

Figure 10. World ammonia consumption in 2013 (IHS, 2014b)



Nitrogen fertilisers account for more than 80 % of the world ammonia market (IHS, 2014c). After the 7.6 % contraction in 2008/09, world fertiliser consumption sharply rebounded in 2009/10 and 2010/11, with growth rates of 5-6 % (IFA, 2012; 2011). In 2012 world consumption was 108.8 Mt_N (IFA, 2013) and in 2013 it reached 110.4 Mt_N (IFA, 2015). World distribution of ammonia consumption in 2013 is shown in Figure 10.

Table 24. Ammonia plants in EU-28 in 2013

Country	Number of plants	Capacity (kt/y)
Belgium	2	1 090
Bulgaria	2	540
Czech Republic	1	347
Germany	5	3 474
Estonia	1	165
Greece	1	150
Spain	2	600
France	4	1 429
Croatia	1	450
Italy	1	600
Lithuania	1	420
Hungary	1	470
Netherlands	2	2 900
Austria	1	515
Poland	5	2 921
Romania	5	2 170
Slovakia	1	355
United Kingdom	3	1 230
Total	39	19 826

World ammonia production in 2012 was 198 Mt_{NH3} according to (IEA, 2013) and 140 Mt_{NH3} according to USGS (2014). In 2013 production increased to 143 Mt_{NH3} (USGS, 2015). Germany, France, Netherlands, Poland and the United Kingdom account for 7.3 % of the global demand, with China at 33 %, India 8.3 % and the US 6.4 % (USGS, 2015). Global ammonia capacity is projected to increase by 16% from 211 Mt_{NH3} in 2013 to

245 Mt_{NH3} in 2018, while potential nitrogen supply is projected at 176 Mt_N (26) and demand at 161 Mt_N (IFA, 2014). The increases are attributed to the declining amount of arable land per person, as a result of urbanisation, soil erosion and nutrient exhaustion, and the growing of the world population (IHS, 2014c). In 2013 the world installed capacity was reported to be 214 Mt_{NH3}, with the EU covering about 9% of it (IHS, 2014a).

The nitrogen market is highly fragmented and regionalised, with Yara being one of the largest producers in Europe (Yara, 2014). In the EU-28 there are 39 ammonia plants in 18 member states, with total production capacity of 19826 kt_{NH3}/y (IHS, 2015a; ICIS, 2012; Ecofys 2009), as shown in Table 24.

About 48% of the global ammonia production is used in the production of urea ($CO(NH_2)_2$), the most commonly used nitrogen fertiliser, 11% in the production of ammonium nitrate, 20% in the production of other fertilisers and 3% directly as fertiliser (CEPS, 2014a). Other uses of ammonia include synthesis of chemicals, explosives, fibres and plastics, refrigeration and others (CEPS, 2014a).

Almost 90% of urea produced worldwide is consumed as fertiliser (Ullmann's Encyclopaedia, 2010a). Urea can also be used as a source of non-protein nitrogen in cattle feeds, in the manufacture of urea–formaldehyde resins and as raw material for melamine and cyanurate synthesis. Another application is in environmental application and in particular as a diesel exhaust fluid in mobile and stationary NO_x reduction systems (Ullmann's Encyclopaedia, 2010a).

Considering that the urea production is based on ammonia and carbon dioxide, which is a by-product of the ammonia production, typically ammonia plants are integrated with urea units. Urea (27) is produced only when integrated with an ammonia plant (EC, 2007b). In the EU-27 there are 25 urea plants distributed over 13 member states, as shown in Table 25 (ICIS, 2012; EC, 2007c).

Table 25. Urea plants in EU-28 in 2013

Country	Number of plants	Capacity (kt/y)
Germany	3	2 600
Estonia	1	220
Spain	2	385
France	2	770
Croatia	1	500
Italy	2	580
Lithuania	1	785
Hungary	1	260
Netherlands	2	1 650
Austria	1	420
Poland	3	1 765
Romania	5	2 240
Slovakia	1	200
Total	25	12 455

Concerning future projections, it is forecasted that up to the end of the decade ammonia will grow with 2.7 (IHS, 2014b; IFA, 2015) and urea 4 % to 2019 (IFA, 2015). For the total fertiliser demand, the IFA foresees a lower growth rate of only 1.7% (IFA, 2015). Projections to 2050 expect that fertiliser consumption in 2050 could be increased by

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(26) Fertilisers are commonly referred per tonne of 100% nitrogen (N) basis. In order to obtain ammonia volume, the information based on 100% N basis should be divided by 0.82 (nitrogen molecular weight / ammonia molecular weight).

(27) Similarly to ammonia, if the information is given as based on 100% N basis, urea volumes are obtained if divided by 0.46 (2 * nitrogen molecular weight / urea molecular weight).

58.4% compared to the 2005/2007 levels, but they involve a continuing slowdown of the overall growth (Alexandratos & Bruinsma, 2012). Especially in the case of industrial countries (including Western Europe) growth is expected to lag significantly behind the one in developing countries. Changes in agricultural policies and increasing awareness and concern about the environmental impacts of fertilisers will play an important role. Total consumption in these parts of the world is expected to have annual growth rates of 0.6% until 2030 and 0.3% in the period 2030-2050 (Alexandratos & Bruinsma, 2012).

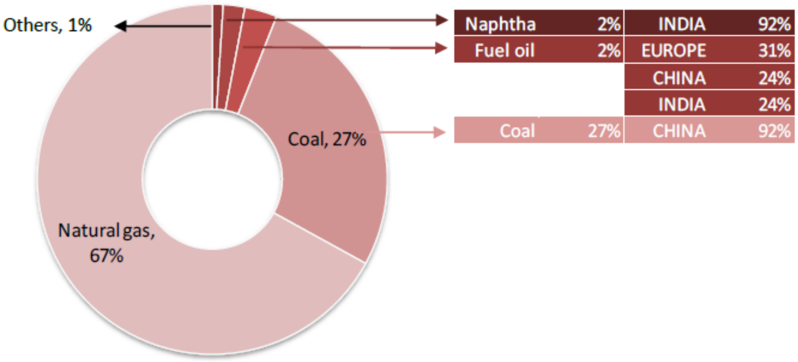
5.2.1 Production processes

Ammonia is synthesised from nitrogen and hydrogen by the following reaction, which is known as the Haber-Bosch process:

$$N_3 + 3\,H_2 \leftrightarrow 2\,NH_3 \qquad \text{(reaction 9)}$$

Nitrogen is obtained from air through liquid air distillation or an oxidative process, where air is burnt and the residual nitrogen is recovered. Hydrogen derives either directly or as a by-product from various feedstocks, mostly fossil fuels (Fertiliser Encyclopaedia, 2009). The feedstocks used worldwide are shown in Figure 11. Depending on the type of fossil fuel, there are two different methods applied to produce hydrogen for ammonia; (1) steam reforming, in the case of light hydrocarbons, such as natural gas, and (2) partial oxidation, used mainly in the case of heavy oils.

Figure 11. World ammonia production by feedstock type (2008) (Carbon Counts, 2010)



In the EU more than 90% of the H_2 for NH_3 is produced by steam reforming of natural gas (Figure 12a) (Ecofys, 2009). Production from natural gas involves the following reactions:

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \qquad \text{(reaction 10)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(reaction 11)}$$

$$CH_4 + \text{air} \rightarrow CO + 2\,H_2 + 2\,N_2 \qquad \text{(reaction 12)}$$

The first reaction takes part in the primary steam reformer and is highly endothermic (Ecofys, 2009). A water gas shift conversion – reaction 11 – also occurs to some extent. The gas leaving the primary reformer contains 5-15% CH_4 and the heat that was not consumed during the reaction (Fertiliser Encyclopaedia, 2009). The third reaction takes place in the secondary steam reformer, and the main objective is to add the nitrogen required for the synthesis and complete the conversion. The reaction is exothermic and the gas outlet temperature is approximately 1 000 °C (EC, 2007b). The catalysts used can be divided into two types: based on non-precious metals (typically nickel) and based on precious metals from Group VIII elements (typically platinum or rhodium). The high costs of precious metals, especially Rh, is driving researchers to develop alternative catalysts, such as cobalt-based (Holladay et al., 2009).

After reforming, the residual CO_2 is removed in a chemical or physical absorption process, with aqueous amine solutions or glycol dimethyl ether as most common solvents respectively (EC, 2007b). The small amounts of CO and CO_2 remaining in the synthesis gas can poison the ammonia reaction catalysts and as a result they are converted to CH_4 by hydrogenation, diminishing them to concentrations less than 10 ppmv (EC, 2007b).

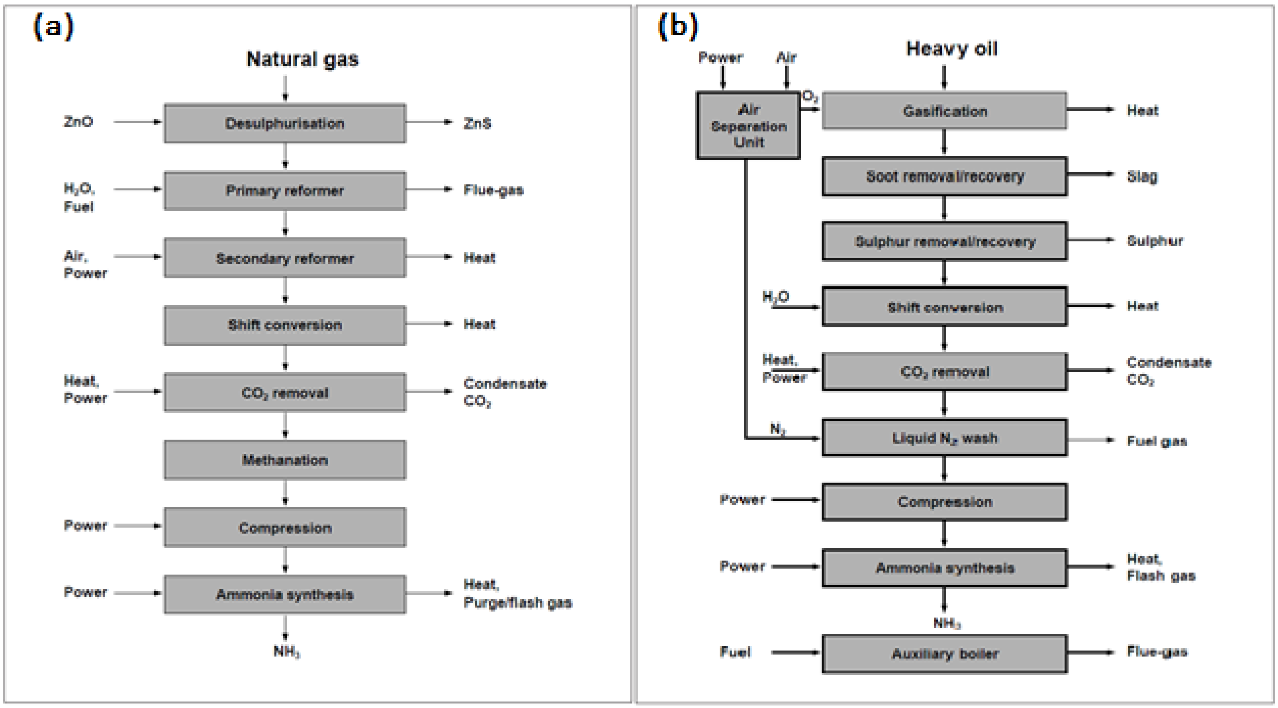
Partial oxidation (Figure 12b) is used for the gasification of heavy feedstocks such as residual oils and coal and its main benefit is its ability to be more widely adaptable to a range of feedstocks (Carbon Counts, 2010). In 2009, there were no coal plants in Europe and only a couple of plants based on heavy fuel oil or LPG, but Poland intended to develop their coal reserves to reduce the dependency on Russian natural gas (Ecofys, 2009). The production of hydrogen is based on a non-catalytic reaction between hydrocarbons, oxygen and steam at pressures up to 80 bar (EC, 2007b). The reactions typically occur with flame temperatures of 1 300-1 500 ^{o}C to ensure complete conversion and to reduce carbon soot formation (Holladay et al., 2009), but are exothermic and they are the following:

(Heavy oil) $C_nH_m + 0.5n\ O_2 \rightarrow n\ CO + 0.5m\ H_2$ (reaction 13)

(Coal) $C + H_2O \rightarrow CO + H_2$ (reaction 14)

$C + 0.5\ O_2 \rightarrow CO$ (reaction 15)

Figure 12. Simplified diagrams of (a) the steam reforming process and (b) the partial oxidation process (EC, 2007b)



Auto-thermal reforming combines partial oxidation and steam reforming, adding steam to catalytic partial oxidation. The oxygen to fuel ratio and the steam to carbon ratio must be properly controlled, in order to control the reaction temperature and product gas composition while preventing coke formation. A significant advantage over steam reforming is that it can be stopped and started very rapidly while producing larger amount of H_2 than partial oxidation alone (Holladay et al., 2009). Another advantage is that there is no direct production of CO_2 emissions because all the heat release is internal (Carbon Counts, 2010).

Steam reforming of natural gas can be up to approximately 85 % efficient in producing hydrogen on higher heating value (HHV) basis (Holladay et al., 2009), but the efficiency can be lower with sources of methane that have higher concentrations of sulphur or other impurities. The hydrogen rich gas contains typically 70-75% H_2 on a dry mass basis, 2-6 % CH_4, 7-10 % CO and 6-14 % CO_2 (Lipman, 2011). Partial oxidation and auto-thermal reforming can have typical efficiencies in the range of 60-75 %, based on HHV (Holladay et al., 2009).

The step following either partial oxidation or steam reforming is ammonia synthesis, which takes place usually at pressures 100-250 bar, temperatures 350-550 ^{o}C and on iron catalyst (Fertiliser Encyclopaedia, 2009). The conversion is incomplete in a single pass (20-30 %), but a large amount of ammonia is produced by its removal from the gas stream and by recycling the unreacted gas (EC, 2007b; Ullmann's Encyclopaedia, 2011a).

CO_2 produced can be captured from the process gas and be used in downstream utilities, which need it as feedstock, such as urea production. The commercial synthesis of urea is achieved by the Basaroff reaction at high pressure and temperature, as following:

$$2\ NH_3 + CO_2 \leftrightarrow NH_2COONH_4 \leftrightarrow CO(NH_2)_2\ \text{(urea)} + H_2O \qquad \text{(reaction 16)}$$

The first reaction is fast and highly exothermic, while the second one is endothermic, but the overall reaction is exothermic (Ullmann's Encyclopaedia, 2010a). The reactions are reversible and therefore the output includes also unreacted ammonia and CO_2. The achievable conversion per pass is influenced by factors as temperature and NH_3:CO_2 ratio. As a function of the latter, urea yield reaches a maximum above the stoichiometric ratio. In most plants all over the world the excess of ammonia and CO_2 is recovered and recycled, achieving conversions up to 96-97%. In conventional recycle processes unconverted CO_2 is recycled as an aqueous solution and the main proportion of unconverted NH_3 is recycled without an associated water recycle. On the contrary, in stripping processes the major part of the recycle of both reactants occurs via the gas phase (Ullmann's Encyclopaedia, 2010a). The final product is usually prills or granules.

5.2.2 Current consumption and emission levels

The typical size of a large single–train ammonia plant is 300-500 kt/d, although new plants can have capacities 1800 t/d and above (EFMA, 2000b). Commercial anhydrous ammonia has two grades of purity: minimum 99.7 wt% (about 0.2 wt% is water) and maximum 99.9 wt% (EC, 2007b).

As explained in 5.2.1, the starting materials for the production of ammonia are fuel as feedstock and air. In the EU, the fuels used are natural gas in the case of steam reforming and residual oil in the case of partial oxidation. The typical feedstock and air requirements are shown in Table 26.

Table 26. Typical consumptions for the ammonia industry (EFMA, 2000b; EC, 2007c)

Input requirements[1]	Steam reforming	Partial oxidation
Feedstock (GJ/t_{NH3})	22 - 25	28.8
Air (kg/kg_{NH3})	1.1 - 2.2	4
Fuel (GJ/t_{NH3})	4 - 9	5.4 - 9.0

[1] The values if expressed in GJ are based on Lower Heating Values (LHV)

Of the different types of steam reforming, conventional reforming has the lowest feedstock consumption and auto-thermal reforming the highest, while the fuel demands follow the reverse order (EFMA, 2000b). In the case of conventional reforming, the nitrogen supply equals the ammonia nitrogen content plus the purge losses, while if excess air is used or in auto-thermal reforming the requirements are about 50 % and 100 % higher, respectively (EC, 2007b). A typical heavy oil-based process uses 1.3 times as much as energy as a gas-based process, while a coal-based process 1.7 times (IEA, 2007). The lower heating values of residual fuel oil and natural gas are shown in Table 6.

The energy requirements for a stand-alone steam reforming plant with no energy export and no other import than feedstock and fuel is 28.8 - 31.5 GJ(LHV)/t_{NH3} (EFMA, 2000). According to the break-down presented by Lako (2009), these energy requirements include feedstock, fuel and electricity and deduct the stream produced in the process. In the case of auto-thermal reforming the electricity consumed is 0.2 GJ/t_{NH3} (Lako, 2009). According to IEA (2009) the electrical consumption is 0.3 GJ/t in the case of ammonia from natural gas, 0.5 GJ/t for ammonia from oil and 3.7 GJ/t for ammonia from coal. In partial oxidation plants the total energy requirement including imported power or auxiliary steam for driving the machinery is 36.9 GJ (LHV)/t_{NH3} (EFMA, 2000b).

Ammonia production accounted for 0.6% of the total EU-28 GHG emissions in 2013 (EEA, 2015). Total emissions of the ammonia industry in 2013 were 26927 $kt_{CO2.eq}$ (EEA, 2015). Germany (25%), Poland (16%) and the Netherlands (14%) had the highest shares in the EU28. There has been a decrease in CO_2 emissions in this industry of 16% since 1990, and between 2012 and 2013 emissions decreased by 3% (EEA, 2015). Estonia, Slovakia and Greece were responsible for the highest emission increases, while high reductions occurred in Romania, Lithuania and the United Kingdom.

From steam reforming plants with a fired primary reformer and partial oxidation plants the emissions occurring are the following:

- Flue-gas from the primary reformer (only in the case of steam reforming),
- Vent gas from CO_2 removal,
- Breathing gas from oil buffers,
- Fugitive emissions,
- Purge and flash gases from the synthesis section,
- Non–continuous emissions (venting and flaring).

There are two major streams of CO_2 emission: fuel-generated and process-generated. The fuel-generated CO_2 results from the combustion of fuel to supply heat for steam reforming, steam boiler process heaters and other equipment. CO_2 produced in the process is primarily recovered. Around 36 % of the CO_2 removed from syngas is used inside the industry, mainly in urea production (33 %), and the remaining 2.2 % is sold for other uses (Carbon Counts, 2010; Benner et al., 2012).

According to IPCC (2006b), in the case of steam reforming of natural gas, the CO_2 emission factor of tier 1 for modern plants in Europe varies between 1.666 and 1.694 t_{CO2}/t_{NH3}, while for partial oxidation it is 2.772 t_{CO2}/t_{NH3}. The values used in our study based on the consumptions and the emission factors for each fuel are shown in Table 27.

Table 27. Emission factors for ammonia and urea production

Process	Emissions ($t_{CO2.eq}/t_{NH3}$)				
	Electricity use	Thermal production	Steam production	Direct process	Total process
Ammonia: Natural gas-based	0.04	0.36	-	1.25	1.65
Ammonia: Heavy residue – based	0.07	0.56	-	2.15	2.77
Urea synthesis	0.03	-	-	0.01	0.04

Ammonia is a benchmarked product, with value 1.619 allowance/t (EC, 2011b). The system boundaries of benchmarking include all steps of the process, as well as emissions related to the production of the electricity consumed. As there is a benchmarking curve available for this product (Ecofys, 2009), the specific emissions for each plant calculated according to literature are calibrated.

Integrating urea production in the ammonia plant has the potential to reduce GHG emissions. According to the stoichiometry, urea production using ammonia requires 0.733 t_{CO2}/t_{urea} and 0.568 t_{NH3}/t_{urea}. On the other hand, it consumes energy in the form of steam and electric power. Average consumption levels are 0.8-1 t_{steam}/t_{urea} and 58 kWh/t_{urea} electricity (EC, 2007b; Ullmann's Encyclopaedia, 2010a; Kojima et al., 2008).

According to most references, the main emissions in urea production are ammonia and dust (Ullmann's Encyclopaedia, 2010a; EC, 2007b; EPA, 1998). In some references, the specific CO_2 emissions of urea plants can vary from 0.323 t_{CO2}/t_{urea} (Kojima et al., 2008) up to 0.785 t_{CO2}/t_{urea} (Wood & Cowie, 2004). But in all these cases, emission factors include the ammonia production step (Wood & Cowie, 2004). It is interesting to note that the emission factors of ammonia production (Table 27), if expressed per tonne of urea, are 0.476 t_{CO2}/t_{urea} for natural gas-based processes and 0.786 t_{CO2}/t_{urea} for heavy residue-based. Some Dutch plants report estimates of diffuse emissions of CO_2 (13-15 t/y) (EC, 2007b), but these values refer only to the particular plants and no further information is given about them. Only one reference has been identified (Bhaskar and Das, 2007), where the only CO_2 emissions mentioned from the urea production process are about 0.038 t_{CO2}/t_{urea} and occur at the medium and low pressure separators.

5.2.3 Best available techniques (BATs)

This paragraph describes the techniques considered generally to have potential of improving the environmental performance of the industry. There have been not many recent studies concerning the ammonia industry. According to (Lako, 2009) state-of-art ammonia plants from the main licensors have net energy use similar to the BAT suggested by the International Fertiliser Association (IFA). There are several possible changes that can lead to reduced energy consumption (Ullmann’s Encyclopaedia, 2011a; Rafiqul et al., 2005; EC, 2007). Table 28 lists an overview of the possible BATs available for the ammonia industry. Most of them are a combination of a number of smaller scale techniques and in these cases, investment costs and energy savings will be calculated from the individual technologies, if not mentioned in the literature for the aggregated technique.

Advanced conventional process

As the ammonia industry has been developing, a considerable reduction in energy consumption has been achieved by improving the process itself. Advanced conventional process plants are usually characterised by improved CO_2 removal systems, preheating of combustion air, indirect cooling of the ammonia synthesis reactor, hydrogen recovery from the purge gas or use of smaller catalyst particles in ammonia converters (EC, 2007b). In general, improved process integration can save 3 GJ/t_{NH3} at additional investment costs of 30 EUR_{2009}/t_{NH3} (Serpec-cc, 2009; de Beer et al., 2001).

Improved CO_2 removal consists of using new solvents or membranes and results in energy savings of about 0.9-1.1 GJ/t_{NH3} at additional investment costs of EUR 15 $_{2009}/t_{NH3}$ (Rafiqul et al., 2005; Serpec-cc, 2009; de Beer et al., 2001).

In the *indirect cooling of the ammonia synthesis reactor* concept, heat from the catalyst beds in the reactor is recovered and then used to produce high-pressure steam or preheat the boiler feed-water. The investment cost reported was YEN 150 $million_{1999}$ for a 300 kt/y reactor and the payback period 1.5 years (IETD, 2015a), which corresponds to EUR 7.14 $_{2013}/t_{NH3}$.

Increasing the air preheat with waste heat can lead to energy savings up to 0.9 GJ/t_{NH3} but NO_x emissions can increase by 120 g/t_{NH3} (EC, 2007b). The ammonia synthesis reaction heat can be used for the production of high pressure steam or by other ways, saving thus energy (up to 0.6 GJ/t_{NH3}) since a higher ammonia conversion rate is achievable and catalyst volumes are reduced (NEDO, 2001).

Hydrogen recovery can be performed using different technologies, such as cryogenic separation, membrane technology or pressure swing absorption (EC, 2007b). The average improvement is 0.8 GJ/t_{NH3} in energy with about EUR 2 $_{2005}$/t_{NH3} additional costs (Rafiqul et al., 2005).

Process with reduced primary reforming and increased process air

Some processes are designed for reduced primary reforming by transferring some of the process to the secondary reformer, which has higher marginal efficiency. This technique is also combining improved CO_2 removal systems, indirect cooling of the ammonia synthesis reactor and use of gas turbine to drive the process air compressor. If *a gas turbine* is used instead of a condensation steam turbine in order to drive the air process compressor, the heat can be used as preheated combustion air in the primary reformer. With this configuration considerable energy savings can be achieved. In revamping of a 1 000 t/d ammonia plant in India, the investment costs reported were USD 2 000 000 $_{2002}$, which is equal to EUR 6.57 $_{2013}$/t_{NH3} (Vaish & Patel, 2002). The total investment costs and performance of this technique are assumed to be the sum of investment costs and the energy savings of the three individual technologies that compose it.

Heat exchange auto-thermal reforming

Developments in the ammonia industry aim to recycle the heat of the secondary reformer outlet gas and the primary reformer flue-gas inside the process itself. Heat exchange auto-thermal reforming can lead to significant reductions in emissions by eliminating the flue-gas, energy savings up to 10 % and NO_x emissions reduction up to 50 % or more (EC, 2007b). Energy consumption though will increase in comparison with other steam reforming concepts.

This technique includes replacing the two reformers by a single isothermal medium temperature shift reactor, and installing improved CO_2 removal systems. By using an *isothermal shift converter*, heat from the catalytic bed is continuously removed and can be used for other purposes, while the catalyst used in high temperature conversion is not needed. The investment cost reported was YEN 500 million $_{1999}$ for a 100 kt facility and the payback period is 0.2 years (IETD, 2015b), which corresponds to about EUR 9.5 $_{2013}$/t_{NH3}. The total investment cost of this technique is estimated from the individual techniques and adds up to about EUR 25.2/t_{NH3}. The net energy savings of these improvements is not quantified (Rafiqul et al., 2005), but for this study it is estimated according to the individual technologies that compose it (isothermal shift reaction and improved CO_2 removal systems) and is assumed to be about 1.4 GJ/t_{NH3}.

Revamp: Increased capacity and energy efficiency

Revamp of old plants aims to improve the efficiency by extensive preheating of the mixed feed entering the furnace and by installing a highly efficient gas turbine. It results in reducing NO_x emissions and total energy consumption by almost 5 GJ/t_{NH3} (EC, 2007b). The investment was EUR 5 700 000 (28) with reference capacity 1 100 t/d and the pay-back time was less than a year (EC, 2007b).

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(28) Concerning this investment cost, there is no clear mention about the reference year in the BREF. As a result, it is assumed that it is 2006, based on the year of publishing of the BREF.

Pre-reforming

A pre-reformer installed before the primary reformer, in combination with a suitable steam saving project, can reduce the heat load up to 5-10% (EC, 2007b). In the case of an Indian ammonia plant with capacity 1000 t/d the investment reported was USD 5.4 million $_{2002}$ (Vaish & Patel, 2002).

Table 28. Overview of the possible BATs and ITs in the ammonia industry

BAT/IT	Description	Investment cost	Energy savings	GHG Reduction
BAT	Advanced conventional processes	EUR 31.5/t	10.0 %	None
BAT	Process with reduced primary reforming and increased process air	EUR 29.4/t	5.0 %	None
BAT	Heat exchange auto-thermal reforming	EUR 25.2/t	6.0 %	None
BAT	Revamp: increase capacity and energy efficiency	EUR 5 235 995 [1]	16.6 %	None
BAT	Pre-reforming	EUR 5 830 684 [2]	7.5 % thermal and steam	None
BAT	Advanced process control	Not included in the study as the savings are <5 %		
BAT	Low pressure catalyst for ammonia synthesis	Not included in the study as the savings are <5 %		
BAT	Use of S resistant catalysts for syngas from partial oxidation shift reaction	No information available		
BAT	Production using hydrogen from water electrolysis	EUR 176/t [3]	-14 400 % electrical 66.3 % rest	98 %
BAT	Improvement of the reforming section	EUR 37/t	13.3 %	None
IT	New reforming concept	EUR 348.1/t [4]	17 % thermal and steam	None
IT	Short contact time catalytic partial oxidation	EUR 835 000 000 [5]	11 % thermal, steam and feedstock	None
IT	CO_2 removal	Not included in the study as the savings are <5 %		
IT	New ammonia synthesis from electricity	EUR 241.4 /t [6]	-9000 % electrical 66.3 % rest	98 %

[1] Reference capacity 361.35 kt/y
[2] Reference capacity 328.5 kt/y
[3] Reference capacity 73 kt/y
[4] Reference capacity 80 kt/y
[5] Reference capacity 500 kt/y
[6] Reference capacity 117 kt/y

Advanced process control

An advanced process control system is model-based or model predictive and provides weighted and hierarchical optimisation, which means that solves optimisation problems by prioritising them. It can also contribute to energy savings of 0.7 GJ/t, obtained at additional costs of EUR 6 $_{2009}$/t_{NH3} (Serpec-cc, 2009). The reduction obtained is only 2.3% and as a result it is excluded from the analysis.

Low pressure catalyst for ammonia synthesis

Conventional catalysts for ammonia synthesis are iron-based. A new catalyst containing ruthenium (Rh) and an alkali promoter has much higher activity, that allows energy reduction of up to 1.2 GJ/t_{NH3}, but the savings might be offset by the need to refrigerate ammonia (EC, 2007b). There is no information about economics available, but since the maximum savings are only about 3.9%, the technique is excluded from the analysis.

Use of sulphur resistant catalysts for shift reaction of syngas from partial oxidation

This is an integrated technique applicable to new partial oxidation plants, which allows for the combined removal of CO_2 and sulphur compounds in one step, instead of separately. There are two configurations available, with different syngas cooling techniques and subsequent differences in the process (EC, 2007b). There is no information available on the level of energy savings and economics and as a result, the BAT is not included in the analysis.

Ammonia production using hydrogen from water electrolysis

Water electrolysis can give an extremely pure hydrogen feed-gas, with only small amounts of oxygen (0.1-0.2%) that has to be removed as it is poisoning the ammonia converter catalyst. This feed-gas can react with nitrogen from the air separation plant. Direct emissions from this process are minimal, but the energy consumption is higher than traditional processes. It is estimated to be 12 MWh/t_{NH3} and the thermal energy and GHG reductions are 20 GJ/t_{NH3} and 98% respectively (Holbrook & Leighty, 2009). The process is generally not considered economically viable due to the actual price for electric power (EC, 2007b), as the price depends on the cost of electricity. With more recent developments an ammonia synthesis plant with 100 MW electrical capacity at a hydropower facility that produces about 73000 t_{NH3}/y will have average cost that can be assumed to be about USD 215 $_{2009}$/t_{NH3} (Holbrook & Leighty, 2009), equivalent of about EUR 176.0 $_{2013}$/t_{NH3}.

Improvement of the reforming section

Conventional steam reforming is carried out in a fired furnace. The implementation of a series of technologies, such as increased pre-heating, the use of enriched air and the installation of a pre-reformer, can lead to reduction of energy consumption. The results depend on the status of the existing plant and according to a study conducted on Indian plants (Trivedi et al., 1998) savings range for plants installed before 1980 between 5 - 13.4 GJ/t, for plants installed until 1990 between 3.3-4.2 GJ/t and plants installed after 1991 there are no significant savings. According to (de Beer et al., 2001), overall the energy loss in the reformer section can be reduced by 3-5 GJ/t_{NH3} and investment costs are estimated at EUR 65 $_{2001}$/GJ saved annually, while according to later studies investment costs for large improvements in the reformer are EUR 24 $_{2009}$/t_{NH3} (Rafiqul et al., 2005; Serpec-cc, 2009) and for moderate improvements EUR 5 $_{2009}$/t_{NH3} (Serpec-cc, 2009). Savings in the case of large improvements are 4 GJ/t_{NH3} and for moderate improvements only 1.4 GJ/t_{NH3}. In this study we consider savings of 4 GJ/t_{NH3} for average investment costs EUR 37 $_{2013}$/t_{NH3}.

5.2.4 Innovative technologies (ITs)

There are a few innovative technologies concerning ammonia production mentioned in the literature and they are summarised in Table 28.

Membrane methane reforming

Conventionally the CH_4 steam reforming reaction is carried out in multi-tubular fixed-bed reactors in high temperatures. The use of reforming membranes can improve energy efficiency and reduce some of the drastic operative conditions. In addition, no traditional CO_2 removal system is needed (Moulijn et al., 2001). The energy savings in hydrogen production can be estimated to be 20 % compared to traditional reforming (Iaquaniello et al., 2008). Since this is fuel reduction respect of hydrogen, corresponding to 85% of the ammonia production energy consumption, the energy savings respect of ammonia are assumed to be 17%. The main disadvantage of this technology is low permeability and the cost of palladium-based membranes. The investment costs are estimated to be about EUR 28.05 million $_{2008}$ for a 20 000 Nm^3/h hydrogen production scheme reforming (Iaquaniello et al., 2008). These investments costs would be about EUR 348.1 $_{2013}/t_{NH3}$ if the ammonia synthesis is based on 100% hydrogen conversion, which is the normal case.

Short contact time catalytic partial oxidation

Short contact time catalytic partial oxidation of natural gas represents an attractive process for syngas production, since it is possible to operate in flameless auto-thermal systems with significantly high conversion and selectivity, compared to existing processes (Reynier et al., 2007). The main advantages of this innovative technology is technical and operational simplicity, flexibility towards feedstock composition and production capacity, reduction in investment costs and energy consumption and reduction of CO_2 production (Iaquaniello et al., 2012). Investment costs are expected to be about 10% lower than those of a steam methane reforming plant of the same capacity and operating costs about 5% less, while the expected reduction in feed and fuel in the hydrogen production is 15% (Iaquaniello et al., 2012). This reduction corresponds to 11% less in the ammonia production energy consumption. Expected investment costs for this technique are EUR 835 000 000 with reference capacity 500 kt/y (OPT Sensor Srl, 2012).

CO_2 removal

New technologies for CO_2 separation are under development, with one of the most promising to be the use of membranes. This technique could potentially save 33% of the separation energy, decreasing the energy use by 1.1 MJ/Nm^3_{CO2} or 0.6 GJ/t_{NH3} (US Department of Energy, 2005). According to (Lako, 2009), the hypothetical upgrading of three ammonia plants in the Netherlands had estimated energy savings 1 PJ/y and tentative investment EUR 50 million $_{2009}$. The study concludes that under the considered assumptions pay-back time is approximately 7 years and it does not warrant economic feasibility. This IT is excluded from the scope of the study as savings are less than 5% and the economic feasibility doubtful.

New ammonia synthesis from electricity

An innovative ammonia synthesis technology is "solid state ammonia synthesis" (SSAS). It combines the functions of the electrolyser and the Haber-Bosch synthesis loop into one process and claims significantly higher efficiency and decreased capital costs, as the process step of producing hydrogen is omitted (Holbrook & Leighty, 2009). The technique is still under development, but it is estimated that the capital costs will be about USD 650 /kW of electricity input and that the electrical energy needs will be about 7.5 MWh/t_{NH3}. A 100-MW ammonia synthesis plant will have about 117 kt/y production and would cost USD 145-445 $_{2009}/t$ depending on the electricity cost (Holbrook & Leighty, 2009), which corresponds to EUR 241.4 $_{2013}/t_{NH3}$. This IT consists improvement of the

"Ammonia production using hydrogen from water electrolysis" BAT, reducing electrical consumption by 37.5 %.

5.3 Steam cracking and Acrylonitrile

Steam cracking is the most important process worldwide to produce high value chemicals (HVCs) by breaking long-chain hydrocarbons into short-chain ones and it is, by far, the most important multi-product process in the chemical and petrochemical sector. As a result, it represents a particular challenge when modelling the energy use and emissions. High value chemicals include ethylene, propylene from pyrolysis gas of steam crackers, benzene, butadiene and hydrogen, according to Solomon Associates (IEA, 2009b). The products analysed in this paragraph include ethylene, propylene, butadiene, 1-butene and acrylonitrile.

Steam cracking has been the major source of light olefins for more than half a century. Olefins are relatively stable compounds that contain one or more pairs of carbon atoms linked by a double bond and the most important ones are ethylene and propylene. Over 85% of the olefins production is used in the production of polymers (Serpec-cc, 2009), as when the double bond is broken, the molecules can quickly form two new single bonds, stimulating thus a variety of reactions. Global ethylene and propylene production in 2012 was 220 MT (IEA, 2013). The ethylene and propylene yields of steam cracking vary between 24-81% and 1.5-25% respectively, depending mainly on the feedstock type and operating conditions (ACC, 2004).

Ethylene (C_2H_4 – $CH_2{=}CH_2$) — ethane according to the International Union of Pure and Applied Chemistry (IUPAC) — is one of the largest-volume commodity chemicals produced worldwide. It is used primarily as raw material in the manufacture of polymer plastics, fibres and other organic chemicals ultimately used in the packaging, transportation and construction industries (Ullmann's Encyclopaedia, 2009). It is the basic chemical for about 30 % of all petrochemicals (Ecofys, 2009). About 60 % of ethylene in Western Europe (29) is used for the production of polyethylene (PE) of different types, such as low density (LDPE), linear low density (LLDPE) and high density (HDPE). Ethylene dichloride (EDC) is the second main derivative of ethylene (15 %), used itself for the production of polyvinylchloride (PVC) (Petrochemicals, 2016). Its product chain is included in Annex 2.

Ethylene is sensitive to both economic and energy cycles and because of the size and broad use of its market, it is often used as a surrogate for the performance of the petrochemical industry at large (IHS, 2014d). Global ethylene consumption reached 129 Mt in 2012 (Eramo, 2013) and since 2009 it has been growing at an average rate of almost 4.5 % (IHS, 2014d). On the other hand, global capacity reached 153.5 Mt in 2013, with the EU accounting for 16.3 %, the United States for 17.8 % and Saudi Arabia for 10.2 % (IHS, 2014a). Projections to 2019 report rates of 4 % per year (IHS, 2014d). Global ethylene demand is usually compared to the average world GDP growth rates and till the end of this decade it is expected to grow faster than the GDP rates (IHS, 2014d), while by 2050 it is expected to grow to 300 % compared to 2010 (ICIS, 2013). GDP is expected to have a growth rate of 1.5 % till the end of this decade (EC, 2013), 63 % slower compared to the ethylene rate. Due to lack of annual rates up to 2050, in this study we assume that the increase in the demand follows the GDP growth rates assumed in (EC, 2013) during the whole simulation period.

Ethylene consumption in western Europe followed the global economic downturn that began in late 2007, managed to rebound in 2010 back to the levels of 2008, but has been decreasing since 2011 (Petrochemicals, 2016). The European ethylene capacity in 2013 was 23 862 kt/year and in 2014 it decreased to 23 378 kt/year, while production was 18 521 kt/year and 19 279 kt/year respectively in these two years (Petrochemicals, 2016). The total EU capacity is about 26 000 kt/year, which is about 20 % of the world ethylene capacity of 130 million tonnes (Cefic, 2013).

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(29) Western Europe in Petrochemicals Europe is EU-15 plus Norway.

Table 29. Steam crackers (ethylene) in EU-28 in 2013

Country	Number of plants	Capacity ($kt_{ethylene}$/y)
Belgium	3	2 240
Czech Republic	1	580
Germany	13	5 655
Spain	3	1 625
France	7	3 140
Italy	3	1 675
Hungary	2	660
Netherlands	5	3 975
Austria	1	500
Poland	1	700
Portugal	1	410
Slovakia	1	240
Finland	1	380
Sweden	1	620
United Kingdom	5	2 715
Total	48	25 125

Steam cracking covers completely the ethylene and butadiene demand in Europe (Ecofys, 2009), while worldwide it accounts for the bulk of the commercial production of ethylene (Ullmann's Encyclopaedia, 2009). In the EU-28 there are 48 steam crackers in operation with a total ethylene production capacity of 25 125 kt/y, as shown in Table 29 (ICIS, 2012; Ecofys 2009; Petrochemicals, 2016; EC, 2014d; IHS, 2015a). The installed capacity considered in this study is in accordance with the Cefic data (Cefic, 2013) and as a result the steam cracking list is considered complete. The majority of installations are located on large chemical sites or refinery sites (EC, 2014d).

Propylene (C_3H_6 – CH_2=$CHCH_3$) — propene according to IUPAC — has similar uses as ethylene and its product chain is included in Annex 2. Polypropylene is the principal driver of propylene demand, as it accounts for 65% of the total global use of propylene (CIEC, 2015). In 2013 56 % of the propylene produced in Western Europe was used for the production of polypropylene and 16 % for propylene oxide (Petrochemicals, 2016).

Most of the world's propylene production and consumption has historically been concentrated in North America and Western Europe, but in recent years China has gained also big share. All three account for about 55 % of global consumption (IHS, 2015b). Propylene is sold in three different quality grades: refinery (55-75 %), chemical (92-96%) and polymer (>99.5 %). Global propylene demand in 2012 was 88 Mt and total capacity was estimated to be 100.4 Mt (Pandia, 2014). In 2013 the installed nameplate propylene capacity was 105.7 Mt for polymer/chemical grade and 45 Mt for refinery grade (IHS, 2014a). Europe accounted for 17.3 % of the polymer/chemical grade capacity, having an equal share with the US, and for 11.4 % of the refinery grade capacity. In Western Europe, nameplate capacity of steam crackers was 12 270 kt/year in 2013 and 12 140 kt/year in 2014, while propylene production (30) was 14 300 kt/year and 14 485 kt/y respectively (Petrochemicals, 2016). World consumption of propylene is forecast to grow on average by 4.6% per year, higher than ethylene (IHS, 2015b).

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(30) Capacity figures relate to steam crackers only, while production figures relate to other sources too (refineries, propane, metathesis) (according to personal communication with Petrochemicals Europe).

Table 30. Propylene producing plants in EU-28 in 2013

Country	Fluid Catalytic Cracking		Steam cracking	
	Number of plants	Capacity (kt/y)	Number of plants	Capacity (kt/y)
Belgium	2	325	5	1 690
Bulgaria	1	70	-	-
Czech Republic	1	60	1	300
Germany	10	1 180	13	3 265
Greece	1	120	-	-
Spain	7	560	4	1 115
France	8	603	7	1 900
Italy	6	610	4	1 010
Lithuania	1	20	-	-
Hungary	1	100	2	355
Netherlands	2	295	5	2 035
Austria	1	115	1	285
Poland	1	120	1	385
Portugal	1	70	1	215
Romania	2	105	-	-
Slovakia	1	30	1	120
Finland	1	90	1	193
Sweden	1	80	1	225
United Kingdom	7	915	4	785
Total	55	5 468	50	1 3878

About 56 % of propylene worldwide production is obtained as a co-product of ethylene manufacture, about 33 % is produced as a by-product of petroleum refining and 7 % is on-purpose product from the dehydrogenation of propane and metathesis. The remaining percentage is from selected gas streams from coal-to-oil processes and from deep catalytic cracking of vacuum gas oil. Metathesis can be applied to convert ethylene and butylenes to propylene as a stand-alone process or being integrated into a steam cracker (Ecofys, 2009). Propylene produced via the refinery catalytic cracking (FCC) process is of refinery grade, while propylene obtained from steam cracking and on-purpose techniques is chemical-grade purity or polymer grade.

In Western Europe, the percentage of propylene from steam crackers is about 70 % (Petrochemicals, 2016). In the EU-28 the 50 steam crackers have a total capacity of 13 878 kt/y in propylene, but as propylene is also produced by fluid catalytic cracking (FCC), there are also 5 468 kt/y produced by 55 plants, as shown in Table 30 (ICIS, 2012). The total propylene capacity is 19 346 kt/y.

Butadiene (C_4H_6 – $CH_2=CH–CH=CH_2$) consumption is driven to a large extent by the automotive industry, as the single largest use of it is in the production of synthetic elastomers, including styrene-butadiene rubber and polybutadiene rubber. In Western Europe butadiene capacity increased from 2 518 kt/y to 2 764 kt/y and production from 1 915 kt/y to 1 991 kt/y between 2013 and 2014 (Petrochemicals, 2016). Global demand was expected to grow at a rate of about 4% per year to 2016 (IHS, 2012a). In Europe all of butadiene demand is covered by steam cracking (Ecofys, 2009).

Butylene (C_4H_8 – $CH_2=CHCH_2CH_3$) – 1-butene according to IUPAC — finds applications in the manufacturing of a variety of chemicals. Co-polymerisation of ethylene and 1-butene produces LLDPE, a form of polyethylene that is more flexible and more resilient. It is also used in the production of polybutene, butylene oxide and in the C4 solvents butyl alcohol and methyl ethyl ketone (MEK).

The steam cracking capacity of Europe was 2808 kt/y concerning butadiene and 703 kt/y concerning butenes in 2013 (ICIS, 2012; Petrochemicals, 2016.

Last but not least, acrylonitrile (C_3H_3N – $CH_2=CH-C\equiv N$) – 2-propenenitrile according to IUPAC – is used mainly as a monomer for products as polyacrylonitrile for acrylic fibres accounting for 42% if its end-uses (Ullmann's Encyclopaedia, 2012). 34 % of acrylonitrile produced is consumed in producing acrylonitrile-butadiene-styrene resins, which are used in numerous automotive, construction and electronics applications thanks to their high strength, colouring characteristics and processing ease (Ullmann's Encyclopaedia, 2012). It is not produced via steam cracking, but it is considered in this study, as it is a derivative of propylene.

Thanks to the above mentioned important uses of it, the global installed capacity of acrylonitrile was in 2010 5.7 Mt (Reliance Industries, 2015). In 2013 only four installations were active in the EU-28 with total capacity 855 kt/y (ICIS, 2012), in comparison with 2000 when there were seven operational installations with a nameplate capacity of 1165 kt/y (EC, 2003a). A plant in Spain has been idle since 2010 (Repsol, 2014). It is obvious, that during the last decade the EU acrylonitrile capacity declined by more than 20 %.

5.3.1 Production processes

As explained already, the most common process applied for lower olefins production is steam cracking and this is the only process described in detail in this study. It is also known as thermal pyrolysis and is a mature technology that has been the industry standard for over 50 years. It can accept a variety of hydrocarbons, ranging from natural gas liquids (ethane, propane and butane) to petroleum liquids (naphtha (31) and gas oils). The choice of feedstock is heavily influenced by market factors and the availability of supplies, but regardless of the feedstock used, steam cracking involves three basic steps (EC, 2014d; EC, 2003a; Ren et al., 2006; Ullmann's Encyclopaedia, 2009):

1. Pyrolysis and cooling,
2. Primary fractionation / compression and
3. Cryogenic cooling and product separation

The feedstock is preheated and vaporised with superheated steam and then passed through tubes where the cracking reactions take place. The process is highly endothermic and requires high temperatures and therefore continuous external heating, usually to 750-900°C (Ren et al., 2006). Temperatures up to 1 100 °C can be achieved (EC, 2014d). The conditions chosen for the furnace temperature and the flow rate of the heated reactants depend on the products that are needed. In order to avoid forming carbon, the residence time is short and the pressure in the tubes low. The vaporisation with steam inhibits carbonisation and prevents mixing with air to form explosive mixtures, a danger in case of leak (due to sub-atmospheric pressure) (CIEC, 2015). In addition, it lowers the hydrocarbon partial pressure, thus enhancing olefin yield (Ullmann's Encyclopaedia, 2009).

The hot mixture leaving the furnace is quenched to prevent loss via side reactions and separated in a series of processes including compression, absorption, drying, refrigeration, fractionation and selective hydrogenation. This further processing depends on the feedstock type and the number and specifications of the desired products (Ullmann's Encyclopaedia, 2009).

In the first end-section the effluent stream is cooled (the waste heat is recovered). It is then condensed to remove heavy hydrocarbon components, compressed and dried,

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(31) Naphtha is the mixture of hydrocarbons in the boiling range of 30 to 200°C.

resulting in a purified gas. Primary fractionation applies only to naphtha and gasoil feed (Ren et al., 2006) and compression takes place in four or five stages, thus removing condensates and acid gases (H_2S, CO_2) by scrubbing the stream near the final stages (Ullmann's Encyclopaedia, 2009). Most of the dilution steam is recovered and recycled (Ren et al., 2006).

The dried gas is led to the main fractionation section, where it is separated into different products. The predominant method in this section is cryogenic separation. There are several configurations that can be used, depending on the feedstock and the design arrangement. The three most common processes are de-methaniser (to remove methane and lighter components), de-ethaniser (to remove ethane, ethylene and some acetylene) and de-propaniser (to remove propane and lighter components) (Ullmann's Encyclopaedia, 2009). During this process, hydrogen is also recovered and used for downstream hydrogenation, hydrotreating of the heavier products or sold (EC, 2014d). The methane-containing gas is usually used as fuel gas internally, while ethane and propane are generally recycled. Acetylene and propadiene are usually undesired and are further processed with hydrogenation so as to yield ethylene and propylene (Ullmann's Encyclopaedia, 2009). Butadiene, C4 compounds and aromatic gasoline are separated in the end (Ren et al., 2006).

The choice of feedstock depends on market factors and the availability of supplies. In 2014, naphtha and condensates provided about 68 % of the feed to European steam crackers, while 21 % came from natural gas liquids and the rest from gasoil and other sources (Petrochemicals, 2016). The final product yields depend on the feedstock and the cracking severity (32). Light olefins are formed primarily from alkanes and naphthenes and as a result, light feedstocks containing mainly *n*-alkanes result in lower co-product yields than the heavier feedstocks (Ullmann's Encyclopaedia, 2009). Generally as the molecular weight of a feedstock increases, ethylene and propylene yields decrease (EC, 2014d; Ullmann's Encyclopaedia, 2009). Typical product streams for the different feedstocks are shown in **Table 31**(33). As naphtha is a mixture of hydrocarbons, the ranges in the case of this feedstock are wide. There is a tendency in the industry to use light naphthas and other feedstocks, lower-severity conditions (high coil outlet temperature, but low hydrocarbon partial oxidation and short residence time) in order to increase the yield of ethylene (Ullmann's Encyclopaedia, 2009).

Concerning propylene production, the four commercially proven routes are: (1) steam cracking, (2) fluid catalytic cracking (FCC), (3) propane dehydrogenation and (4) metathesis of ethylene and butylenes.

Fluid catalytic cracking (FCC) is used in refineries primarily to produce gasoline and distillate from heavy oils, but it also converts a significant portion of the feed to C_1 - C_4 products, including propylene and hydrogen (EC, 2015a). The percentage of propylene produced depends on the operating mode of the FCC: if it is operated in gasoline mode the average propylene yield is about 5 %wt on fresh feed, while if it is operated in propylene mode it can reach up to 20 %wt (Couch et al., 2007). A simplified flow diagram for fluid catalytic cracking is shown in Figure 13.

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(32) Severity refers to the conditions used during cracking and is a function of the temperature and the residence time of the feedstock in the furnace. It depends on the desired product ratios.

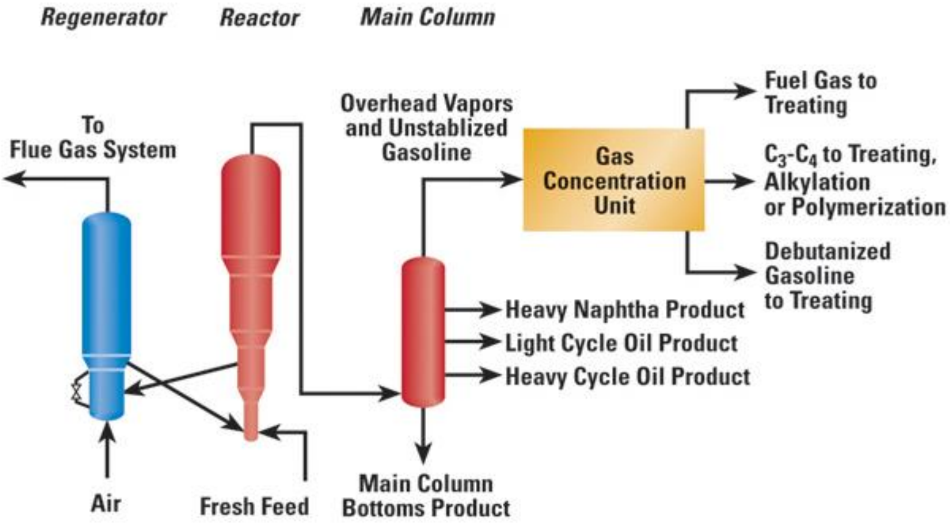
(33) Data representative of relative material balances for an ethylene plant with a capacity of 453 kt per year when feeding one feedstock at the assumed severity conditions. Ethane and propane recycle to extinction is assumed for all feedstock categories.

Table 31. Typical product yields (kt) for different feedstocks for a plant with ethylene capacity 453.6 kt/y (ACC, 2004)

Product (kt)	Feedstock				
	Ethane	Propane	Naphtha	Atmospheric Gasoil	Vacuum Gasoil
Cracking severity	High	Medium to high	Medium to high	Medium to high	Medium
Hydrogen-rich gas	33	17-21	11-14	12-26.5	17-26
Methane-rich gas	39.5	263-296.5	199-222	183 - 196	175-194
Ethylene	453.6	453.6	453.6	453.6	453.6
Propylene[1]	11	166-293.5	181-260	242.5-83	261
Butadiene	10	18-32	56-77	76-82	79
Butenes / Butanes	4.5	13-22	60-128	76-88.5	84
Pyrolysis gasoline	9	47-71	183-494	294-342.5	299.5
Benzene	4.5	17-26.5	51-84	96-109	109
Toluene	0.5	5-5.5	19.5 - 71.5	51-54.5	57
C8 Aromatics	0	0	26.5 - 43	20-43	134
Other	4	25-39	86 - 295	127-136	
Fuel oil	0	4.5-10	29.5 - 51	289-376.5	544-605.5
Total	561	982-1 200	1 173 - 1 670	1 614-1 822	1 897-1 977
Ethylene yield (%)	81	38-46	27 - 39	25-28	23-24

[1] Polymer-grade propylene production is assumed

Figure 13. Simplified fluid catalytic cracking process (UOP, 2014)



The feed in the catalytic cracking unit can be heavy gas oils from the vacuum distillation unit in the refineries or bottom streams from the atmospheric distillation unit. Depending on the feedstock, the process is named either fluid catalytic cracking or residue catalytic cracking, but often units designed for one type of feedstock can also treat some of the other.

Acrylonitrile is produced in Europe exclusively from propylene with the BP/SOHIO process (EC, 2003a), which accounts also for more than 90 % of the worldwide acrylonitrile capacity (IPCC, 2006b). It consists of a vapour phase exothermic ammoxidation of propylene using excess of ammonia and oxygen in the presence of an air–fluidised catalyst bed, according to the following reaction (Ullmann's Encyclopaedia, 2012):

$$C_3H_6 + NH_3 + 1.5\ O_2 \rightarrow C_3H_3N\ +\ 3\ H_2O \qquad \text{(reaction 17)}$$

The conditions of the process are temperatures of 400-510 °C, pressures of 50-200 kPa and residence time of a few seconds and on a mixture of heavy metals on silica, as catalyst. It is a single-pass process with about 98 % conversion of propylene. The reactor effluent is quenched with water and the unreacted ammonia is neutralised with sulphuric acid, resulting in ammonium sulphate that can be used as fertiliser (Ullmann's Encyclopaedia, 2012).

5.3.2 Current consumption and emission levels

Steam cracking is the most energy-consuming process in the chemical industry and globally uses approximately 40 % of the total energy in the entire petrochemical industry (Rahimi and Karimzadeh, 2011). In 2000 it accounted for about 20 % of the final energy use (excluding energy content in chemicals) of the global chemical industry and nearly 200 million tonnes of CO_2 emissions due to combustion of fossil fuels (Neelis et al., 2007; Ren et al., 2008).

Depending on what is considered as final product, there are different ways to express consumptions and emissions in the case of steam cracking. If ethylene is the final product of the process, all energy and feedstock use is allocated only to it and all other by-products are hence energy and feedstock neutral. This is not always the best indicator, as in the comparison of ethane and naphtha cracking, ethylene yield is higher in the case of ethane, but naphtha cracking also yields considerable amounts of other valuable by-products (Table 31). The best indicator would be tonnes of high value chemicals (HVCs), which usually include ethylene, propylene, butadiene and butenes. The feedstock consumptions for steam cracking can be calculated according to the data shown in Table 31 and are summarised in Table 32 in both references for comparison. In our study the goal is to calculate the energy consumption and the GHG emissions of the chemical industry. As a result and in order to avoid double-counting, we will use the allocation of all consumptions and emissions to ethylene, since steam crackers capacity in the industry refers to this product. This way all other by-products are produced without charge but all the consumptions and emissions of this part of the chemical industry are taken into consideration in the study.

Table 32. Feedstock consumption for steam cracking production

Steam cracking	Feedstock	$t/t_{ethylene}$	t/t_{HVC} [1]
Ethane based[2]	Ethane	1.2	1.17
Gas oil based[3]	Gasoil	4.0	2.07
Naphtha based[4]	Naphtha	2.7	1.60

[1] HVCs here include ethylene, propylene, butadiene and butenes

[2] Ethylene yield 81% assumed

[3] Ethylene yield 25% assumed (considering the average of both atmospheric and vacuum gasoil)

[4] Ethylene yield 35% assumed

In the case of acrylonitrile the major raw materials consumed are propylene and ammonia and the average values are shown in Table 33 (EC, 2003a; Ullmann's Encyclopaedia, 2012).

Table 33. Feedstock consumption for acrylonitrile production

Feedstock	Consumption (t/$t_{acrylonitrile}$)
Propylene	1.09
Ammonia	0.50

The process energy use in the case of steam cracking is the sum of the theoretical thermodynamic energy requirement (the minimum energy input requirement for converting feedstock to desired product in an endothermic reaction) together with any energy losses. Losses can occur because of fouling, coking or other reasons. An overview of the specific energy consumptions (SEC) for steam cracking (34) in the case of ethane and naphtha is included in Table 34 (Ren et al., 2006; IEA, 2007).

Table 34. Overview of energy use and CO_2 emissions of ethane and naphtha steam cracking

Feedstock	SEC		CO_2 emissions		Losses	Reference
	(GJ/$t_{ethylene}$)	(GJ/t_{HVC})	(t_{CO2}/$t_{ethylene}$)	(t_{CO2}/t_{HVC})	(wt%)	
Ethane	17-21	16-19	1.0-1.2	1.0-1.2	1-2	(Ren et al., 2006)
	15-25	12.5-21				(IEA, 2007)
Naphtha	26-31	14-17	1.8-2.0	1.6-1.8	1-2	(Ren et al., 2006)
	25-40	14-22				(IEA, 2007)
Gasoil	40-50	18-23				(IEA, 2007)

The breakdown of consumptions and exergy losses can help to identify where energy savings are possible. Concerning naphtha cracking, the step of pyrolysis accounts for approximately 2/3 of the total energy consumption, while the remaining 1/3 is consumed in compression and separation techniques. Compression uses approximately 15% of the total energy use and separation approximately 1/5 of the total energy use (Ren at al., 2006). 75 % of the total exergy losses (about 15 GJ/$t_{ethylene}$) occur in the pyrolysis section, where total temperature drop is more than 1 100 °C and total pressure drop is nearly 70 bar (Ren et al., 2006). Exergy losses in the compression and separation sections, accounting for 25 % of the total losses, are mainly caused by the use of electricity for refrigeration and compression, where the conditions are cryogenic (temperatures as low as -150°C and pressures up to 30 bar) and are estimated to be about 2 GJ/$t_{ethylene}$ (Ren et al., 2006). The additional energy (1-2 %) is needed in decoking/defouling, shutdowns/restarts and related maintenance.

As mentioned earlier, fuel gases containing methane and other fuel-grade by-products from naphtha steam cracking can be combusted to provide process energy. These fuel by-products (amounting to approximately 20-25% of the energy content of naphtha) together with flue gases and waste heat can meet approximately 95% of the process energy demand in naphtha steam crackers (Ren et al., 2006). The LHV of naphtha is 44.5 GJ/t (Table 6), which results in about 10 GJ/$t_{naphtha}$ fuel by-products. Energy for the compression and separation is provided by steam, almost all of which is produced in the heat exchangers after the pyrolysis. Typically, there is no net steam import or export (Ren et al., 2006). A small amount of electricity, about 1 GJ/$t_{ethylene}$ (35), is provided from external sources. Contrary to naphtha cracking, ethane cracking is not self-sufficient in terms of energy and therefore requires energy import of about 15 % of the total SEC (Ren et al., 2006).

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(34) Specific energy consumption refers to process energy use in pyrolysis and separation.

(35) This value refers to primary energy and conversion 40% is considered.

Concerning electricity, according to (IHS, 2014a), naphtha-based steam cracking needs 44 kWh/$t_{ethylene}$ electricity, ethane-based 140 kWh/$t_{ethylene}$ and gasoil-based 300 kWh/$t_{ethylene}$. Using these values and combining all the information in the literature about the specific energy consumption of the different types of steam cracking, the total energy consumption for ethane-based steam cracking is assumed to be 20.5 GJ/$t_{ethylene}$, for naphtha-based to 12 GJ/$t_{ethylene}$ and for gasoil-based to 25 GJ/$t_{ethylene}$, which are in accordance with the aggregated values from literature (Table 34), if the fact that naphtha-based (and also gasoil-based) processes are using by-products for the heating demands. If these consumptions need to be expressed per another product of the steam cracking process, this is based on the relative yields according to Table 31.

A large proportion of Europe's propylene demand can be satisfied by steam cracking, but the rest is supplied from extraction from refinery Fluidised Catalytic Cracker (FCC) off-gas. FCC involves up to 20 % less resources consumption and emissions compared to steam cracking (Ren et al., 2006). The utility consumption of catalytic crackers per tonne of product is estimated to be 120-2 000 MJ of fuel, 2-60 kWh of electricity and 50-20 m^3 of cooling water, while concerning the steam the process consumes about 30-90 kg and produces 40-60 kg (EC, 2015a). Attention should be paid, because FCC is producing gasoline as well as propylene, with a ratio of about 15.3:1 (IHS, 2014c) and since gasoline production is not part of the chemical industry, only the emissions and consumptions attributed to propylene should be taken into consideration. The process consumes 1.7 kWh/$t_{propylene}$ electricity, 0.95 GJ/$t_{propylene}$ fuel for thermal needs and 0.08 t/$t_{propylene}$ medium pressure steam (IHS, 2014a). If medium pressure steam is assumed to be between 3.5-17.5 bar, its average latent heat would be about 2 000 KJ/kg (Engineering Toolbox, 2015a), the steam consumption is converted to 0.16 GJ/$t_{propylene}$. Feedstock consumption of FCC is 26.3 t of distillate fuel oil per tonne products. The amount corresponding to propylene is 1.61 t/$t_{propylene}$, calculated by mass allocation between gasoline and propylene. The emission factor used for direct emissions is 0.21 t_{CO2}/$t_{propylene}$ (IHS, 2014a).

As far as it concerns acrylonitrile, the ammoxidation of propylene is an exothermic reaction. As the heat of reaction is used to generate high pressure steam, acrylonitrile plants are net energy exporters, with a range between 340 and 5 700 MJ/$t_{acrylonitrile}$ (EC, 2003a). This range is wide because of the number of gaseous and liquid effluent streams generated and can be recovered. The electrical demands of the process are 1.51 MJ/$kg_{acrylonitrile}$, based on an LCA study (Plastics Europe, 2005). This value includes also the electricity needed to produce the raw materials, which should be deducted. Ammonia production requires 0.3 GJ/t_{NH3} electricity (see paragraph 5.2.2), while propylene production requires 90.5 kWh/$t_{propylene}$ (calculated according to the procedure explained before). The net electric consumption for ammoxidation is calculated to be 277.8 kWh/$t_{acrylonitrile}$.

During steam cracking, emissions arise from the following principal sources (EC, 2014d):

- Combustion of fuels to provide heat to the steam cracker;
- Decoking of the cracker furnace tubes;
- Regeneration or processing of scrubber liquors used for the clean-up of the cracked gases;
- Fugitive releases of Volatile Organic Carbons (VOCs).

CO_2 emissions of ethylene production from steam cracking can be estimated using the feedstock-specific emission factors shown in Table 35 (IPCC, 2006b). These factors concern total process and energy feedstock use and are based from plant-specific data for steam crackers in Western Europe. As a result, an adjustment factor is necessary for other geographical regions (110 % for Eastern Europe not including Russia). In addition, they do not include emissions from flaring, which amount to about 7 % of total emissions in a well-maintained plant (IPCC, 2006b). The emission factors can be calculated with reference to the other products by using the correlations shown in Table 31.

Table 35. Steam cracking - ethylene production emission factors (IPCC, 2006b)

Feedstock	$t_{CO2}/t_{ethylene}$			
	Naphtha	Gasoil	Ethane	Propane
Ethylene	1.73	2.29	0.95	1.04
— Process feedstock use	1.73	2.17	0.76	1.04
— Supplemental fuel use	0	0.12	0.19	0

Overall VOCs emissions from steam cracking are estimated to be 5 $kg/t_{ethylene}$ produced from naphtha and 10 $kg/t_{ethylene}$ produced from ethane, but due to uncertainties the default values for CH_4 emissions for ethylene production are considered to be 6 $kg/t_{ethylene}$ in the case of ethane as feedstock and 3 $kg/t_{ethylene}$ for all other feedstocks (IPCC, 2006b).

Concerning acetonitrile, process vent CO_2 emissions can be calculated using the emission factors provided in Table 36. These emission factors are based on an average propylene feedstock consumption factor of 1.09 $t/t_{acrylonitrile}$ (Table 33) corresponding to a propylene conversion rate of 70 %. The default emission factor is based on the assumption that secondary products (acetonitrile and hydrogen cyanide) and any hydrocarbon by-product in the main absorber vent gas are either burnt for energy recovery or flared to CO_2 (IPCC, 2006b).

Table 36. Acrylonitrile production CO_2 emission factors (IPCC, 2006b)

Process configuration	Emission factor ($t_{CO2}/t_{acrylonitrile}$)
Secondary products burnt for energy recovery/flare (default)	1.00
Acetonitrile burnt for energy recovery/flare	0.83
Acetonitrile and hydrogen cyanide recovered as product	0.79

Steam cracking products are benchmarked, with value 0.702 $allowances/t_{HVC}$ (EC, 2011b). The system boundaries of the benchmarking include all steps of the processes, including also emissions related to the production of the consumed electricity. Nevertheless, there is no benchmarking curve available for steam cracking (Ecofys, 2009) and as a result, there is no calibration performed in this case.

5.3.3 Best available techniques (BATs)

The goal for the techniques to be considered as BATs is to have potential for achieving high level of environmental protection (Table 37). As olefin production is a mature technology, improvements in terms of energy consumption and GHG emissions that can be achieved are only marginal. In the case of acrylonitrile, BAT is to maximise the re-use of hydrogen cyanide, acetonitrile and ammonium sulphate by-products.

Advanced process control

Advanced process control (APC) has been already implemented in the Shell Chemical Ethylene plant in Texas USA (Haarsma & Mutha, 2008). Some APC features include robust (bi) linear steady state optimisation, advanced modelling capabilities, such as intermediate variables and cascade correction of manipulated variables, and on-line updateable model gains. Typical reported benefits from implementation of APC on an ethylene plant vary from USD 1 to 10 million per year, depending on the plant capacity, its feed slate, the constraints and local economics (Haarsma and Mutha, 2008). The payback time is estimated to be one year or even less. On the reference example plant the benefits on product recovery and energy consumption add up to USD 3.7 million

$_{2007}$/y (Haarsma and Mutha, 2008). Unfortunately, all literature about advanced process control quantifies the benefits only from the financial point of view, but they include savings in feedstock, steam and other parts of the process. As there is no information concerning the investment costs and the exact energy savings of this technique, it is not included in our study.

Table 37. Overview of the possible BATs and ITs in steam cracking and acrylonitrile industry

BAT or IT	Description	Investment cost	Energy savings	GHG Reduction
BAT	Advanced process control	No information available		
BAT	Decoking activities	Not included in the study as the savings are <5 %		
BAT	Implementation of LDAR methods	Not included in the study as the savings are <5 %		
BAT	Improving furnace design	EUR 1 442 430 [1]	10 %	None
BAT	Improving compression and separation section – Advanced distillation columns	Not included in the study as the savings are <5 %		
BAT	Improving compression and separation section – MVR	EUR 0.57/t [2]	5 %	None
BAT	Acetonitrile and hydrogen cyanide recovered as product	No information available		
IT	Adsorption Heat Pump	EUR 5 396 827 [3]	12 %	None
IT	Improving compression and separation sections – VSA	No information available		
IT	Improving compression and separation sections – Membranes	EUR 11 506 984 [4]	8 % electric, thermal and steam	None
IT	Methanol-to-olefin	Not included in the study as the savings are <5 %		
IT	Use of biomass	Not included in the study due to lack of information		

[1] Reference capacity 680 kt/y

[2] Reference capacity 344 kt/y

[3] Reference capacity 500 kt/y

[4] Reference capacity 625 kt/y

Decoking activities

Coke accumulates in the furnace tubes and reduces the heat transfer efficiency. Decoking results in maintaining the furnace at efficient conversion rates without increasing energy demand. Proper design and operation of the furnaces to minimise coke formation is the only technically feasible mean of minimising GHG emissions (Formosa Plastics, 2012; Chevron, 2012; ExxonMobil, 2012). Several licensors are already implementing advanced coil-related furnace features (Ren et al., 2006). This BAT is excluded from our analysis as it determines savings less than 5%.

Implementation of instrument leak detection and repair (LDAR) methods

GHG emissions from piping fugitives can be controlled by techniques such as installation of leak-less technology components, implementation of instrument leak detection and repair (LDAR) programmes, implementing alternative monitoring using remote sensing technology (Formosa Plastics, 2012; Chevron, 2012; ExxonMobil, 2012). However, these methods are only cost-effective for CO_2 prices higher than USD 44/$t_{CO2.eq}$, and the incremental GHG emissions controlled is less than 0.3 % (Chevron, 2012). As a result, this BAT is also excluded from our analysis, due to low savings.

Improving furnace design

In an effort to improve heat transfer and raise severity in the pyrolysis section, several innovations have been developed, such as circulating solids (e.g. sand, coke or other carriers), circulating beds (Picciotti, 1997), selective radiant coils to allow better control of the propylene/ethylene ratio (Nieuwlaar, 2001), ceramic-coated tubes/coils (Kolmetz et al., 2002) and other advanced furnace materials. It is estimated that these advanced materials can achieve approximately 10 % savings on current average SEC (Ren et al., 2006). Some of the innovations aim to decrease coke formation (Brayden et al, 2006), affect olefin selectivity, and increase the skin temperature on the tubes and surface catalytic activity. Total capital costs plus installation costs of a high efficiency coalesce and filtration unit in a 680 kt ethylene plant in 2004 were estimated at USD 1.5 million $_{2004}$ and the payback time was less than a year (Brayden et al., 2006).

Improving compression and separation section

This includes mechanical vapour recompression (MVR), advanced distillation columns, membranes and combined refrigeration systems (Ren et al., 2006). Several advanced distillation columns have been developed with different savings that can range between 60 % and 90 % on the energy consumption of a conventional distillation column (0.1-0.3 GJ/$t_{ethylene}$), while MVR and membranes can lead to approximately 1 GJ/$t_{ethylene}$ and 1.5 GJ/$t_{ethylene}$ savings, respectively (Ren et al., 2006). Capital costs for implementation of an advanced distillation column is about USD 1/$t_{ethylene}$ (Wu et al., 2012) and in the case of MVR costs are almost the same as conventional distillation (Diez et al., 2009), estimated at EUR 0.57_{2012}/$t_{ethylene}$ (OPT Sensor Srl, 2012). Advanced distillation columns are excluded from the scope of the study as BAT, as its maximum savings are 1.5 %, while MVR has savings about 5 % and falls inside the scope.

Acrylonitrile: secondary products recovered

Ammoxidation of propylene to acrylonitrile is not 100 % efficient in utilisation of the propylene feedstock. The primary product yield factor is about 70 % (IPCC, 2006b). However, the acrylonitrile production process may be configured to operate to produce a greater or lesser amount of secondary products (acetonitrile and hydrogen cyanide). In the default case by-products are assumed to be burnt for energy recovery or flared to CO_2 and are not recovered. Nevertheless, if secondary products are recovered for sale and are neither flared nor burnt for energy recovery, the overall process yield factor increases to 85 % (IPCC, 2006b). The emission factors for the cases of secondary products being recovered as products and acetonitrile burnt for energy recovery are shown in Table 36. Unfortunately, there is no cost data available for this technique.

5.3.4 Innovative technologies (ITs)

Possible advances in steam cracking can include modifications in the pyrolysis section to improve heat transfer, reduce coking and raise severity, and introduction of systems for recovery and save or of more efficient techniques of compression and separation.

Adsorption Heat Pump

As steam cracking requires a huge amount of low temperature cooling but at the same time it discharges a large amount of low temperature heat, it can be used to run an Adsorption Heat Pump (AHP) for chilled water generation, of for direct process cooling. A type of AHP has been developed by Mitsubishi Plastics Inc. (Hirata and Kakiuchi, 2011). Chilled water generation from AHP is considered a promising technique to partially replace the existing expensive propylene refrigerant. Applying AHP had a significant impact in reducing energy consumption of the propylene refrigerant compressor by 12 % (Hirata and Kakiuchi, 2011). Investment costs, consisting of the equipment purchase plus the constructions for retrofitting an AHP in an existing plant, are in the order of USD 7.4 million $_{2011}$ (Hirata and Kakiuchi, 2011).

Improving compression and separation section

Possible improvements in these sections include vacuum swing adsorption (VSA) and membranes (Ren et al., 2006).

VSA involves solid sorbents for selective adsorption of ethylene and propylene over paraffins and not a lot of information concerning its performances is available. Membranes, on the other hand, are often made of polymer or inorganic materials and could be used in separation of olefin/paraffin, gases and coke/water (Ren et al., 2006). If membranes are used in the C_2/C_3 separation alone, approximately 8 % savings on process energy is expected (Ren et al., 2006). At present, only hydrogen recovery from the cracked gas is considered feasible and can contribute to reducing the refrigeration load as well as the equipment size of the col-box section. For a 625 kt/y ethylene plant, the net power saving is about 9.3 MW and gives net annual savings of about USD 2 899 000 $_{2001}$/y, while it requires USD 13 521 000$_{2001}$/y capital investment (Al-Rabiah et al., 2001).

Olefin production via methanol

The methanol-to-olefin (MTO) process allows producing olefins from gas or coal instead of oil. SEC in the case of MTO technologies is in the range of 5-8 GJ/$t_{HVC,}$ when conventional naphtha cracking is in the range 14-17 GJ/t_{HVC}, but they require additional 23 GJ/t_{HVC} for the methanol production (IEA, 2013). More efficient methanol synthesis and more selective catalysts for the MTO process will improve the SEC of the process and could lead to GHG savings. For the time being, this technique falls out of the scope of this study, as there are no savings achieved with it.

Use of biomass

Olefins can be produced from biomass, but the primary feedstock needs intermediate transformations. For example, sugar- or starch-rich biomass is fermented to ethanol, which is then converted by dehydration to ethylene. The first part of the process is very energy intensive and the energy consumption of biomass routes can be 3.5-5 times higher than for fossil routes (IEA, 2013). GHG savings could reach 80-90 % compared to steam cracking and about 70 % compared to the industry benchmark (36) (Benner et al., 2012), but it is not yet known to have been applied in industry. This technology is not included in the study as it cannot be quantified yet.

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(36) These calculations are based on the Renewable Energy Directive [EC, 2009], which means that direct and indirect land use change has not been taken into consideration. According to COM(2012) 595 final [EC, 2012], the carbon footprint of some types of biomass (including sugar- and starch-rich feedstocks) will be lower.

5.4 Hydrogen, Syngas and Methanol

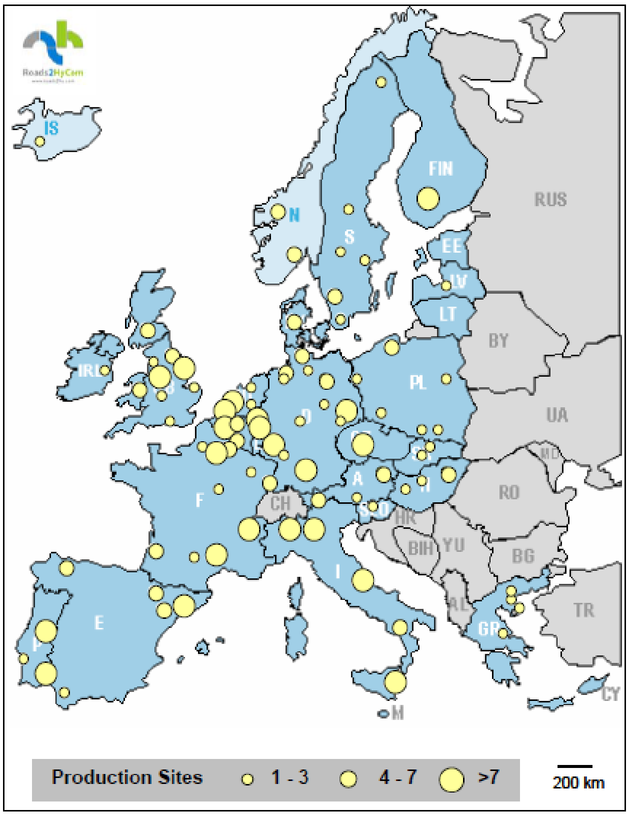
Hydrogen (H_2) is the most abundant element in the universe, and it appears naturally on the earth's crust bound with other elements instead of being in its molecular form. Molecular hydrogen is produced in large quantities both as a principal product and as a by-product.

The term "synthesis gas", usually referred to as syngas, covers all mixtures of carbon monoxide and hydrogen, from pure CO to pure H_2 (Ecofys, 2009). It is mainly used for the synthesis of special chemical products, thus the name (Ullmann's Encyclopaedia, 2000a). In chemical, oil and energy industries hydrogen and synthesis gas are indispensable (Song, 2009).

Globally, around 45 - 50 million tonnes of hydrogen (5.5-6 EJ) (37) were produced in 2010, the majority of which is produced using fossil fuel feedstocks (Carbon Counts, 2010). In 2012, the annual hydrogen production was estimated to be around 6 EJ (IEA, 2012a). Nearly 96% of hydrogen is derived from fossil fuels: natural gas is the most frequently used (about 48 %), followed by liquid hydrocarbons (30 %), coal (18 %) and electrolysis and other by-product sources of H_2 based on electrolysis with 4% (Kothari et al., 2008; IEA, 2012a; IHS, 2015c). Globally, hydrogen is expected to increase by 5-6% until 2020 (IHS, 2015c).

Hydrogen in the refining and chemical industry is almost entirely used as feedstock (IEA, 2012a). Most of it is used in the synthesis of ammonia and methanol and a significant portion in refineries for upgrading crude oils by processes such as hydrocracking and hydrotreating desulphurisation units. In Europe, 50% of the total hydrogen is consumed by the refinery and 32 % by the ammonia industry. If methanol and metal industries are added, these four sectors cover 90 % of the total (Roads2hy, 2007).

Figure 14. Geographic distribution of identified hydrogen production facilities (Roads2hy, 2007)



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(37) For H_2, standard net enthalpy of 121.4 MJ/kg is assumed [Perry's Handbook, 2008].

The hydrogen market is growing, mainly thanks to regulations pertaining to desulphurisation of fuel used in transportation, growth in transportation fuels and decreasing crude oil quality (IHS, 2015c). It is one of a few energy carriers capable of achieving near-zero CO_2 performances (IEA, 2012a) and it is estimated that the overall global demand for hydrogen will increase by about 5-6% during the next five years (IHS, 2015c). The main drivers of the growth are expected to be the lower-quality crude oils that are being processed and the rising demand for distillate fuels (IHS, 2015c).

Around 2005, total European production was estimated at 92 billion m^3, 95% of which was located in EU-28, 2 % in Turkey and 1.8% in Iceland, Norway and Switzerland (Roads2hy, 2007). The captive industry (ammonia and methanol) produced around 64 % of the total, followed by the by-product industry (ethylene, acetylene, styrene and coke-oven gas) with 27 % of the production and merchant companies (38) with 9 % (Roads2hy, 2007). The geographic distribution of the identified hydrogen production sites is shown in Figure 14.

In 2007/08 there were 83 installations included in the EU ETS concerning hydrogen and syngas, including methanol plants and excluding ammonia plants, both in the chemical and in the refinery sectors (Ecofys, 2009). Table 38 summarises an overview of the plants producing hydrogen and methanol in EU-28 (ICIS, 2012; Ecofys, 2009; Roads2hy, 2007).

Table 38. Hydrogen producing plants in the EU-28 in 2013

Country	Capacity (kt/y)
Belgium	372.3
Bulgaria	9.5
Czech Republic	40.3
Denmark	15.7
Germany	1 448.3
Ireland	0.2
Greece	22.5
Spain	348.5
France	352.6
Croatia	58.2
Italy	539.6
Lithuania	58.1
Hungary	38.0
Netherlands	568.6
Austria	89.3
Poland	16.4
Portugal	67.9
Romania	15.2
Slovenia	0.3
Slovakia	31.9
Finland	136.0
Sweden	132.7
United Kingdom	490.0
Total	4 825.0

Methanol (CH_3OH) is the simplest alcohol and is also known as methyl alcohol or wood alcohol. It has a wide range of derivatives (its product chain is included in Annex 2), but it can also be used directly. Its main derivative is formaldehyde accounting for 31% of

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(38) Merchant companies buy hydrogen from captive or by-products industries and sell it back.

the world methanol demand in 2012 (MMSA, 2013). Thanks to its low freezing point (-98°C) and the ability to mix with water in all proportions, it is widely used as antifreeze in heating and cooling circuits and refrigeration systems (Ullmann's Encyclopaedia, 2012b). It is also used as solvent and as absorption agent in gas scrubbers. It is a promising substitute for petroleum products and can be used as fuel, which includes methyl tert-butyl ether (MTBE)/ tert-amyl methyl ether (TAME), biodiesel, gasoline blending and dimethyl ether (DME). The use of methanol in direct fuel applications accounts for 37% of its global demand (MMSA, 2013).

Global methanol installed capacity has been growing since 2009 with an average rate of about 10%, while production with a slightly smaller rate of about 7 %, reaching in 2012 58 Mt according to IEA (2013) and 60.6 Mt according to MMSA (2013). Concerning nameplate capacity installed worldwide, in 2012 it was 95.5 Mt (MMSA, 2013) and in 2013 98.3 Mt, with Europe covering about 3%, most of it residing in Germany (IHS, 2014a). The European installed capacity is shown in Table 39. China owns about 50 % of the world capacity and consumption (IHS, 2014e). China is expected to be the main factor in the growth of methanol capacities, followed by North America, while Europe is expected to be stable (Berggren, 2013). Concerning feedstocks, about 80 % of methanol is natural-gas based, and the rest is coal-based, essentially in China (IEA, 2007).

Table 39. Methanol producing plants in EU-28 in 2013

Country	Number of plants	Capacity (kt/y)
Germany	4	1675
Netherlands	2	500
Romania	1	200
Total	7	2375

Global methanol demand depends on the demand for the main derivatives. In the next five years, global methanol demand for formaldehyde is expected to grow at an average rate just over 5 %, but its demand for fuel applications is expected to be raise more strongly at a rate of about 12.5 % (IHS, 2014e).

5.4.1 Production processes

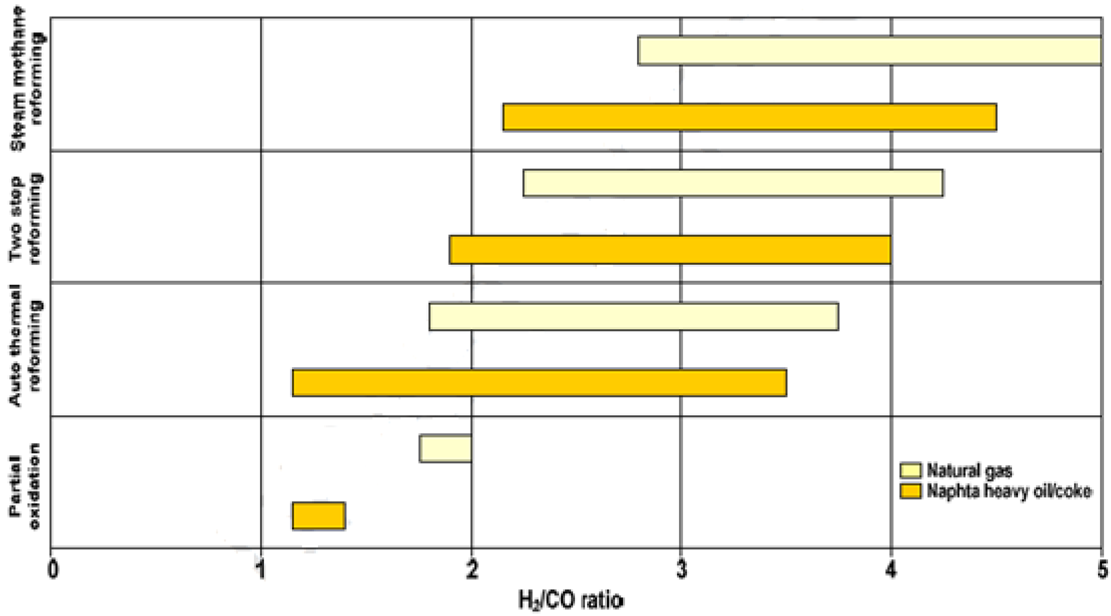
Hydrogen in molecular form can be produced from a variety of feedstocks and by several processes. Feedstocks include fossil resources, such as natural gas, coal and oil, as well as renewable sources, such as solar, wind, wave or hydro-power (IEA, 2006). Processes include chemical, biological, electrolytic, photolytic and thermo-chemical. Electrolysis of water is the oldest known electrochemical process, but the most typical production technology today is through steam reforming of natural gas (Lipman, 2011).

Fuel processing technologies convert a hydrogen containing material, such as hydrocarbons, ammonia or methanol, into a hydrogen rich stream. There are three primary techniques of hydrocarbon reforming: steam reforming, partial oxidation and auto-thermal reforming. The production processes to produce syngas/H_2 are similar to the initial step in the ammonia production (5.2.1) and these hydrocarbon reforming techniques have been presented in detail there already.

An additional way of producing hydrogen from fossil fuels is gasification. The reaction mechanisms of gasification resemble those of partial oxidation (Kothari et al., 2008) and in many cases the two processes are considered to be the same. It involves treatment of coal or heavy hydrocarbon streams with high temperature steam to produce syngas, a catalytic shift conversion and purification of the hydrogen product. Gasification can also have biomass as feedstock, a process that is already mature (Holladay et al., 2009).

The primary advantage of gasification, as well as of partial oxidation, is that useful products can be generated as raw synthesis gas from heavier refinery hydrocarbons or heavy fossil fuels, that otherwise would not have been used (EC, 2015a). However, hydrogen can only be considered as by-product of the gasification process, due to the fact that the H_2/CO ratio can be quite low, since the heavier hydrocarbon streams may not have enough hydrogen to produce the required quantity (EC, 2015a). Figure 15 shows this ratio for the main hydrogen production techniques.

Figure 15. H_2/CO ratio for the main hydrogen production processes and for two types of feedstock (EC, 2015a)



Hydrogen can also occur as by-product in different industries, such as the production of ethylene, chlorine, acetylene and other (Roads2hy, 2007). The case of ethylene production has been already explained in paragraph 5.3.1. Hydrogen is usually produced at a rate of 370 $m^3/t_{ethylene}$ and consumed later at a rate of 180 $m^3/t_{ethylene}$, leading to a net production of 190 $m^3/t_{ethylene}$ (Roads2hy, 2007). The chlor-alkali process will be described in detail in paragraph 5.9 and results typically in producing hydrogen at a rate of 300 $m^3/t_{chlorine}$ (Roads2hy, 2007).

Concerning methanol, there are several alternative processes for its production, such as conventional reforming, combined reforming and partial oxidation. The conventional reforming involves steam reforming and methanol synthesis. The latter is done according to the following reactions:

$$CO + 2\ H_2 \rightarrow CH_3OH \qquad \text{(reaction 18)}$$

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O \qquad \text{(reaction 19)}$$

Conventional reforming process may utilise CO_2 captured from other industrial processes as a supplemental feedstock (IPCC, 2006b).

Combined reforming process combines conventional steam reforming with catalytic partial oxidation and can produce synthesis gas with a more balanced ratio of hydrogen to carbon oxides (IPCC, 2006b), according to the following reaction:

$$CH_4 + \tfrac{1}{2}\ O_2 \rightarrow CO + 2\ H_2 \rightarrow CH_3OH \qquad \text{(reaction 20)}$$

The first catalysts used in the methanol synthesis were ZnO/Cr_2O_3 and operated at 350°C and 250-350 bar, but they have been abandoned since the introduction of $Cu/ZnO/Al_2O_3$ that operates at lower temperatures (220-275°C) and pressure (50-100 bar). The synthesis of the catalyst, usually, varies depending on the manufacturer (Spath & Dayton, 2008).

Due to production economics, primary feedstock for syngas is natural gas (58 % of the world's methanol production in 2013), but it can be produced also from naphtha, petroleum residues, coal and, at least potentially, methane-containing gases from landfills (IPCC, 2006b). The reaction producing methanol is highly exothermic and a major challenge is to remove the excess heat in order to shift the equilibrium towards the products and avoid side reactions and catalyst sintering (Spath & Dayton, 2008; Ullmann's Encyclopaedia, 2012b).

Within the last decade, some new types of large methanol plants have been built, particularly in regions rich in natural gas, such as the Middle East, known as "mega-methanol" plants. These plants offer significant economies of scale and are able to produce methanol at a lower cost (Olah et al., 2009). An example of such a commercial process is the Lurgi MegaMethanol process, developed for methanol plants with capacities greater than 1 million tonnes per year (Air Liquide, 2013).

5.4.2 Current consumption and emission levels

As mentioned already, global hydrogen production relies mainly on processes based on fossil fuels. An overview of the main inputs of the hydrogen production methods is shown in Table 40. Avoided steam is the steam that can be recovered from the excess of heat of some streams. In the case of coal gasification, since the process is exothermic, there is excess of energy that can be recovered as electricity, and therefore the negative value (Dufour et al., 2011).

In order to compare energy consumptions of the different hydrogen production processes, the energy efficiency of each process is needed. The efficiency is defined as the total energy produced by the hydrogen plant divided by the total energy that enters into the plant. According to (Holladay et al., 2009) steam reforming can have efficiencies up to 85% (based on HHV) and auto-thermal reforming and partial oxidation have similar efficiencies 60 - 75% (based on HHV). The efficiency of coal gasification is on average around 60% (Abanades, 2012).

Table 40. Main inputs in the different hydrogen production methods (Dufour et al., 2011; Wu & Tungpanututh, 2012; EC, 2015a; Linde, 2015; LePrince, 2001)

	Steam reforming NG	Steam reforming Naphtha	Auto-thermal reforming NG	Gasification Coal	Partial oxidation
Natural gas (kg/kg_{H2})	2.67		4.12		
Naphtha (kg/kg_{H2})		3.04			
Coal (kg/kg_{H2})				4.34	
Heavy residue (kg/kg_{H2})					3.88
Oxygen (kg/kg_{H2})					5.78
Heat (MJ/kg_{H2})	25	30	20		
Electricity (MJ/kg_{H2})	0.68	0.76	1.24	-8.23	2.13
Steam consumption (kg/kg_{H2})	6.12	6.42	3.0	11.57	0
Avoided steam (kg/kg_{H2})	2.56	N.F.[1]	7.57	7.79	N.F.[1]

[1] N.F.: the value has not been found in the literature or the values found are not in a comparable format to the rest of the production methods.

In the case of some facilities it is not clear which process they follow for producing hydrogen. For these cases a fictional process is considered with the average consumptions of steam reforming and partial oxidation. For feedstock, the average needs in GJ per tonne of hydrogen are calculated and it is assumed that half of them are covered by natural gas and half by heavy residue. For these facilities, the type of fuel used cannot be determined from the process and as a result the energy mix of the country in which they are located is used. The calculation of the energy mix and its characteristics is explained in detail in Annex 3.

The main emissions from hydrogen production are CO_2. The emission factors that occur in the different processes are included in Table 41. Steam reforming has lower emissions than partial oxidation and gasification. It is also obvious that emissions are associated with the chain length of the hydrocarbons, increasing from light to heavy fossil feedstocks (Kothari et al., 2008).

Table 41. CO_2 emissions factors for different hydrogen production processes (Kothari et al., 2008; Spath & Mann, 2001, Dufour et al., 2011)

Process configuration	Emission factor ($t_{CO2}/t_{hydrogen}$)
Steam reforming – Natural gas	8.89
Steam reforming – Methane	7.33
Steam reforming – Naphtha	9.46
Auto-thermal reforming – Natural gas	9.61
Partial oxidation – Octane	12.35
Gasification – Coal	29.33

As mentioned earlier, some of the hydrogen produced derives as by-product and is taken into consideration in the database. These fictitious units do not use any of the processes mentioned earlier and therefore the consumptions and emission levels are not the same. Energy and feedstock consumptions and GHG emissions for these facilities are constructed as the average of two processes: sodium chlorate production process and chlorine electrolysis. The values for these processes have been taken from Ecoinvent v.2.0 (Ecoinvent, 2009).

In the case of the sodium chlorate process, hydrogen is not considered as by-product in Ecoinvent. As a result, the values had to derive by assuming all hydrogen produced as a by-product and re-allocating consumptions and emissions based on the following mass allocation factors: 94.7 for $NaClO_3$ and 5.3 for H_2.

Concerning chlorine electrolysis, hydrogen is produced by three different electrolytic processes: mercury cell, diaphragm cell and membrane cell. Consumptions and emissions have been calculated considering the share of use of these three processes (55% for mercury cell, 24% for diaphragm cell and 21% for membrane cell). The mass allocation factors depend on whether there is NaCl or KCl electrolysed. For NaCl electrolysis, the allocation factors are 46.4% for NaOH, 52.3% for Cl_2 and 1.3% for H_2, while for KCl the allocation factors are 60.5% for KOH, 38.4% for Cl_2 and 1.1% for H_2.

The total emission factors for this cluster of facilities, calculated according to the procedure explained before and based on the Ecoinvent values are: 1.24 $t_{CO2.eq}/t_{hydrogen}$ for emissions from electricity and 0.001 $t_{CO2.eq}/t_{hydrogen}$ for direct process emissions (Ecoinvent, 2009). There is no thermal or steam consumption, so there are no emissions, while emissions due to electricity use are not considered, since the hydrogen produced in these processes is reused to generate the electricity required.

The typical feedstock requirements in the case of methanol production are shown in Table 42. Typical fuel consumption is converted to 0.76 $t_{NG}/t_{methanol}$ for steam reforming without primary reform or 0.70 $t_{NG}/t_{methanol}$ with primary reform and 0.92 $t_{fuel\ oil}/t_{methanol}$ for partial oxidation, by taking into consideration the net calorific values (Table 6). The rest of feedstocks required (water and oxygen if needed), as well as the energy requirements in terms of electricity and heat, are considered to be the same as for hydrogen production.

Table 42. Feedstock consumption and CO_2 emission factors for methanol production (IPCC, 2006b)

	Feedstock Consumption ($GJ/t_{methanol}$)			CO_2 emissions ($t_{CO2.eq}/t_{methanol}$)		
	Conventional steam reforming		Partial oxidation	Conventional steam reforming		Partial oxidation
	without primary reform	with primary reform		without primary reform	with primary reform	
Natural gas	36.5	33.4		0.67	0.497	
Oil			37.15			1.376
Coal			71.6			5.285
Lignite			57.6			5.020

CO_2 emissions from methanol production from steam reforming and partial oxidation processes can be estimated according to the IPCC 2006 default emission factors (Table 42), which are based on the average of plant-specific emissions data (IPCC, 2006b). Conventional steam reforming process for methanol production can be integrated with an ammonia production process, in which case the default CO_2 emission factor is 1.02 $t_{CO2}/t_{methanol}$ (IPCC, 2006b).

5.4.3 Best available techniques (BATs)

The continuous growth of the hydrogen producing industry has led to the necessity of obtaining quality products at the lowest possible costs (Rafiqul et al., 2005). It should be kept in consideration, though, that steam reforming is a mature technology. Table 43 lists an overview of the possible BATs identified during this study. Most of these technologies are common with the ammonia production process and are repeated here.

Air preheat

Combustion air preheating is a method of recovering heat from the exhaust gas of the combustion system through heat exchange with combustion air before it enters the combustion chamber. It results in reduced amount of fuel required in the furnace and therefore energy efficiency improvements, more than 5 % according to the European Commission (EC, 2003b), and typically between 10-15% according to EPA (Air Products, 2012). Reducing the fuel required results in less CO_2 emissions, but increased overall combustion temperatures can give rise in NO_x emissions (EIGA, 2009). As a result the positive effect of air preheating has to be balanced against this negative effect, and in order to be conservative in the present study we consider the lower value for energy efficiency improvement (5 %). Investment costs depend on the specific project situation (EIGA, 2009). The capital cost of a recuperative air preheater used in an integrated hydrogen production of 13 t_{H2}/hr (corresponding to 102.5 kt/y) was USD 640 000 $_{2000}$ (Energy 2000, 2000), corresponding to EUR 693 674 $_{2013}$.

Minimal steam: carbon ratio and associated measures

The molar ratio of steam to hydrocarbon feedstock entering the reformer is of importance. It is not stoichiometric, due to risks with both steam reforming (carbon depositions) and the shift reaction (production of by-products, such as alkanes and alcohols). Too high ratio means more steam than is reacting, and therefore the unreacted portion is heated up only to be cooled down again, so reduced thermal efficiency. Too low ration increases the quantity of unreacted hydrocarbon, thus reducing the plant product efficiency (EIGA, 2009). The optimum operating range is mainly defined by the H_2/CO ratio in the syngas produced and if steam is considered a valuable product or not. Limitation of the maximum operating range of steam/carbon ratio leads to improved thermal efficiency by reducing fuel, cooling water and electricity consumptions, but it might have an effect on NO_x formation and the concentration of some by-products, such as methanol and acetic acid (EIGA, 2009). Energy savings are estimated to be about 0.14 GJ/$t_{hydrogen}$ (Rafiqul et al., 2005), which is less than 5% and as a result the technique falls out of the scope of this study. Reducing the ratio will also reduce both operating and investment costs, but the net investment costs depend on production capacity and the value of steam (EIGA, 2009).

Table 43. Overview of the possible BATs and ITs in the hydrogen and methanol industries

BAT or IT	Description	Investment cost	Energy savings	GHG Reduction
BAT	Air preheat	EUR 693 674 [1]	5 %	None
BAT	Minimal steam/carbon ratio and associated measurements	Not included in the study as the savings are <5 %		
BAT	Isothermal shift conversion	No information available		
BAT	Hydrogen from electrolysis	EUR 729 862 [2]	-12 720 % electrical[3] 100 % rest	100 %
IT	Membrane methane reforming	EUR 27 850 705 [4]	20 % electrical, thermal and steam	None
IT	Biological water gas shift reaction	Not included in the study due to lack of information		
IT	Photosynthetic/Photobiological production	Not included in the study due to lack of information		
IT	Short contact time catalytic partial oxidation	EUR 27 533 784 [5]	15 % thermal, steam and feedstock	None
IT	Biomass pyrolysis and gasification	EUR 2.3 EUR/kg	None	100 %
IT	Sulphur – iodine cycle	No information available		

[1] Reference capacity 102.5 kt/y

[2] Reference capacity 0.33 kt/y

[3] In comparison to the average electrical consumption of natural gas steam reforming and partial oxidation

[4] Reference capacity 14.08 kt/y

[5] Reference capacity39.6 kt /y

Isothermal shift conversion

Lower temperatures favour the strongly exothermic shift conversion. In conventional plants, the head is removed in two stages, but the two reactors can be replaced by a single isothermal medium temperature shift reactor (EC, 2007b). The isothermal shift reaction occurs without a chromium-based catalyst, which is needed in the conventional process, and therefore the risk of hydrogen reacting with CO or CO_2 (Fischer-Tropsch reaction) to form carbon compounds is low. The net energy savings of isothermal shift conversion is not quantified (Rafiqul et al., 2005). Investment costs for a facility with reference capacity 100 kt/y is YEN 500 million $_{1999}$ (IETD, 2014).

Hydrogen from electrolysis

Water electrolysis occurs according to the following reaction:

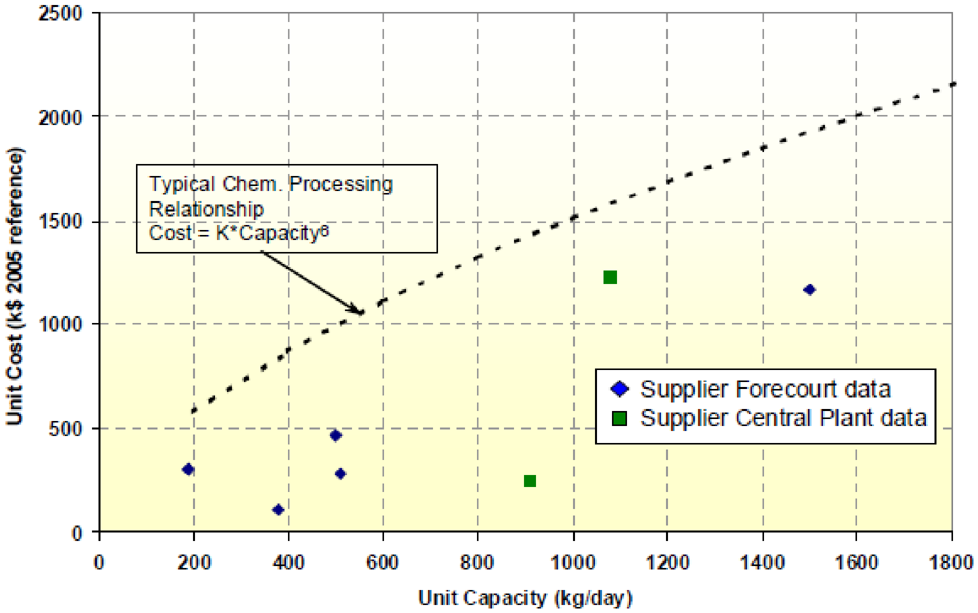
$$H_2O + \text{electricity} \rightarrow H_2 + \tfrac{1}{2}\,O_2 \qquad \text{(reaction 21)}$$

The two most common types of electrolysers are alkaline (use a potassium hydroxide electrolyte) and polymer electrolyte membrane (PEM) (Lipman, 2011). Alkaline electrolysers are suited for stationary applications and are operating at up to 25 bar pressures (IEA, 2006), with efficiencies 50-60 % based on LHV of hydrogen (Holladay et al., 2009). PEM electrolysers require no liquid electrolyte, which simplifies the design and is suited for both stationary and mobile applications, but the membranes have a limited lifetime (IEA, 2006). They are more efficient than alkaline electrolysers (efficiencies of 55-70 %), but cost more (Holladay et al., 2009). Both alkaline and PEM electrolysers have energy requirements in the order of 50 kWh/kg_{H2} (NREL, 2009).

A more recent type of electrolysis is high-temperature electrolysis, based on the fact that the total energy demand for water electrolysis increases slightly with temperature, while the electrical energy demand decreases (IEA, 2006). A typical technology is the solid oxide electrolyser cell (SOEC), operating normally at 700-1 000 ^{o}C. At these temperatures, efficiency is increased by decreasing the power loss in electrolysis (Holladay et al., 2009). An increase in temperature from 100 to 775 ^{o}C reduced the combined thermal and electrical energy requirements by close to 35 % (Holladay et al., 2009). The efficiency of the process depends on temperature and the thermal source, but can be as high as 85-90 % as a function of electrical input only, but if the thermal source is included the efficiency drops significantly to 40-60 % (Holladay et al., 2009).

Due to the variety of technologies it is difficult to establish a relationship between capital cost and capacity. A range of the capital costs as a function of capacity can be seen in Figure 16, according to a study carried out in the US (NREL, 2009). Within the uncertainty of the information collected in the NREL study, the capital cost of electrolysis is estimated to be about USD 800 $_{2005}$ per kg/d unit capacity for an electrolyser not exceeding 1 000 kg/d (forecourt case in Figure 16) (NREL, 2009) (corresponding to EUR 729 862 $_{2013}$ for capacity 328.5 t/y).

Figure 16. Ranges of capital costs of electrolysis (NREL, 2009)



5.4.4 Innovative technologies (ITs)

There is high interest in hydrogen production technologies, especially focusing on the use of biomass or biological ways. Unfortunately, the research in many cases seems to be in too early stages. In this paragraph, a collection of innovative technologies is presented, even if their stage of development is not so close to commercialisation. Some of the technologies that are considered innovative in the hydrogen industry are shared with the ammonia industry and have been already described there, such as the membrane reforming concept and the CO_2 removal concept. From these technologies, only the ones that are taken into consideration in our study are mentioned again and only as far as it concerns the benefits achieved and their economics, so as to be expressed on hydrogen base.

Membrane methane reforming

This innovative technology is about a hybrid system based on the membrane reforming concept to convert natural gas to hydrogen and electricity. It has been described already in the paragraph about ammonia (5.2.4). The technology was still at demonstrative stage, achieving energy savings about 20% and with investment costs about EUR 28.05 million $_{2008}$ for a 20 000 nm^3/h hydrogen production (Iaquaniello et al., 2008).

Biological water gas shift reaction

The biological water-gas shift reaction is an innovative route to hydrogen production via photo-heterotrophic bacteria, such as Rubrivivax gelatinosus. These bacteria are capable of performing water gas shift reactions at ambient temperature and atmospheric pressure by fermentation (Babu et al., 2013). Under normal light phase conditions, they obtain energy through photosynthesis, using solar energy to convert CO_2 and electrons from water to sugars and O_2. In the dark, though, they survive through anaerobic fermentation pathways, performing biological water gas shift reaction (Amos, 2003), which can be explained according to the following reactions (Swanson et al., 2011):

$$CO + H_2O \rightarrow 2\ e^- + 2\ H^+ + CO_2 \qquad \text{(reaction 22)}$$

$$\underline{2\ e^- + 2\ H^+ \rightarrow H_2} \qquad \text{(reaction 23)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(reaction 24)}$$

Hydrogen synthesis rate by biological water gas shift reaction has been found to be 96 $mmol_{H2}/(l*h)$, compared to 20-50 $mmol_{H2}/(l*h)$ by dark anaerobic fermentation (Saxena et al., 2009). According to the same study, processing costs of H_2 production would be USD 3.4/kg. Nevertheless, research of biological processes has not yielded any practical or conceptual process and it is considered to need further advancements before it is economically feasible (Bartels, 2008). As a result, this technology cannot be included in our study, since its year of availability will probably be further than 2030 and there are no information available concerning the energy consumed.

Photosynthetic/Photobiological hydrogen production

Hydrogen can be produced photo synthetically, by reduction of H^+ ions in an aqueous solution to H_2. Green algae contribute to the reduction by producing the catalyst (hydrogenase enzymes) and by providing an electron source. Growth of these algae under controlled conditions can stimulate the production of the hydrogenase enzyme, while electrons are provided by suppression of the first step of photosynthesis (sulphur deprivation), which would normally pull electrons from water to produce oxygen (Melis & Happe, 2001; Hemschemeier et al., 2009). Under anaerobic conditions, hydrogenase can accept electrons and use them to reduce protons to molecular hydrogen, but there are two major research challenges: the optimum level of light intensity and kinetic limitations on electron transport to the enzyme (Allakhverdiev et al, 2010). The technology still needs further research in order to be optimised (Allakhverdiev et al, 2010), as a result its availability cannot be assumed to be before 2030 and there is no estimation of its energy consumption, so it falls out of scope of the present study.

Short contact time catalytic partial oxidation

This technology is also described in the ammonia paragraph (5.2.4). As explained there, expected environmental benefits of it are 15 % reduction in feed and fuel in hydrogen production, accompanied by 15 % lower investment costs compared to steam reforming (Iaquaniello et al., 2012). Direct capital costs of a typical facility producing hydrogen from steam-methane reforming (120500 kg_{H2}/d) were estimated to USD 30 million $_{2002}$ (Molburg & Doctor, 2003), corresponding to EUR 32.4 million $_{2013}$. As a result, capital costs for this innovative technology are estimated at about EUR 27.5 million $_{2013}$.

Biomass pyrolysis and gasification

In biomass conversion processes, a hydrogen-containing gas is produced in a manner similar to coal gasification. The difference between pyrolysis and gasification is that the first is done in an inert environment, while the latter in a reactive environment (Bartels, 2008). The pathways followed are steam gasification (direct or indirect), entrained flow gasification or more advanced concepts such as gasification in supercritical water, application of thermo-chemical cycles, or the conversion of intermediates, such as ethanol, or torrified wood (IEA, 2006). The gasification process typically suffers from low thermal efficiency, since moisture contained in biomass should also be vaporised, and the production of tar if it takes place at high temperatures. Typical efficiencies are between 35 and 50% based on lower heating value (Holladay et al., 2009). The cost of hydrogen from pyrolysis is expected to be USD 2.57 $_{2007}$/kg, while from gasification it is expected to be USD 2.83 $_{2007}$/kg (Bartels, 2008).

Sulphur – iodine cycle

One of the promising approaches to produce large quantities of hydrogen from nuclear energy efficiently is the sulphur – iodine thermochemical water-splitting cycle, which generates hydrogen from water and thermal energy through the following chemical reactions (Brown et al., 2003):

$$2\ H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2\ HI \qquad \text{(reaction 25)}$$

$$H_2SO_4 \rightarrow H_2O + SO_2 + \tfrac{1}{2}\ O_2 \qquad \text{(reaction 26)}$$

$$2\ HI \rightarrow H_2 + I_2 \qquad \text{(reaction 27)}$$

This technology has a lot of advantages, such as no by-products or effluents, except from hydrogen and oxygen, suitability to be used with solar, nuclear or hybrid sources of heat and efficiencies that are about 47%. But it has also serious disadvantages, such as requiring high temperatures (about 800°C) and the presence of corrosive reagents (iodine, sulphuric acid) (Mathias and Brown, 2003). The technology has not been demonstrated outside laboratories and the process economics have not been verified (Mathias and Brown, 2003; Terada et al., 2007).

5.5 Adipic acid

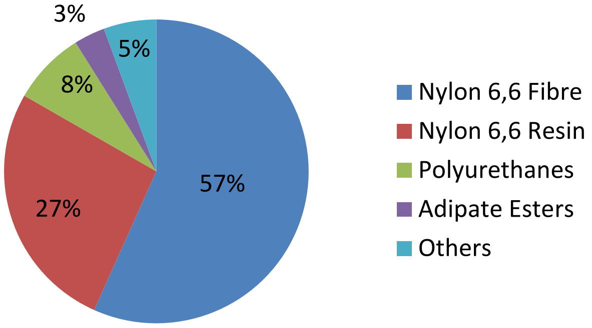
Adipic acid (AA) ($C_6H_{10}O_4$ – $HOOC(CH_2)_4COOH$), is a derivative of benzene and a white crystalline solid with acid taste and very soluble in acetone. Other names of it are 1,4–

butane dicarboxylic acid and according to IUPAC hexanedioic acid. It is used in the manufacture of a large number of products including synthetic fibres, coatings, plastics, urethane foams, elastomers and synthetic fabrics.

Global production in 2014 was 2 839 kt (PCI WoodMackenzie, 2016), with nylon 6,6 fibre and resin accounting for 83.3 % of it (Grand view Research, 2014; Ullmann's Encyclopaedia, 2000b). Other applications of it include polyurethanes, plasticisers, coatings, synthetic lubricants and food additives (PCI WoodMackenzie, 2016). Global market distribution per product in 2013 is shown in Figure 17 (Grand view Research, 2014), while world consumption is expected to have growth rates of 2.8 % per year to 2019 (IHS, 2015d)

Europe and the United States are fairly mature markets for adipic acid, but China and India are dominating the adipic acid consumption, accounting for over 35 % of it in 2013, while Europe accounted for 27 % of the consumption and the US for 24 % (Grand view Research, 2014). The European Union and the Unied States have been the most important exporters and China the largest importer (Schneider et al., 2010), but Asia has been developing rapidly in recent years. Over 60 % of the world's adipic acid supply is owned and operated by four main companies (39), having sites around the world (Grand view Research, 2014).

Figure 17. Adipic acid world market distribution per product in 2013 (Grand view Research, 2014)



In 2010, there were 23 adipic acid plants throughout the world, located mainly in the US (30%), the EU (29%) and China (22%) (Schneider et al., 2010). The rest were in Brazil, Japan, Singapore, South Korea, Ukraine and India (Schneider et al., 2010). In 2013, in the EU-28 there are only 5 adipic acid installations (Table 44), with a total capacity of 969 kt/y (ICIS, 2012; Ecofys, 2009).

Table 44. Adipic acid plants in EU-28 in 2013

Country	Number of plants	Capacity (kt/y)
Germany	3	440
France	1	340
Italy	1	92
Total	5	872

5.5.1 Production processes

Of worldwide adipic acid production, 91 % is made via cyclohexane and the rest mainly from phenol (PCI Wood Mackenzie, 2016). It is manufactured in two steps: during the

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(39) In 2012 BASF, Rhodia, Invista and Ascend Performance Materials accounted for 60% of the total adipic acid production [Grand view Research, 2014]

first one a mixture of cyclohexanone ($(CH_2)_5CO$) and cyclohexanol ($(CH_2)_5CHOH$) is produced either from oxidation of cyclohexane or hydrogenation of phenol, and in the second one this mixture is catalytically oxidised with nitric acid (EC, 2003a). The cyclohexanone - cyclohexanol mixture is known as ketone alcohol oil (KA oil). The reaction producing adipic acid is the following:

$(CH_2)_5CO + (CH_2)_5CHOH + x\ HNO_3 \rightarrow HOOC(CH_2)_4COOH + y\ N_2O + w\ H_2O$ (reaction 28)

The reaction of KA oil requires 50-60% nitric acid and the presence of copper and vanadium catalysts (EPA, 1995; Ecofys 2009). As the reaction is highly exothermic, process control is achieved with the use of large amounts of nitric acid (EPA, 1994). By-products from this reaction are pentanedioic or glutaric acid, butanedioic or a succinic acid and nitrous oxides (Ullmann's Encyclopaedia, 200b; EC, 2003a; Ecofys, 2009).

Following the two reaction steps, the wet adipic crystals are separated from water and nitric acid by a two-stage crystallisation/centrifugation. Water is removed from the reaction mixture by distillation. The yield in adipic acid of the process is more than 90% (Ecofys, 2009; EC, 2003a).

The predominant method of cyclohexane oxidation is metal-catalysed oxidation in moderate temperatures and pressures, with a small amount of cobalt, chromium or copper as catalyst (EPA, 1995). When phenol is the feedstock, it is typically hydrogenated at 140 ^{o}C and 200 - 1800 kPa hydrogen pressures over a nickel, copper or chromium oxide catalyst (EPA, 1995). The phenol route has some advantage such as that the equipment is simpler and the process safer (Chemical Weekly, 2009), but the costs are higher.

In addition to these established approaches, there have been many attempts over the years to improve adipic acid production technologies. In the past, adipic acid was produced via air oxidation, however, this process produced low quality product and is not considered commercial anymore (Ullmann's Encyclopaedia, 200b; EC, 2003a). Some of the new methods include the one developed by Nagoya University and the Asahi Chemical process. The latter is commercialised and is based on partial hydrogenation of benzene to cyclohexene, over a complex ruthenium catalyst under high pressure (Chemical Weekly, 2009).

5.5.2 Current consumption and emission levels

Feedstock (cyclohexane or phenol), nitric acid and air or hydrogen are the raw materials required for adipic acid production. As explained before, the main route for producing adipic acid is from cyclohexane, while a secondary route is from phenol. All but two of the European plants use cyclohexane as feedstock (ICIS, 2012). The consumptions in the two routes are shown in Table 45.

The main environmental issue related to adipic acid production is N_2O that occur during the reaction with nitric acid. Other by-products that constitute emissions are CO, CO_2, non-methane volatile organic compounds (NMVOCs). The default emission factor for the nitric acid oxidation, according to (IPCC, 2006b), is 300 $kg_{N2O}/t_{adipic\ acid}$ ±10 %, which translates to 80.5-98.3 $t_{CO2.eq}/t_{adipic\ acid}$. The uncontrolled emission factors proposed by EPA (1995) for the two steps of the adipic acid production are shown in Table 46. It can be seen that the main emissions are N_2O.

Table 45. Typical consumptions for adipic acid production (US NRC, 1990; IEA, 2009b; Towler & Sinnott, 2013)

Raw materials / Energy	Consumption	
	Cyclohexane KA oxidation[1]	Phenol KA oxidation
Cyclohexane ($t/t_{adipic\ acid}$)	0.74	
Phenol ($t/t_{adipic\ acid}$)		0.72
Nitric acid ($t/t_{adipic\ acid}$)	0.83	0.72
Air ($t/t_{adipic\ acid}$)	1.67	
Hydrogen ($t/t_{adipic\ acid}$)		0.035
Electricity ($kWh/t_{adipic\ acid}$)	388.9	206.0
Fuel ($GJ/t_{adipic\ acid}$)	1.2	1
Steam ($GJ/t_{adipic\ acid}$)	25.7	15.2[2]

[1] Assuming that the overall yield of the process is 90% and that the air in the HNO_3 feed is 25%.

[2] The process needs medium pressure steam (Towler & Sinnott, 2013) and latent heat of 2000 kJ/kg is assumed (Engineering Toolbox, 2015a)

Table 46. Uncontrolled emission factors for adipic acid production (EPA, 1995)

Source		Emissions ($kg/t_{adipic\ acid}$)		
		CO_2	CH_4	N_2O
1st step	High-pressure scrubber	14	0.08	
	Low-pressure scrubber	3.7	0.05	
2nd step	Oxidation reactor	60		290
	Nitric acid tank fume sweep	2.6		1.3

Nevertheless, the adipic acid industry has made effort, applying the BAIs that will be described in the following paragraph, so as to control N_2O emissions. As a result, the values reported in both (EPA, 1995) and (IPCC.2006b) are considered not to represent the current situation of the industry. For the current study, we will assume that the process emissions of the adipic acid production are 60 % lower than the (IPCC, 2006b) values. Taking into consideration the information about consumptions and emissions, the emission factors for the adipic production process are shown in Table 47.

Table 47. Emission factors for adipic acid production

Emissions	Value ($t_{CO2.eq}/t_{adipic\ acid}$)	
	Cyclohexane KA oxidation	Phenol KA oxidation
Electricity use	0.15	0.10
Thermal production	0.07	0.06
Steam production	1.44	0.90
Direct process emissions[1]	32.0	32.0
Total	33.66	33.06

[1] The direct process emissions were assumed to be 60% reduced compared to the lower end of the emission factors according to IPCC is used

Adipic acid is a benchmarked product with value 2.79 allowances/tonne (EC, 2011b), but the industry's emissions have changed remarkably, and therefore no calibration is applied to the specific emissions from this industry.

5.5.3 Best available techniques (BATs)

N_2O, which is the most important contaminant from the adipic acid industry, can be either re-used or abated. The best available techniques for this industry are based exactly on these two possibilities. All the BATs are summarised in Table 48.

Table 48. Overview of the possible BATs and ITs in the adipic acid industry

BAT or IT	Description	Investment cost	Energy savings	GHG Reduction
BAT	Catalytic decomposition	EUR 12 914 914 [1]	None	82.3 %
BAT	Thermal destruction	EUR 9 637 996 [2]	None	95.5 %
BAT	Partial recycling of waste gas	EUR 13 396 814 [3]	None	88.1 %
IT	One-step process	EUR 18 147 900	30 %	99 %
IT	Bio-based techniques	No information available		

[1] Reference capacity 330 kt/y

[2] Reference capacity 88 kt/y

[3] Reference capacity 371 kt/y

The two most widely used end-of-pipe abatement techniques are catalytic decomposition and thermal destruction. For the first one, metal oxide catalysts, such as MgO, are used to decompose N_2O to N_2 and O_2, in a highly exothermic reaction (EC, 2003a). The catalyst needs replacement twice a year. Thermal destruction involves combustion of the off-gases in the presence of methane, thus reducing N_2O to N_2, but giving emissions of NO_x and some residual N_2O (EC, 2003a). The destruction factors in the two cases can be seen in Table 49.

Table 49. N_2O destruction factors for the main abatement techniques (IPCC, 2006b)

Abatement technique	N_2O Destruction factor[1]	Utilisation factor
Catalytic destruction	92.5 %	89 %
Thermal destruction	98.5 %	97 %
Recycle to nitric acid	98.5 %	94 %
Recycle to adipic acid	94 %	89 %

[1] The destruction factor should be multiplied by an abatement system utilisation factor

Abatement costs for the two techniques are reported to range between EUR 0.10-0.40 $_{2010}/t_{CO2.eq}$, with thermal destruction costs to be at the lower range and catalytic destruction costs at the higher range (Schneider et al., 2010). The investment costs of the two abatement techniques from plants that have installed them are EUR 13.4 million $_{2010}$ for catalytic destruction and EUR 10-13.4 million $_{2010}$ for thermal destruction (Schneider et al., 2010).

Another way of reducing the environmental effect of N_2O is to partially recycle the waste gas. The N_2O rich off-gas can be re-used in two ways, either by valorisation as nitric acid or by using it to selectively oxidise benzene to phenol (EC, 2003a).

Valorisation as nitric acid consists of thermal conversion in conditions that encourage the NO_x formation reaction and minimise the reaction to N_2 and O_2, as the NO_x produced are recyclable in the form of nitric acid upstream in the adipic acid process (Klinger, 2001). This technique was tried in a plant in France, where the off-gas was collected and treated in high temperatures for a short period, triggering the decomposition reaction of N_2O. The products gas mixture contains N_2, O_2, CO_2 and NO_x and is converted into nitric acid in an oxyadsorption column. This technique is interesting especially for industrial sites that are lacking in nitric acid (Klinger, 2001).

The alternative route is direct oxidation of benzene with N_2O, a process mainly developed by Solutia in collaboration with the Boreskov Institute of Catalysis in Russia (Parmon et al., 2005). The reaction takes place on zeolite catalysts in the gas phase at 300-450 ^{o}C. The idea behind this technique is also to incorporate the reaction in a new modified adipic acid production scheme, where benzene reacts with N_2O to produce phenol ([40]). It has also been also tested at a pilot plant, in Pensacola, Florida, and its productivity is 400 g phenol per 1 kg of catalyst per hour, but the conversion of N_2O to phenol is only 85 % (Parmon et al., 2005).

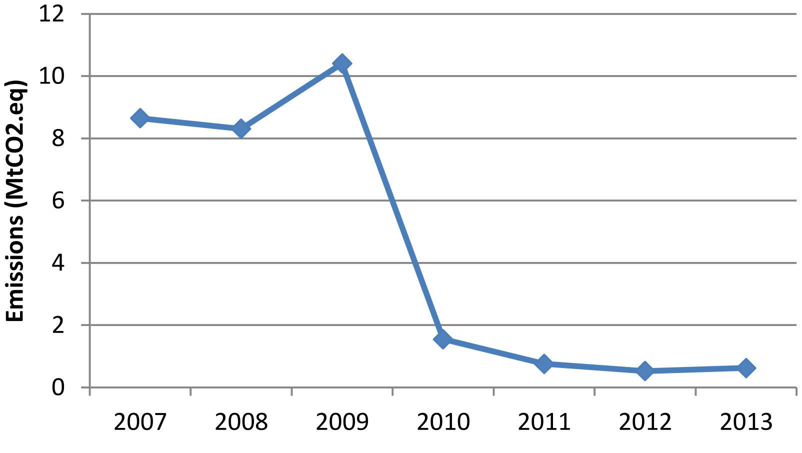
Since the information available in the literature are a bit restricted concerning the two routes of partial recycling, in this study they are considered as one BAT with investment costs about EUR 13.9 million_{2010} (Schneider et al., 2010) and average GHG reduction of 88.13 %.

The theoretical N_2O destruction factors for the abatement techniques mentioned above are summarised in Table 49 (IPCC, 2006b).

It has been common practice since 1990 in Europe and the US to install N_2O abatement technologies on a voluntary basis (Schneider et al., 2010). Three of the plants have installed different technologies (catalytic or thermal destruction, or partial recycling) since 2008 (Schneider et al., 2010). The reported efficiencies achieved vary from 86 % for catalytic destruction (BASF, 2010; 2012a; 2012b; 2013) to 99.99 % for thermal destruction (Schneider et al., 2010).

This practice can explain the reductions in N_2O emissions that have been reported for this industry. N_2O emissions from the EU-28 adipic acid industry have decreased from 8.96 $Mt_{CO2.eq}$ in 2007 (EEA, 2009) to 0.61 $Mt_{CO2.eq}$ in 2013 (Figure 18) (EEA, 2015). Nevertheless, it should be noted that both the nitric and the adipic acid industries have gone through structural changes and decreased their N_2O emissions to quite low levels, but it cannot be expected that this type of change can be replicated in the future.

Figure 18. EU-28 emissions from adipic acid production (EEA, 2015)



5.5.4 Innovative technologies (ITs)

The emerging technologies concerning the adipic acid industry can be divided into techniques that are based on alternative synthetic pathways or innovative catalysts and bio-based techniques.

Research has been aiming at developing a green route for adipic acid that could be environmentally friendly and efficient, as an alternative to the contemporary industrial process, focusing on the direct oxidation of cyclohexane with air or oxygen, also called

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(40) This scheme is explained in detail in [Parmon et al., 2005].

"one-step AA process". Single stage air oxidation has been studied by a number of research groups, typically involving systems with catalysts, such as lipophilic catalyst (Bonnet et al., 2006) metal-doped nanoporous aluminophosphates (Li et al., 2010), carbon nanotubes (Yu et al., 2011), polyoxoanions (Lü et al., 2012) and metalloporphyrins (Li et al., 2012), but only a few of them can be considered environmentally and economically sustainable (Lü et al., 2012). All of these processes are still in the research phase and there is no information about their economic feasibility, with the only exception being the one-step process with H_2O_2 as oxidant, which achieves 30 % lower total energy consumption and 55% lower investment costs (Vural-Güsel et al., 2012). Because of using hydrogen peroxide, the only expected by-product is water, thus achieving clean operation and the investment costs amount to EUR 18.35 million $_{2012}$ (Vural-Güsel et al., 2012).

A fundamental change in chemical synthesis can also be achieved by elaboration of new, environmentally benign routes that can replace environmentally problematic routes. Currently adipic acid is assessed among the most promising bio-based chemicals for market penetration (IEA, 2012b). There have been three biotechnological process suggested within the BREW Project (Brew, 2006) for biotechnical production of adipic acid: (1) biosynthesis of cis,cis-muconic acid from glucose, followed by catalytic hydrogenation to adipic acid, (2) biosynthesis of adipic acid from cyclohexanol and (3) enzymatic conversion of adiponitrile to ammonium adipate by nitrilase. The first one relies on the use of genetically manipulated microbes as synthetic catalysts and begins with the conversion of glucose into cis, cis-muconic acid (Chemical Weekly, 2009). The second one is based on enzymes isolated from Acinetobacter sp., which are expected to convert cyclohexanol to adipic acid. Last but not least, the third one is aiming to convert nitriles to carboxylates enzymatically (Brew, 2006). Only the first of these biotechnological processes, also known as Draths-Frost syntheses, has been tested, but the yields are quite low (15-23 %), since the theoretical yield can be limited by the toxicity of the aromatic intermediates (Brew, 2006).

In the last years several companies have claimed processes for adipic acid (IEA, 2012b), including Verdezyne Inc. with a proprietary metabolic pathways that can utilise carbohydrates, plant-based oils or alkanes (Gibson, 2010), BioAmber with a breakthrough succinic acid purification process to adipic acid (Sheridan, 2011), Genomatica with a patent concerning the third biotechnological process described above (Burgard et al., 2010) and Rennovia developing a chemo-catalytic process for production of adipic acid from renewable raw materials (Westerveld, 2010). All these projects, though, are in early stages and there is no information about their performance and their environmental and economic feasibility. As a result this technology cannot be included in the study.

5.6 Soda ash

Soda ash or sodium carbonate (Na_2CO_3) is the neutral sodium salt of carbonic acid. It is a white crystalline solid and is used as a fundamental raw material to the glass, detergent and chemical industries, as well as the pulp and paper industry. Glass production accounts for about 55% of the world soda ash consumption, while detergents and cleaners account for about 14% and the chemical sector for about 10% (IHS, 2015e). In the chemical industry its main uses are as an alkali source and as feedstock in the production of sodium chemicals.

The annual production of soda ash worldwide in 2013 was about 51.3 Mt, 1.2 % higher than in 2011 (50.7 Mt) (USGS, 2015; 2013). In 2012 42% of the production was concentrated in Asia, 24% in North America and 18% in Europe (IHS, 2012c), while in 2015 China accounted for 46 % of world production and the US for 22% (IHS, 2015e). The percentage of soda ash production in the European Union has slightly decreased during the last decade, as in 2000 it was 18.5 % (Cefic, 2004).

Since the 1920s, several deposits of minerals containing sodium carbonate or bicarbonate have enhanced the production of soda ash from trona (41). Only Botswana, Kenya, Mexico, Turkey and the United States produced soda ash from natural sources in 2013 (USGS, 2015). As trona deposits are not available in Europe, though, soda ash is almost entirely manufactured synthetically (EC, 2007b). In 2013, about 72 % of world soda ash production derived from synthetic processes and 28 % was recovered from natural trona deposits and surface brines (USGS, 2015).

Over many decades demand for Na_2CO_3 had been increasing at an average rate of 2 % per year in the European Union (EC, 2007c), but more recently it is expected to grow slightly slower (around 1.5 – 2.0 % annually) (IHS, 2015e). Local availability of raw materials, the price of energy and the environmental impact of its production are key drivers for improvements in the soda industry worldwide.

In 2013 in the EU-28, 12 plants were in operation with a total production capacity of 8 285 kt, as shown in Table 50 (ICIS, 2012; Ecofys 2009; Cefic, 2004; IHS, 2015a). These plants cover 16% of the global annual production of soda ash. The boundaries of this study exclude plants based on special processes (e.g. soda ash plant in Ludwingshafen, Germany that is based on the production of carpolactam). The European Soda Ash Producers Association (ESAPA) includes also soda producers from Turkey and Bosnia-Herzegovina (ESAPA, 2011).

Table 50. Soda ash plants in EU-28 in 2013

Country	Number of plants	Capacity (kt/y)
Bulgaria	1	1 100
Germany	3	1 710
Spain	1	1 020
France	2	1 300
Italy	1	1 020
Poland	2	1200
Romania	1	435
United Kingdom	1	500
Total	12	8 285

5.6.1 Production processes

As mentioned already, soda ash can be produced from natural sodium carbonate-bearing deposits, referred to as natural processes. The principal ore from which natural soda ash is made is called trona and it is calcinated in a rotary kiln and chemically transformed into crude soda ash, according to the following reaction:

$$2\ N_2CO_3.NaHCO_3.2H_2O\ (\text{Trona}) \rightarrow 3\ Na_2CO_3 + 5\ H_2O + CO_2 \quad (\text{reaction 29})$$

Other natural processes are based on nahcolite, or on mixed minerals (nepheline syenite process). The first one is applied in Colorado USA and the second one in Russia. Small quantities of soda ash are produced also by carbonation of caustic soda and as by-product from the production of carpolactam (EC, 2007c). There are no plants based on natural processes in the EU, as there are no big natural deposits and only one plant (in Germany with capacity 50kt) producing soda ash as co-product of carpolactam (IHS, 2015a).

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(41) Trona ($Na_3(CO_3)(HCO_3)\cdot 2H_2O$) is a naturally occurring mineral known as sodium sesquicarbonate [Mineralogy, 2015].

Practically all European soda ash is produced using the Solvay process, also called the ammonia soda process, which was developed in the 19th century by the Belgian Ernest Solvay and replaced the Leblanc process that was used until then (Ullmann's Encyclopaedia, 2000c). The Solvay process can be summarised by the following theoretical equation:

$2\ NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$ (reaction 30)

Raw materials in this process are salt and limestone ($CaCO_3$). Ammonia is also used in the process, but it is almost totally regenerated and recycled. The reactions taking place in reality follow the pattern shown below (Ecofys, 2009):

$CaCO_3 + heat \rightarrow CaO + CO_2$ (reaction 31)

$CaO + H_2O \rightarrow Ca(OH)_2$ (reaction 32)

$NaCl + H_2O + NH_3 \rightarrow NaCl + NH_4OH$ (reaction 33)

$2\ NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$ (reaction 34)

$(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2\ NH_4HCO_3$ (reaction 35)

$2\ NH_4HCO_3 + 2\ NaCl \rightarrow 2\ NaHCO_3 + 2\ NH_4Cl$ (reaction 36)

$2\ NaHCO_3 + heat \rightarrow Na_2CO_3 + H_2O + CO_2$ (reaction 37)

The ammonia used in the beginning is recovered from the ammonium chloride filtrate (NH_4Cl) by reacting with alkali ($Ca(OH)_2$). The reaction is exothermic and cooling of the liquid is needed in order to maintain efficiency. More information about the Solvay process can be found in the BREF (EC, 2007c), the Cefic Bref for soda ash (Cefic, 2004) and in (Ullman's Encyclopaedia, 2000).

The main advantage of the Solvay process is that the raw materials are available almost everywhere in the world relatively pure and therefore the production can be close to the market (EC, 2007c). Sodium chloride can be obtained by conventional or solution mining, but it contains inorganic impurities that can lead to production problems and should, therefore, be removed.

Soda ash is manufactured in two grades: light soda ash and dense soda ash. The Solvay process produces light soda ash, with a pouring density of about 500 kg/m^3 (EC, 2007c). This grade is used mainly in the detergent industry and for certain chemical intermediates. Dense soda is the preferred form for use in the glass industry and has about double density. It is produced from light soda ash by recrystallisation to sodium carbonate monohydrate and drying, but it is not considered in this study, as the focus is only for the chemical industry.

There are several modifications to the original process, such as the "Akzo" or "dry lime" process, which uses dry lime instead of lime milk for the recovery of ammonia, and the "dual process", which allows co-production of ammonium chloride, which is used as fertiliser in rice cultivation (EC, 2007c).

5.6.2 Current consumption and emission levels

Since almost all the European plants use the Solvay process, the discussion will be focused only on this process. Synthetic production is more energy-intensive and more costly than natural soda.

As mentioned already, the main raw materials needed are salt (in the form of brine), limestone and ammonia. Typical composition ranges of raw brine is 120-125 g/l for Na^+ and 186-192 g/l Cl^-, while a high content of $CaCO_3$ in the limestone can reduce costs and improve production efficiency (Cefic, 2004). There is no typical composition of limestone used in the European plants, as $CaCO_3$ content varies between 84 and 99 % (EC, 2007c). Purification of brine results is losses of about 5 g/l. Ammonia is in the form of aqueous solution 10-35% or as of anhydrous gas or even as aqueous solution of ammonium disulphide. Table 51 provides indicative ranges for the inputs in the Solvay process (Cefic, 2004). The data in this table do not include consumptions concerning brine and limestone extraction or transportation.

Except from raw materials, the process requires also utilities, such as steam, water and electricity. Steam is used at several steps of the Solvay process: Low pressure steam (<5 bar) in ammonia distillation at rates between 1 300 to 2 400 $kg/t_{soda\ ash}$ and intermediate pressure steam (10-14 bar) in thermal decomposition and drying during the reactions at rates between 1100-1300 $kg/t_{soda\ ash}$ (decomposition of bicarbonate) and 350-450 $kg/t_{soda\ ash}$ (drying monohydrate – dense soda ash) (EC, 2007c). Total thermal consumption for the production of soda ash, ranges between 9.25 and 13.2 $GJ/t_{soda\ ash}$ (EC, 2007c), as a result the average thermal consumption of the Solvay process considered in this study is 11,23 $GJ/t_{soda\ ash}$. Electricity is used at the CO_2 gas compressors and consumptions depend on the gas concentration, but range between 50 and 130 $kWh/t_{soda\ ash}$ (Cefic, 2004).

Table 51. Input in the Solvay process

Main input	Range
Limestone ($kg/t_{soda\ ash}$)	1 090-1 820[1]
Raw brine ($kg/t_{soda\ ash}$)	1 530-1 800 (NaCl) / 4 500-5 200 (water)
NH_3 addition ($kg/t_{soda\ ash}$)	0.8-2.1
Electricity ($kWh/\ t_{soda\ ash}$)	50-130 (for dense soda ash)
Thermal Energy ($GJ/t_{soda\ ash}$)	9.25-13.2

[1] This range refers to the plant gate. The quantity entering the lime kilns is reduced by 4-12 % (1 050-1 600 $kg/t_{soda\ ash}$) due to homogenisation.

Water is consumed either in the processes or for cooling. The quantity of process water is in the range of 1.9-2.4 $m^3/\ t_{soda\ ash}$ and is normally taken from the outlet of the cooling system. Cooling water is in the range of 50-100 $m^3/t_{soda\ ash}$ depending on the temperature (Cefic, 2004). The main quantity of water enters the process in the form of brine, which is in liquid phase and represents 4500-5200 $kg/t_{soda\ ash}$ (Cefic, 2004).

Concerning emissions, CO_2 is generated in two pyrolysis reactions (reaction 31 and reaction 37), but it is captured, compressed and directed back to be used in the carbonation stage, so in theory the Solvay process is neutral. In practice, though, some CO_2 is emitted because its production is higher than what is stoichiometrically necessary (IPCC, 2006b). In a stand-alone soda ash process, these emissions range between 200 and 300 $kg/t_{soda\ ash}$. The calcination process also produces some CO (4-20 $kg/t_{soda\ ash}$), depending on the extent of the conversion of CO into CO_2 (Boudart reaction (Cefic, 2004).

Other emissions include nitrogen, sulphur oxides and ammonia, but the first two are rather limited, as the temperatures in the kiln are rather moderate and the sulphur content of the fuels used in limestone burning is low (EC, 2007c). Ammonia slip is usually less than 1.5 kg/$t_{soda\ ash}$, but there are fluctuations depending on the performance of the process (Cefic, 2004).

The emissions factors used in this study are summarised in Table 52. There are big differences in the emission factors of the different plants, depending on the fuel type used. The most emission intensive plants, using coal as fuel, report specific emission factor of about 2 t_{CO2}/$t_{soda\ ash}$, while the most emission efficient plant emits only about 0.7 t_{CO2}/$t_{soda\ ash}$ (Ecofys, 2009). For the present study, we assume that the total emission factor for soda ash production is the average of this range (1.35 t_{CO2}/$t_{soda\ ash}$)

Table 52. Emissions from the Solvay process for production of soda ash

Emissions	Value ($t_{CO2.eq}$/$t_{soda\ ash}$)
Electricity use	0.04
Thermal production	0.63
Direct Process emissions	0.68
Total	1.350

Soda ash is a benchmarked product, with value 0.843 allowance/t (EC, 2011b). The system boundaries of the benchmarking include all steps of the process, but exclude emissions related to the production of the consumed electricity. The specific emissions for each facility producing soda ash are calibrated according to the benchmarking curve for this product.

5.6.3 Best available techniques (BATs)

This paragraph describes the techniques considered generally to have potential in achieving high level of environmental protection in the soda ash industry, with focus mainly on the techniques referring to air emission abatement and on reducing energy consumption.

Table 53 lists an overview of the possible BATs available for the soda ash industry. In general, improvements in this industry are usually long term investments as a common characteristic of all abatement techniques is the high capital cost due to the large volumes involved. In addition technologies are usually interdependent, which means that they might be mutually exclusive (Cefic, 2004).

Soda ash plants do not require often shut downs for planned maintenance and can maintain continuous steady operation for a number of years. An integrated design of the plants with a required degree of standby equipment allows for operational flexibility, which is characteristic of this industry (EC, 2007c). The benefits from careful designing are higher raw materials and energy savings and a reduced environmental impact. The lower values of the consumptions (Table 51) and emissions presented in the previous paragraph can only be achieved via integrated design and operation of the plant (Cefic, 2004). The plant in Spain can be considered as example of this BAT (EC, 2007c) and the estimated investment costs are EUR 13 200 000 for reference capacity 330 kt/y (OPT Sensor Srl, 2012).

Since large amounts of steam are required for the production of soda ash, the inclusion of a cogeneration unit is a favourable technique. Higher energy efficiency is achieved, resulting also in lower emissions. The efficiency levels achieved are about 90 %, since almost all the steam leaving the turbines can be used in the process (EC, 2007c). The applicability of CHP in soda plants does not depend on the type of fuel used and the data concerning the presence of CHP in the European soda ash industry are based on the databases available (ESAP, 2012).

Table 53. Overview of the possible BATs and ITs in the soda ash industry

BAT/IT	Description	Investment cost[1] (EUR)	Energy savings (%)	GHG Reduction (%)
BAT	Integrated design and operation	13 200 000	44.6 Electric 17.6 Thermal	None
BAT	Energy conversion of primary fuels (CHP)	General reference in 4.5.1		
BAT	Optimisation of the process to avoid excessive CO_2 emissions	54 280 000	None	48.15
BAT	Vertical shaft kiln for the production of concentrated CO_2 gas and reactive lime	5 280 000	2.7 Thermal	None
BAT	Centrifugation of crude sodium carbonate	Not included in the study as the savings are < 5%		
BAT	Ammonia recovery in the distillation section	0	24 Feedstock	None
IT	Integration with ammonia plant	No information available		
IT	Innovation in the carbonation section	No information available		
IT	Soda ash production from Na_2SO_4	No information available		

[1] Reference capacity 330 kt/y.

As mentioned earlier, CO_2 emissions at this industry occur due to excessive production and are relatively moderate, but the main part of CO_2 stored in soda ash is emitted in the downstream industries, such as the glass industry (EC, 2007c). Optimisation of the soda ash process can therefore lead to substantial savings in the global sense of environmental protection and to decrease in the manufacturing cost of production. The optimisation includes actions such as narrow possible temperature profile in the kiln, the selection of optimum quality limestone and fuel and if the market permits, an increased degree of integration with refined sodium bicarbonate plants (EC, 2007c). The financial benefit for the soda ash plant, can be calculated according to the CO_2 pricing, whose average in 2013 was EUR 4.38/t_{CO2} (Figure 4) (EEX, 2015), while the environmental benefit can be estimated from the range of emissions in the different European plants (Ecofys, 2009). There are several plants (in Spain, France, Italy and the UK) that are considered as examples for this BAT (EC, 2007c) and the estimated investment costs are EUR 54 280 000 for reference capacity 330 kt/y (OPT Sensor Srl, 2012).

Another BAT is the choice of vertical shaft kiln, instead of the other types available. The decomposition of limestone to produce soda ash sets a number of constraints on the type and design of the kiln to be used. Most European plants were already using vertical shaft kilns before 2007 that satisfy all the constraints placed by the decomposition of limestone (42) (EC, 2007c). The main environmental benefit from this type of kiln is a higher concentration of CO_2 in the lime kiln gas that has an important impact on the energy efficiency of the soda ash process. Energy intensity in the lime kiln section of a typical plant amounts to 2.2-2.8 GJ/$t_{soda\ ash}$, and vertical shaft kilns can achieve the lowest value

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(42) These constrains include for example maximum thermal efficiency, sufficient supply of CO_2, ability to accept a wide particle size distribution of limestone, high yield to reactive lime etc. More information can be found in the literature [EC, 2007; Cefic, 2004].

of the emissions range (EC, 2007c). Estimated investment costs for this BAT are about EUR 5 280 000 for reference capacity 330 kt/y (OPT Sensor Srl, 2012).

Another technique involves the centrifugation of the crude sodium bicarbonate before the calcination section. Centrifugation decreases the water content in the sodium bicarbonate, thus minimising the steam requirements for its thermal decomposition. As a result, besides decreased energy consumption, the emissions of CO_2, SO_x and NO_x are also reduced (EC, 2007c). The average water content in crude sodium bicarbonate in Europe is 15-19 %, but after centrifugation contents of 12-14 % H_2O can be achieved, reducing the energy required for its decomposition by 5-6 % (EC, 2007c). The Polish plants had already installed this technology before 2007 (EC, 2007c).

The last technique examined in this study is ammonia recovery in the distillation section. Ammonia is in principle a reaction aid, which can be recovered in most part, although some quantity still needs to be added (Table 51). Distillation is the primary abatement technique for ammonia recovery, with efficiencies over 99.5% and ammonia slip ranging between 0.3 and 1.9 kg/$t_{soda\ ash}$, if operated properly (EC, 2007c). The environmental benefit can be calculated from this range. Proper operation also minimises the impact of liquid effluents. The lowest ammonia slip is achieved with the highest quantity of steam, but an increase in energy used will lead to increased CO_2 emissions and as a result an optimum to be reached between the two effects (EC, 2007c).

5.6.4 Innovative technologies (ITs)

No emerging techniques were reported based on the Solvay process (EC, 2007c), but a few potential improvements have been identified in the literature.

The first one is utilisation of excess CO_2 from the ammonia process for production of soda ash, by integrating the soda ash plant with an ammonia plant. The ammonia industry emits approximately 1.25 t_{CO2}/t_{NH3}, if it is not integrated with a downstream urea plant (EC, 2007c) and can therefore be used in the production of soda ash. The application of this technique has many restrictions, as the ammonia and soda plants need to be in proximity, the ammonia plant should not be integrated with urea production and a cheap source of lime should be also available. As a result, it cannot be considered generally applicable and it falls out of the scope of this study. An example plant of this technology is though mentioned to exist in Haldia, India (EC, 2007c).

The second technique concerns innovations in the carbonation section of the soda ash plant (reaction 34). In Japan a new type of carbonator was reported in 1983, with production capacity of 250 $t_{soda\ ash}$/d in each carbonation tower, with the ability to operate more than 8 months, overall heat transfer coefficient five times higher than the one is Solvay towers and remarkably reduced equipment costs (EC, 2007c). The two plants mentioned as examples, though, were closed (EC, 2007c) and therefore the innovative technique is not considered due to lack of information on performances.

In addition to these improvements to the Solvay process, an alternative route based on the Leblanc process has been suggested. According to this process, soda ash can be produced from sodium sulphate, according to the following reactions:

$$Na_2SO_4 + 2\ NH_4HCO_3 \rightarrow 2\ NaHCO_3 + (NH_4)_2SO_4 \qquad \text{(reaction 38)}$$

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \qquad \text{(reaction 39)}$$

This process has 50-65% less investment costs than the conventional Solvay process, but 60-89% higher production costs (Kumar et al., 2013). In addition, it is not economical for producing soda ash, but for producing baking soda (sodium bicarbonate). Based on this conclusion, as well as the fact that there is no information available for its environmental performance compared to the Solvay process, this technique is also not considered in this study.

5.7 Aromatics

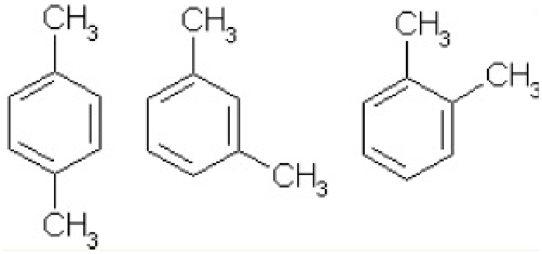
The term ‘aromatics’ is mainly used to describe benzene, toluene and xylenes, also known as BTX. They all have the common characteristic of an aromatic ring (a six-member Kekule ring) in their molecule, named like this due to a specific smell that they have. Nevertheless, aromatic chemical plants also produce a number of intermediate chemicals, apart from BTX, including cyclohexane (EC, 2014d). They are all important in the production of polymers, other chemicals and several consumer products, such as solvents, paints, polishes, pharmaceuticals. They are often produced together in the same process, mainly from fractions obtained by oil distillation (CIEC, 2015), so they can be considered as a group (Kirk-Othmer, 1999).

Benzene (C_6H_6) is one of the largest-volume petrochemicals and the largest of the aromatics. It is used as raw material for a wide range of other chemical products (its product chain is included in Annex 2). In 2013, global production of benzene increased to 43.7 Mt (IHS, 2014f) from 43 Mt, in 2012 (IEA, 2013). Western Europe, China and the US accounted for about 50% of the total world consumption (IHS, 2014g). Benzene has been used as solvent and as a component of motor fuel for improving gasoline quality, but because of its high toxicity its use has decreased drastically (Ullmann's Encyclopaedia, 2000d). In Europe, the maximum benzene present in petrol can be 3.7 % m/m (EC, 2009c). The main application of benzene is as chemical feedstock. 70-75 % of benzene is consumed globally for the production of ethyl benzene and cumene (IHS, 2014g) Ethylbenzene is used primarily for the production of polystyrene and cumene for phenol and acetone (CIEC, 2015). Cyclohexane and nitrobenzene account for about 15-20 % (IHS, 2014f). Benzene consumption growth rates are expected to be around 2-3 % up to 2019 (IHS, 2014f).

Toluene (C_6H_5-CH_3) is used as a raw material to produce benzene and xylenes, solid-state resins and toluene diisocyanates (TDI) for polyurethane applications (EC, 2014d). Its product chain can be found in Annex 2. Some of the toluene produced is added in gasoline not isolated in its pure form, but as a mixture with other aromatics (Ullmann's Encyclopaedia, 2011b). Over 50 % of toluene produced in the refinery is converted into benzene by dealkylation and disproportionation (CIEC, 2015).

Xylene (C_8H_{10}) is the name of three isomeric forms, depending on the relative place of the methyl groups: ortho–xylene or 1,2–dimethyl benzene, meta–xylene or 1,3–dimethyl benzene and para–xylene or 1,4–dimethyl benzene (Figure 19). The most widely used isomers are ortho**–** and para**–**xylene, the latter being the main focus of producers as it is used in the production of polyethylene terephthalate (PET) (EC, 2014d). Ortho**–**xylene is used almost entirely to make phthalic anhydride, an intermediate in the synthesis of PVC plasticisers, pharmaceuticals and other chemicals (US Department of Energy, 2000). Xylene product chain is included in Annex 2. Mixed xylenes contain a blend of the three isomers, in varied compositions, but typically rich in m-xylene, which is the least valuable component (IHS, 2015f). Consumption of p-xylene accounted for 81 % of global mixed xylenes demand in 2015 (IHS, 2015f). During 2010-2015 both consumption and capacity of mixed xylenes increased globally, the first one at an average annual rate of 3.5 % and the latter by 23 % (IHS, 2015f). In the period 2015-2020, consumption of mixed xylenes is expected to grow at an average rate of 4.5 % per year (IHS, 2015f).

Figure 19. Xylene isomers: para–, meta– and ortho–



Information about aromatics production and capacity is reported by Petrochemicals Europe, but only about their members, which include EU-15, Norway and Switzerland. In 2013 benzene capacity and production was 10.1 Mt and 6.9 Mt respectively, while in 2014 they were 9.8 Mt and 6.7 Mt respectively (Petrochemicals, 2016). Concerning toluene, total capacity in 2013 was 2.1 Mt, while total production amounted to 1.80 Mt, while in 2014 they were 2.2 Mt and 1.66 Mt respectively (Petrochemicals, 2016). Mixed xylenes capacity in 2014 was 4.3 Mt (48 % para–xylene and 13.2% ortho–xylene) and production reached 2.7 Mt (70.1 % para–xylene and 18.7 % ortho–xylene) (Aromatics Online, 2016; Petrochemicals, 2016).

Like most petrochemicals, the demand of BTX is strongly linked with consumer demand for plastics (US Department of Energy, 2000). Benzene is expected to grow at a rate of 3 % annually until 2018 (IHS, 2014f), while the estimated growth in overall toluene consumption was less than 3% per year (ThyssenKrupp, 2009b). In the case of xylenes, consumption is expected to grow at 4.5 % annually until 2020 (IHS, 2015f).

There are aromatics plants in 15 member states in the EU-28 as shown in Table 54 (IHS, 2015a; ICIS, 2012; EC, 2003a). Not all plants are producing all three BTX, but since most countries have more than one plants, usually in the aggregated case, all BTX are produced in most member states. Since there are three products to be taken into consideration, the databases are not reporting individual plants but production lines. As a result, Table 54 does not include the number of plants. In the analysis each production line has been considered separately.

In 2013 total benzene toluene and xylenes capacities were 10.4 Mt/y, 3.0 Mt/y and 8.7 Mt/y respectively (IHS, 2015a; ICIS, 2012; EC, 2003a). The capacities per product included in the database, if compared with the capacities reported by Cefic (Petrochemicals, 2016), are slightly higher, since the data from Cefic refer only to EU-15, but the database is considered to be complete. In the case of xylenes, the difference is higher, since (Petrochemicals, 2016) report only mixed xylenes, but in our analysis we have taken into consideration also the production of p-xylene and o-xylene.

Table 54. Aromatics plants in EU-28 in 2013

Country	Benzene (kt/y)	Toluene (kt/y)	Xylenes (kt/y)
Belgium	885	95	1 085
Czech Republic	350	31	10
Germany	2 720	980	900
Spain	981	330	250
France	900	96	580
Italy	470	325	400
Hungary	195	110	85
Netherlands	2 515	325	1 140
Austria		4	
Poland	390	220	100
Portugal	95	245	220
Romania	40	85	
Slovakia	30	86	60
Finland	150		
United Kingdom	650	80	100
Total	10 371	2 967	4 930

Most of the units in Table 54 are built geographically close to or inside a refinery and therefore they can share most of the environmental abatement installations with the refinery (EC, 2014d).

5.7.1 Production processes

There is a large variety of plant configurations for the production of aromatics and aromatic complexes are often designed and built with different plant arrangements depending on the feedstocks used and the mix of products. The processes are usually not selective and produce a mixture of benzene, toluene and xylenes that has to be separated and purified (IL&FS, 2010). However, the routes producing aromatics often have some scope for upgrading the products according to the market needs, so the choice of production route depends on the feedstock availability, its cost and the aromatics demand (EC, 2003a).

Benzene was originally produced as a by-product from coal in the process to produce coke for the steel industry, until new processes began to emerge in the 1930s (Ullmann's Encyclopaedia, 2000d). Currently, the two main sources of feedstock for the production of aromatics are pyrolysis gasoline (43) and reformate from reformers (Ecofys, 2009). About 72 % of aromatics came from reformate, 24 % from pyrolysis gasoline (pygas) and the remaining 4 % from coke oven light oil from coke oven plants (IEA, 2007). Reformers are typically located in refineries and as a result refineries produce a significant proportion of the overall aromatics production. The fraction coming from coke oven operations is minor and this operation is not typically associated to conventional petrochemical industries, but rather with the iron and steel industry (EC, 2003a).

The main processing schemes in aromatic production are:

- Catalytic reforming of naphtha or steam cracking of naphtha for production of pygas
- Solvent extraction for separation of non-aromatics from aromatics

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(43) Pyrolysis gasoline or pygas is a naphtha-range product with a high aromatic content. It is produced in naphtha or gasoil steam crackers (not from ethane-based steam crackers).

- Pre-treatment of pygas, which includes two stage selective hydrogenation
- Separation of benzene, toluene and C_8 fractions
- Further separation of C_8 hydrocarbons

Pyrolysis gasoline (pygas) is produced by steam cracking of naphtha or paraffin gases and contains a high proportion of aromatics, primarily benzene and toluene, and a smaller amount of C_8 aromatics that contain up to 40 % ethyl benzene (Table 55). The yield in aromatics depends on the feedstock chosen (Table 31). This process has been already described in paragraph 5.3, with the steam cracking products. Raw pygas contains large quantities of diolefins and olefins.

The main purpose of reforming is to upgrade the octane of the streams for use as a gasoline blendstock (EC, 2015a). In a typical case, naphtha feed enters one or a series of reactors containing platinum catalysts in a gas atmosphere, after being hydrotreated to remove sulphur, nitrogen and metallic contaminants. Products from a reformer include hydrogen, refinery fuel gas, LPG, isobutene, n-butane and reformate. Reformate can be blended to gasoline or further separated into BTX and naphtha cracker feeds (EC, 2015a).

Table 55. Typical composition of the aromatics feedstocks (ThyssenKrupp, 2009b)

Component (% w/w)	Pygas	Reformate	Light reformate	Coke oven Light oil
Benzene	30	3	24	65
Toluene	20	13	46	18
Xylenes	4	18	< 0.5	6
Ethylbenzene	3	5	< 0.5	2
C_{9+} aromatics	3	16	0	7
Naphthenes	High	Low	Low	High
Olefins	High	High	Low	High
Paraffins	Low	High	High	Low
Sulphur	Up to 1 000 ppm	< 1 ppm	Low	Up to 1% wt

The following step is aromatics extraction, regardless of the feedstock. Since the composition of the aromatics mix is dictated by the feedstock (Table 55), the composition of the different feedstocks dictates different procedures to be followed.

Raw pygas has high concentrations in olefins and ethyl benzene and low concentration in xylenes, therefore it is mainly used to recover benzene or benzene/toluene (ThyssenKrupp, 2009b). The first step is hydrogenation in order to avoid polymerisation of the diolefins, followed by a series of distillation operations to prepare the desired cuts (C_6 for benzene and C_7 for toluene) for extraction (Ecofys, 2009). Olefins and impurities, such as nitrogen, sulphur and other components, are then completely hydrogenated and the H_2S containing off-gas is separated. Aromatics are extracted using either liquid – liquid extraction or extraction distillation technologies (Ecofys, 2009; ThyssenKrupp, 2009b). If C_{7+} aromatics are to be converted into benzene, a thermal hydrodealkylation unit is integrated in such a way that the extracted toluene is dealkylated to form benzene (ThyssenKrupp, 2009b).

Reformate has relatively lower benzene content and relatively higher toluene and xylenes content (Table 55). It is therefore used mainly for producing p-xylene (ThyssenKrupp, 2009b). Since (light) reformate contains lower quantities of olefins and sulphur impurities, hydrogenation is not required as first step. On the contrary, the typical process route includes fractionation by distillation to produce a C_{7-} and a C_{8+} fraction. From the C_{7-} fraction benzene and toluene are extracted from the non-aromatics with the same technologies as described before, while the C_{8+} fraction is sent to the p-xylene loop without extraction since the non-aromatics content in this fraction is very low (ThyssenKrupp, 2009b). The product, either extracted benzene and toluene or mixed xylenes, is treated with clay to remove olefins and then distilled (Ecofys, 2009). C_8

aromatic isomers have close boiling points and chemical properties, so the separation in individual xylenes needs techniques such as shape selective adsorption of p-xylene or crystallisation of the p-xylene molecule at temperatures between -4 and -60 °C (Ecofys, 2009). The remaining xylenes are sent to the isomerisation unit to be converted to p-xylene. If o-xylene is also a desirable product; it must be removed as pure product by distillation before isomerisation (ThyssenKrupp, 2009b).

5.7.2 Current consumption and emission levels

As already explained, aromatics feedstocks are reformate, pyrolysis gasoline and coal tar processing. It should be noted that there are several different configurations for aromatic plants even for the same feedstock and the characteristics of all individual processes are not always available.

Table 56. Overall material balances of aromatics complexes

	Feed Basis	Arabian Light Crude	Mideast Naphtha Heartcut
	Product objectives	Maximise p-xylene	
Naphtha feedstock properties	Specific gravity	0.735	0.753
	Initial boiling point (°C)	83	82
	Endpoint (°C)	166	176
	Paraffins/naphthenes/ aromatics (vol%)	66/23/11	48/37/15
Overall material balance (kt/y)	Naphtha	940	1535
	Benzene	164	238
	p-xylene	400	700
	o-xylene		100
	C_{10+} aromatics	50	9
	Sulfolane raffinate	140	174
	Hydrogen–rich gas	82	
	Pure hydrogen		40
	LPG	68	22
	Light ends	36	252

Due to the variety of available configurations, typical product compositions can also vary. Typical products yields of solvent extraction from naphtha reformate are 8.5 % benzene, 26.3 % toluene, 26.1 % xylenes (Energetics, 2000). According to (Serpec-cc, 2009), reformate can typically contain 12-23% benzene, up to 30% toluene and 23-48% p-xylene. Overall material balances for typical aromatics complexes with configuration for maximising p-xylene production are shown in Table 56, along with the properties of the naphtha feedstock used to prepare the cases (Meyers, 2004; UOP, 2006). The typical yields from pyrolysis gasoline were already included in Table 31.

Aromatics extraction is a process that yields several products and therefore there are several measures of consumptions and emissions, depending on what is considered the final product, as in the case of steam cracking (paragraph 5.3.2). Contrary to steam cracking, the aromatics industry is not only benzene orientated, but all three aromatics are considered as products. Even in the database, the aromatic plants are recorded according to the production lines for each aromatic (IHS, 2015a; ICIS, 2012; EC, 2003a). As a result, in this case consumptions and emissions are allocated to each one of them based on their mass ratio. Of course with this general allocation, it is not possible to account for each of the different plant configurations. We have to assume that aromatics are produced by a generic process. If a facility is reporting producing only benzene, then the values per tonne of benzene will be used, but if it is reporting producing toluene, xylenes or all BTX the values per tonne of aromatics will be applied, attributed to each aromatic by mass allocation based on the ratios mentioned before.

In order to apply mass allocation, the ratio of benzene: toluene: xylenes is needed. This ratio in the case of pygas-based is 85:49.2:33.2 (44) and in the case of reformate-based 25:0:75 in the case of p-xylene oriented configuration (Table 56), 14:43.2:42.8 in the case of solvent extraction (45) and 23:30:48 according to (Serpec-cc, 2009). For our study, we will apply the ratio by (Serpec-cc, 2009), as the values used are also from the same source.

Feedstock and energy consumptions are shown in Table 57 for both references: total aromatics and only benzene. Feedstock consumptions in the case of pygas and naphtha can be calculated according to the average of the data reported in Table 31 and Table 56 respectively, while utilities consumptions are average consumptions in European benzene plants (Serpec-cc, 2009) adjusted to the material balances of the two processes.

Table 57. Feedstock and average energy consumption for aromatics production processes

	Aromatics pygas based		Aromatics reformate based	
	Unit/$t_{aromatics}$	Unit/$t_{benzene}$	Unit/$t_{aromatics}$	Unit/$t_{benzene}$
Feedstock				
Pygas (t)	2.31[1]	4.74		
Naphtha (t)			1.5[2]	6.08
Utilities[3]				
Fuel (GJ)	1.47	2.9	0.35	1.5
Steam (GJ)	3.9	7.8	3.45	15.0
Electricity (kWh)	15.0	30	9.2	40

[1] Calculation based on Table 31 (the average of naphtha and atmospheric gasoil pygas)

[2] Calculation based on the average of the two types of feedstock in Table 56

[3] Values per tonne benzene from (Serpec-cc, 2009). The values per tonne of aromatics are calculated according to the ratio or BTX, as explained in the text.

Emissions from aromatic plants are mainly due to energy needed by aromatics separation processes, combustion processes (to supply energy) (EC, 2003a; EC, 2014d), or leakages (Energetics, 2000). As aromatic plants are usually integrated into refinery auxiliary facilities, the process emissions of the aromatic plant will most commonly go to the end-of-pipe devices shared with or belonging to the refinery (EC, 2014d).

In 2011, the total process and steam emissions related to the aromatics production process were estimated to add up to 6.6 $Mt_{CO2.eq}$, on a total BTX production of 11.7 Mt, which equals an average value of 0.56 $t_{CO2}/t_{aromatics}$ (Benner et al., 2012). Each process has different benchmark emissions that are shown in Table 58. The range of the value occurs due to two methods identified by Cefic in the case of BTX from pygas (Ecofys, 2009).

Table 58. Benchmark values for BTX production in Europe (Ecofys, 2009)

Benchmarked section	Region	Direct + heat ($t_{CO2}/t_{aromatics}$)	Direct + heat + electricity ($t_{CO2}/t_{aromatics}$)
BTX from pygas	Europe	0.34-0.38	0.37-0.43
BTX from reformate	World	0.26	0.28
Xylenes loop	Europe	0.50	0.65

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(44) Calculation based on Table 31 (the average of naphtha and atmospheric gasoil pygas).

(45) Calculation based on the information in [Energetics, 2000].

Table 59 shows the emission factors used in this study, which are calculated according the energy consumptions (Table 57) and the emission factors shown in Table 58. The average of the two processes (from pygas and reformate) is 0.34 $t_{CO2}/t_{aromatics}$, thus about 40% less than the average emission factor according to real emissions. This difference is taken into consideration too.

Table 59. Emission factors for the processes producing aromatics

Emissions	Aromatics pygas based	Aromatics reformate based
	Value ($t_{CO2.eq}/t_{aromatics}$)	Value ($t_{CO2.eq}/t_{aromatics}$)
Electricity use	0.007	0.005
Thermal production	0.08	0.02
Steam production	0.28	0.27
Direct Process	0.19	0.09
Total	0.56	0.39

Aromatics are benchmarked products, but in order to ensure a level playing field for their production in refineries and in chemical plants, the free allocation of emission allowances is based on the 'CO_2 weighted tonne' (CWT) approach and the benchmark value of the refineries product benchmark should be applied (EC, 2011b). The benchmark value for refinery products is 0.0295 $allowances_{CWT}/t_{prod}$ and the CWT factor for aromatic solvent extraction is 5.25 kt/y covering all feeds including pygas after hydrotreatment. Pygas hydrotreating is accounted under naphtha hydrotreatment with 1.10 kt/y CWT factor, while p-xylene production has CWT factor 6.40 kt/y (EC, 2011b). There is no benchmarking curve available for aromatics and therefore no calibration can be performed for the specific emissions per facility.

5.7.3 Best available techniques (BATs)

The majority of the techniques used in aromatic plants are horizontal or generic and some of them are shared with the steam cracking process (paragraph 5.3.3). An overview of the techniques that have been identified as having potential for reducing GHG emissions and improve energy efficiency is summarised in Table 60.

As mentioned several times already, aromatic plants can be built close to or inside a refinery, since refineries are usually integrated with other petrochemical processes. Process integration originates from the petrochemical industry, where it has been applied successfully (Serpec-cc, 2009). The general aim is to reduce energy requirements and it involves schemes such as heat recovery from product streams and use of waste heat. Typical savings achieved are 20 % in energy consumption, but can reach 50 % (Serpec-cc, 2009). It is a technique applicable to aromatic plants, as well as surrounding units (EC, 2003a). Process integration applied in a refinery, with capacity of 2 10^5 barrels per day, including aromatics extraction and BTX fractionation, resulted in energy consumption reduction by more than 422 GJ/hr, worth more than USD 20 million/y (Wolschlag et al., 2009). It has been applied also at the Samsung Total Aromatics Complex in Daesan, Korea with 2006 capacity 480 $kt_{p\text{-}xylene}/y$, 240 $kt_{benzene}/y$ and 100 $kt_{toluene}/y$. The complex-wide revamping project for energy optimisation reports energy savings 20% that sum up to USD 12 million $_{2006}$/y, while the investment costs were USD 9.1 million $_{2006}$ and the payback time less than a year (AspenTech, 2006). The energy consumption achievable if such a BAT is applied is estimated to be at 7.1 $GJ/t_{benzene}$ steam and 0.03 $MWh/t_{benzene}$ electricity for the production of aromatics from pygas and at 12.0 $GJ/t_{benzene}$ steam and 0.03 $MWh/t_{benzene}$ for the production of aromatics from reformate (Serpec-cc, 2009).

Table 60. Overview of the possible BATs and ITs in aromatics production

BAT/IT	Description	Investment cost (EUR)	Energy savings (%)	GHG Reduction (%)
BAT	Energy integration – reformate based process	7 780 383 [1]	25 % electric 20 % thermal	None
	Energy integration – pygas based process		9 % thermal	
BAT	Styrene recovery from pygas	No information available		
IT	Xylenes separation processes	No information available		
IT	Split–feed two–stage parallel aromatisation for maximum p–xylene yield	No information available		
IT	Composite solvent for extraction distillation	No information available		
IT	Conversion of methane to higher hydrocarbons	No information available		
IT	Bio–based aromatics	No information available		

[1] Reference capacity 820 kt$_{aromatics}$/y

Styrene is present in the pyrolysis gasoline, but it cannot be purified by conventional distillation because of the presence of other components or isomers with similar boiling points (IHS, 2005). It is usually hydrogenated to ethyl benzene in order to reduce the gum-forming potential of gasoline. New technologies, though, that recover styrene from pygas via extractive distillation are being commercialised (Gentry and Zeng, 2009). A proprietary solvent system is used to change the relative volatility of the pygas components and allow styrene to be selectively extracted (Lee et al., 1998). This process has been successfully tested in a pilot plant, but has not yet been demonstrated on a commercial scale (IHS, 2005). The extraction technology provides profitable production of styrene at relatively small capacities and is appropriate for at least 15 kt/y contained styrene in pygas (Gentry and Zeng, 2009). The prospective economics of the process for reference capacity 250 kt$_{styrene}$/y includes capital cost of USD 30 million $_{2009}$ (Gentry and Zeng, 2009), but since there are no data concerning its GHG or energy savings, the technique cannot be included in this analysis.

5.7.4 Innovative technologies (ITs)

In recent years various studies have been carried out aiming at improving the performances of aromatics production processes, focusing mainly on increasing product yield or on new feedstocks that can substitute petroleum derivatives. Recovery techniques can increase the product yield and membranes can have an outstanding role in separation industries in the near future, thanks to their simplicity, low energy cost and not causing environmental pollution (Takht Ravanchi et al., 2009).

Xylenes are difficult to be isolated, because the three isomers, as well as ethyl benzene have close boiling points. Various commercial processes for separation of p-xylene from C_8 aromatics have been developed as alternative to fractional distillation, which include fractional crystallisation (differences of the freezing points) or zeolites for selective absorption (Huff et al., 2005). Separation using aromatic-selective polymeric membranes can be proved to particularly useful for recovery of m-xylene and p-xylene (Miller et al., 2008). The technique sounds promising, but there is no information concerning its performances available.

Increased p-xylene yield can also be achieved via split-feed two-stage parallel aromatisation (Nacamuli and Thom, 1998). This invention relates to a process for reforming a full–boiling range hydrocarbon feed to enhance p-xylene and benzene production and it is based on the fact that an adverse effect on production of p-xylene can happen with the help of catalysts. The catalysts comprise of at least one Group VIII metal and a non-acidic zeolite support, in the case of C_6-C_7 cuts catalytic aromatisation, and of at least one Group VII metal and a metallic oxide support, in the case of C_{8+} cut catalytic aromatisation (Nacamuli and Thom, 1998). Also for this technology there are no data available that refer to its performances.

Improvements in extractive distillation involve new solvents. A new application provides a composite solvent that has higher solubility and relatively wide boiling range, so that it allows moderation of the operation conditions and therefore energy savings (Tian et al., 2006). The composite solvent comprises a main solvent, a modifier, which can be selected from sulpholane derivatives, N–formyl morpholine and N–methyl pyrrolidone provided that the acidity and basicity of the modifier are opposite to those of the main solvent, and a solutiser, which can be selected from aromatics C_8-C_{11}.

An innovative possible utilisation of CH_4 is the production of higher hydrocarbons with a number of strategies that include among others the syngas pathway followed by Fischer – Tropsch chemistry and the direct conversion to aromatics and hydrogen in the absence of oxygen (Lunsford, 2000). Currently, no direct processes have progressed to a commercial stage, probably due to the fact that product yields are generally small and the considerable difficulties existing in an economical way (Lunsford, 2000; Eliasson et al., 2000).

Biomass is considered to be a feedstock possible to substitute petroleum resources. A potential breakthrough technology is catalytic pyrolysis of lignin. Some routes that are being explored are catalytic hydrocracking, catalytic pyrolysis over a zeolite catalyst and liquefaction with a mixture of supercritical water and phenol (Benner et al., 2012). Catalytic fast pyrolysis seems to be the most advanced technology for direct conversion of biomass to olefins and aromatics in one reactor. Zeolite catalysts with micropores present good catalytic characteristics in this process, but large-molecule oxygenates that are produced during pyrolysis cannot enter their pores and form coke on the catalyst surface, thus deactivating it (Zhang et al., 2013). The initial estimations of the investment costs amount to USD 220 million (Bennet et al., 2012). Another possibility is bio-based p-xylene, of which there are few scale–up production units (Lin et al., 2013). Gevo Inc. is converting isobutanol derived from biomass fermentation (Peters et al., 2011), Virent Energy system Inc. developed a process to convert a series of chemical via hydrocarbon oxidation (Cortright & Blommel, 2011) and Lin et al. (2013) suggest producing p-xylene from 5–hydroxymethylfurfural an intermediate deriving from lignocellulosic biomass. The overall yield has been reported to be up to 88 % and its capital costs have been estimated to be USD 100.63 million (Lin et al., 2013). Unfortunately, the data available for these technologies are quite restricted and as a result they cannot be considered in this study.

5.8 Carbon black

Carbon black (CB) is the name of a group of manufactured fine-particle products that have a variety of different trade names and physicochemical properties, but share a chemical composition of nearly pure elemental carbon. It is usually in the form of colloidal particles and is produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions. Its chemical composition is shown in Table 61 (Long et al., 2013).

Rubber applications dominate carbon black uses worldwide. Approximately 90 % of carbon black is used in the tire and automotive industry, while the remaining 10 % is divided among other special carbon black applications that include pigment, UV absorbing, conducting agent in inks, coatings and plastics (EC, 2007c).

Table 61. Carbon black chemical composition

Component	Content
Total carbon	97-99 %
Elemental carbon	>97 %
Organic carbon	<1 %
Hydrogen to Carbon ratio	<0.008
Inorganic Species	<1 %

Since carbon black is predominantly used in rubber products, most carbon black production facilities are located in countries with large automotive industries. Until middle 2014, 17 carbon black installations have been reported in the EU-28 (Table 62). Their total capacity was 1 248 kt/y (ICIS, 2012).

Table 62. Carbon black plants in EU-28 in 2013

Country	Number of plants	Capacity (kt/y)
Belgium	1	10
Czech Republic	1	135
Germany	3	330
Spain	2	60
France	2	165
Croatia	1	38
Italy	3	240
Hungary	1	100
Netherlands	1	90
Poland	1	40
Sweden	1	40
Total	17	1 248

5.8.1 Production processes

Carbon black can be produced by two chemical processes: (1) incomplete or partial combustion, or (2) thermal cracking. The main difference between the two types of processes is that in partial combustion, air is used to burn part of the feedstock, thus producing the energy required to carry out the pyrolysis, whereas in thermal cracking processes, heat is generated externally and introduced into the process.

The main manufacturing processes for producing carbon black belong to the partial combustion processes and are the following three (Ecofys, 2009):

Furnace black process

It allows the production of all grades of carbon black required by the rubber industry. Carbon black is produced by injecting the primary feedstock (petrochemical or chemo-chemical heavy aromatic oils), usually as an atomised spray, into a high temperature zone of high energy density, which is achieved by burning a secondary feedstock (natural gas, oil or other gases) with air. The oxygen present is not sufficient for complete combustion of the primary feedstock, which is therefore pyrolysed to form carbon black. Yields depend on the type of carbon black and of primary feedstock and range from 40 to 65 % (EC, 2007c).

Gas black process

This process was developed in order to exploit coal tar oils as feedstock, which are partially vaporised and transported to the production apparatus by a combustible carrier gas (hydrogen, coke oven gas or methane). The type of burner used influences the carbon black properties. The production rate and the yield depend on the grade of carbon black produced, but for a typical reinforcing black, the yield is 60 %. In the case of high quality pigment blacks the yield is considerably lower.

Lamp black process

It is the oldest industrial scale production process.

The yield in general depends strongly on the produced quality. More information about the carbon black manufacturing processes can be found in the BREF for Large Inorganic Chemicals – Solids and others (EC, 2007b).

The furnace black process is currently the most important production route and accounts for more than 95 % of the production worldwide. It is a continuous process, with great flexibility and better economy compared to other processes. Within the EU-ETS scheme, most carbon black plants use the black furnace process. The gas black and the lamp black processes are only used in order to produce special grades of carbon black that cannot be manufactured through the furnace black process, and account for less than 5 % of worldwide production. In 2009 only two plants in Europe were reported to use the latter two processes, one each (Ecofys, 2009).

5.8.2 Current consumption and emission levels

Since the majority of black carbon plants use the furnace black process, our discussion will be focused on only this process.

An accurate mass and energy balance for the black furnace process is challenging, due to the fact that it is not clearly known which part of the feedstock is converted into products. In addition, feedstock and operating conditions depend on the grade of carbon black produced and are frequently changed, while energy recovery for internal and external use can be done under different forms (EC, 2007c).

Table 63. Typical raw materials consumption in a furnace black plant (Ullmann's Encyclopaedia, 2010b)

Raw material	Semi-reinforcing Carbon Black	Reinforcing Carbon Black	Average (t/t_{CB})
Oil	2.5-3.3 t/h	1-1.5 t/h	1.83
Natural gas	300-550 m^3/h	280-440 m^3/h	0.21[1]
Air	7 000-10 000 m^3/h	6 000-7 500 m^3/h	6.15[2]
Carbon black	1.5-2 t/h	1-1.5 t/h	

[1] For the EU-mix natural gas 0.8 kt/Nm^3 is assumed (JEC, 2014)

[2] Density of air is assumed to be 1.2 kg/m^3 in STP (Engineering toolbox, 2015b)

Natural gas is the most important fuel in the furnace black process, but other gases and oils can also be used. These can be oil from fluid catalytic cracking of gas oils, ethylene tar or ethylene cracker residue. Typical raw material consumption of a furnace black plant is shown in Table 63.

Table 64. Energy consumption and emission factor for the carbon black manufacturing process

Process	Energy consumptions[1]			Emission factor [2]
	Electrical (kWh/t)	Thermal (GJ/t)	Steam (GJ/t}	($t_{CO2.eq}/t_{CB}$)
Furnace black	500	52.7	0.00	2.62

[1] (IEA, 2009b)
[2] (IPCC, 2006b)

The electrical consumption for carbon black plants depends on production and ranges from 430 kWh/t_{CB} for production more than 75 kt/y to 550 kWh/t_{CB} for production less than 50 kt/y (EC, 2007c). Table 64 reports the values of energy consumption for the furnace black process used in this study.

As mentioned earlier, the yield and therefore the emissions depend on the quality of carbon black produced. Under normal operating conditions, the furnace black process does not form toxic solid or liquid by-products (EC, 2007c). An important potential source of emissions to the air is the tail-gas, which comes from the reactor after product separation and is a low calorific gas with high moisture that can vary from 30 to 50 vol-% wet. Its composition depends on the feedstock used, as well as on the CB quality grade. Typical tail-gas contains mainly moisture, nitrogen (32-46 vol- % wet), hydrogen (6.6-14 vol- % wet) and carbon monoxide (6-11.7 vol-% wet) (EC, 2007c). The total emission factor used in this study is shown in Table 64.

Carbon black produced by furnace black is a benchmarked product, with the value of 1.954 allowances/t. The system boundaries of the benchmarking are all processes directly or indirectly linked to the production of furnace carbon black as well as finishing, packaging and flaring (EC, 2011b). In particular the emissions included are: (i) the CO_2 emissions related to the combustion of tail-gas, (ii) the CO_2 emissions due to combustion of fuels used, (iii) emissions related to purchase heat from external suppliers and (iv) the indirect emissions from electricity consumption.

5.8.3 Best available techniques (BATs)

In this paragraph the possible Best Available Technologies (BATs) available for the carbon black industry are described. Table 65 lists an overview of the possible BATs available for the carbon black industry.

Most of the BATs mentioned are not widely used in the European carbon black industry. NO_x and SO_x emissions are mainly related to combustion of the tail-gas in dedicated combustors. Primary NO_x reduction is considered only for the use in enclosed thermal combustors and not in the carbon black reactor, as it interferes with the production process and not useful, due to the relatively low amount of such type emissions in the reactor. There is very little experience within the carbon black industry with the application of this BAT (EC, 2007c) and as a result it will not be considered for this study. The main process-integrated mechanism for SO_x reduction is the use of low sulphur feedstock, but this is a technique that is not included inside the boundaries of the carbon black industry, and therefore cannot be considered for this study either.

Table 65. Overview of the possible BATs and ITs in the carbon black industry

BAT/IT	Description		Investment cost (EUR)	Energy savings (%)	GHG Reduction (%)
BAT	Primary NO_x reduction		No information available		
BAT	Primary SO_x reduction		Outside the scope of this study		
BAT	Selective catalytic reduction		Not applicable in this industry		
BAT	Selective non-catalytic reduction		No information available		
BAT	Dust removal/ separation operation		No savings		
BAT	Tail-gas combustion devices and energy recovery	Flare	No savings		
		CHP	16 118 600	General reference in 4.4	
IT	Hydrocarbon decomposition by plasma		Outside the scope of this study		

Selective Catalytic Reduction (SCR) is not used in the carbon black industry, due to low NO_x level in the gases from the reactor and expected interferences with the operation of the plant, while Selective Non-Catalytic Reduction (SNCR) is reported to exist only in the carbon black plant in Sweden, and as a result neither is considered as successfully demonstrated techniques (EC, 2006). Dust removal/separation is not a BAT affecting energy efficiency or GHG emissions, and therefore falls out of the scope of this study.

The most common technique in Europe is the use of tail-gas combustion devices with energy recovery. The main source of emissions, as mentioned before, is tail-gas. It is not allowed to vent uncombusted tail-gas unless in case of emergency. Nearly all carbon black plants reuse part of the tail-gas in dryers, but the remaining tail-gas can be used in different ways. Some plants sell it directly, whereas others combust it in a CHP or a boiler. There are four types of devices, currently in use to combust tail-gases at carbon black facilities: (1) product dryer combustion chambers, (2) boilers or combined heat and power (CHP) installations, (3) flares and (4) other thermal combustors. In general, this technique is included in this study uniformly as CHP.

From the 16 CB plants in the EU-28, at least 9 have CHP installed (EC, 2007c). CHP capacities were provided in the general case by ESAP (ESAP, 2012). In the special case of these plants, though, data were available for only 4 of them. The CHP installed capacities of the plants for which no data were available was, therefore, calculated, by using the weighted average of the four known CHP capacities.

If tail-gas is burnt in boilers, high pressure superheated steam can be generated and subsequently used, but usually the carbon black industry cannot use all of the steam produced itself, and therefore exports it. Flares are also used in the industry, where tail-gas is combusted without energy recovery. Therefore it is used only to facilitate the disposal of excess tail-gas.

Energy recovery from the tail-gas affects the energy efficiency of the plant. The potential energy that can be recovered depends on the calorific value of the tail-gas and can vary between 17 and 30 GJ/t_{CB} (EC, 2007c). In addition, combustion of the tail-gas results in reducing GHG emissions, as it reduces NO_x emissions.

The economic viability of a CHP is depending on the local electricity costs and the price that can be obtained for the surplus electricity, while in the case of a boiler, it depends on the need for steam in the plant and the revenues that can obtained by selling the excess. Investment costs of a boiler producing steam (100 bar, 530°C) varies between EUR 115 000 $_{2002}$/(t_{steam}/h) for an installation of 100 t/h and EUR 70 000 $_{2002}$/(t_{steam}/h) for an installation of 200 t/h. Units in the carbon black industry are rather in the range of

100 t/h. The gross investment cost in the CB industry is estimated to be for flares in the range EUR 0.5-1.5 million $_{2002}$, for incinerators EUR 5-15 million $_{2002}$, for boilers EUR 10-15 million $_{2002}$ and for CHP units EUR 15-25 million $_{2002}$ (EC, 2007c).

5.8.4 Innovative technologies (ITs)

As mentioned already, carbon black can be produced also by thermal cracking, but this process is not used in the industry. New developments in technologies tend to improve this category of chemical processes. According to literature (Sun et al., 2016; Yuan et al., 2014), methods have been proposed for producing carbon black from decomposition of hydrocarbons, usually methane, by plasma. The different plasma technologies can be generally distinguished in two main categories: thermal plasma and non-thermal plasma.

The thermal-plasma concept for carbon black production has induced the development of two patented and competing processes and several other non-patented processes. The first patented process was developed in Norway by Kvaerner Engineering and is converting methane to hydrogen and CB on the basis of a direct current carbon electrode plasma generator (Gaudernack and Lynum, 1998; Bakken et al., 1998). The second one was developed in France at Ecole de Mines de Paris in partnership with CNRS and TIMCAL Belgium and consists of a 3-phase plasma process (Fulcheri et al., 1997; 2002). A team from Seoul National University, South Korea has also developed a continuous production of carbon black and hydrogen by thermal decomposition of methane using direct current – radio frequency hybrid thermal plasma (Kim et al., 2005), which has the advantage of synthesising new nanostructured materials by providing high-temperature environment and longer residence time for reactant gases. CNRS and TIMCAL Belgium have developed another variation of the thermal dissociation of methane, using solar energy (Rodat et al., 2011a; 2011b).

Concerning the non-thermal plasma processes, a novel process was introduced by a team in France at Ecole de Mines de Paris (Moreno-Couranjou et al., 2009), based on low current-high voltage discharges. This process can also produce a broad range of products.

From all these processes, only the "Carbon Black and Hydrogen" process by Kvaerner Engineering has been scaled up and it is based on a graphite plasma torch invented by SINTEF with coaxial graphite electrodes. Its benefit is environmental, as there are no CO_2 or NO_x emissions from this process. There are three patterns concerning this process (Kvaerner Engineering, 1992; 1993a; 1993b) and was commercially utilised in a plant outside Montreal, Canada for the period 1998-2001. The designed operational capacity of the Kvaerner's Karbomont plant was 20 kt_{CB}/y and 2.5 billion cubic feet of hydrogen per year, which was used in an adjacent petroleum refinery. The plant is though decommissioned and no information on it is available.

Gasplas AS has also configured this plasma technology to produce a novel reactor design, with shorter residency time, higher quality output and efficiency at small scale, compared to the Kvaerner reactor (Gasplas, 2011). They report the following performance: 4 kg $CH_4 \rightarrow$ 1 kg H_2 + 3 kg C with electric energy consumption 10 kWh_{el}. The total OPEX is EUR 920/t_{CB} with reference capacity 200 kg H_2/d and 600 kg C/d. The economic aspects of the process are based on hydrogen production and the carbon black produced is considered only in the form of by-product credits.

As mentioned earlier, this is the only innovative technology that has been scaled up, but from the economics of the technology it is made clear that there is also hydrogen produced. This makes the IT appropriate for carbon black plants that have a market for hydrogen too, as it was demonstrated by the pilot plant of Kvaerner. As a result, it cannot be regarded as a possible solution for all plants, and therefore it is not considered to be inside the scope of this study.

5.9 Chlor-alkali

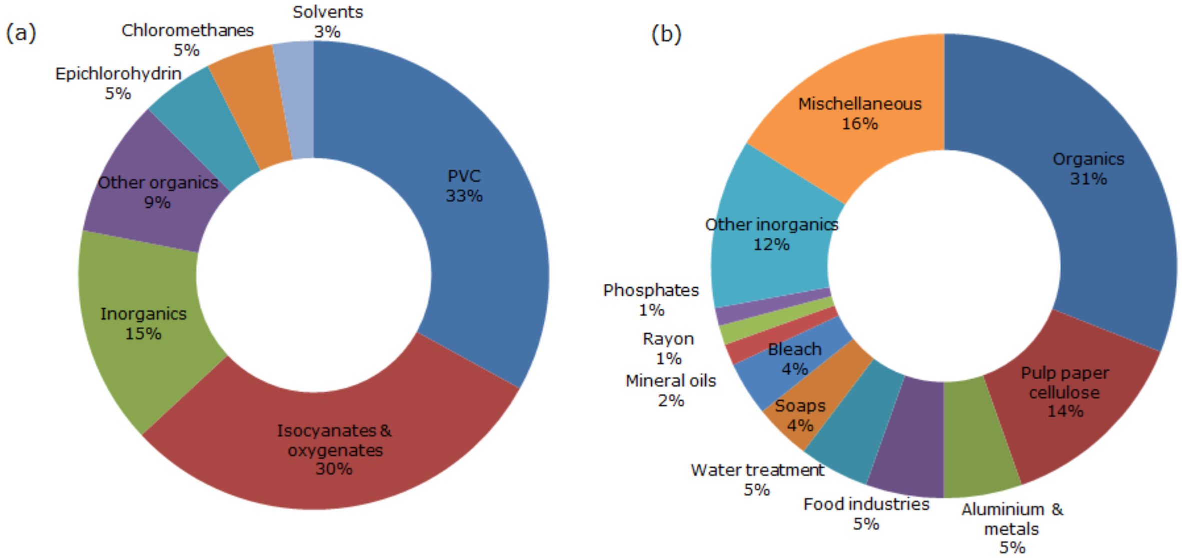
Chlorine (Cl) is a chemical element with atomic number 17 and belonging to the halogen group in the periodic table. Molecular chlorine (Cl_2) is a greenish gas, but due to its high reactivity, in nature it is usually found bound with other elements (Euro Chlor, 2014). It is one of the most abundant elements on earth, with about 50 quadrillion tonnes of dissolved sodium chloride (NaCl) found in oceans and seas. However, the majority of salt comes from rock saltmines (Euro Chlor, 2014). From the readily available rock salt, chlorine and sodium hydroxide (NaOH, also known as caustic soda) is produced; as a result, the industry co-produces both these substances and is called chlor-alkali.

Chlorine is an essential component in many industrial and commercial applications, as it can be seen in its product chain in Annex 2. World chlorine installed capacity in 2012 was estimated to be about 76.8 Mt (EC, 2014c), but the global annual production in 2011 was estimated to be about 56 Mt (CIEC, 2015) and in 2013 about 65 Mt (CEPS, 2014b). China was the driver of global chlor-alkali capacity expansion with a share of 41% in 2012. U.S and Europe are following with shares of 18 % and 16 % respectively (EC, 2014c). Most new larger chlorine plants are built to supply feedstock to ethylene dichloride facilities (IHS, 2014h).

In the EU-28+ (46) total capacity in 2012 was 12.2 MT/y (EC, 2014c) and production 9.7 Mt (Euro Chlor, 2013). In 2013 production decreased to 9.5 Mt (Euro Chlor, 2014), but in 2014 it increased by 1.7 % (Euro Chlor, 2015). 3-4 % of the chlorine production capacity is coupled with the production of potassium hydroxide and approximately 96-97 % with the production of sodium hydroxide (EC, 2014c).

Chlorine is well known for its use in sterilising drinking water and swimming pool water, but it has a huge variety of uses. It is largely used in the synthesis of chlorinated organic compounds with polyvinylchloride (PVC) and isocyanates being the major drivers of the industry (EC, 2014c). Chlorinated substances intervene in many agrochemicals and in the manufacturing of pharmaceuticals, as well as paints, rubbers and detergents. The main chlorine applications in the EU-28+ are shown in Figure 20(a) and amounted in total to 9.6 Mt (Euro Chlor, 2014).

Figure 20. (a) Chlorine and (b) caustic soda applications in the EU-28+ in 2013



The output of sodium hydroxide is proportional to that of chlorine and equal to the ratio of molecular weights 1.128, but is influenced by factors side-reactions and factors that depend on the method of production (EC, 2014c). It is usually produced commercially in the form of 50 % wt solution and its main uses are shown in Figure 20(b) in (Euro Chlor,

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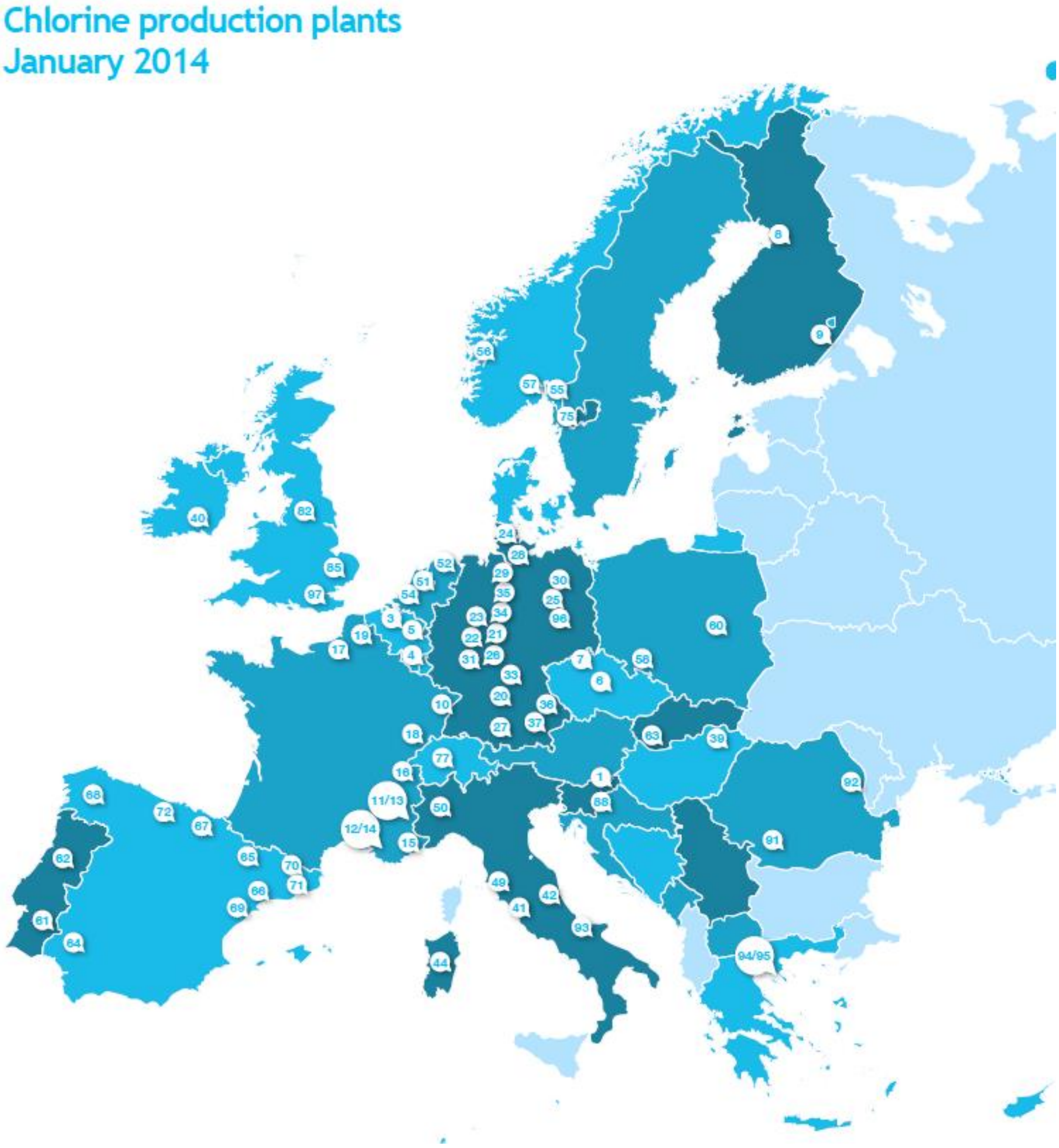
(46) EU-28+ includes EU-28, Iceland, Norway, Switzerland and Lichtenstein.

2014). In 2013 the applications of caustic soda in the EU-28+ were 9.3 Mt in total (Euro Chlor, 2014). Large quantities are used within the chemical industry, but two specific end uses are influencing its demand: alumina production and the pulp and paper industry.

Chlorine and caustic soda are co-products and the demand for one highly influences the demand for the other. Over the last several decades, the industry has proved to be cyclical, with chlorine demand driving it mainly, as it can be noticed by comparing the EU-28+ consumptions of the two co-products (Euro Chlor, 2013; 2014; 2015). Another forcing affecting the market is environmental regulations, but as long as no non-chlorine replacement for PVC is developed, demand will remain strong (US Department of Energy, 2000).

The EU-28+ chlor-alkali industry consisted in 2013 of 66 sites in 21 countries, 19 of which are members of the EU-27, with total capacity of 12.36 Mt and 12.55 Mt respectively (Figure 21) (Euro Chlor, 2012; 2013). More than 40 % of the nominal capacity is located in Germany, followed by Belgium and the Netherlands (15%) and France (more than 10%). Almost 2 million jobs are directly or indirectly related to chlorine and caustic soda (Euro Chlor, 2012).

Figure 21. Chlor-alkali production sites in EU-28+ in January 2014 (Euro Chlor, 2014)



In our study only the 19 member states of the EU-28 are taken into consideration. The overview of these plants is given in Table 66 (ICIS, 2012; Euro Chlor, 2014). The number of production lines is slightly higher than the sites reported by Euro Chlor, due to the fact that the different production process accounts as a different production line, but the nominal capacities are consistent.

Table 66. Chlor-alkali plants in EU-28 in 2013

Country	Number of production lines	Capacity (kt/y)
Belgium	5	1 109
Czech Republic	2	196
Germany	21	5 063
Ireland	1	9
Greece	2	24
Spain	10	717
France	12	1 474
Italy	6	301
Hungary	2	323
Netherlands	3	847
Austria	1	70
Poland	3	340
Portugal	3	142
Romania	3	384
Slovakia	1	76
Slovenia	1	16
Finland	2	115
Sweden	1	120
United Kingdom	3	729
Total	82	12 055

5.9.1 Production processes

Since the 1960s electrolysis has been the predominant technique employed to produce chlorine and sodium hydroxide (US Department of Energy, 2000). In the chlor-alkali electrolysis process, a chloride salt solution (brine) is decomposed electrolytically by direct current, according to the following reaction:

$$2\ NaCl + 2\ H_2O \rightarrow Cl_2 + H_2 + 2\ NaOH \qquad \text{(reaction 40)}$$

The most common feedstock is sodium chloride (NaCl), but also potassium chloride (KCl) can be used. KCl involves much higher raw material costs; it is therefore only used when KOH is the desired product and represents only 3-4 % of the European chlorine production capacity (EC, 2014c).

There are three electrolysis technologies for producing chlorine and caustic soda: membrane, mercury and diaphragm. All cells produce elemental chlorine gas at the anode and a solution of NaOH at the cathode. Brine is continually fed to the anode compartment, liberating chlorine gas and flows through the separator to the cathode compartment, forming hydroxide. The three technologies differ in the separator, causing different electrode reactions and keeping the co-products separate differently (EC, 2014c; CEPS, 2014b).

Mercury flows along the floor of a chamber with the anode suspended from the top and acts as cathode, causing the following reactions in cathode and decomposer respectively:

$$Na^+ + e^- + Hg_x \rightarrow Na\text{–}Hg_x \qquad \text{(reaction 41)}$$

$$2\ Na\text{–}Hg_x + 2\ H_2O \rightarrow 2\ NaOH + H_2 + 2\ Hg_x \qquad \text{(reaction 42)}$$

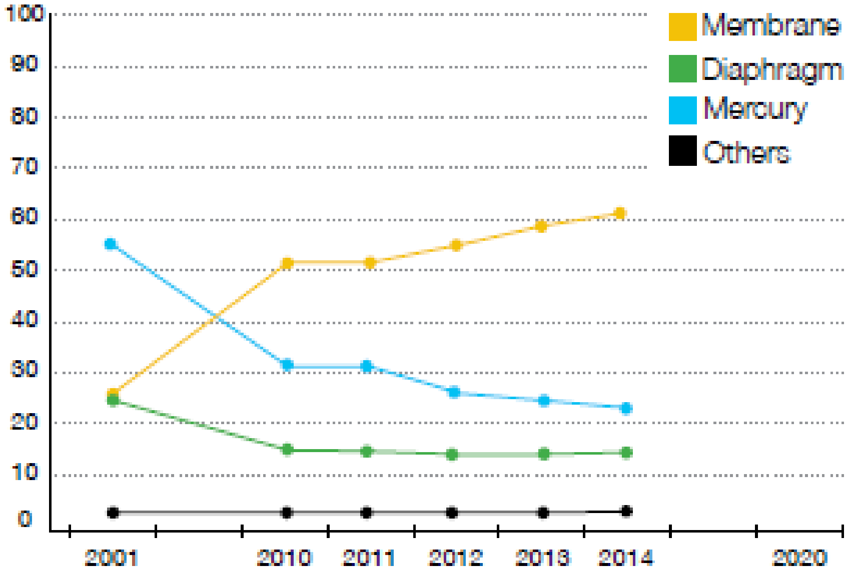
A porous diaphragm divides the electrolytic cell in the two compartments, allowing the flow of the brine through it from the anode to cathode. The membrane cell is similar to the diaphragm one, but the two electrodes are separated by an ion-selective membrane and not a diaphragm. The cathode reaction occurring in both cases is the following:

$$2\ Na^+ + 2\ e^- + 2\ H_2O \rightarrow 2\ NaOH + H_2 \qquad \text{(reaction 43)}$$

The products of electrolysis are proportional in a fixed ratio: 1 070-1 128 $kg_{NaOH\ (100\%\ wt)}/t_{Cl2}$ and 28 kg_{H2}/t_{Cl2}. The ratio for the production of KOH is about 1.583, but in both cases it is influenced by side reactions taking place at the electrodes and in the case of the diaphragm and membrane cells, the diffusion of hydroxide through the separator (EC, 2014c).

The mercury cell technique is the oldest and has the advantage of producing Cl_2 gas with nearly no oxygen and a 50% wt NaOH solution, but operates in higher voltage and current density than the other techniques. It also requires high brine purity, in order to avoid the risk of explosion through H_2 generation in the cell, and of course involves environmental releases of Hg. On the contrary, the diaphragm cell has low electrical consumptions, but high steam consumption and although the brine purity is not important, the quality of NaOH and Cl_2 produced is low. If asbestos diaphragm is used, it involves environmental releases of asbestos. Last but not least, the membrane cell technique is the least energy consuming of the three cells and produces very pure NaOH, but it may require evaporation to increase its concentration. It also requires high brine purity and the chlorine produced contains oxygen, but since brine depletion in membrane cells is two or three times greater than mercury cells, it allows lower recycling rates and less equipment is needed. The advantages and disadvantages of these three technologies are summarised in Table 67.

Figure 22. Chlorine manufacturing technologies in Europe (Euro Chlor, 2014)



In 2000, the mercury process accounted for 54% of the European capacity, but in 2013 it was only 25 % and in 2014, 22.6 % (Euro Chlor 2014; 2015). On the contrary membrane process is increasing and accounted in 2013 for 59% of the European capacity (Euro Chlor, 2014). Global chlorine installed capacity of mercury cell plants in 2012 was estimated to be about 5 Mt/y (UNEP, 2013). In the EU-28, 13 of the member states are still using mercury cells with total capacity about 3.0 Mt/y (Euro Chlor, 2014), equivalent to 25.1 % of the total chlor–alkali capacity. The downward trend in using the mercury cell technique is depicted in Figure 22 and can be attributed to environmental reasons connected with mercury emissions and energy efficiency (CEPS, 2014b). In 2013 only one plant in the EU-27 was still using asbestos diaphragms (EC, 2014c).

5.9.2 Current consumption and emission levels

Consumptions and emissions in the chlor-alkali industry depend on the cell technique used and on the specifications of the products and the purity of the brine (EC, 2014c).

As mentioned earlier, the most common feedstock to produce brine is NaCl, and secondary KCl. The stoichiometric consumption of the salts is 1.65 t_{NaCl}/t_{Cl2} and 2.10 t_{KCl}/t_{Cl2} respectively, but the real consumption can be either higher (due to losses via the brine purge) or lower (due to addition of HCl and hydroxide to the brine system). Salt consumption in European plants is shown in Table 67 (EC, 2014c). Most plants use brine recirculation, thus saving raw material consumption. If a once-through brine process is used, salt consumption is about twice and according to reports it ranges from 3.1 to 3.8 t_{NaCl}/t_{Cl2} (EC, 2014c). Due to the higher price of KCl, plants using it do not waste brine.

Besides brine, raw materials are also water, which is added in the process in order to prepare the brine, and some reagents used for its purification. Water is used for the production of caustic, its dilution if needed and the cooling of chlorine (EC, 2014c).

The main energy source for the production process is electricity, which fuels the electrolysis process. The amount required depends on the design of the cell, the operating current, the electrolyte concentration, temperature and pressure (US Department of Energy, 2000). The chlor-alkali industry is an energy-intensive one and consumed in 2010 total electricity equal to 35 TWh, equivalent to 17% of the total final electrical consumption of the European chemical and petrochemical industry (EC, 2014c).

Table 67. Consumptions, emissions and advantages and disadvantages of chlor–alkali production technologies

	Mercury cell	Diaphragm cell	Membrane cell
Raw materials			
NaCl (kg/t_{Cl2})		1 610-2 340	
KCl (kg/t_{Cl2})		2 070-2 200	
Water (m^3/t_{Cl2})		0-2.7	
Utilities			
Electricity (kWh/t_{cl2})	3 000-4 400	2 600-3 100	2 300-3 000
Steam (t/t_{Cl2}) [1]	–	2.7-5.3	0.5-1.7
Emissions			
Electricity use ($t_{CO2.eq}$/t_{Cl2})	1.721	1.325	1.232
Steam production ($t_{CO2.eq}$/t_{Cl2})	-	0.123	0.036
Total	1.721	1.448	1.269
Advantages and disadvantages			
Advantages	High purity products and simple brine purification	Low quality requirements of brine and low electrical consumption	Low total energy consumption, low investment and operation costs, high purity NaOH
Disadvantages	Use of Hg, high costs, costly environmental protection and large floor space	High steam consumption, low purity NaOH, low Cl_2 quality and in some cases asbestos based	High purity brine required, low Cl_2 quality and high costs of membranes

[1] For producing NaOH 50% wt

Other processes that require energy are the preparation and purification of raw materials, the preparation of caustic soda (or potash) to commercial concentrations and other auxiliary equipment (EC, 2014c). Except for electricity, energy in the form of heat (steam) is also needed to produce the salt and concentrate the NaOH solution. As mercury cells produce directly caustic soda in commercial requirements, there is no need for steam, but in the case of diaphragm and membrane cells steam consumptions are 2 196 MJ/t_{Cl2} and 648 MJ/t_{Cl2} respectively (Euro Chlor, 2010; IEA, 2007). The energy consumption of the chlor-alkali process is summarised in Table 67 (EC, 2014c).

Concerning emissions, all three technologies emit chlorine to air, about 0.010-15 g/t_{Cl2}, through leakages and channelled emissions (EC, 2014c). In addition, mercury cells can be significant sources of environmental pollution, due to losses of mercury, usually at a range of 0.1-1.78 g/t (EC, 2014c). Overall European emissions in 2013 amounted to about 0.68 g_{Hg}/t_{Cl2}, with only one plant being above the target of 1.5 $g_{Hg/t}Cl_2$ for total emissions (Euro Chlor 2014).

None of the emissions mentioned above are considered to be GHG emissions. The only GHG emissions from chlor-alkali plants are fugitive CO_2 emissions that can occur due to brine acidification, but they are very low and are not taken into account (EC, 2014c). The emissions considered in this study are summarised in Table 67, based on the consumptions of the processes and with the relevant emission factors.

5.9.3 Best available techniques (BATs)

This paragraph consists of a short description of the techniques that have been identified as having potential to improve energy efficiency and reduce GHG emissions, without implying that the list summarised in Table 68 is exhaustive.

Table 68. Overview of the possible BATs and ITs in the chlor-alkali industry

BAT/IT	Description	Investment cost	Energy savings (%)	GHG Reduction (%)
BAT	Conversion of mercury cell plants to membrane cell plants	EUR 426.2/t [1]	28.4 % electric & – 68 400% steam	None
BAT	Conversion of asbestos diaphragm cell plants to membrane cell plants	EUR 367/t [2]	7.02 % electric & 70.5 % steam	None
BAT	Asbestos-free diaphragms	Not included in the study as the savings are < 5 %		
BAT	High performance bipolar membrane cells	EUR 21/t [3]	13.6 % electric	None
BAT	High performance electrodes and coatings	Not included in the study as the savings are < 5 %		
BAT	Use of hydrogen	Not included in the study as the savings are < 5 %		
IT	Oxygen-depolarised cathodes	EUR 89/t [4]	15 % electric & steam	None
IT	Four-stage caustic evaporator in membrane plants	No information available		

[1] Reference capacity 100 kt/y

[2] Reference capacity 160 kt/y

[3] Reference capacity 500 kt/y

[4] Reference capacity 100 kt/y

The chlor-alkali industry consumes big quantities of electricity. About 90% of the electric current used is raw material, though, and cannot be substituted, limiting therefore the reduction potential (Euro Chlor, 2010). Reduction can be achieved due to a technology shift from mercury and diaphragm cell technologies to membrane technology. Besides energy reductions, which can be in the range of 20-45%, also prevention of emissions can be achieved, mercury in the case of mercury cells and asbestos in the case of diaphragm cells. However, total energy consumptions also depend on the steam consumption, which in the case of mercury cells is increased if it is transformed to membrane cell. Average energy savings in electricity are calculated according to the data in Table 67 and are shown in Table 68. Conversions include changes in electrolysers, transformers and rectifiers, additional brine purification and dechlorination, and inclusion of a cell room caustic soda recirculation system (EC, 2014c). Investment costs depend on a lot of factors, such as current density, plant size and others. For converting a mercury cell plant with chlorine capacity of 100 kt/y and design current density variation of 4-6 kA/m^2, the total investment costs range is EUR 203-610$_{2009}$/t$_{Cl2}$ (EC, 2014c) or on average about EUR 400/t$_{Cl2}$ (Serpec-cc, 2009), while the conversion of a diaphragm cell plant requires investment costs of EUR 300-400 $_{2009}$/t$_{Cl2}$ (EC, 2014c). For comparison, the costs of a completely new membrane cell plant are estimated to be about EUR 1000 $_{2009}$/t$_{Cl2}$ (EC, 2014c).

Another technique concerning diaphragm cells is using asbestos–free ones. They are often referred to as synthetic diaphragms and are typically made of perfluorinated polymeric fibres and metal oxide fillers that are resistant to the corrosive environment of the operating chlor-alkali cell (Bachot and Stutzmann, 1995; DuBois and Dilmore, 1997). Asbestos-free diaphragms have longer lifetimes and show stability to load variations (EC, 2014c). Their environmental benefits constitute of reductions in energy consumption and avoiding asbestos emissions and wastes. The specific electrical energy consumptions is reduced by 100-150 kWh/t$_{Cl2}$ (4.4% savings) and the cost for converting a diaphragm cell plant with chlorine capacity 160 kt/y to a non-asbestos diaphragm was, in 1999, EUR 1.4-2 million (EC, 2014c).

Within the membrane cells there are a couple of configurations or materials that can be considered as BATs. These are:

High–performance bipolar membrane cells

These cells make use of serial electrical arrangement and small gaps between the electrodes, instead of parallel electrical arrangement that is characteristic of monopolar cells. Due to the shorter current path in bipolar cells, ohmic losses are much lower than in equivalent monopolar electrolysers, leading to decreased energy consumption, that range from 2 280 to 2 535 kWh/t$_{Cl2}$ for current densities range of 4 to 7 kA/m^2 (EC, 2014c). Typical costs of membranes are EUR 20 $_{2009}$/t$_{Cl2}$ (EC, 2014c)

High–performance electrodes and coatings

Developments in the performance of electrodes and coatings include improvements in gas release, leading to reduced electrical resistance caused by gas bubbles for the first and optimisation in terms of mechanical and electrochemical robustness for the latter, leading to lower overpotentials and lower production of chlorate (EC, 2014c). These changes result in reductions of energy consumption and chlorate emissions. Overall energy reductions reported amount to 3-4% and the costs of electrode recoatings may amount to several thousand euros per m^2 (EC, 2014c).

As already mentioned, the chlor–alkali process has hydrogen as second by-product, produced in a ratio of about 28 kg/t$_{Cl2}$. Hydrogen can be either used as a chemical reagent, for example in the production of NH_3, methanol, H_2O_2 or hydrochloric acid or in hydrogenations and hydrosulphurisations, or as fuel for the production of steam and electricity, or it can be emitted in the atmosphere. The use of hydrogen is considered to be a BAT, with potential to reduce energy consumption, raw material consumption for the production of hydrogen and of course hydrogen emissions (EC, 2014c). From the hydrogen produced, approximately 12 % in 2012 and 2013 was not valorised as chemical reagent or fuel and was emitted to air (Euro Chlor 2014). This technique depends on the presence of a market for hydrogen close to the chlor-alkali plant and on the demand for chemicals or steam. References from a plant in Austria with chlorine capacity 70 kt/y mention fuel oil savings of approximately 500 t/y (EC, 2014c). Steam production from hydrogen, which can be used to generate electricity, requires considerable investments for boilers and turbines and it is typically seen as an unattractive investment for a 'non–core' business with a limited quantity of hydrogen compared to what industrial gas companies are handling (EC, 2014c). Due to small savings achieved and the restrictions in applicability, this technique is not taken into consideration in this study.

Except from the BATs described above, there are several more in the literature, for whom though not enough data are available for a complete economic and environmental evaluation, so they are not considered in the analysis. For these techniques, more information can be found in the BREF for the chlor-alkali industry (EC, 2014c).

5.9.4 Innovative technologies (ITs)

Two emerging technologies have been identified concerning the chlor-alkali industry:

Oxygen–depolarised cathodes

This technology is a variant of membrane electrolysis, but differs in the fact that the conventional cathode is replaced by an oxygen depolarised cathode (ODC), in which added oxygen reacts with water in a 3-phase process, forming hydroxyl ions (Martelli & Federico, 2004). The reaction takes place at voltage roughly one volt lower than standard electrolysis process, which is the reason for reduced electrical consumption, at the range of 1 600-1 700 kWh/t_{Cl2} (Woltering et al., 2013), which means savings more than 30% (Woltering et al., 2013; US Department of Energy, 2006). However, the overall reduction of energy consumption is lower, as some energy is required to produce pure oxygen and because the savings due to hydrogen cannot be claimed as there is no hydrogen co-produced (EC, 2014c). If a modern membrane cell is converted to the ODC technology, energy savings are estimated to be 15 %, with the condition that hydrogen is produced via steam reforming (Bulan et al., 2009). Investment costs for converting a chlor-alkali plant with capacity 100 kt/y to the ODC technology would be EUR 0.7-1.0 million $_{2009}$ (Moussallem et al., 2009). The viability of the technology depends on the price of electricity and oxygen and the lower the price of electricity, the more attractive the technology (Moussallem et al., 2009).

Four-stage caustic evaporator in membrane cell plants

This technology is aiming at improving the step of producing caustic soda in 50 % wt solution. In the membrane cell technology the NaOH solution produced is about 32 % wt and requires concentration. This innovative technology has been installed in an AkzoNobel plant in Germany and it is claimed to achieve 20 % energy savings (AkzoNobel, 2012). In general, the more stages a system has, the less heating steam is required, but due to increased investment costs, sometimes a three-stage evaporation plant is more economical than a four-stage one (Körting, 2014). There is no data concerning the economical assessment of this technology, and therefore it cannot be included in this study.

5.10 Ethylene oxide and Ethylene glycol

Ethylene oxide (EO – C_2H_4O) – oxirane according to IUPAC but also known as epoxyethane – is the simplest cyclic ether and a colourless gas (at temperatures above 11°C) with a sweet smell. It is frequently used as an intermediate in the chemical industry, as it contains a strained epoxy (47) group that can be easily broken (Ullmann's Encyclopaedia, 2001). It is, though, also highly toxic and flammable and has been involved in a number of serious incidents (Ullmann's Encyclopaedia, 2001).

Ethylene oxide can directly be used as a disinfectant, sterilising agent and as a fumigant when in non-explosive mixtures with N_2, CO_2 or diclorofluor methane. It is used also as an intermediate for the production of ethylene glycols, ethylo amines and glycol ethers. It was first produced by eliminating hydrochloric acid from ethylene chlorohydrin using potassium hydroxide solution, but direct catalytic oxidation of ethylene has replaced the first production route totally (Ullmann's Encyclopaedia, 2001).

In 2000, the global capacity of ethylene oxide was around 15 000 kt (Ullmann's Encyclopaedia, 2001), while in 2011 it approximated 27 Mt (Business Wire, 2012). In 2012, 25% of the global capacity was located in the Middle East, 16% in China and 12% in the United States (IHS, 2013d). In 2011, consumption reached 22.5 Mt (Business Wire, 2012), with the largest market being mono-, di- and tri-ethylene glycols, representing in 2012 more than 75 % of the total ethylene oxide consumption (IHS,

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(47) Epoxy groups contain a bond of –C–C– triangulated with oxygen.

2013d). The ethylene oxide market was projected to grow at an annual rate of 5.7 % between 2013 and 2018 (Global processing, 2013).

Information concerning Europe is available by Petrochemicals Europe, but it covers only Western Europe (Petrochemicals, 2016) In 2013 ethylene oxide capacity was 2.9 Mt and has not changed since 2010, while production reached 2,6 Mt (Petrochemicals, 2016). In EU-28 there were 12 production sites, with total capacity 3.0 Mt/y as shown in Table 69 (ICIS, 2012).

Table 69. Ethylene oxide production sites in EU-28 in

Country	Number of plants	Capacity (kt/y)
Belgium	2	940
Germany	4	1 070
Spain	1	100
France	1	220
Netherlands	2	500
Poland	1	115
Sweden	1	100
Total	12	3 045

Ethylene glycols or dihydroxy alcohols, as mentioned earlier, are the main derivative of ethylene oxide. Monoethylene glycol (MEG – $C_2H_6O_2$) – ethane-1,2-diol according to IUPAC – is the simplest diol and is usually referred to with the name of group (ethylene glycol) or just glycol. It is a clear, colourless, odourless liquid with a sweet taste and it is used in the production of polyester fibres and polyethylene teraphtalate (PET) or as antifreeze in automobile radiators (Ullmann's Encyclopaedia, 2000e). In 2013, 86 % of MEG produced globally was consumed in the production of PET, 7.5% as antifreeze and 6.5 % in other uses (IHS, 2013e). Concerning world distribution of MEG consumption, 75 % was in Asia, 10 % in North America and only 6 % in Western Europe (IHS, 2013e).

Due to its relation with ethylene oxide, production plants of the two substances are located close to each other. It is estimated that about 60% of the total world production of ethylene oxide is converted to MEG (Ullmann's Encyclopaedia, 2000e). In 2010 MEG capacity was 25 Mt, with operating rates averaging about 77% (Chemweek, 2011). In 2012 global capacity was estimated to be about 28 000 kt with global demand of 22 000 kt (CPMA, 2012). Its annual growth by 2018 was projected at 6.1 % (Global processing, 2013).

In western Europe, capacities of MEG have been stable between 2010 and 2013 at 1227 kt, while production has been growing from 926 kt in 2010 to 1 016 kt in 2013 (Petrochemicals, 2016). In EU-28 in 2013 there were 9 plants producing ethylene glycol, with total capacity 1365 kt (Table 70) (ICIS, 2012).

Table 70. Ethylene glycol production sites in EU-28 in 2013

Country	Number of plants	Capacity (kt/y)
Belgium	2	665
Germany	2	300
Spain	1	75
France	1	25
Netherlands	1	155
Poland	1	110
Sweden	1	10
Total	9	1 340

5.10.1 Production processes

Ethylene oxide used to be produced via a chlorohydrin route, but this method is totally out of use in industrial scale, due to its pollution problems. It is produced by direct oxidation of ethylene over a silver oxide catalyst, according to the following reaction (Ullmann's Encyclopaedia, 2001; EC, 2003a; IPCC, 2006b):

$$C_2H_4 + ½\ O_2 \rightarrow C_2H_4O \qquad \text{(reaction 44)}$$

Oxygen can be supplied either through air or as pure oxygen. The reaction is exothermic and is carried out at elevated temperatures (200-300°C) and pressure (15-25 bar) with residence times of one second. Although the reactor contains metallic silver, the actual catalyst is silver oxide that precipitates under the reaction conditions. Excess heat is recovered to produce steam for the process.

Besides the production of ethylene oxide (partial oxidation), also complete oxidation (or combustion) of ethylene takes place:

$$C_2H_4 + 3\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O \qquad \text{(reaction 45)}$$

This reaction is also highly exothermic. The ratio between the two reactions defines the selectivity of the EO process. Control of the temperature in the reactor is important to ensure that complete oxidation is minimised (US Department of Energy, 2000). As temperature increases reaction 45 is favoured and it produces about 15 times more energy than reaction 44 (enthalpy of partial oxidation -106.7 kJ/mol and enthalpy of complete oxidation -1 323 kJ/mol at 250 °C and 15 bar) (Ullmann's Encyclopaedia, 2001). The selectivity to EO is 65-75 % in the case of air or 70-80 % in the case of oxygen, at an ethylene conversion of 8-10% (EC, 2003a). For ethylene conversion 7-15%, the EO selectivity in the oxygen-based process reaches 80-90 % (Ullmann's Encyclopaedia, 2001). Selectivity decreases almost linearly with increasing ethylene conversion, thus the highest selectivities are achieved with minimum conversion (Ullmann's Encyclopaedia, 2001).

The gases from the reactor are cooled and the ethylene oxide produced in dissolved in water together with small amounts of CO_2, N_2 and aldehydes (US Department of Energy, 2000). EO is obtained from this mixture by distillation. The gases, on the other hand, are rich in ethylene, as the per-pass conversion to EO is low. As a result, recycling of these gases is essential to improve the yield and the economics of the process (US Department of Energy, 2000).

In industrial scale monoethylene glycol (MEG) is produced only by hydrolysis of ethylene oxide, according to the following reaction (Ullmann's Encyclopaedia, 2000e; EC, 2003a; US Department of Energy, 2000):

$$C_2H_4O + H_2O \rightarrow C_2H_6O_2\ (OH{-}C_2H_4{-}OH) \qquad \text{(reaction 46)}$$

The reaction is exothermic and takes place either without catalyst at temperature 200 °C, pressure 12.5 bar and with residence time of one hour, or with sulphuric acid as catalyst at temperature 50-70 °C and residence time of 30 minutes (Speight, 2002). The non-catalytic process is preferred, as it needs no corrosion resistance and no acid separation step (US Department of Energy, 2000).

Although the main product is MEG, also diethylene glycol (DEG) and triethylene glycol (TEG) or heavier glycols can be formed from consequent reactions of the lighter glycols, as the following reactions:

$OH{-}C_2H_4{-}OH + C_2H_4O \rightarrow OH{-}C_2H_4{-}O{-}C_2H_4{-}OH$ (DEG) (reaction 47)

$DEG + C_2H_4O \rightarrow OH{-}C_2H_4{-}O{-}C_2H_4{-}O{-}C_2H_4{-}OH$ (TEG) (reaction 48)

These reactions are inevitable, as EO reacts more readily with MEG than with water, but their production can be minimised if excess of water is used (Ullmann's Encyclopaedia, 2000e). The yield of the process in MEG is usually more than 80 % with molar ratio EO:water higher than 1:10. Usually a 20-fold molar excess is employed. MEG is separated from water and the higher glycols by successive distillations with decreasing pressures. The glycols are separated by vacuum distillation.

The modern ethylene oxide/ethylene glycols plants are highly integrated units, focusing either on producing one of the two products or both. Focusing on producing both high purity EO and MEG is usually adopted, as MEG, the most important product of EO, is safer to transfer than EO itself and this configuration provides efficient heat integration for the two processes. Although all the reactions are exothermic, the purification of MEG is highly energy consuming.

5.10.2 Current consumption and emission levels

As explained before, ethylene oxide is produced from the reaction of ethylene with oxygen and there are two processes, based on the way oxygen is provided: as pure oxygen or as air. Typical raw material consumptions of the EO production processes can be seen in Table 71:

Table 71. Typical raw materials consumption for ethylene oxide production (EC, 2003a)

Raw material	Oxygen-based process	Air-based process
Selectivity (%)	75-85	70-80
Ethylene (kg/t_{EO})	750-850	800-900
Oxygen (kg/t_{EO})	750-1100	

Both ethylene and oxygen are required to be of high purity (Ullmann's Encyclopaedia, 2001).

For the production of monoethylene glycol, ethylene oxide reacts with water, as explained before. For molar ratio water:EO 20:1, MEG yield of 90 % can be assumed (Ullmann's Encyclopaedia, 2000e). Raw materials consumption calculated according to these assumptions is used in this study and is shown in Table 72.

Table 72. Typical raw materials consumption for monoethylene glycol production

Raw material	MEG production
Ethylene oxide (kg/t_{MEG})	789
Water (kg/t_{MEG})	322

The integrated EO/MEG process is both producing and consuming energy. As explained in the previous paragraph, production of ethylene oxide is typically a net energy producer and production of monoethylene glycol is typically a net energy consumer, due to the distillation part (EC, 2003a). The energy produced in the first section of the process depends on selectivity (the ratio between partial and total oxidation), which is highly dependent itself on the type and age of the catalyst.

The total performance of the plant depends on the relative sizes of the EO and MEG sections (EC, 2003a). As a result, different performances are reported from different plants. In the present study, the energy consumptions estimated by (IEA, 2009b) are used (Table 73).

Table 73. Energy consumption for producing ethylene oxide and monoethylene glycol (IEA, 2009b)

Consumption	Ethylene oxide production	Monoethylene glycol production
Electricity (kWh/t)	333.3	83.3
Thermal (GJ/t)	3.1	1.1
Steam (GJ/t)		8

Primary emissions from the formation of ethylene oxide by direct oxidation are ethylene, ethylene oxide, carbon dioxide and ethane. The default emission factors suggested in the literature (Table 74) depend on the catalyst selectivity and derive by using stoichiometric principles and are based on the assumption that all carbon contained in the ethylene feedstock is converted either into ethylene oxide or to CO_2 emissions (IPCC, 2006b).

Table 74. Default emission factors for the production of ethylene oxide (IPCC, 2006b; EC, 2003a)

	Oxygen-based process			Air-based process		
Selectivity (%)	75	80	85	70	75	80
Ethylene consumption (t/t_{EO})	0.85	0.80	0.75	0.90	0.85	0.80
CO_2 emission factor ($t_{CO2.eq}/t_{EO}$)	0.663	0.5	0.35	0.863	0.663	0.5
CH_4 emission factor (kg_{CH4}/t_{EO})	1.79 (without thermal treatment) 0.79 (with thermal treatment)					

Small amounts of CH_4 might also be present in the emissions (EC, 2003a). The default emission factors are also shown in Table 74. In many cases, the gaseous effluent stream is flared, oxidised (thermally or catalytically) or sent to a boiler or a power plant, thus decreasing final emissions.

Table 75 includes the detailed emission factors used in this study. In Europe only the first generation of EO plants used air-based processes and since then most of them have been converted to oxygen-based process (EC, 2003a). In 2013, only direct oxidation using oxygen is used in the EU (EC, 2014d). Thus only the case of oxygen-based production will be considered. According to the information in Table 71, the average selectivity in the case of the oxygen-based process is 80% and the average ethylene consumption 800 kg/t_{EO}, thus the emission factor used in this study is 0.55 $t_{CO2.eq}/t_{EO}$, taking in consideration also methane emissions. Information concerning MEG production emissions refer to particular plants in the Netherlands and only ethylene and acetaldehyde are identified (EC, 2003a). Since no general conclusion can be reached, in this study we assume the same emission factor as in the ethylene oxide production, as in general plants are integrated. The conversion to emissions per tonne of MEG is done according to the stoichiometry of reaction, considering yield 90 %, as explained before.

Table 75. Emission factors in the case of ethylene oxide production and monoethylene glycol production

Emissions	Ethylene oxide production	Monoethylene glycol production
	Value ($t_{CO2.eq}/t_{EO}$)	Value ($t_{CO2.eq}/t_{MEG}$)
Electricity use	0.16	0.04
Thermal production	0.17	0.06
Steam production		0.58
Direct Process	0.55	0.43
Total	0.88	1.11

Ethylene oxide is a benchmarked product, with value 0.512 allowance/t (EC, 2011b). The benchmark covers besides EO, also mono-, di- and tri-ethylene glycols. The system boundaries of benchmarking include all steps of the process, as well as the emissions related to the production of the electricity consumed. The specific emissions per plant, calculated according to the literature vales explained in this paragraph, are calibrated according to the benchmarking curve.

5.10.3 Best available techniques (BATs)

This paragraph includes the techniques considered generally to have potential of improving the environmental performance or the energy efficiency of the industry (Table 76). According to the BREF still in force (EC, 2003a), BAT for ethylene oxide (EO) production is direct oxidation of ethylene by pure oxygen and BAT for monoethylene glycol (MEG) production is the hydrolysis reaction of ethylene oxide.

Table 76. Overview of the possible BATs and ITs in the ethylene oxide/ethylene glycols industry

BAT	Description	Investment cost (EUR)	Energy savings (%)	GHG Reduction (%)
BAT	OMEGA process	134 626 790 [1]	-10 % electric, 20 % steam & 19 % feedstock	None
BAT	METEOR process	No information available		

[1] Reference capacity 600 kt_{MEG}/y

There are several licenses for EO production by companies including Shell, Scientific Design and Japan Catalytic (Ullmann's Encyclopaedia, 2001). Scientific Design, Union Carbide, Japan Catalytic and Chemische Werke Hüls have developed air-based processes, while Shell and later Scientific Design developed oxygen-based processes (Zomerdijk & Hall, 1981).

Shell offers two version of its process: the Shell MASTER process and the Shell OMEGA process (Shell, 2015). The former is based on a high-selectivity EO catalyst and thermal conversion of EO to ethylene glycols, while the latter also on a catalyst but an only-MEG producing technology. Although MASTER process is a traditional process, OMEGA process is more innovative. It is designed to use the CO_2 produced during the EO reaction, so as to convert EO into ethylene carbonate ($(CH_2O)_2CO$), which is then treated with water to produce MEG, without the presence of higher glycols (Chemicals technology, 2015). EO is produced by the conventional Shell technology, using a proprietary silver-based catalyst. This process is expected to have selectivity 90 % with ethylene conversion 10-15 %, while the yield of MEG is as high as 99 % (IHS, 2009). Ethylene consumption is estimated to be 0.51 t/t_{MEG} (Chemicals technology, 2015), compared to 0.63 t/t_{MEG} of the conventional method (48). Capital investment is estimated to be 15 % less than for the conventional process for a 400 kt MEG plant (IHS, 2009) and in 2004 it was estimated to be at USD 120-160 million for a 600 kt/y MEG plant (Shell, 2015), corresponding to 134.6 million EUR_{2013}. The process consumes 20% less steam than the conventional thermal conversion (Chemical Processing, 2009), but 10 % more electricity compared to the standard process (Chemsystems, 2009a). This process is fully commercialised with a 400 kt/y plant in Korea, a 600 kt/y plant in Saudi Arabia and a 750 kt/y plant in Singapore (Chemical Processing, 2009).

Dow also owns a newly commercialised technology, the METEOR process, which includes a single EO reactor combined with Ag-based catalysts with high selectivity, high activity and long life, thus reducing capital investments compared to the multiple reactors configuration (Dow, 2015). Savings are estimated to be about 11 % for a 400 kt ethylene glycols plant (IHS, 2009). They claim higher production of oxide/glycol per

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(48) The calculation is based on the information of Table 71 and Table 72.

tonne of feedstock (Aker, 2008). EO selectivity is 89% with ethylene conversions of 8-13%, while overall MEG yield in the ethylene glycols product is 90-93 % (IHS, 2009). Due to limited information concerning its energy or GHG savings, this process is not taken into consideration.

5.10.4 Innovative technologies (ITs)

There are a few innovative technologies concerning these two products. Alternative routes from ethylene to ethylene oxide can be found in the literature (Ullmann's Encyclopaedia, 2001), such as electrochemical oxidation (Stoukides and Vayenas, 1981; Cooker & Cochran, 1996), thallium(III) catalysed oxidation in solution (Diamond et al., 1982) and enzymatic oxidation (van Ginkel et al., 1986). But these routes have not evolved closer to industrial application and the information concerning their performances is restricted.

5.11 Ethylene dichloride and Vinyl chloride monomer

Ethylene dichloride (EDC - $C_2H_4Cl_2$) – 1,2–dichloroethane according to IUPAC – is an important ethylene derivative. It is a clear, colourless oily liquid with a sweet pleasant chloroform-like odour and a highly volatile, toxic and flammable chemical (Ullmann's Encyclopaedia, 2011c). EDC is mainly used in the production of vinyl chloride monomer (VCM), nearly all of which goes into polyvinyl chloride (PVC) (EC, 2003a; IHS, 2015g). Small quantities of EDC are also used in the production of solvents such as trichloroethylene, ethylene amines and thrichloroethane, or in the production of tetrachloroethylene (ICIS, 2007). In addition to these uses, it has also been used as a solvent in the textile, metal cleaning and adhesive industries (EPA, 2013).

Global EDC capacity in 2009 was 42.6 Mt (Business Wire, 2010a). 40.8 % of global capacity was in North America, while Europe followed with a share of 24.8 % (Business Wire, 2010a). Asia, Middle East and the rest of America had 22.9 %, 7 % and 4.4 % respectively (Business Wire, 2010a)..Since 2010 the world EDC production has followed a rising trend, reaching in 2011 almost 46.2 Mt (Dow, 2013a). In 2013, North America accounted for almost 37.9 % of the overall production, followed by Europe with 28.7 % and Asia – Pacific with 20.3 % (Merchant Research, 2014). Belgium, Germany, France, China and USA are the five countries producing about 65.1 % of the world EDC production in 2013 (Merchant Research, 2014).

Most EDC plants are integrated upstream to chlor-alkali units and downstream to VCM plants. About 95 % of EDC produced in the EU is used to manufacture VCM (Ecofys, 2009). Vinyl chloride (C_2H_3Cl) – chloroethane according to IUPAC – is a colourless gas with characteristic mild, sweet odour. It is a toxic and hazardous material and is characterised as human carcinogen (Ullmann's Encyclopaedia, 2011c). As mentioned already, almost all of VCM is used in the production of PVC, but small quantities are also used in chlorinated solvents manufacture (EC, 2003a).

Global VCM capacity in 2009 was 40.0 Mt (Business Wire, 2010b).). 45.1 % of global capacity was in Asia-Pacific, while Europe followed with a share of 25.8 % (Business Wire, 2010b). North America, Middle East and the rest of America had 20.0 %, 5.2 % and 3.9 % respectively (Business Wire, 2010b). In 2010 it increased to about 47 Mt (Dow, 2013b). VCM consumption is projected to grow at an average rate of 3.7 % till 2020 (IHS, 2015h).

In 2013, in EU-28 there were 47 production lines producing ethylene dichloride with total capacity 11.9 Mt and 23 plants producing vinyl chloride with total capacity 6 810 kt (Table 77) (ICIS, 2012, EC, 2014d). In the case of ethylene chloride production lines are reported because there are two processes and if both are applied in the same location, each one is counted separately.

Table 77. Ethylene dichloride and vinyl chloride plants in EU-28 in 2013

	Ethylene Dichloride		Vinyl chloride	
Country	Number of production lines	Capacity (kt/y)	Number of plants	Capacity (kt/y)
Belgium	5	1 980	2	1 050
Czech Republic	2	300	1	150
Germany	15	3 599	7	2 070
Spain	3	680	2	470
France	7	1 845	4	1 200
Italy	1	180		
Hungary	3	640	1	400
Netherlands	2	965	1	620
Poland	2	520	1	300
Slovakia	2	85	2	100
Sweden	3	365	1	150
United Kingdom	2	700	1	300
Total	47	11 859	23	6 810

5.11.1 Production processes

Worldwide almost all ethylene dichloride (EDC) is produced from ethylene either by direct chlorination or by oxychlorination, or combination of the two processes (IPCC, 2006b).

Direct chlorination is the classic method, where chlorine is added to the double bond of ethylene, according to the following reaction:

$$CH_2{=}CH_2 + Cl_2 \rightarrow (CH_2Cl)_2 \qquad \text{(reaction 49)}$$

The reaction can give several mixed derivatives, such as di-, tri or tetra-chloroethylene and chloromethanes. Usually, though, the final product consists of more than 99 % EDC and less than 1 % other chlorinated hydrocarbons (EC, 2003a).

The reaction is catalysed by metal chlorides, usually ferric chloride, and it is exothermic (EC, 2003a). It takes place in temperatures 50-120°C and pressure 1-5 bar. Based on the EDC boiling point (~85°C) and the temperature the reaction is carried out, there are two variants: low temperature chlorination at temperatures below the boiling point and high temperature chlorination at temperatures over the boiling point. In the first case the EDC produced is in liquid phase and is washed to eliminate the catalyst, thus requiring in further steps drying and distillation. The advantage of this variant is that there are slightly less by-products and it has low requirements in materials, but is high in energy consumption. In the second case, the EDC produced is in the gas-phase and can be sent to thermal cracking directly. The vapour is hot and as a result energy can be recovered (EC, 2003a).

Oxychlorination of ethylene involves hydrogen chloride and oxygen and EDC is produced according to the following reaction:

$$2\ CH_2{=}CH_2 + 4\ HCl + O_2 \rightarrow (CH_2Cl)_2 + H_2O \qquad \text{(reaction 50)}$$

Catalysts for this reaction are cupric chloride ($CuCl_2$), potassium chloride (KCl) and alumina (Al_2O_3) or silica (SiO_2). The range of temperature and pressure is 220-250 °C and 2-6 bar, respectively (EC, 2003a). The reaction is highly exothermic and temperature control is required in order to avoid undesirable by-products.

Oxygen can be provided either as pure oxygen or as ambient air, or as a mixture of both. Air systems require air and ethylene in slight excess of stoichiometric quantities to ensure high conversion of HCl, but this also increases the formation of by-products (EC, 2003a). On the other hand, in oxygen systems ethylene needs to be in larger excess and the operation can be in lower temperatures. This leads to higher EDC yields and reduced by-products and vented gases volumes. However, pure oxygen needs energy to be produced from air.

VCM is produced by thermal cracking of dry, pure EDC, according to the following reaction:

$$(CH_2Cl)_2 \rightarrow CH_2CHCl + HCl \qquad \text{(reaction 51)}$$

EDC is heated to temperatures approximately 500 °C and then splits to VCM and HCl with conversion rates of 50-65 % (EC, 2003a). Unconverted EDC is recycling to the cracking furnace, as a result almost total conversion is assumed. It is essential if EDC is highly pure (more than 99.5 %wt), so as to reduce coke and fouling of the reactor, and dry, so as to avoid corrosive reactions with HCl. The pyrolysis gases require fast cooling, otherwise tars and heavy by-products may be produced (EC, 2003a).

Combination of direct chlorination for EDC production with cracking to produce VCM produces a surplus of hydrogen chloride. Oxychlorination, on the other hand, provides a sink for HCl. It is therefore, common, in the industry to combine both direct chlorination and oxychlorination. This is called "balanced" process (IPCC, 2006b) and is applied in approximately 90 % of the plants worldwide (EC, 2014d).

Since direct chlorination and oxychlorination are both highly exothermic, while EDC cracking is endothermic, process integration provides opportunities for energy recovery and re-use (EC, 2003a). Heat can be recovered from the furnace combustion gases, the gas leaving the cracking furnace and the gaseous vents of the oxidisers. In addition, steam can be generated at the oxychlorination reactor or in the case of high temperature chlorination; the low level heat of the reaction can be used in the vaporisation or distillation of EDC.

5.11.2 Current consumption and emission levels

As mentioned before, the most common configuration of EDC/VCM plants is the balanced process (EC, 2014d). In this case, the raw materials needed are ethylene, chlorine and oxygen (or air).

Typical yields on ethylene for direct chlorination are 96-98%, for oxychlorination 93-97 % (EC, 2003a), while in the balanced process selectivities are in the range of 93-96 %. On chlorine the yields reported are 98% for direct chlorination and 96-99 % for oxychlorination (EC, 2003a). In order to calculate the raw materials needed according to stoichiometry, in the case of integrated plants we assume an average yield of 95 % on ethylene and 98% on chlorine. As a result and according to reactions 49 and 50, in the case of direct chlorination one tonne EDC requires 0.29 t ethylene and 0.73 t chlorine, while in the case of oxychlorination one tonne EDC requires 0.30 t ethylene, 0.73 t chlorine and 0.16 t oxygen. These consumptions can be transformed per tonne of VCM by taking into consideration the difference in molecular weights (49) if conversion is assumed to be 100 % and correspond to 0.46 t/t_{VCM} for ethylene.

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(49) Molecular weights: EDC = 98.96 g/mol and VCM = 62.50 g/mol

Table 78. Typical raw materials and energy consumption in integrated vinyl chloride monomer production

Raw material	Value (t/t$_{VCM}$)	Source
Ethylene	0.46	(EC, 2014d; ThyssenKrupp, 2012)
Chlorine	0.58	
Oxygen	0.13	
Energy	Value	
Steam	0.25 t/t	(ThyssenKrupp, 2012)
	0.3-1.7 GJ/t	(EC, 2014d)
Fuel gas	2.7 GJ/t	(ThyssenKrupp, 2012)
	3.4-4.2 GJ/t	(EC, 2014d)
Electricity	0.11-0.21 MWh/t	(EC, 2014d)

These calculations are in accordance with the consumptions reported by the industry (Table 78). Chlorine and oxygen consumptions are lower in the case of the balanced process thanks to recirculation of HCl. The values used in this study for raw materials are summarised in Table 79.

Table 79. Raw materials consumptions used in the present study for ethylene dichloride and vinyl chloride monomer production

Feedstock	Process	Value
Ethylene	Direct chlorination	0.30 t/t$_{EDC}$
	Oxychlorination	0.29 t/t$_{EDC}$
Chlorine	Direct chlorination/ Oxychlorination	0.73 t/t$_{EDC}$
Oxygen	Oxychlorination	0.16 t/t$_{EDC}$
EDC	EDC cracking	1.6 t/t$_{VCM}$

EDC is rather an intermediate used to manufacture VCM and other products. Activity data for the production of EDC may not be complete, as it could be directly converted to VCM. It may be that the VCM production activity data is more complete (IPCC, 2006b). This is the case for energy consumptions; all references are reporting the values for the final product, which is VCM (ThyssenKrupp, 2012; EC, 2003a; EC, 2014d). According to (EC, 2003a) typical values are 0.2 t/t$_{VCM}$ steam, 1 MWh/t$_{VCM}$ natural gas and 0.2 MWh/t$_{VCM}$ electricity, while according to (EC, 2014d) steam consumption ranges between 0.3 and 1.7 GJ/t$_{VCM}$, thermal energy 3.4-4.2 GJ/t$_{VCM}$ and electricity 0.11-0.21 MWh/t$_{VCM}$.

One way of handling this issue is to treat EDC/VCM as a single entity. But regarding VCM data as a surrogate for EDC data also has issues related to completeness, because not all of EDC is used to produce VCM (IPCC, 2006b). In such a case, adjustment is needed. EDC utilisation for products other than VCM amounts to about 5 % of total EDC production, according to data from North America and Europe (IPCC, 2006b; Ecofys, 2009).

Table 80 shows the values of energy consumptions for both EDC and VCM according to (IEA, 2009b). By comparing the values for VCM production in this table with the values according to (EC, 2014d), it can be seen that they are in accordance, but these values are rather at the lower edge of the ranges in (EC, 2014d). Since there is limited information for the non-integrated process, it is assumed that the values of Table 80 do not include EDC production and they will be used for this study.

Table 80. Energy consumptions for ethylene dichloride and vinyl chloride monomer production (IEA, 2009b)

Product	Electricity	Thermal	Steam
Ethylene dichloride	83.3 kWh/t_{EDC}	5.3 GJ/t_{EDC}	
Vinyl chloride monomer	194.4 kWh/t_{VCM}	3.6 GJ/t_{VCM}	0.5 GJ/t_{VCM}

Concerning emissions, most concern arises from VCM, which is a carcinogen. They may occur as fugitive emissions and losses (EC, 2003a). Most of emissions in air are volatile organic carbon compounds. As a result, the emission factors that are used in this study (Table 81) are based on the energy consumed for the processes. They are calculated by combining the information in Table 80 with the emission factors in Table 6.

Table 81. Emission factors for ethylene dichloride and vinyl chloride production

Emissions	Process	
	Ethylene dichloride	Vinyl chloride monomer
Steam		0.036 t_{CO2}/t
Electricity	0.04 t_{CO2}/t	0.09 t_{CO2}/t
Thermal	0.3 t_{CO2}/t	0.2 t_{CO2}/t
Total	0.34 t_{CO2}/t	0.33 t_{CO2}/t

The specific emissions that are calculated according to the emission factors of Table 81 are calibrated with benchmarking curve for VCM to reflect actual emissions from the industry.

5.11.3 Best available techniques (BATs)

This paragraph includes the techniques considered generally to have potential of improving the environmental performance or the energy efficiency of the industry.

Table 82. Overview of the possible BATs and ITs in the ethylene dichloride/vinyl chloride monomer industry

BAT/IT	Description	Investment cost (EUR)	Energy savings (%)	GHG Reduction (%)
BAT	Process optimisation	Considered as standard technology		
BAT	Heat transfer	Considered as standard technology		
BAT	Pigging system	101 568	19% electricity	
BAT	Cogeneration	General reference in 4.5.1		
IT	Ethane-based VCM	Not considered in the study		
IT	Avoid oxychlorination	No information available		

Process optimisation concerning the chlorination process (direct and oxy-) can lead to lower emissions (EC, 2014d). Optimisation may include techniques such as by-products minimisation. In direct chlorination, a slight excess of chlorine or ethylene is ensuring complete ethylene conversion, and in the case of pyrolysis, by-products can be avoided by using additives, controlling the EDC feed purity or rapid cooling of the products. The use of catalysts in direct or oxychlorination also increases the selectivity (EC, 2003a). This technique is too general and depends on each plant. As a result the benefits of it are difficult to quantify and therefore it cannot be taken into consideration for the study. In any case it is rather improbable that the industry is not already applied most of these techniques, since average yields on ethylene are 98%.

Both direct and oxy-chlorination are exothermic reactions. The removed heat of reaction can be used to produce low pressure steam for preheating purposes or other internal usage. On the other hand, heat recovered from the process gas leaving the cracking furnace can be used to vaporise the EDC feed to the furnace or to generate steam. As in the previous case, this technology is considered to be applied to all plants and therefore it is not included in the study.

Pigging technology is considered to be a cleaning technique. It involves pushing the contents of a pipe by a close fitting plug, named pig, almost completely out of the pipe (EC, 2007d). It leads to reduced loss of valuable product and lower load in rinsing waters. It has no cross media effects and it is generally applicable in long pipelines, multiproduct plants and batch operations (EC, 2007d). In the case of 100 m pipeline with diameter 3 in, the total investment costs of a pigging system was estimated to be about EUR 105 000 $_{2003}$ for a 10 year service life (EC, 2007d). There is no information available about the savings in energy efficiency, especially in the case of EDC/VCM plants, but a 19 % electric reduction is assumed, according to expert judgement (OPT Sensor, 2012).

As is the case in most of the chemical industry, the use of cogeneration systems is considered as a best technique also in the case of EDC/VCM plants, especially with the potential of these plants. The applicability of CHP does not depend on the type of fuel used and the data concerning the presence of CHP in the European EDC/VCM industry are based on the databases available (ESAP, 2012).

5.11.4 Innovative technologies (ITs)

Two emerging technologies have been identified concerning the ECD/VCM industry:

Ethane-based production processes

There has been interest to directly convert ethane to vinyl chloride monomer. The conversion can be performed by various routes (Ullmann's Encyclopaedia, 2006):

$$C_2H_6 + 2\ Cl_2 \rightarrow CH_2CHCl + 3\ HCl \qquad \text{(reaction 52)}$$

$$C_2H_6 + HCl + O_2 \rightarrow CH_2CHCl + 2\ H_2O \qquad \text{(reaction 53)}$$

$$2\ C_2H_6 + 1.5\ O_2 + Cl_2 \rightarrow 2\ CH_2CHCl + 3\ H_2O \qquad \text{(reaction 54)}$$

The driver of this innovative technology is economics, as it would eliminate ethylene crackers and EDC production from the PVC chain. Several attempts have failed during scale-up for various reasons, such as poor conversions, catalyst instability and corrosion caused by high reaction temperatures (Chemical Online, 1999).

EVC International NV had patented a process and in a junction with Bechtel Group Inc. started in May 1998 a 1000 t/y pilot plant at Wilhelmshaven, Germany (Chemical Online, 1999), while they were planning the first industrial plant for 2005 (EC, 2003a). This process operated at less than 500 ^{o}C, which is a relatively low temperature, meaning reduced corrosion and extended catalyst life. Conversions are reported to be 100 % on chlorine, 99 % on oxygen and more than 90 % on ethane (Chemical Online, 1999). It also reported 30 % reduction of energy consumption and recycling of the chlorinated by-products (EC, 2003a).

Nevertheless, there is no information for further information about the building of the industrial plant and it seems that this experimental technology has not been developed further. As a result there can be no assumption about its deployment and therefore it is not considered in the study.

Alternatives to avoid oxychlorination

The motive behind these alternatives is to avoid the oxychlorination step which generates most by-products, by converting HCl to Cl_2 (EC, 2014d). This is done via the classical Deacon reaction:

$$2\ HCl + 0.5\ O_2 \rightarrow Cl_2 + H_2O \qquad \text{(reaction 55)}$$

This technique results in lower waste generation and lower emissions from incineration, but it is not considered to be safer than oxychlorination, as Cl_2 has to be manipulated in high pressures (EC, 2014d). In addition, replacing oxychlorination with direct chlorination will decrease the energy that can be recovered, as the former is more exothermic than the latter. Investment costs are expected to be quite high, as very costly construction materials are needed because of the high risks of HCl (EC, 2014d).

5.12 PVC

Polyvinyl chloride (PVC) is a polymer prepared from vinyl chloride monomer (VCM). Its molecular formula is $(CH_2CHCl)_n$, where n=700-1 500 (Ullmann's Encyclopaedia, 2014). It is relative inexpensive and is the most versatile of all thermoplastics because it can be used in such a wide range of applications (Ullmann's Encyclopaedia, 2014; IHS, 2014i). It is the third highest volume polymer, slightly behind polyethylene and polypropylene (EC, 2007d).

PVC comes in two main sizes that depend on the production process used. If suspension and mass polymerisation is used particles of 100-180 μm in diameter are produced (S-PVC), while by emulsion a latex (50) of particle size 0.1-3.0 μm is derived (E-PVC) (Ullmann's encyclopaedia, 2014). It can be converted into either rigid products to give pipes, conduit, sheet and window profiles, or flexible formulations for flexible sheet, flooring, cable coverings, hoses etc. in 2013, rigid applications accounted for 63 % of total production (IHS, 2014i). It has been used as a replacement for materials such as wood and metals, an application that has been increasing in later years.

In 2012, world installed capacity for PVC was 53.4 Mt and production 37.5 Mt (Ullmann's Encyclopaedia, 2014). Europe accounted for 15.4 % of the installed capacity, North America for 15.1% and China 43.9%. Europe produced 6.6 Mt PVC and consumed 6.2 Mt, owing almost 18% of global exports, while China produced 13.1 Mt and consumed 13.9 Mt, importing 16.6 % of global exports (Ullmann's Encyclopaedia, 2014). In 2012, the European Union had capacity, production and consumption 7.3 Mt, 5.8 Mt and 4.8 Mt respectively, while its operational rate was 80 % (Ullmann's Encyclopaedia, 2014).

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(50) PVC lattices are colloidal dispersions of spherical particles [Ullmann's Encyclopaedia, 2014]

Table 83. PVC plants in the EU-28 in 2013

	S-PVC		E-PVC	
Country	Number of plants	Capacity (kt/y)	Number of plants	Capacity (kt/y)
Belgium	2	445	1	30
Czech Republic	1	135		
Germany	10	1 620	8	470
Spain	3	490	1	42
France	6	1 410	1	80
Italy	1	180		
Hungary	1	400		
Netherlands	2	675		
Poland	2	340		
Portugal	2	200	1	15
Romania	2	305		
Slovakia	1	40	1	50
Sweden	1	150	1	82
United Kingdom	3	340	1	45
Total	37	6 550	15	814

5.12.1 Production processes

There are three different processes for manufacturing PVC:

- Suspension polymerisation
- Emulsion polymerisation
- Bulk or mass polymerisation

In the suspension polymerisation process liquid VCM is dispersed in water by vigorous stirring, resulting in droplets, inside which polymerisation takes place (Ullmann's Encyclopaedia, 2014; EC, 2007d). The reaction requires the presence of an initiator, such as per esters, per carbonates or peroxides, and a suspension agent, usually partially hydrolysed polyvinyl acetates. In order to achieve optimum morphology, also additives are also employed, such as oxygen, buffers, granulating agents and others. Besides these, the quality of S-PVC is determined from the level of agitation and homogenisation, the charging procedure and timing of each additive addition (Ullmann's Encyclopaedia, 2014).

In 2013, in EU-28 there were 52 facilities producing PVC with total capacity 7.4 Mt (Table 83) (ICIS, 2012, EC, 2007d). As mentioned before there are two types of PVC based on the production process and the table distinguishes between the two cases.

In emulsion processes, polymerisation of the monomer takes place in an aqueous medium that contains surfactant and an initiator. The product (E-PVC) is in the form of aqueous latex, which is then spray dried and milled to fine powder (agglomerates of the latex particles) (Ullmann's Encyclopaedia, 2014). There are three polymerisations processes that are used in order to produce different size distributions: batch emulsion, continuous emulsion and micro-suspension (EC, 2007d). The particles size will determine the rheology profiles of the final product. Balch emulsion produces narrow width unimodal latex of a small size, while by continuous emulsion lattices with a wide particle size distribution are produced. Wide particle size corresponds to low plastisol viscosities (EC, 2007d). Micro-suspension produces latex with a wide particle size distribution too, but requires lower quantities of emulsifier, which makes the product more suitable for food applications (EC, 2007d).

Mass or bulk polymerisation is practically identical to the suspension polymerisation, differing only in the mechanical operation of the process (Ullmann's Encyclopaedia, 2014). For this reason, in this study, it is considered as one with suspension polymerisation.

More information and detailed descriptions of the production processes can be found in the literature (Ullmann's Encyclopaedia, 2014; EC, 2007d).

5.12.2 Current consumption and emission levels

The main raw material for the production of PVC is vinyl chloride monomer (VCM), which is polymerised in an aqueous medium. Polymerisation is a strongly exothermic reaction (-1 540 KJ/kg) and removal of heat is needed in order to control it (Ullmann's Encyclopaedia, 2014; EC, 2007d). Conversions achieved are at the range of 85-95% (EC, 2007d). As conversion increases beyond 85%, the reaction rate is decreased due to monomer starvation (Ullmann's Encyclopaedia, 2014).

Besides VCM, also water and additives are also needed for the reaction to take place. In a basic recipe for suspension polymerisation, the ratio between VCM and water is usually 1 to 0.9-1.3 (Ullmann's Encyclopaedia, 2014). In the case of emulsion, this ratio is slightly higher (1 to 1.1-1.4) (Ullmann's Encyclopaedia, 2014). For stabilisation of the dispersion surfactants, emulsifiers and colloids are used, typically in quantities of 1 kg/t in suspension and 10 kg/t in emulsion (EC, 2007d). All the chemicals needed for the reaction of polymerisation are summarised in Table 84.

Table 84. Raw materials, chemicals and energy consumed in PVC production (Ullmann's Encyclopaedia, 2014; EC, 2007d)

Feedstock	Suspension	Emulsion
VCM	1.1 t/t_{PVC}	
Water	0.9-1.3 t/t_{VCM}	1.1-1.4 t/t_{VCM}
Surfactants, emulsifiers etc.	1 kg/t_{VCM}	10 kg/t_{VCM}
Initiator	> 1 kg/t_{VCM}	
Chemicals to stop the reaction	> 1 kg/t_{VCM}	
Energy		
Thermal energy	2-3 GJ/t_{PVC}	6-9 GJ/t_{PVC}
Electricity	194-305 kWh/t_{PVC}	389-611 kWh/t_{PVC}

Production of PVC requires energy in the form of steam for heating or stripping and electricity for refrigeration units, pumps and compressors. Typical energy consumptions are included in Table 84.

Pollution from PVC production includes VCM emissions, PVC dust, VCM in water and hazardous waste (EC, 2007d). The European PVC industry (EU-28. Norway and Switzerland) has made important efforts towards sustainability. In 1995 the European Council of Vinyl Manufacturers (ECVM) issued an industry charter, according to which the signatories were obliged to reduce their environmental impact (PVCplus, 2012). In 2001 the four major European associations concerning PVC (manufacturers of PVC, PVC plasticisers and PVC stabilisers and plastics converters) signed a sustainable development commitment entitled "Vinyl 2010". According to the final report in 2010, between 2000 and 2010 there had been impressive progress in waste management, recycling technologies, stakeholder engagement and handling of additives (PVCplus, 2012).

Since 2011, a new initiative has been launched, named "VinylPlus". The main goals are to recycle 800 kt/y of PVC by 2020, to develop innovative recycling technologies, especially addressing concerns about organochlorine emissions, to use sustainably additives, to increase energy efficiency and to promote sustainability through the entire PVC value chain (PVCplus, 2012; Vinylplus, 2016).

The boundaries of this study include only GHG emissions. As a result, the only emissions considered are those one due to electricity and thermal energy generation. As thermal energy is mainly in the form of steam, the emissions are calculated by using the steam emission factor and not by assuming natural gas. The values used are shown in Table 85.

Table 85. Emission factors for PVC production

Polymerisation	Electricity	Thermal	Steam	Total
Suspension	0.12 t_{CO2}/t_{PVC}		0.18 t_{CO2}/t_{PVC}	0.30 t_{CO2}/t_{PVC}
Emulsion	0.23 t_{CO2}/t_{PVC}		0.54 t_{CO2}/t_{PVC}	0.77 t_{CO2}/t_{PVC}

Both PVC products are benchmarked products, with values 0.085 allowances/t for PVC-S and 0.238 allowances/t for PVC-E. The system boundaries of the benchmarking include all steps of the process, but exclude emissions related to the production of the consumed electricity.

5.12.3 Best available techniques (BATs)

This paragraph includes the techniques considered generally to have the potential of improving the environmental performance or the energy efficiency of the PVC industry (Table 86).

Table 86. Overview of the possible BATs and ITs in the PVC industry

BAT/IT	Description	Investment cost (EUR)	Energy savings (%)	GHG Reduction (%)
BAT	Heat recovery	Not enough information available		
BAT	Pigging system	101 568	19 % electricity	
BAT	Cogeneration	General reference in 4.5.1.		
BAT	Emissions prevention measures	Outside the scope of this study		
IT	Recycling technologies	Recycling is considered separately		

As mentioned before, polymerisation is a strongly exothermic reaction. Heat needs to be removed to control the reaction and it can be used to generate low pressure steam for preheating purposes or other internal use. This practise results in reductions of energy consumptions. It is mainly applied in integrated sites where the produced steam can be sold to available customers (EC, 2007d). The technique requires the use of heat exchangers. There are several correlations for estimating investment costs of heat exchangers in the literature (Slavkovic et al., 2014), but usually they are a function of the heat transfer surface. As there is no information about the savings achieved concerning the PVC industry in particular and there are no generic data about the heat exchangers needed, neither investment costs, nor environmental benefits can be calculated.

Pigging technology is considered to be a cleaning technique. It has already been explained in 5.11.3 and it involves pushing the contents of a pipe by a close fitting plug, named pig, almost completely out of the pipe (EC, 2007d). The same values are used also in this industry.

Of course, cogeneration is considered also for this industry, but as it is the case for the whole study, it is treated generally for the whole of the chemical industry.

There are a number of available techniques to reduce emissions and pollution from this industry. These include environmental management tools, monitoring and maintenance of equipment, minimisation of plant stops and start-ups, emission prevention and others (EC, 2007d). But as the emissions are not of greenhouse gases, these techniques are outside the scope of this study.

Last but not least, recycling can be considered as a technique to save both energy and emissions. PVC recycling will be described in the following section and the savings will be calculated.

5.12.4 Innovative technologies (ITs)

As mentioned already, the European PVC industry has focused on encouraging innovative technologies concerning end of life recycling (PVCplus. 2012). Recycling is handled in the following paragraph, separately from PVC newly produced.

5.13 PVC recycling

PVC compounds are suitable for end-of-life recycling and it offers the possibility to change formulation parameters, a characteristic that enables the reuse of PVC in new products. The PVC industry around the world has been active in recycling for decades (Vinylplus, 2016; Vinylinfo, 2016; Vinyl Council Australia, 2016).

As mentioned already the European PVC industry has adopted initiatives that include end-of-life treatments (PVCplus, 2012). "VinylPlus", the latest initiative since 2011, includes the following targets (Recovinyl, 2016):

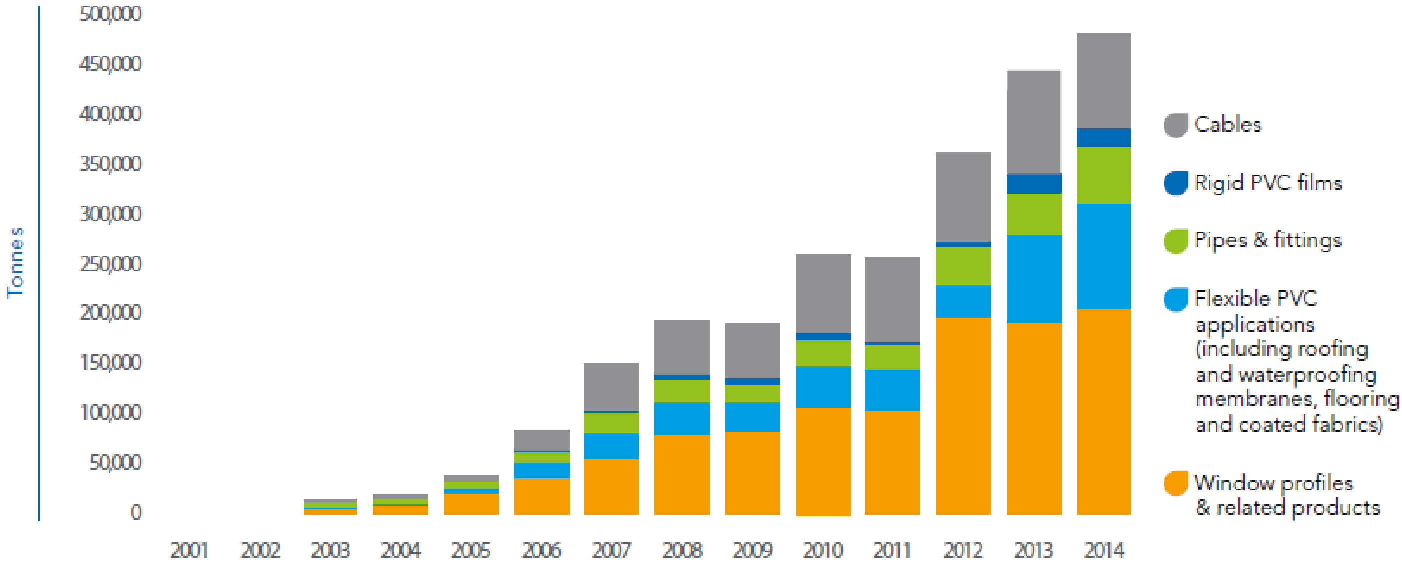
- recycle 800 kt/y by 2020; and
- develop and exploit innovative technologies to recycle 100 kt/y of difficult to recycle PVC material.

Generally in Europe, recycling and energy recovery from post-consumer plastics have increased since 2006, the former by 40 % and the latter by 27 % (Plastics Europe, 2015). In 2006 only 4.7 Mt of plastics was recycled, while in 2012 the volume has increased to 6.6 Mt

In 2013, 444.5 kt of PVC were recycled in Europe within the VInylPlus framework (VinylPlus, 2014) and in 2014 that amount increased to 481.0 kt (VinylPlus, 2015). Figure 23 shows the type of PVC recycled in Europe, as well as the evolution during the last decade (VinylPlus, 2015).

In order to analyse the recycled PVC industry, the recycled quantities are needed. These depend on the total annual quantity of PVC in wastes and the recycled fraction of it (Prognos, 2000). A big part of PVC applications are long-lived products, a fact that can explain the big bust in recycling observed in later years (Figure 23).

Figure 23. PVC recycled within the Vinyl 2010 and VinylPlus frameworks (VinylPlus, 2015)



The recycling potential of PVC is determined to a large extent by contamination and the technical characteristics that the final product should have, as well as by legal and economic factors (Prognos, 2000).

Two major groups of waste can be distinguished, based on type: pre-consumer and post-consumer waste (Prognos, 2000). Pre-consumer waste is either production waste, which is generated during the production of PVC final and intermediate products, or installation waste, from handling or installing PVC products. Post-consumer waste is usually end-of-life products (pipes, windows, packaging) and therefore, mixed waste fractions or part of composite materials. Pre-consumer waste may have defined composition, while this is rather impossible for post-consumer waste, and as a result, pre-consumer waste has higher potentials for recycling (Prognos, 2000).

For this study, the focus is on high-quality PVC recyclates, or recyclates that can serve as substitutes of virgin PVC. As a result, low-quality or mixed plastic products are outside the boundaries. As pre-consumer waste yields high-quality products, while post-consumer waste results in products of rather low level purity (Prognos, 2000). It is assumed that the annual amount of products that can be considered as substitutes for virgin PVC consists of 90 % pre-consumer waste and 10 % post-consumer waste. Unfortunately pre-consumer waste is usually dealt inside the industry and not through the usual waste management systems, so national authorities do not have information about it (DG Env, 2011).

The European plastics recycling industry is rather new and consists of rather small- and medium-sized companies (Plastics Recyclers Europe, 2012). There are more than 1 000 companies in Europe. Since there is no official data on plants performing PVC recycling, for the present study, we have decided to allocate a fictitious plant per country, whose production capacity is equal to the recycling potential of this country. Although the year of analysis for all products has been 2013, in this particular study, the analysis is done for 2012, as it is the last year for which there is available information. The methodology followed is explained in this section.

Table 87. Estimation of PVC waste streams (kt/y) in EU-28 by country for 2012

Country	Total plastics waste[1]	Estimated PVC waste[2]	Post-consumer waste[3]		Pre-consumer waste[3]	
			Total	Recyclable	Total	Recyclable
Belgium	611.0	65.4	57.5	23.0	7.8	6.7
Bulgaria	99.9	10.7	9.4	2.7	1.3	1.1
Czech Republic	325.6	34.8	30.7	14.7	4.2	3.6
Denmark	107.2	11.5	10.1	2.9	1.4	1.2
Germany	2 530.5	270.8	238.3	100.1	32.5	27.6
Estonia	22.7	2.4	2.1	0.9	0.3	0.2
Ireland	126.2	13.5	11.9	4.3	1.6	1.4
Greece	133.2	14.3	12.5	3.0	1.7	1.5
Spain	1 142.9	122.3	107.6	37.7	14.7	12.5
France	1 646.8	176.2	155.1	37.2	21.1	18.0
Croatia	39.2	4.2	3.7	1.1	0.5	0.4
Italy	2 733.1	292.4	257.3	95.2	35.1	29.8
Cyprus	74.3	7.9	7.0	1.6	1.0	0.8
Latvia	21.6	2.3	2.0	0.7	0.3	0.2
Lithuania	50.6	5.4	4.8	1.8	0.7	0.6
Luxembourg	26.3	2.8	2.5	0.5	0.3	0.3
Hungary	185.8	19.9	17.5	5.1	2.4	2.0
Malta	4.4	0.5	0.4	0.1	0.1	0.0
Netherlands	609.6	65.2	57.4	29.3	7.8	6.7
Austria	357.6	38.3	33.7	9.8	4.6	3.9
Poland	969.7	103.8	91.3	36.1	12.5	10.6
Portugal	213.7	22.9	20.1	6.2	2.7	2.3
Romania	649.3	69.5	61.1	24.2	8.3	7.1
Slovenia	47.8	5.1	4.5	1.9	0.6	0.5
Slovakia	108.1	11.6	10.2	4.5	1.4	1.2
Finland	91.3	9.8	8.6	2.0	1.2	1.0
Sweden	175.8	18.8	16.6	7.2	2.3	1.9
United Kingdom	3 986.2	426.5	375.3	110.7	2.3	43.5
EU 28	17 090.6	1 828.7	1 609.3	564.4	219.4	186.5

[1] Source (Eurostat, 2016b)

[2] It is assumed that PVC share = 10.7%

[3] It is assumed that 88% of PVC waste is post-consumer and 12% pre-consumer

Eurostat reports plastic waste generation per country, which in 2012 amounted to 17 Mt (Eurostat, 2016b). Since there is no further information concerning the composition of this waste, it was assumed that the PVC share in it is the same as its share in plastics demand. According to (Plastics Europe, 2015), in 2013 PVC covered 10.7 % of the total EU-27, Norway and Switzerland plastics demand. Based on this information and this assumption, the total production of PVC waste per country was estimated (Table 87).

Based on the forecasts provided by (Prognos, 2000), over the period 2000-2020 the post-consumer PVC waste was expected to cover 88 % of the total PVC waste production in the EU, while the remaining 12 % would be pre-consumer PVC. Taking this forecast into consideration, the estimated PVC waste can be distinguished as pre- and post-consumer (Table 87).

Table 88. Estimated volumes of high-quality PVC waste (kt/y) in EU-28 for 2012

Country	Pre-consumer waste (kt/y)	Post-consumer waste (kt/y)	Total (kt/y)
Belgium	6.0	2.3	8.3
Bulgaria	1.0	0.3	1.3
Czech Republic	3.2	1.5	4.7
Denmark	1.1	0.3	1.3
Germany	24.9	10.0	34.9
Estonia	0.2	0.1	0.3
Ireland	1.2	0.4	1.7
Greece	1.3	0.3	1.6
Spain	11.2	3.8	15.0
France	16.2	3.7	19.9
Croatia	0.4	0.1	0.5
Italy	26.8	9.5	36.4
Cyprus	0.7	0.2	0.9
Latvia	0.2	0.1	0.3
Lithuania	0.5	0.2	0.7
Luxembourg	0.3	0.1	0.3
Hungary	1.8	0.5	2.3
Malta	0.0	0.0	0.1
Netherlands	6.0	2.9	8.9
Austria	3.5	1.0	4.5
Poland	9.5	3.6	13.1
Portugal	2.1	0.6	2.7
Romania	6.4	2.4	8.8
Slovenia	0.5	0.2	0.7
Slovakia	1.1	0.4	1.5
Finland	0.9	0.2	1.1
Sweden	1.7	0.7	2.4
United Kingdom	39.2	11.1	50.2
EU 28	167.9	56.4	223.8

Recycling rates are calculated according to the following equation:

$$\text{Recyclable PVC waste}_i = \text{PVC waste}_i * \text{Recycling rate}_i$$

where ‘i’ can be either pre- or post-consumer waste. Since pre-consumer waste is comparatively easy to recycle and is collected separately in defined qualities (Prognos, 2000), an average recycling rate of 85 % is assumed. For post-consumer waste for each country the rate is assumed to be equal to the rate of plastic packaging recycling, reported by (Plastics Europe, 2015). This way the recyclable post- and pre-consumer waste is calculated (Table 87).

As explained before, the boundaries of this study are covering only recycled PVC with potential to replace virgin PVC. The final assumption is that after sorting and separation, 90% of the total amount of pre-consumer waste and 10 % of post-consumer waste is of a quality sufficient for 'high-quality waste'. The estimated volumes of high-quality PVC waste for 2012 is shown in Table 88.

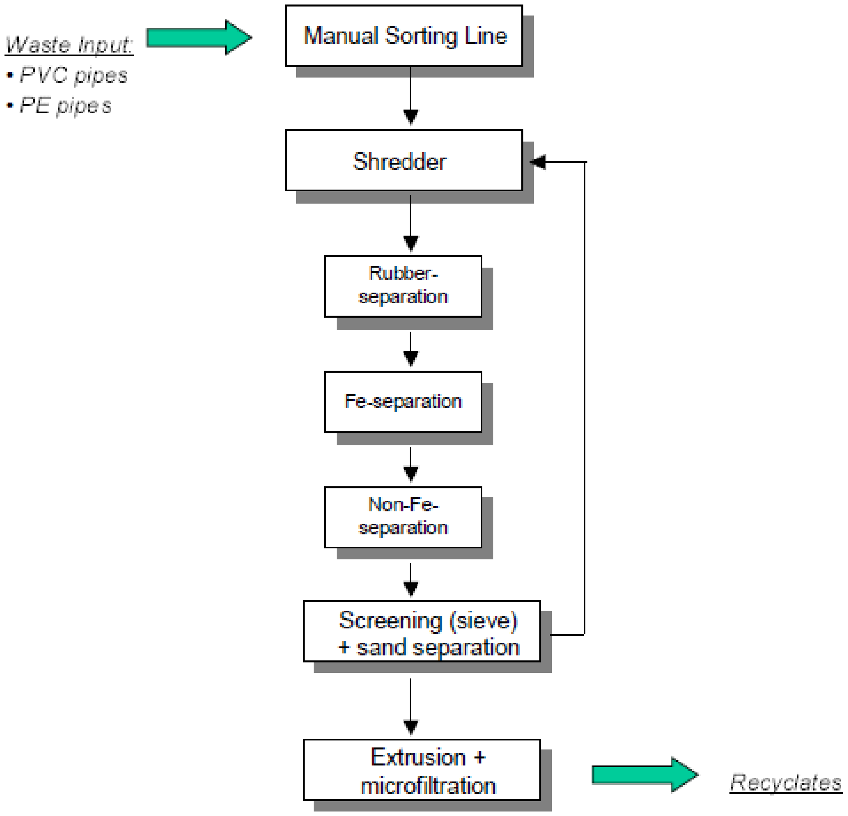
5.13.1 Production processes

There are two main options for recycling PVC: mechanical and chemical (TNO, 1999; Prognos, 2000). Besides these there are some competing technologies, such as municipal solid waste incineration and cement kilns, but these are not considered to be recycling technologies and as such are out of the scope of this paragraph.

Mechanical recycling includes operations where plastics waste is treated with mechanical processes, such as grinding, sieving and screening (Prognos, 2000). Recyclates are produced, which can be converted into new plastic products and substitute virgin plastics.

Only thermoplastic materials (51) are of interest for this type of recycling and homogeneous, single polymer stream is needed, as generally different plastics are not compatible with each other (Plastics Recyclers Europe, 2012). The purer the collected PVC material, the higher the quality of the recyclates produced. Important factors are both the degree PVC is in mixture with other materials when collected, and the differences in composition of the collected PVC itself. Usually rigid PVC (S-PVC) contains lower additives than soft PVC applications (Prognos, 2000).

Figure 24. Flow diagram for recycling PVC pipes (Prognos, 2000)



The first step of recycling is collection and, if PVC wastes are collected in mixed fractions, also sorting. In general mechanical treatment consists first of shredding units that reduce the size and separation units that extract specific sizes or materials Polymeric materials are then re-melted and reprocessed into products by mills and extruders. A typical flow diagram for recycling PVC pipes can be seen in Figure 24.

Chemical recycling, also known as feedstock recycling, includes technologies that are less sensitive to unsorted or contaminated waste products and aim to chemically degrade the

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(51) A thermoplastic material becomes soft when heated and hard when cooled.

material into their monomers or other basic chemicals. Examples of such technologies are hydrogenation, pyrolysis or gasification (PVC, 2016). The output may be reused for polymerisation into new plastics, for the production of other chemicals or as an alternative fuel.

Several initiatives exist in the market concerning chemical recycling. There are processes for mixed plastic waste (52) and others for PVC-rich waste. Detailed descriptions of these processes can be found in (TNO, 1999).

Most of the chemical recycling processes operating currently are for mixed plastic waste from packaging with PVC content less than 10% (PVC, 2016). Some of these processes are (TNO, 1999):

- Texaco gasification process: The plastic waste is first mildly thermally cracked into synthetic heavy oil and some gas fractions in a liquefaction step. Non-condensable gases are used as fuels, while the heavy oil is filtered to remove inorganic particles and is then injected in an entrained bed gasifier together with the condensable gases. The final product after cleaning is synthesis gas with small amounts of CH_4, CO_2, H_2O and some inert gases.
- Polymer cracking process: The plastic waste is pre-treated to reduce size and remove non-plastics and is then fed directly into a heated fluidised bed reactor. There it is thermally cracked to hydrocarbons that vaporise and leaves the reactor as gas. The gas is purified and then condensed, resulting in valuable distillate feedstock.
- BASF conversion process: The plastic waste is first grounded, separated from materials such as metals and agglomerated. A multi-stage melting and reduction process follows. The liquefied plastic is then cracked into components of different chain lengths, which are separated by distillation. The products include naphtha, monomers such as ethylene and propylene, high boiling oils that can be processed to syngas and residues.
- Use of mixed plastic waste in blast furnace: Plastic waste can replace the conventional reducing agents of iron ore to iron, so as to be used for steel. The plastic waste is injected in the blast furnace in a similar way as coal.
- Veba combi cracking process: Mixed plastic waste from packaging is firstly kept at temperatures 350-400 °C to effect depolymerisation and dechlorination. It is then hydrogenated in the Veba Combi Cracker section at 400-450 °C and the product is led to separation. The process yields a synthetic crude oil that can be processed in any refinery and a residue with heavy hydrocarbons contaminated with ashes metals and inert salts. The latter can be blended with coal for coke production.
- Pressurised fixed bed gasification of SVZ: Plastic waste is fed in a solid bed gasification kiln together with lignite and waste oil and synthesis gas, liquid hydrocarbons and effluent are produced. The liquid hydrocarbons are further processed by oil pressure gasification.

Mechanical and chemical recycling should not be considered as competing with each other, but rather as complementary. Mechanical recycling is appropriate for as pure PVC waste as possible, while chemical recycling can process contaminated products with less restrictions than mechanical recycling.

5.13.2 Current consumption and emission levels

Since we focus on high-quality recyclables, mechanical recycling is the most possible recycling process to be followed. As a result, the analysis will be based on these processes and not on chemical recycling.

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(52) These processes accept plastic waste with PVC contain from >2% up to >10%, depending on the process [TNO, 1999].

For PVC that is entering recycling processes recovery rates are generally high, usually about 95% (Brown et al., 2000). Based on this rate, the specific feedstock consumption due to mechanical recycling is 1.05 tonne high quality PVC waste per tonne of high quality PVC recyclate.

Energy requirements for processing polymers with mechanical means typically range between 10 and 15 MJ/kg (Brown et al., 2000). The exact energy consumed depends on the steps followed. It is assumed that high quality recycling is closer to the upper limit and that all of the energy is consumed as electricity (Brown et al., 2000). As a result, the energy requirements of PVC recycling for this study are 4.17 MWh/$t_{PVC.recycled}$.

Concerning emissions, volatile material may be produced during heating, melting and blending, but total emissions from these stages are considered to be relatively insignificant (Brown et al., 2000). Emissions from PVC recycling are estimated to be in total about 17.65 $kg_{CO2}/t_{PVC.recycled}$, but they occur during transportation (Brown et al., 2000). Transportation is outside the boundaries of this study and as a result process emissions are considered to be zero. The only emissions taken into consideration are indirect ones, due to electricity consumption and they amount to 1.9 $t_{CO2}/t_{PVC.recycled}$.

Recycled PVC could replace virgin PVC and therefore the two processes should be considered between them, so as to decide the savings. The energy consumption and emissions of PVC recycling should be compared with the ones of PVC produced new. But the latter should include the whole production pathway from ethylene to PVC. This pathway can have several configurations. Table 89 shows the different configurations of the pathway and the way the total energy consumptions are calculated. The average energy consumption is 22.2 GJ/t_{PVC}, while the average emission factor is calculated accordingly and amounts to 2.8 t_{CO2}/t_{PVC}. As a result, the savings achieved from recycled PVC are 32.5% for energy and 32.1 % for emissions.

Since recycled PVC is considered as replacement of virgin PVC, its price is also important. According to (Plastics News, 2016), the price of recycled PVC (resin grade: clear industrial flake) in 2012 ranged between 0.41 and USD 0.55 $_{2012}$/lb. In general the price of recyclate is set by the price of virgin compound (Brown et al., 2000). Therefore, it is assumed that the annual growth rate for price of high quality PVC recyclates varies according to the price of virgin PVC.

5.13.3 Best available techniques (BATs)

Since the industry is rather new (Plastics Recyclers Europe, 2012), there are not so many best available techniques or innovative technologies that will not be analysed. The only technology that can be considered as best available, different from that which is currently used, is the VinyLoop process.

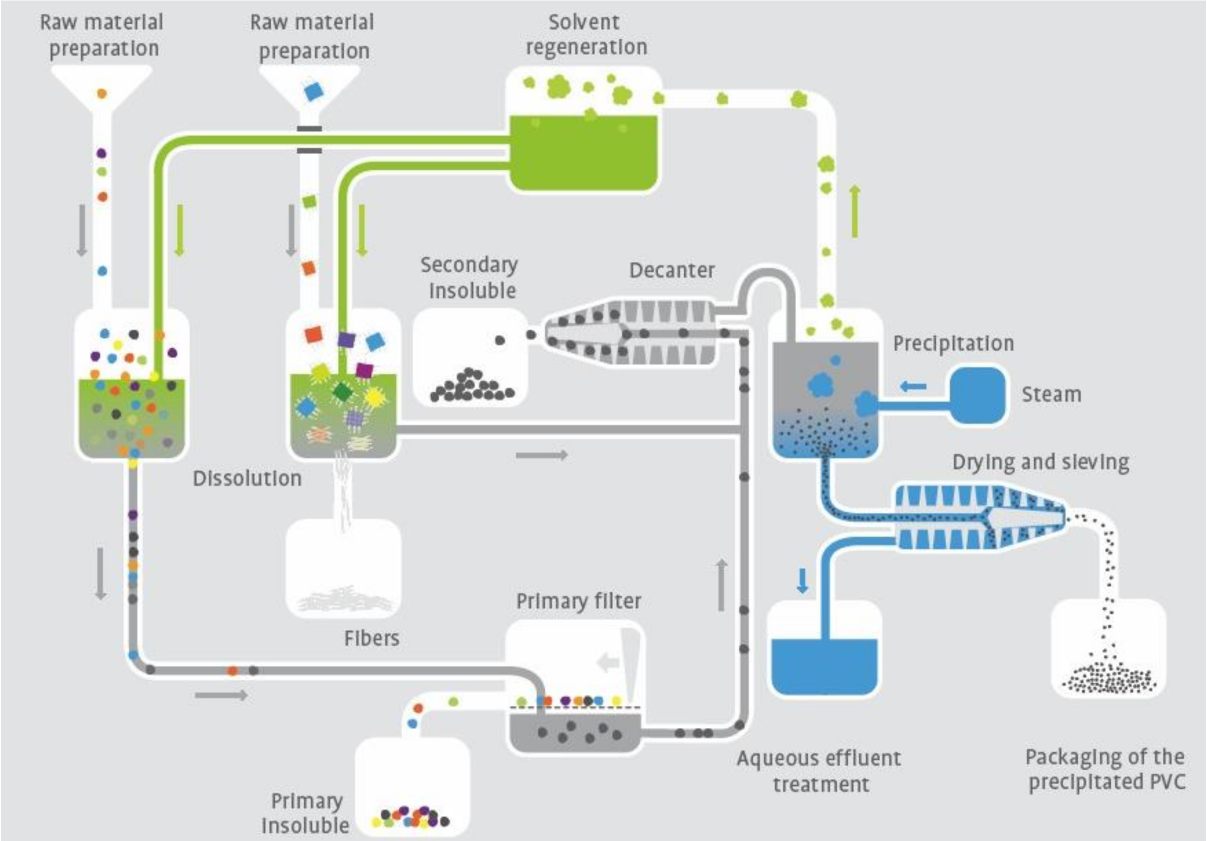
VinyLoop is developed by the Solvay group in order to recycle difficult-to-treat composite PVC waste and is based on physical principles (TNO, 1999; VinyLoop, 2013). It is suitable for composites with at least 70% PVC.

Table 89. Schematic representation of the different configurations for virgin PVC production and energy consumptions

Ethylene → EDC → VCM → PVC								
Ethylene			EDC		VCM	PVC		
Energy consumption								
Steam cracking (GJ/$t_{ethylene}$)			Chlorination		EDC cracking	Polymerisation (GJ/t_{PVC})		Total energy consumption (GJ/t_{PVC})
Naphtha-based	Ethane-based	Gasoil-based	Direct	Oxy		Suspension	Emulsion	
12	20.5	25	Balanced process 5.4 GJ/t_{VCM}			3.4	9.3	
+			+			+		15.4
+			+				+	21.3
	+		+			+		19.7
	+		+				+	25.6
		+	+			+		22.0
		+	+				+	27.9

PVC and its additives are selectively dissolved in a solvent that allows them to separate from other elements. PVC is recovered by precipitation and then dried (TNO, 1999; VinyLoop, 2013). Figure 25 shows the process flow diagram (VinyLoop, 2013).

Figure 25. The VinyLoop process (VinyLoop, 2013)



A first plant based on this technology was inaugurated in 2002 in Italy with a capacity of 10 kt/y of PVC scraps and nominal production of 27 t_{PVC}/d (VinyLoop, 2002). It is designed to process electric cable waste and tarpaulin (53). In 2014 the plant produced in total 5.2 kt of recycled PVC and in 2013, 4.9 kt (Vinylplus, 2016). The final investment for this plant amounted to EUR 10.6 million $_{2001}$ (VinylLoop, 2002), which corresponds to EUR 7.95 million $_{2013}$. According to a study comparing VinyLoop with the conventional PVC producing route (virgin PVC and incineration), savings can reach 47 % for energy and 40 % for GHG emissions (Solvay, 2013). Since the system boundaries are wider than the PVC production process alone and there is no way to assess the actual savings of the process for stricter boundaries, the process is not taken into consideration in our analysis.

5.13.4 Innovative technologies (ITs)

Concerning PVC recycling, research efforts from the industry focus mainly on novel waste separation techniques. The aim is to bring mixed or difficult waste streams to the point of being handled by conventional mechanical recycling. Examples of such technologies include Neidhardt Recycling GmbH (for PVC-aluminium composite materials), R-Inversatech (for PVC in waste such as tarpaulins), the technique from Hemawe/Caretta (separating fabric and tissue from soft PVC foils) and others (Vinylplus, 2013) The whole sector is rather new and these technologies are only preparing the PVC waste for recycling, so they will not be considered in this study.

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(53) Tarpaulin is a composite PET textile (woven fibres) coated with PVC compound.

5.14 Ethylbenzene and Styrene

Ethylbenzene (C_8H_{10} – $C_6H_5CH_2CH_3$) is a single-ring alkyl aromatic compound that is almost exclusively used for the production of styrene (C_8H_8 – $C_6H_5CH=CH_2$). As a result, these two chemical substances will be treated together.

Commercially, ethyl benzene is produced by alkylation of benzene with ethylene (Ullmann's Encyclopaedia, 2005). It is a colourless liquid with an odour similar to gasoline. As already mentioned, it is mainly used for the production of styrene. Other uses include paint solvent and reactant for the production of other chemicals (diethyl benzene and acetophenone), but these uses amount to less than 1 % (IHS, 2015i, Ullmann's Encyclopaedia, 2005). In 1999, the global installed capacity of ethyl benzene was around 25 Mt (Ullmann's Encyclopaedia, 2005), while in 2002 it had already reached 28 Mt (Cefic, 2012), while global ethylene demand was expected to increase at an average rate of 2.1 % in the period 2014-2019 (IHS, 2015i)

Styrene – phenylethene according to IUPAC – is a colourless liquid with a distinctive, sweetish odour. It is used as feedstock for several polymer products. About 60 % of styrene produced is used to derive polystyrene (54), 18 % for styrene-acrylonitrile copolymer (SAN) (55) and acrylonitrile-butadiene-styrene copolymer (ABS) (56), 5 % for styrene-butadiene rubber elastomers (57) (Ullmann's encyclopaedia, 2011d). The remaining is used in miscellaneous uses. In 2012, global styrene capacity was estimated to be more than 32.7 Mt. while production exceeded 26.4 Mt (Merchant Research, 2013). Asia accounted for about half of the world styrene capacity, and Europe for about 18 % (Merchant Research, 2013).

Concerning future growth, polystyrene, which drives styrene consumption, receives high competition from polypropylene, PET and other substitutes. As a result polystyrene growth rates to 2019 are low (around 1.6% per year) (IHS, 2015j). On the other hand, expandable polystyrene, another application, was expected to grow faster, with rates around 2.3% and ABS resins even faster with rates of 3.6 % (IHS, 2015j).

Table 90. Ethylbenzene and styrene plants in the EU-28 in 2013

	Ethylbenzene		Styrene	
Country	Number of plants	Capacity (kt/y)	Number of plants	Capacity (kt/y)
Belgium	2	890	2	500
Czech Republic	1	300	1	170
Germany	2	930	2	850
Spain	1	505	1	450
France	1	720	1	600
Italy	2	720	2	595
Netherlands	3	2 005	4	2 170
Poland			1	120
Slovakia	1	15		
United Kingdom	1	160		
Total	14	6 245	14	5 455

Information concerning Europe is available by Petrochemicals Europe, but it covers only Western Europe (Petrochemicals, 2016) In 2013, ethyl benzene capacity was 5.9 Mt, which decreased by 10 % compared to 2012, while production is not reported (Petrochemicals, 2016). Concerning styrene installed capacity was 5.2 Mt in 2013, 9 %

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(54) Polystyrene is used to make from toys, housing for air conditiners and television cabinets to furniture parts, insulation boards and disposable food containers.

(55) SAN is used for drinking tublers and battery cases.

(56) ABS is used for piping, automotive components, shower stalls etc.

(57) These rubber elastomers are used as passengers car tires, industrial hoses and footwear.

less than 2012. Styrene production reached 4.5 Mt, decreased only by 3.6 % compared to the previous year (Petrochemicals Europe, 2016). In the EU-28, there were 14 plants for each product, with a total capacity 6.2 Mt/y for ethyl benzene and 5.5 Mt/y for styrene as shown in Table 90 (ICIS, 2012).

5.14.1 Production processes

Alkylation of benzene with ethylene is the process used globally for the production of ethyl benzene. The traditional catalyst is aluminium chloride ($AlCl_3$), but new technologies are based on heterogeneous zeolites (Ullmann's Encyclopaedia, 2005; EC, 2014d). Although the $AlCl_3$ route has several drawbacks (costly disposal of waste streams and corrosion of equipment), a considerable part of worldwide ethyl benzene production still utilises variations of it. Nevertheless, there is a general trend in the industry to change to zeolite technology.

Alkylation can be either in the liquid- or in the vapour-phase. Vapour phase zeolites have the advantages of better selectivities and simpler catalyst management, while aqueous waste streams can be avoided (Ullmann's Encyclopaedia, 2005; EC, 2014d). it is particularly suited for dilute ethylene streams, such as refinery off-gas from fluid catalytic cracking units. Liquid-phase alkylation on zeolite catalyst was commercialised in 1990 and operates below critical benzene temperature (around 290°C).

The principles of all alkylation processes, regardless of the catalyst or the phase, are the same and the process steps are similar. The reaction occurs by mixing an excess of benzene with ethylene in the presence of catalyst and it is exothermal. Benzene excess does not totally prevent side-reactions of ethylene, which can further react with the ethyl benzene produced to form mostly isomers of di- and thri-ethyl benzene (EC, 2014d). These by-products can be separated and recycled in a trans alkylation section.

In the case of styrene, the feedstock for all commercial processes has been ethyl benzene (Ullmann's Encyclopaedia, 2011d; EC, 2014d). 85% of styrene production is done by catalytic dehydrogenation. The main reaction is the following:

$$C_6H_5CH_2CH_3 \leftrightarrow C_6H_5CH{=}CH_2 + H_2 \qquad \text{(reaction 56)}$$

This reaction is endothermic and reversible and occurs in the vapour phase with steam and over a catalyst consisting primarily of iron oxide. Due to the stoichiometry reaction and the fact that it takes place in the gas phase, lower pressures and higher temperatures favour the conversion to styrene. It can be carried out either adiabatically or isothermally. The main difference is the way the endothermic reaction heat is supplied.

Adiabatic operation is applied in over 75% of all operating styrene plants (Ullmann's Encyclopaedia, 2011d; EC, 2014d). The necessary heat is introduced at the inlet either by injection of superheated steam or by indirect heat transfer. Ethylbenzene conversion can vary with the system but it is usually 65% overall (Ullmann's Encyclopaedia, 2011d).

In isothermal dehydrogenation, the reactor is built like a shell and tube heat exchanger. The tubes are packed with a catalyst and steam and ethyl benzene flow through them. The necessary heat is supplied by hot flue-gas on the shell side of the reactor. Steam temperatures are lower than in the case of adiabatic dehydrogenation, but there are practical limitations of size for the reactor.

The product from the reaction is crude styrene that can include - besides styrene - (typically 64 %), also benzene, toluene, ethyl benzene (typically 32 %) and others (Ullmann's encyclopaedia, 2011d). The pure product needs to be separated by distillation. Styrene and ethyl benzene have similar boiling points (145 °C and 136 °C respectively), so 70-100 trays are required for separating them. Residence time is of importance, as styrene may start polymerising.

Most commercial styrene plants are based on either the Lummus/UOP (UOP, 2004) or the Fina/Badger technologies (Badger, 2012), although there are some more commercial technologies available (Woodle, 2006).

The rest of styrene is produced commercially via the styrene-propylene oxide process. It involves co-production of propylene oxide, but it involves large capital investment and has higher costs of production, but credits from selling the co-produced propylene oxide can make the process profitable (EC, 2014d). Due to its low percentage of application in the industry, it will be assumed that all EU plants are produced via ethylene dehydrogenation.

5.14.2 Current consumption and emission levels

As described before, ethyl benzene is produced by alkylation of benzene with ethylene. Typical consumptions for feedstock and energy consumptions are shown in Table 91 (EC, 2014d; MacFarlane, 1977). If the catalyst is zeolite, deactivation is slow and is due to coke formation, while if the catalyst is $AlCl_3$ continuous replacement of the losses is required. Alkylation is exothermic and heat can be recovered. It can be used to preheat the reactors for alkylation and trans alkylation or as steam in the styrene production.

Table 91. Typical feedstock and energy consumptions in the case of ethyl benzene production

Raw material	Value ($t/t_{ethylbenzene}$)	Source
Ethylene	0.26-0.28	(EC, 2014d; MacFarlane, 1977)
Benzene	0.74-0.78	
Energy	**Value**	
Steam	0.34-1.72 GJ/t	(EC, 2014d)
Electricity	25-32 kWh/t	(EC, 2014d)
Fuel	1.95 GJ/t	(MacFarlane, 1977)
Heat recovery	2.45-2.63 GJ/t	(EC, 2014d)

In the case of styrene, feedstock and energy consumptions are summarised in Table 92. The only feedstock is ethyl benzene. The catalyst used in the reaction deteriorates over time, thus affecting energy efficiency and needs to be replaced (EC, 2014d).

Table 92. Typical feedstock and energy consumptions in the case of styrene production

Raw material	Value ($t/t_{styrene}$)	Source
Ethylbenzene	1.04-1.17	(EC, 2014d)
Energy	**Value**	
Steam	4.86-8.28 GJ/t	(EC, 2014d)
Electricity	70-170 kWh/t	(EC, 2014d)
Heat recovery	0-2.88 GJ/t	(EC, 2014d)

Concerning emissions during ethyl benzene production, they are usually VOCs such as ethylene, ethyl benzene and others. They are estimated to be about 1.3 $kg_{VOC}/t_{ethylbenzene}$, but they are not released in the atmosphere, as they have sufficient calorific value to be used as fuel (EC, 2014b). As a result, the emissions considered in this study are because of the utilities used. They are calculated according to the average value of consumption for each utility and using the appropriate emission factors (Table 6). Emissions in the case of styrene are also calculated accordingly (Table 93). These values are considered to be in accordance with the values reported by (Ecofys, 2009), where the total EU average emissions for ethyl benzene/styrene production is estimated to be 0.887 t_{CO2}/t of both ethyl benzene and styrene (58).

Table 93. Emission factors in the cases of ethyl benzene and styrene production

Emissions	Process	
	Ethylbenzene	Styrene
Steam	74.2 kg_{CO2}/t	460.0 kg_{CO2}/t
Electricity	13.2 kg_{CO2}/t	55.8 kg_{CO2}/t
Thermal	109 4 kg_{CO2}/t	
Total	196 8 kg_{CO2}/t	515.8 kg_{CO2}/t

In the case of integrated plants, consumptions and emissions are assumed to be equal to the sum of the individual plants once the heat recovery from the ethyl benzene process is deducted.

Styrene is a benchmarked product, with value of 0.527 allowance/t (EC, 2011b). The system boundaries of benchmarking include all steps of the process, as well as the emissions related to the production of the electricity consumed. The specific emissions per plant that were calculated according to the literature vales explained in this paragraph were calibrated according to the benchmarking curve.

5.14.3 Best available techniques (BATs)

This paragraph consists of a short description of the techniques that have been identified as having potential to improve energy efficiency and reduce GHG emissions, without implying that the list summarised in Table 94 is exhaustive.

Table 94. Overview of the possible BATs and ITs in the ethyl benzene/styrene industry

BAT/IT	Description	Investment cost (EUR)	Energy savings (%)	GHG Reduction (%)
BAT	Advanced control and optimisation	2 328 300	5 % for all	
BAT	Styrene Advanced reheat technology	Not enough information available		
BAT	Radial flow reactor system	Considered as standard technology		
BAT	Styrene recovery from pygas	No information available		
IT	Simultaneous dehydrogenation of ethyl benzene and ethane	No information available		
IT	Exelus styrene process	46 032 400	40 % for all	

As in all processes, a series of process design decisions lead to either lower emissions or energy savings or both. There are in the market solutions for advanced control and optimisation. The one proposed by Honeywell covers both the ethyl benzene and the styrene production units (Honeywell, 2007). It introduces controllers in the different sections of the integrated process, so as in the first part to maximise the ethylene feed and the ethyl benzene yield and in the second part to maximise the feed to the dehydrogenation reactor while minimising energy consumption in the steam superheater. Another controller aims at maximising the styrene recovery. The benefits achieved are improved product quality control and increase in styrene yield by 0.2 % and in

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(58) The total specific CO_2 emissions from ethyl benzene and styrene production reported in [Ecofys, 2009] is 0.854 $t_{CO2}/t_{products}$, but they have used different emission factors for electricity, fuel and steam than in the current study. By using the values of Table 6, total emissions are 0.887 $t_{CO2}/t_{products}$. The molecular weight of the two substances is 106.17 g/mol for ethyl benzene and 104.15 g/mol for styrene.

operational efficiency (Honeywell, 2007). It has been applied already at a plant in China of SECCO Petrochemical Company Limited. There is no official documentation of the costs of this technology, but an estimation is about EUR 2 to 3 million $_{2012}$, referring to a medium styrene plant of about 380 kt/y (OPT Sensor Srl, 2012). The savings achieved are assumed to reach 5 % for electricity, steam and feedstock.

In modern styrene production plants, managing the operating conditions of the ethyl benzene dehydrogenation reactor so as to minimise thermal reactions is considered important. Thermal reactions can become a significant problem if temperatures are over 655 ^{o}C (Woodle, 2006). Thermal reactions can be hindered if ethyl benzene is not heated directly to the reaction inlet temperature until coming into contact with the catalyst. This is achieved if ethyl benzene comes into contact with the main stream of steam that is preheated to the appropriate temperature just before the catalyst (Woodle, 2006). Reactor design and catalyst configuration are factors that control thermal reactions too (EC, 2014d).

As has been explained already, due ethyl benzene dehydrogenation is favoured by lower pressure and higher temperature. The use of minimum pressure drop radial bed reactors leads to lower operating pressure and therefore lower ethyl benzene feed consumption and reducing by-product formation. It has been the main type of reactor used in the Lummus/UOP technologies (UOP, 2004; Woodle, 2006). The system contains two reactors in the series. The main stream of steam is superheated and is mixed with ethyl benzene (which is already diluted with steam) immediately before entering the first stage reactor. It is also used to reheat the reaction mixture for the second reactor. The cooled steam is then superheated again. The reactor effluent is cooled in a series of three waste heat exchangers. The first stage of waste heat recovery is used in superheating the feedstocks and subsequent stages to produce steam in different pressures. This patented way of heat recovery that does not require compression equipment leads to energy savings. The Fina/Badger styrene process has similar characteristics (Woodle, 2006). This technology has been introduced in the market for several decades and is already applied in more than 50 plants worldwide (Woodle, 2006); as a result, it is considered as standard technology.

Lummus/UOP has developed the Styrene Monomer Advanced Reheat technology (SMART) process based on an oxidative reheat technology and combining it with adiabatic dehydrogenation (UOP, 2004). It is most usually applied as a revamp to existing plants, in order to achieve up to 60 % increased styrene production with minimal capital investment costs (Woodle, 2006). The main characteristic of this technology is that hydrogen is oxidised in the oxidative reheat section to supply the heat needed in the dehydrogenation reaction. This results in elimination of the costly interstage reheater and reduction of the superheated steam requirements (UOP, 2004). Ethylbenzene conversions achieved can be more than 80 %, as consumption of hydrogen shifts the reaction equilibrium toward styrene production (Woodle, 2006). The application of this technology is less appealing, because of its safety risks due to high the temperature mixture of oxygen and hydrogen. Due to its limitations in application and the fact that there is not enough information available concerning its performances and economics, this technology cannot be considered in this study.

As has already been mentioned in the aromatics section (5.7.3), styrene is also present in the pyrolysis gasoline. It is usually not recovered, but new technologies exist and they are based on extractive distillation for recovering it (Gentry and Zeng, 2009). This available technology has been described already in paragraph 5.7.3, so it will not be repeated here. Although there is enough information for its economics, data concerning savings are limited and it is not included in the analysis.

5.14.4 Innovative technologies (ITs)

Two technologies have been identified as emerging for this industry (Table 94).

The first one involves simultaneous dehydrogenation of ethyl benzene and ethane, Ethane is fed to the dehydrogenation reactor along with ethyl benzene and a catalyst capable of producing both styrene and ethylene is used (ChemSystems, 2009b). Ethylene is recovered and used as feed to the alkylation. Ethane is cheaper than ethylene, but according to a study by SRI Consulting, operating and capital cost charges related to the separation and recycling of ethane/ethylene offset any price advantage (Baker et al., 2005). It would make sense only in areas of the world where ethane and ethylene differences of about 90% in pricing. More recently, though, there has been a new styrene production process, starting from a gas mixture of ethane and ethylene (Saipem SpA, 2010). The process is described in detail in the patent submitted (Saipem SpA, 2010) and the stream at the end of the dehydrogenation reactor consists of styrene (2-35 %w/w), ethylene (1-20 %w/w), ethane (25-75 %w/w) and ethyl benzene (2-40 %w/w). The advantage of this technology is that the ethane and ethylene do not need to be separated after steam cracking and as a result, energy is saved because of the distillation that is avoided. The technology has only been tested in pilot plant level, as a result there is no available information concerning performances.

The second one is a novel catalytic technology to produce styrene from toluene and methanol, called the Exelus styrene monomer process (ExSyM) (US Department of Energy, 2012). It aims to produce styrene from lower cost raw materials than ethylene with a use of a novel catalyst in a single-step process. It is based on the alkylation reaction of toluene with methanol to produce styrene, hydrogen and water (Exelus, 2013). The reaction has been known for years, but yields have been low. Exelus, with the support of the US Department of Energy, developed a proprietary solid catalyst and reactor design improvements that enable styrene production in mild conditions (1 atm and 425 ^{o}C) that achieve styrene selectivity 80 % (Exelus, 2013). Feedstock consumptions are 1.38 $t_{toluene}/t_{styrene}$ and 0.92 $t_{methanol}/t_{styrene}$.

The benefits from ExSyM process are lower cost feedstocks and energy savings due to elimination of dehydrogenation of ethyl benzene that is energy demanding (Exelus, 2013). The endothermic alkylation reaction of toluene is about 50 % less endothermic than the equivalent of ethylene and energy savings are estimated to be about 40 % (US Department of Energy, 2012). Environmentally, the process has 40 % lower GHG emissions and the hydrogen produced may be recovered and reused (US Department of Energy, 2012). As it is not clear from which part of the process the GHG emissions are saved and in order to avoid double counting of the benefits of the innovative technology, in the present study we have chosen to follow the conservative choice of taking into consideration only the energy savings. Investment costs to build a new plant based on ExSyM process with capacity 250 kt/y was about USD 63 million $_{2012}$, while retrofitting would cost USD 10-15 million $_{2012}$, while the cost of a conventional plant was USD 125 million (US Department of Energy, 2012). The technology is currently in long term testing of the catalyst (Exelus, 2013).

6 Model

This chapter describes the model developed to analyse prospective scenarios of the industry up to 2050. The goal of the model is to illustrate the potential trend of energy consumption and GHG emissions for the European chemical industry. As the first part of the study, the model follows a bottom-up approach, basing the prospective trend of the industry as a whole on an analysis at plant level of the cost-effectiveness of potential retrofits. Therefore, the model individually analyses the cost-effectiveness of new investments in the best available techniques and innovative technologies for each European chemical plant. The potential retrofits are the ones described for each product in chapter 5. The model has been implemented in MatLab (matrix laboratory) and was developed in its primary form by ALTRAN under the auspices of contract no. 108530 to the European Commission, JRC-IET Petten.

The basic assumptions in the model are:

- it does not deal with international trade in the chemical sector;
- all investment costs are expressed in EUR_{2013}.

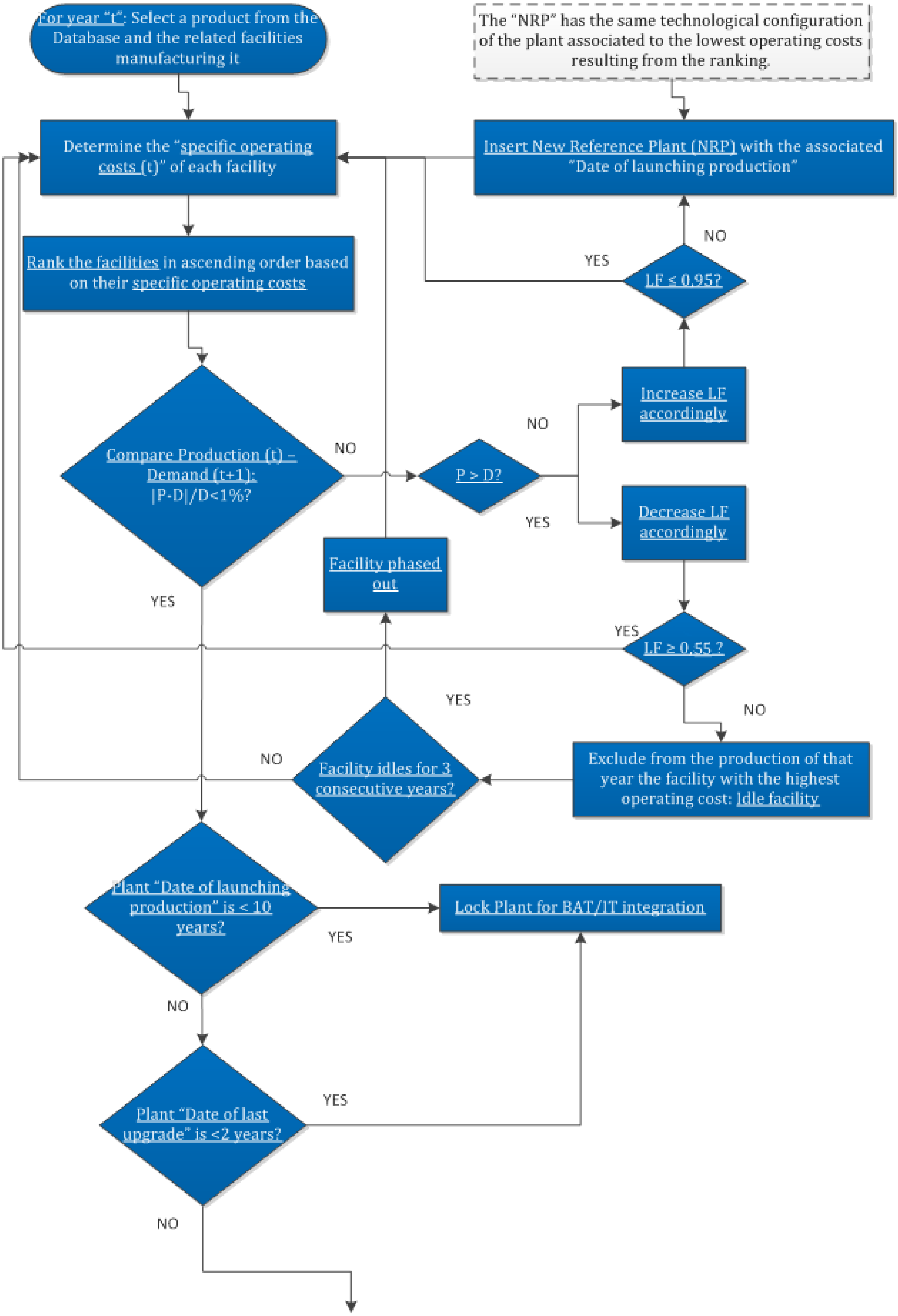
The starting year of the simulation is 2013, as it corresponds to the latest information collected for the current status of the industry, and it works in an iterative way up to 2050, which means that the cost effectiveness-analysis is carried out year by year. The core of the model is the decision-making criterion of investments in new BATs and ITs.

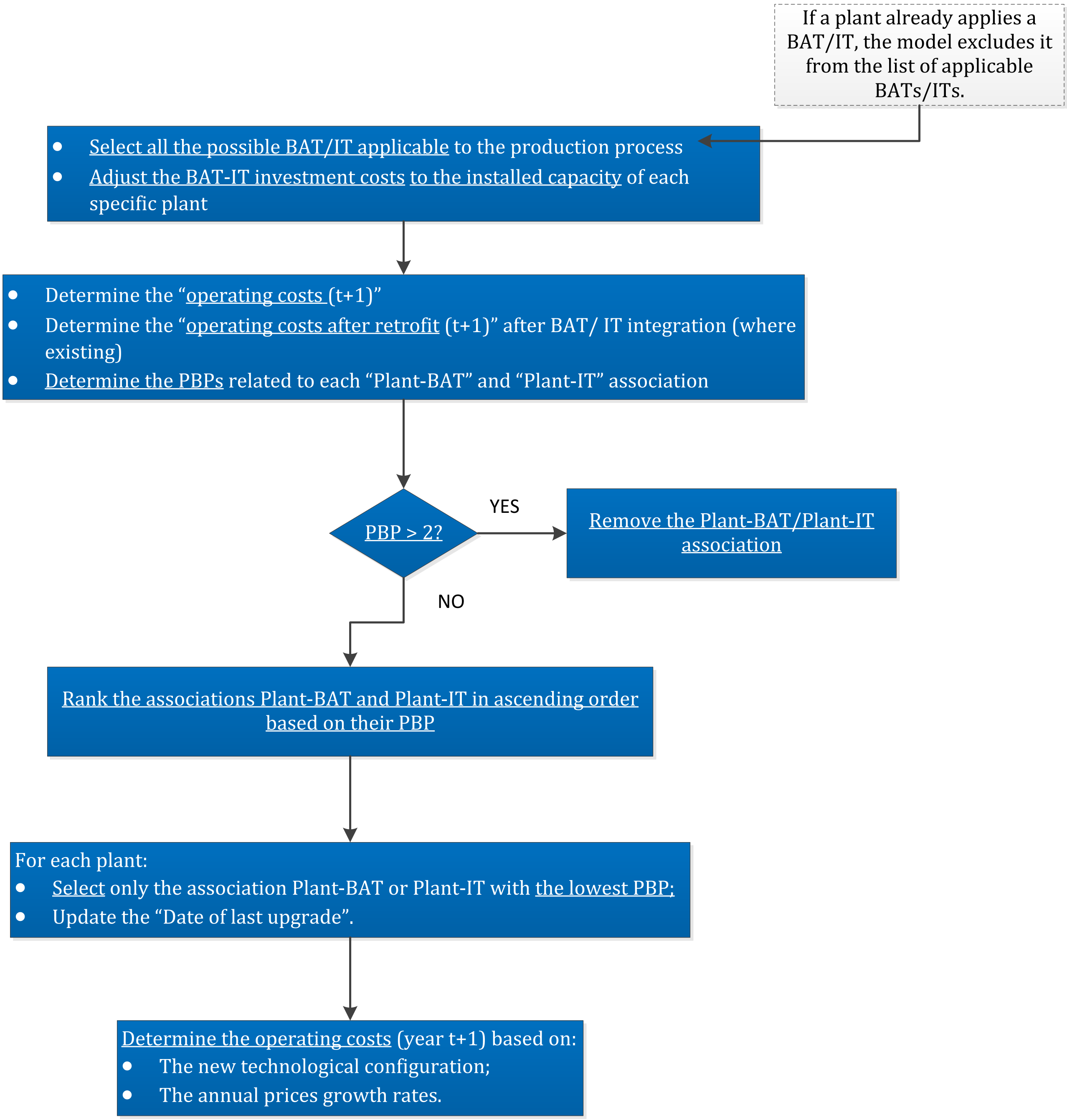
Figure 26 illustrates the logical path followed by the model for the determination of the annual technological configuration of the industry. This logical path can be divided in the following steps:

1. Calculation of operating costs,
2. Comparison of production and expected demand and
3. Cost-effectiveness analysis

These steps are detailed in sections 6.2, 6.3 and 6.4. Once all steps are completed, the loop restarts for the next year.

Figure 26. Flow chart of the logical path of the model





6.1 Basic input in the model

For each year, the model operates at plant level considering a series of input data from the database compiled during the first part of the study. The values for these input data are based on literature and commercially available.

The data that are related to the plant are:

- Plant name and location
- Installed capacity
- Type of product produced
- Type of process in use

- Year the plant started operation and year of last update
- Load factor
- Fuels in use
- Plant performances in terms of energy consumptions, GHG emissions and feedstock use
- List of BAT measures already installed in this plant
- BATs/ITs applicable to each process

Regarding the BAT/ITs, the information included is:

- The process to which it can be applied
- Investment costs
- Operation costs
- Savings in terms of energy and feedstock consumption
- Savings in terms of emissions
- Year of availability (only in the case of ITs)

Future trends taken into consideration are:

- Trends in demand of the products
- Trends in the prices of fuels and products
- Trends in the price of CO_2 emissions

For the future projections used in the modelling, the general assumptions followed are based on the Reference Scenario of the European Commission at the time of writing (EC, 2013).

Concerning the products, studies projecting trends to 2050 forecast that global chemical sales will grow by about 3% per year (UNEP, 2012). For the individual products, future projections available in the literature extend usually only up to five years ahead. Notwithstanding the short-term projections for the evolution of the global demand described in chapter 5, it is assumed that during the simulation period 2013-2050 the demand follows the GDP growth rates according to the Reference Scenario (EC, 2013).

6.2 Step 1: Calculation of operating costs

When starting the simulation, the model selects all the plants that produce a specific product. A first estimation of operating costs is performed and the plants are ranked based on their specific costs. The production is first allocated to plants with the lowest operating costs and then gradually assigned according to increasing operating costs.

The calculation of operating costs is based on the following equation:

$$\text{Annual operating costs} = \text{Annual variable costs} + \text{Annual fixed costs}$$

Variable costs are associated with the manufacturing of the products; therefore they depend on the annual production and on the facility technological configuration. They are composed of the costs for:

Raw materials

They are evaluated for each plant, based on the feedstock consumption associated to the process used in that facility. The estimation incorporates the effect of BATs already present, and it is done according to:

*Annual raw material costs = Σ(Process Feedstock consumption * Feedstock price)*(1-BAT feedstock reduction)*Production*

Electricity bought from the grid

The cost for electricity is based on the specific electricity consumption of each process, the production and the price of electricity. The estimation of the amount of electricity bought from the grid takes into account the self-production, calculated as explained in Chapter 4. The value for the price is based on Eurostat (Eurostat, 2016c) and it corresponds to the average of the price for industrial users weighted according to the facilities producing ammonia, steam cracking and methanol, as indicative of the chemical industry.

Fuels consumed in the process

As in the case of electricity, energy costs due to fuel consumption are determined by the process thermal requirements, the production and the price of fuels. The presence of CHP affects the thermal requirements and its effect is incorporated into the model following the methodology explained in Chapter 4.

CO2 emissions allowances

If the CO_2 emissions of any plant exceed its free allowances defined by (EC, 2011b; EC, 2012d) and provided in Table 7, the extra emissions generate costs. These costs are calculated according to the formula:

$$\textit{Annual } CO_{2.eq} \textit{ emissions allowances costs} = (\textit{Specific } CO_{2\cdot eq} \textit{ emissions} - \textit{Benchmark emission value}) * \textit{Production}$$

On the other hand, fixed costs are connected to (Sinnott, 2005):

- Operating labour: Costs of operating labour would not normally exceed 15% of the total operating costs;
- General overhead: 50-100% of operating labour costs;
- Supervision: 20% of operating labour costs;
- Local rates: It covers local taxes and is typically 1-2% of capital costs;
- Insurance costs: Typically 1-2% of capital costs;
- Maintenance: 5-10% of capital costs;
- Royalties: 1% of capital costs.

Investment data for each type of facility included in this study are collected from the literature and are summarised in Table 95. These investment costs are adjusted to different capacities according to the following formula (Perry's Handbook, 2008):

$$\textit{Investment cost} = \textit{Investment cost}_{Ref} * (\textit{Capacity} / \textit{Capacity}_{Ref})^{n}$$

The exponent n may vary from 0.4 to 0.9, but the average value for chemical equipment is 0.6 (Perry's Handbook, 2008).

Capital costs are then determined considering the depreciation of the initial investment. An operating lifetime of 10 years is assumed, corresponding to a depreciation rate of 10% (Sinnott, 2005). The equation applied is:

$$Capital\ cost = Investment\ cost * Depreciation\ rate * \frac{(1 + Depreciation\ rate)^{Lifetime}}{(1 + Depreciation\ rate)^{(Lifetime-1)}}$$

Table 95. Investment costs and reference capacity of new plants for each product

Product	Reference capacity (kt/y)	Investment cost (million EUR$_{2013}$)	Data Origin
Nitric acid	324	39.8	(Hydrocarbon Processing, 2001)
Steam cracking [1]	300	297.6	
Acrylonitrile	80	94.7	
Ammonia	400	158.2	
Urea	1 120	223.9	
Adipic acid [2]	160	182.8	(Chemicals Technology, 2012f)
Hydrogen	20	27.3	(Hydrocarbon Processing, 2001)
Methanol	500	153.8	
Soda ash [3]	800	211.0	(Process Worldwide, 2012)
Aromatics [4]	1 070	543.8	(Chemicals Technology, 2012e)
Carbon black	130	100.7	(Chemicals Technology, 2012)
EO	20	14.8	(Hydrocarbon Processing, 2001)
MEG	300	178.7	(Oil & Gas Journal, 2001)
EDC [5]	550	550.9	(Chemicals Technology, 2012b)
VCM	180	119.6	(Hydrocarbon Processing, 2001)
PVC [6]	300	170.0	(Chemicals Technology, 2012d)
Ethyl benzene	450	47.2	(Hydrocarbon Processing, 2001)
Styrene	180	66.1	
Chlorine	800	105.8	(Chemicals Technology, 2012b)

[1] Ethylene production

[2] Complex that manufactures both adipic and nitric acid, with a total production capacity equal to 160 kt/y

[3] Plant manufacturing both soda ash and calcium chloride, with a total installed capacity equal to 800 kt/y

[4] Aromatics complex; production capacity of 655 kt/y of paraxylene (PX), 355 kt/y of benzene and 60 kt/y of toluene;

[5] Ethylene dichloride (EDC) and caustic soda complex, with a production capacity of 300 kt/y of EDC and 250 kt/y of concentrated caustic soda;

[6] PVC included the production of PVC-S, PVC-E and PVC Recycled.

6.3 Step 2: Production vs expected demand

Once the facilities are ranked based on their specific operating costs, the overall production capacity is verified and compared to the product demand. In case of a mismatch, the code modifies the load factors, accordingly. In this phase, some plants may be mothballed or new ones can be included, depending on the value assumed for the load factor. In case of decreased demand, the model idles the facilities with the highest operating costs. If a facility idles for more than 3 years, the facility is phased out.

If the demand of a product increases from year ‘t’ to the following year ‘t+1’, the model increases the load factor, exploiting the potential production of the sector. The upper limit for the load factor has been defined based on the highest value of load factor in 2013 for the processes considered in the study (equal to 0,89), that, for a major flexibility, was further increased, taking as ‘maximum load factor value’ a load factor equal to 0,95.

If the demand for a product decreases from year ‘t’ to following year ‘t+1’, the model reduces the value of the load factor until an estimated fixed minimum value. This ‘minimum load factor’ is estimated based on the lowest value of load factors in 2013 (equal to 0.63 for xylenes). As in the upper case, we allow a further decrease adopting 0.55 as the ‘minimum load factor value’ feasible.

Modeling of the future technological asset of the chemical and petrochemical facilities in the EU-28 during the observation period (2013-2050) required the introduction of new plants. Those plants have been allocated in the European domain in order to satisfy the future foreseen demand for each specific product, whenever the process load factor reached the defined upper limit.

The technological features associated to the new reference plants (NRP) have been based on the specific operating costs of current plants and the prevailing production process for each chemical product. These two conditions assure that all of the NRPs related to the manufacturing of the same product have the same technological asset: type of process, use of BATs (including CHP), use of ITs, type of fuel, capacity. This way, the model selects annually as NRPs exclusively plants that have the most economic operational costs for each product.

Nevertheless, the technologic configurations of NRPs change over-time, based on the effects of retrofits on the specific operating costs in the previous year. Eventually, the load factor of the process in use in the NRPs will be the one resulting from the balancing of production and demand for a product in a determined year.

6.4 Step 3: Cost-effectiveness analysis for integrating BATs and ITs

Once the demand is satisfied, a cost-effectiveness analysis is performed at plant level to assess the new BATs/ITs integration.

In order for a facility to be considered able to revamp, its technological configuration through the integration of a BAT or an IT, it should satisfy both the following requirements:

- A facility has started operation more than 10 years ago and
- The last upgrade in it was more than 2 years ago.

These conditions are based on the assumptions that new plants have already the best available efficiency and that the initial investment for them has not been totally depreciated yet.

For each eligible facility, the software selects the corresponding BAT/IT applicable to the production process in use, excluding those already applied and checking the compatibility with the other processes in use within the plant. By definition a BAT is available from the first year of the simulation, while ITs can be incorporated only after their assumed year of availability.

The decision-making criterion selected to establish the profitability of an investment in BAT-IT is the payback period (PBP). The payback period is defined as the period of time during which the initial capital expenditure of an investment is recouped (Perry's Handbook, 2008). It is calculated according to the following formula, based on the investment costs for the retrofitting and the difference of the annual operational costs before and after retrofit:

$$\text{Payback Period} = \text{Investment cost}_{Retrofit} / (\text{Operational costs}_{Old} - \text{Operational costs}_{New})$$

The investment costs for retrofit are determined in a similar way as the investment costs of new plants, explained before. The information for the reference case derives from the literature and these values are scaled for the capacity of each facility in the database.

The model restricts retrofitting to only one per year for each facility. For this reason, in the case that several retrofits for the same plant comply with the illustrated criterion, the model selects the technology with the lowest PBP and verifying if this value is lower than 2 years:

- If YES, the software integrates in the plant the selected BAT/IT, updating in the database the date of last upgrade;
- If NOT, the integration of the BAT/IT is not accepted and the final OUTPUTS can be issued.

As application of BATs/ITs may lead to reductions on consumptions or GHG emissions, thus resulting in a decrease in operating costs, the OPEX is re-calculated. Once the cost-effectiveness of all potential retrofits in each plant is analysed for each year, the year number is increased by one and the cycle starts again.

7 Input scenarios

This chapter includes the description of the scenarios developed to model the energy consumption and GHG emissions trends in the industry up to 2050.

The following chapter analyses the results of following scenarios:

1. Baseline scenario

   It is based on the information presented so far. The state of the industry in 2013 is taken into consideration and the trends are based on the 2013 EU Energy and GHG emissions reference scenario (EC, 2013).

2. Fuel price variations (AS1)

   Since fuels costs represent one of the largest expenses for the chemical industry, variations in their prices are expected to affect the facilities in an important way. The three variations in this case are:

- Low fuels prices, corresponding to the prices of the baseline scenario;
- Medium fuels prices, where the final prices of the fuels in 2050 is twice the baseline prices (AS1a);
- High fuels prices, where the final prices of the fuels in 2050 are five times the corresponding prices of the baseline scenario (AS1b);
- Very high fuel prices, where the final prices of the fuels in 2050 are ten times the corresponding prices of the baseline scenario (AS1c).

3. CO_2 price variations (AS2)

   The ETS is expected to play an important role in the EU and affect the industries that fall under its scope. Therefore, the price of CO_2 is an important input for the model and the respective scenarios. Despite the fluctuation in the price of CO_2 in Europe in the recent years (Figure 4), the EU reference scenario foresees an increase in these prices at a level as high as EUR 100/t_{CO2} in 2050 (EC, 2013). Other sources provide more conservative projections and even a total collapse of the CO_2 price (IHS CERA, 2012). As a result, we analyse three cases with respect the price of CO_2:

- Low CO_2 price, corresponding to the prices of the baseline scenario;
- Medium CO_2 price, in which the final CO_2 price in 2050 is twice the baseline price (AS2a);
- High CO_2 price, in which in 2050 the final CO_2 price is 5 times the baseline price. (AS2b);
- Very high CO_2 price, in which the final CO_2 price in 2050 is ten times the baseline price (AS2c).

As explained in Chapter 6.4, the driver selected to establish the profitability of an investment in BAT-IT is the payback period (PBP). In all of the above mentioned scenarios, the Payback time is set to be up to 2 years.

8 Results

This chapter includes the simulation results and the analysis of the energy consumption and GHG emissions trends of the chemical industry in the EU up to 2050, under all the assumptions and scenarios explained in the previous chapters of this study. The first section includes the overall energy consumption and GHG emissions in the baseline scenario for the whole sector.

8.1 Total energy consumption and GHG emissions trends

The baseline scenario takes as reference the evolution of the chemical and petrochemical industry, assuming that the future demand for the products and the prices for $CO_{2.eq}$ allowances, fuels and feedstocks follow the assumptions of the 2013 EU Energy and GHG emissions reference scenario (EC, 2013).

Figure 27 provides an overview of the trends of the total energy consumptions resulting from the simulation for the baseline scenario. Total energy includes all electricity and thermal energy, as well as energy incorporated as feedstock. It includes two cases, in the first one (red line) no retrofits are allowed in the sector, while in the second case (blue line) retrofits are happening, and as a result BATs or ITs are integrated in the facilities. In 2050 the chemical and petrochemical sector is expected to use in total 5 740 PJ if retrofits do not take place and 5 515 PJ if BATs/ITs are installed, resulting in 225 PJ or 4 % savings. Compared to 2013, the total energy consumption will increase 39.2 % if retrofits are installed, whereas the production will increase 45.6 %.

Figure 27. Trends of the total energy consumption (electricity, thermal and feedstock) in the EU chemical and petrochemical industry, according to the baseline scenario

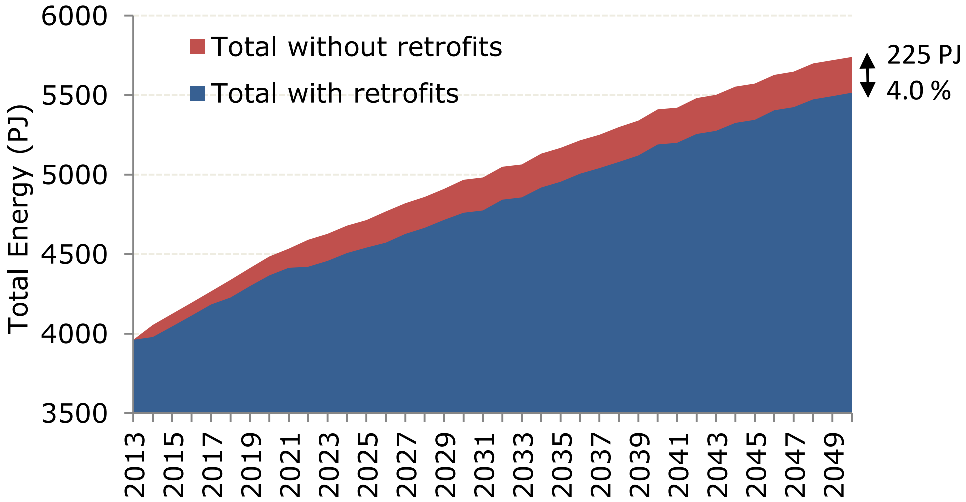


Figure 28 shows the trends of the energy incorporated in the products as feedstock, thermal energy and electricity directly accounted in this study. From 2013 to 2050, electricity and thermal energy consumption grow 14.5 % and 17.2 %, respectively; whereas the energy incorporated as feedstock grows 47.2 %.

Figure 28. Trends of production, electricity, thermal energy consumption and energy incorporated as feedstock in the EU chemical and petrochemical industry if retrofits are allowed, according to the baseline scenario

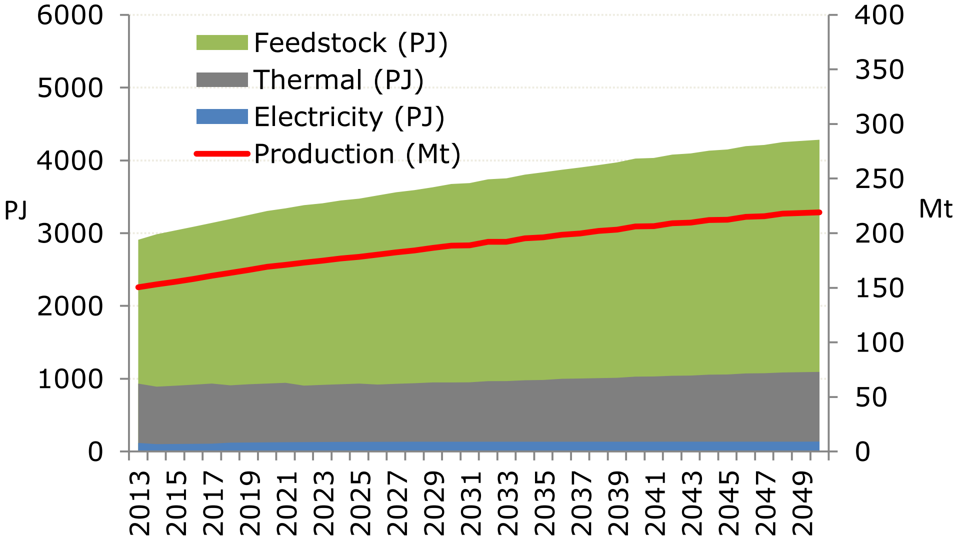
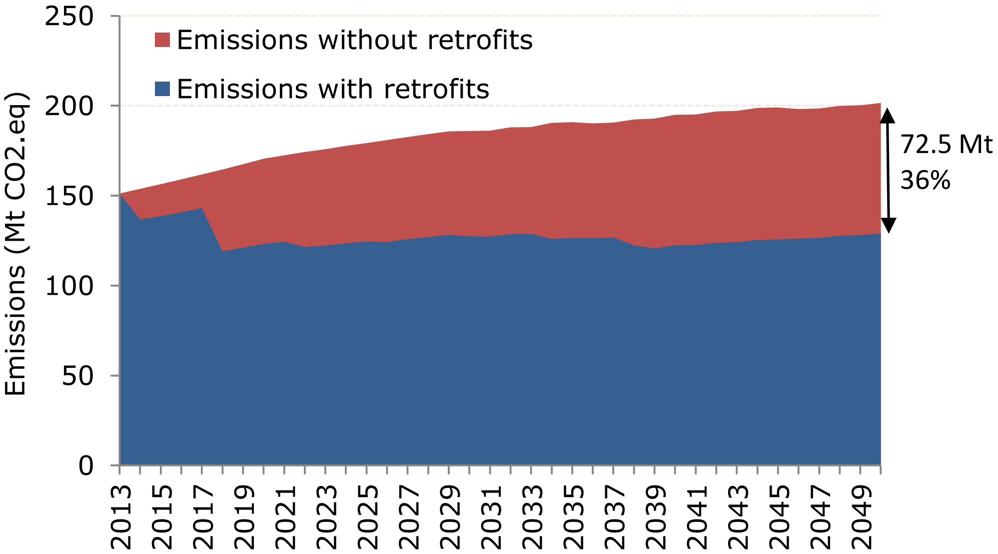


Figure 29 depicts the trends of GHG emissions with or without retrofits. The savings between the two cases are more remarkable than in total energy consumption. If the industry did not incorporate any retrofits in the period 2013-2050, by 2050 the GHG emissions would amount to 201.5 Mt $CO_{2.eq}$. The installation of BATs/ITs will reduce this amount to 129 Mt $CO_{2.eq}$, that is, delivering 75.5 Mt $CO_{2.eq}$ or 36 % savings.

Figure 29. Trends of total GHG emissions ($Mt_{CO2.eq}$) in the EU chemical and petrochemical industry, according to the baseline scenario



The first set of alternative scenarios (AS1) analyses the impact of the prices of energy and feedstock in the sector. Two cases are considered. In both of them the price of any type of energy (fuels or electricity) in 2050 is increased. In AS1a the increase is twofold, in AS1b fivefold and in AS1c tenfold compared to the baseline scenario. In both cases the initial values in 2013 are the same, but the annual growth rates have been increased by a constant increment per type of energy, so that the appropriate price in 2050 is reached. However, none of the alternative scenarios varying the energy price offers any remarkable difference compared with the baseline scenario. The reason behind this apparently strange behaviour is that: with the values considered in the baseline scenario the industry already incorporates practically all BATs at hand; as well as all potential ITs as soon as they become available. This makes that the more favourable conditions to energy-efficiency investments of the alternative scenarios are not able to foster additional savings to the already achieved in the baseline scenario

The second set of alternative scenarios (AS2) analyses the impact of the prices of CO_2 allowances in the sector. Again several cases were considered, with increasing values for the allowances, twice, five and ten times the final value of the CO2 allowances in the baseline scenario. And again, the results are quite similar to the baseline scenario; the maximum saving provided by the most favourable scenario delivers 0.8% of additional CO2 to the baseline 36.8 % instead of 36 %.

The behaviour of the individual chemical products in the different scenarios will be presented in detail in the following section. Although there is a variety of technologies that can serve as BATs or ITs, the ones that have been identified to be influenced by both the increase in fuel and CO_2 allowances prices concern ammonia and hydrogen.

8.2 Results per product

The following paragraphs demonstrate in detail the results disaggregated per product. As a starting point, the trend in total energy consumption and total GHG emissions in the baseline scenario are discussed and the analysis of the influence of the alternative scenarios in the specific energy consumption and GHG emissions follows. Due to the large amount of graphs and results that are produced, only the cases which show some interest are presented. The application of the available best or innovative techniques is also argued.

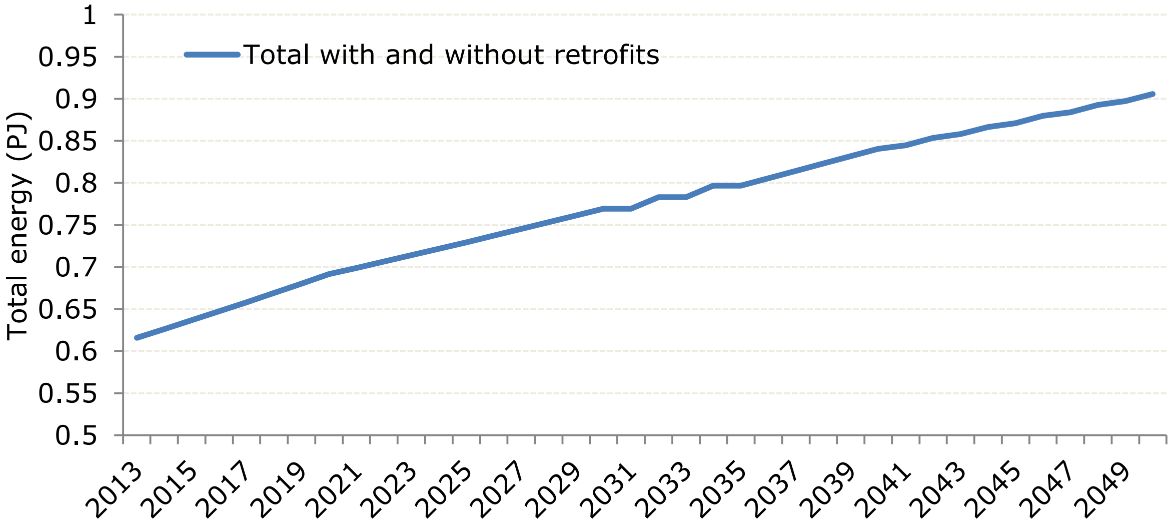
Concerning the two cross-cutting technologies (Chapter 4.5), CHP is already installed to a large extent in the chemical industry. The results show new CHP is foreseen installed in facilities producing: adipic acid, benzene, ethylbenzene, ethylene dichloride, vinyl chloride monomer, PVC-S and PVC-E. In total, there will be 2750 MW new electrical capacity, producing 9.4 TWh/y electricity. The new the CHP units are dimensioned according to the thermal needs of the processes. Only 12% of the electricity produced via CHP is consumed inside the processes. The excess (88 %) is assumed to be sold, so as to return financial benefit to the facilities. Most of the new capacity is installed in the first years of the simulation.

On the other hand, CCS is installed in all three subsectors that are sources of high purity CO_2. In the case of ammonia the technology becomes popular only in the part of the industry that is not integrated with urea production, but it is only expected, as CO_2 is usually consumed in producing urea. In the hydrogen industry, about half of the facilities install CCS, while in the ethylene oxide subsector 70 %.

8.2.1 Nitric acid

The production of nitric acid is based on a strongly exothermic reaction, and therefore the amount of energy consumed for heating is low, but the process results in production of N_2O emissions. As described in Chapter 5.1.3, the BATs applicable in this industry have an effect exclusively on $CO_{2.eq}$ emissions.

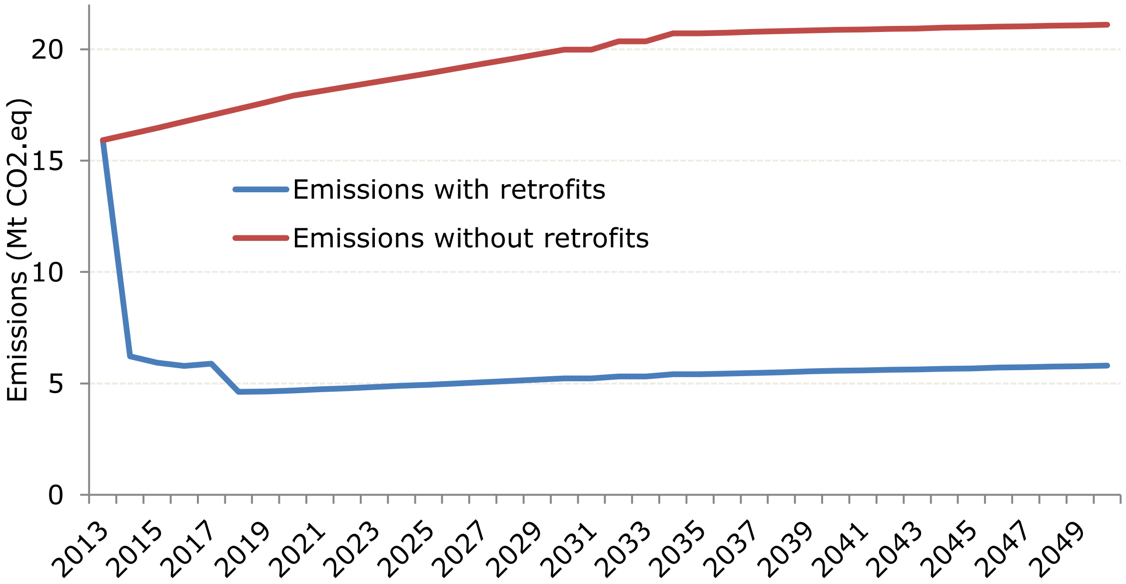
Figure 30. Trends of total energy consumption in the nitric acid industry, according to the baseline scenario



Due to these characteristics the energy consumption curves with or without retrofits (Figure 30) overlapp each other under all different scenarios of this study. The results are similar for all different alternative scenarios, so only the trends according to the baseline scenario are presented.

On the other hand, the application of BATs leads to substantial decrease in the GHG emissions from the early years of the simulation (Figure 31). The savings reach up to 75%. The reason for this change is the great interest in the chemical industry to decrease N_2O emissions. The specific emissions have the same behaviour as the total emissions and they are not depicted in a figure. By considering the production in 2050 and the specific emission factors in 2013 and 2050 if retrofits are allowed, the savings in emissions will be 75 % or in absolute terms 17.5 $Mt_{CO2.eq}$.

Figure 31. Trends of total GHG emissions ($Mt_{CO2.eq}$) in the nitric acid industry, according to the baseline scenario



As a conclusion, all the changes are decided in the first years of the simulation. Before 2020 more than 80 % of the nitric acid plants will have adopted at least one of the three available BATs, favouring primary and secondary abatement measures, mostly due to the higher cost of tertiary measures.

8.2.2 Ammonia and Urea

For the production of ammonia there are seven BATs available, while for urea none other than CHP, as described in Chapter 5.2.3. According to the baseline scenario, in 2050 the ammonia industry can save 26 % in total energy and 48 % of GHG emissions if BATs are adopted compared to the case without BATs. The trends in total energy is depicted in Figure 32 while the ones in total GHG emissions in Figure 33. the case of urea, since there are no specific BATs available and the industry has already installed to a large extent CHP, the results do not show any difference between allowing or not BATs or alternative scenarios.

Figure 32. Trends of total energy consumption in the ammonia industry, according to the baseline scenario

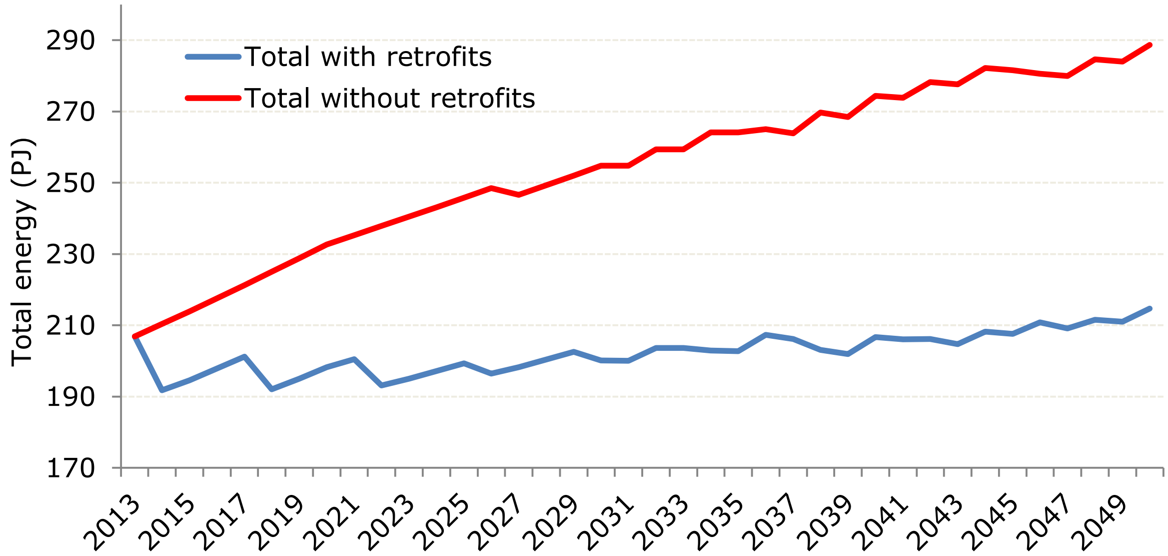
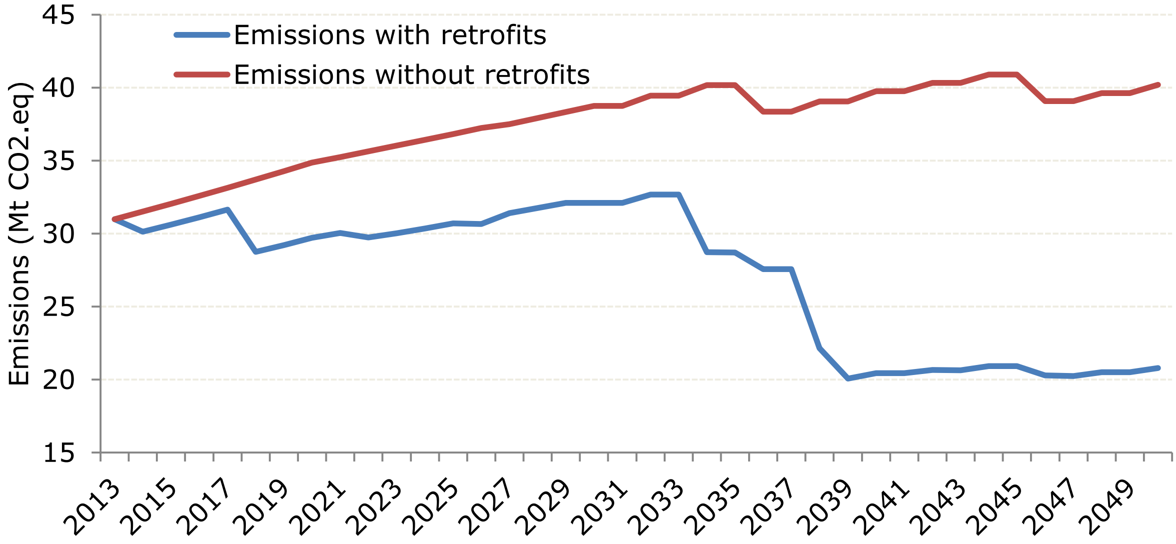


Figure 33. Trends of total GHG emissions ($Mt_{CO2.eq}$) in the ammonia industry, according to the baseline scenario



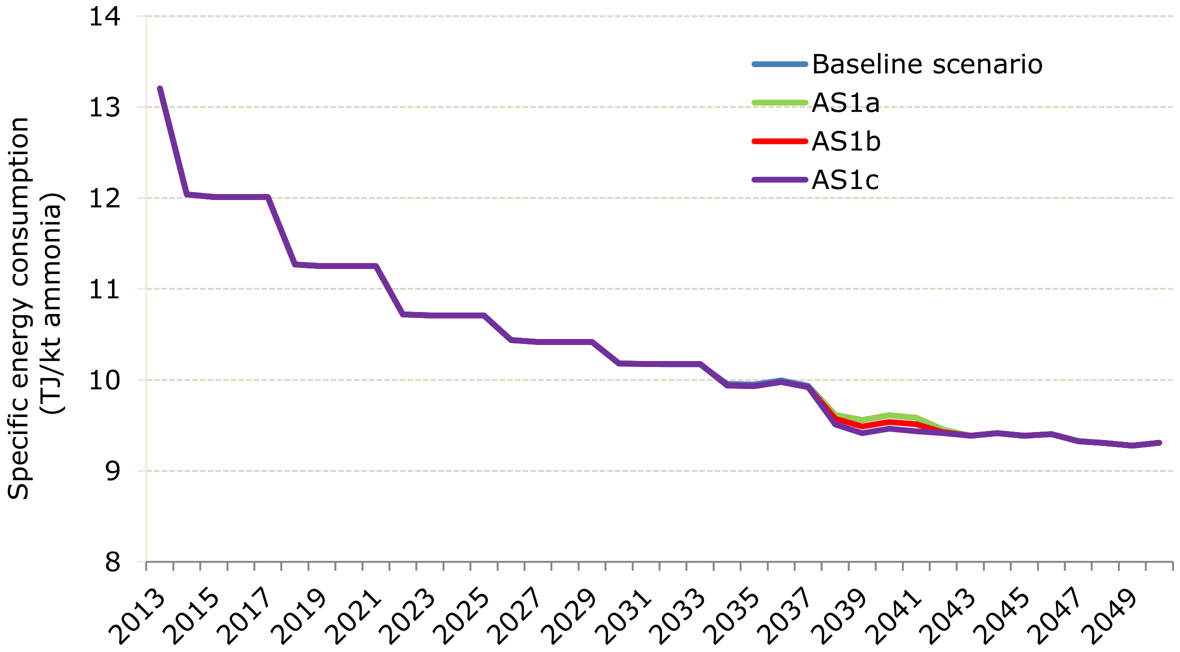
Concerning the type of BATs adopted, by 2020 about 85% of the facilities will have been revamped so as to improve their efficiency and 90% will have adopted improvements in the reforming section. On the other hand, BATs such as heat exchange auto thermal reforming becomes cost effective after 2025; pre-reforming, and the process with reduced primary reforming and increased process air, after 2030. Based on the assumptions done in this study, production of ammonia using hydrogen from water electrolysis is not adopted before 2050 because of its high investment costs.

Besides CCS, there are three ITs available in the ammonia industry. 90 % of the facilities are foreseen to adopt the new reforming concept from 2040 onwards, while at the same period CCS becomes interesting for the plants that are not integrated with urea production. In the case of 2 facilities hydrogen from natural gas catalytic partial oxidation becomes cost-effective, while ammonia synthesis from electricity does not get adopted before 2050, as seen for the water electrolysis BAT.

Ammonia is one of the few chemical products considered in this study that is affected by higher fuel and CO_2 allowances prices. If fuel prices increase adoption of pre-reforming is slightly delayed until 2035 and CCS is applied in 27 % less facilities until 2040 and 18 % onwards. It should be noted that the ammonia industry consisted of 39 facilities in 2013 and it is foreseen to remain rather constant until 2050, so in absolute values CCS does not become cost effective for one fifth of the industry. The behaviour in the case of CCS is opposite if CO_2 allowances prices increase, but the re-reforming concept is less adopted.

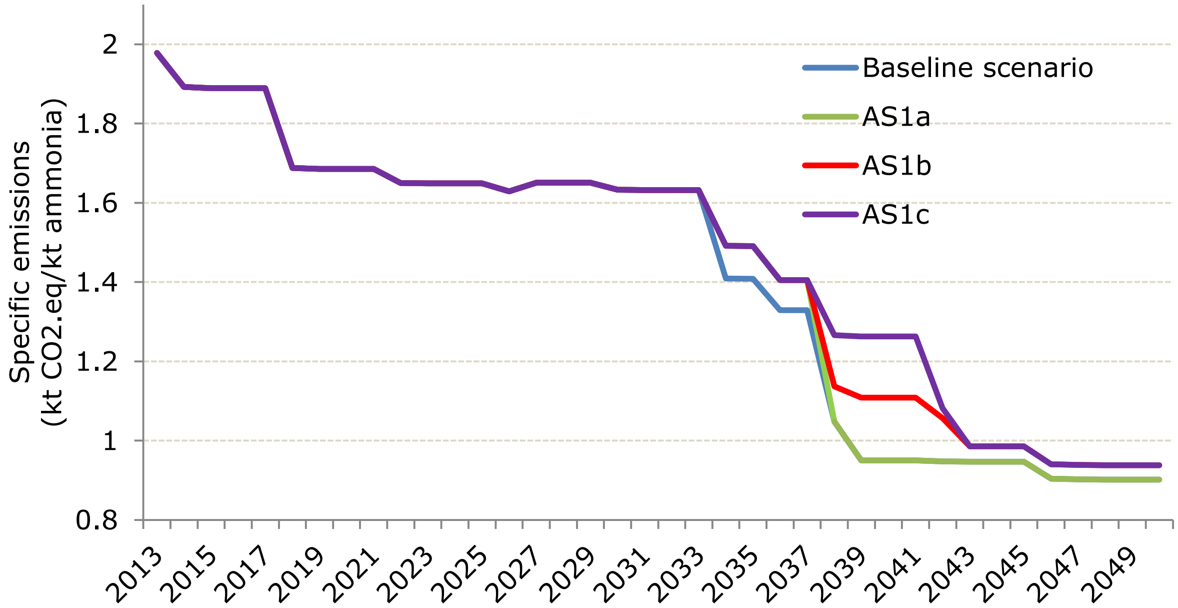
The specific energy consumption decreases as the production increases and BATs are adopted (Figure 34), but the rate of decrease is hardly influenced by the price of fuels or CO_2 allowances. The difference among the scenarios in the period 2038-2042 can be attributed in the delays in adopting the technologies, as discussed in the previous paragraph. The savings if we compare the specific emissions in 2013 and 2050 multiplied with the production in 2050 reach 54 % and in absolute terms 24.8 $Mt_{CO2.eq}$.

Figure 34. Evolution of the specific energy consumption (TJ/kt_{NH3}) in 2013-2050, according to the baseline scenario and the fuel prices alternative scenarios



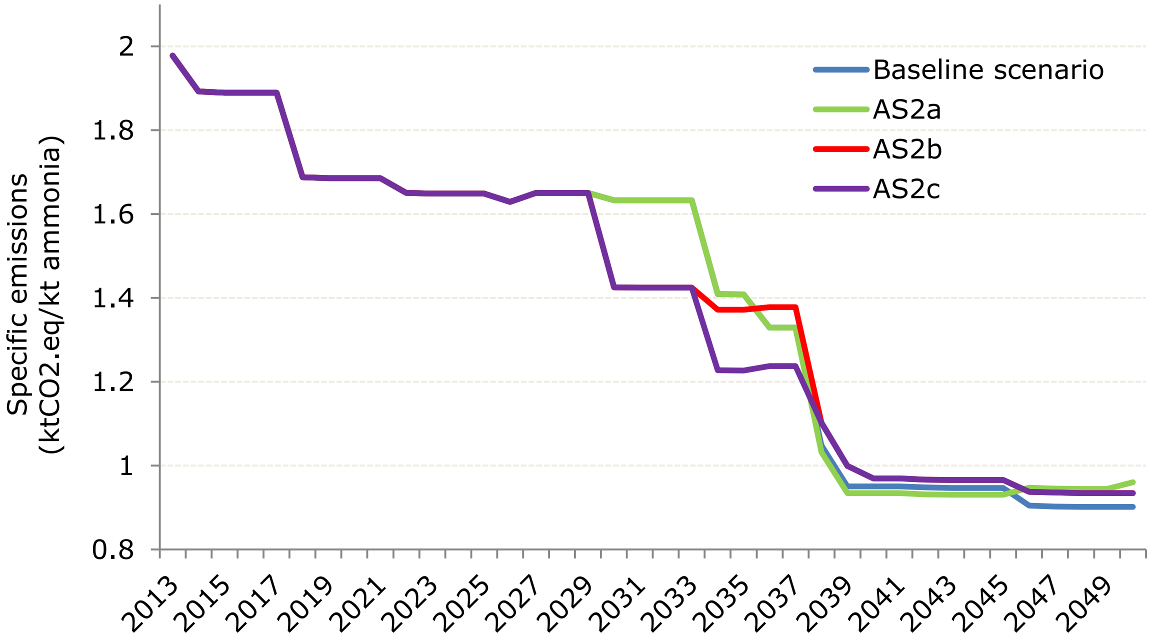
The fact that increasing the fuel prices results in slower adoption of the BATs affects the specific emissions of the industry (Figure 35). In 2050, the final value in the baseline and AS1a scenarios is 0.9 $kt_{CO2.eq}/kt_{NH3}$; in the AS1b and AS1c scenarios is 0.94 $kt_{CO2.eq}/kt_{NH3}$. The initial value in 2013 is 1.98 $kt_{CO2.eq}/kt_{NH3}$

Figure 35. Evolution of the specific emissions ($kt_{CO2.eq}/kt_{NH3}$) in 2013-2050, according to the baseline scenario and the fuel prices alternative scenarios



For the alternatives scenarios where the price of CO_2 allowances is increased, the specific emissions decrease faster and reach a lower minimum than in the case of the baseline scenario (Figure 36), clearly due to CCS. In 2050 the specific emissions in all scenarios is around 0.93 $kt_{CO2.eq}/kt_{NH3}$..

Figure 36. Evolution of the specific emissions ($kt_{CO2.eq}/kt_{NH3}$) in 2013-2050, according to the baseline scenario and the allowances prices alternative scenarios

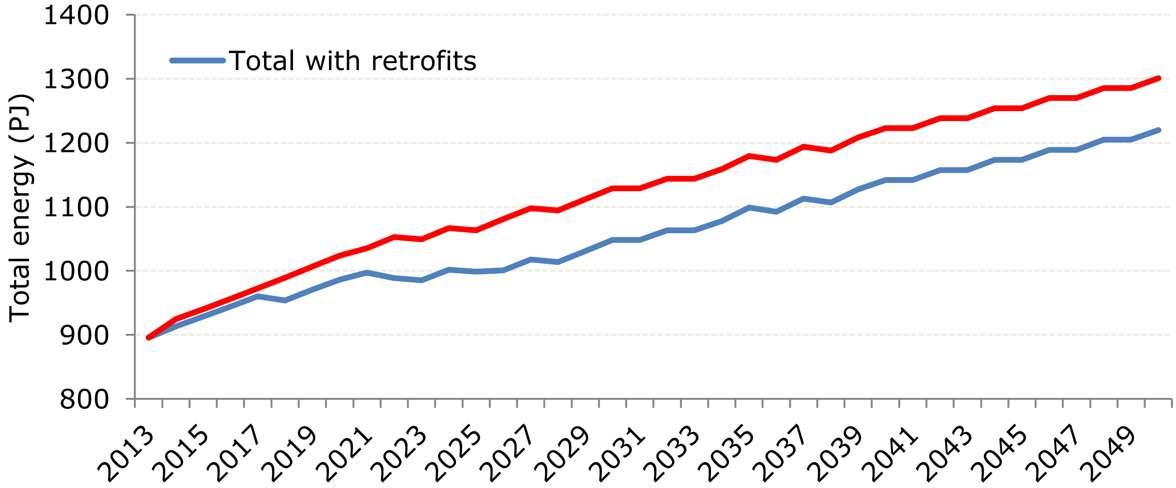


In the case of urea there is no difference in the behaviour of the industry among the alternative scenarios; while in the case of ammonia facilities integrated with urea production, CCS is only marginally adopted and after 2035. This result is rather expected, as CO_2 is used in the production of urea. Comparing the specific emissions in 2013 and 2050 and based on the production of 2050, the savings are only 3.7% or in absolute terms 18 $kt_{CO2.eq}$.

8.2.3 Steam cracking

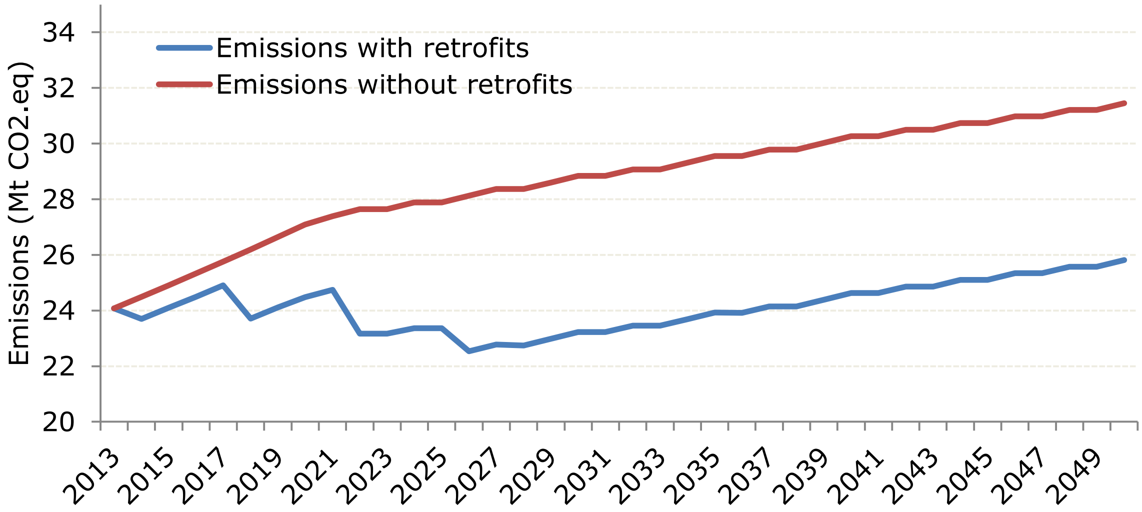
As has been explained already, steam cracking is one of the basic processes in the chemical industry and it has been the major source of light olefins for more than half a century. As a result this sector has already gone through several optimisation cycles.

Figure 37. Trends of total energy consumption in ethylene production, according to the baseline scenario



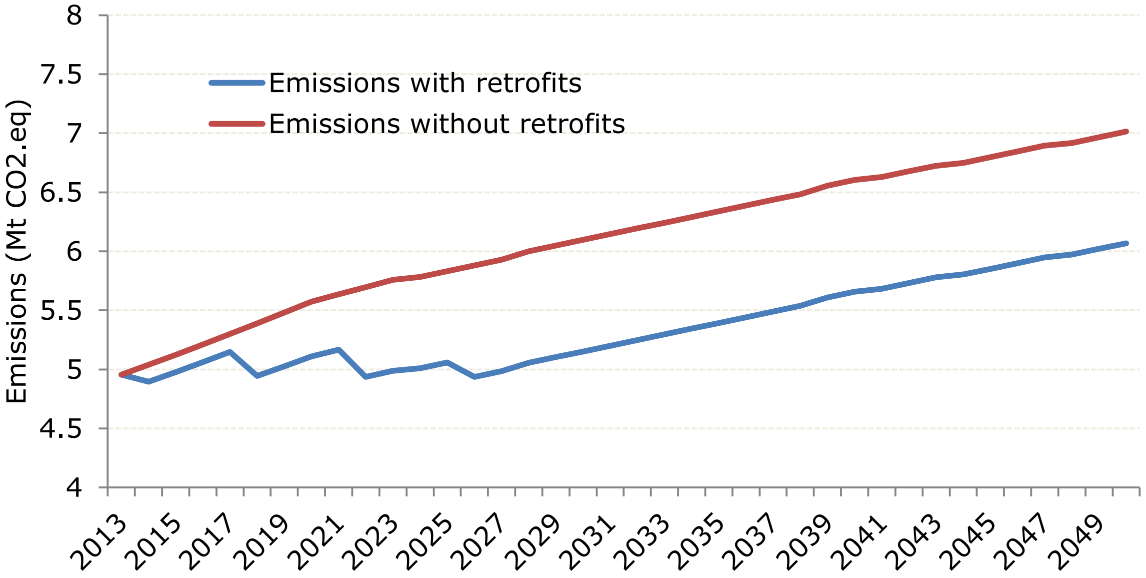
Ethylene is the main product of steam cracking. According to the baseline scenario, if the ethylene producing industry adopts BATs the savings in energy will be from 1 % to 3 % until 2020, will reach 7 % by around 2030 and 6.2% by 2050 (Figure 37). When comparing this figure with (Figure 27) we can check the relevant role if this subsector in the whole industry. On the other hand, in total GHG emissions the savings build up to 20 % until 2025 and 18 % by 2050 (Figure 38).

Figure 38. Trends of total GHG emissions ($Mt_{CO2.eq}$) in ethylene production, according to the baseline scenario



The second product of steam cracking considered in this study is propylene, which can be produced also via fluid catalytic cracking, as explained in Chapter 5.3.1. There are no savings in the trends of total energy consumption for this product if BATs are installed or not, while the savings in total GHG emissions reach maximum 16 % in 2025 and are expected to be 13.5 % in 2050 in the baseline scenario (Figure 39).

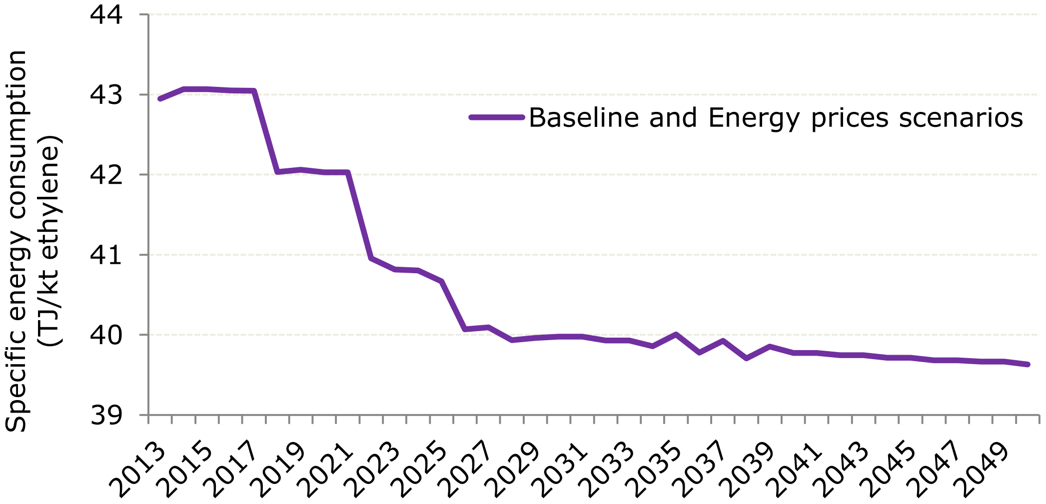
Figure 39. Trends of total GHG emissions ($Mt_{CO2.eq}$) in propylene production, according to the baseline scenario



Concerning the type of BATs available, there are two technologies involving improvements in steam cracking, the first one in the furnace design and the second one in the compression and separation section (Chapter 5.3.3). Until 2020 both of them are adopted by at least half of the industry that includes both steam crackers and FCC.

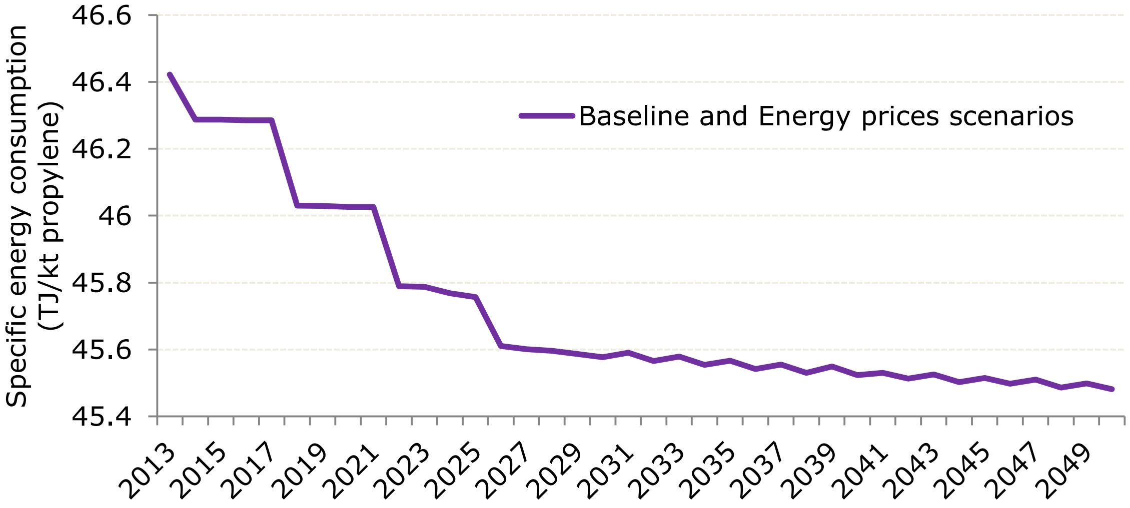
Besides BATs, there are also two innovative technologies for steam cracking, explained in detail in chapter 5.3.4. The adsorption heat pump seems to be adopted by big part of the industry in the period 2020-2035, while improvements in the separation and compression section via membranes application occurs from 2027 to 2040. These technologies decrease both the energy consumption and the GHG emissions, contributing to half of savings obtained at the end of the simulation. The rest of the savings are thanks to the BATs.

Figure 40. Evolution of the specific energy consumption (TJ/$kt_{ethylene}$) in 2013-2050, according to the baseline scenario and the fuels prices alternative scenarios



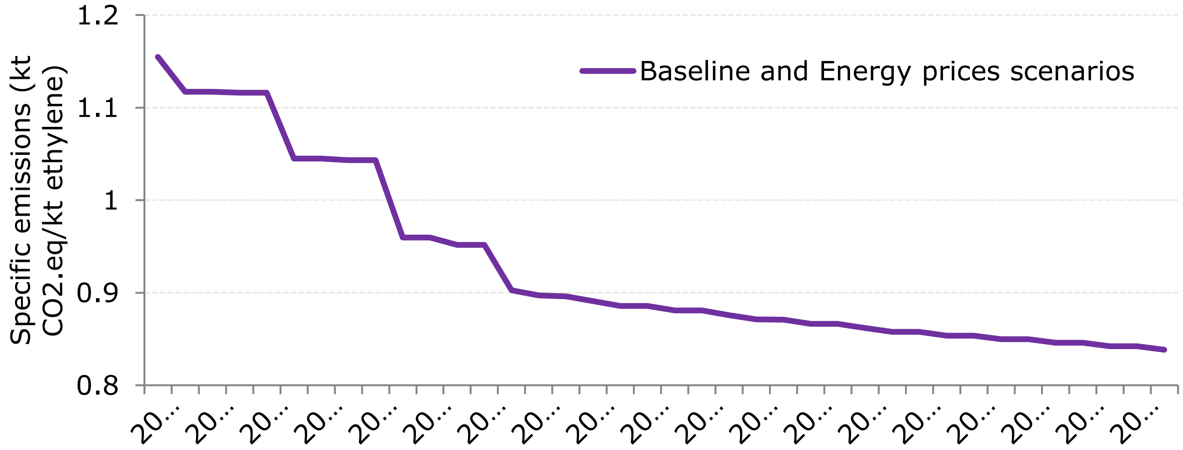
The specific energy consumption in both ethylene and propylene production is decreasing as the volumes produced increase and BATs are adopted (Figure 40 and Figure 41). The decrease rates of specific energy consumption for the ethylene or propylene are not influenced by the price of fuels or CO_2 allowances.

Figure 41. Evolution of the energy consumption (TJ/$kt_{propylene}$) in 2013-2050, according to the baseline scenario and the fuels prices alternative scenarios



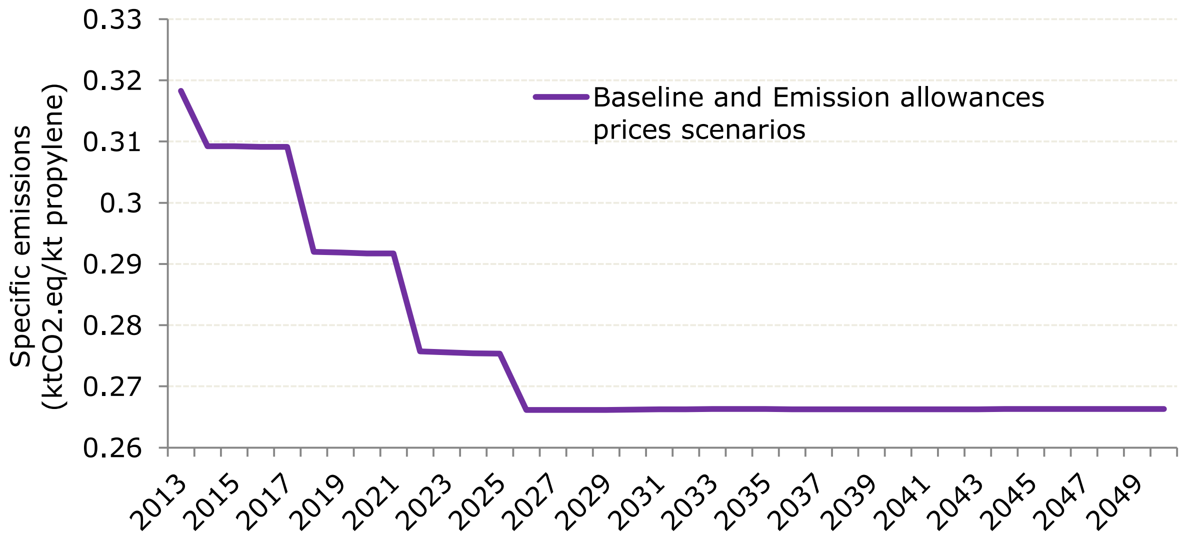
In the case of specific emissions in ethylene production (Figure 42), increasing the price of fuel prices or CO_2 allowances does not influence the rate of achieving the minimum emission factor. In 2050 the ethylene emission intensity is 0.83 $kt_{CO2.eq}/kt_{ethylene}$, while in 2013 1.12 $kt_{CO2.eq}/kt_{ethylene}$. Based on these values multiplied with the ethylene production in 2050, the savings calculated amount in 8.6 $Mt_{CO2.eq}$ or almost 25%.

Figure 42. Evolution of the specific emissions ($kt_{CO2.eq}/kt_{ethylene}$) in 2013-2050, according to the baseline scenario and the fuels prices alternative scenarios



In the case of the specific emissions of propylene, the influence of both fuel and CO_2 allowances prices is not significant. The industry achieves the minimum emission factor in all scenarios around 2026 and it is 0.267 $kt_{CO2.eq}/kt_{propylene}$ (Figure 43).

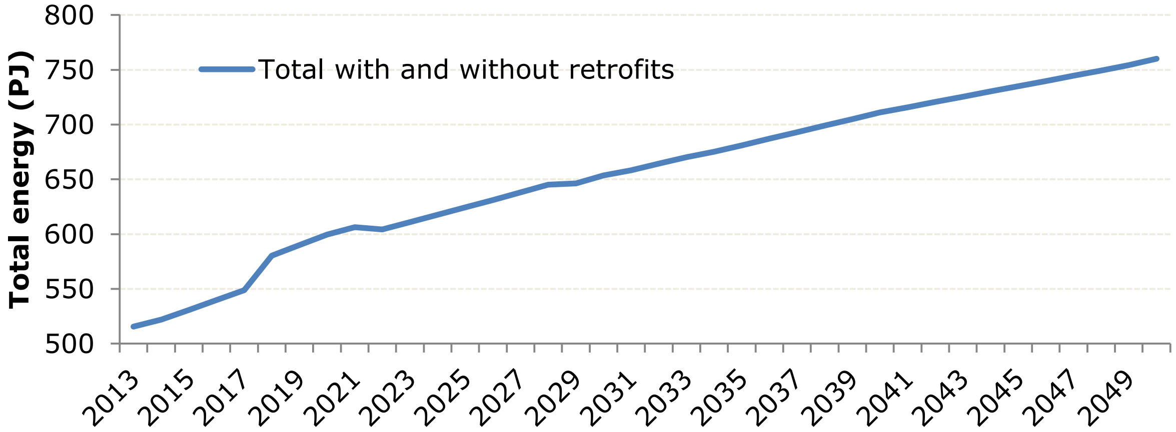
Figure 43. Evolution of the specific emissions ($kt_{CO2.eq}/kt_{propylene}$) in 2013-2050, according to the baseline scenario and the allowances prices alternative scenarios



8.2.4 Hydrogen and Methanol

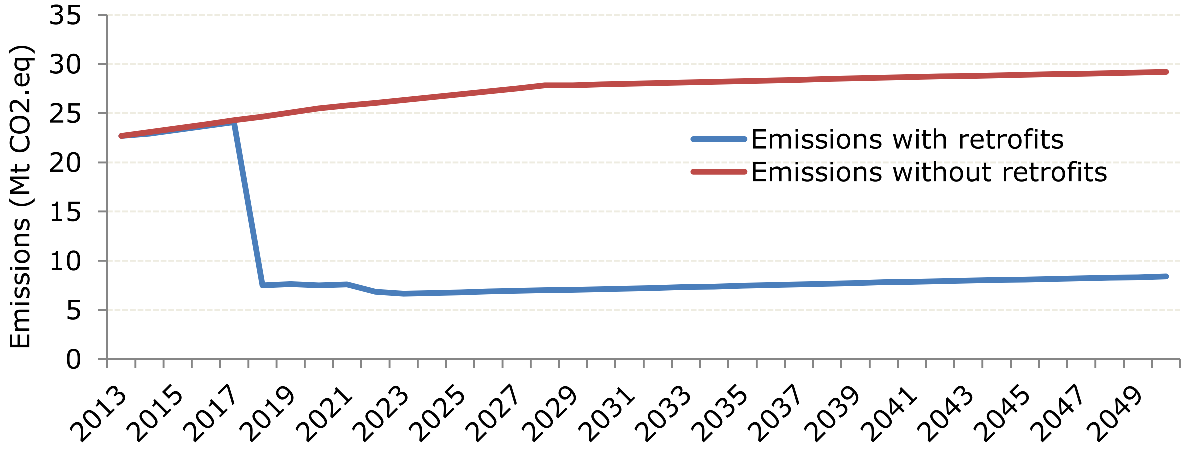
In order to model the complex hydrogen industry, five different processes were considered (Chapter 5.4.1), together with two processes for methanol production, which utilises hydrogen as feedstock. It is also one of the subsectors in the chemical industry with promising processes affecting the non-energy use, such as electrolysis that decreases the fossil fuel used and the GHG emissions, but increases significantly the electricity consumption of the facility. As a result its adoption is not widespread (less than 10% of the industry coverts to it) and the total energy consumption of the hydrogen industry does not appear to decrease with or without retrofits (Figure 44). Another BAT that is adopted by a large part of the industry is preheating of the combustion air, thus recycling energy, but its influence in the energy consumption is not noticeable.

Figure 44. Trends of total energy consumption in hydrogen production, according to the baseline scenario



On the other hand, total GHG emissions are influenced by the adoption of BATs or ITs (Figure 45). Regarding innovative technologies, there are four that are considered in this study: the use of biomass as feedstock, improvements in the steam methane reforming, catalytic partial oxidation of natural gas and CCS. They are all described in detail in Chapter 5.4.4 and Chapter 4.6.2. The use of biomass of feedstock does not seem to become cost effective so as to be adopted by the industry, but about 40 % of the hydrogen industry retrofits improvements in the steam methane reforming from 2020 onwards. In addition, catalytic partial oxidation of natural gas is adopted by a few facilities as early as 2018. The most important IT is CCS, which is already available in the case of hydrogen. Its adoption is foreseen to start around 2020 by as much as 70 % of the industry at that time (about 140 facilities (59)). This is the reason why GHG emissions in Figure 45 decrease in 2018. Production of hydrogen from electrolysis results in 20 PJ more energy consumed (in the form of electricity) compared to the current status of this subsector. The small increase in emissions in the period 2020-2030 is due to the parallel adoption of improvements in the steam methane reforming, which offsets a bit the savings.

Figure 45. Trends of total GHG emissions in hydrogen production, according to the baseline scenario



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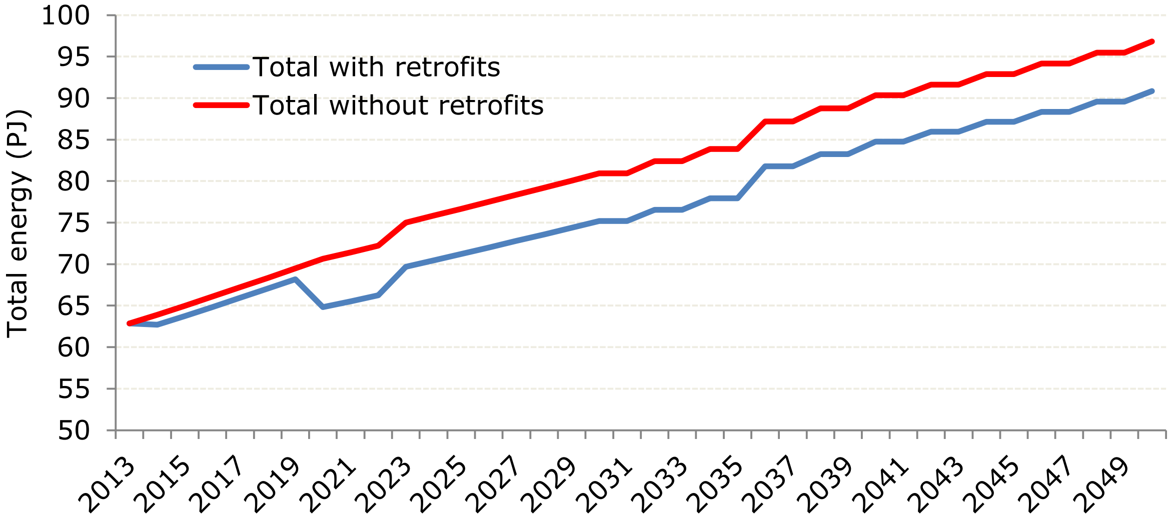
[59] It should be noted that the number of facilities in this study for the hydrogen industry does not correspond to the actual facilities. This is because the production of hydrogen as by-product has been modelled as one fictitious facility per country including all the capacity that is known per country.

Methanol production has also the hydrogen from electrolysis as BAT and shares the innovative technologies with the hydrogen production, with the only exception of CCS. The trends of total energy consumption for this subsector are shown in Figure 46, while the trends in GHG emissions follow a similar behaviour as the energy. Innovative technologies are responsible for 81 % of the emission savings in the case of hydrogen and 75 % in the case of methanol.

Figure 46. Trends of total energy consumption in methanol production, according to the baseline scenario



The effect of electrolysis is even clearer in the specific energy consumption, with the pick observed in 2018 (Figure 47). As production increases and thanks to the rest of the BATs, the specific energy is then decreasing. In the case that fuel prices increase five or ten times more than the baseline scenario, the adoption of natural gas catalytic partional oxidation and CCS is slightly hindered, as a result in 2050 the specific energy in these two scenarios is about 1 % higher. The influence of CO_2 allowances prices in the behaviour of the industry is similar to the fuel prices,

Figure 47. Evolution of the energy consumption (TJ/kt_{H2}) in 2013-2050, according to the baseline scenario and the fuels prices alternative scenarios

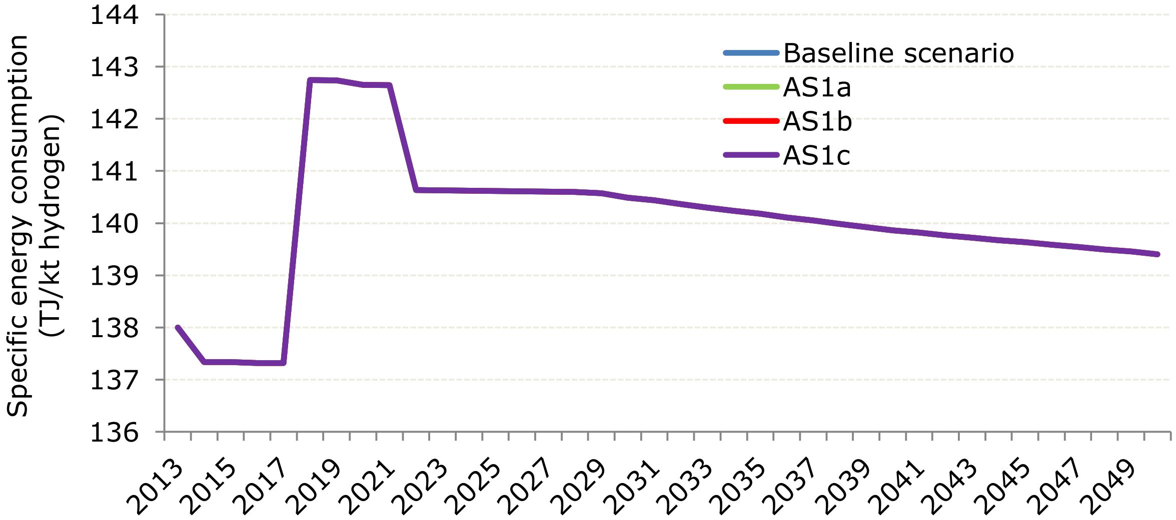
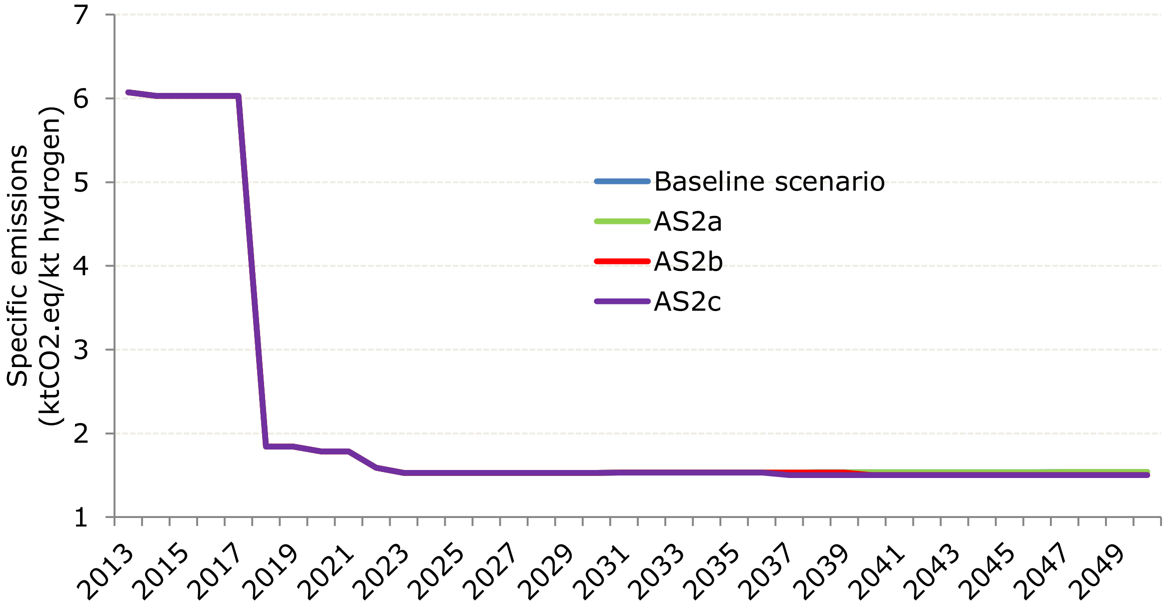


Figure 48 shows that the broad adoption of electrolysis and CCS in the early years of the simulation leads to a sharp decrease of the emission intensity, making ineffective the higher allowances prices considered in the alternative scenarios.

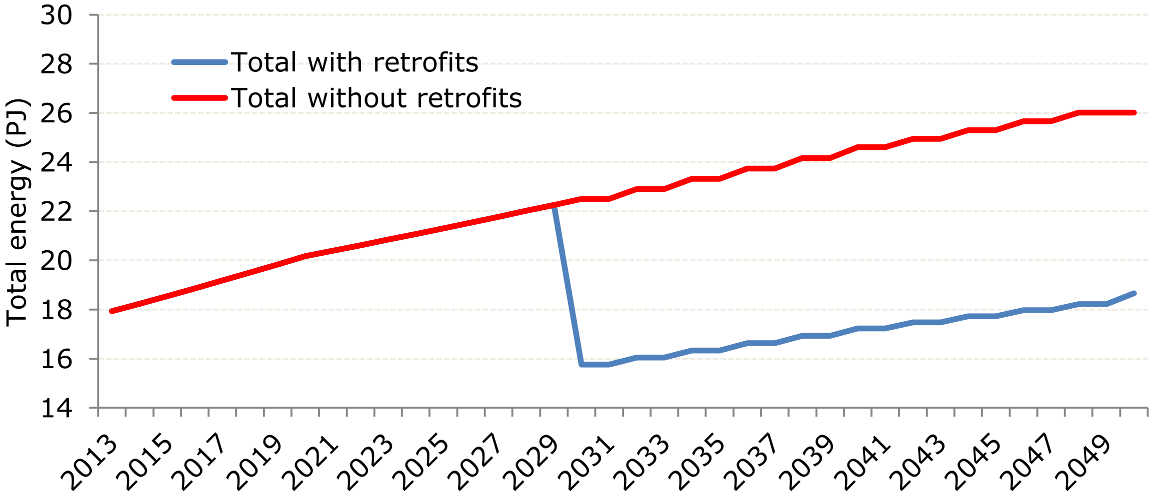
Figure 48. Evolution of the specific emissions ($kt_{CO2.eq}/kt_{hydrogen}$) in 2013-2050, according to the baseline scenario and the allowances prices alternative scenarios



8.2.5 Adipic acid

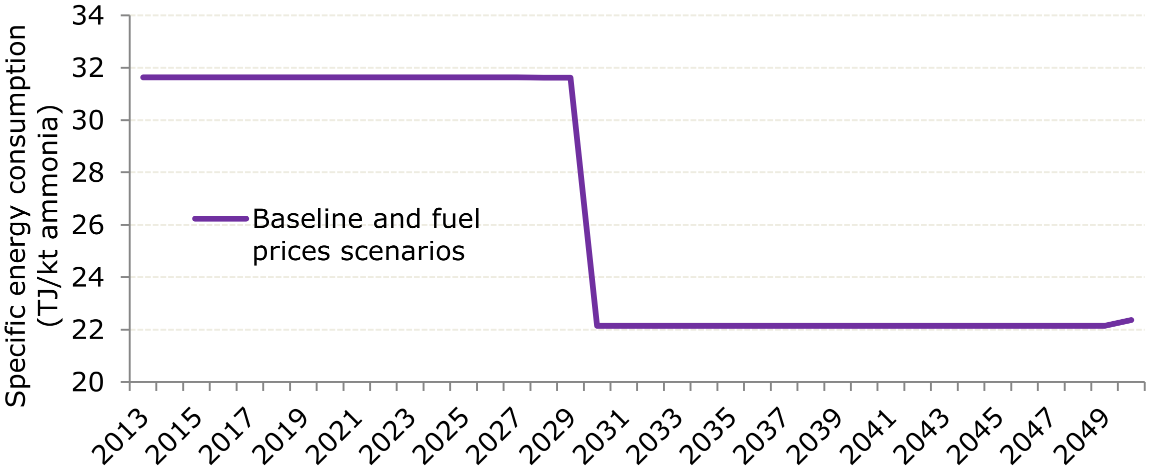
Adipic acid is one of the products in the chemical industry, where changes have already been taking place, as explained in Chapter 5.5, due to the great interest in decreasing N_2O emissions. This subsector consists of only a few plants that have shown interest in adopting end-of-pipe BATs. Only two plants have not been reported to have one of the available BATs in 2013. If these plants also adopt a BAT, the difference in emissions could reach 70 %.

Figure 49. Trends of total energy consumption in adipic acid production, according to the baseline scenario



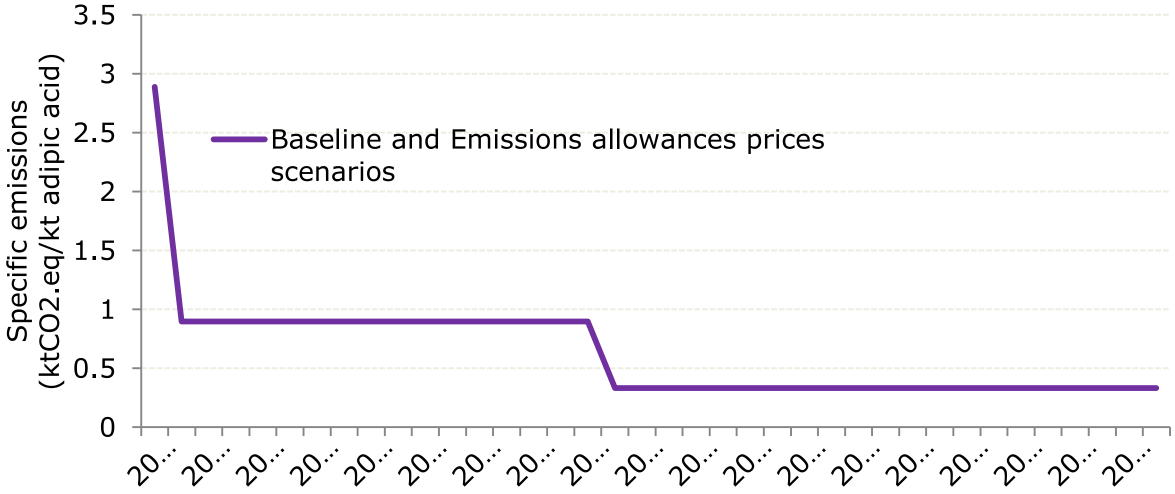
There are three BATs available for N_2O abatement and, according the model, both plants install tertiary measures as early as 2014. CHP is also further installed in the facilities producing adipic acid, adding in total about 20 MW electrical capacity. From the electricity produced per year from CHP 87 % is consumed inside the facilities and the rest (7500 MWh) is sold out. In 2030 there is the next change taking place, when the efficient and environmentally friendly "one-step adipic acid process" becomes available and is adopted by almost all the plants. The description of the IT is done in Chapter 5.5.4. This innovative technology is responsible of the abrupt decrease in the total energy consumption shown in Figure 49.

Figure 50. Evolution of the specific energy consumption (TJ/$kt_{adipic\ acid}$) in 2013-2050, according to the baseline scenario and the fuels prices alternative scenarios



As far as the specific energy consumption and GHG emissions are concerned, the presence of BATs or ITs decrease them significantly, but the adipic acid industry is not sensitive to fuel (Figure 50) or CO_2 allowances prices (Figure 51), as the same changes take place irrespective of the scenario. Specific energy consumption decreases from 31.6 TJ/kt in 2013 to about 22.4 TJ/kt in 2050, thanks to the "one-step" process. Equivalently, the specific emission factors decrease from 2.9 $kt_{CO2.eq}/kt_{adipic\ acid}$ to 0.3 $kt_{CO2.eq}/kt_{adipic\ acid}$, corresponding to 89% savings or in absolute terms 2.1 $Mt_{CO2.eq}$ (based on the 2050 production of adipic acid).

Figure 51. Evolution of the specific emissions ($kt_{CO2.eq}/kt_{adipic\ acid}$) in 2013-2050, according to the baseline scenario and the allowances prices alternative scenarios



8.2.6 Soda ash

All European soda ash is produced using the Solvay process, also called the ammonia soda process (Chapter 5.6.1). For this process there are four BATs available, all described in detail in Chapter 5.6.3. From these four, integrated design and operation is the technology adopted by 11 out of the 17 facilities in 2050, while optimisation of the process to avoid excessive CO_2 emissions by 9 and the vertical shaft kiln by only 3. As a result, if retrofits are allowed, the soda ash industry decreases in 2050 its total energy consumption by about 13 %, as can be seen in Figure 52, and its total emissions by 39 % (Figure 53).

Figure 52. Trends of total energy consumption in soda ash production, according to the baseline scenario

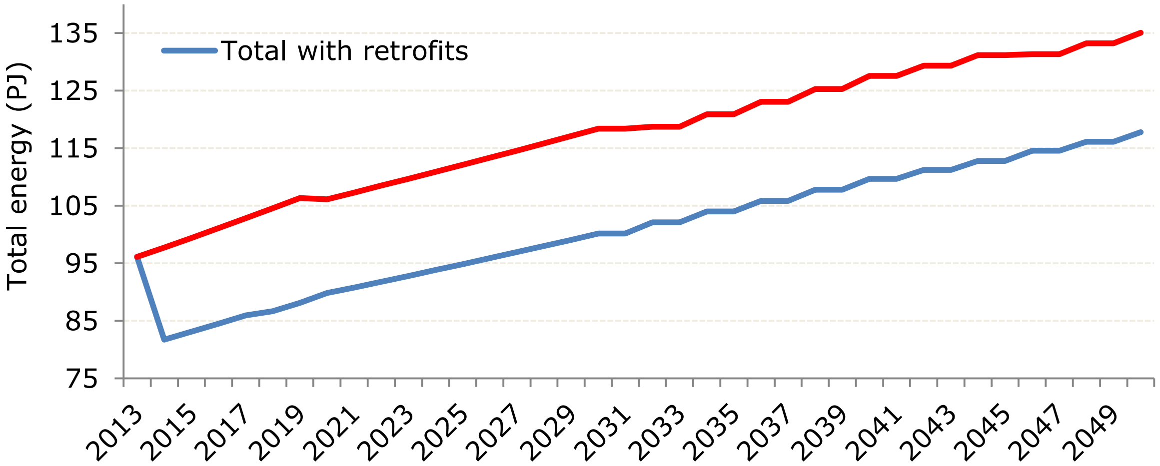
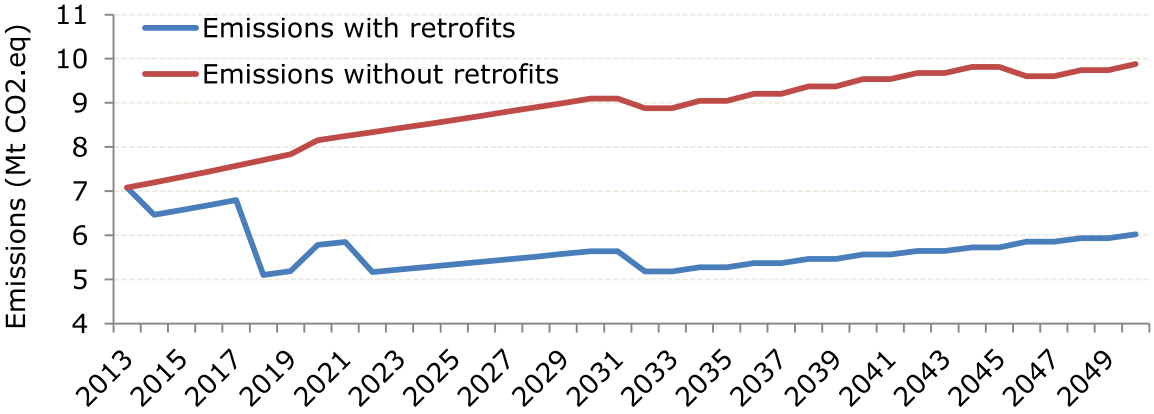
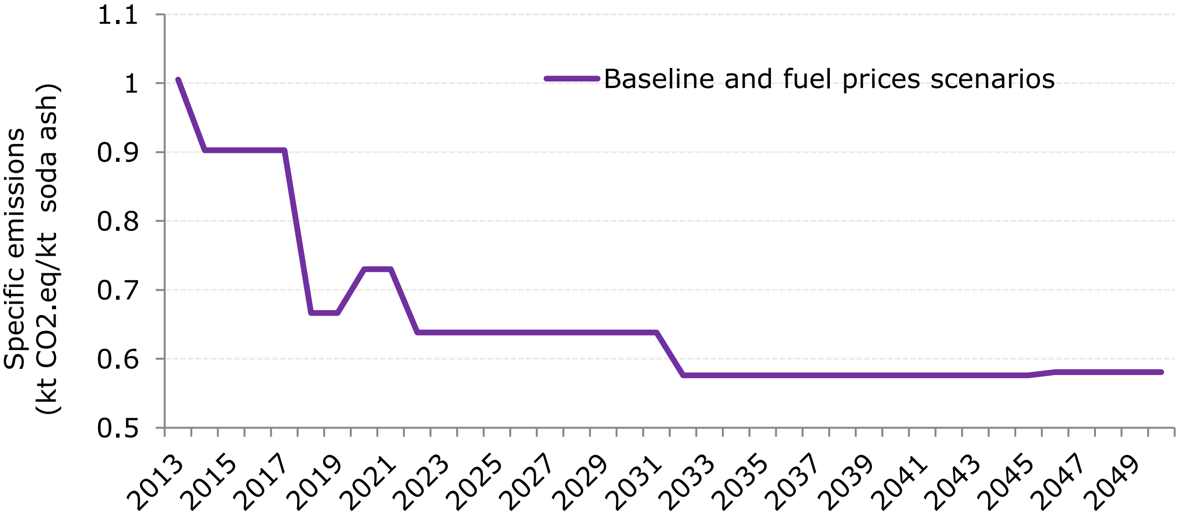


Figure 53. Trends of total GHG emissions in soda ash production, according to the baseline scenario



In 2050, the specific energy consumption is around 11.4 TJ/kt$_{soda\ ash}$ and is affected mostly by the application of integrated design and operation. On the contrary, specific emissions are more influenced by the increase in production and the fact that the facilities are becoming more emission efficient (Figure 54). Increasing the fuel or emission allowances prices does not result in any difference in the evolution of the specific energy or emissions. In 2050 the specific emission intensity is 0.59 kt$_{CO2.eq}$/kt$_{soda\ ash}$, while in 2013 1.0 kt$_{CO2.eq}$/kt$_{soda\ ash}$. Taking into consideration the production of soda ash in 2050, 42 % savings are achieved and in absolute terms 4.3 Mt$_{CO2.eq}$.

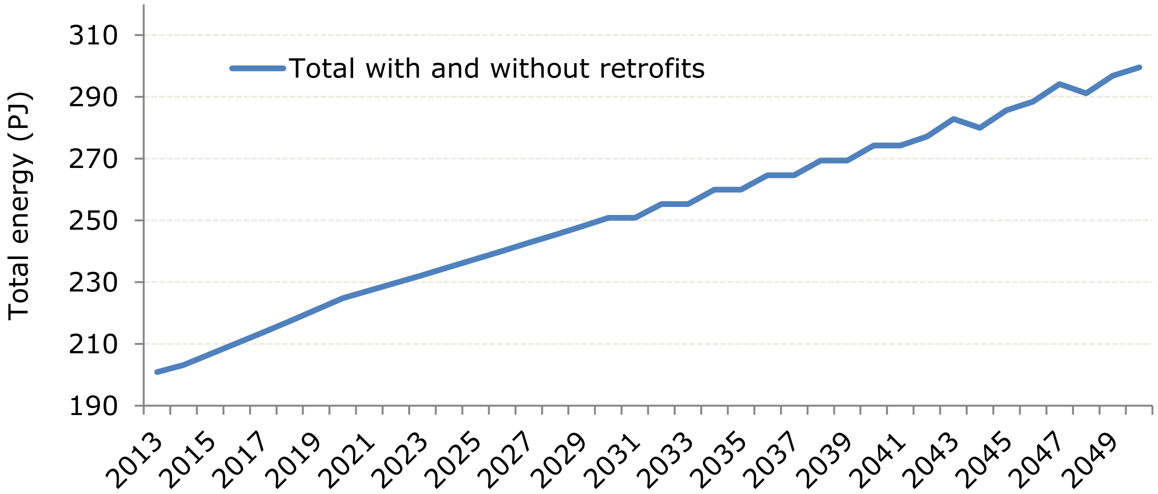
Figure 54. Evolution of the specific emissions (kt$_{CO2.eq}$/kt$_{soda\ ash}$) in 2013-2050, according to the baseline scenario and the fuel prices alternative scenarios



8.2.7 Aromatics

Aromatics include benzene, toluene and xylenes. There are two different processes to produce them depending on the feedstock. There are practically only two BAT available for these products: energy integration and CHP. Although the aromatics industry is prone to install both these BATs, this does not seem to affect either the total GHG emissions or energy consumed (indicative Figure 55). This is the case for all three of the aromatics.

Figure 55. Trends of total energy in benzene production, according to the baseline scenario



Since, in the case of aromatics, our database does not include actual number of facilities but actual number of production lines, the two terms are not directly comparable. As an indication of the level of adoption of energy integration, 60 % of the benzene productions lines adopt this technology. Regarding CHP, the newly installed electrical capacity is 76.7 MW attributed to the aromatics production. From the electricity produced, 65 % is sold, while the rest is used internally. Attention should be given when quantifying the CHP installations in the aromatics industry, as they are produced both in the chemical and in the refining industries.

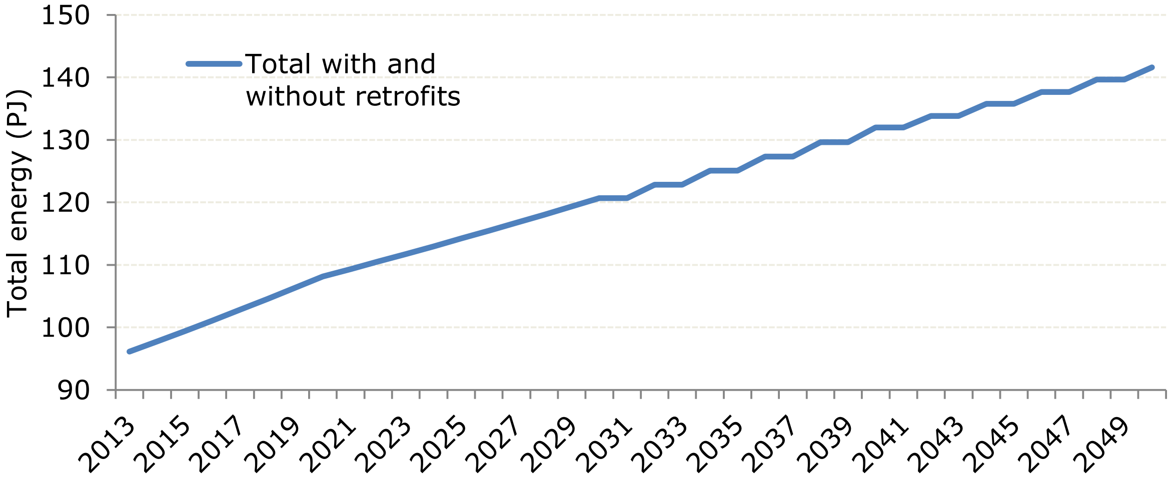
Concerning the specific energy consumption, there is only small variations in the period 2013-2020 and they do not depend on fuels or allowances prices. For benzene the average energy consumption is 28 $TJ/kt_{benzene}$, while for toluene and xylenes, it is 42.2 $TJ/kt_{toluene}$ and 43 $TJ/kt_{xylenes}$ respectively. In 2050 the specific emissions for the three aromatics are 0.78 $kt_{CO2.eq}/kt_{benzene}$, 0.15 $kt_{CO2.eq}/kt_{toluene}$ and 0.17 $kt_{CO2.eq}/kt_{xylenes}$. There is rather an increase in the emissions in the aromatics industry that can be attributed to the installation of CHP.

8.2.8 Carbon black

Carbon black is produced via the furnace black process (Chapter 5.8.1) and there are not BATs or ITs available that are considered in this study, as the available ones either were outside of the scope of this study or there was limited information about their performances, as explained in detail in Chapter 5.8.3 and 5.8.4. The only exception is CHP.

Already more than 60 % of the carbon black industry has been identified to have CHP installed in 2013. According to the model, no further installations are foreseen. As a result, both total energy and GHG emissions are similar with or without retrofits and they grow in parallel with the production (Figure 56).

Figure 56. Trends of total energy in carbon black production, according to the baseline scenario

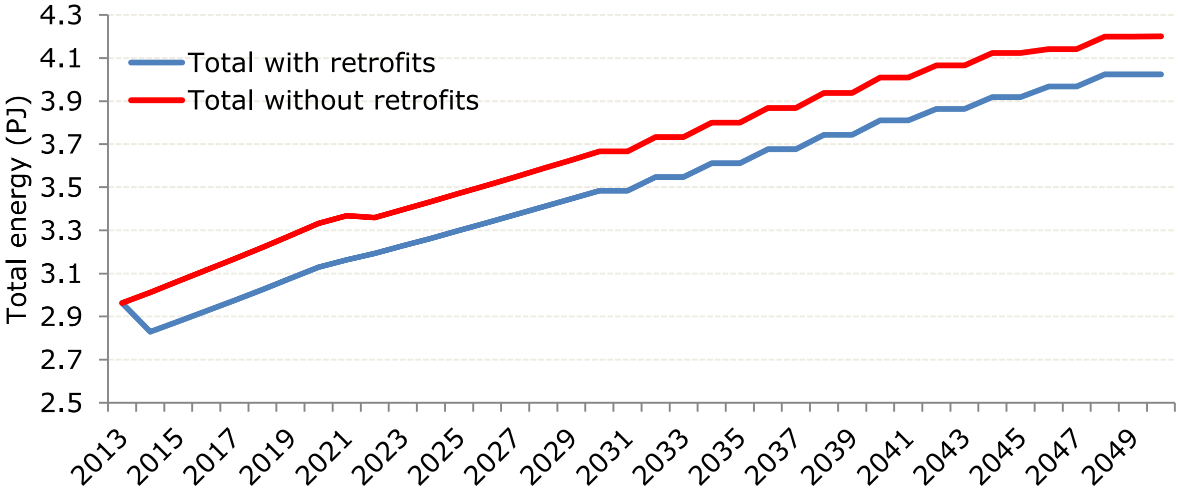


Varying the prices of fuels or CO_2 allowances does not affect the performance of this subsector of the chemical industry.

8.2.9 Ethylene oxide and Monoethylene glycol

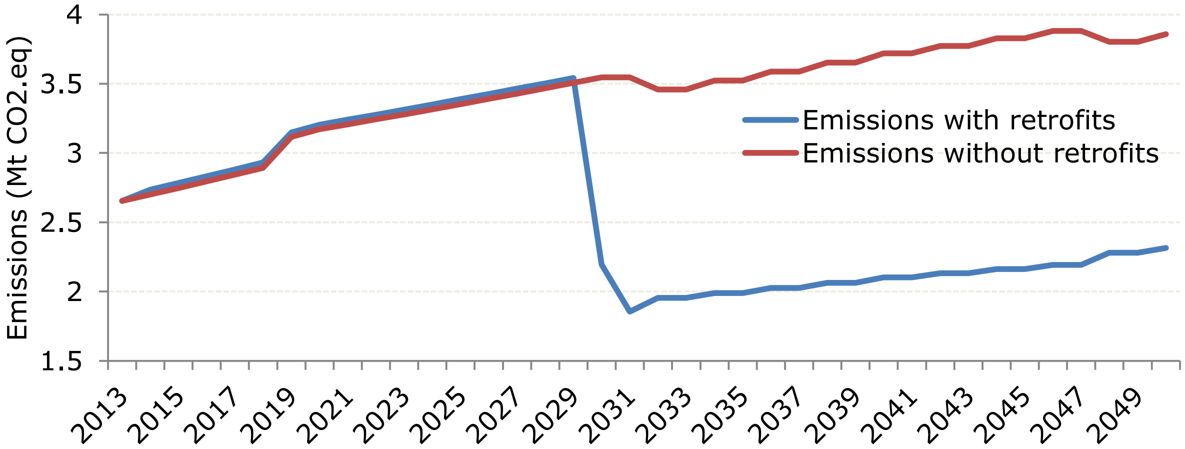
Ethylene oxide (EO) and monoethylene glycol (MEG) are two connected processes. The main BAT available for this sub-sector of the chemical industry is the OMEGA process, whose final product is MEG, as a result any savings in energy are more obvious in the MEG production part (Figure 57). About 70 % of the MEG industry adopts the new process, since it avoids the production of higher glycols, but its effect in energy savings is dual. From one side it decreases the feedstock and steam consumed, but it increases the electricity consumption. In the baseline scenario and for 2050, the energy savings between allowing retrofits and not are 4.2 % and in absolute terms 0.2 PJ.

Figure 57. Trends of total energy consumption in MEG production, according to the baseline scenario



On the other hand, as far as the ethylene oxide production part is concerned, CCS is a possible technology for this subsector and is installed in facilities after 2030. By 2050 70% of the facilities practice CCS, which leads to emission savings as illustrated in Figure 58. In 2050 the savings between allowing retrofits and not in the baseline scenario reach 40 % and in absolute terms 1.6 $Mt_{CO2.eq}$.

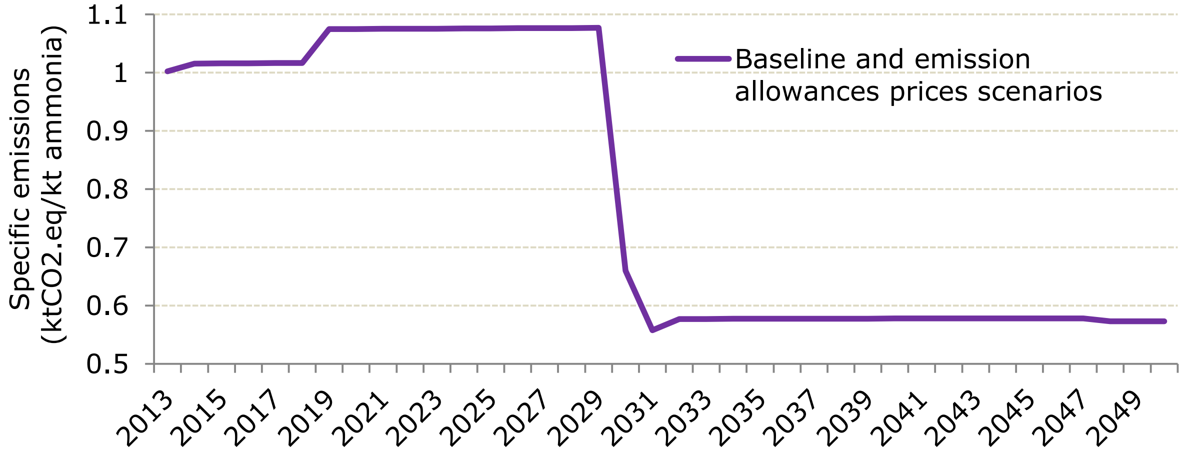
Figure 58. Trends of total GHG emissions in ethylene oxide production, according to the baseline scenario



As far as the specific energy consumptions for the two chemicals is concerned, in 2050 for ethylene oxide is 25.3 TJ/kt_{EO} and for monoethylene glycol 2.5 TJ/kt_{MEG}. Variations of fuels or allowances prices do not affect the behaviour of the industry for the energy point of view.

Equivalently, the specific GHG emissions in 2050 for monoethylene glycol are 1 $kt_{CO2.eq}/kt_{MEG}$ and for ethylene oxide 0.6 $kt_{CO2.eq}/kt_{EO}$ and remain the same with varying fuels or allowances prices. In 2013 they were 1 $kt_{CO2.eq}/kt$ for both products. If the production of the two chemicals in 2050 is taken into consideration, the combined savings of GHG emissions for the ethylene oxide and MEG amounts up 1.6 $Mt_{CO2.eq}$. The evolution in the specific GHG emissions in the case of ethylene oxide for the different allowances alternative scenarios is shown in Figure 59. The sharp decrease is thanks to CCS.

Figure 59. Evolution of the specific emissions ($kt_{CO2.eq}/kt_{EO}$) in 2013-2050, according to the baseline scenario and the allowances prices alternative scenarios



8.2.10 Ethylene dichloride and Vinyl chloride monomer

As in the case of ethylene oxide and MEG, ethylene dichloride (EDC) and vinyl chloride monomer (VCM) are also connected processes. The main BAT available for this sub-sector of the chemical industry is the pigging technology, which is really a cleaning technology, leading to lower loss of valuable products. It is described in detail in Chapter 5.11.3. About 60% of the facilities producing EDC and 50 % of the ones producing VCM install this technology in the period 2013-2050. Besides pigging, the industry adopts CHP. 1710 MW electrical capacity is attributed to the ethylene dichloride industry and 730 MW to the VCM industry. From the electricity produced via CHP 94 % in the EDC part and 80 % in the VCM part is sold out.

The effect of adopting BATs is neither visible in total energy nor in total GHG emissions. Any decrease in emissions achieved thanks to the pigging technology is offset by the increase due to CHP (Figure 60). As the pigging technology decreases mainly the electricity consumption, the savings in energy are not so obvious either, since feedstock is the main contributor to the energy consumption. In 2050, the energy savings between allowing retrofits and not are only 0.6 % in EDC production and 2% in VCM production. Similarly, the emissions savings are 1.4 % in EDC and 0.4 % in VCM.

Figure 60. Trends of total GHG emissions in EDC production, according to the baseline scenario

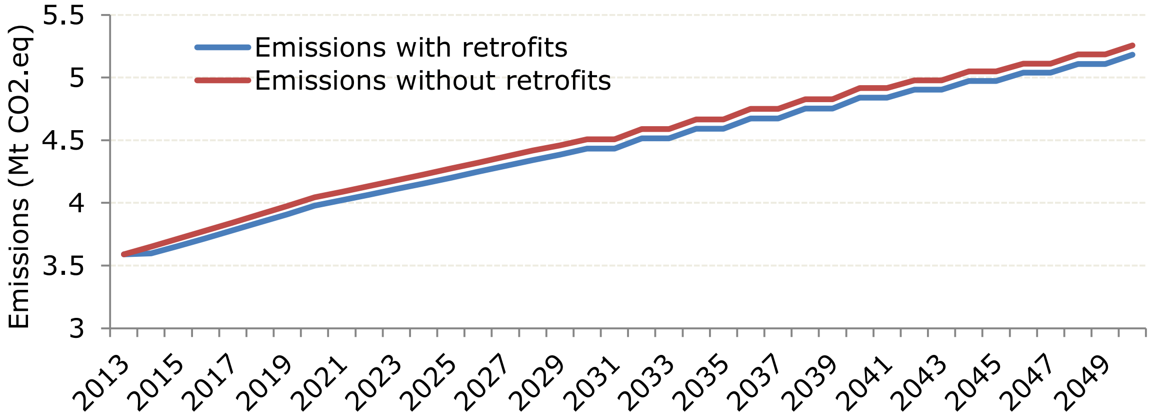
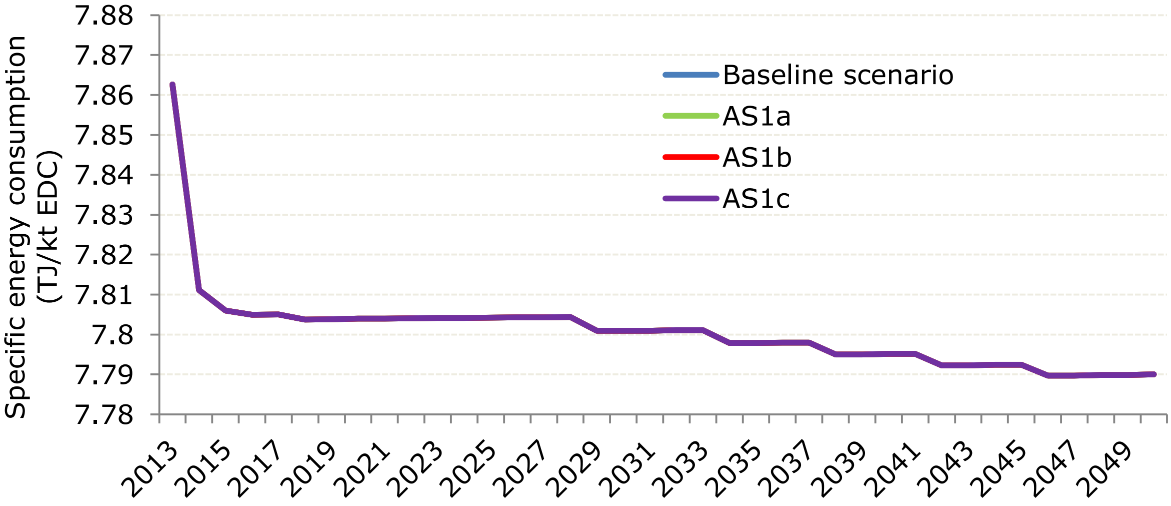


Figure 61. Evolution of the specific energy consumption (TJ/kt$_{EDC}$) in 2013-2050, according to the baseline scenario and the fuels prices alternative scenarios



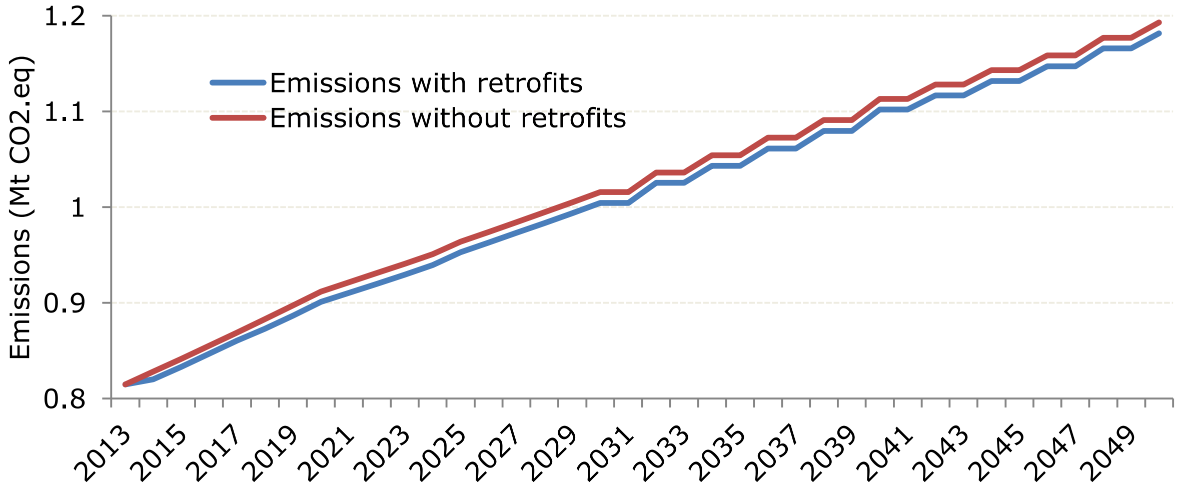
Concerning the specific energy consumptions for ethylene dichloride, it hardly changed the 7.8 TJ/kt_{EDC} from 2013-2050, which corresponds to 104 PJ for the 2050 production of 2050. In the case of vinyl chloride monomer the savings are only 1 PJ or about 3 %, since the specific energy consumptions in 2013 and 2050 are 5.8 TJ/kt_{VCM} and 5.6 TJ/kt_{VCM} respectively.

On the other hand, the specific GHG emissions in the case of VCM decreased from 0.48 $kt_{CO2.ew}/kt_{VCM}$ in 2013 to 0.47 $kt_{CO2.ew}/kt_{VCM,}$in 2050 leading to 3% savings (based on the 2050 production). For EDC the specific emission intensity decreased only marginally, resulting in only 2 % emissions savings. Variations of fuels prices or CO_2 allowances prices do not affect the industries for energy or emissions.

8.2.11 PVC

PVC is an interesting set of products, as there are two configurations (suspension or PVC-S and emulsion or PVC-E), as well as a recycled product, which is considered to be the innovative technique of the subsector.

Figure 62. Trends of total GHG emissions in PVC-S production in the baseline scenario



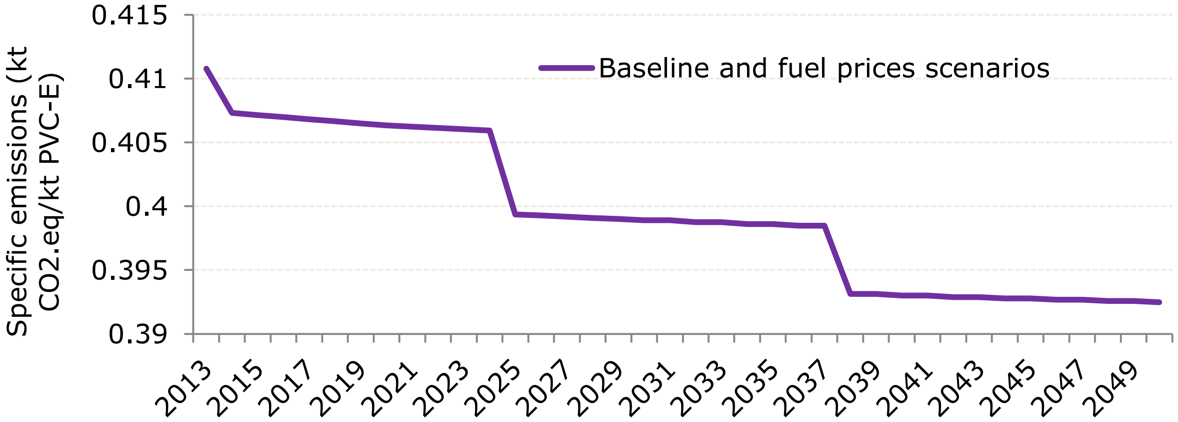
Actually, there is only one BAT available for the two types of PVC and that is the pigging technology, of course, besides CHP. The industry adopts this technology at a percentage more than 90 % for both PVC-S and –E. As already explained before, this BAT minimises the loss of valuable products and affects mainly the total emissions. On the other hand, CHP is slightly increasing the emissions if adopted and in the case of the two virgin PVC there are new installations. The new electrical capacity in PVC-S amounts to 5 MW and in PVC-E to 39 MW. All electricity produced via CHP is consumed internally in this industry and it covers 17 500 MWh in the case of PVC-S and 132 000 MWh in PVC-E.

Figure 62 is indicative of the trends in total emissions for PVC-S and PVC-E is similar. In 2050 the savings in GHG emissions between allowing retrofits and not reach only 0.9 % and 0.7 % for PVC-S and –E respectively. Similar is the situation in the case of total energy is only 0.5 % and 0.9 % respectively.

PVC recycling is a rather new technology and there are no variations besides mechanical recycling considered in this study. It is, after all, a better technology than producing virgin PVC. The only trend that can be mentioned in this case is that production is foreseen to increase and by 2050 to be 3 times higher than currently.

Concerning the specific energy consumptions, adopting BATs would save about 1.5 PJ in the PVC-S process and 273 TJ in the PVC-E one (considering the 2050 production and the emission intensities in 2013 and 2050). Based on similar calculations, the specific emissions in the case of PVC-S change only marginally and lead to 1.5 % or 18 $kt_{CO2.eq}$. Whereas in the PVC-E industry the savings reach 4.5 % or 17.5 $kt_{CO2.eq}$, as they decrease from 0.41 $kt_{CO2.eq}/kt_{PVC-E}$ in 2013 to 0.39 $kt_{CO2.eq}/kt_{PVC-E}$ in 2050 (Figure 63). Variations of fuels prices or CO_2 allowances prices do not affect the industry, as can be seen in Figure 63.

Figure 63. Evolution of the specific energy consumption GHG emissions ($kt_{CO2.eq}/kt_{PVC-E}$) in 2013-2050, according to the baseline scenario and the fuel prices alternative scenarios



8.2.12 Ethylbenzene and Styrene

Figure 64 and Figure 65 display the trends in total energy consumption and GHG emissions in the case of ethyl benzene production. Advanced control and optimisation is considered as BAT in this subsector of the chemical industry, as well as CHP. Both are being adopted and it is the reason why allowing retrofits leads to savings compared to the case where retrofits do not take place. These savings in 2050 correspond to 0.9 PJ or 2.7% in energy and 50 $kt_{CO2.eq}$ or 3.2 % in emissions between allowing retrofits and not.

CHP is further adopted in the ethylbenzene industry. The new CHP electrical capacity amounts to 165 MW and from the electricity produced 63 % is sold out and the rest consumed internally.

Figure 64. Trends of total energy consumption in ethyl benzene production according to the baseline scenario

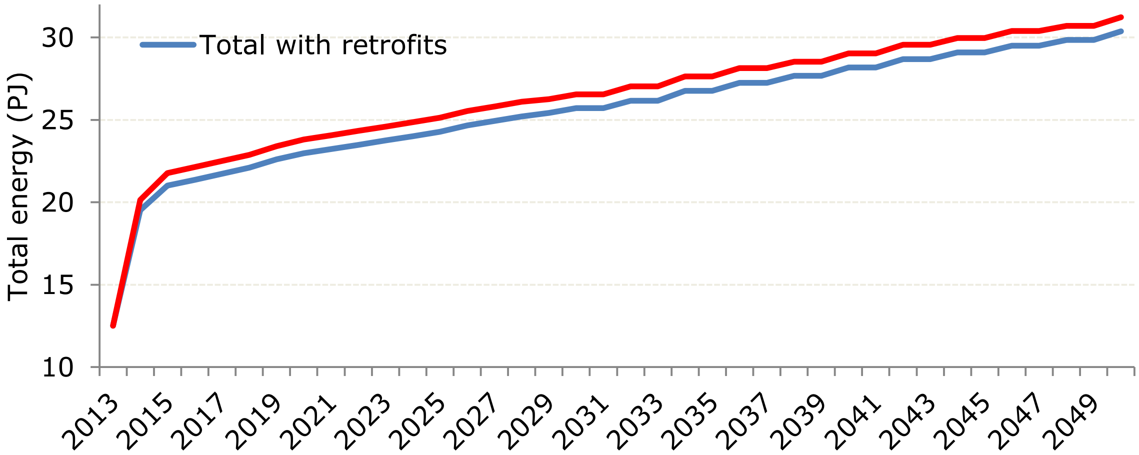


Figure 65. Trends of total GHG emissions in ethyl benzene production according to the baseline scenario

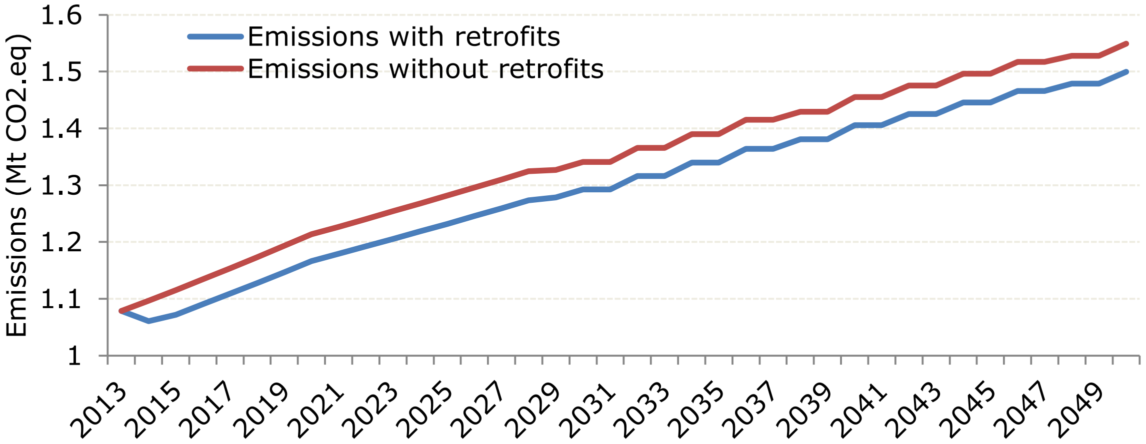
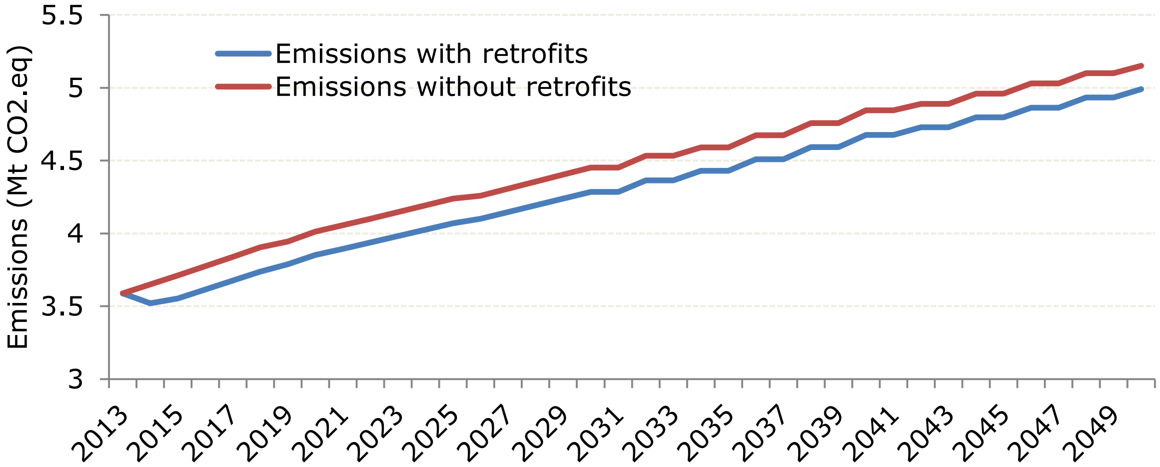


Figure 66 shows the trend of total GHG emissions for the styrene industry, which grow linearly with production. It has the same BATs as the ethyl benzene industry, as the two processes are connected. The savings from retrofits in 2050 amount to 1.6 PJ or 0.5 % in energy and 163 kt$_{CO2.eq}$ or 3.1 % in emissions.

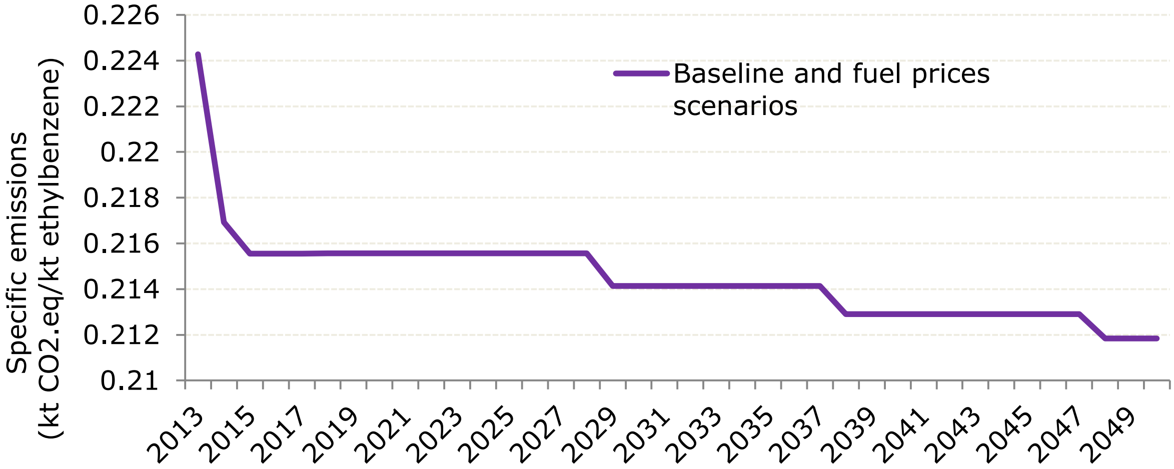
Figure 66. Trends of total GHG emissions in styrene production in the baseline scenario



There is also an innovative technology available, the Exelus styrene process, but it does not become cost efficient, so as to be adopted by the industry.

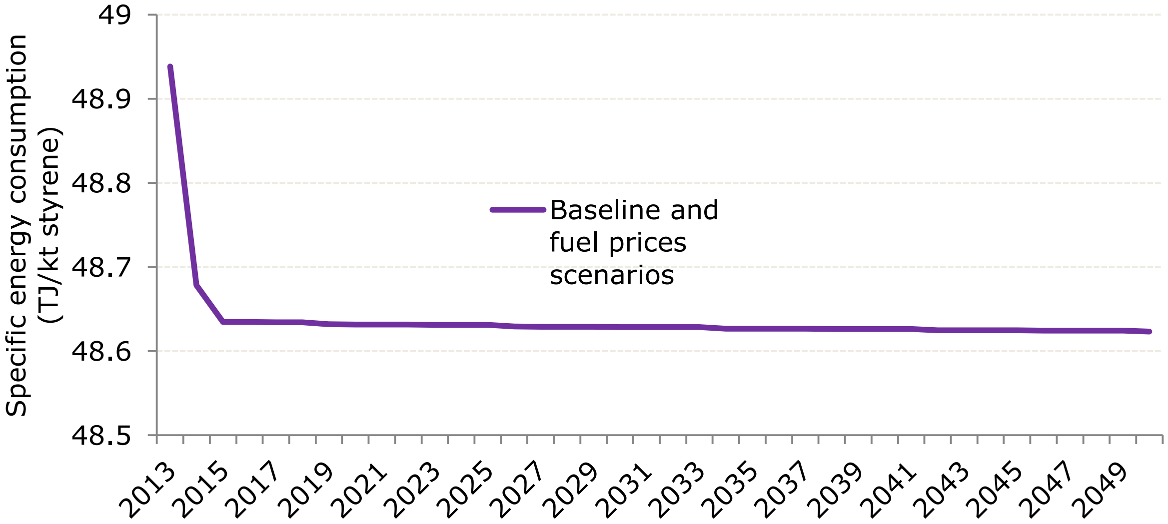
The specific emissions intensity between 2013 and 2050 decreases marginally both in the case of ethylbenzene (Figure 67) and styrene. If the production of each product of 2050 is taken into consideration, the savings in emissions correspond to 90 $kt_{CO2.eq}$ or 5.5 % for ethylbenzene and 290 $kt_{CO2.eq}$ or 5.5 % for styrene,

Figure 67. Evolution of the specific GHG emissions ($kt_{CO2.eq}/kt_{ethylbenzene}$) in 2013-2050, according to the baseline scenario and the fuels prices alternative scenarios



Equivalently, the specific energy consumption for the two products is also changing marginally. Based on the same calculations as for emissions, in the case of styrene 2.1 PJ or 0.6 % is saved (Figure 68), but for ethylbenzene 12 PJ more are needed.

Figure 68. Evolution of the specific energy consumption ($TJ/kt_{styrene}$) in 2013-2050, according to the baseline scenario and the fuel prices alternative scenarios



8.2.13 Chlor-alkali

Chlorine is one of the most electricity-intensive subsectors of the chemical industry. It can be produced by three processes of which the membrane cells are considered to be best available technique, as they are less energy intensive and, hence, less impacting in terms of GHG emissions (Chapter 5.9.3). The facilities with mercury cells convert readily to membrane cells, while asbestos diaphragm cells are also abandoned throughout the whole period of the study. CHP on the other hand does not get installed in the industry further than the current situation.

Besides the conversion of the other two types in membrane cells and CHP, high performance bipolar membrane cells are also considered as BAT in the current study. It becomes cost-effective quite early in the simulation period and gets installed in about half the plants producing chlorine.

In addition to these BATs, there is also an innovative technology considered in the study: the oxygen–depolarised cathodes. It is a variant of the membrane cells and is described in detail in Chapter 5.9.4. It is installed in a few facilities until 2020, but after this point the interest of the industry in it grows.

Figure 69. Trends of total energy consumption in chlorine production according to the baseline scenario

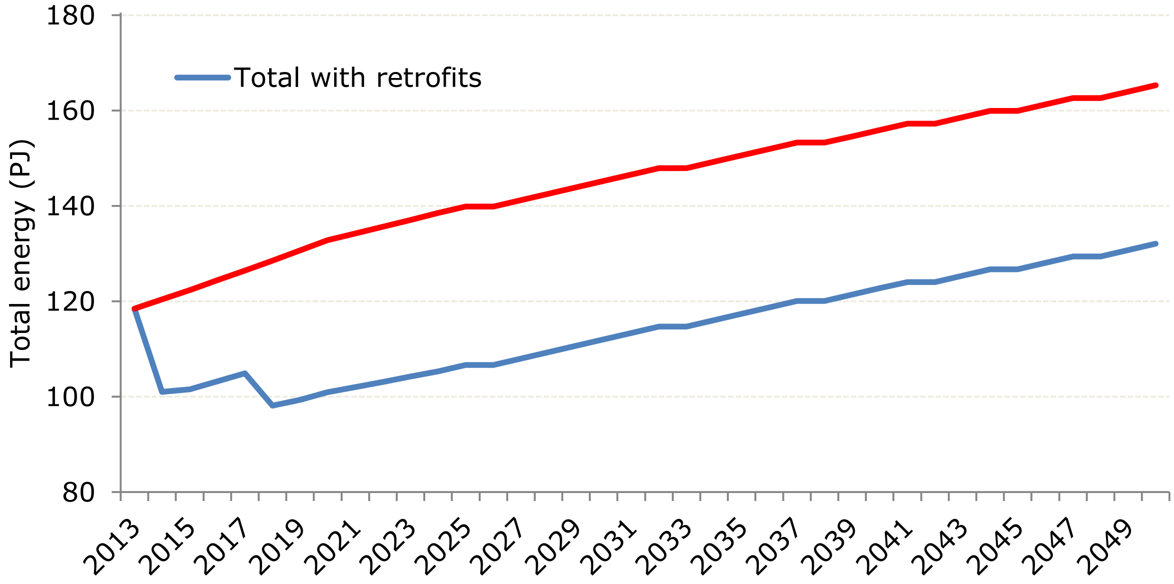
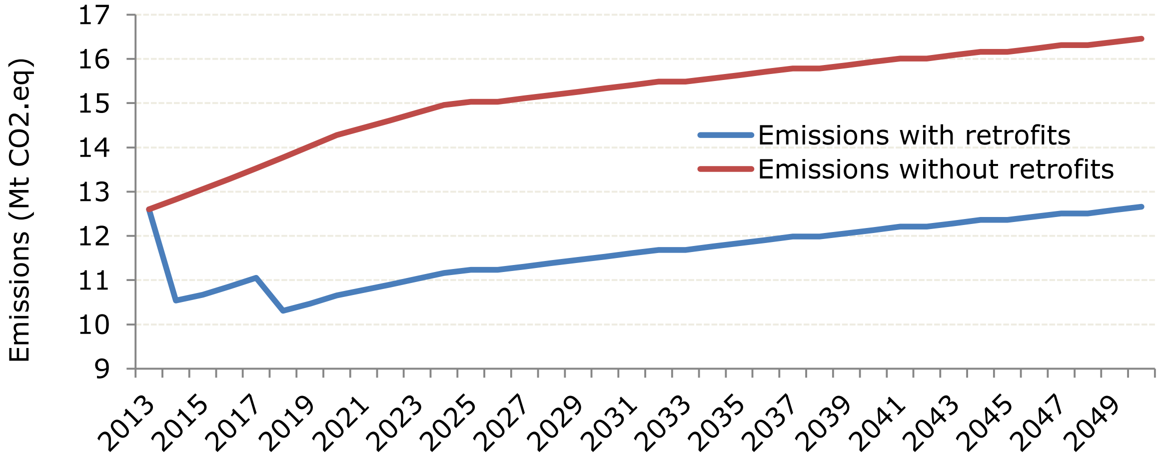


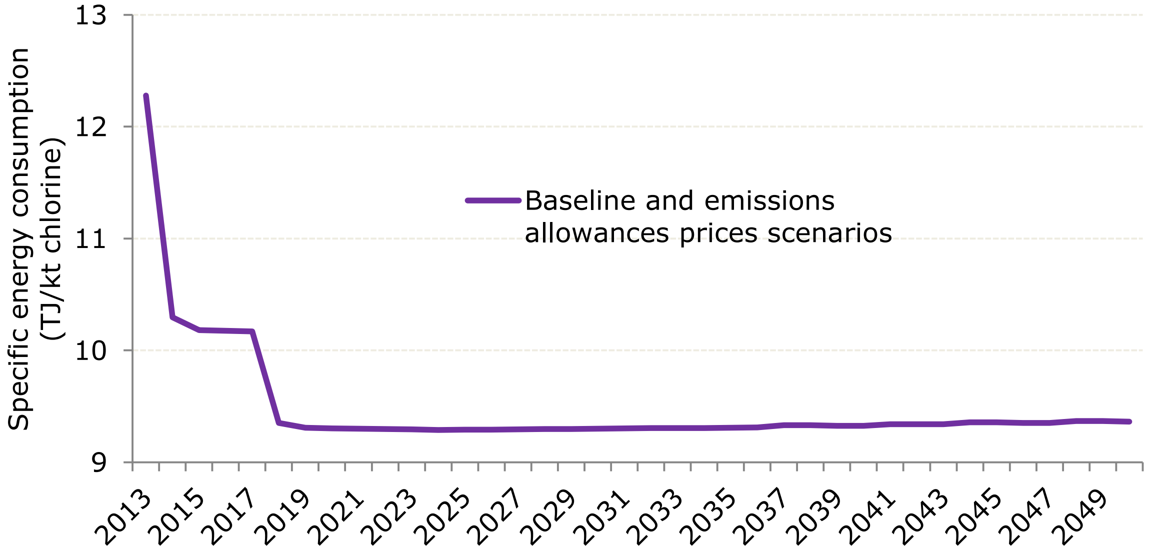
Figure 69**Error! Reference source not found.** and Figure 70 depict the trends in total energy consumption and total GHG emissions for the chlor-alkali industry. Both quantities grow linearly with the production. If BATs are installed, the savings in 2050 add up to 33.2 PJ or 20 % in energy and 3.8 $Mt_{CO2.eq}$ or 16.5 % in emissions.

Figure 70. Trends of total emissions in chlorine production in the baseline scenario



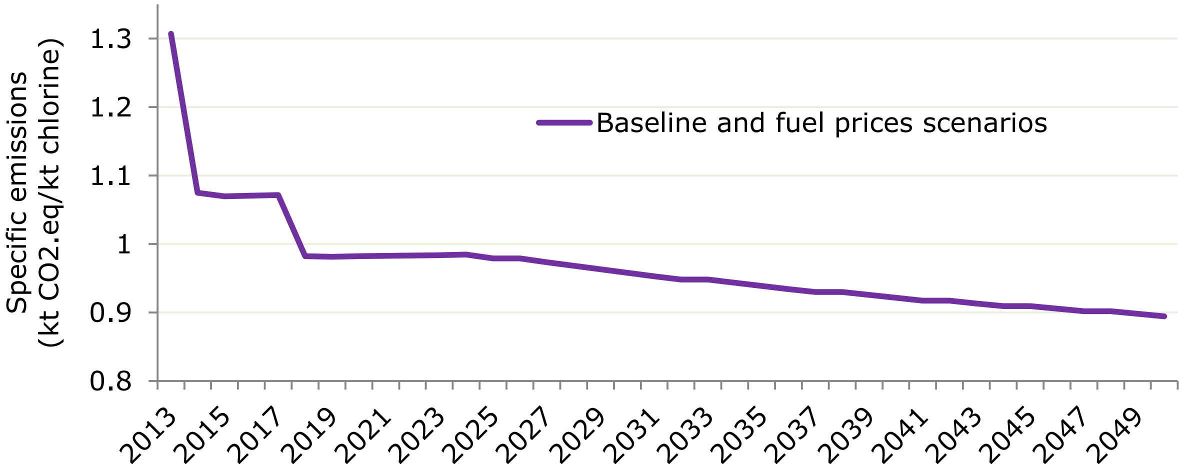
As far as it concerns the specific energy consumption, the value in 2013 was 12.3 $TJ/kt_{chlorine}$, while in 2050 it is 9.3 $TJ/kt_{chlorine}$ and is rather insensitive to changes in fuel or CO_2 allowances prices (Figure 71). Based on the chlorine production of 2050, there will be 41.8 PJ or 24 % energy savings between 2013 and 2050.

Figure 71. Evolution of the specific energy consumption ($TJ/kt_{chlorine}$) in 2013-2050, according to the baseline scenario and the emissions allowances prices alternative scenarios



On the other hand, the specific GHG emissions decrease more strongly. Figure 72 shows the evolution of the specific emission factors for the different variations in CO_2 allowances prices. The specific emission intensity in 2013 was 1.3 $kt_{CO2.eq}/kt_{chlorine}$ and in 2050 is foreseen to become 0.9 $kt_{CO2.eq}/kt_{chlorine}$. By multiplying these values with the chlorine production in 2050, almost 32 % emissions savings are calculated, corresponding to 5.8 $Mt_{CO2.eq}$.

Figure 72. Evolution of the specific GHG emissions ($kt_{CO2.eq}/kt_{chlorine}$) in 2013-2050, according to the baseline scenario and the fuel prices alternative scenarios



9 Conclusions

Before drawing any conclusions about this study, some precautions should be highlighted. This document reflects the potential trend in energy consumption and GHG emissions of the chemical industry under some assumptions. Deviation from these assumptions will make the actual trends differ from the results estimated. The first and most demanding assumption is that the European industry remains globally competitive, and therefore, we assume that the European demand for chemicals is met by the European production in the same way as currently. This can be challenging for some of the scenarios analysed, if there are not similar global conditions (especially in the high fuel prices and allowances prices). The rationale of those scenarios is to analyse what the industry could provide in a cost-effective fashion to reduce GHG emissions and energy consumption under those circumstances. This potential is analysed without assigning more or less credibility to those scenarios. In any case, and as the communication on the Energy Union states (EC, 2015d) the policies to prevent carbon leakage should reflect the degree of efforts undertaken in other major economies. The Commission, together with Member states, will engage with other major economies to convince them to join Europe's ambition, which is reflected in the agreement on the 2030 and 2050 climate and energy framework. The EU has committed to at least 40 % of domestic reduction in GHG emissions, compared to 1990 by 2030; and 80 % by 2050.

In addition, although the uncertainty of some potential factors affecting the interest in adopting technological improvements has been tackled varying those factors in different scenarios, the values assigned to some of the detailed characteristics of the technologies are not exempt from uncertainty. Moreover, the list of technologies cannot be comprehensive, as for some of them there is no information publicly available.

Keeping in mind these precautions, we also have to asset the ambition and degree of detail of this exercise. The chemical and petrochemical industry is a very diversified and complex sector in terms of portfolio of manufactured products, processes and technologies in use or under development, differences in production capacities, performances etc. Nevertheless, this study analyses the energy consumption and GHG emissions trends of the industry based on detailed information at facility level for all plants involved in the production of 26 major chemical products. These 26 products cover 75 % of the total energy and non-energy use of the EU-28 chemical industry in 2013, and most of the emissions in the same year. As such, this model can be considered the first-of-its-kind for this industry.

The baseline scenario indicates that the adoption of best available and innovative technologies would mean annual savings of 72.5 $Mt_{CO2.eq}$ and 225 PJ (5.4 Mtoe) by 2050. Including these savings, the total annual emissions and energy consumption by 2050 of the products covered in this study amounts up to 129 Mt $Mt_{CO2.eq}$ and 5515 PJ (131.7 Mtoe). In absolute terms, from 2013-2050 the total energy consumption increases by 39.2 % and the GHG emissions' decrease by 14.7 %; these values include the effect (and depend on) a demand increase of 45.6 %. The different scenarios, varying significantly the fuel prices and the price of the CO2 allowances, hardly change these results; meaning that, practically all the savings potentials are materialised under the assumptions of the baseline scenario.

The small improvement of just only 4% (225 PJ) of total energy consumption by 2050 can be partly explained by the fact that non-energy consumption is not affected a lot by the new technologies, while it represents on average 77% of the total energy consumption. In fact, the peculiarity of the chemical and petrochemical industry of incorporating most of the energy consumed in its products is unique among the energy-intensive industries. Most BATs and ITs reduce the electricity, thermal energy or steam consumed in the processes, but not directly the energy consumed as feedstock. Big changes in non-energy consumptions are expected only from technologies that replace the fossil feedstock with some more sustainable alternative, such as production of hydrogen from electrolysis or if chemicals could be produced by biomass. Electrolysis unfortunately increases the electricity consumption of the facilities, while break-through technologies such as biomass as feedstock are so early in research stages that either will not be available before 2050 or there is no information available for the performances, so they could not be included in the current study. A small fraction of the savings identified, about 16%, can be attributed to savings of feedstock, while the rest 84% (corresponding to 189 PJ in 2050) is savings in the electricity or fuels (used for thermal needs or steam in the processes). If only this part is taken into consideration for the calculation, then the percentage of savings is 13% in the case of the baseline scenario.

Concerning the chemical products that contribute the most to the savings of GHG emissions between 2013 and 2050, nitric acid and adipic acid play an important role ; their specific emission factors in 2050 is 75% and 90% lower than in 2013, respectively. This is an expected result, as the chemical industry has shown already great interest in reducing the nitrous oxide emissions, which have a really high global warming potential. In the case of nitric acid, the industry prefers installing primary and secondary abatement measures; while the adipic acid subsector, tertiary measures. It is assumed that, after 2030, there will be an innovative technology in the adipic acid industry that will contribute in decreasing the process emissions not related to nitrous oxide.

Ethylene, chlorine, ammonia and hydrogen are important as they are the most produced chemicals (16% of the total production in 2050 for ethylene, 11% for chlorine and 6% for ammonia). The reduction of the specific GHG emissions of these four chemicals is estimated to be 27% for ethylene, 31% for chlorine, 54% for ammonia and 75% for hydrogen. Advanced process control is already considered as a default technology for steam crackers, but savings can be attributed mainly to improvements in the compression and separation section and the use of adsorption heat pumps, and secondarily to improved furnace design and the use of membranes in the separation section. In the case of chlorine, all of the three BATs special for this industry (conversion of mercury and asbestos diaphragm cells to membrane ones and high performance bipolar membrane cells) are being installed in big part of the industry. Further improvements are thanks to oxygen-depolarised cathodes, which is though not available before 2020.

Soda ash, ethylene oxide and monoethylene glycol have also high reduction potentials, but their importance is smaller as their production volumes represent a smaller share in the whole production. For soda ash the most important BAT is integrated design and operation, while for ethylene oxide/monoethylene glycol the savings are firstly due to adoption of the OMEGA technology and further installing CHP, but mainly thanks to CCS. The potentials for them were estimated at around 42% for soda ash and for ethylene oxide and 1% for MEG.

The specific energy consumption of the chemical industry is foreseen to decrease in 2050 compared to 2013, with only few exceptions. The highest improvements happen for ammonia (24% lower), which can be attributed to the high extent of revamping the plants so as to improve energy efficiency, for adipic acid (29% lower), thanks to the innovative technology that is based on alternative synthetic pathways or innovative catalysts, chlorine (24% lower), mainly because the older and less efficient cell-types are abandoned for more efficient and environmentally friendly options..

There are two cross-cutting technologies considered in this study: combined heat and power (CHP) and carbon capture and storage (CCS). Although CHP is already installed to a large extent in the chemical industry, the model foresees the installation of additional 2750 MW of electrical capacity. Mainly in the production of: adipic acid, benzene, ethylbenzene, ethylene dichloride, vinyl chloride monomer, PVC-S and PVC-E. Only 12% of the 9.4 TWh/y electricity produced via CHP is consumed inside the processes, while the excess is sold. On the other hand, the model installs CCS in all three subsectors that are sources of high purity CO_2. In the case of ammonia the technology becomes popular only in the part of the industry that is not integrated with urea production, but it is only expected, as CO_2 is usually consumed in producing urea. In the hydrogen industry, about 70% of the facilities install CCS, while in the ethylene oxide subsector 80%.

It is worth noting that the model also relies on the hypothesis that some technology innovations will become available at some point in the future. Since these key technologies include carbon capture and storage (CCS), these findings confirm the critical nature of these technologies (EC, 2015d) in order to achieve the 2050 climate objectives cost-effectively. In particular, CCS in processes resulting in near-pure CO_2 streams (e.g. ammonia, hydrogen, ethylene oxide etc.) has a considerable contribution in terms of GHG emissions reductions. In some cases, it is a technically ready technology (e.g. ammonia), but the rest of the cases are of more importance for the chemical industry. Therefore, one of the main conclusions of this study is the clear need for a decisive push for some technologies and to create the right conditions to make these potential savings happen.

References

(Abanades, 2012) Abanades A., The challenge of hydrogen production for the transition to a CO_2-free economy, Agronomy Research – Biosystem Engineering Special Issue 1 (2012), p. 11 – 16.

(ACC, 2013) American Chemistry Council (ACC), 2013 Guide to the Business of Chemistry, Washington DC, 2013.

(ACC, 2004) American Chemical Council (ACC), Ethylene: Product Stewardship Guidance Manual, December 2004.

(Air Liquide, 2013) Air Liquide, Methanol and derivatives – Technology for methanol and derivatives, 2013, available at http://www.engineering-solutions.airliquide.com/en/about-us-global-engineering-and-construction-solutions/technologies-air-liquide-lurgi-cryo-zimmer/methanol-and-derivatives.html (last accessed December 2014)

(Air Products, 2012) Air Products and Chemicals Inc., Application for an Air Permit for the Delaware City Hydrogen Facility Project, Prepared by Environmental Resources Management, April 2012, available at http://delaware.sierraclub.org/sites/delaware.sierraclub.org/files/documents/2012/05/air_products_hydrogen_facility.pdf (last accessed August 2014)

(Aker, 2008) AkerSolutions, The METEOR^{TM} EO/EG Process, 2008, available at https://akersolutions.com/Global/PandC/Process/Petrochemical/Chemical%20Intermediates/Meteorflyer%20A4%20version.pdf (last accessed April 2015)

(AkzoNobel, 2012) AkzoNobel, Pressemitteilung – AkzoNobel setzt einzigartiges Eindampfsystem für Natronlauge ein, Frankfurt, Germany, June 2012, available at https://www.akzonobel.com/Frankfurt/system/Images/AkzoNobel_setzt%20einzigartiges%20Eindampfsystem%20f%C3%BCr%20Natronlauge%20ein_20120628_tcm156-77331.pdf (last accessed August 2014)

(Alexandratos & Bruinsma, 2012) Alexandratos N. and Bruinsma J., World agriculture towards 2030/2050: the 2012 revision, ESA working paper no. 12-03, Rome, FAO

(Allakhverdiev et al, 2010) Allakhverdiev S. I., Thavasi V., Kreslavski V. D., Zharmukhamedov S. K., Klimov V. V., Ramakrishna S., Los D. A., Mimuro M., Nishihara H., Carpentier R., Photosynthetic hydrogen production, Journal of Photochemistry and Photobiology C: Photochemistry Reviews 11 (2010), p. 101 – 113.

(Al-Rabiah et al., 2001) Al-Rabiah A. A., Timmerhaus K. D., Noble R. D., Membrane technology for Hydrogen separation in ethylene plants, 6th World Congress of Chemical Engineering, Melbourne Australia, September 2001, available at http://faculty.ksu.edu.sa/alrabiah/Documents/article12.pdf (last accessed August 2014)

(Amos, 2003) Amos W. A., Biological water-gas shift conversion of carbon monoxide to hydrogen, Milestone completion report, National Renewable Energy Laboratory (NREL), September 2003.

(Aromatics Online, 2016) Aromatics Online, Aromatics, In a nutshell, available at http://www.aromaticsonline.eu/aromatics/in-a-nutshell (last accessed March, 2016)

(AspenTech, 2006) AspenTech, Holistic approach to capturing and sustaining energy savings, December 2006, available at http://texasiof.ceer.utexas.edu/showcase2006/FinalPres/PDFs/Galleon%20III/Desouza%20Aspentech%20TxTech%20Showcase%20Dec06%20Rev2.pdf (last accessed August 2014).

(Attenberger, 2011) Attenberger P., Universally applicable: Polyvinyl Chloride (PVC), Kunststoffe International 2011/10, p. 7 – 10.

(Babu et al., 2013) Babu V., Thapliyal A., Patel G. K., Biofuels Production, Schrivener Publishing and John Wiley & Sons, November 2013.

(Bachot & Stutzmann, 1995) Bachot J. and Stutzmann P., Microporous asbestos-free diaphragms/cathodes for electrolytic cells, United States Patent US 5470449 A, November 1995.

(Badger, 2012) Badger, Styrene, 2012, available online at http://www.badgerlicensing.com/TechServices_PC_Styrene.html (last accessed April 2016)

(Baker et al., 2005) Baker L., Bent M., Bush J., Heslinga M. Jones A., Engineering an alternative route to styrene, Chemical Engin- EARS, December 2005, available online at https://www.calvin.edu/academic/engineering/senior-design/SeniorDesign05-06/team07/PPFS.pdf (last accessed April 2016)

(Bakken et al., 1998) Bakken J. A., Jensen R., Monsen B., Raaness O. Waernes A. N., Thermal plasma process development in Norway, Pure and Applied Chemistry 70 (1998), p. 1223 – 1228.

(Bartels, 2008) Bartels J. R., A feasibility study of implementing an Ammonia economy, Graduate thesis, Iowa State University, 2008, available at http://lib.dr.iastate.edu/cgi/viewcontent.cgi?article=2119&context=etd (last accessed August 2014)

(de Beer et al., 2001) de Beer J., Phylipsen D., Bates J., Hendriks C., Economic evaluation of sectoral emission reduction objectives for climate change – Economic evaluation of carbon dioxide and nitrous oxide emission reductions in industry in the EU – Bottom up analysis, January 2001.

(Benner et al., 2012) Benner J., van Lieshout M., Croezen H., Identifying breakthrough technologies for the production of basic chemicals: A long term view on the sustainable production of ammonia, olefins and aromatics in the European region, Delft, CE Delft, January 2012.

(Berggren, 2013) Berggren M., Global Methanol outlook capacity calling, 16th IMPCA Asian Methanol Conference, Singapore, October 2013.

(Bhaskar & Das, 2007) Bhaskar K. and Das P. C., Manufacture of Urea, Bachelor thesis, National Institute of Technology, Rourkela, India, 2007.

(Bonnet et al., 2006) Bonnet D., Ireland T., Fache E., Simonato J.P., Innovative direct synthesis of adipic acid by air oxidation of cyclohexane, Green Chemistry 8 (2006), p. 556 – 559.

(Brayden et al, 2006) Brayden M., Wines T. H., Del Giudice K., Improve steam cracking furnace productivity and emissions control through filtration and coalescence, Scientific & Technical report, Pall Fuels and Chemicals, GDS138, April 2006.

(Brew, 2006) The Brew Project, Medium and long-term opportunities and risks of the biotechnological production of bulk chemicals from renewable resources – the Potential of white biotechnology, A collaboration of academy and industry partners under the European Commission's GROWTH Programme, Utrecht, September 2006.

(Brown et al., 2000) Brown K.A., Holland M.R., Boyd R.A., Thresh S., Jones H., Ogilvie S.M., Economic evaluation of PVC waste management, AEA Technology, June 2000.

(Brown et al., 2003) Brown L.C., Lentsch R.D., Besenbruch G.E., Schultz K.R., Funk J.E., Alternative flowsheets for the sulphur-iodine thermochemical hydrogen cycle, AIChE spring national meeting, New Orleans, April 2003 available at http://www.osti.gov/scitech/servlets/purl/821952 (last accessed August 2014).

(Bulan et al., 2009) Bulan A., Jörissen J., Jung J., Kiefer R., Lochhaas H., Röttger-Heinz J., Turek T., Wagner N., CO_2-reduktion bei der Herstellung chemischer Grundstoffe – Einsatz von sauerstoffverzehrkathoden bei der chlorherstellung, Klimaschutz und

Anpassung an die Klimafolgen – Strategien, Maßnahmen und Anwendungsbeispiele, 2009, pp. 61-68.

(Burgard et al., 2010) Burgard A.P., Pharkya P., Osterhout R.E., Microorganisms for the production of adipic acid and other compounds, Patent US 7799545 B2, September 2010.

(Business Wire, 2010a) Research and Markets: Ethylene Dichloride (EDC) global supply dynamics to 2020 – The US sustains the leading position in global production, November 2010, available at http://www.businesswire.com/news/home/20101103006868/en/Research-Markets-Ethylene-Dichloride-EDC-Global-Supply (last accessed March 2016)

(Business Wire, 2010b) Research and Markets: Vinyl Chloride Monomer (VCM) global supply dynamics to 2020 – Production from coal derivatives emerging as a cheaper alternative in China, November 2010, available at http://www.businesswire.com/news/home/20101124005595/en/Research-Markets-Vinyl-Chloride-Monomer-VCM-Global (last accessed March 2016)

(Business Wire, 2012) Research and Markets: China Ethylene oxide (EO) industry report 2012 – 2014, November 2012, available at http://www.businesswire.com/news/home/20121120005746/en/Research-Markets-China-Ethylene-Oxide-EO-Industry#.VRk_fGM1AxE (last accessed April 2015)

(Carbon Counts, 2010) Zakkour P. and Cook G., CCS Roadmap for industry: High-purity CO_2 sources – Sectorial Assessment – Final report, Carbon counts Company Ltd, UK, September 2010.

(CCC, 2009) Committee on Climate Change (CCC), Meeting Carbon Budgets – the need for a step change, Progress report to the UK Parliament, October 2009 available at http://archive.theccc.org.uk/aws2/21667%20CCC%20Report%20AW%20WEB.pdf (last accessed August 2014)

(Cefic, 2004) Cefic, IPPC BAT Reference Document – Large volume solid inorganic chemicals family: Process BREF for Soda Ash, March 2004.

(Cefic, 2012) Cefic, Ethylbenzene: Environmental, health and safety guidelines, 2012, available online at http://www.ethylbenzene.org/content/1.html (last accessed April 2016)

(Cefic, 2013) Mosquera J., Competitiveness of the EU Chemical Industry, a key sector in the Refining value chain, Presentation in the 2nd meeting of the EU Refining Forum, Brussels, Belgium, November 2013, available at http://ec.europa.eu/energy/observatory/oil/doc/refining/20131127_2nd_meeting_cefic_competitivenes.pdf (last accessed August 2014)

(Cefic, 2014) Cefic, Facts and figures 2013, January 2014, available at http://www.cefic.org/Facts-and-Figures/ (last accessed March 2016).

(Cefic, 2015) Cefic, Facts and figures 2014, January 2015, available at http://www.cefic.org/Facts-and-Figures/ (last accessed March 2016).

(CEH, 2007) Suresh B. and Fujita K., CEH Marketing Research Report – Ammonia, Chemical Economics Handbook, SRI Consulting, July 2007.

(CEH, 2005) Devanneu M. T., CEH Marketing Research Report – Ethylene, Chemical Economics Handbook, SRI Consulting, September 2005

(CEH, 2004) Lauriente D.H. and Yagi K., CEH Marketing Research Report – Nitric Acid, Chemical Economics Handbook, SRI Consulting, September 2004.

(CEPS, 2014a) Egenhofer C., Schrefler L., Rizos V., Infelise F., Luchetta G., Simonelli F., Stoefs W., Timini J., Colantoni L., Final report for a study on composition and drivers of energy prices and costs in energy intensive industries: the case of the Chemical Industry – Ammonia, Framework Contract No ENTR/2008/006 LOT4 for the procurement of studies and other supporting services on the Commission Impact Assessment and evaluation, Centre for European Policy Studies (CEPS), Brussels, Belgium, January 2014

(CEPS, 2014b) Egenhofer C., Schrefler L., Rizos V., Infelise F., Luchetta G., Simonelli F., Stoefs W., Timini J., Colantoni L., Final report for a study on composition and drivers of energy prices and costs in energy intensive industries: the case of the Chemical Industry – Chlorine, Framework Contract No ENTR/2008/006 LOT4 for the procurement of studies and other supporting services on the Commission Impact Assessment and evaluation, Centre for European Policy Studies (CEPS), Brussels, Belgium, January 2014

(Chemical Engineering 2009) Chemical Engineering Plant Cost Index (CEPCI), Chemical Engineering, March 2009

(Chemical Engineering 2014) Chemical Engineering Plant Cost Index (CEPCI), Chemical Engineering, March 2014

(Chemical Online, 1999) Brown A.S., New VCM plant will use ethane, Chemical Online, September 1999, available online at http://www.chemicalonline.com/doc/new-vcm-plant-will-use-ethane-0001 (last accessed April 2016)

(Chemical processing, 2009) Chemical Processing, Shell showcases emerging technologies, 2009, available at http://www.chemicalprocessing.com/articles/2009/236/ (last accessed April 2015)

(Chemical Weekly, 2009) Special Report, Adipic acid: A techno-commercial profile, Chemical Weekly, April 7, 2009, available at http://www.chemicalweekly.com/Profiles/Adipic_Acid.pdf (last accessed August 2014)

(Chemicals technology, 2015) Chemicals Technology, Shell mono-ethylene glycol plant Singapore, 2015, available at http://www.chemicals-technology.com/projects/shell-monoethylene/ (last accessed April 2015)

(ChemSystems, 2009a) Chemsystems Perp Program, Ethylene oxide / ethylene glycol, Nexant, 2009, available online at http://database.thinking.nexant.com/reports/search.cfm?order=title&keyword=ethylene%20oxide/ethylene%20glycol (last accessed April 2016)

(ChemSystems, 2009b) ChemSystems Per Program, Styrene/Ethylbenzene, Nexant, 2009 available online at http://database.thinking.nexant.com/about/cs/news/items/PERP%200708_4_StyreneEB.cfm (last accessed April 2016)

(Chemweek, 2011) Chemical Week, Ethylene glycol market firms; Players bullish on outlook, MEGlobal, September 2011, available at http://www.meglobal.biz/news/2011/08/09 (last accessed April 2015)

(Chevron, 2012) Chevron Phillips Chemical Company, Greenhouse Gas Air Permit Application – Gulf Coast Steam Cracker, Submitted to EPA Region 6, Response, March 2012 available at http://www.epa.gov/region6/6pd/air/pd-r/ghg/chevron_response031912.pdf (last accessed August 2014)

(CIEC, 2015) CIEC Promoting Science, The Essential Chemical Industry – online, University of York, York, UK, available at http://www.essentialchemicalindustry.org/ (last accessed March 2015).

(Cooker & Cochran, 1996) Cooker B. and Nochran R.N., Electrochemical oxidation to olefin; alkaline oxide produced at both electrodes, United States Patent US 5527436 A, June 1996.

(Cortright & Blommel, 2011) Cortright R.D. and Blommel P.G., Conversion of hydrocarbon oxidates to hydrocarbons, ketones and alcohols useful as liquid fuels, such as gasoline, jet fuel or diesel fuel, and industrial chemicals; hydrocarbon oxidates can originate from biomass; e.g. using aqueous phase reforming hydrogen; biofuels, United States Patent US 8053615 B2, March 2011.

(Couch et al., 2007) Couch K.A., Glavin J.P., Wegerer D.A., Qafisheh J.A., FCC propylene production, Petroleum Technology Quarterly (PTQ) Q3 2007, p. 33 – 43.

(CPMA, 2012) Chemicals & Petrochemicals Manufacturers' Association India (CPMA), MEG – Monoethylene glycol, 2012, available at http://cpmaindia.com/meg_about.php (last accessed April 2015)

(Deloitte, 2010) Deloitte, PVC markets of Europe and South-East Asia: analysis of profitability and production cost, Deloitte Consulting 2010.

(Diamond et al., 1982) Diamond S.E., Mares F., Muccigrosso D.A., Solar J.P., Producing epoxide from olefin using metal nitro complexes, United States Patent US 4356311 A, October 1982.

(Diez et al., 2009) Diez E., Langston P., Ovejero G., Dolores Romero M., Economic feasibility of heat pumps in distillation to reduce energy use, Applied Thermal Engineering 29 (2009), p. 1216 – 1223.

(DG Env, 2011) European Commission DG ENV, Plastic waste in the environment, April 2011

(Dow, 2013a) The Dow Chemical Company, Product safety assessment: ethylene dichloride, March 2013, available at http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08cb/0901b803808cb0a6.pdf?filepath=productsafety/pdfs/noreg/233-00295.pdf&fromPage=GetDoc (last accessed March 2016)

(Dow, 2016b) The Dow Chemical Company, Product safety assessment: vinyl chloride monomer, June 2013, available at http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08d7/0901b803808d77d0.pdf?filepath=productsafety/pdfs/noreg/233-00271.pdf&fromPage=GetDoc (last accessed March 2016)

(Dow, 2015) Dow Technology Licensing, Dow Technology Licensing METEOR^{TM} Ethylene oxide/glycol process technology, 2015, available at http://www.dow.com/licensing/offer/meteor.htm (last accessed April, 2015)

(DuBois & Dilmore, 1997) DuBois D.W., Dilmore C.R. Jr., Method for preparing asbestos-free chlor-alkali diaphragm, United States Patent US 5683749 A, November 1997.

(Dufour et al., 2011) Dufour J., Serrano D. P., Galves J. L., Moreno J., Gonzalez A., Hydrogen production from fossil fuels: Life cycle assessment of technologies with low greenhouse gas emissions, Energy & Fuels 25 (2011), p. 2194 – 2202.

(EC, 2003a) European Commission, Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry, JRC Institute for Prospective Technological Studies Sustainable Production and Consumption Unit, European IPPC Bureau, February 2003.

(EC, 2003b) European Commission, Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries, JRC Institute for Prospective Technological Studies Sustainable Production and Consumption Unit, European IPPC Bureau, February 2003.

(EC, 2006) European Commission, Regulation No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the registration, evaluation, authorisation and restriction of chemicals (REACH), establishing a European Chemicals Agency, Official Journal of the European Union L136, 29/5/2007, p. 3-280.

(EC, 2007a) European Commission, Limiting Global Climate Change to 2 degrees Celsius – The way ahead for 2020 and beyond, COM(2007)2, Brussels, Belgium, January 2007.

(EC, 2007b) European Commission, Reference Document on Best Available Techniques (BAT) for the Manufacture of Large Volume Inorganic Chemicals – Ammonia, Acids and

Fertilisers, JRC Institute for Prospective Technological Studies Sustainable Production and Consumption Unit, European IPPC Bureau, August 2007.

(EC, 2007c) European Commission, Reference Document on Best Available Techniques (BAT) for the Manufacture of Large Volume Inorganic Chemicals – Solids and Others Industry, JRC Institute for Prospective Technological Studies Sustainable Production and Consumption Unit, European IPPC Bureau, August 2007.

(EC, 2007d) European Commission, Reference Document on Best Available Techniques (BAT) for the Manufacture of Polymers, JRC Institute for Prospective Technological Studies Sustainable Production and Consumption Unit, European IPPC Bureau, August 2007.

(EC, 2008) European Commission, NACE Rev. 2 Statistical classification of economic activities in the European Community, Luxembourg, 2008.

(EC, 2009a) European Commission, Directive 2009/28/EC of the European Parliament and the Council of 23 April 2009 on the promotion of the use of energy from renewable sources, Official Journal of the European Union L140, 5/6/2009, p. 16-62.

(EC, 2009b) European Commission, Reference Document on Best Available Techniques (BAT) for Energy Efficiency, JRC Institute for Prospective Technological Studies Sustainable Production and Consumption Unit, European IPPC Bureau, February 2009.

(EC, 2009c) European Commission, Directive 2009/30/EC of the European Parliament and the Council of 23 April 2009 as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions, Official Journal of the European Union L140, 5/6/2009, p. 88 – 113.

(EC, 2009d) European Commission, Directive 2009/31/EC of the European Parliament and the Council of 23 April 2009 on the geological storage of carbon dioxide, Official Journal of the European Union L140, 5/6/2009, p. 114 – 135.

(EC, 2010a) European Commission, 2020 climate and energy package, . Available at http://ec.europa.eu/clima/policies/package/index_en.htm

(EC, 2010b) European Commission, Directive 2010/75/EU of the European Parliament and the Council of 24 November 2010 on industrial emissions (integrated pollution an control), Official Journal of the European Union L334, 17/12/2010, p. 17-119.

(EC, 2011a) European Commission, A Roadmap for moving to a competitive low carbon economy in 2050, COM(2011) 112, Brussels, Belgium, March 2011.

(EC, 2011b) European Commission, Commission Decision of 27 April 2011 determining transitional Union-wide rules for harmonised free allocation of emission allowances pursuant to Article 10a of Directive 2003/87/EC of the European Parliament and the Council, Official Journal of the European Union L130, 17/5/2011, p. 1-43.

(EC, 2012a) European Commission, Directive 2012/27/EU of the European Parliament and of the Council of 25 October 2012 on energy efficiency, Official Journal of the European Union L315, 14/11/2012, p. 1-56.

(EC, 2012b) European Commission, Commission Regulation (EU) No 601/2012 of 21 June 2012 on the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC, Official Journal of the European Union L181, 12/7/2012, p. 30-104

(EC, 2012c) European Commission, Impact Assessment Report accompanying the document "Guidelines on certain State aid measures in the context of Greenhouse Gas Emission Allowance Trading Scheme", SWD(2012) 130 final, 22/5/2012.

(EC, 2012d) European Commission, Communication from the Commission amending the Communication from the Commission Guidelines on certain State aid measures in the context of the greenhouse gas emission allowance trading scheme post-2012, 2012/C387/06, Official Journal of the European Union C 387, 15/12/2012, p. 5-13

(EC, 2013) European Commission, EU energy, transport and GHG emissions, Trends to 2050 – Reference Scenario 2013, Luxembourg, 2013 doi:10.2833/17897

(EC, 2014a) European Commission, State of the Industry, Sectoral overview and Implementation of the EU Industrial Policy accompanying the document COM(2014)14, SWD(2014)14/3, Brussels, Belgium, January 2014.

(EC, 2014b) European Commission, Commission Regulation No 206/2014 of 4 March 2014 amending Regulation No 601/2012 as regards global warming potentials for non-CO_2 greenhouse gases, Official Journal of the European Union L65, 5/3/2014, p. 27-28.

(EC, 2014c) European Commission, Best Available Techniques (BAT) Reference Document for the production of Chlor–alkali, JRC Institute for Prospective Technological Studies Sustainable Production and Consumption Unit, European IPPC Bureau, 2014.

(EC, 2014d) European Commission, Best Available Techniques (BAT) Reference Document in the Large Volume Organic Chemical Industry – Draft 1, JRC Institute for Prospective Technological Studies Sustainable Production and Consumption Unit, European IPPC Bureau, April 2014.

(EC, 2015a) European Commission, Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas, JRC Institute for Prospective Technological Studies Sustainable Production and Consumption Unit, European IPPC Bureau, 2015.

(EC, 2015b) European Commission, Climate Action, The EU Emissions Trading System, available at http://ec.europa.eu/clima/policies/ets/index_en.htm (last accessed January 2015).

(EC, 2015c) European Commission, Commission delegated regulation 2015/2402 of 12 October 2015 reviewing harmonised efficiency reference values for separate production of electricity and heat in application of Directive 2012/27/EU of the European parliament and of the Council and repealing Commission implementing decision 2011/877/EU, Official Journal of the European Union L33, 19/12/2015, p. 54 – 61.

(EC, 2015d) European Commission, Communication from the Commission to the European Parliament, the Council, European Economic and Social committee of the Regions and the European Investment Bank, A framework strategy for a resilient Energy Union with a forward-looking climate change policy, Energy Union Package COM(2015) 80 final, available at http://eur-lex.europa.eu/resource.html?uri=cellar:1bd46c90-bdd4-11e4-bbe1-01aa75ed71a1.0001.03/DOC_1&format=PDF (last accessed January 2017)

(EC, 2016a) European Commission, Climate Action, 2020 climate and energy framework, 2016, available at https://ec.europa.eu/clima/policies/strategies/2020_en (last accessed February 2017)

(EC, 2016a) European Commission, Climate Action, 2030 climate and energy framework, 2016, available at https://ec.europa.eu/clima/policies/strategies/2030_en#tab-0-0 (last accessed February 2017)

(EC, 2016b) European Commission, Cumulative cost assessment for the EU Chemical industry – Final report, Ref. Ares(2016)3304226 – 11/10/2016, available at http://ec.europa.eu/DocsRoom/documents/17784/attachments/1/translations/en/renditions/pdf (last accessed January 2017)

(EC, 2016c) European Commission, Climate Action, Carbon leakage, 2016, available at https://ec.europa.eu/clima/policies/ets/allowances/leakage_en#tab-0-0 (last accessed December 2016)

(EC, 2016d) European Commission, Climate Action, Carbon Capture and Geological Storage, 2016, available at http://ec.europa.eu/clima/policies/lowcarbon/ccs/index_en.htm (last accessed August, 2016)

(ECHA, 2014) European Chemicals Agency (ECHA), Nitric acid, available at http://echa.europa.eu/ (last accessed August 2014).

(Ecofys, 2009) Ecofys, Fraunhoffer Institute for Systems and Innovation Research and Öko-Institut, Methodology for the free allocation of emission allowances in the EU ETS post 2012 – Sector report for the chemical industry, November 2009 available at http://www.ecofys.com/files/files/091102_chemicals.pdf. (last accessed March 2016)

(Ecofys & TNO, 2004) Ecofys in cooperation with TNO, Global carbon dioxide storage potential and costs, EEP-02001, 2004

(Ecoheatcool, 2005-2006) Ecoheatcool and Euroheat & Power, Ecoheatcool working package 1 – The European Heat market Final report, Euroheat & Power, Belgium, 2005 – 2006.

(Ecoinvent, 2009) Ecoinvent, Ecoinvent database v.2.0, in: Inventories SCfLC, editor, Dübendorf, Switzerland, 2009.

(EEA, 2015) European Environmental Agency (EEA), Annual European Union greenhouse gas inventory 1990 – 2013 and inventory report 2015, Technical report No 19/2015, Denmark, November 2015.

(EEX, 2016) European Energy Exchange (EEX), European Emission Allowances Auction (EUA) – Global Environmental Exchange: Primary Market data, available at https://www.eex.com/en/market-data/emission-allowances/auction-market (last accessed March 2016)

(EFMA, 2000a) European Fertiliser Manufacturers' Association (EFMA), Booklet No.2: Production of nitric acid, Brussels, Belgium, 2000.

(EFMA, 2000b) European Fertiliser Manufacturers' Association (EFMA), Booklet No.1: Production of ammonia, Brussels, Belgium, 2000.

(EIGA, 2009) European Industrial Gases Association (EIGA), Best available techniques for hydrogen production by steam methane reforming, IGC Document 155/09/E, Brussels, Belgium, 2009.

(Eliasson et al., 2000) Eliasson B., Liu C.J., Kogelschatz U., Direct conversion of methane and carbon dioxide to higher hydrocarbons using catalytic dielectric-barrier discharges with zeolites, Industrial and Engineering Chemical Research 39 (2000), p. 1221 – 1227.

(Energetics, 2000) Energetics, Energy and Environmental Profile of the U.S. Chemical industry — Chapter 4, U.S. Department of Energy, May 2000.

(Energy 2000, 2000), Breault R.W., McClaine A.W., Rolfe J., Konduri R., Miskolczy G., Integrated hydrogen production and storage with chemical hydride slurry for energy in the 21st century, in Energy 2000: Beginning of a new millennium, Catania P. (editor), Technomic Publishing Company, 2000.

(Engineering Toolbox, 2015a) The Engineering Toolbox, Properties of saturated steam, available at http://www.engineeringtoolbox.com/saturated-steam-properties-d_457.html (last accessed March 2015)

(Engineering Toolbox, 2015b) The Engineering Toolbox, Air – Density and specific weight, available at http://www.engineeringtoolbox.com/air-density-specific-weight-d_600.html (last accessed March 2015)

(Entec, 2008). Entec UK Limited, Report for the European Commission – Support for the development and adoption of monitoring and reporting guidelines and harmonised benchmarks for N_2O activities for unilateral inclusion in the EU ETS for 2008 – 12, Final report, February 2008.

(EPA, 2013) U.S. Environmental Protection Agency (EPA),Ethylene dichloride, October 2013, available at http://www.epa.gov/airtoxics/hlthef/di-ethan.html (last accessed April 2015)

(EPA, 2010) U.S. Environmental Protection Agency (EPA), Available and Emerging Technologies for reducing Greenhouse Gas Emissions from the Nitric Acid production industry, Office of Air Quality Planning and Standards, North Carolina, USA, December 2010.

(EPA, 2015) U.S. Environmental Protection Agency (EPA), Catalog of CHP Technologies, March 2015, available at https://www.epa.gov/sites/production/files/2015-07/documents/catalog_of_chp_technologies.pdf (last accessed April 2016)

(EPA, 1998) U.S. Environmental Protection Agency (EPA), Compilation of Air pollutant emission factors AP – 42, Chapter 8: Inorganic Chemical Industry (Nitric acid / Urea), 5th edition, February 1998.

(EPA, 1995) U.S. Environmental Protection Agency (EPA), Compilation of Air pollutant emission factors AP – 42, Chapter 6: Organic Chemical Process Industry – Adipic acid, 5th edition, January 1995.

(EPA, 1994) U.S. Environmental Protection Agency (EPA), Background report AP-42 section 6.2 – Adipic acid production, U.S., July 1994.

(E-PRTR, 2016) European Environmental Agency (EEA), The European Pollutant Release and Transfer Register (E-PRTR), Industrial Activity, 2013, available at http://prtr.ec.europa.eu/#/industrialactivity (last accessed March 2016)

(Eramo, 2013) Eramo M., Global Ethylene Market Outlook: Low cost feedstocks fuel the next wave of investments in North America and China, Inaugural Ethylene Forum, November 2013, available online at http://media.corporate-ir.net/media_files/IROL/11/110877/05_Global_Ethylene_Market_Outlook_Eramo.pdf (last accessed October 2014).

(ESAP, 2012) Energy System Analysis & Planning (EPIC), Electricity Production Information & Capacity (EPIC) Database, 2012.

(ESAPA, 2011) European Soda Ash Producers Association (ESAPA), Position papers, 2011, available online at http://esapa.eu/position-papers.aspx (last accessed March 2015)

(Euro Chlor, 2010) Euro Chlor, The European chlor–alkali industry: an electricity intensive sector exposed to carbon leakage, Brussels, Belgium, December 2010.

(Euro Chlor, 2012) Euro Chlor, Chlorine Industry Review 2012 – 2013 – Towards a new European Industrial policy for more competitiveness, Brussels, Belgium, 2013.

(Euro Chlor, 2013) Euro Chlor, Chlorine Industry Review 2011 – 2012 – Will Europe fuel our future?, Brussels, Belgium, 2012.

(Euro Chlor, 2014) Euro Chlor, Information about chlorine and the chlor-alkali industry in Europe, available at http://www.eurochlor.org/the-chlorine-universe/what-is-chlorine.aspx (last accessed August 2014)

(Eurostat, 2006) Danko J., Lösönen P., Statistics in focus – Combined Heat and Power (CHP) electricity generation in the EU-25 in 2002 totalled 299.2 TWh, 9.9% of total gross electricity generation, Eurostat , European Commission, Luxembourg, 2006.

(Eurostat, 2013) Eurostat, Energy balance sheets 2010-2011, Luxembourg, April 2013, doi:10.2785/43236 .

(Eurostat, 2014a) Eurostat, Annual detailed enterprise statistics for industry (NACE Rev.2, B-E), Number of persons employed, last update 13/6/2014, available at http://epp.eurostat.ec.europa.eu/portal/page/portal/product_details/dataset?p_product_code=SBS_NA_IND_R2

(Eurostat, 2014b) Eurostat, Energy balance sheets 2011 – 2012, Luxembourg, 2014.

(Eurostat, 2014c) Eurostat, Combined Heat and Power (CHP) data, Luxembourg, September 2014.

(Eurostat, 2015) Eurostat, Combined heat and power (CHP) data 2005 – 2013, Luxembourg, June 2015

(Eurostat, 2016a) Eurostat, Complete energy balances – annual data (nrg_110a), 1st updated February 2016

(Eurostat, 2016b) Eurostat, Generation of waste – Plastic wastes (env_wasgen), last updated July 2015

(Eurostat, 2016c) Eurostat, Electricity prices for industrial consumers from 2007 onwards – bi-annual data, last update 7/11/2016

(Exelus, 2013) Exelus, ExSyM technology, 2013, available online at http://www.exelusinc.com/exsymchem.shtml (last accessed April 2016)

(ExxonMobil, 2012) ExxonMobil Chemical Company, Greenhouse Gas Prevention of significant deterioration Permit Application for Ethylene Expansion Project Baytown Olefins Plant, Baytown, Texas, Prepared by SAGE Environmental Consulting, May 2012 available at http://www.epa.gov/region6/6pd/air/pd-r/ghg/exxonmobil-baytown-olefins-app.pdf (last accessed August 2014)

(Farmosa Plastics, 2012) Formosa Plastics Corporation, Greenhouse Gas Permit Application Prevention of significant deterioration: 2012 Expansion Project – Olefins Expansion: Olefins 3 and propane dehydrogenation plant, Point Comfort, Texas, Submitted to EPA Region 6, Prepared by Zephyr Environmental Corporation, November 2012 available at http://www.epa.gov/region6/6pd/air/pd-r/ghg/formosa-olefins-expansion-app.pdf (last accessed August 2014)

(Fertiliser Encyclopaedia, 2009) Gowariker V., Krishnamurthy V.N., Gowariker S., Dhanorkar M., Paranjape K., The Fertilizer Encyclopaedia, Wiley, ISBN: 978-0-470-41034-9, February 2009, p. 35 – 41.

(Fertiliser Europe, 2012) Fertiliser Europe Hoxha A., Personal communication, 2012.

(Fulcheri et al., 2002) Fulcheri L., Probst N., Flamant G., Farby F., Grivei E., Bourrat X., Plasma processing: a step towards the production of new grades of carbon black, Carbon 40 (2002), p. 169 – 176.

(Fulcheri et al., 1997) Fulcheri L., Schwob Y., Flamant G., Comparison between new carbon nanostructures produced by plasma with industrial carbon black grades, Journal de Physique III 7 (1997), p. 497 – 503.

(Garcia Villaluenga & Tabe-Mohammadi, 2000) Garcia Villaluenga J.P. and Tabe-Mohammadi A., A review on the separation of benzene/cyclohexane mixtures by pervaporation processes, Journal of Membrane Science 169 (2000), p. 159 – 174.

(Gasplas, 2011) Risby P., Espen Stoknes P., Gasplas Presentation, Gasplas AS, UK – Norway, 2011, available at http://www.gasplas.com/w3/attachments/160_110608_GasPlas_Presentation_UEA-email%201.pdf (last accessed July 2014).

(Gaudernack & Lynum, 1998) Gaudernack B. and Lynum S., Hydrogen from natural gas without release of CO_2 to the atmosphere, International Journal of Hydrogen Energy 23 (1998), p. 1087-1093.

(Gentry & Zeng, 2009) Gentry J.C. and Zeng M., Pygas upgrading for European steam crackers, www.digitalrefining.com/article/1000578, PTQ Q1, 2009.

(Gibson, 2010) Gibson L., Verdezyne proves adipic acid production process, Biomass magazine 4 (2010), p. 25, available at http://biomassmagazine.com/articles/3608/verdezyne-proves-adipic-acid-production-process (last accessed August 2014)

(Global CCS Institute, 2016) Global CCS Institute, Industrial CCS, available online at http://www.globalccsinstitute.com/content/industrial-ccs (last accessed August 2016)

(Global processing, 2013) Global processing, Prospects look good for global ethylene oxide, ethylene glycol markets, August 2013, available at http://www.processingmagazine.com/articles/126001-prospects-look-good-for-global-ethylene-oxide-ethylene-glycol-markets (last accessed April 2015)

(Grand view Research, 2014) Grand view Research, Adipic Acid market analysis and segment forecasts to 2020 – Report summary, February 2014, available at http://www.grandviewresearch.com/industry-analysis/adipic-acid-market?gclid=CIuwg4j9nsACFQgYwwod5G0AjQ (last accessed August 2014)

(Haarsma & Mutha, 2008) Haarsma G. and Mutha R., Implementation of unit wide Advanced Process Control in ethylene plant, paper 151b, AIChE spring national meeting, New Orleans, April 2008 available at http://www.kemco.or.kr/up_load/blog/Advance%20Process%20Control.pdf (last accessed August 2014)

(Hemschemeier et al., 2009) Hemschemeier A., Melis A., Happe T., Analytical approaches to photo biological hydrogen production in unicellular green algae, Photosynthesis Research 102 (2009), p. 523 – 540.

(Hirata & Kakiuchi, 2011) Hirata K. and Kakiuchi H., Energy saving for ethylene process by Adsorption Heat Pump, Applied Thermal Engineering 31 (2011), p. 2115 – 2122.

(Holladay et al., 2009) Holladay J.D., Hu J., King D.L., Wang Y., An overview of hydrogen production technologies, Catalysis Today 139 (2009), p. 244 – 260.

(Holbrook & Leighty, 2009) Holbrook J.H. and Leighty W.C., Renewable fuels: Manufacturing ammonia from hydropower, January 2009, available at http://www.hydroworld.com/articles/hr/print/volume-28/issue-7/articles/renewable-fuels-manufacturing.html (last accessed August 2014)

(Honeywell, 2007) Honeywell, Success story: SECCO maximises EBSM unit profitability with Honeywell's optimisation solution, 2007. Available online at https://www.honeywellprocess.com/library/marketing/case-studies/Success%20Story_SECCO_Optimization.pdf (last accessed April 2016)

(Huff et al., 2005) Huff G., Chen B., Colling G., Miller J., Xylene process using perm-selective separations, United States Patent US 20050171395 A1, August 2005.

(Iaquaniello et al., 2012) Iaquaniello G., Antonetti E., Cucchiella B., Palo E., Salladini A., Guarinoni A., Lainati A., Basini L., Natural gas catalytic partial oxidation: A way to syngas and bulk chemicals production, http://dx.doi.org/10.5772/48708, 2012.

(Iaquaniello et al., 2008) Iaquaniello G., Giacobbe F., Morico B., Cosenza S., Farace A., Membrane reforming in converting natural gas to hydrogen: Production costs, Part II, International Journal of Hydrogen Energy 33 (2008), p. 6595 – 6601.

(ICF, 2015), ICF International, Study on energy efficiency and energy saving potential in industry and on possible policy mechanism, December 2015.

(ICIS, 2007) ICIS, Ethylene dichloride uses and Market data, November 2007, available at http://www.icis.com/resources/news/2007/11/02/9075704/ethylene-dichloride-edc-uses-and-market-data/ (last accessed April 2015)

(ICIS, 2012) ICIS, Database, 2012.

(ICIS, 2013) ICIS, Market outlook: Speedy growth for chemicals by 2050, October 2013, available at http://www.icis.com/resources/news/2013/10/13/9714353/market-outlook-speedy-growth-for-chemicals-by-2050/ (last accessed July 2016)

(IEA, 2006) IEA, Hydrogen production and storage- R&D Priorities and Gaps, OECD/IEA, Paris, 2006

(IEA, 2007) IEA, Tracking Industrial Energy Efficiency and CO_2 emissions, OECD/IEA, Paris, 2007

(IEA, 2008) IEA, Combined Heat and Power – Evaluating the benefits of greater global investment, IEA publications, France, February 2008

(IEA, 2009a) IEA, Energy technology transitions for industry, IEA publications, France, 2009

(IEA, 2009b) Saygin D., Patel M. K., Tam C., Gielen D. J., Chemical and Petrochemical sector: Potential of best practice technology and other measures for improving energy efficiency, IEA information paper, France, September 2009

(IEA, 2012a) IEA, Energy Technology Perspectives 2012: Pathways to a Clean Energy System, IEA Publications, France, 2012

(IEA, 2012b) de Jong E., Higson A., Wlash P., Wleishc M., Bio-based Chemicals – Value added products from bio refineries, IEA Bioenergy – Task 42 Bio refinery, February 2012

(IEA, 2013) IEA, Technology roadmap: Energy and GHG reductions in the chemical industry via catalytic processes, IEA Publications, France, May 2013

(IEA, 2014) IEA, Energy Technology Perspectives 2014: Harnessing electricity's potential, IEA Publications, France, 2014

(IEA, 2015) IEA, Extended world energy balances, Edition 2015/1, Database, DOI: http://dx.doi.org/10.1787/95e22f23-en (last accessed June 2016)

(IEA, 2016a) IEA, Energy prices and taxes, Vol. 2016/1, OECD Publishing, Paris, DOI: http://dx.doi.org/10.1787/energy_tax-v2016-1-en

(IEA, 2016b) IEA, Spot market and crude oil import costs: Crude oil import costs and index, IEA Energy Prices and Taxes Statistics Database, DOI: http://dx.doi.org/10.1787/data-00446-en (last accessed June 2016)

(IEA ETSAP, 2010) IEA Energy Technology Systems Analysis Programme, Technology Brief E04, Combined Heat and Power, May 2010, available at http://www.iea-etsap.org/web/e-techds/pdf/e04-chp-gs-gct_adfinal.pdf

(IETD, 2015a) Industrial Efficiency Technology Database (IETD), Indirect cooling, Institute for Industrial Productivity, 2015, available at http://ietd.iipnetwork.org/content/indirect-cooling (last accessed March 2015)

(IETD, 2015b) Industrial Efficiency Technology Database (IETD), Shift Conversion, Institute for Industrial Productivity, 2015, available at http://ietd.iipnetwork.org/content/shift-conversion (last accessed March 2015)

(IFA, 2013) Heffer P. and Prud'homme M., Fertiliser Outlook 2013 – 2017, 81st IFA Annual Conference, Chicago USA, May 2013, International Fertiliser Industry Association (IFA), June 2013 available at http://www.fertiliser.org/MarketOutlooks (last accessed August 2014)

(IFA, 2012) Heffer P. and Prud'homme M., Fertiliser Outlook 2012 – 2016, 80th IFA Annual Conference, Doha Qatar, May 2012, International Fertiliser Industry Association (IFA), June 2012 available at http://www.fertiliser.org/MarketOutlooks (last accessed August 2014)

(IFA, 2011) Heffer P. and Prud'homme M., Fertiliser Outlook 2011 – 2015, 79th IFA Annual Conference, Montreal Canada, May 2011, International Fertiliser Industry Association (IFA), June 2011 available at http://www.fertiliser.org/MarketOutlooks (last accessed August 2014)

(IHS, 2005) Recovery of styrene from pyrolysis gasoline, Abstract from PEP Review 2005 – 15, December 2005, available at http://www.ihs.com/products/chemical/technology/pep/reviews/recovery-of-styrene-from-pyrolysis-gasoline.aspx (last accessed August, 2014).

(IHS, 2009) IHS Chemical, Ethylene glycol, Abstract from the Process Economics Program Report 2I, September 2009, available at https://www.ihs.com/products/chemical-technology-pep-ethylene-glycol-2009.html (last accessed April 2015).

(IHS, 2011a) IHS Chemical, Propylene – Abstract from the Report, August 2011, available at http://www.ihs.com/products/chemical/planning/ceh/propylene.aspx (last accessed August 2014).

(IHS, 2011c) IHS Chemical, Benzene – Abstract from the Report, October 2011, available at http://www.ihs.com/products/chemical/planning/ceh/benzene.aspx (last accessed August 2014).

(IHS, 2011d) IHS Chemical, Chlorine/Sodium Hydroxide – Abstract from the Report, June 2011, available at http://www.ihs.com/products/chemical/planning/ceh/chlorine-sodium.aspx (last accessed August 2014).

(IHS, 2012a) IHS Chemical, Butadiene – Abstract from the Report, December 2012, available at http://www.ihs.com/products/chemical/planning/ceh/butadiene.aspx (last accessed August 2014).

(IHS, 2012b) IHS Chemical, Adipic acid – Abstract from the Report, January 2012, available at http://www.ihs.com/products/chemical/planning/ceh/adipic-acid.aspx (last accessed August 2014).

(IHS, 2012c) IHS Chemical, Sodium Carbonate – Abstract from the Report, December 2012, available at http://www.ihs.com/products/chemical/planning/ceh/sodium-carbonate.aspx (last accessed August 2014).

IHS, 2012d)) IHS Chemical, Ethylene Dichloride – Abstract from the Report, April 2012, available at https://www.ihs.com/products/ethylene-dichloride-chemical-economics-handbook.html (last accessed April 2015).

(IHS, 2013a) IHS Chemical, Hydrogen – Abstract from the Report, August 2013, available at http://www.ihs.com/products/chemical/planning/ceh/hydrogen.aspx (last accessed August 2014).

(IHS, 2013b) IHS Chemical, Xylenes – Abstract from the Report, July 2013, available at http://www.ihs.com/products/chemical/planning/ceh/xylenes.aspx (last accessed August 2014).

(IHS, 2013c) IHS Chemical, Toluene – Abstract from the Report, January 2013, available at http://www.ihs.com/products/chemical/planning/ceh/toluene.aspx (last accessed August 2014).

(IHS, 2013d) IHS Chemical, Ethylene oxide – Abstract from the Report, May 2013, available at https://www.ihs.com/products/ethylene-oxide-chemical-economics-handbook.html (last accessed April 2015)

(IHS, 2013e) IHS Chemical, Ethylene glycols – Abstract from the Report, November 2013, available at https://www.ihs.com/products/mono-di-and-triethylene-chemical-economics-handbook.html (last accessed April 2015)

(IHS, 2014a) Information provided by IHS Chemical in the form of a Chemical Plant Database, September 2014.

(IHS, 2014b) IHS Chemical, Nitric Acid – Abstract from the Chemical Economics Handbook, June 2014, available at http://www.ihs.com/products/chemical/planning/ceh/nitric-acid.aspx (last accessed August 2014).

(IHS, 2014c) IHS Chemical, Ammonia – Abstract from the Report, February 2014, available at http://www.ihs.com/products/chemical/planning/ceh/ammonia.aspx (last accessed August 2014).

(IHS, 2014d) IHS Chemical, Ethylene – Abstract from the Report, October 2014, available at https://www.ihs.com/products/ethylene-chemical-economics-handbook.html (last accessed March 2015).

(IHS, 2014e) IHS Chemical, Methanol – Abstract from the Report, May 2014, available at http://www.ihs.com/products/chemical/planning/ceh/methanol.aspx (last accessed August 2014).

(IHS, 2014f) IHS Chemical, Global demand for benzene increased to 43.7 million metric tons in 2013, February 2014, available online at http://press.ihs.com/press-release/aromatic-chemicals/global-demand-benzene-primary-chemical-building-block-chemical-indu (last accessed March 2016)

(IHS, 2014g)) IHS Chemical, Benzene – Abstract from the Report, December 2014, available at https://www.ihs.com/products/benzene-chemical-economics-handbook.html (last accessed March 2016).

(IHS, 2015a) Information provided by IHS Chemical in the form of a Database, October 2015.

(IHS, 2015b) IHS Chemical, Propylene – Abstract from the Report, February 2015, available at https://www.ihs.com/products/propylene-chemical-economics-handbook.html (last accessed July 2016).

(IHS, 2015c) IHS Chemical, Hydrogen – Abstract from the Report, June 2015, available at https://www.ihs.com/products/hydrogen-chemical-economics-handbook.html (last accessed July 2016).

(IHS, 2015d) IHS Chemical, Adipic acid – Abstract from the Report, April 2015, available at https://www.ihs.com/products/adipic-acid-chemical-economics-handbook.html (last accessed July 2016).

(IHS, 2015e) IHS Chemical, Sodium carbonate – Abstract from the Report, December 2015, available at https://www.ihs.com/products/sodium-carbonate-chemical-economics-handbook.html (last accessed July 2016).

(IHS, 2015f) IHS Chemical, Xylenes – Abstract from the Report, October 2015, available at https://www.ihs.com/products/xylenes-chemical-economics-handbook.html (last accessed July 2016).

(IHS, 2015g) IHS Chemical, Ethylene Dichloride – Abstract from the Report, September 2015, available at https://www.ihs.com/products/ethylene-dichloride-chemical-economics-handbook.html (last accessed July 2016).

(IHS, 2015h) IHS Chemical, Vinyl Chloride Monomer (VCM) – Abstract from the Report, April 2015, available at https://www.ihs.com/products/ethylbenzene-chemical-economics-handbook.html (last accessed July 2016).

(IHS, 2015i) IHS Chemical, Ethylbenzene – Abstract from the Report, November 2015, available at https://www.ihs.com/products/vinyl-chloride-monomer-chemical-economics-handbook.html (last accessed July 2016).

(IHS, 2015i) IHS Chemical, Styrene – Abstract from the Report, July 2015, available at https://www.ihs.com/products/styrene-chemical-economics-handbook.html (last accessed July 2016).

(IL&FS, 2010) IL & FS Ecosmart Limited, Technical EIA guidance manual for petrochemical complexes, Prepared for the Ministry of Environment and Forests, Government of India, Hyderabad, September 2010.

(IPCC, 2005) Intergovernmental Panel on Climate Change (IPCC), IPCC special report on Carbon dioxide capture and storage, prepared by Working group III of the IPCC (Metz B., Davidson O., de Coninck H.C., Loos M. and Meyer L.A. (eds.)), Cambridge University Press, Cambridge UK, 2005.

(IPCC, 2006a) Intergovernmental Panel on Climate Change (IPCC), 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Volume 2 – Energy, Chapter 2 – Stationary Combustion.

(IPCC, 2006b) Intergovernmental Panel on Climate Change (IPCC), 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Volume 3 – Industrial Processes and Product Use, Chapter 3 – Chemical Industry Emissions.

(IPCC, 2007a) Solomon S., Qin D., Manning M., Chen Z., Marquis M., Averyl K.B., Tignor M., Miller H.L. (eds.) Working Group I contribution to the 4th Assessment Report of the IPCC. Chapter 2: Changes in atmospheric constituents and in radiative forcing.

(IPCC, 2007b) Intergovernmental Panel on Climate Change (IPCC), Climate change 2007 – Mitigation of Climate change: Working Group III contribution to the 4th Assessment Report of the IPCC. Chapter 4 – Energy supply.

(IPCC, 2013) Climate Change 2013: The physical science basis. Contribution of Working Group I to the 5th Assessment Report of the Intergovernmental Panel on Chemical Change, Cambridge University Press, Cambridge, United Kingdom.

(JEC, 2014) JEC – Joint Research Centre, EUCAR, CONCAWE collaboration, Well-to-tank Appendix 1, Version 4a, 2014.

(Kim et al., 2005) Kim K.S., Seo J. H., Nam J. S., Ju W. T, Hong S. H., Production of hydrogen and carbon black by methane decomposition using DC-RF hybrid thermal plasmas. IEEE Transactions on Plasma Sciences 33 (2005), p. 813 – 823.

(Kirk-Othmer, 1999), Kroschwitz J.I (executive editor), Howe-Grant M. (editor), Kirk-Othmer Encyclopaedia of Chemical Technology, 4th edition, Wiley, 1999.

(Klinger, 2001) Klinger F., Session 7: Control of N_2O emissions from various sources – Valorisation of nitrous oxide emitted by adipic acid unit, Rhodia Alsachimie, Chalempe, France, 2001, available at https://www.yumpu.com/en/document/view/11811141/valorisation-of-nitrous-oxide-emitted-by-adipic-acid-units-infomil (last accessed August 2014).

(Kojima et al., 2008) Kojima Y., Morikawa H., Sakata E., Urea production reduces greenhouse gas by energy saving and carbon dioxide recovery, Toyo Engineering Corp, 2008.

(Kolmetz et al., 2002) Kolmetz K., Kivlen J., Gray J., Phaik Sim C., Soyza C. A., Advances in cracking furnace technology, Refining Technology Conference, Dubai, December 2002, available at http://kolmetz.com/pdf/articles/AICFT.pdf (last accessed August 2014)

(Körting, 2014) Körting Hannover AG, Changing mercerising waste water into money – caustic recovery for mercerising lye, 270-Caustic Recovery-131204, available at http://www.koerting.de/docs/default-source/brochures-process/caustic-recovery-view-%28brochure%29.pdf?sfvrsn=16 (last accessed August 2014)

(Kothari et al., 2008) Kothari R., Buddhi D., Sawhney R. L., Comparison of environmental and economic aspects of various hydrogen production methods, Renewable and Sustainable Energy Reviews 12 (2008), p. 553 – 563.

(Kumar et al., 2013) Kumar S., Kalita A. Uppaluri R., Economic feasibility study of sodium bicarbonate and soda ash production from Na_2SO_4, International Journal of Engineering Research and Science and Technology 2 (2013), p. 21 – 40.

(Kvaerner Engineering, 1993a) Kvaerner Engineering, System for the production of carbon black, International Patent, PCT No. 93/00057, 1993.

(Kvaerner Engineering, 1993b) Kvaerner Engineering, Production of carbon black, International Patent, PCT No. 93/00058, 1993.

(Kvaerner Engineering, 1992) Kvaerner Engineering, A method for decomposition of hydrocarbons, International Patent, PCT No. 92/00196, 1992.

(Lako, 2009) Lako P., Energy conservation potential of the nitrogen fertiliser industry, ECN, The Netherlands, March 2009.

(Lee et al., 1998) Lee F.M., Gentry J.C., Wright Wytcherley R., Recovery of styrene from pyrolysis gasoline by extractive distillation, United States Patent US 5849982 A, December 1998.

(LePrince, 2001) LePrince P., Petroleum refining vol 3: Conversion Processes, Technip, 2001.

(Li et al., 2012) Li H., She Y., Wang T., Advances and perspectives in catalysts for liquid-phase oxidation of cyclohexane, Frontiers of Chemical Science and Engineering 6 (2012), p. 356 – 368.

(Li et al., 2010) Li J., Li X., Shi Y., Mao D., Lu G., Selective oxidation of cyclohexane by oxygen in a solvent-free system over lanthanide-containing $AlPO_5$, Catalysis Letters 137 (2010), p. 180 – 189.

(Lin et al., 2013) Lin Z., Ierapetritou M., Nikolakis V., Aromatics from lignocellulosic biomass: economic analysis of the production of p-xylene from 5-hydroxymethylfurfural, AIChE Journal 59 (2013) p. 2079 – 2087.

(Linde, 2015) Linde, Hydrogen available at http://www.linde-engineering.com/internet.global.lindeengineering.global/en/images/H2_1_1_e_12_150dpi19_4258.pdf (last accessed March 2015).

(Lipman, 2011) Lipman T., An overview of Hydrogen production and storage systems with renewable hydrogen case studies – A clean energy States Alliance report, Clean Energy States Alliance, USA, May 2011.

(Lloyd, 2011) Lloyd L., Handbook of Industrial Catalysts, Springer, 2011, DOI 10.1007/978-0-387-49962-8

(Long et al., 2013) Long C. M., Nascarella M. A., Valberg P. A., Carbon black vs. black carbon and other airborne materials containing elemental carbon: Physical and chemical distinctions, Environmental Pollution 181 (2013), p. 271 – 286.

(Lü et al., 2012) Lü H., Ren W., Liu P., Qi S., Wang W., Feng Y., Sun F., Wang Y., One-step aerobic oxidation of cyclohexane to adipic acid using an Anderson-type catalyst $((C_{18}H_{37})_2N(CH_3)_2)_6Mo_7O_{24}$, Applied Catalysis A: General 441 – 442 (2012), p. 136 – 141.

(Lunsford, 2000) Lunsford J.H., Catalytic conversion of methane to more useful chemicals and other fuels: a challenge for the 21st century, Catalysis Today 63 (2000), p. 165 – 174.

(Martelli & Federico, 2004) Martelli G. and Federico F., Electro catalytic composition for oxygen-depolarised cathode, United States Patent US 20040069622 A1, April 2004.

(Mathias & Brown, 2003) Mathias P.M., Brown L.C., Thermodynamics of the sulphur-iodine cycle for thermochemical hydrogen production, 68th Annual meeting of the Society of Chemical Engineers, Japan, March 2003, available at http://www.aspentech.com/publication_files/TP51.pdf (last accessed August 2014).

(Melis & Happe, 2001) Melis A. and Happe T., Hydrogen production. Green algae as a source of energy, Plant Physiology 127 (2001), p. 740 – 748.

(Merchant Research, 2013) Merchant Research & Consulting ltd, Global styrene production exceeded 26.4 million tonnes in 2012, August 2013, available online at http://mcgroup.co.uk/news/20130830/global-styrene-production-exceeded-264-million-tonnes.html (last accessed April 2016)

(Merchant Research, 2014) Merchant Research & Consulting ltd, North America ranks first in worldwide ethylene dichloride market, November 2014, available at http://mcgroup.co.uk/news/20141121/north-america-ranks-worldwide-ethylene-dichloride-edc-market.html (last accessed April 2015)

(Meyers, 2004) Meyers R., Handbook of Petroleum Refining Processes, McGraw – Hill, 3rd edition, 2004.

(Miller et al., 2008) Miller J.T., Chen B., Colling C.W., Huff G.A. Jr, Henley B., Koros W.J., Chafin R.W., Separation process using aromatic-selective polymeric membranes, Patent WO 2008100270 A1, August 2008.

(Mineralogy, 2015) Antony J.W., Bideaux R.A., Bladh K.W., Nichols M.C. (eds.), Handbook of Mineralogy, Mineralogical Society of America, Chantilly VA 20151–1110, USA, available online at http://www.handbookofmineralogy.org/ (last accessed March 2015)

(MMSA, 2013) Methanol Market Services Asia (MMSA), Methanol Supply and Demand Balance 2008 – 2013E, 2013 available at http://www.methanol.org/getattachment/827c8c64-fb2a-4520-aa5a-210612b903cd/MMSA-Supply---Demand-Tables-2008---2013.pdf.aspx (last accessed October 2014)

(MNP, 2008) Milieu- en Natuurplanbureau (MNP), Wisselink L.G., Eerens H., Vis J., EU 2020 climate target: 20% reduction requires five-fold increase in impact of CO_2 policies, MNP report 500094007, Netherlands Environmental Assessment Agency, Netherlands, 2008.

(Molburg & Doctor, 2003) Molburg J.C. and Doctor R.D., Hydrogen from steam-methane reforming with CO_2 capture, 20th Annual International Pittsburgh Coal Conference, September 2003.

(Moreno-Couranjou et al., 2009) Moreno-Couranjou M., Monthioux M., Gonzalez-Aguilar J., Fulcheri L., A non-thermal plasma process for the gas phase synthesis of carbon nanoparticles. Carbon 47 (2009)., p. 2310 – 2321.

(Moulijn et al., 2001) Moulijn J.A., Makkee M., van Diepen A., Chemical process technology, John Willey & Sons, 2001.

(Moussallem et al., 2009) Moussallem I., Pinnow S., Turek T., Möglichkeiten zur Energierückgewinnung aus Wasserstoff bei der Chlor-Alkali-Elektrolyse, Chemie Ingenieur Technik 81 (2009), p. 489 – 493.

(Nacamuli & Thom, 1998) Nacamuli G.J. and Thom B.J., Split-feed two-stage parallel aromatisation for maximum para-xylene yield, Patent WO 1998058041 A1, December1998.

(NEDO, 2001) New Energy and Industrial Technology Development Organization (NEDO). FY2000 Study Report: *"Survey of Energy Saving in Japan",* March 2001.

(Neelis et al., 2005) Neelis M.L., Patel M.K., Bach P.W., Haije W.G., Analysis of energy use and carbon losses in the chemical and refinery industries, ECN-I-05-008, September 2005.

(Neelis et al., 2007) Neelis M., Patel M., Blok K., Haije W., Bach P., Approximation of theoretical energy-saving potential for the petrochemical industry using energy balances for 68 key processes, Energy 32 (2007), p. 1104 – 1123.

(Nieuwlaar, 2001) Nieuwlaar E., ICARUS-4 Sector study for the chemical industry, Report nr. NWS-E-2001-19, Department of Science, Technology and Society, Utrecht University, The Netherlands, September 2001.

(NREL, 2009) National Renewable Energy Laboratory (NREL), Current (2009) state-of-art hydrogen production cost estimate using water electrolysis, NREL/BK-6A1-46676, Colorado, USA, September 2009.

(OECD, 2014) OECD, Biofuels in OECD and FAO, OECD-FAO Agricultural Outlook 2014, OECD Publishing, Paris, 2014, DOI: http://dx.doi.org/10.1787/agr_outlook-2014-6-en (last accessed June 2016)

(Olah et al., 2009) Olah G., Goeppert A., Surya Prakash G.K., Beyond Oil and Gas: the methanol economy, 2nd edition, Wiley VCH, 2009.

(OPT Sensor Srl, 2012) OPT Sensor S.r.l. Personal communication, 2012.

(Pandia, 2014) Pandia R.M., Markets and potential for non-polymer derivatives of propylene, March 2014, Presentation available at http://platts.com/IM.Platts.Content/ProductsServices/ConferenceandEvents/2014/xc450/presentations/PropyleneIts%20Derivatives-Feb%202014.PDF (last accessed October 2014).

(Parmon et al., 2005) Parmon V.N., Pnov G.I., Uriarte A., Noskov A.S., Nitrous oxide in oxidation chemistry and catalysis: application and production, Catalysis Today 100 (2005), p. 115 – 131.

(PBL, 2014) PBL Netherlands Environmental Assessment agency, Trends in global CO_2 emissions, 2014 report, available at: https://encrypted.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&ved=0ahUKEwi4xv7Or_HRAhULcBoKHUaiBWAQFggeMAA&url=http%3A%2F%2Fwww.pbl.nl%2Fsites%2Fdefault%2Ffiles%2Fcms%2Fpublicaties%2FPBL_2014_Trends_in_global_CO2_emisions_2014_1490_0.pdf&usg=AFQjCNE2SZo9QAIc5AsrYThevmOllWiBQg&sig2=P4OqJ2_S9XsAKA95bzdmVw&bvm=bv.146073913,d.ZGg

(PCI Wood MacKenzie, 2016) PCI nylon, Adipic Acid, available at http://www.pcinylon.com/index.php/markets-covered/adipic-acid (last accessed March 2016).

(Perry's Handbook, 2008) Green D. W., Perry R. H. (editors), Perry's Chemical Engineering Handbook, 8th edition, Mc-Graw Hill, 2008, p. 9-4 – 9-21.

(Peters et al., 2011) Peters M.W., Taylor J.D., Jenni M., Manzer L.E., Henton D.E., Integrated process to selectively convert renewable isobutanol to p-xylene, United States Patent US 20110087000 A1, April 2011.

(Petrochemicals, 2016) Petrochemicals Europe, Capacity and Production data – Ethylene and derivatives, available at http://www.petrochemistry.eu/about-petrochemistry/facts-and-figures/capacity-and-production-data.html (last accessed March 2016).

(Phylipsen et al., 2002) Phylipsen D., Blok K., Worrell E., de Beer J., Benchmarking the energy efficiency of Dutch industry: an assessment of the expected effects on energy consumption and CO_2 emissions, Energy Policy 30 (2002), p. 663-679.

(Picciotti, 1997) Picciotti M., Ethylene Technologies – 1: Novel ethylene technologies developing, but steam cracking remains king, Oil & Gas Journal, 23 June 1997, available at http://www.ogj.com/articles/print/volume-95/issue-25/in-this-issue/petrochemicals/ethylene-technologies-1-novel-ethylene-technologies-developing-but-steam-cracking-remains-king.html (last accessed August 2014)

(Plastics Europe, 2005) Boustead I., Eco-profiles of the European Plastics Industry – Acrylonitrile, A report for Plastics Europe, March 2005 available at http://www.plasticseurope.org/plasticssustainability/eco-profiles/browse-by-list.aspx (last accessed August 2014)

(Plastics Europe, 2015) Plastics Europe, Plastics – the Facts 2014/2015, 2015, available online at http://www.plasticseurope.org/documents/document/20150227150049-final_plastics_the_facts_2014_2015_260215.pdf (last accessed April 2015)

(Plastics News, 2016) Plastics News, Historical resin pricing: PVC, available online at http://www.plasticsnews.com/resin/recycled-plastics/historical-pricing?grade=1341001|Vol2 (last accessed April 2016)

(Plastics Recyclers Europe, 2012) Plastics Recyclers Europe, How to boost plastics recycling and increase resource efficiency?, 2012, available online at http://www.plasticsrecyclers.eu/sites/default/files/EuPR%20Strategy%20Paper%202012_0.pdf (last accessed April 2016)

(Prognos, 2000) Plinke E., Wenk N., Wolff G., Castiglione D., Palmark M., Mechanical recycling of PVC wastes – Final report, January 2000

(PVC, 2016) PVC, PVC-recycling technologies, available online at http://www.pvc.org/en/p/pvc-recycling-technologies (last accessed April 2016)

(PVCplus, 2012) PVCplus, PVC from A to Z, May 2012, available online at http://www.renolit.com/fileadmin/renolit/corporate/images/Everything_about_PVC.pdf (last accessed April 2016)

(Rafiqul et al., 2005) Rafiqul I., Weber C., Lehmann B., Voss A., Energy efficiency improvements in ammonia production – perspectives and uncertainties, Energy 30 (2005), p. 2487 – 2504.

(Rahimi & Karimzadeh, 2011) Rahimi N. and Karimzadeh R., Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: a review, Applied Catalysis A: General 398 (2011), p. 1 – 17.

(Recovinyl, 2016) RecoVinyl, Vinyl Plus, available online at http://www.recovinyl.com/vinylplus (last accessed April 2016)

(Reliance Industries, 2015) Reliance Industries Limited, Other petrochemicals, available at http://www.ril.com/html/business/other_petrochemicals.html (last accessed March 2015)

(Ren et al., 2006) Ren T., Patel M., Blok K., Steam cracking and methane to olefins: Energy use, CO_2 emissions and production costs, Energy 33 (2008), p. 817 – 833.

(Ren et al., 2006) Ren T., Patel M., Blok K., Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes, Energy 31 (2006), p. 425 – 451.

(Repsol, 2014) Repsol S.A. and Subsidiaries, Auditors' report consolidated financial statements for the year ended 31 December 2013 and consolidated management report, February 2014, available online at https://www.companyreporting.com/sites/default/files/annual-report-index/repsol-sa-annual-report-2013.pdf (last accessed March 2016)

(Reynier et al., 2007) Reynier E., Specchia S., Saracco G., Specchia V., Syngas production via short contact time catalytic partial oxidation reactors based on Rh catalysts, Third European Combustion meeting ECM, 2007.

(Roads2hy, 2007), Maisonnier G., Steinberger-Wilckens R., Deliverable 2.1 and 2.1.a "European Hydrogen Infrastructure Atlas" and "Industrial Excess Hydrogen Analysis"-Part II: Industrial surplus hydrogen and markets and production, www.roads2hy.com, March 2007, available at http://www.ika.rwth-aachen.de/r2h/images/d/df/Roads2HyCom_R2H2006PU_-_(Part_II)_-_Industrial_Surplus_H2.pdf (last accessed March 2016)

(Rodat et al., 2011a) Rodat S., Abanades S., Grivei E., Patrianakos G., Zygogianni A., Konstandopoulos A., Flamant G., Characterisation of carbon blacks produced by solar thermal dissociation of methane. Carbon 49 (2011), p. 3084 – 3091.

(Rodat et al., 2011b) Rodat S., Abanades S., Flamant G., Methane decarbonisation in indirect heating solar reactors of 20 and 50 KW for a CO_2-free production of hydrogen and carbon black. Journal of Solar Energy Engineering 33 (2011), p. 031001.

(Saipem SpA, 2010) Buonomo F., Donati G., Micheli E., Tagliabue L., Process for the simultaneous dehydrogenation of ethane and ethyl benzene, Saipem S.p.A., European Patent EP1199293B1, December 2010, available online at http://www.google.com/patents/EP1199293B1?cl=en (last accessed April 2016)

(Saygin et al., 2011) Saygin D., Patel M.K., Worrell E., Tam C., Gielen D.J., Potential of best practice technology to improve energy efficiency in the global chemical and petrochemical sector, Energy 36 (2011), p. 5779-5790.

(Saxena et al., 2009) Saxena R.C., Adhikari D.K., Goyal H.B., Biomass-based energy fuel through biochemical routes: A review, Renewable and Sustainable Energy Reviews 13 (2009), p. 167 – 178.

(SBC, 2012) SBC Energy Institute and Schlumberger Business Consulting: Leading the energy transition: Bringing Capture & Storage to Market. Available at: https://encrypted.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&ved=0ahUKEwjZk92jqPHRAhVIrRoKHU6oDqMQFggZMAA&url=http%3A%2F%2Fwww.globalccsinstitute.com%2Fsites%2Fdefault%2Ffiles%2Fpublications%2F56466%2Fsbc-energy-institute-ccs-factbook.pdf&usg=AFQjCNE5oblqX08gbJU67GVVY02VGH7wcw&sig2=4QOqg8j908Coefec3UOfLw&bvm=bv.146073913,d.ZGg

(Schneider et al., 2010) Schneider L., Lazarus M., Kollmuss A., Industrial N_2O projects under the CDM: Adipic Acid – A case of carbon leakage?, Stockholm Environment Institute (SEI), Working paper WP-US-1006, USA, October 2010.

(Serpec-cc, 2009) Overgaag M., Harmsen R., Schmitz A., Industry and refineries sector, Sectorial Emission Reduction Potentials and Economic Costs for Climate Change (SERPEC-CC), Ecofys and JRC-IPTS, October 2009.

(Shell, 2015) Shell Global, Ethylene oxide / ethylene glycol (EO/EG) processes, 2015, available at https://www.shell.com/global/products-services/solutions-for-businesses/globalsolutions/refinery-chemical-licensing/petrochemical-technology/ethylene-oxide-processes.html (last accessed April 2016)

(Sheridan, 2011) Sheridan K., BioAmber and CELEXION announce exclusive licensing partnership, 2011, available at http://www.celexionbio.com/pdf/BioAmberRelease20110315.pdf (last accessed August 2014)

(Sinnott, 2005) Sinnott R., Chemical Engineering Design, 4th Edition, *in* Chemical Engineering Volume 6, Elsevier Butterworth-Heiemann, 2005.

(Slavkovic et al., 2014) Slavkovic G., Budimir S.J., Rakonjac I.M., Jaric M.S., Budimir N.J., Techno-economic analysis of heat exchangers with parallel helical tube coils, Technical Gazette 21 (2014), p. 861 – 866.

(Solvay, 2013) Solvay, The eco-footprint of VinyLoop, October 2013, available online at http://www.vinyloop.com/en/environmental-solutions-en/eco-footprint-study.html (last accessed April 2016)

(Song, 2009) Song C., Introduction to Hydrogen and Syngas production and purification technologies, in: Hydrogen and Syngas Production and Purification Technologies, Liu K., Song C., Subramani V. (editors), Willey Online Library, November 2009, p. 1 – 13.

(Spath & Dayton, 2007) Spath P. and Dayton D., Products from Syngas – Methanol (Catalyst), SunGrant BioWeb and the University of Tennessee, 2007, available at http://bioweb.sungrant.org/Technical/Bioproducts/Bioproducts+from+Syngas/Methanol/Default.htm (last accessed December 2014).

(Spath & Mann, 2001) Spath P. L. and Mann M. K., Life cycle assessment of hydrogen production via natural gas steam reforming, NREL/TP-570-27637, National Renewable Energy Laboratory (NREL), Colorado, USA, February 2001, available at http://www-pord.ucsd.edu/~sgille/mae124_s06/27637.pdf (last accessed August 2014)

(Speight, 2002) Speight J.G., Chemical and process design handbook, McGraw-Hill, 2002

(Stoukides & Vayenas, 1981) Stoukides M. and Vayenas C.G., The effect of electrochemical oxygen pumping on the rate and selectivity of ethylene oxidation on polycrystalline silver, Journal of Catalysis 70 (1981), p. 137 – 146.

(Sun et al., 2016) Sun D.L., Wang F., Hong R.Y., Xie C.R., Preparation of carbon black via arc discharge plasma enhanced by thermal pyrolysis, Diamond and Related Materials 61 (2016), p. 21 – 31.

(Swanson et al., 2011) Swanson S., Wawrousek K., Yu J., Maness P.-C., Growth and hydrogen production of Rubrivivax gelatinosus CBS, National Renewable Energy Laboratory (NREL), U.S.A., 2011, available at http://digitalcommons.calpoly.edu/cgi/viewcontent.cgi?article=1086&context=star (last accessed August 2014).

(Takht Ravanchi et al., 2009) Takht Ravanchi M., Kaghazchi T., Kalgari A., Application of membrane separation processes in petrochemical industry: a review, Desalination 235 (2009), p. 199 – 244.

(Terada et al., 2007) Terada A., Iwatsuki J., Ishikura S., Noguchi H., Kubo S., Okuda H., Kasahara S., Tanaka N., Ota H., Onuki K., Hino R., Development of hydrogen production technology by thermochemical water splitting IS process – Pilot test plan, Journal of Nuclear Science and Technology 44 (2007), p. 477 – 482.

(ThyssenKrupp, 2014) ThyssenKrupp Industrial Solutions, Nitric Acid – Technical data: Consumption figures, available at http://www.thyssenkrupp-industrial-solutions.com/en/products-solutions/chemical-industry/nitrates/nitric-acid/process/technical-data.html (last accessed August 2014)

(ThyssenKrupp, 2012) ThyssenKrupp Industrial Solutions, Vinyl chloride and polyvinyl chloride, available at http://www.thyssenkrupp-industrial-solutions.com/fileadmin/documents/brochures/uhde_brochures_pdf_en_8.pdf (last accessed April 2016)

(ThyssenKrupp, 2009a) Groves M. and Frank C., EnviNOx: Process for N_2O ad NO_x abatement in nitric acid plants – Setting emission standards for nitric acid plants, Prepared for presentation at Nitrogen and Syngas Conference 2009, Uhde, Germany 2009.

(ThyssenKrupp, 2009b) ThyssenKrupp Technologies, Aromatics, RT 645e, April 2009, available at http://www.thyssenkrupp-uhdemexico.com/fileadmin/documents/brochures/259c5237-1918-41f7-894f-9b34e3bcc10e.pdf (last accessed August 2014)

(Tian et al., 2006) Tian L., Tang W., Zhao M., Zhang Y., Bian Z., Sun H., Wu S., Process for separating aromatics by extractive distillation and a composite solvent used therein, United States Patent US 7078580 B2, July 2006.

(TNO, 1999) Tukker A., de Groot H., Simons L., Wiegersma S., Chemical recycling of plastics waste (PVC and other resins), TNO-report STB-99-55 Final, 1999.

(Towler & Sinnott, 2013) Towler G. and Sinnott R., Chemical engineering design – Principles, practice and economics of plant and process design, 2nd edition, Elsevier, 2013.

(Trivedi et al., 1998) Trivedi A.N., Sathaye J., Mykhopadhaya M., Energy efficiency and environmental management and options in the Indian fertiliser industry, ADB Technical Assistance Project , Forest Knol, California, 1998.

(Ullmann's Encyclopaedia, 2000a) Häussinger P., Lohmüller R., Watson A.M., Hydrogen 6. Uses, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., January 2000.

(Ullmann's Encyclopaedia, 2000b) Tuttle Musser M., Adipic acid, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., June 2000.

(Ullmann's Encyclopaedia, 2000c) Thieme C., Sodium Carbonates, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., June 2000.

(Ullmann's Encyclopaedia, 2000d) Folkins H.O., Benzene, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., June 2000.

(Ullmann's Encyclopaedia, 2000e) Rebsdat S. & Mayer D., Ethylene glycol, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., June 2000.

(Ullmann's Encyclopaedia, 2001) Rebsdat S. & Mayer D., Ethylene oxide, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., March 2001.

(Ullmann's Encyclopaedia, 2005) Welch V.A., Fallon K.J., Gelbke H.-P., Ethylbenzene, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., October 2005.

(Ullmann's Encyclopaedia, 2006) Rossberg M., Lendle W., Pfleiderer G. Tögel A., Dreher E.-D., et al., Chlorinated Hydrocarbons, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., July 2006.

(Ullmann's Encyclopaedia, 2009) Zimmermann H. & Walzl R., Ethylene, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., April 2009.

(Ullmann's Encyclopaedia, 2010a) Meesseen J. H., Urea, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., October 2010.

(Ullmann's Encyclopaedia, 2010b) Voll M., Kleinschmit P., Carbon 6: Carbon Black, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., January 2010.

(Ullmann's Encyclopaedia, 2011a) Appl M., Ammonia 2: Production processes, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., October 2011.

(Ullmann's Encyclopaedia, 2011b) Fabri J., Graeser U., Simo T.A., Toluene, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., October 2011.

(Ullmann's Encyclopaedia, 2011c) Dreher E.L., Torkelson T.R., Beutel K.K., Chloroethanes and chloroethylenes, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., October 2011.

(Ullmann's encyclopaedia, 2011d) James D.H. and Castor W.M., Styrene, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., October 2011.

(Ullmann's Encyclopaedia, 2012a) Brazdil J. F., Acrylonitrile, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., July 2012.

(Ullmann's Encyclopaedia, 2012b) Ott J., Gronemann V., Pontzen F., Fiedler E., Grossmann G., Kersebohm B., Weiss G., Witte C., Methanol, Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., October 2012.

(Ullmann's Encyclopaedia, 2014) Fischer I., Schmitt W.F., Porth H.-C., Allsopp M.W., Vianello G., Poly(vinyl chloride), Ullmann's Encyclopaedia of Industrial Chemistry, Willey-VCH Verlag GmbH & Co., May 2014.

(UNEP, 2013) United Nations Environment Programme (UNEP), Global estimate of global mercury cell chlorine capacity, Global inventory, last updated in 2013.

(UNIDO, 2010a) United Nations Industrial Development Organization (UNIDO), Global industrial energy efficiency benchmarking: An energy policy tool, Working paper, November 2010.

(UNIDO, 2010b) United Nations Industrial Development Organization (UNIDO), Carbon Capture and Storage in industrial applications: Technology Synthesis Report, Working paper, November 2010.

(UNIDO, 2010c) United Nations Industrial Development Organization (UNIDO), Global Technology roadmap for CCS in industry – Background paper prepared for the sectoral workshops, Vienna, 2010.

(UNFCCC, 2016) UNFCCC, National emission reported to the UNFCCC and to the EU Greenhouse Gas monitoring mechanism, available at http://www.eea.europa.eu/data-and-maps/data/national-emissions-reported-to-the-unfccc-and-to-the-eu-greenhouse-gas-monitoring-mechanism-12 (last accessed October 2016)

(UOP, 2004) UOP, Lummus/UOP Classic SM Process, 2004, available online at http://www.dequi.eel.usp.br/~barcza/EstirenoUOP.pdf (last accessed April 2016)

(UOP, 2014) UOP, UOP RFCC Resid FCC Process, 2014 available at http://www.uop.com/fcc/ (last accessed December 2014).

(UOP, 2006) UOP LCC, Aromatics Complex, 2006, available at http://www.scribd.com/doc/162158824/42-Aromatics-Complex (last accessed August 2014).

(US Department of Energy, 2000) US Department of Energy, Energy and environmental profile of the U.S. Chemical Industry, May 2000 available at http://energy.gov/sites/prod/files/2013/11/f4/profile_full.pdf (last accessed August 2014)

(US Department of Energy, 2005) US Department of Energy, Materials for separation technologies: Energy and Emission reduction opportunities, May 2005 available at http://www1.eere.energy.gov/manufacturing/industries_technologies/imf/pdfs/separationsreport.pdf (last accessed August 2014)

(US Department of Energy, 2006) US Department of Energy, Advanced chlor–alkali technology, Office of Energy Efficiency and renewable energy, January 2006 available at https://www1.eere.energy.gov/manufacturing/industries_technologies/imf/pdfs/1797_advanced_chlor-alkali.pdf (last accessed August 2014)

(US Department of Energy, 2012) US Department of Energy, New process for producing styrene cuts costs, saves energy and reduces greenhouse gas emissions, 2012, available online at https://www1.eere.energy.gov/office_eere/pdfs/exelus_case_study.pdf (last accessed April 2016)

(USGS, 2014) U.S. Geological Survey (USGS), Nitrogen (fixed) – Ammonia, Mineral Commodity Summaries, February 2014 available at http://minerals.er.usgs.gov/minerals/pubs/commodity/nitrogen/mcs-2014-nitro.pdf (last accessed August 2014)

(USGS, 2013) U.S. Geological Survey (USGS), 2012 Minerals Yearbook – Soda ash, September 2013 available at http://minerals.usgs.gov/minerals/pubs/commodity/soda_ash/ (last accessed August 2014)

(USGS, 2012) U.S. Geological Survey (USGS), 2011 Minerals Yearbook – Soda ash, November 2012 available at http://minerals.usgs.gov/minerals/pubs/commodity/soda_ash/ (last accessed August 2014)

(US NRC, 1990) U.S. National Research Council, Tracking toxic substances at industrial facilities – Engineering mass balance versus materials accounting, Committee to evaluate mass balance information for facilities handling toxic substances, National Academy Press, Washington D.C., 1990

(Vaish & Patel, 2002) Vaish V.S. and Patel M.R., Stretching the capacity of a 23 year-old Kellogg ammonia plant, Technical Conference – IFA, International Fertilizer Industry Association, 2002.

(van Ginkel et al., 1986) van Ginkel C.G., Welten H.G.J., de Bont J.A.M., Epoxidation of alkenes by alkene-grown Xantobacter spp., Applied Microbiology and Biotechnology 24 (1986), p. 334 – 337.

(Vinyl Council Australia, 2016) Vinyl Council Australia, Collaborating for a step change in recycling, available at http://www.vinyl.org.au/sustainability/recycling-pvc/recycling-strategy (last accessed April 2016)

(Vinylinfo, 2016) Vinyl Institute USA, available at http://www.vinylinfo.org/ (last accessed April 2016)

(VinyLoop, 2002) VinyLoop, A new process to regenerate PVC compounds from composite residues: a new product the precipitated PVC compound, Presentation, 2002, available online at http://infohouse.p2ric.org/ref/38/37438.pdf (last accessed April 2016)

(VinyLoop, 2013) VinyLoop, Smart recycling, 2013, available online at http://www.vinyloop.com/en/the-vinyloop-process-en/smart-recycling-en.html (last accessed April 2016)

(Vinylplus, 2013) Vinylplus, PVC recycling technologies, 2013, available online at http://www.vinylplus.eu/documents/6/68/PVC-recycling-technologies (last accessed April 2016)

(Vinylplus, 2014) Vinylplus, Progress report 2014: Reporting on 2013 activities, 2014, available online at http://www.vinylplus.eu/uploads/Modules/Documents/Executive_Summary/Progress%20report%202014/VinylPlus-PR2014_EN.pdf (last accessed April 2016)

(Vinylplus, 2015) Vinylplus, Progress report 2015: Reporting on 2014 activities, 2015, available online at http://www.vinylplus.eu/uploads/docs/VinylPlus_Progress_Report_2015_English.pdf (last accessed April 2016)

(Vinylplus, 2016) Vinylplus, The programme – Voluntary commitment, 2016, available online at http://vinylplus.eu/programme/voluntary-commitment (last accessed April 2016)

(Vural-Güsel et al., 2012) Vural-Güsel I., Wang Q., Noël T., Hessel V., Process–design intensification – direct synthesis of adipic acid in flow, Chemical Engineering Transactions 29 (2012), p. 565 – 571.

(Weber, 2013) Weber S., The US Petrochemical industry: impact of new energy and feedstock sources on aromatics supply, Argus DeWitt, May 2013, available online at https://argusmedia.com/~/media/Files/PDFs/Presentations/Aromatics-Forum-SW-2013.pdf?la=en (last accessed March 2015)

(Westerveld, 2010) Westerveld R., Rennovia targets bio-based route to adipic acid, Chemical Week, October 18, 2010, available at http://www.rennovia.com/LinkClick.aspx?fileticket=-Q5uwX-Ayhc%3D&tabid=62 (last accessed August 2014)

(White, 2009) White D. C., Olefin plant energy savings through enhanced automation, AIChE paper number 110f, Prepared for presentation at the 2009 Spring National Meeting Tampa, Florida, April 2009 available at http://www.emersonprocessxperts.com/papers/Olefin-Plants-Automation-and-Energy-AIChE-Doug-White.pdf (last accessed August 2014)

(Wolschlag et al., 2009) Wolschlag L.M., Couch K.A., Zhu F., Alves J., UOP FCC design advancements to reduce energy consumption and CO_2 emissions, UOP LCC, USA, 2009.

(Woltering et al., 2013) Woltering P., Hofmann P., Funck F., Kiefer R., Bäumer S., Donst S, Schmitt C., Energy–saving chlorine production: Chlor – alkali electrolysis using innovative cathode technology, ThyssenKrupp Technoforum, Issue 1, 2013, p. 18 – 23.

(Wood & Cowie, 2004) Wood S. and Cowie A., A review of greenhouse gas emission factors for fertiliser production, IEA Bioenergy Task 38, June 2004

(Woodle, 2006) Woodle G.B., Styrene, Encyclopedia of Chemical Processing, Taylor & Francis, 2006, p. 2859 – 2869.

(Wu et al., 2012) Wu G., Huang K., Chen H., Wang S., Wei N., Wang S.J., Simplified design and control of an ideal heat-integrated distillation column (idea HIDiC), Asia-Pacific Journal of Chemical Engineering 7 (2012), p. 912 – 927.

(Wu & Tungpanututh, 2012) Wu W. and Tungpanututh C., Optimisation of a methane auto thermal reforming-based hydrogen production system with low CO_2 emissions, 8th IFAC Symposium on Advanced Control on Chemical Processes, Singapore, July 2012, available at http://www.nt.ntnu.no/users/skoge/prost/proceedings/adchem-2012/files/0023.pdf (last accessed August 2014)

(Yara, 2014) Yara, Yara Fertiliser Industry Handbook, February 2014

(Yu et al., 2011) Yu H., Peng F., Tang J., Hu X., Wang J., Yang J., Zheng W., Selective catalysis of the aerobic oxidation of cyclohexane in the liquid phase by carbon nanotubes, Angewandte Chemie 123 (2011), p. 4064 – 4068.

(Yuan et al., 2014) Yuan J.J., Hong R.Y., Wang Y.Q., Feng W.G., Low-temperature plasma preparation and application of carbon black nanoparticles, Chemical Engineering Journal 253 (2014), p. 107 – 120.

(ZEP, 2008) European Technology Platform for Zero Emission Fossil Fuel Power Plants, EU demonstration programme for CO_2 capture and storage (CCS) – ZEP's proposal, November 2008.

(Zhang et al., 2013) Zhang H., Xiao R., Jin B., Xiao G., Chen R., Biomass catalytic pyrolysis to produce olefins and aromatics with a physically mixed catalyst, Bioresource Technology 140 (2013), p. 256 – 262.

(Zomerdijk & Hall, 1981) Zomerdijk J.C. and Hall M.W., Technology for the manufacture of ethylene oxide, Catalysis Review Science and Engineering 23 (1981), p. 163 – 185.List of abbreviations and definitions

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Annex 1: Abbreviations

AA	Adipic acid
AHR	Adsorption heat pump
APC	Advanced process control
BAT	Best available technique
BTX	Benzene, toluene, xylenes
CB	Carbon black
CCS	Carbon Capture and Storage
Cefic	Conseil Européen des Fédérations de l'Industrie Chimique
CEPCI	Chemical engineering plant cost index
CHP	Combined heat and power
CWT	CO_2 weighted tonne
DEG	Diethylene glycol
DME	Dimethyl ether
ECVM	European Council of vinyl manufacturers
EDC	Ethylene dichloride
EEA	European Environmental Agency
ELV	Emission limit value
EMS	Energy management systems
EO	Ethylene oxide
E-PRTR	European Pollutant Release and Transfer Register
ESAPA	European Soda Ash Producers Association

EU	European Union
EU-ETS	EU Emissions Trading System
FCC	Fluid catalytic cracking
GDP	Gross domestic product
GHG	Greenhouse gas
HDPE	High density polyethylene
HFCs	Hydro-fluorocarbons
HHV	Higher heating value
HVC	High value chemicals
IGCC	Integrated gasification combined cycle
IED	Industrial Emissions Directive
IPPC	Integrated Pollution Prevention and Control
IT	Innovative technology
KA oil	Ketone alcohol oil (mixture cyclohexanone – cyclohexanol)
LHV	Lower heating value
LDAR	Leak detection and repair (programmes)
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
LPG	Liquefied petroleum gas
MEK	Methyl ethyl ketone
MEG	Monoethylene glycol
MTBE	Methyl tert-butyl ether
MTO	Methanol to olefin

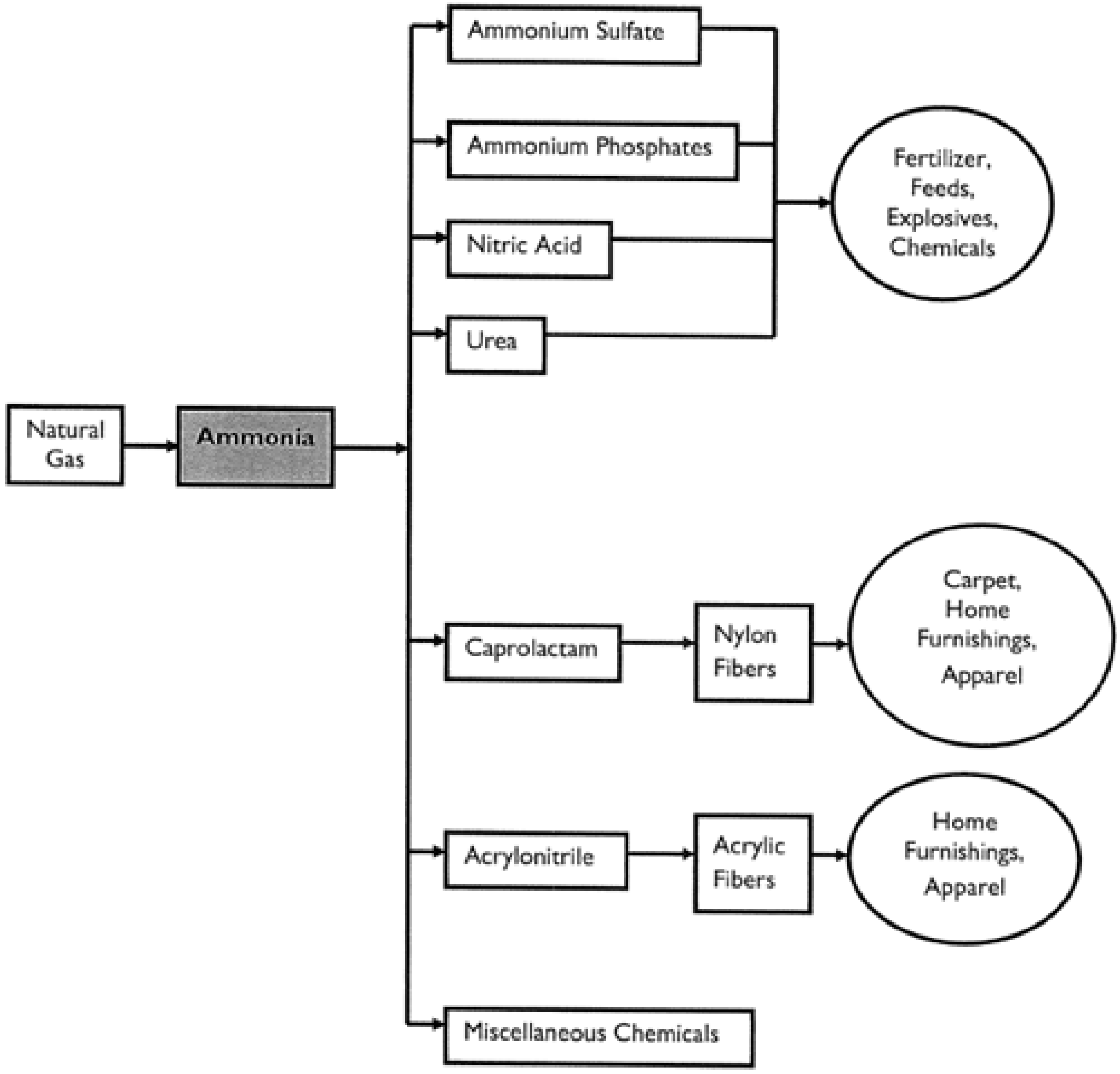
MVR	Mechanical vapour recompressing
NGCC	Natural gas combined cycle
NGL	Natural gas liquids
NRP	New reference plant
NSCR	Non selective catalytic reduction
OE	Overall efficiency
OECD	Organisation for economic co-operation and development
ODC	Oxygen depolarised cathode
OPEX	Operating expenses
PBP	Payback period
PE	Polyethylene
PEM	Polymer electrolyte membrane
PES	Primary energy savings
PFCs	Perfluorocarbons
PET	Polyethylene terephthalate
PVC	Polyvinylchloride
REACH	Registration, evaluation, authorisation and restriction of chemicals
SC	Steam cracking
SCR	Selective catalytic reduction
SEC	Specific energy consumption
SNCR	Selective non-catalytic reduction
SOEC	Solid oxide electrolyser cell
TAME	tert-Amyl methyl ether

TDI	toluene diisocyanates
TEG	Triethylene glycol
toe	Tonne of oil equivalent
UNFCCC	United Framework Convention on Climate Change
VCM	Vinyl chloride monomer
VSA	Vacuum swing adsorption

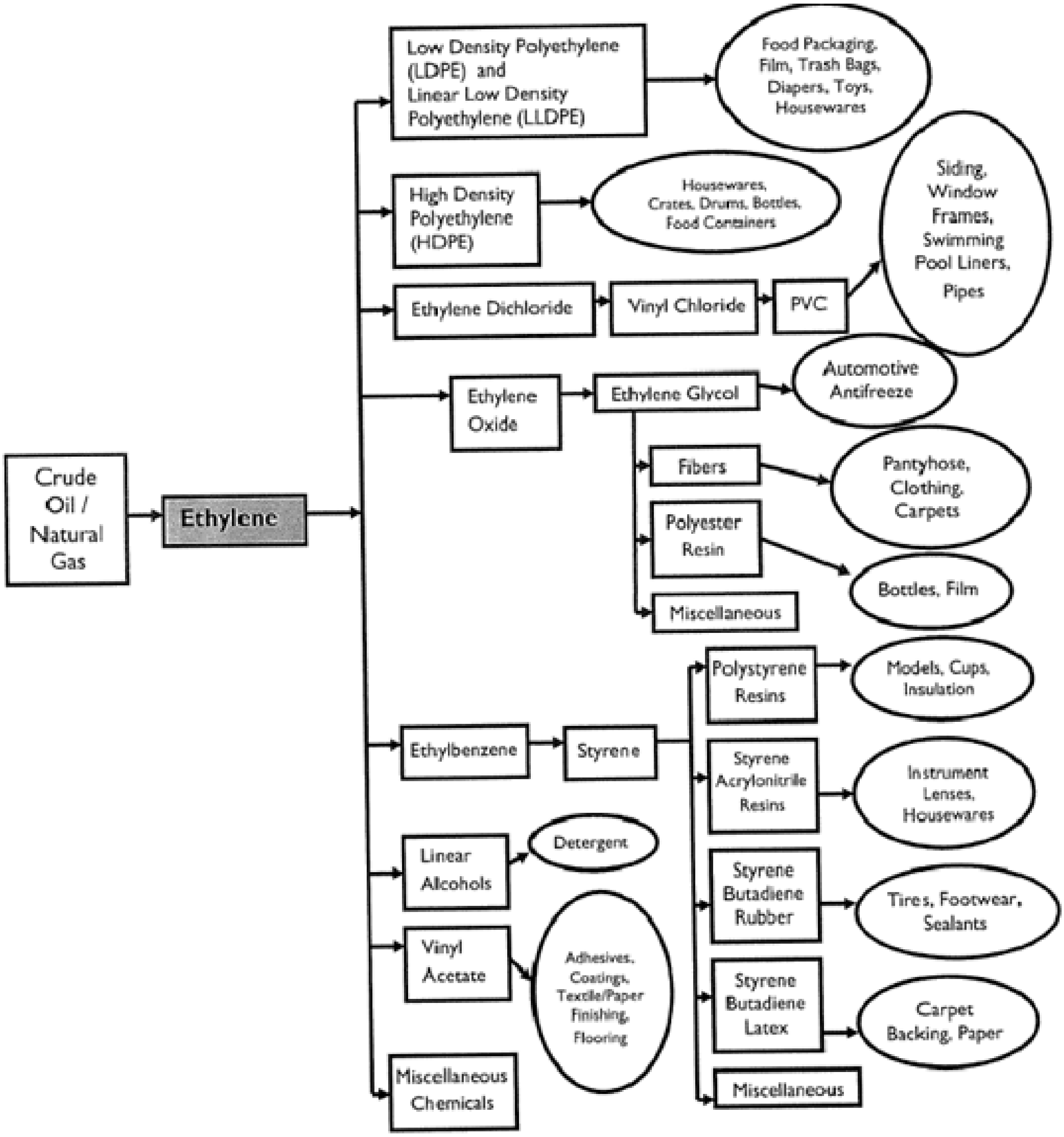
Annex 2: Basic chemical product chains

This annex presents the range of products from the basic chemical substances. The pictures belong to the American Chemical Council (ACC, 2013).

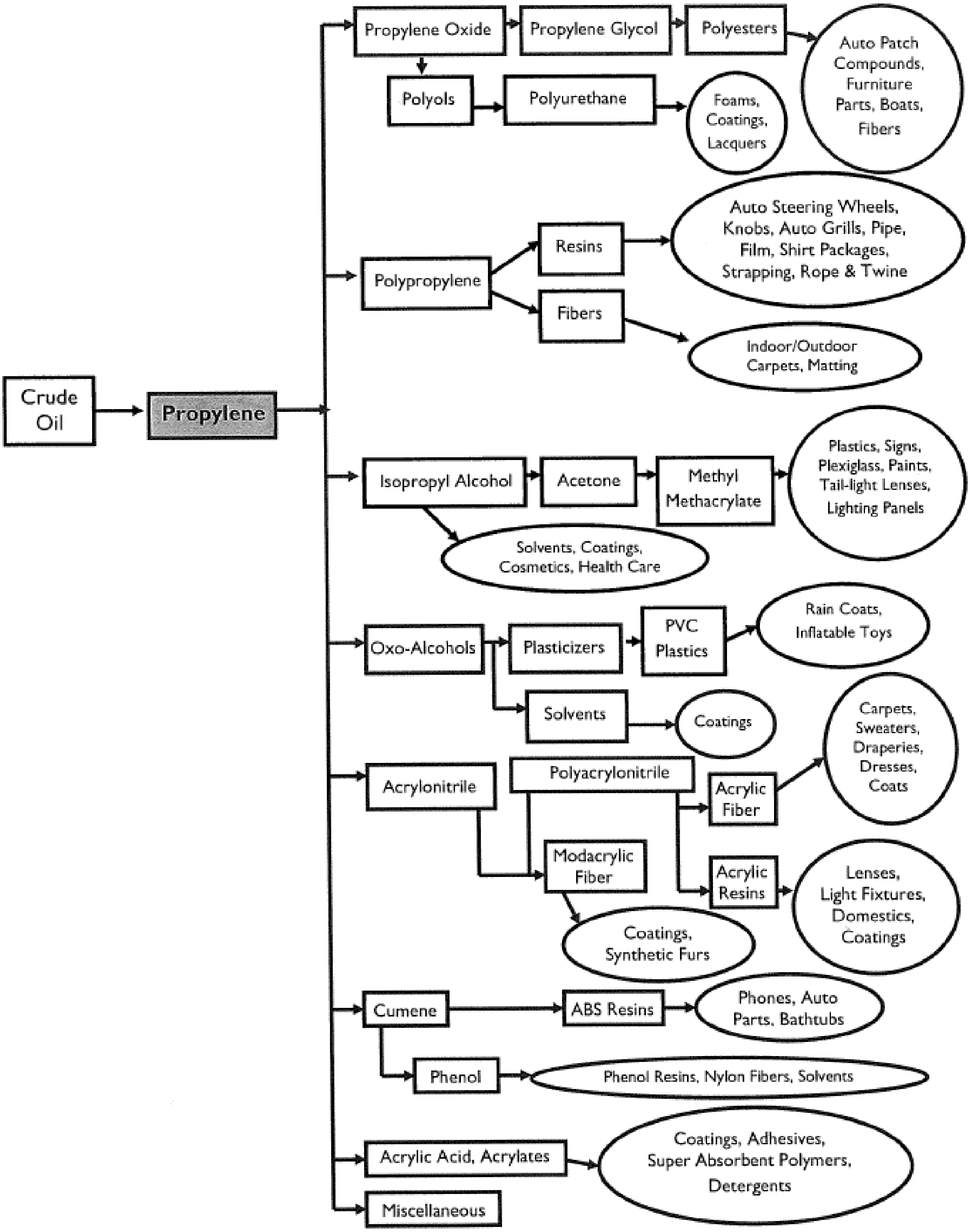
Ammonia



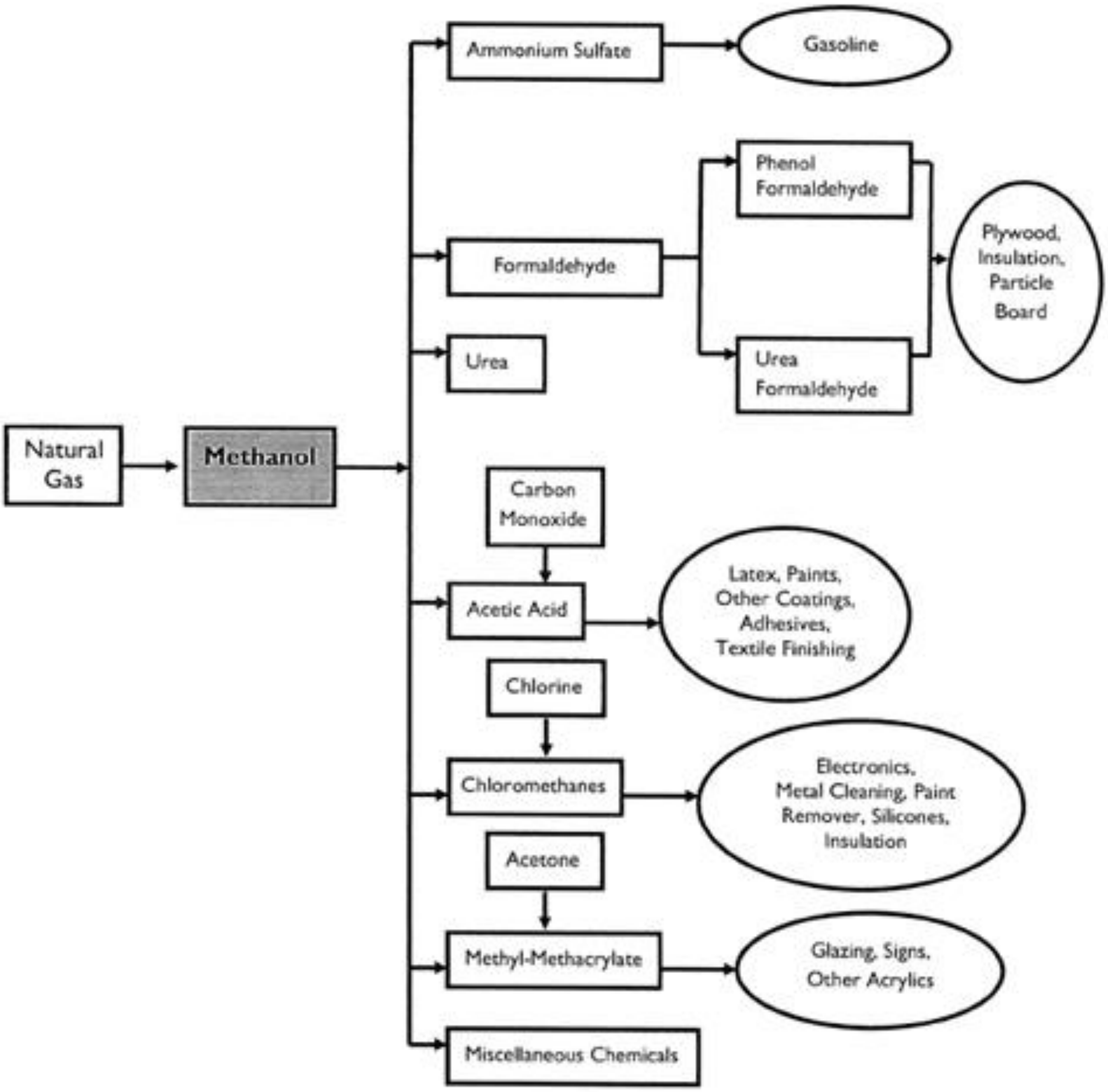
Ethylene


Crude Oil / Natural Gas
Ethylene
Low Density Polyethylene (LDPE) and Linear Low Density Polyethylene (LLDPE)
Food Packaging, Film, Trash Bags, Diapers, Toys, Housewares
High Density Polyethylene (HDPE)
Housewares, Crates, Drums, Bottles, Food Containers
Ethylene Dichloride
Vinyl Chloride
PVC
Siding, Window Frames, Swimming Pool Liners, Pipes
Ethylene Oxide
Ethylene Glycol
Automotive Antifreeze
Fibers
Pantyhose, Clothing, Carpets
Polyester Resin
Bottles, Film
Miscellaneous
Ethylbenzene
Styrene
Polystyrene Resins
Models, Cups, Insulation
Styrene Acrylonitrile Resins
Instrument Lenses, Housewares
Styrene Butadiene Rubber
Tires, Footwear, Sealants
Styrene Butadiene Latex
Carpet Backing, Paper
Miscellaneous
Linear Alcohols
Detergent
Vinyl Acetate
Adhesives, Coatings, Textile/Paper Finishing, Flooring
Miscellaneous Chemicals

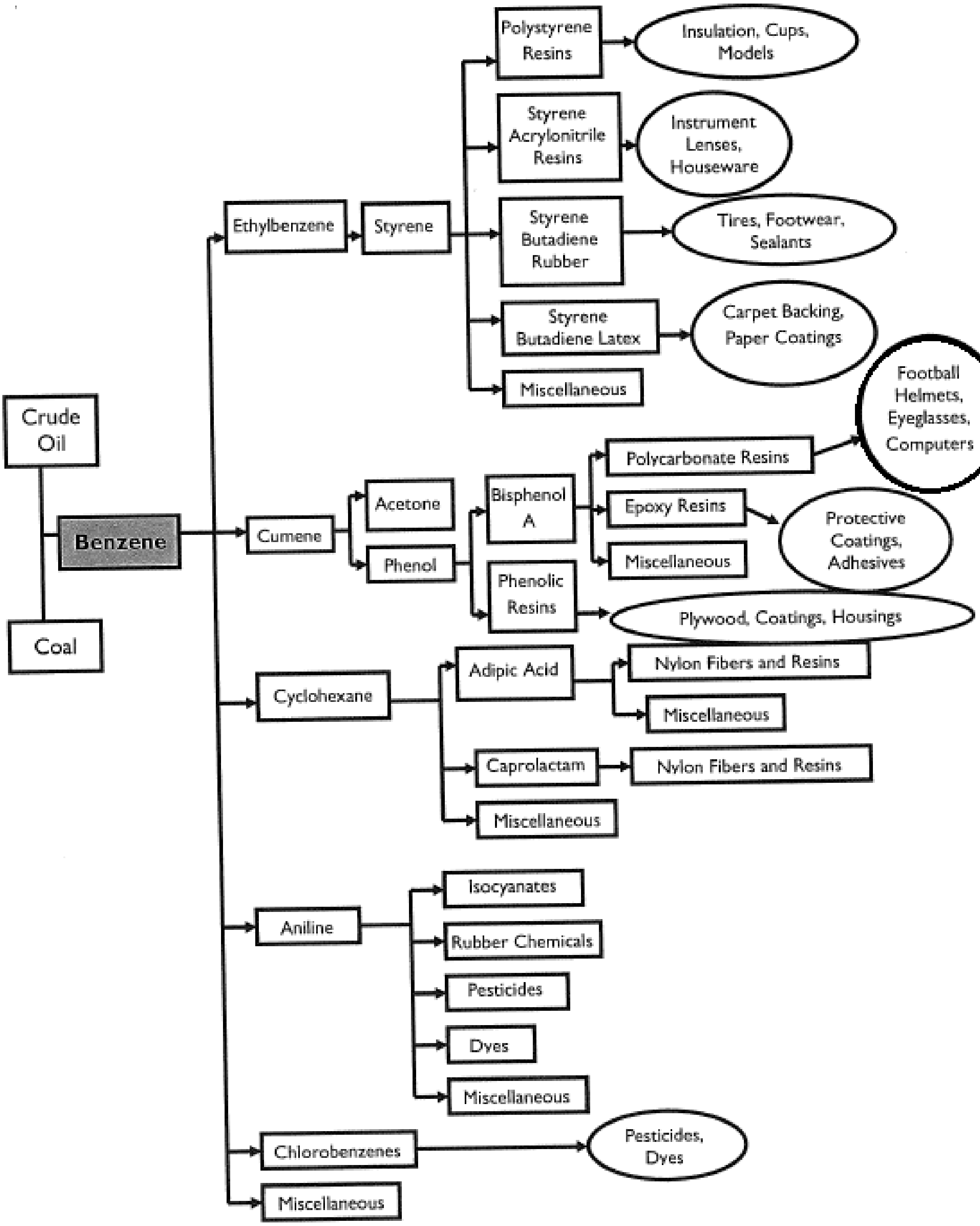
Propylene


Crude Oil
Propylene
Propylene Oxide
Propylene Glycol
Polyesters
Auto Patch Compounds, Furniture Parts, Boats, Fibers
Polyols
Polyurethane
Foams, Coatings, Lacquers
Polypropylene
Resins
Auto Steering Wheels, Knobs, Auto Grills, Pipe, Film, Shirt Packages, Strapping, Rope & Twine
Fibers
Indoor/Outdoor Carpets, Matting
Isopropyl Alcohol
Acetone
Methyl Methacrylate
Plastics, Signs, Plexiglass, Paints, Tail-light Lenses, Lighting Panels
Solvents, Coatings, Cosmetics, Health Care
Oxo-Alcohols
Plasticizers
PVC Plastics
Rain Coats, Inflatable Toys
Solvents
Coatings
Acrylonitrile
Polyacrylonitrile
Acrylic Fiber
Carpets, Sweaters, Draperies, Dresses, Coats
Modacrylic Fiber
Acrylic Resins
Lenses, Light Fixtures, Domestics, Coatings
Coatings, Synthetic Furs
Cumene
ABS Resins
Phones, Auto Parts, Bathtubs
Phenol
Phenol Resins, Nylon Fibers, Solvents
Acrylic Acid, Acrylates
Coatings, Adhesives, Super Absorbent Polymers, Detergents
Miscellaneous

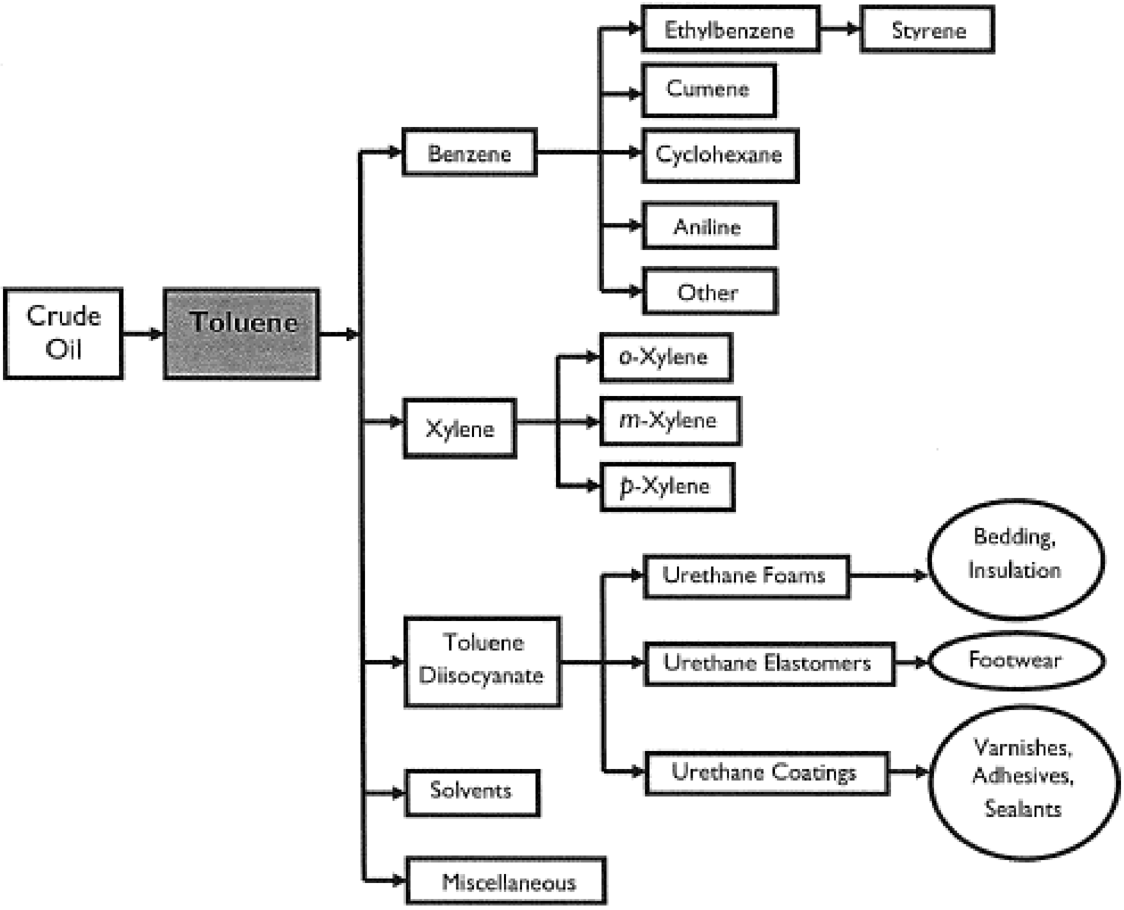
Methanol


Natural Gas
Methanol
Ammonium Sulfate
Gasoline
Formaldehyde
Phenol Formaldehyde
Urea Formaldehyde
Plywood, Insulation, Particle Board
Urea
Carbon Monoxide
Acetic Acid
Latex, Paints, Other Coatings, Adhesives, Textile Finishing
Chlorine
Chloromethanes
Electronics, Metal Cleaning, Paint Remover, Silicones, Insulation
Acetone
Methyl-Methacrylate
Glazing, Signs, Other Acrylics
Miscellaneous Chemicals

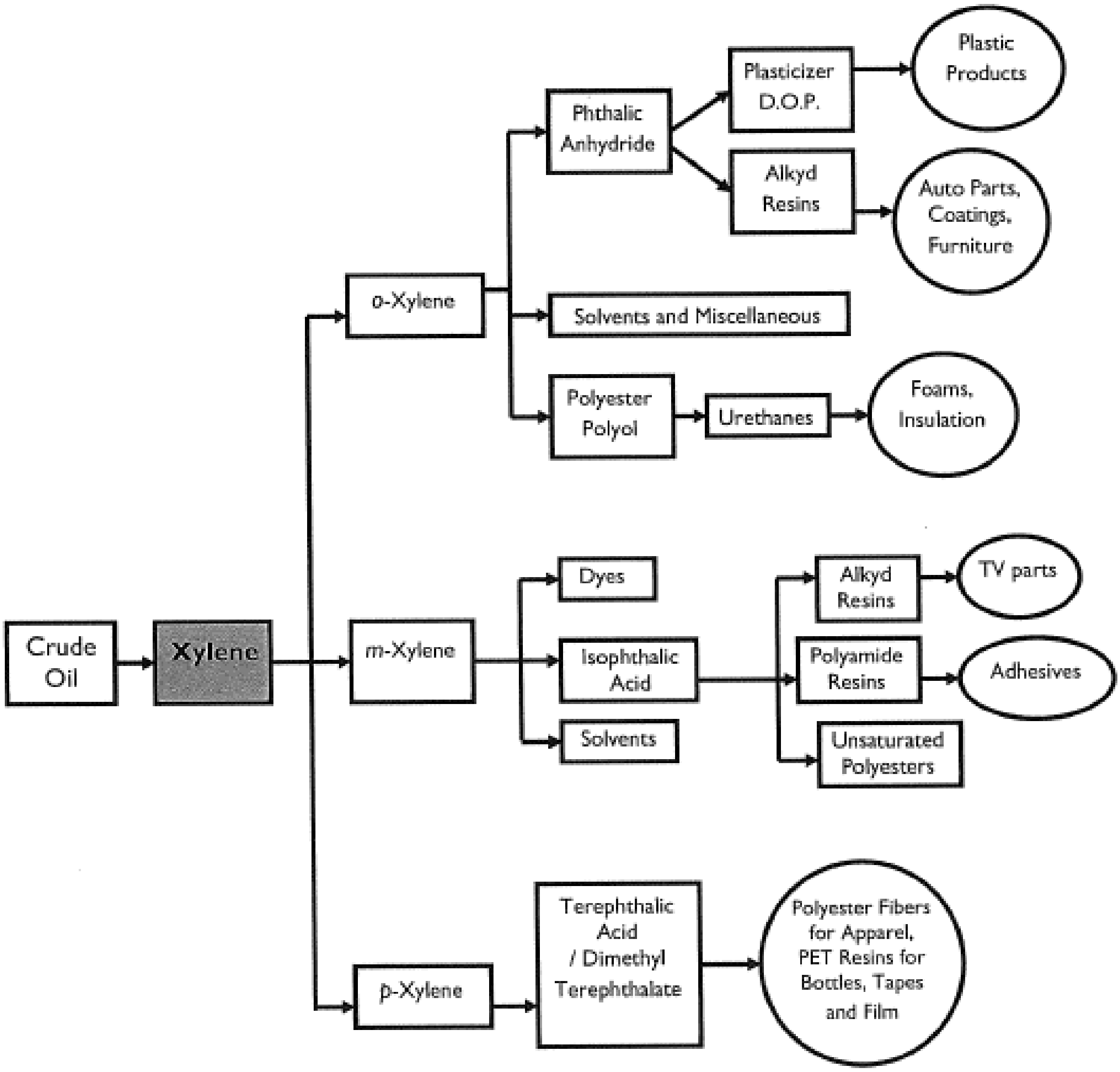
Benzene


Crude Oil
Coal
Benzene
Ethylbenzene
Styrene
Polystyrene Resins
Insulation, Cups, Models
Styrene Acrylonitrile Resins
Instrument Lenses, Houseware
Styrene Butadiene Rubber
Tires, Footwear, Sealants
Styrene Butadiene Latex
Carpet Backing, Paper Coatings
Miscellaneous
Cumene
Acetone
Phenol
Bisphenol A
Polycarbonate Resins
Football Helmets, Eyeglasses, Computers
Epoxy Resins
Protective Coatings, Adhesives
Miscellaneous
Phenolic Resins
Plywood, Coatings, Housings
Cyclohexane
Adipic Acid
Nylon Fibers and Resins
Miscellaneous
Caprolactam
Nylon Fibers and Resins
Miscellaneous
Aniline
Isocyanates
Rubber Chemicals
Pesticides
Dyes
Miscellaneous
Chlorobenzenes
Pesticides, Dyes
Miscellaneous

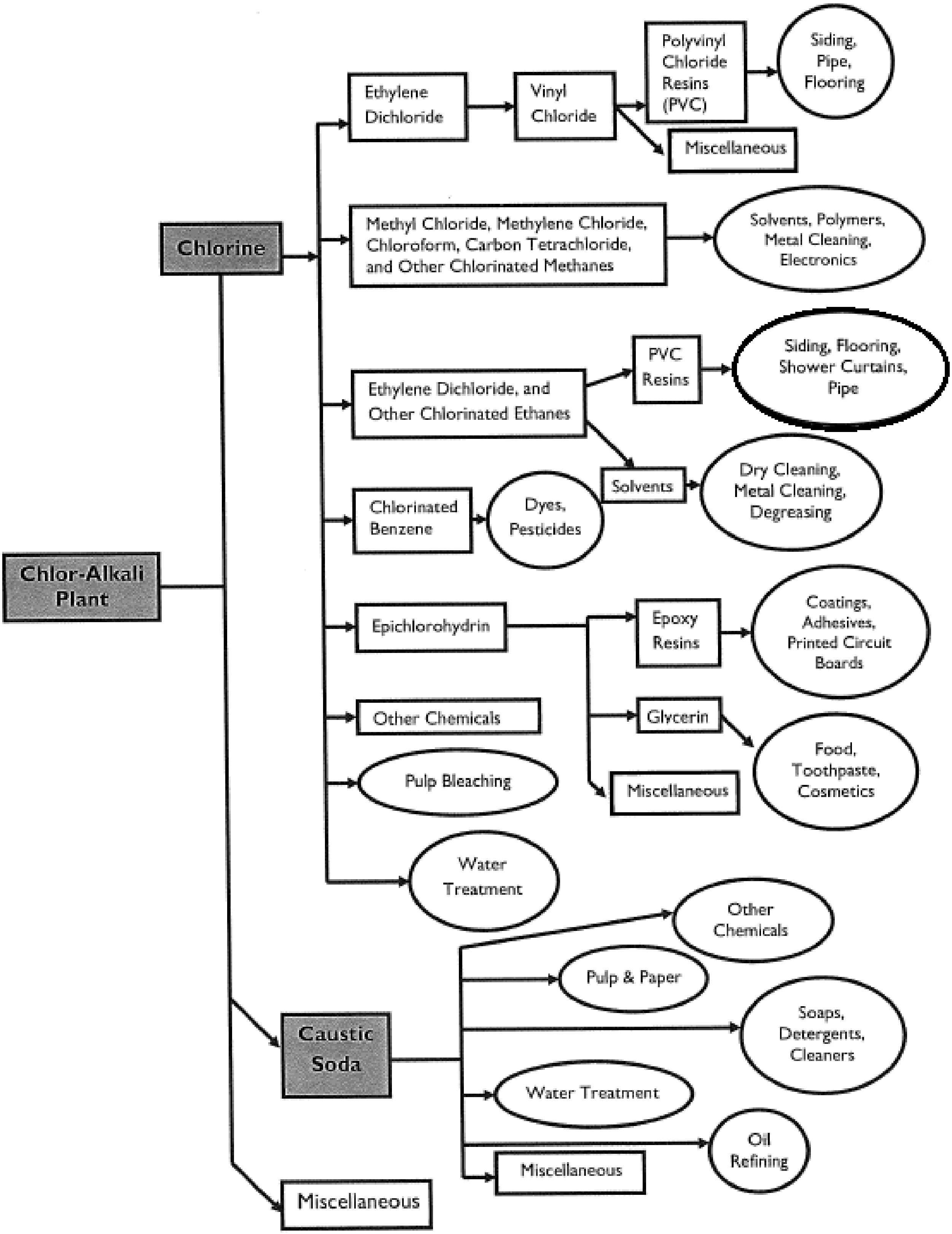
Toluene


Crude Oil
Toluene
Benzene
Ethylbenzene
Styrene
Cumene
Cyclohexane
Aniline
Other
Xylene
o-Xylene
m-Xylene
p-Xylene
Toluene Diisocyanate
Urethane Foams
Bedding, Insulation
Urethane Elastomers
Footwear
Urethane Coatings
Varnishes, Adhesives, Sealants
Solvents
Miscellaneous

Xylene


Crude Oil
Xylene
o-Xylene
Phthalic Anhydride
Plasticizer D.O.P.
Plastic Products
Alkyd Resins
Auto Parts, Coatings, Furniture
Solvents and Miscellaneous
Polyester Polyol
Urethanes
Foams, Insulation
m-Xylene
Dyes
Isophthalic Acid
Solvents
Alkyd Resins
TV parts
Polyamide Resins
Adhesives
Unsaturated Polyesters
p-Xylene
Terephthalic Acid / Dimethyl Terephthalate
Polyester Fibers for Apparel, PET Resins for Bottles, Tapes and Film

Chlor-alkali



Annex 3: Calculation of national energy mixes

For some products, such as hydrogen and PVC recycling, fictitious facilities are used. In these cases the fuel used is not clearly defined and as a result it is assumed that the national energy mix of the country they are located in is the fuel used in the process. It should be noted that this methodology is used only for these fictitious facilities and nowhere else in the study.

In order to decide the energy mix of the different European member states in 2013, the information for the chemical and petrochemical sector available from the IEA World energy balances are used (IEA, 2015). Only coal, peat, crude oil, oil products, natural gas and biofuels and waste are taken into consideration. The percentage of each one of them in the fuel use of 2013 is shown in the table below.

Fuel use in the EU-28 chemical and petrochemical sector in 2013

Product	Coal / coal products	Peat / peat products	Crude, NGL	Oil products	Natural gas	Biofuels / waste
Country			(%)			
Belgium				1.67	97.42	0.91
Bulgaria	26.24			4.71	68.80	0.25
Czech Republic	44.88			0.20	53.88	1.04
Denmark	0.51			6.41	93.06	0.02
Germany	6.90			20.97	69.11	3.02
Estonia				2.92	97.01	0.06
Ireland				33.30	66.70	
Greece				43.60	56.40	
Spain	5.39		0.15	4.49	89.81	0.15
France	13.82			14.03	68.82	3.33
Croatia				2.81	97.19	
Italy	0.09			29.31	65.74	4.86
Cyprus				100.00		
Latvia				18.91	51.78	29.31
Lithuania				1.63	96.03	2.34
Luxembourg				4.74	95.26	
Hungary	0.34			9.73	89.87	0.06
Netherlands			51.99	1.36	46.62	0.03
Austria	2.81			6.34	69.27	21.58
Poland	57.04			25.22	16.47	1.28
Portugal	6.81			6.33	85.57	1.29
Romania	7.98		0.29	21.60	68.16	1.97
Slovenia				10.23	69.71	20.05
Slovakia				7.16	87.47	5.37
Finland				88.20	4.94	6.86
Sweden		3.71		39.79	52.75	3.75
United Kingdom	3.89			7.16	88.94	

Based on the information of this table, we are able to calculate characteristics such as emission factors, lower heating values (LHV) and prices for the fuel mix of each country. The following table includes these values. For emission factors and LHVs the values in Regulation 601/2012 (EC, 2012b) are used, while prices are the weighted average of the fuel prices per country according to (IEA, 2016a) and (IEA, 2016b). Information about biofuels is restricted, as a result for all countries the average value between bioethanol and biodiesel was used, as these are reported in (OECD, 2014).

Lower heating values, emission factors and prices 2013 for each country fuel mix

Product	Lower heating value	Emission factor	Price 2013
Country	(GJ/t)	(t_{CO2}/ GJ)	(EUR/GJ)
Belgium	47.66	0.05584	8.57
Bulgaria	41.51	0.06689	9.91
Czech Republic	37.04	0.07305	8.63
Denmark	47.60	0.05724	12.95
Germany	44.57	0.06021	11.45
Estonia	47.86	0.05650	10.26
Ireland	16.58	0.06104	14.52
Greece	46.15	0.06257	15.78
Spain	46.48	0.05880	9.78
France	43.13	0.06171	11.40
Croatia	47.88	0.05652	10.81
Italy	45.28	0.05776	15.05
Cyprus	43.75	0.07095	18.57
Latvia	38.42	0.04246	14.58
Lithuania	47.23	0.05503	10.92
Luxembourg	47.80	0.05680	11.58
Hungary	47.49	0.05764	9.90
Netherlands	45.46	0.06286	11.57
Austria	40.61	0.04603	12.37
Poland	33.03	0.08137	7.70
Portugal	45.73	0.05898	12.11
Romania	44.59	0.06135	12.16
Slovenia	41.56	0.04637	14.27
Slovakia	46.09	0.05415	11.27
Finland	42.20	0.06535	23.63
Sweden	43.77	0.06176	17.27
United Kingdom	46.77	0.05868	9.46

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