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DECARBONISATION OPTIONS FOR LARGE VOLUME ORGANIC CHEMICAL PRODUCTION, SHELL PERNIS

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MIDDEN

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Decarbonisation options for Large Volume Organic Chemical Production, Shell Pernis

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MIDDEN project coordination and responsibility
The MIDDEN project (Manufacturing Industry Decarbonisation Data Exchange Network) was initiated and is also coordinated and funded by PBL and TNO EnergieTransitie. The project aims to support industry, policymakers, analysts, and the energy sector in their common efforts to achieve deep decarbonisation. Correspondence regarding the project may be addressed to:
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This report was reviewed by Shell, as far as the descriptions of the production facilities is concerned. All energy efficiency improvement and decarbonisation options and related parameters are determined by PBL and TNO and have explicitly not been verified by Shell. PBL and TNO remain responsible for the content.

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FINDINGS

Summary

This MIDDEN report covers the production of chemicals at the Pernis location of Shell Nederland Chemie (SNC). The scope excludes the Shell refinery, which is covered by the MIDDEN report related to the Dutch refineries (Oliveira & Schure, 2020). The table below shows the different products, processes, feedstocks and capacities of SNC Pernis. The total energy use for these processes amounts to 4.4 PJ/year, subdivided in 3.1 PJ steam, 0.5 PJ hot oil, 0.4 PJ electricity and 0.2 PJ fuel gas.

Table S.1 Production capacities at the Pernis location of Shell Nederland Chemie

Main Product	Main Feedstock	Process	Capacity [kt/year]	Final energy use [PJ]
Propylene	Propane/propylene (P-P) mix	Distillation P-P splitter	280	0.12
Various hydrocarbon (HC) solvents	HC's mix	Distillation and Hydrogenation	820	0.34
Isopropyl Alcohol (IPA)	Propylene	Propylene Hydration	150	1.12
Methyl Isobutyl Ketone (MIBK)	Acetone (DMK)	DMK Hydrogenation	35	0.47
Di-isobutyl Ketone (DIBK)	Acetone (DMK)	DMK Hydrogenation	5	0.07
Methyl Isobutyl Carbinol (MIBC)	MIBK	MIBK Hydrogenation	2.5	0.03
PO-Glycol ethers (POGE's)	PO/Ethylene Oxide (EO)	Propylene Oxide (PO) etherification	247	0.35
Methyl Tertiary – Butyl ether (MTBE)	Raffinate-1	Reaction of Isobutene and Methanol	170	0.54
Secondary Butyl Alcohol (SBA)	Raffinate-2	Sulphuric acid hydration of n-butene	105	0.57
Methyl Ethyl Ketone (MEK)	SBA	SBA dehydrogenation	90	0.39
Polyether Polyols	PO	Polyether Polyols	200	0.24
Styrene acrylonitrile (SAN) Polyols	PO, SAN	SAN Polymerisation	50	0.12
Total				**4.37**

Energy supply is closely linked to the adjacent Shell Pernis refinery. The direct emissions reported for the chemical activities amount to 30.3 kilotonnes (kt) CO_2 in 2018. Around half of these emissions come from fuel combustion for the furnaces, the other half from combustion of residual gases.

Decarbonisation options to address direct emissions include CCS and avoiding combustion of fuel in furnaces by electric heating. As far as residual flows are combusted, alternative uses of these flows could be investigated. Hydrogen for hydrogenation could be supplied by green or blue hydrogen, thus avoiding emissions in hydrogen production from fossil fuels. Hydrogen may also be an alternative fuel for combustion in furnaces. Energy efficiency may still have room for improvement by further optimising the systems for process heating, including distillation and drying. Electrification may be part of these efforts, by applying heat pumps, or replacing steam driven compressors by electrically driven ones. Also geothermal energy is an option for renewable heat generation.

Biobased feedstocks can be further applied for several of the processes at SNC Pernis. For the imported methanol and acetone (DMK) feedstocks, there are biobased versions available. For products such as polyols and propylene glycol ethers, there are alternative processes using biobased glycerol.

FULL RESULTS

Introduction

This report describes the current situation for the Pernis location of Shell Nederland Chemie (SNC). It deals with the production of several basic chemicals in the Netherlands and the options and preconditions for its decarbonisation. The study is part of the MIDDEN project (Manufacturing Industry Decarbonisation Data Exchange Network). The MIDDEN project aims to support industry, policymakers, analysts, and the energy sector in their common efforts to achieve deep decarbonisation. The MIDDEN project will update and elaborate further on options in the future, in close connection with the industry.

Scope

Products include: Propylene; Various Hydrocarbon Solvents; Methyl Tertiary – Butyl ether; Secondary Butyl Alcohol; Methyl Ethyl Ketone; Isopropyl Alcohol; Methyl Isobutyl Ketone; Di-isobutyl Ketone; Methyl Isobutyl Carbinol; Propylene Oxide Glycol ethers; Polyether Polyols; Styrene acrylonitrile (SAN) Polyols.

Production processes include: distillation; hydrogenation; dehydrogenation; hydration; etherification; polymerisation.

The main options for decarbonisation are: electrification; biobased feedstocks; CCS. The decarbonisation strategy is strongly dependent on the decarbonisation of the Shell refinery at Pernis.

Reading guide

Chapter 1 introduces Shell Nederland Chemie at Pernis. Chapter 2 describes the current situation for the production processes, and chapter 3 describes the feedstocks, products and applications of these processes, while options for decarbonisation are systematically quantified and evaluated in chapter 4. The feasibility of and requirements for those decarbonisation options are discussed in chapter 5.

1 Shell Nederland Chemie Pernis

1.1 Location

Shell Pernis petrochemical complex is located in the Industrial Area in the Port of Rotterdam It is comprised by the refinery (owned and operated by Shell Nederland Raffinaderij B.V.) and the chemicals plants of Shell Nederland Chemie B.V. (SNC), where crude oil is processed into usable products such as gasoline, kerosene, diesel and raw materials for the chemical industry. Both refinery and chemicals sites at Pernis occupy a total area of 550 hectares (Shell, 2019a), surrounded by large and small residential areas like Pernis, Hoogvliet, Spijkenisse,Rhoon/Poortugaal, Vlaardingen and Schiedam. The Shell refinery itself is covered in the MIDDEN report related to the refineries (Oliveira & Schure, 2020).

Figure 1 Pernis Petrochemical complex location

In addition to the chemical plants in Pernis, SNC owns a second site located in Moerdijk (which is covered in another MIDDEN report (Wong & Van Dril, 2020)), approximately at 33 km distance from Pernis, between the industrial centres of Antwerp and Rotterdam. In the late 1960's, the Pernis site ran out of space for the installation of new chemical plants, therefore the acquisition of the site in Europoort near Moerdijk was required due to the growing demand for chemical products. The sites of Pernis and Moerdijk are interconnected by underground pipelines to facilitate the exchange of feedstocks and products (Public Affairs department of Shell Nederland Raffinaderij B.V., 2003).

1.2 History

Shell Chemicals history began in The Netherlands in 1929, with the establishment of a partnership named "NV Mekog" manufacturing ammonia from coke-oven gas. In 1936, the refinery came on stream at Pernis and since then, Shell has been manufacturing a growing number of petroleum products from crude oil at this location. In 1949, the petrochemical plants came into operation, where raw materials for PVC were produced, as well as Teepol, an industrial detergent (Shell, 2019b). In 1959, the chemical branch was transferred to SNC. Over the years, regular investments have been made at Pernis to expand the capacity of propylene production, for example, and to enhance product quality. The latest additions are the propylene oxide glycol ether plant, on-stream in 2001, and a polymer polyols plant, on stream in mid-2003 (Shell, 2019b; Port of Rotterdam Authority, 2019). In the last two decades, a number of petrochemical plants in Pernis were sold to new owners and/or dismantled e.g. isoprene and styrene rubber were dismantled in 2010. The lubricants plant was closed in 2014 (Engineeringnet, 2019). Other plants on the Pernis site are: Shin Etsu (production of PVC) and Hexion UK Ltd (basic chemicals) (Port of Rotterdam Authority, 2019). "*SNC continues to supply many of the feedstocks for these plants, and both SNC and SNR (Shell Nederland Raffinaderij) provide various services to these new owners*" (Public Affairs department of Shell Nederland Raffinaderij B.V., 2003).

1.3 Main Activities

The SNC Pernis manufacturing plants are operated by Shell owned companies or by partners within joint ventures. SNC Pernis manufactures basic and intermediate chemicals to sell in large volumes to other chemicals companies or industries. The main products are lower olefins, chemical solvents, hydrocarbon solvents, and polyols (Shell, 2019c).

SNC Pernis is part of a fully integrated petrochemical complex with connections to and from the Shell Refinery, SNC Moerdijk, other plants located in the vicinity of their site and other transport systems for their products. More detailed descriptions of the processes and manufactured products at SNC – Pernis site are included in chapter 2 and 3 in this report.

2 SNC–Pernis Processes

Shell Chemicals has played a significant role in the growth of the global petrochemicals sector and have developed an important number of their own key manufacturing processes (Shell, 2019c). In this chapter, the main manufacturing processes taking place in SNC Pernis are described, followed by a brief description of the energy system in these plants and the corresponding carbon dioxide emissions.

A total of 12 main chemical manufacturing processes take place in SNC Pernis in two locations namely, "Chemie, Oplosmiddelen en Derivaten" (COD) and "Chemie, verlading en polyolen" (CVP). The raw material flows come from the adjacent Shell Refinery and SNC-Moerdijk, as well as from external suppliers.

Table 1 presents a list of the main products manufactured by SNC Pernis categorized by type.

Table 1 Overview of main products and processes in SNC Pernis site (Shell, 2019c; Port of Rotterdam Authority, 2019)

Main Product	Category	Location	Main Feedstock	Process	Capacity kt/year
Propylene	Lower Olefin	COD	Propane/ propylene (P-P) mix	Distillation P-P splitter	280
Various Hydrocarbon (HC) solvents	Hydrocarbon Solvent	COD	HC's mix	Distillation and Hydrogenation	820
Isopropyl Alcohol (IPA)	Chemical Solvents	COD	Propylene	Propylene Hydration	150
Methyl Isobutyl Ketone (MIBK)	Chemical Solvents	COD	Acetone (DMK)	DMK Hydrogenation	35
Di-isobutyl Ketone (DIBK)	Chemical Solvents	COD	Acetone (DMK)	DMK Hydrogenation	5
Methyl Isobutyl Carbinol (MIBC)	Chemical Solvents	COD	MIBK	MIBK Hydrogenation	2.5
PO-Glycol ethers (POGE's)	Chemical Solvents	COD	PO/Ethylene Oxide (EO)	Propylene Oxide (PO) etherification	247
Methyl Tertiary – Butyl ether (MTBE)	Chemical Solvents	COD	Raffinate-1	Reaction of Isobutene and Methanol	170
Secondary Butyl Alcohol (SBA)	Chemical Solvents	COD	Raffinate-2	Sulphuric acid hydration of n-butene	105
Methyl Ethyl Ketone (MEK)	Chemical Solvents	COD	SBA	SBA dehydrogenation	90
Polyether Polyols	Polyols	CVP	PO	Polyether Polyols	200
Styrene acrylonitrile (SAN) Polyols	Polyols	CVP	PO, SAN	SAN Polymerisation	50

Figure 2 illustrates the activities taking place on the SNC-Pernis premises by showing the products, processes and the in- and output flows. These include interaction with the refinery, the SNC-Moerdijk site, third parties located either in the Netherlands (e.g. Port of Rotterdam) or abroad such as the interaction with liquified gas products from Shell Qatar or the supply of feedstock from Europe.

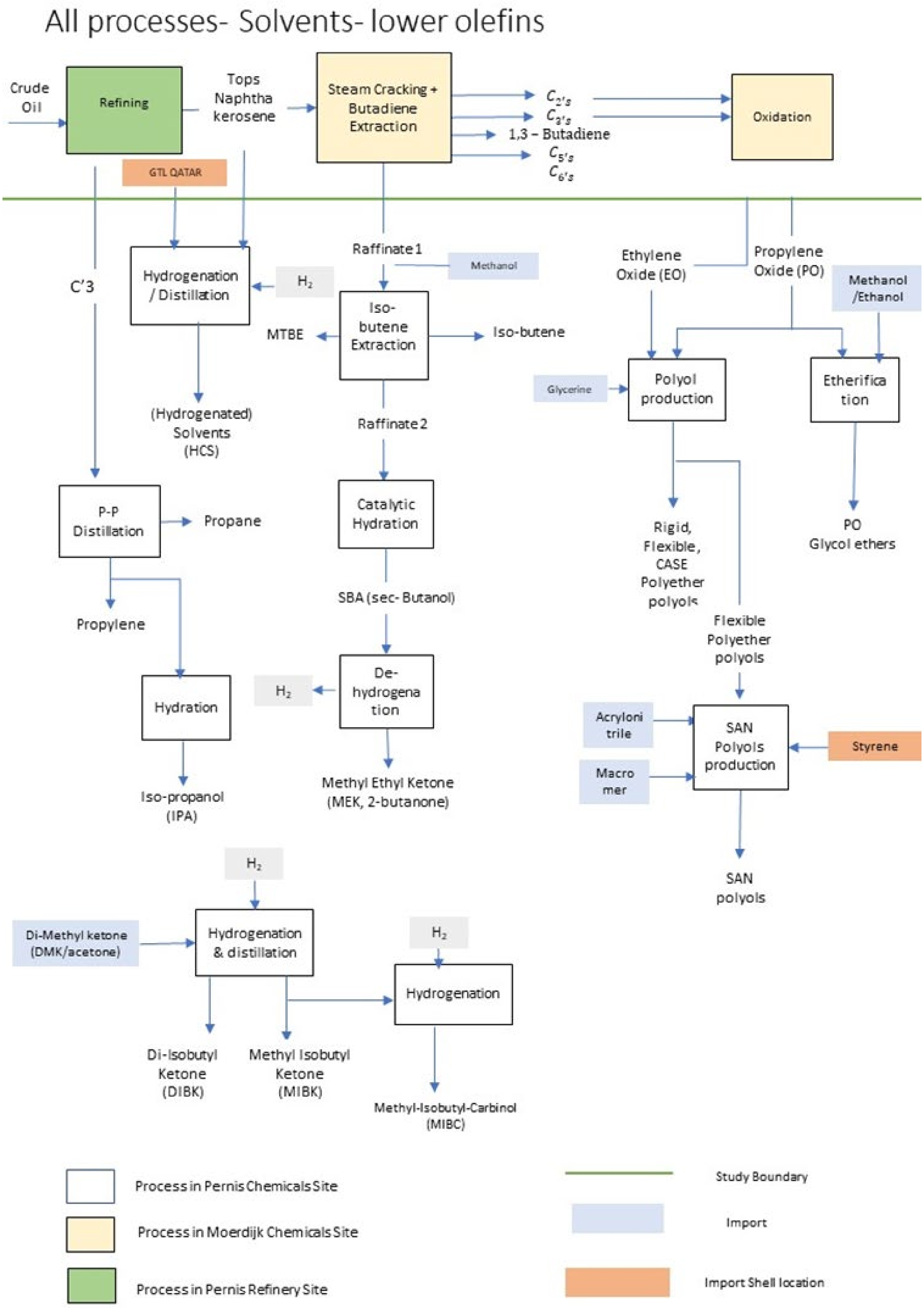

Figure 2 Overview of main processes flow in SNC Pernis site

In general, the production of chemical feedstock in the refineries, from fossil fuel materials, typically involve endothermic processes demanding a large amount of energy for both endothermic reactions as well for separation and purifications processes. However, the subsequent processes downstream in the production chain, as the ones occurring at SNC-Pernis site, go from high to low energy level products with mostly exothermic chemical reactions and relatively high yields (Matar & Hatch, 2000).

2.1 Main manufacturing processing routes in SNC-Pernis

This report section has been divided in four subsections considering what has been identified as “production routes” or main material flows as shown in Figure 2. The definition of these routes is based on the main feedstocks groups and their conversion processes into final commercial products, namely, C-3’s stream from the refinery, the C4’s mix (Raffinate - 1) stream from Moerdijk, imported dimethyl ketone (DMK or Acetone) and Propylene Oxide from Moerdijk.

Among the first two groups of process routes, one may find processes that are usually considered to take place in the refinery, for example, propane-propylene distillation, continuous distillation of hydrocarbon solvents and MBTE synthesis (Barthe, Chaugny, Rouidier, & Delgado Sancho, 2015). They are included in this study because these processes were excluded from the MIDDEN study on refineries (Oliveira & Schure, 2020).

2.1.1 C3’s and refinery streams processing route

Figure 3 displays the process to be described in this sub-section, distillation on C3’s mix from SNR and distillation and for some products Hydrogenation of GTL from Qatar and C5 cuts and naphtha from the refinery. Propylene hydration for the propylene of Isopropyl alcohol (IPA) is also included.

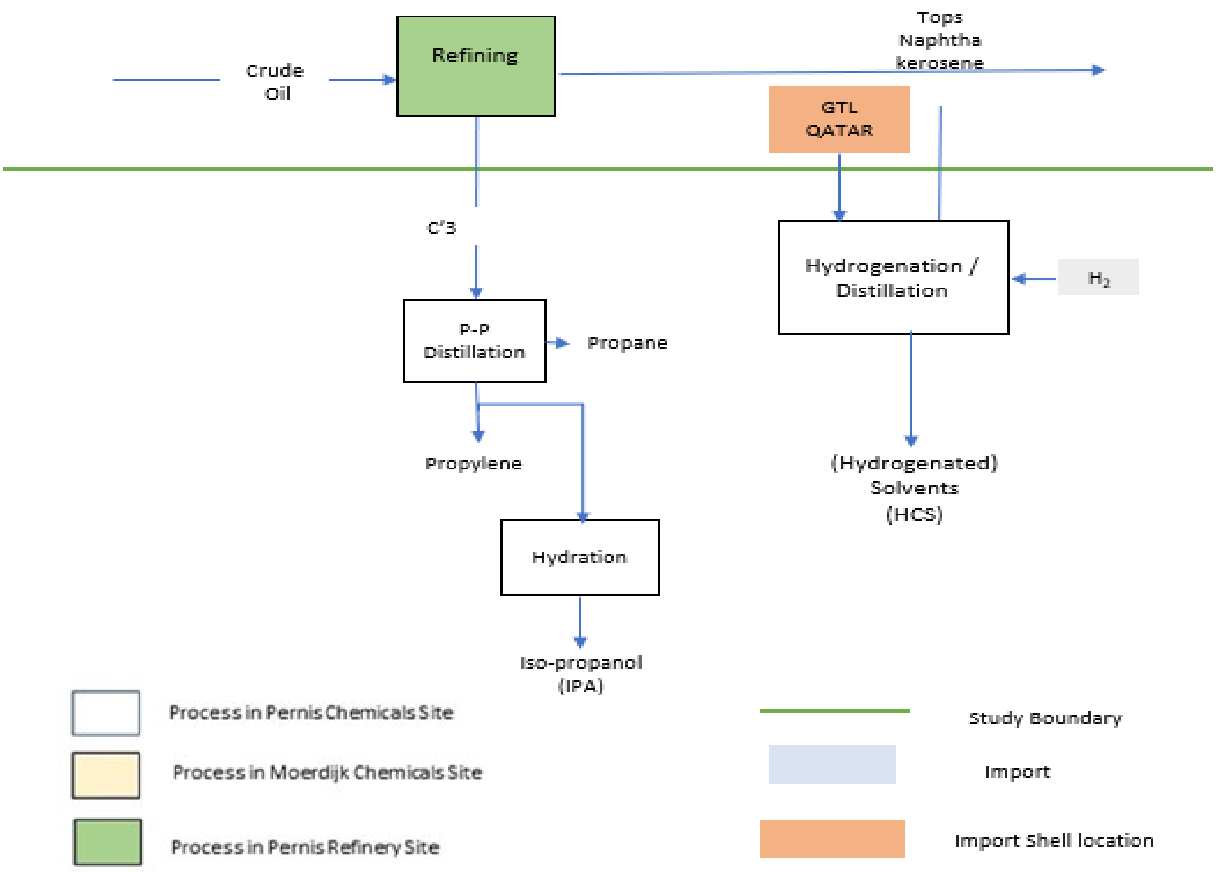

Figure 3 C3's and other Refinery streams processing route

Catalytic cracker feed Distillation (High Purity Propylene)

Distillation is a separation process of liquid mixtures based on their boiling points or relative volatility. It is physical separation process not a chemical reaction (Perry & Green, 1997). In petrochemical plants and refineries, distillation is commonly used to separate olefins, for example ethane/ethylene, propane/propylene, and butane/butene. It is also used to upgrade refinery grade product into a polymer grade propylene, a more diverse and commercial end-product.

The purifying units are usually referred to as splitters or superfractionators, as they contain a number of separations stages (Koch-Glitsch L.P., 2019). The propane/propylene (C3) splitter in SNC-Pernis produces polymer grade propylene (98 to 99.9% purity) from a feed (60 to 95% propylene) from catalytic crackers of the refinery and third parties. The splitter contains various columns and purification beds, including the main columns with heat pump (Shell, 2019d; Obenaus, Droste, & Neumeister, 2010; Shell Global Solutions B.V., 2019).

The propane/propene splitter is equipped with a heat pump (compressor) which supplies the energy required for the separation of the propane and propylene. This heat pump runs at a fixed speed, and it is driven by an electro motor, which represents the highest energy consumption of this unit.

Figure 4 depicts the C3 splitters with heat pump technology developed by Shell.

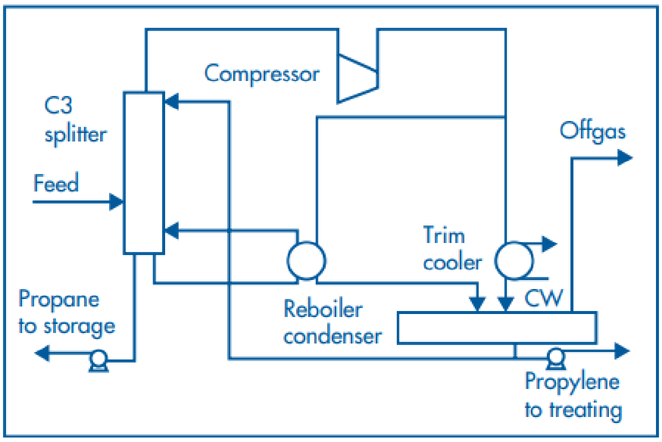

Figure 4 Distillation Process Flow diagram of C3 splitters with heat pump technology (Shell Global Solutions B.V., 2019)

The produced propylene serves as feed for the production of IPA, acrylonitrile (ACN) and epichlorohydrin (ECH). The latter is manufactured in the plants of Hexion B.V. which are also located at the SNC Pernis site. Propylene is also feedstock for the production of propylene oxide (PO) in SNC Moerdijk. This in turn is returned to Pernis for the production of polyols and POGE. The remaining propylene is pumped into the propylene grid to Botlek, Moerdijk and Antwerp. The produced propane is sent back to the refinery.

Continuous Distillation of Hydrocarbon mixture (Hydrocarbon Solvents)

Hydrocarbon Solvents (HCS) are generally manufactured by the continuous distillation of crude oil, similar to the process used for motor fuels. The resulting hydrocarbon solvents contain paraffinic, naphthenic and aromatic components in various proportions. The composition of individual products within this group is determined by the refining parameters (Shell, 2019e).

At SNC-Pernis, solvents from hydrocarbons are produced in the HCS units, manufacturing both low-aromatic and high-aromatic solvents. Isoparaffinic, iso and normal pentanes, and aromatic solvents are produced in SNR premises. The feedstock for the HCS units comes from SNR, Shell Rheinland (Germany) and Shell Qatar Gas to Liquid (GTL) plants.

The HCS are manufactured in two major stages, hydrogenation and distillation. The hydrogenation reaction leads to the conversion to low-aromatic products. The remaining light hydrocarbon and any remaining hydrogen and hydrogen sulphide are then removed in a stripper[1] by distillation. Except for high aromatic solvents (>99% aromatics), all HCS are de-aromatised by hydrogenation.

After intermediate storage, the bottom product is further processed in three distillation units where the low-aromatic intermediates are separated according to their boiling ranges. Additionally, any high-aromatic material that has not passed through the hydrogenation unit (HGU) is distilled in a fourth unit as well. The temperature range of these operations varies from 60 to 250 °C, as illustrated in Figure 5.

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[1] Steam Stripping is essentially a physical separation process where one or more components are removed from a liquid stream by a vapour stream (steam). Steam strippers allow for the removal of heavy soluble organic compounds that air strippers cannot remove. The temperature of these columns is usually very close to the boiling point of water. This is commonly done in a tray or packed tower (College of Chemical Engineering at University of Michigan, 2019 a).

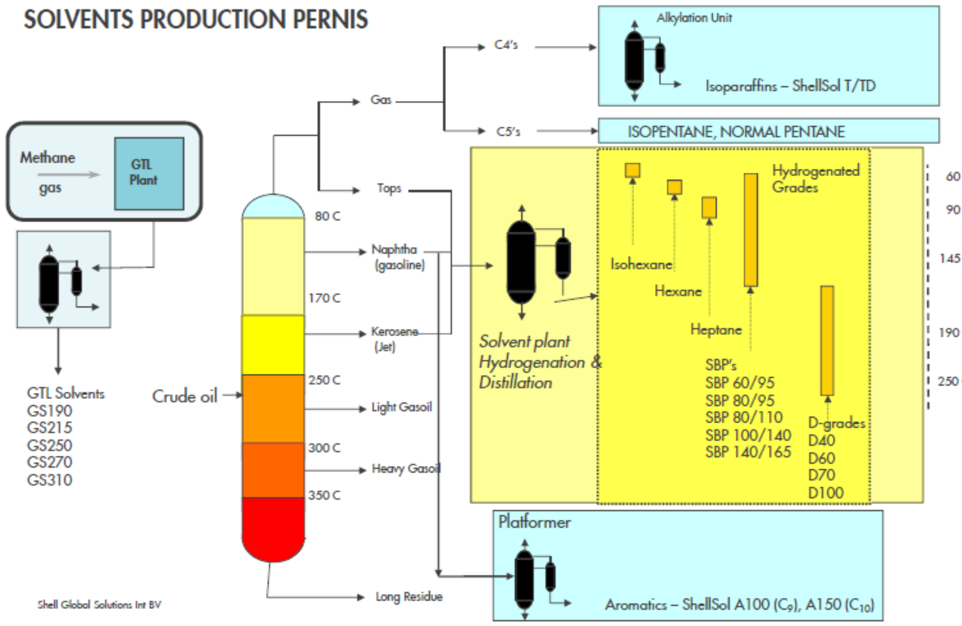


Figure 5 Schematic representation of High and Low paraffinic Hydrocarbons Solvent Production in Shell Chemicals Pernis (Shell Global Solutions B.V., 2018)

Hydrogenation of aromatics is exothermic, so the HGU does not consume much energy. The process energy consumption is determined by the fractioning of low and high aromatic hydrocarbon solvents in distillation units. Separation processes using conventional heat integrated distillation units with furnaces, gas turbines and boilers, are energy intensive processes. The energy requirements may change on a yearly basis, due to the variability in composition of the raw materials (a hydrocarbon mixture) and the market product demands.

Direct hydration of propylene to produce Isopropyl alcohol (IPA)

Isopropyl Alcohol is produced by the chemical grade propylene direct hydration. The modern route avoids the need for sulphuric acid, as it is the case in - older - indirect production methods based on refinery grade propylene. Worldwide, a relatively small amount of IPA is produced by the hydrogenation of acetone in the liquid phase. This process is only suitable where excess acetone is available (Papa, 2002)

Direct hydration is more commonly used in Europe and it consists of the reaction of propylene and water, either in gas phase or in liquid phase. It is applied in the preparation of ethanol from ethylene, and the manufacturing of isopropyl alcohol from propylene, the production of tertbutyl alcohol from isobutene, and production of SBA (2-butanol) from a mixture of butenes (Raffinate II) (Falcke, et al., 2017). More information on the latter is given in the next subsection (2.1.2) of this chapter.

The direct hydration of propylene is carried out according to the following reversible equation:

$$CH_3CH{=}CH_2 + H_2O \rightarrow CH_3CHOHCH_3$$

Equation 1 Propylene hydration to Iso-propylene Alcohol (Nawaz, 2017, p. 1)

The reaction is exothermic, the heat of the reaction calculated from available thermochemical data is about 12 kcal/mol (approx. 50 kJ/mol) over a range of 127 to 326 °C in vapour phase (Tokuyama Soda, 1973).

From the operational point of view, the liquid phase process is carried out at pressures of 80-100 bar and 150 °C whereas the vapour phase reaction is generally carried out at approximately 180 °C and 35 bar (Falcke, et al., 2017) or 200 °C and 25 bar over a catalyst (Matar & Hatch, 2000).

Figure 6 shows a typical process diagram for the manufacturing of IPA at liquid phase conditions where: (1) propylene recovery column, (2) reactor, (3) residual gas separation column, (4) aqueous isopropanol azeotropic distillation column, (5) drying column, (6) isopropyl ether separator, (7) isopropyl ether extraction (Petrochemical Handbook, 1991). *"An isopropanol yield of 93.5% can be realized at 75% propylene conversion. The only important by-product is diisopropyl ether (about 5%)"* (Matar & Hatch, 2000, p. 227)

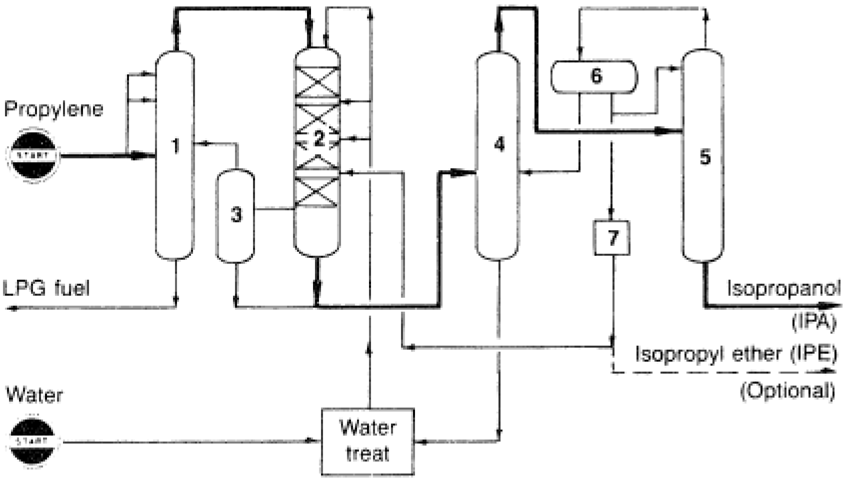


Figure 6 A flow diagram for the Liquid Phase Hydration of propylene to the isopropanol process (Petrochemical Handbook, 1991)

At SNC-Pernis, part of the propylene stream from the C3 splitter is fed together with reaction water into a circulation stream of reactants. The reaction product is led to a washing tower where the non – converted propene is removed and recycled. Subsequently, IPA is obtained from the aqueous solution by distillation, where components such as di-isopropyl ether (IPE), normal propyl alcohol (NPA) and an excess amount of water are removed. Since IPA and water constitute an azeotropic mix, cyclohexane is used as entrainer for separation in a closed cycle.

In the IPA manufacturing process, a large part of the energy use is determined by a medium pressure steam turbine driving a compressor used to circulate reactants. The rest steam is used for the separation of the reaction products from the reactor. Medium Pressure (MP) steam networks typically operate within pressures values ranging from 7-20 bar whilst temperatures vary within 200-350 °C (Barthe, Chaugny, Rouidier, & Delgado Sancho, 2015).

2.1.2 C4's stream processing routes

C_4's hydrocarbon stream from the refinery or from steam cracking units comprises a mix of butane and butenes. The latter are unsaturated olefinic hydrocarbons (alkenes) and are frequently referred to as "butylenes". There are four butene isomers: 1-butene, cis-2-butene, trans-2-butene and 2-methyl propene isobutene, also known as "isobutylene". Butenes cannot be found separately in nature and cannot be separated by distillation since their boiling points are very similar (Obenaus, Droste, & Neumeister, 2010). Therefore the separation of isobutylene from a mix of C4 hydrocarbons is usually integrated in the manufacturing of MTBE and in other cases, with the production of sec-butanol and MEK for maximizing product yields (Streich, Geng, & Renger, 2016). An overview of the C4 stream process route is depicted in Figure 7, from the C4's mix to Sec-Butanol and the Methyl–Ethyl–Ketone production routes.

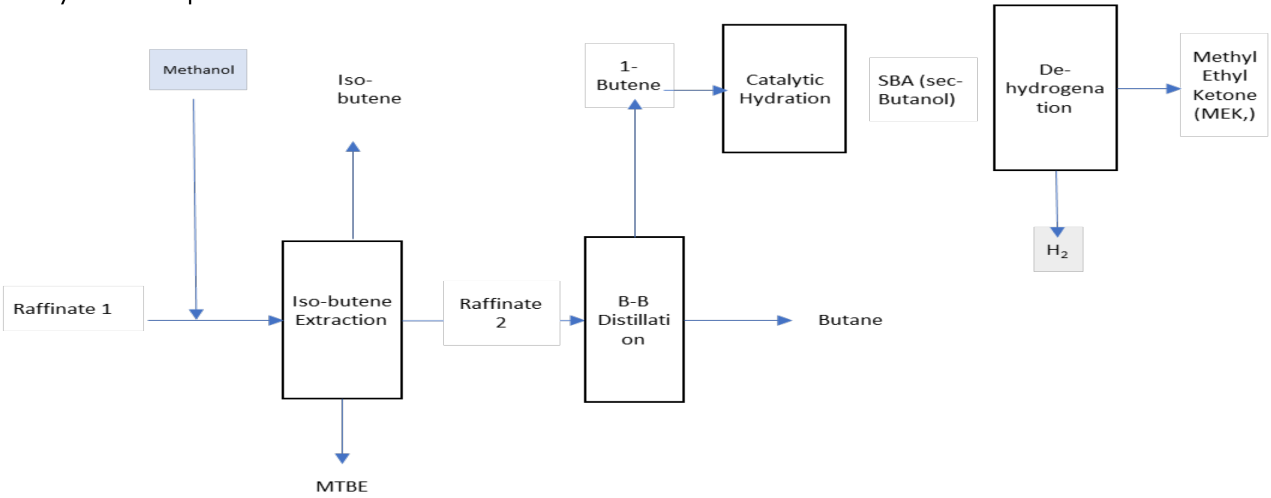


Figure 7 From C4's mix to Sec-Butanol and Methyl – Ethyl – Ketone production routes

Etherification of C4's mix (Raffinate -1) to Methyl tert-butyl ether (MTBE)

There are multiple variations of commercial processes to produce MTBE. Most commercially available processes are comparable, and consist of a reaction and a refining section (Winterberg, Schulte-Körne, Peters, & Nierlich, 2010)

Generally, MTBE is produced from the reaction of isobutene and methanol. MTBE synthesis is an exothermic liquid phase reversible reaction. Typically, five reactions occur in the synthesis of MTBE, the main reaction is presented in equation 2. According to the reviewed literature, the MTBE yield may vary in between 83 % (Nawaz, 2017) and 98% (Matar & Hatch, 2000). The reaction occurs in the presence of an acidic ion-exchange resin catalyst at temperatures between 38-93 °C and a pressure range of 7 to 14 bar (Institute for Health and Consumer Protection, 2002).

$$\text{MTBE: } CH_3OH + (CH_3)_2C{=}CH_2 \leftrightarrow (CH_3)_3COCH_3$$

Equation 2 Isobutene and Methanol Reaction (Nawaz, 2017, p. 1)

Table 2 Typical composition (in wt. %) of Raffinate-1 and 2 related to integrated steam cracking, the Hüls MTBE synthesis process and isobutane removal (Obenaus, Droste, & Neumeister, 2010)

Component	Raff.-I	Raff.-II	*n*-Butene conc.
Isobutane	3	6	< 0.05
Isobutene	45	< 0.1	< 0.1
1-Butene	25	45	48
1,3-Butadiene	< 0.5	< 0.8	< 0.001
n-Butane	11	19	20
trans-2-Butene	9	17	18
cis-2-Butene	7	13	14

*Related to the Hüls process (Fig. 1)

The reaction consists in the synthesis of MTBE by the etherification of isobutene contained in Raffinate-1, with methanol, resulting in a new stream with almost non isobutene content, also called Raffinate 2. In the distillation phase, the raffinate 2 is then fractioned to separate isobutane together with water. Through selective hydrogenation, Raffinate-2 is then stripped the residues 1-3 butadiene present, ending with a typical composition of about 60 to 90 wt.% of linear butenes and butane (Winterberg, Schulte-Körne, Peters, & Nierlich, 2010). Table 2 also shows the typical composition of raffinate 2 after isobutane removal. A version of the Raffinate-1 etherification process flowsheet is presented in Figure 8, licensed by Uhde GmbH (Gulf Publishing Company, 2004).

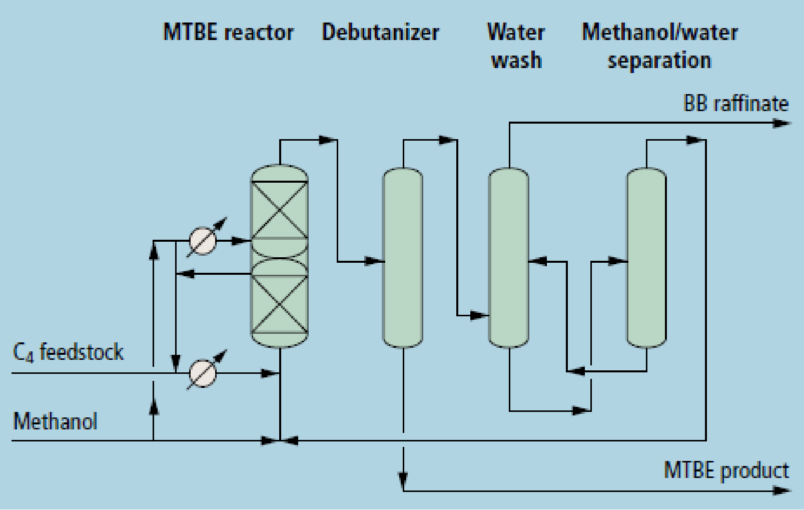
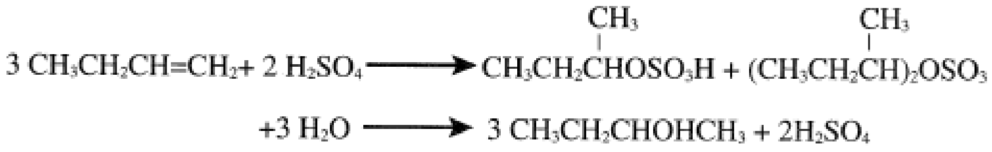


Figure 8 Uhde GmbH. MTBE production processes (Gulf Publishing Company, 2004)

In SNC-Pernis the produced MTBE is sent to the refinery or exported. It is mainly used as additive in the transport fuel production process. The resulting Raffinate 2 (Shell, 2019d) is a chemical building block used in the manufacture of secondary butyl alcohol (SBA) and methyl ethyl ketone (MEK) as described in the following sub-sections.

From Raffinate 2 indirect hydration to Sec-butyl alcohol (SBA)

All alkenes react with water in the presence of dilute sulfuric acid to produce alcohols. SBA made by hydration is, after 1-3 butadiene, the second largest volume product from n-butenes (Obenaus, Droste, & Neumeister, 2010). Industrially, two variants of the hydration reaction are used, indirect and direct processes. The direct hydration process occurs in the gas phase (Falbe, Bahrmann, Lipps, & Mayer, 2013). At SNC-Pernis, SBA or 2-butanol is produced by the hydration of Raffinate-2 using the indirect process, in which the liquid-phase reaction takes place in two steps. The first step is the reaction of the feedstock with sulfuric acid at a temperature of 35 °C to form mono- and dialkylsulfates i.e. fat acids. In the second step, the resulting mix (fat acids) is separated from residual gas in a phase separator to later be diluted with water (hydrolysis) and forming SBA. This raw SBA is upgraded to pure SBA to be fed to the MEK plant (Falbe, Bahrmann, Lipps, & Mayer, 2013). Reportedly, an 85 wt% alcohol yield could be realized. The main by-product is di-sec-butyl ether, which may be recovered (Matar & Hatch, 2000). The reactions are as follows:



$$3\ CH_3CH_2CH{=}CH_2 + 2\ H_2SO_4 \longrightarrow CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HOSO_3H + (CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}H)_2OSO_3$$

$$+3\ H_2O \longrightarrow 3\ CH_3CH_2CHOHCH_3 + 2H_2SO_4$$

Equation 3. Chemical Reactions for SBA manufacturing (Matar & Hatch, 2000, p. 222)

The SBA production unit requires sulfuric acid to catalyse the hydrolysis reaction. The energy demand is driven by the amount of steam required in three steps of the process, these are:

(1) the amount of low pressure (LP) and medium pressure (MP) steam to recirculate sulfuric acid over the unit (Barthe, Chaugny, Rouidier, & Delgado Sancho, 2015). (2) LP steam required to remove sulfuric acid from the SBA and water mixture, and (3) the amount of LP steam required to separate SBA and water through vaporization. The latter is decisive for the energy consumption of the unit (Dennebos & Zwart, 2019). Usual operating ranges of industrial low-pressure steam vary within a pressure range of 3.5 to 5 bar and temperatures in between 150 to 200 °C.

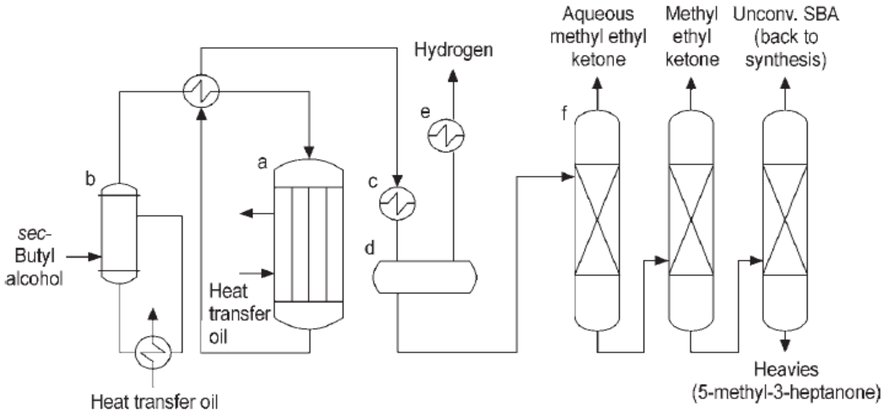
SBA dehydrogenation for the Synthesis of Methyl Ethyl Ketone (MEK)

Methyl Ethyl Ketone (MEK) or 2-butanone is the second most commercialised ketone next to acetone. MEK is mainly produced by the dehydrogenation of SBA. By 2006, approximately 92% of all production capacities worldwide used this process technique (Hoell, et al., 2012).

$$\underset{\text{sec-butyl alcohol}}{CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_2CH_3} \xrightarrow[400\text{-}550^{\circ}C]{ZnO\text{ or brass}} \underset{\text{MEK}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_3} + \underset{\text{hydrogen gas}}{H_2}$$

Equation 4. SBA Chemical Reactions for MEK manufacturing (Environmental Protection Agency (EPA), 1994)

In the most commonly used production method, SBA dehydrogenation occurs in the vapour phase. The majority of the reaction takes place in furnaces at 400-550 °C and pressures lower than 4 bar (ICIS, 2019b). Other authors indicate that typical conditions for this reaction are 220 to 450 °C and 1 to 6 bars (Barnicki, 2012). The alcohol vapour is then fed into a multi-tubular reactor containing zinc or copper oxides as catalysts, and subsequently, the hydrogen is flashed off (ICIS, 2019b). Copper catalysts provide high selectivity, typically greater than 90% (Barnicki, 2012). After the hydrogen separation, the MEK is purified by distillation. "*The main fraction (methyl ethyl ketone) is typically obtained at an 85 to 90 percent yield based on the mass of secondary butyl alcohol charged*" (Environmental Protection Agency (EPA), 1994, pp. 4-6). Another source reports a higher yield of approximately 95% (Matar & Hatch, 2000). The produced hydrogen may be re-used, burned in a furnace, or flared. Figure 9 depicts a process technology developed by Deutsche Texaco based on dehydrogenation of anhydrous sec-butyl alcohol on a copper-based precipitation catalyst at 240–260 °C under normal pressure (Stahmer, 1984) (DE Patentnr. 1147933, 1958).



a) A multitube reactor; b) Evaporator; c) Condenser; d) Separator; e) Refrigerator; f) Distillation column system

Figure 9 Gas Phase dehydrogenation of sec-butyl alcohol developed by Deutsche Texaco (Hoell, et al., 2012)

The Environmental Protection Agency reports reactors to be maintained between 400°C and 550 °C at normal atmospheric pressures for conversion from secondary-butyl alcohol using a catalytic bed of zinc oxide or brass (zinc-copper alloy) (Environmental Protection Agency (EPA), 1994). For the manufacturing of MEK, most of the energy use is used to supply heat to the reactor where the indicated temperatures are required for the dehydrogenation process (Environmental Protection Agency (EPA), 1994). SNC is assumed to apply gas phase dehydrogenation technology.

Alternatively, a liquid phase technology for MEK manufacturing is also employed in Europe using Raney nickel or copper chromate at 150 ºC, at atmospheric pressure (ICIS, 2019b). The selectivity is typically three percent higher than the vapour phase process (Barnicki, 2012; Environmental Protection Agency (EPA), 1994). It also has a longer catalyst life, simpler product separation, and lower energy consumption than the vapour phase process (Environmental Protection Agency (EPA), 1994)

2.1.3 Acetone (DMK) processes route

At Shell Pernis Chemicals, the main feedstock to produce MIBK and DIBK is acetone supplied by a third party. MIBK is produced from acetone through a hydrogenation process with Diisobutyl ketone as by-product. The hydrogenation of (raw) MIBK is the process applied to manufacture methyl isobutyl carbinol (MIBC) (Shell, 2019f).

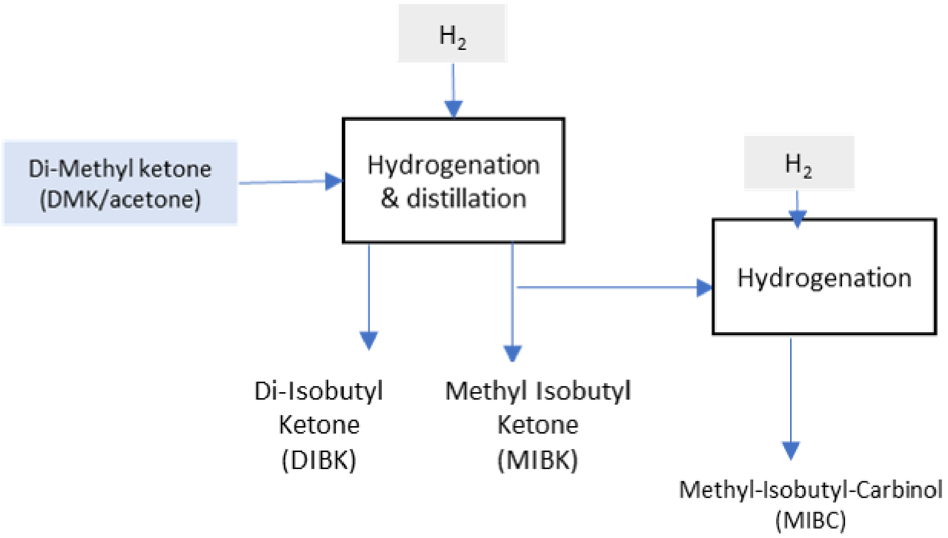


Figure 10 From DMK to MIBK, DIIBK and MIBC production routes

Methyl isobutyl ketone (MIBK) (4-methyl-2-pentanone) is an industrially important solvent and chemical intermediate, and the third most produced acetone-derivative after methyl methacrylate and bisphenol-A. There are four different processes to produce MIBK: MIBK and DIBK can be co-produced by the catalysed reaction of hydrogen and acetone (DMK) and/or IPA. SNC currently does not apply IPA as feedstock. The other two routes are single or multi-step and multi-feed processes (Muthusamy & Fisher, 2019). The most commercial process with more than 60 percent of MIBK production is a three step process of aldol condensation of acetone and derivative intermediates diacetone alcohol and mesityl oxide (ICIS, 2019a), it implies the combination of three subprocesses such as condensation, dehydration and hydrogenation, and also separation and purification of intermediate products (such as diacetone alcohol and mesityl oxide) to ultimately provide a relatively low conversion rate.

Hydrogenation is the main process unit used to manufacture MIBK and DIBK. Generally, the process involves elevated temperature and relatively high pressure in the presence of a catalyst (Speight, 2002). In hydrogenation processes, it is usually a best practice to heat the materials before they enter the reactor and have the reactor itself thermally insulated. Hydrogenation is usually an exothermic reaction, which requires temperature control (by heat removal) at the beginning of the reaction.

Di-isobutyl ketone (DIBK) is a heavy-end by-product of producing MIBK. Characterization of the production processes of MIBK/DIBK is deemed difficult since "*The MIBK to DIBK ratio is not constant and decreases as steps are taken to increase MIBK production by increasing reactant conversion*" (Europe Patentnr. EP1931615A1, 2008). Additionally, the production capacities tend to vary because some of the equipment used in the manufacture of MIBK can be used to manufacture other ketones as well.

The MIBK manufacturing process energy use is determined by the fuel required for heat generation and the energy required for compressors for the hydrogenation process (IHS-Markit, 2019 h; Speight, 2002).

2.1.4 Propylene Oxide Processing Routes

Ethylene oxide and mainly propylene oxide (also called epoxides) are processed in SNC–Pernis to manufacture glycol ethers through an etherification process using methanol, and depending upon the desired end product, ethanol might be added to the reaction. Epoxides may also follow a different production line for the manufacturing of polyols at the CVP location in the SNC-Pernis site as depicted in Figure 14.

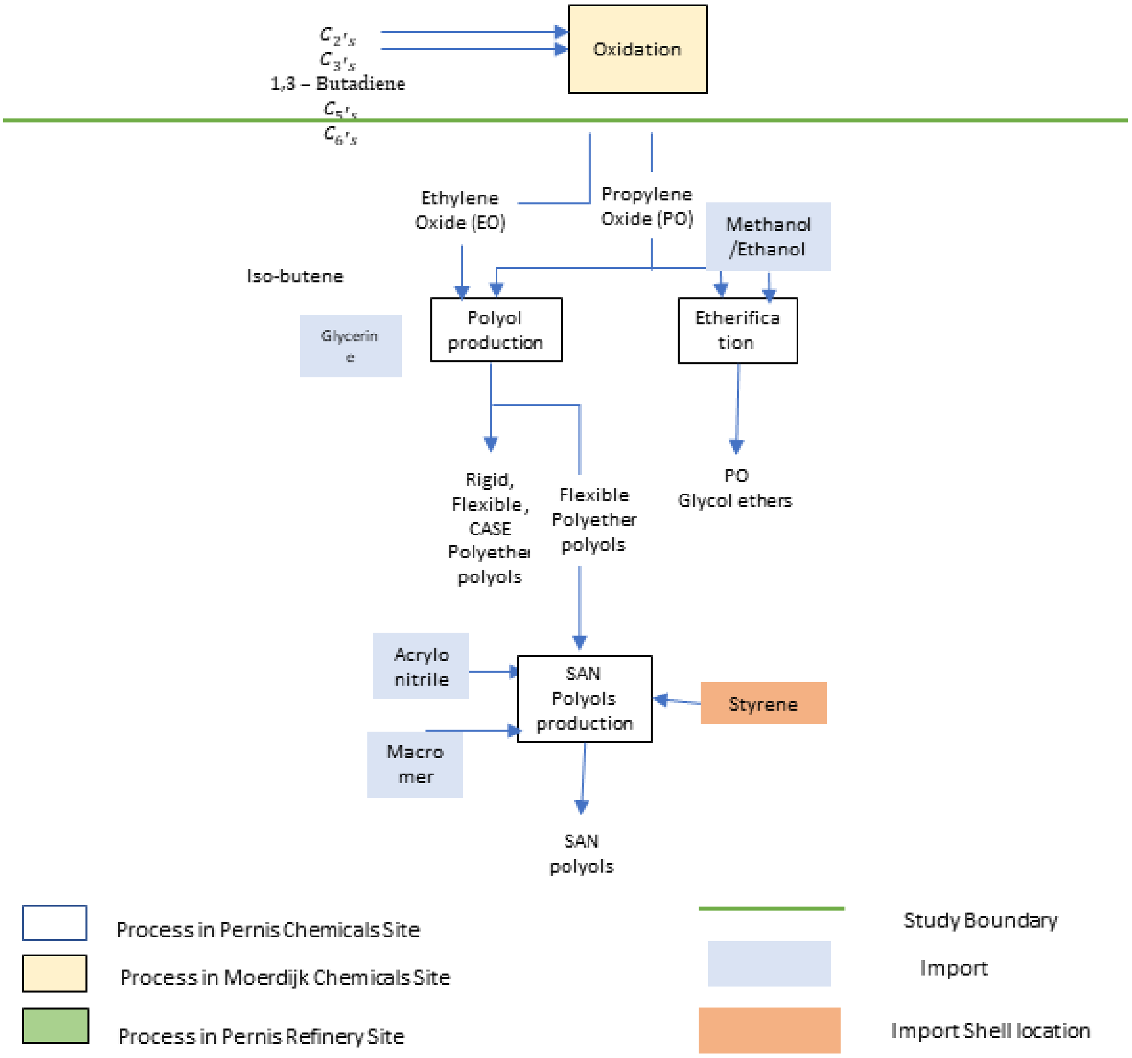


Figure 11 From Propylene Oxide to Glycol Ethers and (SAN) Polyols

Epoxides etherification route to manufacture Glycol ethers

Glycol ethers are solvents that have been manufactured since the 1930's. Glycol ethers are generally produced through the etherification of epoxides, there is a wide variety of this type of solvents because of the different proportion in which the epoxides can be mixed, in consequence, the end products (Glycol ethers) are classified in two groups depending upon the epoxide used for its production, namely E-series for ethylene based glycol ethers and P-series for those made out of propylene. The type of alcohol utilised, methanol or ethanol, also defines what type of glycol ether will be produced. For instance, the reaction of propylene oxide with methanol yields propylene glycol methyl ether (Barnicki, 2012).

SNC-Pernis produces glycol ethers and glycol ether acetates using propylene oxide (PO) as feedstock, which is manufactured by SNC-Moerdijk (Shell, 2019g). PO is added to an excess of alcohol in a reactor (methanol, ethanol). The process has two steps, reaction and separation section. In a number of distillation towers, the reaction product is separated into mono or possibly di-propylene glycol ethers and heavy ends. The reaction conditions typically are in between 170 -220 °C and 1.0–1.5 MPa (10-15 bar) depending on the alcohol and epoxide. The etherification of an epoxide is an exothermic reaction, with an average heat of reaction of about -80 to -100 kJ/mole (Barnicki, 2012).

PO polymerisation for Polyether Polyols Manufacturing

Polyether polyols are manufactured in the CVP location through the catalytic polymerization of propylene oxide (PO)) and/or ethylene oxide (EO) (produced in SNC-Moerdijk). The most common catalyst is potassium hydroxide.

The process needs an initiator having active hydrogens, and a starter such as glycerine, sucrose, water, amines or mono-propylene glycol (MPG). SNC-Pernis has seven product lines for the manufacturing of different grades of polyols with specific applications based on their molecular weight.

Polyether polyols may be classified depending on their application in three main categories: coatings, adhesives, sealants and elastomers (CASE) polyols, flexible foams and rigid foams. CASE polyols are the result of the combination of mono propylene glycol and propylene oxide. Polyols for flexible foams are prepared by conducting a reaction of glycerine with propylene oxide (PO) and optionally, ethylene oxide (EO) or amine. Polyols for rigid foams are prepared by conducting a reaction of various basic raw materials, such as trimethylolpropane or sucrose/sorbitol with propylene oxide (PO) (Ionescu, 2005).

Recent research (Fernández-Dacosta, Stojcheva, & Ramirez, 2018) describes the conventional polyether polyol manufacturing process as the reaction of propylene oxide (PO), glycerol (G) and mono-propylene glycol (MPG), equivalent to a CASE polyol, taking place at 135 °C and 3 bar. Double metal cyanide (DMC) is used as catalyst and recovered in a filter after the reaction. In a vacuum-stripping step (140 °C, 25 mbar) odours and other impurities are separated, and polyol is obtained as final product (40 °C, 1 bar). Figure 12 shows the process configuration.

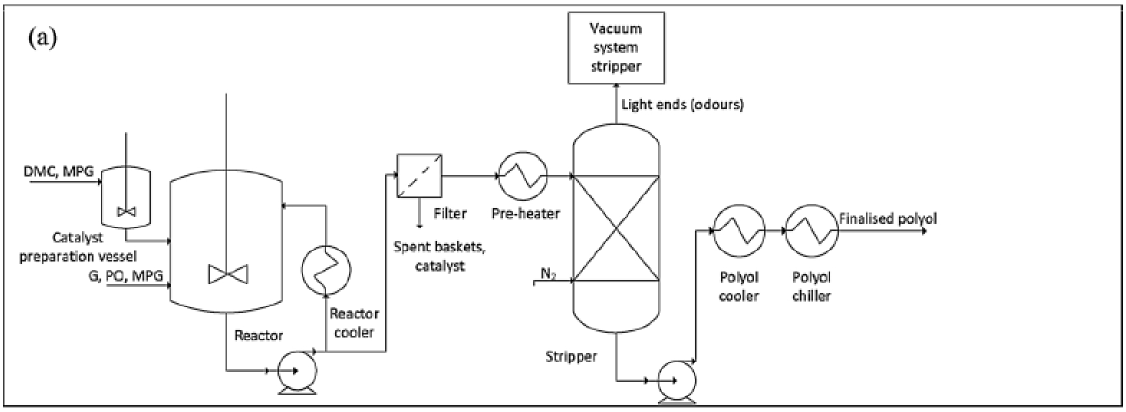


Figure 12 Conventional CASE polyether polyol manufacturing process diagram (Fernández-Dacosta, Stojcheva, & Ramirez, 2018)

Propylene Polyether Polyols conversion to Styrene Acrylonitrile (SAN) Polymer Polyols

SAN Polymer production starts with the use of styrene, acrylonitrile and a macromer usually presented in the form of pellets or beads. Figure 13 shows a continues bulk polymerization process developed by Toyo Engineering Corp (Gulf Publishing Company, 2010). The temperature in the reactor is carefully monitored and kept constant in order to meet a steady flow condition. At the exit of the reactor, the mixture is preheated and transported to a devolatilizer in which the separation of volatile components from the polymer mix by evaporation under vacuum conditions occurs. Finally, a viscous liquid polymer is produced and delivered to clients. At Pernis the product is not extruded and cut into pellets.

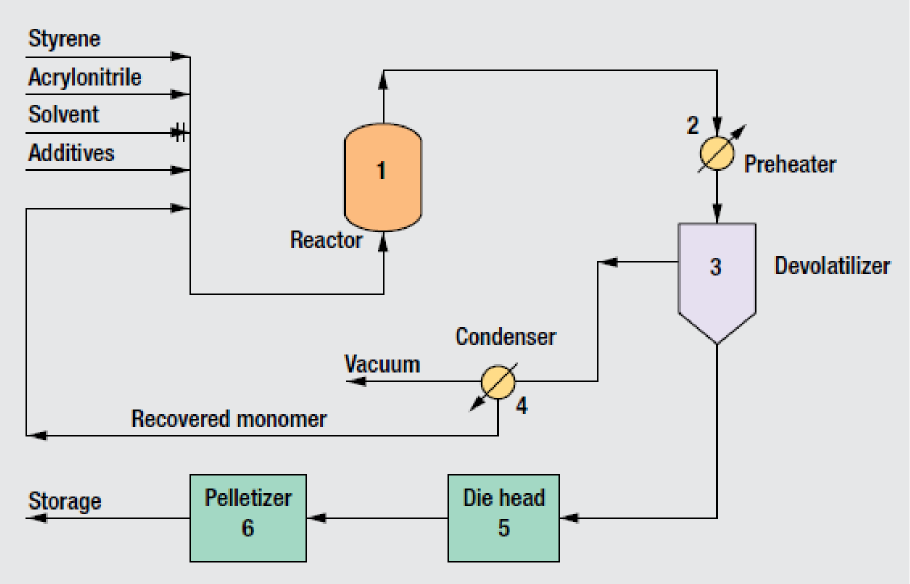


Figure 13 SAN Polymer process developed by Toyo Engineering Corp (TOYO) (Gulf Publishing Company, 2010; Gulf Publishing Company, 2004)

At SNC-Pernis, the SAN beads are produced in a batch process with styrene, acrylonitrile, a catalyst and the stabilizer as ingredients, and polyol as solvent. Hereby the polymer is 'graved' on the stabilizer. If desired, the result can be diluted with extra polyol. The dilution process is quite critical, as a relatively high viscosity is required to improve the suspension stability but also should be low enough for processability. In order to minimise storage capacity requirements, Shell uses inline blending for all polyols. This means that the components are stored separately. The dosing pumps that assemble the end product also pump it directly into a tanker ship or a truck. Static mixers in the discharge pipes ensure the necessary mixing controlled by pumps and valves. The main application of SAN polyols is the manufacturing of flexible foam (C2W, 2020).

SAN polymer polyols manufacturing consumes more energy than the polyol manufacture itself. In the Shell process unconverted styrene and acrylonitrile need to be stripped off as they are toxic compounds in the end application. This stripping involves evaporation with steam of the unconverted compounds, and subsequent incineration with roof combustors. with steam.

2.2 Energy Consumption in SNC-Pernis manufacturing plants

Chemicals production processes require the use of principal utilities such as electricity, heat and cooling water. Heat can be provided to reactors or distillation units in a direct or indirect manner, the former by using dedicated furnaces and boilers, and the latter through heat oil and steam distribution systems. Electricity is required by electrical compressors, pumps control systems and valves. Typically, these plants are part of an integrated petrochemical and /or refining complex where central facilities provide the common utilities (Falcke et al., 2017; Falbe & al, 2013).

SNC-Pernis receives energy in the form of electricity, heat and gas from the refinery. The adjacent refinery supplies heat in the form of steam and thermal oil. The refinery also supplies fuel gas to fire furnaces and incinerators Energy Consumption in SNC-Pernis manufacturing plants.

The energy consumption levels are highly dependent on the feedstock composition, specific processes design and the desirable products and by-products of the petrochemical process. The total energy use of SNC plants in 2015 and its allocation per manufactured product (or group of) was provided by the company, this information is presented in Table 3.

Table 3 SNC plants total energy use in 2015 per groups of manufactured products, calculated based on Shell information on shares

Main Process	Main Product	Total Energy Use SNC-Pernis (TJprimary/y)	Energy Use Product Share (%)
Distillation P-P splitter	Propylene	221	5
Distillation and Hydrogenation	HCS	397	8
Propylene Hydration	IPA	1,678	34
DMK Hydrogenation	MIBK		
DMK Hydrogenation	DIBK	1,060	22
MIBK Hydrogenation	MIBC		
Propylene Oxide (PO) etherification	POGE's		
Reaction of Isobutene and Methanol	MTBE		
Sulphuric acid hydration of n-butene	SBA	1,060	22
SBA dehydrogenation	MEK		
TOTAL COD LOCATION		**4,416**	**90**
Propylene Oxide (PO) polymerisation	Polyether Polyols	**491**	**10**
SAN Polymerisation	SAN Polyols		
TOTAL CVP LOCATION		**491**	**10**
TOTAL ENERGY USE SNC-PERNIS 2015		**4,907**	**100**

The highest energy demand is regarded to the processes occurring at the COD location. The processes represent about 90% of the yearly total energy consumption of the chemical plants operated by SNC-Pernis. More specifically, the IPA, MIBK, SBA and MEK manufacturing consume slightly over 55% of the energy supplied to SNC plants, followed by the major distillation processes for propylene and hydrocarbon solvents manufacturing, which together consume about 13%. MTBE, Glycol-Ethers, and MIBC processes require approximately a quarter of the annual energy use of the COD location. The polyether and SAN polyols production in the CVP location is estimated to consume around 10% of the total energy demand in SNC-Pernis plants. Total primary energy consumption of the SNC–Pernis facilities in 2015 was 4,907 TJprim. Table 4 provides a breakdown of the energy use in these plants in which steam and hot oil delivered by the refinery represent together about 75% of the total primary energy use in one year (SNC, 2019).

Table 4 Primary Energy Consumption in SNC 2015 – Pernis (SNC, 2019)

Energy Carrier	Primary Energy Consumption (TJ)	Primary Energy Consumption (%)
Steam	3,125	64
Electricity	1,018	21
Hot oil	545	11
Fuel gas	219	4
Total	4,907	100

For energy efficiency improvement, Shell Pernis uses an Energy Management System that helps operators identify processes with low efficiency by highlighting the five largest causes of inefficiency at any given time. With the help of this monitoring system, operators can find solutions more effectively and with higher added value (Shell, 2019a).

2.3 Material and energy balances

The estimations of energy balances for each process in this section are the result of the combination of actual energy use data for SNC-Pernis processes in 2015 (Table 3) and literature values shown in Table 5.

Table 5 Theoretical energy consumption values per ton of product for relevant LVOC manufacturing processes

Main Process	Main Product	Total (GJ/ton)	Steam (GJ/ton)	Electricity (GJ/ton)	Fuel (GJ/ton)	SOURCE
Distillation P-P splitter	Propylene	-	-	-	-	-
Distillation and Hydrogenation	HCS	-	-	-	-	-
Propylene Hydration	IPA	10.69	5.4	0.09	5.2	(Neelis, Patel, Blok, Haije, & Bach, 2007b)
DMK Hydrogenation	MIBK	-	-	-	-	-
DMK Hydrogenation	DIBK	-	-	-	-	-
MIBK Hydrogenation	MIBC	-	-	-	-	-
Propylene Oxide (PO) etherification	POGE’s	-	-	-	-	-
Reaction of Isobutene and Methanol	MTBE	3.66	3.6	0.06	0	(Neelis, Patel, Blok, Haije, & Bach, 2007b)
Sulphuric acid hydration of n-butene	SBA	12.65	12	0.65	0	(Streich, Geng, & Renger, 2016)
SBA dehydrogenation	MEK	6.91	6	0.05	0.86	(Streich, Geng, & Renger, 2016)
Propylene Oxide (PO) polymerisation	Polyether Polyols	1.42	1.29	0.13	0	(Neelis, Patel, Blok, Haije, & Bach, 2007b)
SAN Polymerisation	SAN Polyols	-	-	-	-	-

The energy data of the processes are divided in three categories: complete information, partial information and very limited information (Figure 14).

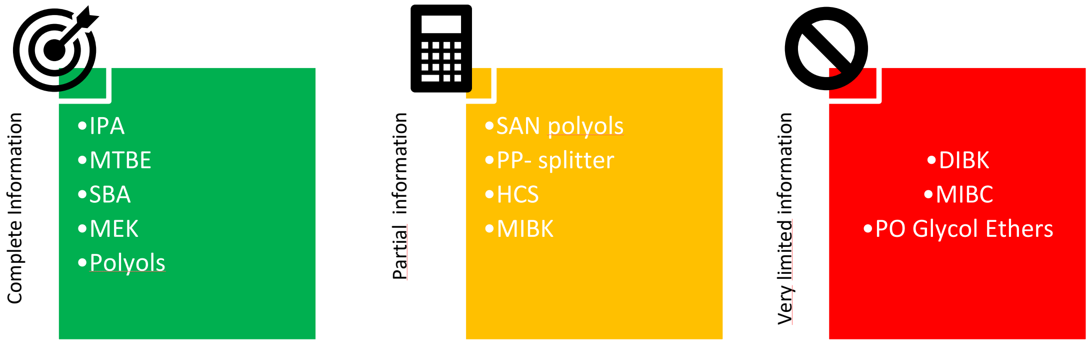


Figure 14 Selection of processes for energy and material balance estimations.

Processes with complete information were calculated and checked against the actual values. When only partial information was available an estimation was performed. For the processes with very limited information about material flows and/or energy use, assumptions were made.

To calculate annual energy flows, it is necessary to combine literature values with an estimate of the produced mass in a year or mass flows. The core inputs for the material balance are: plants capacity (in Table 3), the main product yields and annual capacity utilisation rate. Table 6 indicates the products yields found in the literature.

Table 6 Main product yields found in literature

Main Process	Main Product	Main Product Yield (%)	SOURCE
Distillation P-P splitter	Propylene	98-99.9[2]	(Shell Global Solutions B.V., 2018)
Distillation and Hydrogenation	HCS	60-80	(SNC, 2019)
Propylene Hydration	IPA	94	(Matar & Hatch, Chemistry of Petrochemical Processes, 2000)
DMK Hydrogenation	MIBK		
DMK Hydrogenation	DIBK		
MIBK Hydrogenation	MIBC		
Propylene Oxide (PO) etherification	POGE's		
Reaction of Isobutene and Methanol	MTBE	83-98	(Gulf Publishing Company, 2004; Matar & Hatch, 2000)
Sulphuric acid hydration of n-butene	SBA	30-90	(Environmental Protection Agency (EPA), 1994; Matar & Hatch, 2000)
SBA dehydrogenation	MEK	85-98	(Environmental Protection Agency (EPA), 1994)
Propylene Oxide (PO) polymerisation	Polyether Polyols		
SAN Polymerisation	SAN Polyols	-	-

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[2] Purity of the split propylene. The feed from the refinery contains 60-95% propylene.

The results for the material balance are summarized Table 7. Note that the numbers represent tentative estimates, and do not represent actual realisations. The yields per process shown in table 7 fall within the theoretical yield ranges shown in table 6. It was assumed that the capacity of the plant expressed in kt of product per year already includes the product yield and high selectivity. Therefore, product yield data are used only for the feedstock requirements. For the capital utilisation rate, (Neelis, Patel, Blok, Haije, & Bach, 2007b) suggests a typical value of 86% for the plants in the Netherlands. Shell indicates lower utilisation rates for HCS and IPA, which are set at 70%. Based on the material balance estimates, the total net hydrogen use of SNC Pernis is calculated at 7 kt per year.

Table 7. Material flow of main products at SNC-Pernis in 2015[3]

Main Product	Capacity [kt/year]	Capacity utilisation rate [%]	Annual Production (kt/y)	Estimated yields [%]	Main feedstock	Feedstock use (kt/y)
Propylene	280	86%	241	98%	P-P-mix	307[4]
Various HC solvents	820	70%	574	95%	HC's mix	604
Isopropyl Alcohol (IPA)	150	70%	105	94%	Propylene	78
Methyl Isobutyl Ketone (MIBK)	35	86%	30	93%	Acetone (DMK)	38
Di-isobutyl Ketone (DIBK)	5	86%	4.3	93%	Acetone (DMK)	5.7
Methyl Isobutyl Carbinol (MIBC)	2.5	86%	2.2	93%	MIBK	2.3
PO-Glycol ethers (POGE's)	247	86%	212	85%	PO/EO	150[5]
Methyl Tertiary – Butyl ether (MTBE)	170	86%	146	99%	Raffinate-1	94[6]
Secondary Butyl Alcohol (SBA)	105	86%	90	80%	Raffinate-2	85
Methyl Ethyl Ketone (MEK)	90	86%	77	90%	SBA	88
Polyether Polyols	200	86%	172	90%	PO	191
Styrene acrylonitrile (SAN) Polyols	50	86%	43	90%	PO, SAN	48

Based on the Shell data in Table 3 and Table 4, literature values in Table 5 and the mass flows in Table 7, a further allocation of final energy consumption to specific processes is made. For electricity, final energy use is calculated based on a primary factor of 2.3 as used in current energy efficiency monitoring. Final electricity use is estimated at around 10% of total use, except for the P-P-splitter heat pump and the SAN polyol compounding, where a 60% share is estimated. Direct fuel use is only reported for the MEK furnaces. The results are presented in Table 9.

The IPA production process (hydration) is the process with the highest energy consumption, SBA's manufacturing process (dehydrogenation) ranks in second place. MTBE synthesis ranks third closely followed by MEK's production process (hydrogenation). These results are

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[3] Figures in bold style were estimated to match the annual energy use, based on literature review; Sources: Capacities (Shell, 2019c; Port of Rotterdam Authority, 2019) and Capacity Utilisation Rate (Neelis, Patel, Blok, Haije, & Bach, 2007b).

[4] Assuming 80% propylene in the P-P-mix.

[5] Plus 100 kt methanol and ethanol.

[6] Plus 59 kt methanol.

expected according to the description of the process in the reviewed literature (Speight, 2002; Matar & Hatch, 2000).

Table 8 Calculated energy use per process and energy carrier

Main Process	Main Product	Steam and hot oil [PJ]	Fuel [PJ]	Electricity final use [PJ]	Total final energy use [PJ]
Distillation P-P splitter	Propylene	0.04	-	0.08	0.12
Distillation (and Hydrogenation)	HCS	0.30	-	0.04	0.34
Propylene Hydration	IPA	1.11	-	0.01	1.12
DMK Hydrogenation	MIBK	0.41	-	0.06	0.47
DMK Hydrogenation	DIBK	0.06	-	0.01	0.07
MIBK Hydrogenation	MIBC	0.03	-	0.00	0.03
Propylene Oxide (PO) etherification	POGE's	0.31	-	0.04	0.35
Reaction of Isobutene and Methanol	MTBE	0.53	-	0.01	0.54
Sulphuric acid hydration of n-butene	SBA	0.51	-	0.07	0.57
SBA dehydrogenation	MEK	0.17	0.22	0.00	0.39
Polyether Polyols	Polyether Polyols	0.22	-	0.02	0.24
SAN Polymerisation	SAN Polyols	0.04	-	0.08	0.12
Totals		3.73	0.22	0.42	4.37

2.4 EU ETS carbon dioxide emissions

In the overall petrochemical complex, a large number of units within SNC-Pernis contribute to the carbon dioxide emissions. Energy requirements, raw material composition, use of auxiliary materials and their chemical reactions are among the factors influencing the CO_2 emissions of the manufacturing process and energy use. SNC uses chemical gas for heat generation. Further, SNC Pernis operates incinerators and flares for combustion of unwanted residuals (Public Affairs department of Shell Nederland Raffinaderij B.V., 2003).

The direct CO_2 emissions from processes mainly originate from the fuel-fired furnace operation at the SBA/MEK production units. These are fired with residual gases from the C_3 PP-splitter. Additionally, CO_2 emissions may be generated by gas flaring, yet on a non-regular basis, as flaring is only used in start-up /shut-down operations and in case of equipment failures. The main objective of flaring is to prevent unburnt fuel gas from entering the atmosphere. This allow for a safe shutdown or maintenance of plants. Hence the undesired gas is burned and emissions are released at a height to avoid any annoyance to the neighbourhoods surrounding the facilities (Public Affairs department of Shell Nederland Raffinaderij B.V., 2003). A report by the Dutch National Institute for Public Health and the Environment (RIVM) indicates "*Shell's environmental annual report does report the CO emissions from some incinerators and from the processes (flaring)*" (Mennen, Mooij, & van Dijk, 2008, p. 54), however, the breakdown of these figures is not publicly disclosed (Mennen, Mooij, & van Dijk, 2008). The total CO_2 emissions reported by SNC-Pernis to the Dutch Emission Authority in 2018 are 30,323 tonnes/y (Permit number NL-201100012). It is assumed based on the RIVM report that emissions from flaring and incinerators are included in these figures.

Typically, the fuel used in integrated petrochemicals complexes are "refinery" gas and/or "chemical waste" gas. Table 10 includes the energy content and CO_2 emissions factors extracted from the "list of fuels and standard CO_2 emission factors" for The Netherlands published by The Netherlands Enterprise Agency (RVO) in 2018, following the 2006 IPPC guidelines for Emissions estimations (Zijlema, 2018). These values are country specific (Zijlema, 2018), but actual values are site specific. It is assumed the SNC plants use a fuel with characteristics resembling refinery gas.

Table 9 Energy content and CO_2 emissions factors of Gas fuels used in Dutch refineries and chemical plants. (Zijlema, 2018)

Fuel	Net Calorific Values (MJ/kg)	CO_2 emission factors (kg CO_2/GJ)
Refinery Gas	45.2	67.0
Chemical Waste Gas	45.2	62.4

The emission for the SNC-Pernis site in 2015 are 27,193 ton as reported in the EU ETS repository (Nederlandse Emissieautoriteit, 2019). The calculated direct emissions from the MEK process furnaces amount to 14 kt. The remaining emissions as shown in Table 11 are assumed to represent the residuals incineration in roof combustors and flares.

Table 10 Calculated results for CO_2 emissions

Process	2015 CO_2 emission (kt/y)
SBA dehydration (MEK production)	14
Incinerators and other sources	13.2
Total	27.2

3 SNC-Pernis main products and application

The majority of the products manufactured in SNC–Pernis are intermediates for the rest of the chemical industry. The main products are propylene, chemical solvents from propylene and butene streams, and propylene oxide derivates (such as glycol ethers and polyols). Hydrocarbon solvents are also manufactured in these facilities. All these materials are key building blocks for the chemical industry to manufacture everyday products. In some processes, additional raw materials are combined with the main feedstock. The process integration and optimization may allow for certain low value streams or by products *"to be processed into sealable co-products or utilized as feedstock or fuels, thus eliminating the need for disposal."* (Falcke, et al., 2017, p. 60). For example, hydrogen may be recycled to be used as feedstock in the hydrogenation process or propane and butane can be used as fuel gas or commercialized as such. Table 11 provides an overview of main feedstocks and products, as well as additional raw materials and some of the by-products present in the 12 processes operated by SNC–Pernis.

Table 11 Overview of feedstock and products for SNC-Pernis processes

Process	Main Feedstock	Additional Raw Materials	Main Product	By-Product
Distillation P-P splitter	C3[7] /import[8]		Polymer grade Propylene	Propane
Distillation and Hydrogenation	GTL[9]; Tops/Naphtha Kerosene Cuts [7]	Hydrogen	Various HC solvents	
Propylene Hydration	Propylene	Water	Isopropyl Alcohol (IPA)	
DMK reaction	DMK import[10]	Hydrogen	Methyl Isobutyl Ketone (MIBK)	Water
DMK reaction	DMK import[10]	Hydrogen	Di-isobutyl Ketone (DIBK)	Water
MIBK hydrogenation	MIBK	Hydrogen	Methyl Isobutyl Carbinol (MIBC)	
Propylene Oxide (PO) etherification	PO	Methanol; Ethanol	Propylene Glycol ethers	
Reaction of Isobutene and Methanol	Raffinate -1[7]	Methanol	Methyl Tertiary – Butyl ether (MTBE)	Raffinate 2 (75% butenes)
Sulphuric acid hydration of n-butene	Raffinate 2	Water, Sulfuric Acid	Secondary Butyl Alcohol (SBA)	Butane
SBA dehydrogenation	SBA		Methyl Ethyl Ketone (MEK)	Hydrogen
Propylene Oxide (PO) etherification	PO/EO	Glycerine	(flexible and CASE) Polyether Polyols	
	PO		Rigid Polyols	

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[7] Export from SNR- Pernis, 86% butenes

[8] Import refers to feedstock provided by an external supplier

[9] Import Shell Qatar

[10] IPA is not used by SNC for this purpose

SAN Polymerisation	Flexible Polyols	Macromer, Acrylonitrile, Styrene[1]	Styrene acrylonitrile Polymer Polyols	

This chapter will describe the most common applications, properties, and market value of the feedstocks and products handled at SNC-Pernis. For the main feedstocks and a few products listed in this section, recent technical developments in production methods are briefly described, since they may have an influence in current and future market trends. Commodity prices are also indicated for those substances for which publicly open data is found.

3.1 Feedstocks

As presented in Table 12, three of the chemical building blocks come from manufacturing processes in SNC-Moerdijk, namely Raffinate-1, ethylene oxide and propylene oxide (Wong & Van Dril, 2020). Raw materials come also from the GTL plant in Qatar, SNR and Rhineland refineries, among others for the production of polymer grade propylene and hydrocarbon solvents. The feedstock materials that have not been included in previous MIDDEN studies, more specifically DMK or acetone, products from the Qatar GTL plant and methanol are briefly described in the following sub-sections.

3.1.1 Dimethyl Ketone (DMK) or Acetone

Acetone is an organic compound and it is the simplest example of the ketones. It is a colourless, volatile flammable liquid that is miscible with water and has a pungent, irritating and presents a relatively sweet odour (IHS-Markit, 2019 a).

Main Production Methods

Acetone is produced directly or indirectly from propylene or as a by-product from phenol production. Approximately 83% of acetone in The Netherlands is produced via the cumene process, the most frequently used method worldwide (VNCI, 2019).

Main Applications

Acetone is a chemical intermediate in the manufacture of some polymers, high molecular glycol, chemical solvents as MIBK and alcohols (such as IPA). Acetone serves as an important solvent itself of most plastic and synthetic fibres, paints and varnishes. It is widely used in the pharmaceutical industry, for medical and for cosmetic applications; it is also used as a food additive and for packaging. Acetone is a heavy-duty degreaser. Familiar household uses of acetone are as the active ingredient in nail polish remover and as paint thinner (Petrochemicals Europe, 2019) (VNCI, 2019a).

Market Value and trends

In the last three years, the global acetone demand has been driven mainly for use as a solvent and for the production of methyl methacrylate (MMA) and bisphenol A (BPA) (IHS-Markit, 2019 a). The production of solvents from acetone represented 26% of the total worldwide demand in 2016 (Centre for Industry Education Collaboration, University of York., 2019).

In 2015, the European market price for acetone varied from 500 to 800 EUR/tonne, the lowest value reached at the end of the year due to oversupply (ICIS - Chemical Business, 2017).

3.1.2 Hydrogen

Hydrogen is a colourless and odourless gas at normal conditions, it is non-toxic and does not cause environmental damage, therefore it is considered environmentally neutral (Shell Deutschland Oil GmbH, 2017). The boiling point is low (–252.76 °C) at normal pressure (1.013 bar); this is close to the absolute zero temperature of –273.15 °C.
Hydrogen gas (H_2) has the highest energy content of any common fuel by weight and its combustion properties make hydrogen an interesting combustion fuel.

In 2018, nearly 96% of all hydrogen was derived from fossil fuels, natural gas being the most commonly used feedstock (representing 49%), followed by liquid hydrocarbons at 29% and coal at 18%. Four percent of the total hydrogen production came from electrolysis and as a by-product from sources of hydrogen (IHS-Markit, 2019 b).

Main Applications

In the chemical industry, hydrogen is a fundamental building block for the synthesis of ammonia, representing about 55% of the total 2016 worldwide hydrogen production, and also for the production of methanol (10%), which takes place by means of the catalytic hydrogenation of carbon monoxide (University of York Centre for Industry Education Collaboration, York, UK., 2019; Hydrogen Europe, 2019). The processing of intermediate oil products is another hydrogen application which takes place in refineries (representing about 25%) whereas hydrogen is used to process crude oil into refined fuels, such as gasoline and diesel, and also for removing contaminants, such as Sulphur from these fuels. The remaining 10% of the global hydrogen production is used in the manufacturing of polymers and other applications, like hydrogenation for solvents at SNC Pernis (Hydrogen Europe, 2019). Approximately 75% of the hydrogen currently consumed worldwide by oil refineries is supplied by large hydrogen plants that generate hydrogen from natural gas or other hydrocarbon fuels.

Hydrogen is increasingly seen as energy carrier. Hydrogen is a highly efficient, low-polluting fuel that can be used for transportation, heating, and power generation whereas it is challenging to use electricity. Hydrogen from different origins, either blue or green hydrogen, could replace natural gas in the future depending on multiple factors, such as economic, governmental policies, safety, infrastructure and market regulations. For energy purposes, hydrogen can help industrial and electricity generation sectors to decarbonize without the need to make major investments themselves (Mulder, Perey, & Moraga, 2019).

Market Value and trends

The industrial sector is both the main producer and consumer of hydrogen, with more than 90% of market share amongst the EU28, and a total consumption of 7 Mt (Fraile, Lanoix, Maio, Rangel, & Torres, 2015).

Recent growth in both hydrogen global and European markets is driven primarily by regulations pertaining to the desulfurization of fuel used in transportation (i.e. diesel), the growth in transportation fuels, and a decrease in the crude oil quality, requiring more hydrogen for processing. Likewise, hydrogen generation as a by-product from crude processing is also decreasing because of poor quality crudes. This has caused refineries to look for hydrogen availability from external sources that are set up on-site or adjacent to the refining facilities. (IHS-Markit, 2019 b). Another reason for the worldwide increase in hydrogen demand in refineries is the increased oil consumption in developing economies such as China and India (Hydrogen Europe, 2019).*"Overall global demand for hydrogen for "conventional" industrial is expected to increase at a rate of around 4–5% per year during the next five years, primarily as a result of demand from petroleum refinery operations, and the production of ammonia and methanol*" (IHS-Markit, 2019 b).

Hydrogen prices are mainly determined by large industrial actors and depend on the purity of the product and the relative physical location from the production site to the final consumer's location. The larger dedicated production plants are often joint ventures of a producer and consumer. Prices in joint ventures are assumed to be cost based with commonly used margins. Currently, prices are set via net back gas and oil formulas.

3.1.3 Methanol

Methanol is a light, colourless, volatile and flammable liquid. It is miscible in water and presents a distinctive odour. Methanol is considered toxic for human consumption. The boiling point of Methanol at atmospheric pressure is 64.7 °C.

There are many production methods for methanol. It can be produced from coal, natural gas, coke-oven gas, hydrogen and biomass, among other feedstocks. The main commercial production method is from synthesis gas (carbon monoxide and hydrogen), "syngas" might be derived from oil, coal or, increasingly, biomass. The latter is becoming central to the development of biorefineries as an intermediate in the conversion of biomass to useful products. For more information on methanol, biorefineries and biofuels in the Netherlands please refer to the MIDDEN study Decarbonisation Options for The Dutch Biofuels Industry (Khandelwal & van Dril, 2020).

Main Applications

As a chemical intermediate, the most important application is for manufacturing of Polymers (PTA, a precursor of PET plastics), followed by MTBE synthesis, acetic acid, glycol ethers and formaldehyde. Within the everyday uses are windshield cleaning fluid, gas line antifreeze, perfumes, food warming fuel, coy machine or printer toners.

The use of methanol as fuel for cars has increased rapidly in recent years, either as a liquid fuel or mixed with petrol in internal combustion engines cars. In China, a mix of 15 % methanol to petrol is used in cars without engine modification. A larger concentration (85%) of methanol (M85) can be used in vehicles with modified engines. The use of methanol as a fuel in China showed an annual increase of 25% annually from 2000 to 2015. (Centre for Industry Education Collaboration, University of York., 2019). In more recent developments, methanol is used in direct methanol fuel cells or, after reforming, in Proton-exchange Membrane (PEM) fuel cells also for mobility purposes. Moreover, fuel additives are produced from methanol, and it is used to trans-esterify vegetable oils to form methyl esters (biodiesel) (Hydrogen Europe, 2019).

Market Value and trends

Methanol is among the top five chemical commodities in the chemical sector. In between 2012 and 2017, world capacity for methanol expanded at an average rate of almost 5% per year, driven by new plants built in Northeast Asia. China alone accounted for 75% of the new additions over the same time period. The overall market expanded at an average rate of 6.5% per year over the last five years.

Despite the demand reduction of methanol for fuel applications, overall, the global demand increased mainly due to expansions in China in the methanol-to-olefins (MTO)/methanol-to-propylene (MTP) sector, which is the fastest growing downstream application. Other relatively new applications include dimethyl ether (DME) and fuel blending (IHS-Markit, 2019 c).

Over the next three years, methanol consumption is expected to grow further, albeit at a slower average rate of about four percent per year. The continuing development of MTO/MTP

production in China, as well as the increasing global production of formaldehyde, are expected to drive methanol market growth through 2022.
In Europe, the trend is to keep manufacturing methanol through traditional processes, such as synthesis gas (syngas) in a reformer and from methane by steam and catalytic autothermal reforming. However, in recent years, BioMCN a Netherlands based facility, became the first company in the world to produce methanol from biogas. "*Bio-methanol can also be used as a chemical building block for a range of future-oriented products, including bio-MTBE, bio-DME, bio-hydrogen and synthetic biofuels (synthetic hydrocarbons)*" (OCI N.V., 2019).

3.1.4 Acrylonitrile

Acrylonitrile is an organic compound with the formula CH_2CHCN. In terms of its molecular structure, it consists of a vinyl group linked to a nitrile. It is clear, (colourless to pale-yellow), liquid at room temperature and has an unpleasant odour. (National Institutes of Health (NIH), 2019). It evaporates quickly when spilled.

Acrylonitrile is produced through the reaction of propylene and ammonia known as Ammoxidation, which is the process of conversion of a methyl group to a nitrile in the presence of a heterogeneous catalyst.

Main Applications

Acrylonitrile is used in the production of primarily ABS/SAN resins, acrylic fibres, acrylamide, nitrile rubber, adiponitrile, and carbon fibres. It is also used as an intermediate in the production of pharmaceuticals and dyes, and as a fumigant.

Market Value and trends

In the European market, supply and demand fundamentally play a large role in determining developments in the ACN spot market. This commodity prices in the European market showed an important drop in 2015, going from about 1400 USD per tonne (ca. 1262 EUR/tonne – 2015 conversion rate[11]) down to approximately 830 USD/tonne (ca. 748 EUR/tonne – 2015 conversion rate). This trend continued with declining spot prices in January 2016 (ICIS - Chemical Business, 2017).

In 2017, an increase in demand was expected to be strong in North America, Northeast Asia and the Middle East (IHS-Markit, 2019 d).

3.1.5 Gas-to-Liquid products – Shell Qatar

Shell's Gas-to-Liquids (GTL) technology converts natural gas into high-quality hydrocarbon liquid products including transportation fuels, motor oils and the feedstock for everyday needs such as plastics, detergents and cosmetics. GTL fluids and solvent grades are sourced from Qatar. The liquids contain mainly paraffins (97%), with molecular structure C16 and higher (Shell, 2020b).

3.2 SNC – Pernis Main Products and Uses

3.2.1 Propylene

Propylene (Propene) is a major building block for a large number for the production of organic chemicals such as polypropylene, acrylonitrile, propylene oxide, and oxo alcohols, as

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[11] All conversion rates used in this report may be found at De Nederlandsche Bank website (DNB, 2019)

well as for a large variety of industrial products. Unlike ethylene, propylene readily undergoes substitution reactions, which leads to a wide range of important chemicals, as displayed in Figure 15. Propylene demand comes second after ethylene's, despite of the greater variety of derivatives from propylene (Matar & Hatch, 2000).

Production Methods

Traditionally, propene has been largely manufactured by two processes: steam cracking of naphtha and catalytic cracking of gas oil. Both processes also produce many other products such as ethene in large amounts. These processes have been extensively documented in other MIDDEN studies, e.g. SNC-Moerdijk. In 2010, steam cracking accounted for ca. 56% of the global production and catalytic cracking of gas oil for 37% of the global production (Centre for Industry Education Collaboration, University of York., 2019).

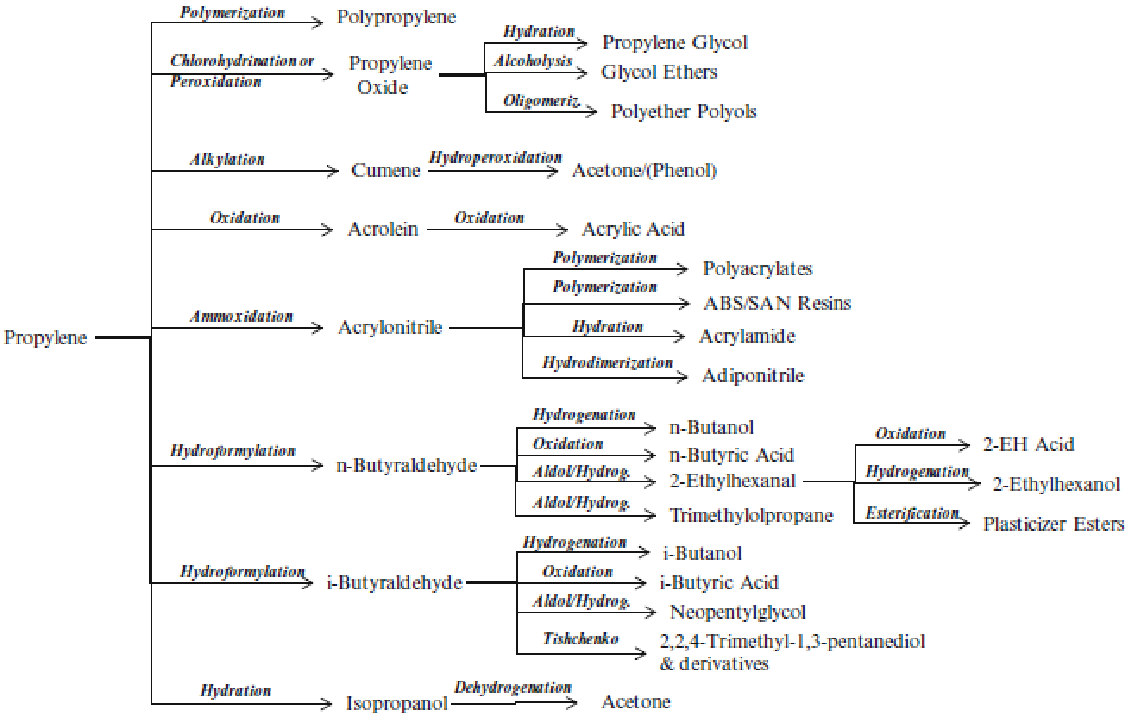

Figure 15 Main Propylene Derivatives Chart (Barnicki, 2012)

In recent years, the demand for propene in comparison with ethene has increased. Much research and development has concentrated on finding methods of producing propene without ethene. These novel manufacturing methods are known as "On Purpose Propene" (OPP) processes. Three of these OPP processes are well used in large-scale, these are: the catalytic cracking of propane, the Methanol to Olefins (MTO) process and the reaction between bio-ethene and bio-butene. Another process to produce propene is via syngas and ethanol. Synthesis gas is used to convert bioethanol to propanol which is subsequently dehydrated to propene (Centre for Industry Education Collaboration, University of York., 2019).

Main Applications

Propylene is the second-largest-volume chemical produced globally. In 2016, about 65% of total propylene produced for chemical uses worldwide went into the manufacture of polypropylene. About 8% of the world's propylene is consumed in the production of propylene oxide, while the third-largest end-use segment, acrylonitrile, accounts for about 6% of total consumption. The remainder went into the manufacture of chemical intermediates such as acrylic acid, cumene, and oxo alcohols.

Market Value and trends

Propylene comes in three grades: polymer grade with 99.5% minimum purity, chemical grade with 93-94% minimum purity and refinery grade with a purity 60-70% purity. Spot Markets prices depend upon the propylene grade, among other factors.

In 2015, polymer grade polymer in the European spot market showed an increasing trend, ranging from 530 USD/tonne to approximately 900 USD/tonne (ca. 478 EUR/tonne to 811 EUR/tonne – 2015 conversion rate) at its peak (ICIS - Chemical Business, 2017).

Propylene consumption has been increasingly linked to emerging countries (China, in particular), where the improvement in living standards and growing urbanization are driving the increasing use of polymers and chemicals. In consequence, between 2012 and 2017, the propylene demand growth rate was sustained at about 4% per year, with Northeast Asia accounting for 67% of the new requirements (ICIS - Chemical Business, 2017).

It is expected that new propylene capacity will be developed primarily in the regions where most of the demand growth will take place, in Northeast Asia and North America. Its production is expected to further increase globally. On-Purpose Propylene (OPP) production might also increase in the coming three years, accounting for as much as 29% of the global propylene production by 2021 (ICIS - Chemical Business, 2017).

3.2.2 Hydrocarbon Solvents (HCS)

SNC manufactures a wide range of HCS with numerous applications in industrial processes and in the production of final goods for commercial and household use. The different HCS products categories are: aliphatic mineral spirits, Isoparaffins, special boiling point solvents (SBP) and pentane sprays. Every HCS type is manufactured in different grades to accommodate specific customer needs and product use.

Main Applications (Shell, 2019e)

The aliphatic mineral spirits main characteristic is their flash point range lying within 35 and 120 °C. The de-aromatized "D-grades" may be made with an extremely narrow boiling range. They are used in lighter fluids, lamp oil, metal rolling oils and oil drilling fluids.
The Isoparaffins – synthetic HCS are practically odourless, have high purity and also relatively high boiling point (174 -215 °C.). They are ideal for the manufacturing of odour free painting, wallpaper, household sprays and hand cleaners.

Pentanes solvents have a narrow and relatively boiling point range (28 to 35 °C) as well as a very low flashing point, below -50 °C. Moreover, the composition of these solvents and fast evaporation allowed them to be primarily used as aerosols propellants, blowing agent in foams and reaction media in chemical polymerisation processes.

Special Boiling point solvents feedstock is a group of heavier hydrocarbon chains (C_6 to C_{10}), however, due to the deep hydrogenation technology used in their manufacturing process, the aromatic content is nearly untraceable. There are at least 10 grades of SBP's sold in Europe with boiling points ranging from 40 to 165 °C.

GTL solvents are the next generation high purity paraffinic fluids and solvents with unique synthetic composition, low aromatics content and practically odourless. These characteristics may enhance various properties in cosmetics coating and paintings formulations. They have many other applications such as: heating and lighter fluids, manufacturing of aerosols, polishes, cleaners, crop protection products, drilling muds formulation, metal working, institutional cleaning products, mining solvents, aluminium rolling oils, process diluents, polymer extender oils, defoamers, sealants, heat transfer fluid (Shell, 2019k).

3.2.3 Isopropyl alcohol (IPA)

Isopropanol is a colourless liquid that has a pleasant odour and is soluble in water. It is a medium evaporating solvent and is completely miscible with most solvents. It is more soluble in hydrocarbon liquids than methanol or ethanol. For this reason, small amounts of isopropanol may be mixed with methanol-gasoline blends used as motor fuels to reduce phase separation. It has a boiling point of 82 °C at atmospheric pressure conditions.

Main Applications

IPA is a solvent for epoxy and acrylic resins, ethyl cellulose, polyvinyl butyral, alkaloids, gums, shellac, natural resins, and many essential oils. It is also used in the manufacture of MIBK and acetone (DMK), but not at Shell Pernis anymore (Shell, 2019i).

Isopropanol is used in cosmetics, other personal care products and pharmaceuticals. electronic grade includes the use in the electronics industry, primarily as a cleaner for printed circuit boards (PCBs), flat panel displays, and other electronic devices (IHS-Markit, 2019 e).

Production Methods

Main production methods were presented in chapter 2. As mentioned, the direct hydration of chemical grade (90+%) propylene, which avoids the need for sulphuric acid, is the most widely used process (ICIS - Chemical Business, 2017).

Market Value and trends

In Europe, IPA’s use as a raw material for DMK manufacturing has been reduced since acetone production as a by-product in phenol production has increased. The market share for this application has decreased to a very low amount. In the European market, the feedstock price direction is seen as uncertain because of the volatility in crude oil prices. There is no new capacity expansion planned in Europe in the immediate future, as the European market is considered mature (ICIS - Chemical Business, 2017). Shell is one of the major European producers of IPA, it has around a third of the region’s nameplate capacity (ICIS, 2019c). The IPA market price tends to move in line with feedstock propylene when the market is well balanced.

In 2015, technical grade-IPA prices in the European market ranged in between 600 and 1000 EUR/tonnes, however, the average price over the course of the year hovered around 750 EUR/tonnes (ICIS - Chemical Business, 2017). IPA prices increased between 2017 and 2018, ranging from ca. 850 EUR/tonne to 1600 in the first year to later stabilize in approximately 1200 EUR/tonne towards the end of the two-year period (ICIS, 2019c).

3.2.4 Methyl tert-butyl ether (MTBE)

Methyl tert-butyl ether is a colourless, readily mobile liquid with characteristic terpene-like odour. It has unlimited miscibility with all common organic solvents and all hydrocarbons. Its normal boiling point is 55.3 °C.

Main Applications

MTBE is widely used as the oxygenated additive to improve the characteristics of petrol. Isobutylene serves as a raw material for MTBE and ETBE, as well as for isooctane. MTBE is also used as a chemical intermediate to produce high purity isobutylene. Other favoured octane enhancing compounds are alcohols (methanol and ethanol), ETBE (ethyl t-butyl ether), and TAME (t-amyl methyl ether) (Centre for Industry Education Collaboration, University of York., 2019).

Production Methods

MTBE is typically manufactured in petroleum refineries but also in plants manufacturing industrial organic chemicals such as SNC-Pernis. MTBE is produced principally by reacting isobutene with methanol. It can also be produced from methanol, tert-butyl alcohol (TBA) and diazomethane (Institute for Health and Consumer Protection , 2002).

Ethyl t-butyl ether (ETBE) is an alternative to MTBE as an oxygenate to enhance the octane rating of petrol. It is used mainly in Europe, particularly in France. This accounts for over 90% of the world's annual production of ca. 3 million tonnes. It is manufactured from 2-methylpropene and ethanol.

Market Value and trends

In the United States, ethanol or, more recently, bio-ethanol are the preferred gasoline enhancers, since the banning of MTBE due to seepages from storage tanks at petrol stations leading to contamination of underground water. Nearly all MTBE and all of the ETBE produced in the United States is exported to other countries as gasoline octane improvers (IHS-markit, 2019 f). In Europe, however, ethers are still authorized in the relevant EU Directives relating to their use as a fuel component. However, recent regulations about fuel specification (Fuel Quality Directive) and renewable energies (Renewable Energy Directives) will inevitably lead to an increased biofuel use (Winterberg, Schulte-Körne, Peters, & Nierlich, 2010).

European methanol prices and demand are largely dictated by the gasoline market, in which MTBE is blended. In this market, MTBE competes with other gasoline components such as toluene and reformate (ICIS - Chemical Business, 2017).

The MTBE prices are subject to a seasonal demand, rising in summer when gasoline requires more octane boosters. Summer demand is higher, as well as prices. In 2014, the Europe MTBE spot FOB Rotterdam market price moved from a low of approximately 500 USD/tonne (ca. 376 EUR/tonne – 2014 conversion rate) to a maximum price slightly over 1000 USD/tonne (ca. 752 EUR/tonne – 2014 conversion rate). This peak was reached around summertime. For most of the year, prices hovered around 750 USD/tonne (ca. 565 EUR/tonne – 2014 conversion rate). In between September 2015 and September 2016, the summer peak was significantly lower than it was the previous year (about 650 USD per tonne) (ca. 586 EUR/tonne – 2015 conversion rate). Prices at the end of the period were approximately 580 USD /tonne (ca. 524 EUR/tonne – 2016 conversion rate) (ICIS - Chemical Business, 2017; DNB, 2019).

3.2.5 Sec-butyl alcohol (SBA)

Sec-Butanol (2-butanol, sec-butyl alcohol) is a liquid with a strong characteristic odour. Its normal boiling point is 99.5 °C. The alcohol is soluble in water, but in a lesser degree compared to isopropyl and ethyl alcohols. The main production methods were presented in chapter 2. There is no publicly available market data on this product.

Main Applications

The main application is as intermediate product for the production of MEK by dehydrogenation. SBA is also used as a solvent, a paint remover and an intermediate in the production of industrial cleaning compounds and oil treating chemicals.

3.2.6 Methyl Ethyl Ketone (MEK)

Methyl ethyl ketone (MEK or 2-butanone) is a colourless, flammable liquid similar to acetone. Its boiling point (79.5 °C) is higher than the one of acetone and it is classified as a low-boiling, fast evaporating solvent. MEK is only partially miscible with water, whereas it is completely miscible with most organic solvents. The main commercial route to MEK production is the dehydrogenation of secondary butanol.

Main Applications

Methyl ethyl ketone is a powerful, commercially important industrial solvent for many substances, especially resinous materials.
MEK is used in surface coatings, adhesives, thinners, printing inks and cleaning agents. Other industrial uses are in pharmaceuticals, extraction, dewaxing, and as a chemical intermediate (Shell, 2019i). Another MEK application is as the solvent in polymerisation processing of acrylonitrile-butadiene-styrene (ABS), styrene-butadiene rubber (SBR) and polystyrene (PS).

Market Value and trends

The MEK market is fairly concentrated, 80% of global MEK production is provided by the Top 10 producers. In geographical terms, China, Japan and Western Europe are the three largest global suppliers of MEK, accounting for nearly 85% of the total global capacity as of mid-2018. In 2013, The United States ceased production of methyl ethyl ketone despite being a major MEK producer at that time. The US market is currently supplied entirely through imports. (IHS-markit, 2019 f). SNC B.V. has more than 25% of the installed MEK capacity in Europe.

"*MEK is a volatile market in Europe, and is prone to unpredictable price spikes driven by availability shortages*". (ICIS - Chemical Business, 2017, p. 128). This volatile price behaviour has been observed in between 2017 and 2018, as demonstrated in Figure 16 showing how European MEK spot prices.

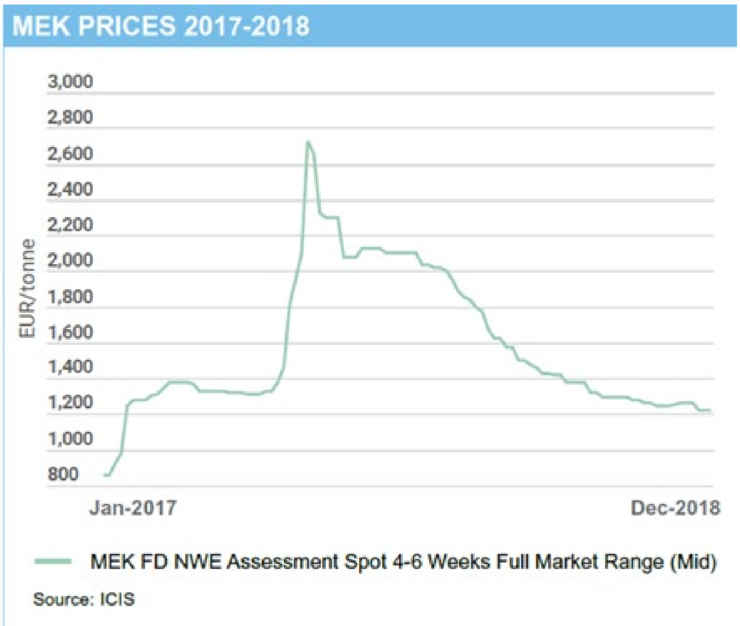

Figure 16 European Spot Market – MEK Prices (ICIS, 2019c, p. 106)

At the beginning of the calendar year (2017) prices were MEK slightly above 800 EUR/tonne. However, MEK spot prices spiked to their highest level since 2015 due to a high demand and low supply in Europe. By the end of April 2017, MEK prices reached historically high levels (ca. 2,700 EUR/tonne) as a result of availability shortage from the Netherlands. By the end of 2018 prices stabilized slightly over 1,200 EUR/tonne (ICIS, 2019).

3.2.7 Methyl Isobutyl Ketone (MIBK)

Methyl Isobutyl Ketone (MIBK) is a colourless liquid solvent with a characteristic mild odour. MIBK is, after methyl methacrylate and bisphenol A, the third largest tonnage product obtained from acetone. Its boiling point is 118 °C. Main production methods were presented in chapter 2.

Main Applications

MIBK is an industrially important solvent due to its chemical compatibility with other organic solvents. It is used as a solvent, in the manufacture of many chemicals, in many chemical processes, in paints, and in dry cleaning products. It is also used as a flavouring agent and in food-contact packaging products. It is also an intermediate chemical for di-isobutyl carbinol production.

Market Value and trends

Worldwide, MIBK solvent application consumed about half of the total MIBK production whereas rubber antiozonants use accounts for about a third of the total. Over half of global MIBK is consumed in Asia, with China accounting for half of the regional consumption. MIBK use for solvent and rubber antiozonant are the key drivers for the growth of the demand in Asia due to the rapid development of the automobile industry in China and MIBK's high solvent power.

MIBK European market prices showed historical highs at the beginning of 2017 , it went from 1,200 to almost 2,600 EUR/tonne due to production shortages from one of the main market suppliers (ICIS, 2019a). By the end of 2018 prices decreased to nearly 1,400 EUR/tonne.
In developing countries such as China, MIBK use in coatings is expected to increase at more than 3% per year in 2019–2022 because of MIBK's high solvent power. Consumption in the developed regions may stay relatively stable or even slightly decrease because of increasing environmental concerns about volatile organic compounds (VOCs), as well as the trend towards more waterborne solvent systems. Demands for rubber applications are expected to grow as well.

MIBK prices are significantly affected by feedstock costs (acetone and propylene) and since the production of MIBK is energy intensive (IHS-markit, 2019 g). Shell Chemicals is one of the major European producers for all of MIBK. It has 50% of the region's nameplate capacity (ICIS, 2019).

3.2.8 Methyl Isobutyl Carbinol (MIBC)

Methyl Isobutyl Carbinol (MIBC) is a high purity oxygenated chemical solvent. MIBC has excellent solvency, a relatively high boiling point and a medium evaporation rate. The Main production methods were presented in chapter 2.

Main Applications

MIBC's major application is in the production of lube oil additives, followed by its purpose as the principal flotation frother in treating copper and other ores. Coatings constitute a small portion of MIBC consumption (Dow Chemical Company, 2002).

Market Value and trends
"World MIBC statistics are difficult to estimate, but overall, MIBC will experience positive growth in lube oil applications and as a flotation frother (especially in actively mined regions)" (IHS-Markit, 2019 h).

Just like MIBK prices, MIBC are significantly affected by feedstock costs (acetone and its raw material propylene) and the price of natural gas.

3.2.9 Diisobutyl Ketone (DIBK)

Diisobutyl ketone is a slow evaporating ketonic solvent which is immiscible with water, but miscible with other organic solvents. It is a light-coloured liquid with a mild, characteristic odour. Shell's DIBK is a mixture of two isomers: 2,6-dimethyl-4-heptanone and 4,6-dimethyl-2-heptanone in the ratio 2:1 (Shell, 2019j). Main applications include commercial printing inks, general industrial coatings, paints and coatings and process solvents.

3.2.10 Propylene Oxide Glycol Ethers (POGE's)

Propylene oxide glycol ethers (POGEs) and their acetates are high purity, high performance industrial chemical solvents. There are 6 different types of PO glycol ethers commercialized by Shell in Europe with boiling points varying from 120 to 194 °C. Shell's POGE's *"are designed to meet the increasing technical and environmental demands of solvent-based formulations including low aromatic, high solid and waterborne technologies".* (Shell, 2019g)

Main Applications
POGEs and their acetates are mainly used in surface coatings, inks, cleaners, cosmetics and agrochemical formulations. Additionally, they are used as extractants, coalescing agents and flow improvers.

Shell's trade name for these products is Proxitols™, mainly used as solvents for the paint and ink industry.

3.2.11 Propylene Oxide Polyether Polyols and SAN Co-polymer polyols

Polyols are compounds with multiple hydroxyl groups. Shell's trade name for polyether polyols is Caradol™. They are manufactured in a wide range of molecular weights to meet the application and processing needs foam and CASE manufacturers (Shell, 2019h).

Main Applications
The main use of polyols is in polyurethane (PU) foams, flexible or rigid. Flexible foams are primarily used in cushioning applications such as furniture, bedding and car seats. Rigid foam's largest application is in the construction industry, as insulation material. Rigid foam is also used in commercial refrigeration and packaging. Smaller uses for polyether polyols include elastomers, adhesives and sealants, surface coatings and PU fibres (ICIS - Chemical Business, 2017). Polyols can also be used in non-urethane applications such as surfactants and oil demulsifiers (Shell, 2019h).

SAN polymer polyols are made by SNC, where SAN is in-situ reacted in an emulsion polymerisation. These mixes are used to produce polyurethane foam, automotive parts, battery cases, kitchenware, appliances, furniture and medical supplies. SAN polyols are also used for pharmaceutical and cosmetic packaging.

Production Methods

Polyether polyols are produced by the catalyzed addition of epoxides, mainly propylene oxide or ethylene oxide (EO), to an initiator having active hydrogens. The most common catalyst is potassium hydroxide.

Most major polyether polyols producers are in the process of developing or have already developed natural oil–based polyols (NOPs). The main feedstocks for these products are renewable (vegetable) oils including rapeseed, soybean, castor, and corn oils.

Market Value and trends

The Eurozone economic crisis during 2012 and 2014 impacted negatively the polyurethane market in Western Europe. Since 2015, the consumption of polyether polyols has increased and it is expected that this upwards trend will continue until 2023.

Globally, the consumption of polyether polyols in global markets will grow particularly in in Asia (excluding Japan, South Korea, and Taiwan), led by China and India (IHS-Markit, 2019 h; IHS-Markit, 2019 i).

The North American Polyols market is considered mature, nonetheless it is expected to continue to grow in line with the economic recovery after the recession. The outlook for Latin America is uncertain due to political and economic conditions. (ICIS - Chemical Business, 2017).

Generally, polyols prices follow feedstock costs closely. Additionally, the supply-demand balance of the polyol or of its raw materials may influence polyether polyols prices. As a reference, polyether flexible foam prices in the American region dropped from 3150 USD/tonne in July 2015 (ca. 2839 EUR/tonne – 2015 conversion rate) to 2700 USD/tonne to June 2016 (ca. 2439 EUR/tonne – 2016 conversion rate) (ICIS, 2019; DNB, 2019).

4 Options for decarbonisation

This chapter presents potential options for reduction of energy use and/or CO_2 emissions for SNC-Pernis site by 2050. Table 12 summarizes the decarbonisation options investigated for the sites discussed in this report. This is not an exhaustive list, and many options are under development and therefore not yet commercially available. Moreover, some of the options might be mutually exclusive or could be combined using different system configurations. Most of the options should also be assessed in view of the decarbonisation strategy of the neighbouring Shell refinery site. Brief descriptions of the proposed technologies and potential applications are presented in this chapter. These options have been determined by the authors and have not been verified by Shell.

Table 12 Summary of decarbonisation options for SNC – Pernis

Technology	Category	Relevant to process
Electrification	Alternative energy supply for furnaces	Might be applicable to all processes that present gas-fired equipment (SAB/MEK)
	Alternative energy supply for boilers	Steam boilers for process specific boilers
	Alternative energy supply for distillation units	Further heat integrated distillation units might be applicable to processes that require distillation units (MTBE, IPA).
	Alternative energy supply and process modification	Heat pumps may be applicable to produce hot water (wet steam). (Crosscutting) Electric motors replacing steam turbines for propulsion
Blue hydrogen as fuel	Fuel Substitution	Might be applicable to all processes that use gas-fired equipment (SAB/MEK)
Green hydrogen as fuel	Fuel Substitution	Might be applicable to all processes that use gas-fired equipment
Blue hydrogen as feedstock	Feedstock substitution	Applicable to hydrogenation Process for HCS, MIBK manufacturing
Green hydrogen as feedstock	Feedstock substitution	Applicable to the hydrogenation Process for HCS, MIBK manufacturing
Ultra-Deep geothermal	Alternative energy supply	Might be applicable to all processes that require low to medium temperature heat / alternative heat generation
Energy efficiency	Low waste heat recovery	Including further heat optimisation, district heating (export), Organic Rankine Cycles to generate electricity from heat sources
	Catalyst innovation	Reduce heat requirements per process
	Integrated control systems based on artificial intelligence or mathematical rule-based methods	Overall Real time-processes optimisation
Bio-methanol	Feedstock substitution	Increase production of Bio-MTBE Polyols and POGE's with lower CO_2 footprint

Technology	Category	Relevant to process
On Purpose Propylene	Feedstock substitution	(Bio) propylene produced from (bio) methanol
Sugars and bio-glycerol or Bio-propylene	Feedstock substitution	Polyols and POGES manufacturing
Bio-Acetone	Feedstock Substitution	MIBK, DIBK and IPA production
Carbon capture and storage	CCS	Might be applicable to all current stacks
Carbon capture and use	CCSU/Alternative process	Applicable for polyols

4.1 Electrification Technology

As it was established in the previous section, about 80% of the energy demand in SNC - Pernis facilities is related to heat requirements for processes that run on low (less than 100 °C) or medium temperature heat (100 °C to 500 °C). This implies a large potential to reduce CO_2 emissions by implementing electricity for the generation of heat in the petrochemical chemical industry

4.1.1 Electric furnaces

Typically, electric furnaces may achieve very high temperatures above 1,000 °C and in some cases up to 10,000 °C (Sandalow, et al., 2019). This temperature range is well above the chemical processes' operation requirements in SNC-Pernis.

4.1.2 Electric boilers for steam generation

Electric boilers can be used for steam generation instead of natural gas or refinery gas fired boilers. Another application is to power electric motors replacing steam turbines for propulsion (Rotterdam-Moerdijk Industry Cluster Work Group, 2018). Electric boilers are good alternative for medium temperature heat (McKinsey, 2018). They can be also used to produce low heat in the form of hot water (wet steam) and hot thermal oil. As this electrification mainly applies to utility-related processes it does not require a complete redesign of primary processes (Berenschot, EnergyMatters, CE Delft, Industrial Energy Experts, 2017). However, its implementation might be more complicated when it comes to the generation of superheated steam and high pressure steam, due to high electrical capacity (in the order of MW) which might bring operational complications and additional space requirements (Rotterdam-Moerdijk Industry Cluster Work Group, 2018).

The most commonly used industrial electric boilers systems are those with a resistance heating element boiler and the electrode boilers. The latter uses the conductive properties of water as it heats up when electric current flows through it. Pressure in the boiler is also controlled by the flow rate in which water is pumped into the vessel. It can operate at 10 bars or higher pressures. Typically, electrode boilers' electrical capacity ranges from 3 to 70 MW whereas electric boilers have a lower capacity range up to 5 MW (TNO, 2019).
The application of these technologies "*is already or even operated by large chemical producers, because it can be flexibly employed as demand-side management measure to use low-cost intermittent power supply from renewables"* (Dechema E.V., 2017, p. 26). The utility generation potential of electric boilers for SNR (the steam supplier for SNC-Pernis) is presented in detail in the MIDDEN study for the refinery sector (Oliveira & Schure, 2020).

SNC uses mostly steam from the refinery steam system, and the associated emissions are not part of the SNC emissions.

4.1.3 Heat pumps in utilities

A heat pump uses energy from a low temperature heat source to increase the temperature in the heat sink to a desired level using an electric compressor. There are many types of heat pumps available in the market with multiple thermodynamic cycles and wide operating temperature range (ECN, 2017), as shown in Figure 17. This figure indicated that the maximum reachable temperature with the current commercially available technology is about 140 °C. This is achievable by custom made reverse Rankine cycles heat pumps, which may have a maximum thermal capacity of 20 MW (ECN, 2017). However, *"Heat requirements exceeding +/- 100 °C are generally too high for the currently available heat pumps"* (Hers, Afman, Cherif, & Rooijers, 2015, p. 13). According to the ECN study (ECN, 2017), generally, a temperature match does not imply a match in required capacity.

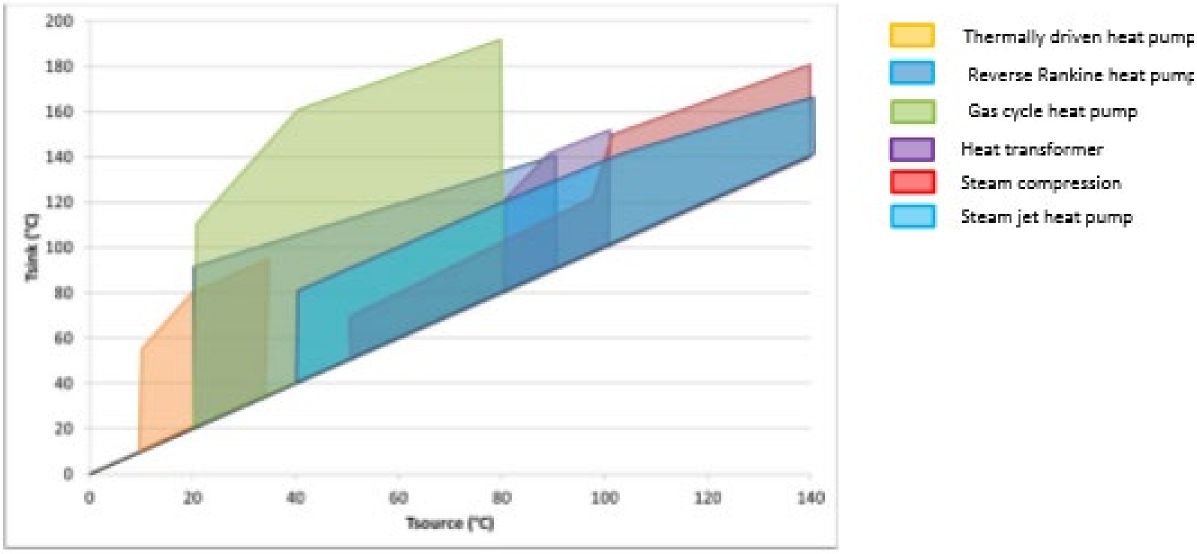

Figure 17 Different heat pumps operational windows (ECN, 2017)

High Temperature (HT) heat pumps that provide heat above 130 °C for industrial application are a highly promising technology for electrification, nevertheless, technology readiness is currently a limiting factor for industrial (megawatt) application (Berenschot, EnergyMatters, CE Delft, Industrial Energy Experts, 2017).

4.1.4 Integrated heat pumps

Heat pumps may be operated as a stand-alone device to deliver heat to a process , for example, production of wet steam (hot water) or it can be process integrated in different configurations to assist distillation processes, such as, a Vapour Compression Column (VC), the (Mechanical) Vapour Recompression ((M)VRC), and the heat integrated distillation columns (HIDiC) Steam recompression, as depicted in Figure 18.

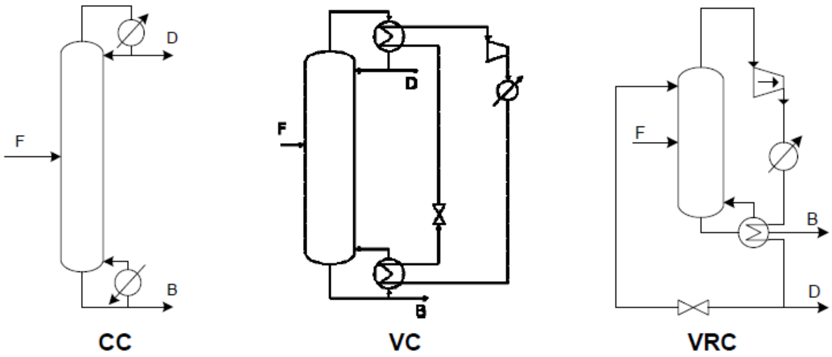

Figure 18 Heat Pump Assisted Distillation Columns: the conventional column (CC), the vapour compression column (VC) and the vapour recompression column (VCR) (Bruinsma & Spoelstra, 2010)

The application of each distillation configuration is driven by the temperature lift, required by the process. The ECN study "Heat pumps in distillation" (Bruinsma & Spoelstra, 2010) indicates, based on pinch analyses for reboilers duties in distillation columns in the Netherlands, that VRC heat pumps should be applied for lifts below 30 °C, moreover, compact heat exchangers are critical for the performance of the heat pump system for temperatures below 20 °C. Same source suggests that HIDiC's are suitable for temperatures in between 15 to 45 °C, partly overlapping with VRC, nevertheless, presenting higher savings efficiency.

The MVRC technology is already applied in SNC-Pernis since 1995 for the propylene-propane distillation column as presented in section 4.1.4, resulting in reduced energy and cooling water use, and an increase in distillation yield. *"Energy savings add up to 1.2 PJ yearly, equivalent to 37.8 mln m^3 of natural gas. A very short payback time of two years was realised."* (Van Kranenburg, et al., 2016, p. 13). A study by ECN (Marina, Smeding, Zondag, & Wemmers, 2017) identified MTBE and IPA process as potential candidates to use the Heat pump assisted distillation technology.

4.2 Blue and green hydrogen

Hydrogen is produced by SNR and supplied to SNC-Pernis as feedstock to produce HCS, MIBK, DIBK and MIBC. Currently in the Netherlands, more than 85% of the hydrogen is mainly produced from natural gas (through steam methane reforming) and as a by-product in the production of chlorine and crude oil refining (H-vision, 2019, p. 27). When combined with carbon capture sequestration or use (CCS(U)) technologies, the process emissions can be reduced significantly (blue hydrogen). Moreover, if hydrogen is produced with renewable electricity through electrolysis, the resulting "green" hydrogen is a carbon-free energy carrier or feedstock.

There are existing plans framed in the H-vision project to develop a large-scale production and utilisation of blue hydrogen in the Rotterdam cluster. Shell is one partner of the consortium of companies behind the project. The estimated emissions reduction potential for the H-vision project corresponds mainly to the current H_2 production in the refinery domain (SNR and others), it excluded the combustion emissions of small process furnaces. Nevertheless, if the blue hydrogen production is realised, it will have a positive impact in the SNC-Pernis operations and emissions, as they are part of an integrated system. Indirect emissions from electricity generation were excluded too, except for those from one electricity supplier of Shell Pernis. The same source also indicates that the supply of carbon free hydrogen produced by electrolysis using renewable energy sources will be feasible only in the future, given the current electrolyser technology readiness levels (TRL's varying from 6 to 8 for different electrolysers types), their limited electricity generation capacities (for refinery scale purposes) and economy of scale (Dechema E.V., 2017). More specifically, the potential benefits and costs of the manufacturing of blue and green hydrogen by SNR are documented in detail in the MIDDEN's decarbonisation options for the refinery sector study (Oliveira & Schure, 2020).

The use of hydrogen as a fuel is an alternative in situations where full electrification is complex or because of technology readiness limitations, which is the case for the electrification of furnaces for the petrochemical industry (H-vision, 2019).

At the refinery and SNC-Pernis, carbon free hydrogen could replace the use of fuel gas in process furnaces and boilers resulting in a reduction of CO_2 emissions. Considering the current configuration of the petrochemical complex, the fuel (hydrogen) generation and CO_2 capturing (in the blue hydrogen case) would take place centrally at the refinery (SNR). This would imply modifications for the SNC-Pernis units using residual gases, mainly the MEK furnaces and roof combustors.

The primary technical modification would be the replacement of gas burners into furnaces and the adjustment of operating conditions. The technical feasibility of these options still needs to be proven, especially because of the possible increment of NO_x emissions from the combustion process of hydrogen; however, field tests have been performed to technically asses the hydrogen firing of process heaters by John Zink Co., LLC and the Chevron Energy Technology Company. This study tested two different types of burners, one of them designed to reduce NO_x emissions, known as Ultra-low NO_x COOLstar™, a technology that is currently commercially available, even for 100% hydrogen fuels (John Zink Co., 2020). The results of the Chevron study (Lowe, Brancaccio, Batten, Leung, & Waibel, 2011) indicate that no major modification needs to be done in the equipment, other than process temperature control in the furnace and burners. It was also demonstrated that, when using the ultra-low NO_x burners, there was a NO_x emission reduction when firing 95% hydrogen fuel instead of refinery gas. A slight increase in heating efficiency on a lower heating value basis, was observed when replacing refinery fuel gas with hydrogen fuel. With respect to the fuel pipeline system, a change from refinery fuel gas to hydrogen yields less than a 1 psig (~0.07 bar) difference along the piping system, thus no significant piping material modifications are required (Lowe, Brancaccio, Batten, Leung, & Waibel, 2011).

Alternatively, the installation of flexible burners that allow the combustion of natural gas and hydrogen might represent another technically feasible option given that the ratio between the calorific value of hydrogen and its density is comparable to the natural gas ratio (Oliveira & Schure, 2020).

4.3 Ultra-Deep geothermal (UDG) heat

Geothermal energy is heat generated in the subsurface of the earth, this heat is transferred to the surface by water and/or steam. This geothermal energy may be used to generate emissions free electricity or for heating and cooling applications. It can be used as a continuous source of heat independently from seasonal variations. There are different geothermal technologies with distinct levels of maturity.

Ultra-deep technology refers to the extraction of thermal energy at depths beyond 4,000 m, where water temperature may reach 120 °C or higher. The UDG heat from this source may be used for industrial heat purposes to produce steam, and the residual heat could be used to heat homes and greenhouses through a regional heat network. For industrial applications (medium heat demand) only UDG at a depth between 4,000 and 8,000 m is applicable. Preliminary research has identified a potential geothermal reservoir at depths around 5,000 m in the port of Rotterdam area.

Harvesting the thermal energy from the underground requires drilling two wells (producer/ injector doublets) into a water bearing rock (aquifer). The hot water from the aquifer is extracted to the surface through one well (producer), subsequently, the heat is transferred to a heat network through a heat exchanger. The cooled water is then injected to the aquifer through the second well (injector) to be reheated in the aquifer. In the subsurface, 1 to 2 Km distance in between the two wells is required to prevent rapid cool water breakthrough in the production well. When using electrical pumps or heat pumps powered with green electricity, also indirect CO_2 emissions are zero. Overall, for an average geothermal project, the CO_2 reduction is 88% compared to natural gas (Platform Geothermie, DAGO, Warmtenetwerk, EBN, 2018).

Technologies for direct uses geothermal energy such as district heating, geothermal heat pumps, greenhouses and others are widely used and can be considered mature. The main technical challenge for the application of this option is to successfully and safely drill a well at such large depths. Geothermal energy has already been utilised in the Netherlands for the last 10 years, however, the deepest geothermal well reached no more than 2,500 m depth. Furthermore, prior to 2016, a total of 41 wells for the exploration and/or production of oil and gas wells have reached depths in between 4 to 5 km depth, 6 wells have a total depth ranging from 5 to 6 Km. The deepest well drilled in the Netherlands reached almost 6 Km depth (Boxem, Veldkamp, & Van Wees, 2016). This indicates that there is little technical expertise and, possibly, limited rigs availability with the appropriate capacity to drill new wells at the desired target depths in the Rotterdam area.

Another technical requirement is the construction of heat networks to distribute the thermal heat to the final users, especially in urban and industrial environments such as Botlek. Increasing the network capacity must be a priority in the next couple of years together with the exploration of suitable aquifers and the execution of UDG pilot projects for technology assessment. This option would be considered for processes with low/medium heat requirements in installations where no own waste heat is available or where there is a deficit of heat supply (Platform Geothermie, DAGO, Warmtenetwerk, EBN, 2018). Feeding geothermal energy into (waste) heat networks is an option considered by the Rotterdam Moerdijk industry Cluster working group for the Climate agreement (Rotterdam-Moerdijk Industry Cluster Work Group, 2018).

4.4 Energy efficiency

Energy efficiency is increased by all measures that reduce energy use per unit of product (energy intensity) (Ecofys, Berenschot, 2018; Shell, 2020a). Shell has a continuous improvement of energy efficiency in its operation for years by regular maintenance practices, smart scheduling of the maintenance activities and installing more energy efficient equipment, for example, by replacing steam turbines drives with electrical motor (Shell, 2020a). Additionally, Shell-operated refineries and chemical plants have invested in combined heat and power units and have implemented heat integration and waste gas recovery systems (Shell Global Solutions B.V., 2019; Shell, 2020a).

There is a high potential to increase energy efficiency by emerging heat recovery technologies. The application of electrical heat pumps to upgrade low quality steam was previously mentioned in this report (Section 4.1). The VNCI's roadmap for the Dutch Chemical industry assumes that electrification technologies such as MVR and high temperatures heat pumps combined, may provide an energy efficiency annual increase in between 0.5% an 1 % and typical payback times of 5 years or less (Ecofys, Berenschot, 2018).

The European Commission Directorate-General Energy published a study on energy efficiency and energy saving potentials of eight energy intensive industrial sectors in the EU28 member states. Among other things, they studied the energy saving potential of different technologies by 2030 and 2050 (ICF Consulting Limited, 2015). This study ranks low waste heat recovery as the one with the highest energy saving technical potential for the chemicals sector. It reports that Organic Rankine Cycles (ORC) may be used for generating electricity from low-temperature waste heat (as low as 80 ◦C) e.g. from a gas turbine or reciprocating engine exhaust, hot exhausts from furnaces or flue gas condensation of waste incinerators. Innovation in working mediums (fluids) to be used in ORC's will help to further increase the overall efficiency of the cycle. The potential of energy savings from these waste recovery technologies is 12% by 2030 of the identified total technical potential for the European chemical industry of 66% (ICF Consulting Limited, 2015).

Alternatively, waste heat recovery is used for district heating in neighbouring areas and greenhouse horticulture. Shell has implemented a project of this kind to supply heat to 16,000 households in the Rotterdam area (Port of Rotterdam Authority, 2020). This can contribute to a maximum of 1.5 Mtonnes/year of CO_2 emissions reduction outside the petrochemical sector (mainly for buildings) (Ecofys, Berenschot, 2018).

Continued research efforts are oriented to develop catalysts to replace heat as a reaction accelerator, their energy savings potential according to ICF's report is 10% by 2030 increasing only to 11% by 2050 (ICF Consulting Limited, 2015; U.S. Department of Energy, 2011).

Integrated control systems using sensors to collect data and artificial intelligence or mathematical rule-based models, can be implemented to control and adjust process conditions, reducing energy consumption of the overall system. The potential associated technical savings are estimated at 10% by 2030 (ICF Consulting Limited, 2015).

4.5 Feedstock replacement

Feedstock substitution in the manufacturing processes may have impact on the direct and/or indirect GHG emissions of the plant. In the second chapter of this report, it was stablished that practically none of the CO_2 emissions are related to the chemical reactions occurring in the SNC-plants, most of the CO_2 emissions are generated by the combustion of fuels in furnaces or by waste incineration equipment. Indirectly, emissions from steam generation for the SNC processes is substantially larger (Oliveira & Schure, 2020). Moreover, total emissions in the product chain may add to the carbon footprint. Therefore, the substitution of feedstock of fossil origin, for example, methanol produced form natural gas, by another bio or waste-based product would imply the reduction of indirect emissions in the overall product supply chain. These combined options are of particular interest for integrated companies such as Shell since they can reduce the overall product carbon footprint. For example, Shell is currently investing in the waste-to-chemicals (W2C) project (see 4.5.1).

4.5.1 Bio or waste-based methanol as a feedstock for MTBE and Polyols

Methanol is produced on a large commercial scale from natural gas. Methanol is the base chemical for the synthesis of MTBE and polyols in SNC–Pernis, but has many other applications (see 3.1.3).

A route for producing methanol is to use hydrogen, made by electrolysis, together with CO_2 in a methanol synthesis reactor. Another way to produce methanol is using biogas. Bio-methanol is chemically identical to the methanol that can be used both as a fuel and as a feedstock. Bio-methanol is currently commercially produced in The Netherlands by Bio-methanol Chemie Nederland B.V (BioMCN) (OCI N.V., 2019). More information can be found in the "Decarbonisation Options for The Dutch Biofuels Industry" MIDDEN report (Khandelwal & van Dril, 2020).

Bio-MTBE, "produced out of second-generation bio-methanol, is a renewable fuel additive that results in a more than 50% reduction in CO_2 emissions compared to its pure fossil-fuel alternative" (SABIC, 2019). Bio-methanol could be used as feedstock in the manufacturing of propylene oxide polyols as well.

Reportedly, a consortium in which Shell is partner with Nouryon, Enerkem, Air Liquide, and the Port of Rotterdam Authority, has announced the planning of the construction of a Waste to Chemicals (W2C) plant to produce methanol from non-recyclable waste. The facility, using Enerkem[12]'s proprietary technology, converts non-recyclable mixed waste including plastics into syngas. Subsequently, the syngas is used to produce clean methanol with applications in both the chemical and transportation sector. The plant's estimated cost (CAPEX) is around 200 mln EUR and the planned plant will be in Botlek (Port of Rotterdam). The planned capacity is 220,000 tonnes of methanol manufactured from 360,000 tonnes of waste, supplied by 700,000 households. Reportedly, the main customers of the future plant will be Shell and Nouryon (ECSPP, 2020). By replacing the use of fossil fuel, the CO_2 emission reduction is estimated at about 300,000 tonnes per year for the manufacturing of methanol. (Process Control, 2020; ECSPP, 2020). The project is said will to contribute to develop a circular economy and help The Netherlands to achieve its goal of becoming carbon-neutral by 2050. CO_2 emissions can be substantially reduced if the methanol is made of green hydrogen and captured CO_2.

4.5.2 On Purpose Propylene (OPP)

In recent years, research and development has concentrated on finding methods of producing propylene without ethylene. These novel manufacturing methods are known as "On Purpose Propylene" (OPP) processes. Propane dehydrogenation (PDH) is the primary on-purpose technology in use in China and the U.S. (Marsh & Wery, 2020; ICIS, 2020). Other methods include methanol to olefins plus olefin cracking (MTO + OC), and methanol to propylene (MTP™). "*All of these options produce propylene yields that are at least double those of the traditional technologies. PDH has the highest propylene yield of all, at 85%*" (Marsh & Wery, 2020). The emission reduction is then predominately based on providing low-carbon methanol as feedstock (Dechema E.V., 2017).

MTO technology for the manufacturing of ethylene/propylene in SNC-Moerdijk plants is presented as a decarbonisation option in the MIDDEN study for this location (Wong & Van Dril, 2020). Currently, there are no MTO plants in Europe (Dechema E.V., 2017). Reportedly,

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[12] Enerkem is a Canadian company and *"the first company in the world to produce renewable methanol and ethanol from non-recyclable, non-compostable municipal solid waste at full commercial scale"* (Enerkem, 2020)

this process may convert methanol to propylene and ethylene in a ratio between 1.3 and 1.8 to 1 (ICIS, 2020). CO_2 emissions can be substantially reduced if the methanol is made of green hydrogen and captured CO_2.

MTP is a variation of the MTO process, it uses different catalyst and different operational conditions to produce propylene. Currently, MTP is an alternative to the MTO process in locations where there is availability of low cost ethylene from ethane crackers, as it was the case in China (Process Worldwide, 2020). It is not yet commercially deployed in Europe (Dechema, 2017; Clariant, 2019).

4.5.3 Biomass for polyols and propylene glycols manufacturing

An alternative to traditional polyols production methods is the partial substitution of fossil raw materials by biomass-based options maintaining the main product properties and qualities. R&D work is ongoing on natural oil polyols. At present, not all of the polyol grades can be substituted as this will heavily impact product performance and consistency. The biobased raw materials can be grouped in three categories, depending upon its origin: sugars, vegetable oil and lignin options.

Sugar based polyols have been manufactured for decades to manufacture polyether polyols for rigid polyurethanes applications, as it is the case in SNC-Pernis. Generally, they can be manufactured using sugar beet, sugarcane or starch. Alternatively, cellulose or hemicellulose are preferred since they do not interfere with the food supply chain (Gómez-Jiménez-Aberasturi & Ochoa-Gómez, 2017). Currently, the renewable material content in polyols is up to 30% . However, new ways to produce polyols with up to 100% of renewable materials have been recently developed using high functionality monomers derived from biomass. For example, 2-3 butanediol, used for manufacturing of polyurethanes and antifreeze agents, is produced by the fermentation of glucose. Currently, new industrial processes for low cost bio 2-3 butanediol are under development which can boost its future demand (Gómez-Jiménez-Aberasturi & Ochoa-Gómez, 2017).

Glycerol is the simplest vegetable oil based polyol. It is widely used as a starter for the synthesis of polyether polyols for polyurethane production. It is currently the main source for producing bio-based polyurethanes (Desroches, Escouvois, Auvergne, Caillol, & Boutevin, 2012). Recently, glycerol prices have been reduced due to the surplus of glycerol from the production of biodiesel. These lower prices have favoured the conversion of glycerol into other chemical building blocks such as 1-3 propanediol (Propylene glycol), as shown in figure 19. 1-3 propanediol is an important commercial intermediate chemical, a solvent commonly used in laundry and dishwashing products, personal care, anti-freeze products and e-cigarettes.

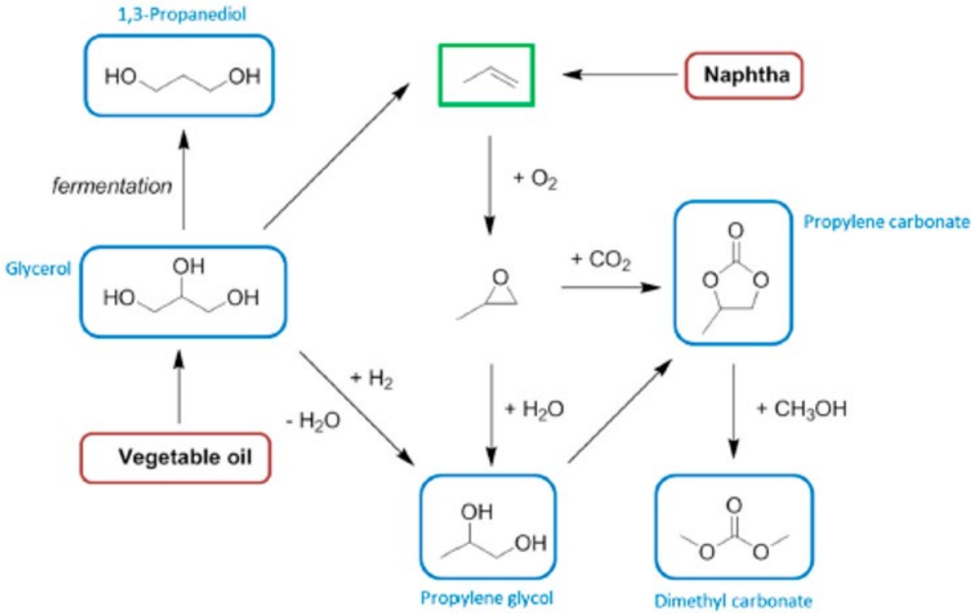


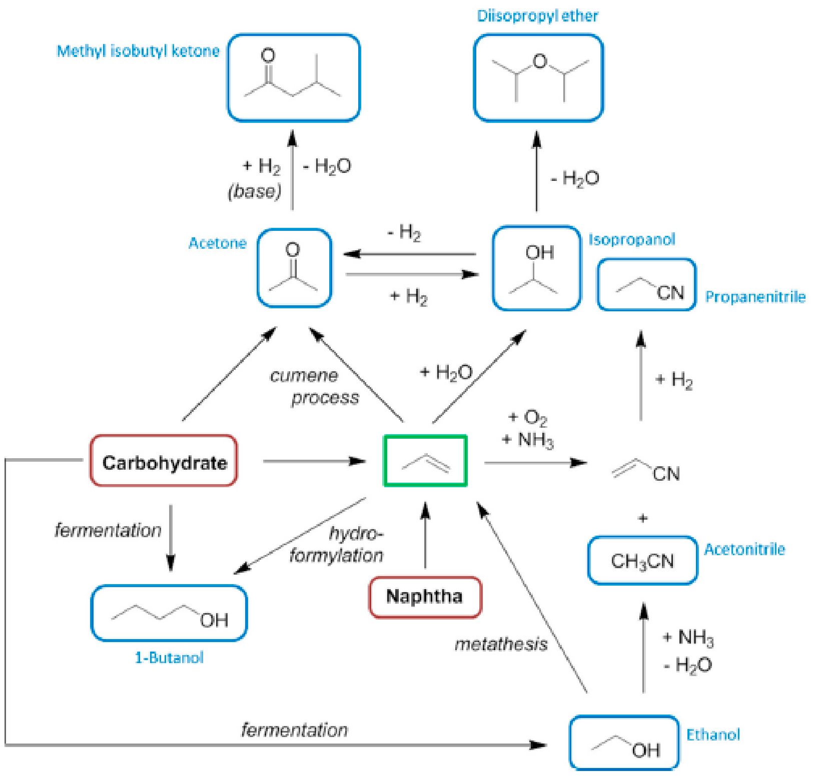
Figure 19 Bio-glycerol use for propylene glycol manufacturing (Clark, Farmer, Hunt, & Sherwood, 2015) (feedstocks are red, key intermediates green, solvents blue).

For SNC Pernis, changing the polyols manufacturing process to use biomass based feedstocks might limit the number of products that can be manufactured in the existing production lines. An alternative could be the substitution of fossil based propylene oxide (PO) by a PO made with OPP technology. This implies changing the manufacturing process of PO at the Moerdijk plants, as explained in section 4.5.2. Using green PO and bio-methanol would also reduce emissions of POGE's manufacturing.

4.5.4 Biobased acetone for MIBK, DIBK and IPA

Acetone could be produced from the essential oils of citrus fruit. The route is long for the manufacture of a currently low priced commodity and investments are required to replace the common method based on cumene (Clark, Farmer, Hunt, & Sherwood, 2015). This route can be unattractive since bio-DMK would have to be produced on purpose while it is a widely available by-product from phenol production.

Bio-based acetone can be converted into bio-based isopropanol or MIBK, as required (see Figure 20). Propanol can also be directly produced by the hydrogenolysis of glycerol (Zhu, et al., 2012). Applying these manufacturing methods would substitute the process of IPA in SNC-Pernis, currently based in the hydration of propylene.



Scheme 5. Propylene solvent synthesis tree. Key: red = feedstocks, green = key intermediate, blue = solvents.

Figure 20 Bio–acetone-based route for MIBK and IPA manufacturing

Based on Clark et al.'s article (Clark, Farmer, Hunt, & Sherwood, 2015) bio-based propylene might not be necessary for the manufacturing of acetone based solvents and IPA. However, there might be a large increase of bio-propylene demand as monomer for the manufacturing of bio-plastics and bio-polyurethane products (Clark, Farmer, Hunt, & Sherwood, 2015; Gómez-Jiménez-Aberasturi & Ochoa-Gómez, 2017).

4.6 Carbon capture, sequestration and utilisation CCS(U)

CCS(U) for Shell Pernis would typically include larger CO_2 sources on the refinery site, but could also include emissions from the smaller sources of the SNC, like furnaces and incinerators. As far as residual flows are combusted, alternative applications of these flows could be investigated.

There are three commonly used technologies to capture carbon dioxide for industrial and power plants applications namely, pre-combustion, post-combustion, oxyfuel combustion (IPCC, 2005a).

Capture

Pre-combustion systems process the primary fuel in a reactor to produce separate streams of H_2 to be used as a fuel, CO_2 for storage or utilisation and water. This capturing method is commercially used in fertilizer manufacturing and refining processes to produce low carbon fuels (IPCC, 2005a). This method is the principle behind Steam Methane Reforming to produce Blue hydrogen (H-vision, 2019). The main advantages of pre-combustion capture are the total high pressure and concentrations of the H_2 and CO_2 mix, resulting in a less energy intensive separation process. Commercially used separation processes are the use of solvents/solid sorbents or membranes. The separation process with sorbent/solvents is realised by the intimate contact of gas containing CO_2 with a liquid or a solid that will capture the CO_2. This is later released in an additional step named regeneration that may occur in the same or a different vessel. The regeneration process may be achieved by changing the conditions of the sorbent, e.g. by heat or a pressure decrease. Membranes are permeable surfaces manufactured with materials that will allow selective flow of gas through them, which is usually dependent on the pressure difference across the membrane. Typical materials used in membranes are ceramic, metal or polymers (IPCC, 2005b). These separation methods and their associated costs are explained in more detail in the MIDDEN's refineries study (Oliveira & Schure, 2020).

Post-combustion capturing is the separation of CO_2 from combustion products (flue gas, exhaust gas, or stack gas). The primary components of flue gas are CO_2, nitrogen, water and pollutants such as particulate matter (dust), sulphur oxides, nitrogen oxides, and carbon monoxide. Strict environmental regulations require the treatment of the flue gas before releasing it to the atmosphere with flue gas cleaning systems such as gas scrubbers and dust filters. Typically, flue gas is released to the atmosphere with a low CO_2 concentration (less than 10% by volume) resulting in a more energy intensive separation process than pre-combustions methods. Because of these concentration and pressure differences, pre-combustion methods are preferred despite their higher costs (IPCC, 2005a). However, a major advantage of using post combustion is that "*they can be applied as an "end of pipe" solution for almost any stationary process using any fuel*" (Sandalow, et al., 2019, p. 30). Therefore, post combustion is more suitable for existing installations.

An option that is still under development, is the replacement of air with oxygen for combustion, creating a stack gas mainly composed of water and CO_2. This method is known as Oxyfuel capturing, which requires smaller and more efficient equipment as airborne nitrogen is avoided in the separation step. It has been demonstrated at industrial relevant scale in the glass industry, not yet in petrochemicals plants (IPCC, 2005a; Sandalow, et al., 2019).

Transport and storage

The transportation of the captured carbon can be done via pipelines for distances up to 1,000 km. Shipping might be an economically attractive alternative for larger distances overseas, if applicable (IPCC, 2005a).

The underground CO_2 storage process is a commercially mature technology, it has been used in the oil and gas industry as an Enhanced Oil Recovery (EOR) method since 1960. The first dedicated geological storage project started in 1996. Since then, government supported research has allowed to develop tools and methods for monitoring and predict the behaviour of the CO_2 in the underground, which has been essential for the definition of industrial standards in recent years (ISO, 2020). Nevertheless, several uncertainties associated with the interaction of the injected CO_2 with fluids and rocks in depleted gas reservoirs and potential leakage from the reservoir rock needs further research.

Shell has developed large-scale CCS projects with different level of maturation. Two of them in Canada are already in operating phase, having research partnerships with industry and leading academic institutes.. The CCS project in Australia is in an earlier stage of development (Shell, 2020b). Moreover, Shell is a partner in the Technology Centre Mongstad (TCM) in Norway, which is the largest demonstration facility for CO_2 capture at a relatively large scale with a maximum capturing capacity of 100,000 tonnes of CO_2 per year using an ammonia unit and amine plant. This centre has been in operation since 2012. Currently a new module-based test site is under construction (expected to be completed in 2020) in which capturing emerging technologies such as carbon activated materials will be tested. (Technology Centre Mongstad, 2020).

In late 2019, Shell, ExxonMobil, Air Liquide and Air Products signed up a joint development agreement for the CCS Porthos project, to be located in the port of Rotterdam (Porthos Project, 2020). Companies will capture carbon dioxide produced during their manufacturing process to be transported via pipelines to an existing platform in the North Sea to be injected in depleted gas fields, about 3 km deep from the seabed (Porthos Project, 2020).

Utilisation

Utilisation of captured CO_2 is an additional step that might bring new opportunities to carbon dioxide emissions mitigation, since it can be used as feedstock in the manufacturing of chemicals, fuels and polymers. *"CO_2 use is not expected to deliver emissions reductions on the same scale as carbon capture and storage (CCS) but can play a role in meeting climate goals as part of an all technologies approach"* (IEA, 2019).

Captured CO_2 is currently used to enhance plant growth in greenhouse horticulture. It is not permanently stored, but avoids separate natural gas-based CO_2 production by the horticulture companies. Since 2005, SNR has been partnering in the OCAP project, supplying carbon dioxide for the horticulture industry in the Westland. CO_2 is captured in the Pernis refinery and transported through the NPM (Nederlandse Pijpleidingmaatschappij) pipeline, which can be used as a buffer as well (temporary storage unit). The pipeline runs from the Botlek area to the port area of Amsterdam. The future Porthos pipeline could be used for the same purpose, transporting captured CO_2 to the horticulture industry around Rotterdam (Porthos Project, 2020).

The utilisation of CO_2 to manufacture polyols for polyurethanes, known as polyether carbonate polyol (PPC), is possible and the manufacturing process has been described in several patents (U.S. Patent No. US7977501B2, 2008) (U.S. Patent No. US8324419B2, 2008). The main difference with respect to the traditional polyether polyols production process is that part of the propylene oxide is replaced by CO_2. Other differences are the catalyst used, double metal cyanide (DMC) and the reaction conditions (135 ◦C and 25 bar) (U.S. Patent No. US8324419B2, 2008). Recent research (Fernández-Dacosta, et al., 2017) has assessed the technical, economic and environmental feasibility of manufacturing PPC at a refinery by implementing CCU in combination with carbon storage, showing promising results from the techno-economic and perspective. By utilising the captured CO_2, the propylene oxide demand was reduced which also translates into a better environmental performance than the base case (conventional polyol manufacturing) (Fernández-Dacosta, et al., 2017). For SNC-Pernis, implementing this pathway in the manufacture of polyols for rigid foam applications may imply capital investments to modify the existing processing facilities. A limitation of this method is that the CO_2 content in the resulting polyol is 20% in weight, increasing its viscosity, and therefore making it unsuitable for flexible PU foam application (Langanke, et al., 2014). The option has been studied by the Shell Projects and Technologies department, but work has stopped due to the large capital investment. The process may even have a larger CO_2 footprint than the CO_2 processed.

5 Discussion

The decarbonisation options for petrochemical manufacturing processes presented in this report were identified with the aim of reducing carbon dioxide emissions by 2050 in the SNC-Pernis manufacturing plants. They include technologies for electrification, energy efficiency, blue/green hydrogen for fossil fuel substitution, bio-based solutions and CCS(U). The feasibility of their successful and, more importantly, sustainable implementation will depend of the overall benefits of an integrated energy and supply chain system. Social acceptance will also play a role when using CCS, biomass and geothermal technologies.

The direct emissions of SNC Pernis are low compared to the refinery emissions. They originate mainly from combusting residual process flows. Alternative uses for these residuals would have to be found to avoid combustion. CCS may play a role in the reduction of these direct emissions in SNC-Pernis from furnaces and waste incinerators. If post-combustion capture of CO_2 directly from the SNC furnaces is too complex, gas flows may be routed to central processing installations and the MEK furnaces can be heated with blue or green hydrogen. This hydrogen can be produced externally or at the refinery. It means that the use of hydrogen as a fuel will depend on new facilities for hydrogen production at large scale. The production of green hydrogen, requiring large availability of renewable electricity, seems less attractive at an early stage but could be achievable in the longer term, as long as the technology maturation occurs satisfactorily.

Captured CO_2 at SNC-Pernis could be applied for the manufacturing of polyols for rigid applications. However, this option will deliver new products with different and insufficient specifications.

Many products manufactured in SNC-Pernis are intermediates derived from propylene or propylene oxide. Methanol, hydrogen and acetone are also important feedstocks in the studied processes. These feedstocks are mostly manufactured using fossil raw materials. The use of alternative greener feedstocks is possible with minor modifications to the SNC-plants, as described in section 4. It will however, require major capital investments for bio-methanol production and subsequent biobased production of propylene and propylene oxide. This may substitute the fossil naphtha based SNC-Moerdijk plants in the longer term. Currently, Shell plans to develop a bio-waste methanol plant in the Rotterdam cluster. The availability of this feedstock will be a major enabler for the reduction of the carbon footprint of SNC products such as polyether polyols and glycols produced on both the Moerdijk and Pernis sites. Finally, the use of blue hydrogen as a feedstock seems feasible and its application depends on how the Rotterdam plans for blue hydrogen production develop.

In general, two disadvantages of biomass-based options are the impact on land use and feedstock availability. Consequently, the uncertainties regarding availability and feedstock price are an issue for its short-term implementation. Additionally, achieving current product qualities with biomass-based feedstock would require further development.

Energy efficiency options such as the development of new catalysts and heat pumps, and the integration of geothermal energy in the system would reduce the steam demand and therefore reduce emissions from the refinery steam generating units.

The solutions described in the document were listed and presented as stand-alone solutions. Nevertheless, a fully integrated assessment for the Shell Pernis refinery and chemical plants is required to quantify benefits of possible combinations of solutions. Some of the choices may compete with others, or certain combinations are not technically viable or mutually exclusive. Moreover, the choices must consider alignment not only with Shell shareholders and business partners, but also the directly connected company sites in the Rotterdam cluster and the local authorities and communities.

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