PBL Netherlands Environmental
Assessment Agency

DECARBONISATION OPTIONS FOR LARGE VOLUME ORGANIC CHEMICALS PRODUCTION, SHELL MOERDIJK

Louise Wong, Ton van Dril

09 November 2020

MIDDEN

Manufacturing Industry Decarbonisation Data Exchange Network

Decarbonisation options for large volume organic chemicals production, Shell Moerdijk

© PBL Netherlands Environmental Assessment Agency; © TNO
The Hague, 2020
PBL publication number: 3483
TNO project no. 060.33956 / TNO 2020 P11258

Authors

Wong, L.; van Dril, A.W.N.

Acknowledgements

Special thanks to Arend de Groot, Rajat Bhardwaj (TNO)

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:
D. van Dam (PBL), Dick.vanDam@pbl.nl, or S. Gamboa Palacios (TNO), Silvana.Gamboa@tno.nl.

This publication is a joint publication by PBL and TNO and can be downloaded from: www.pbl.nl/en. Parts of this publication may be reproduced, providing the source is stated, in the form: Wong, L., and Van Dril, A.W.N. (2020), Decarbonisation options for large volume organic chemicals production, Shell Moerdijk. PBL Netherlands Environmental Assessment Agency and TNO EnergieTransitie, The Hague.

PBL Netherlands Environmental Assessment Agency is the national institute for strategic policy analysis in the fields of the environment, nature and spatial planning. We contribute to improving the quality of political and administrative decision-making by conducting outlook studies, analyses and evaluations in which an integrated approach is considered paramount. Policy relevance is the prime concern in all of our studies. We conduct solicited and unsolicited research that is both independent and scientifically sound.

TNO EnergieTransitie has a twofold mission: to accelerate the energy transition and to strengthen the competitive position of the Netherlands. TNO conducts independent and internationally leading research and we stand for an agenda-setting, initiating and supporting role for government, industry and NGOs.

This report was reviewed by Shell Nederland Chemie. PBL and TNO remain responsible for the content.

Contents

FINDINGS

Summary

Shell Nederland Chemie (SNC) B.V. Moerdijk operates a naphtha cracker and several downstream processes, including the fractionation of olefins and benzene, and the production of ethylene oxide, ethylene glycols, ethylbenzene, styrene monomer and propylene oxide. The Moerdijk site is linked by pipelines to the Shell refinery site in Rotterdam.

Table S.1 Production capacities at SNC Moerdijk

Product	Capacity (kilotonnes per year)	Main process/reaction
Ethylene	910	Steam cracking
Propylene	500	Steam cracking
Butadiene	115	Separation from C_4 fraction of steam cracker
Benzene	500	Extraction from pyrolysis gasoline of steam cracker
Ethylene oxide	305	Oxidation of ethylene to ethylene oxide
Ethylene glycol	155	Hydration of ethylene oxide to ethylene glycol
Ethylene benzene	640	Alkylation of benzene to ethylbenzene
Styrene Monomer and Propylene Oxide	1,000/460	Co-production via propylene epoxidation and ethylbenzene hydroperoxidation

The energy is largely supplied by fuel gases and liquids separated from the naphtha cracking process, and other residual streams, estimated at 34 PJ. The site operates a utilities unit with steam boilers and a combined heat and power (CHP) plant, mainly using around 6-8 PJ natural gas, and 7 PJ cracker fuel gases and liquids. The estimated final net demand for steam is 12 PJ; final direct use of fuel gases is estimated at 26 PJ, electricity at 2.4 PJ annually. Total CO_2 emissions amount to 2,280 kilotonnes (kt) in 2019.

The main decarbonisation options are: heat integrated distillation columns and heat pumps, heat recovery, process control, coalesce-filtration units, membranes (for gas separation), adsorption heat pumps, electrification, hydrogen as fuel, biomass to bio-ethylene process, methanol to olefin process, carbon capture and storage or utilization. Shell recently announced cracker furnace replacements that would reduce CO_2 emissions with 10% by 2025.

FULL RESULTS

Introduction

This report describes the current situation for the Dutch Large Volume Organic Chemical (LVOC) and derivatives production in the Netherlands and the options and preconditions for its decarbonisation. Specifically, this concerns the situation of Shell Moerdijk. 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

Part of the MIDDEN initiative is to compile a database of material and energy uses of industrial processes at a plant level for the Dutch manufacturing industry. The scope of this research will focus on the manufacturing of large volume organic chemicals at the Moerdijk complex owned by Shell Nederland Chemie (SNC) B.V., Chemieweg 25, 4782 SJ Moerdijk. Processes include lower olefin production via steam cracking, butadiene hydrogenation and extraction, benzene extraction, ethylene oxide and ethylene glycol production, and the co-production of styrene monomer and propylene oxide. Products include ethylene, propylene, butadiene, benzene, ethylene oxide, ethylene glycols, ethylbenzene, styrene monomer and propylene oxide.

The main decarbonisation options investigated are: heat integrated distillation columns, heat recovery, process control, coalesce-filtration units, mechanical vapour recompression, membranes for gas separation, adsorption heat pumps, electrification, hydrogen as fuel, biomass to bio-ethylene, methanol to olefin process, carbon capture and storage or utilization.

Reading guide

Chapter 1 gives a general introduction to the LVOC industry in the Netherlands and Shell Moerdijk in particular. In Chapter 2 we describe the current situation of Shell Moerdijk, based on recent representative data and in Chapter 3 we describe the relevant products to these processes. Options for decarbonisation are systematically quantified and evaluated in Chapter 4. The feasibility and barriers of those decarbonisation options are discussed in Chapter 5.

1 Large Volume Organic Chemicals production in the Netherlands

1.1 The Dutch chemical industry

In 2018, the Dutch chemical industry consumed over 800 PJ of energy and feedstock and was responsible for over 19 million tonnes (Mt) CO_2eq greenhouse gas (GHG) emissions (CBS, 2018). Mapping the chemical industry and the various decarbonisation options proves a difficult task due to the wide range of products and technologies. Within the chemical industry, a large portion of energy demand and emissions are attributed to a relatively small number of processes. One of the processes with the highest share of GHG emissions and energy consumption is the steam cracking process for olefin production. Other processes in chemical industry with large emissions include the production of ammonia, chlor-alkali, methanol and hydrogen (Ecofys; Fraunhofer ISI; Oeko-Institut, 2009).

Shell operates a steam cracker and several of the other processes at the Moerdijk site. In the EU-28 countries, 51 operating steam crackers had an ethylene nameplate capacity of about 25,000 kt/year in total in 2015 (Table 1.1). Many of these plants are located in western Europe, with the Dutch steam cracking installations having a total production capacity of about 4,000 kt/year for ethylene. In the Netherlands, three more steam crackers are operated in Terneuzen (Dow Chemical) and two more in Geleen (SABIC).

Table 1.1 Steam cracking installations and capacities in the EU-28 in 2015 (Koottungal, 2015; Petrochemicals Europe, 2020; Boulamanti & Moya Rivera, 2017)

Country	Number of plants	Capacity ($kt_{ethylene}$/y)
Austria	1	500
Belgium	3	2,230
Czech Republic	1	544
Finland	1	330
France	7	3,050
Germany	12	5,757
Greece	1	20
Hungary	2	660
Italy	3	1,420
Netherlands	6	4,037
Poland	1	700
Portugal	1	330
Romania	4	844
Slovakia	1	220
Spain	3	1,280
Sweden	1	625
United Kingdom	3	1,995
Total	51	24,542

Most steam cracking installations are located on large chemical sites in relative proximity to a refinery site. Figure 1.1 shows the Antwerpen-Rotterdam-Rijn-Ruhr-area (ARRRA) cluster where extensive network of pipelines ensures secure supply of products to and from refineries, steam crackers and olefin consumers to/from the Netherlands, Germany, Belgium, and Luxembourg.

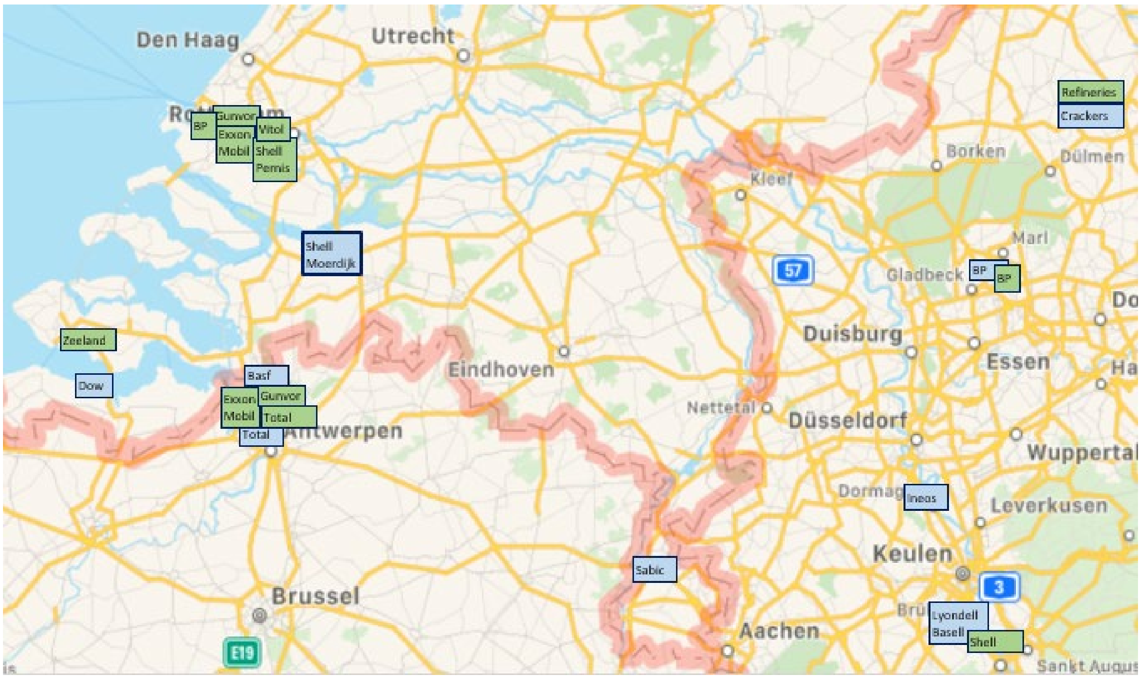

Figure 1.1 Locations of refineries and olefin producer/consumers in the ARRRA cluster (Petrochemicals Europe, 2020)

Located in the center of the cluster is the Port of Rotterdam which is the largest seaport in Europe. As of 2020, the total length of the port area spans 42 km and consists of 1,500 km of pipelines. The port's main value chains associated with energy use are fuel, chemicals, and electricity production. Five refineries in this area transport fuels and feedstock to various markets where supply is facilitated easily by a pipeline network, large volume storage and loading docks for shipping, rail and road transports. Crude oil, fuel and feedstock flows are mostly contained within the Netherlands, Belgium and three western states of Germany (North Rhine-Westphalia, Rhineland-Palatinate and Hessen). Emphasis on raw materials processing and chemicals manufacturing means that the port largely consists of crude oil refineries, chemical plants, gas production for industrial use, storage terminals for tanks, pipelines networks, and multiple other service companies (Samadi, et al., 2016).

1.2 Shell Moerdijk

1.2.1 Location and infrastructure

Shell Moerdijk is located within the Rotterdam/Moerdijk petrochemical cluster, within easy access to the sea, and connected to other major chemical and refinery sites at Pernis and Antwerp. Its proximity to other major petrochemical producers and consumers means the site benefits from reduced transport costs and efficient use of feedstock and products. On average, 70% of products from Moerdijk are transported via pipelines, 25% is transported via ship (>2,400 shipments annually), and the remaining 5% via rail (1,650 wagons) and by road (11,000 freight trucks). Crude oil is processed in the refinery at Shell Nederland

Raffinaderij BV (“Shell Pernis”), and the resulting feedstocks are routed to Shell Moerdijk for further transformation into bulk chemicals. The underground pipeline network interconnects the sites so that commodities can be transported between sites for further processing as needed (Shell, 2018b).

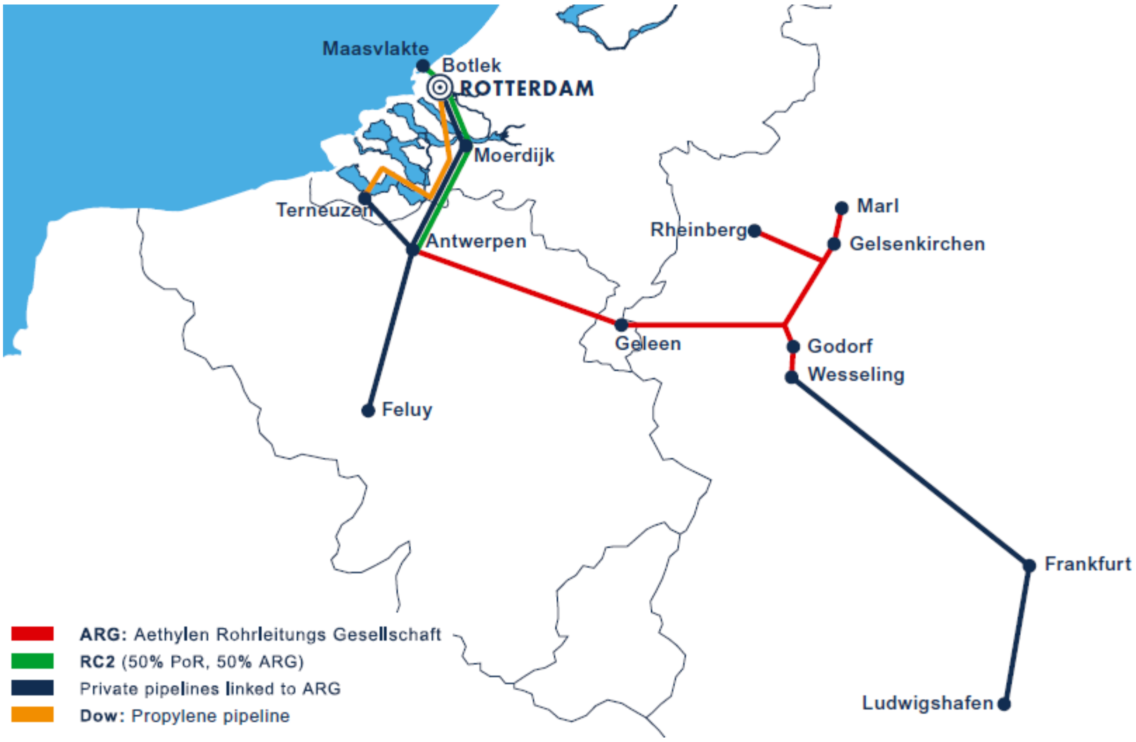

Figure 1.2 Ethylene and propylene pipelines in the ARRRA cluster (Port of Rotterdam, 2010)

The RC2 pipeline (Figure 1.2) transports ethylene between Rotterdam and Antwerp. It is a single common carrier pipeline which means that it can be used by multiple users simultaneously. Pipelines owned by Äthylen Rohrleitungsgesellschaft (ARG) cover a distance of approximately 500 km and transport ethylene between producers and consumers in the Netherlands, Germany, and Belgium (ESCPP, 2010). The MultiCore pipeline system is a joint venture of the Port of Rotterdam Authority (75%) and Vopak (25%). The system is comprised of 4 x 20 km underground pipelines which transport chemicals and gases between the Europoort, Botlek and Pernis sites within the Rotterdam area (Samadi, et al., 2016). This pipeline system transports isoprene (IP extraction feed) from the steam cracker at Moerdijk. The IP feed is also sent to the Rubis Terminal in the Botlek, where it is shipped to the United States for further processing (Port of Rotterdam, 2010).

The Shell Moerdijk site covers a total area of 325 hectares, of which 250 are currently used for production and a further 75 hectares have potential to accommodate growth. In 2019, Shell opened a 27 MW solar PV installation on its site, supplying electricity to the production facilities. The workforce at the petrochemical complex consists 1,300 staff, of which 800 are permanent, and 500 are contractors for maintenance and projects (Shell, 2018a; Shell, 2018b).

1.2.2 History and current plans

Shell Moerdijk is the name of the complex that houses several petrochemical production plants in the Moerdijk port and industrial area. After there was a lack of expansion space at the Pernis site, Shell buys the initial 250 hectares at Moerdijk and construction of the facility started in 1969. 1973 marked the official start-up of on-site activities when the first commercial products were shipped. The second phase of construction began in 1976, and the first plant for co-production of styrene monomer and propylene oxide (MSPO-1) started production in 1980. This was followed by the third phase of expansion in 1996. The second MSPO-2 plant started up in 1999 and is a joint venture from Shell (50%) and BASF (50%) (Shell, 2018a). In 2000, the Moerdijk Lower Olefins (MLO) section of the plant was expanded where the ethylene cracker capacity is increased with four larger furnaces from 650 kt/y to 900 kt/y. Cost of expansion was 136 million euro (Chemicals Technology, 2016). An aromatics unit extracting benzene from the pyrolysis gasoline stream of the steam cracker was added in 2002, and a third reactor was added to the MEOD unit to increase the ethylene oxide capacity. In 2009, the four newer furnaces were adjusted to process hydrowaxes from Pernis and other Shell refineries. In 2016, an aromatics unit (solvent deasphalter) entered operation at Shell Pernis. Benzene from this unit is routed to Shell Moerdijk for styrene monomer production (Shell, 2016).

Recently, September 2020, plans to replace the 16 older cracking furnaces built in 1972 by 8 new units with the same overall capacity were announced (Petrochem, 2020). The investment is said to involve several hundred million euros. The plant will remain in operation and the modular replacement is expected to be completed in 2025.

Another relevant investment for an air separation unit (ASU) south of the Shell site was announced by Air Liquide (Chemicals Technology, 2020). This 125 million euro ASU will produce 2,200 tonnes of oxygen per day, which could cover the demand of both the Shell ethylene oxide and styrene production. The electricity driven unit features flexible operation with an oxygen storage, equivalent with 40 MWh of electricity storage. The ASU is planned to be operational in 2022 and will be connected to the Air Liquide pipeline network.

1.2.3 Principal activities

The main processes and products are detailed in Table 1.2, with the nameplate capacity of the unit. Principal activities are centered around the steam cracker located in the Moerdijk Lower Olefins (MLO) section (Figure 1.3). This section produces the basic lower olefin chemicals from feedstocks, including; ethylene, propylene, butadiene. A benzene extraction unit is linked to the steam cracker to obtain benzene from the pyrolysis gasoline streams of the cracker. The products and by-products from the MLO section are either sold, reused in the process, or routed to various other plants on site where intermediate chemicals are manufactured (MEOD, MSPO-1 & 2) (Shell, 2018a).

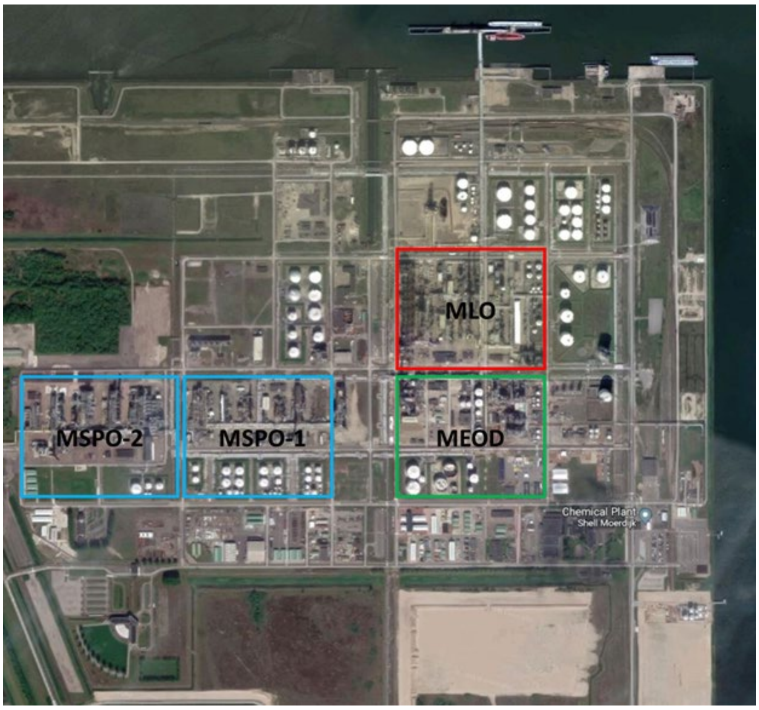

Figure 1.3 Shell Moerdijk site with main activities/plants indicated (MLO = Moerdijk Lower Olefins, MSPO = Moerdijk Styrene monomer and Propylene Oxide, MEOD = Moerdijk Ethylene Oxide and Derivatives)

Table 1.2 Products and capacities of plants at Shell Moerdijk (Shell, 2018a)

Product	Capacity (kt/y)	Main process/reaction
Moerdijk Lower Olefins (MLO) and aromatics		
Ethylene	910	Steam cracking
Propylene	500	Steam cracking
Butadiene extraction	115	Separation of butadiene from C_4 fraction of the steam cracker
Butadiene hydrogenation	105	Hydrogenation of C_4 fraction to be further converted to butylene derivatives
Benzene extraction	550	Extraction from pyrolysis gasoline fraction of the steam cracker
Moerdijk Ethylene Oxide and Derivatives (MEOD)		
Ethylene oxide	305	Oxidation of ethylene to ethylene oxide
Ethylene glycol	155	Hydration of ethylene oxide to ethylene glycol
Moerdijk Styrene Monomer and Propylene Oxide Plants (MSPO 1 & 2)[1]		
Ethylene benzene	640	Alkylation of benzene to ethylbenzene
Styrene Monomer/Propylene Oxide 1	450/250	Co-production via epoxidation of ethylbenzene hydroperoxide
Styrene Monomer/Propylene Oxide 2	550/210	
Other plant operations		
Moerdijk Utility Company		Supplies steam, air, water
Moerdijk Filling & Dispatch (MFD)		Product delivery

---

[1] Also abbreviated SMPO 1 & 2.

2 LVOC processes

Shell Moerdijk is a multi-plant complex which also contains multi-product processes. Furthermore, in the case of naphtha steam cracking, fuel grade by-products are recycled into the fuel network or by-products can be reused as feedstock. The ETS emissions, energy use and process descriptions for each of the major plants (MLO, MEOD, SMPO), are described in the following sections. The main inputs and outputs, specific energy consumption, and emissions of the processes are described. This is followed by a section describing the utilities onsite.

2.1 ETS Emissions

Table 2.1 lists the emissions for all units onsite reported under the ETS from the Dutch Emissions Authority (NEa, 2020). As expected, a large share of emissions is contributed from the steam cracker unit. The utilities and other supporting units combined emitted over 600 kt CO_2 per year in 2016-2019. The styrene monomer/propylene oxide plants 1 & 2, and aromatics section are also emitting significant amounts of GHGs.

Table 2.1 ETS emissions for plants at Shell Nederland Chemie B.V., Moerdijk for 2016-2019 (NEa, 2020)

SNC B.V. Moerdijk	Activity/production unit	ETS emissions (kt/y)			
		2016	2017	2018	2019
BKG 1	Steam cracker	1,178	1,196	1,210	924
BKG 2	Styrene monomer 1, ethylbenzene	141	172	172	158
BKG 3	Styrene monomer 2	211	220	221	189
BKG 4	Aromatics, high pressure (HP) steam boiler	206	324	336	239
BKG 5	Ethylene oxide, ethylene glycol	95	85	90	93
BKG 6	Propylene oxide 1	36	43	44	36
BKG 7	Propylene oxide 2	21	20	20	18
BKG 8	Utilities: Two HP steam boilers; Other supporting units: butadiene hydrogenation, catalyst preparation, flaring torch	665	623	662	622
Total		2,553	2,683	2,755	2,280

2.2 Moerdijk Lower Olefins

Commercially, the two main production processes to obtain these lower olefins are catalytic cracking, or the pyrolysis of hydrocarbons in the form of steam cracking. Steam cracking of petroleum fractions is the main process applied in Europe and also at Moerdijk. Long-chain saturated hydrocarbon molecules are thermally "cracked" to produce a mixture of smaller chain unsaturated compounds. After separation the olefins can be sold themselves or subjected to further processing and functionalization to produce other useful chemicals such as oligomers, polymers and other ethylene derivatives (Zimmerman & Walzl, 2012; Falcke, et al., 2017).

The Moerdijk Lower Olefins (MLO) section consists of the steam cracker, utilities (steam turbine and gas turbine) and butadiene and benzene extraction units. The main products are ethylene, propylene, butadiene, and benzene. The steam cracking reaction results in more than one product which makes it difficult to standardize the energy use and emissions accurately for each product. Therefore, benchmarking studies from Solomon and Associates has defined the term High Value Chemicals (HVCs) which includes ethylene, propylene, benzene, butadiene, acetylene and hydrogen. Due to the variation in reaction conditions and multiple products formed, aggregation of these chemicals makes it easier to assess the overall performance of a site compared to others. In this study the energy use and emissions are standardized to this term for simplicity and consistency with literature.

The description below is based on steam cracking processes (Figure 2.1) outlined by Falcke et al. (Falcke, et al., 2017), Boulamanti & Moya (2017) and Spallina et al. (2017). The "P" streams (P01 etc.) are liquid or gas process streams, "S" represents the steam flows, "U" are residual fuel streams, and "A" are air streams. The description is illustrative for Shell Moerdijk, it serves as a default where Shell data are missing. Certain process elements are reported according to the process at Shell Moerdijk and sourced from industrial experts.

2.2.1 Pyrolysis

The hydrocarbon stream (P01) is pre-heated and mixed with steam (S03) to reach a steam-to-naphtha ratio of 0.5. The mixture is further heated to 500ºC (P02) and enters the cracker where temperatures of ~850 ºC are reached at a pressure of 1 bar. The tubes are externally heated by gas fired burners. The endothermic nature of the reaction means that extremely high energy inputs are required. A residence time of ~0.6 seconds is reported to maximize olefin yields (Zimmerman & Walzl, 2012). The cracked gas leaves the cracker (P03) at 850ºC and cooled to 230ºC (P04). This cooling produces high (S01) and medium (S02) pressure steam which is used for power generation (e.g. driving compressors). The gas is quenched with water (and some recirculated oil) and cooled and routed to the primary fractionation section (P05). Due to the high temperatures in the furnace, heat recovered is used for pre-heating the reactants and for steam generation in the reboilers. From the exhaust gas, the steam (S03) is generated at 100 bar and superheated up to 500ºC. However, throughout the process steam is produced and consumed at different temperature and pressure levels.

2.2.2 Primary fractionation and compression

Heavy components (C_9+) are removed (P08), and the light components (P06) are cooled and separated into gas and liquid streams. The gaseous stream (P07) is compressed in a multistage compressor, from which the liquid knockout is sent to the stripper for aromatics recovery (P26). Usually in the last gas compression stage, the gas is scrubbed with caustic soda for acid gas (CO_2, hydrogen sulfide) removal. The gas is dried with a molecular sieve and sent to the product separation section of the plant.

2.2.3 Ethylene and propylene separation

This section involves several distillation columns to separate the individual hydrocarbon products and other treatment steps which process the various streams such as cooling or hydrogenation. The dried gas enters the cryogenic cooler (P10) where it is cooled to -50ºC and fed to the de-methanizer. The incondensable elements of the stream are removed from the top of the column and expanded to 1 bar. The incondensable stream is used in the plant fuel network as fuel for the furnace (U02) and fuel for the boiler (U01). The bottom stream enters the de-ethanizer (P12), from which the bottom stream enters the de-propanizer (P13), and similarly that bottom stream enters the de-butanizer (P14).

The distillate of the de-ethanizer (P15) undergoes a hydrogenation reaction (H_2-1) where the acetylene (C_2H_2) is converted into ethylene. The mixture of C_2 species (P16) are separated in the C_2 splitting column and polymer grade ethylene is obtained after heat recovery (P17).

The distillate of the de-propanizer (p20) is hydrogenated to convert methyl-acetylene (C_3H_4) to propylene (C_3H_6), and sent to the propylene purification column where polymer grade propylene is obtained (P22). The bottom streams of the C_2 and C_3 splitting columns (P19 and P23) contain ethane and propane which are typically recycled as cracker feedstock. Different from most other mixed-feed crackers, acetylene is recovered in a separate section using extractive distillation and is subsequently used on-site for the production of vinyl esters for Hexion Specialty Chemicals B.V.

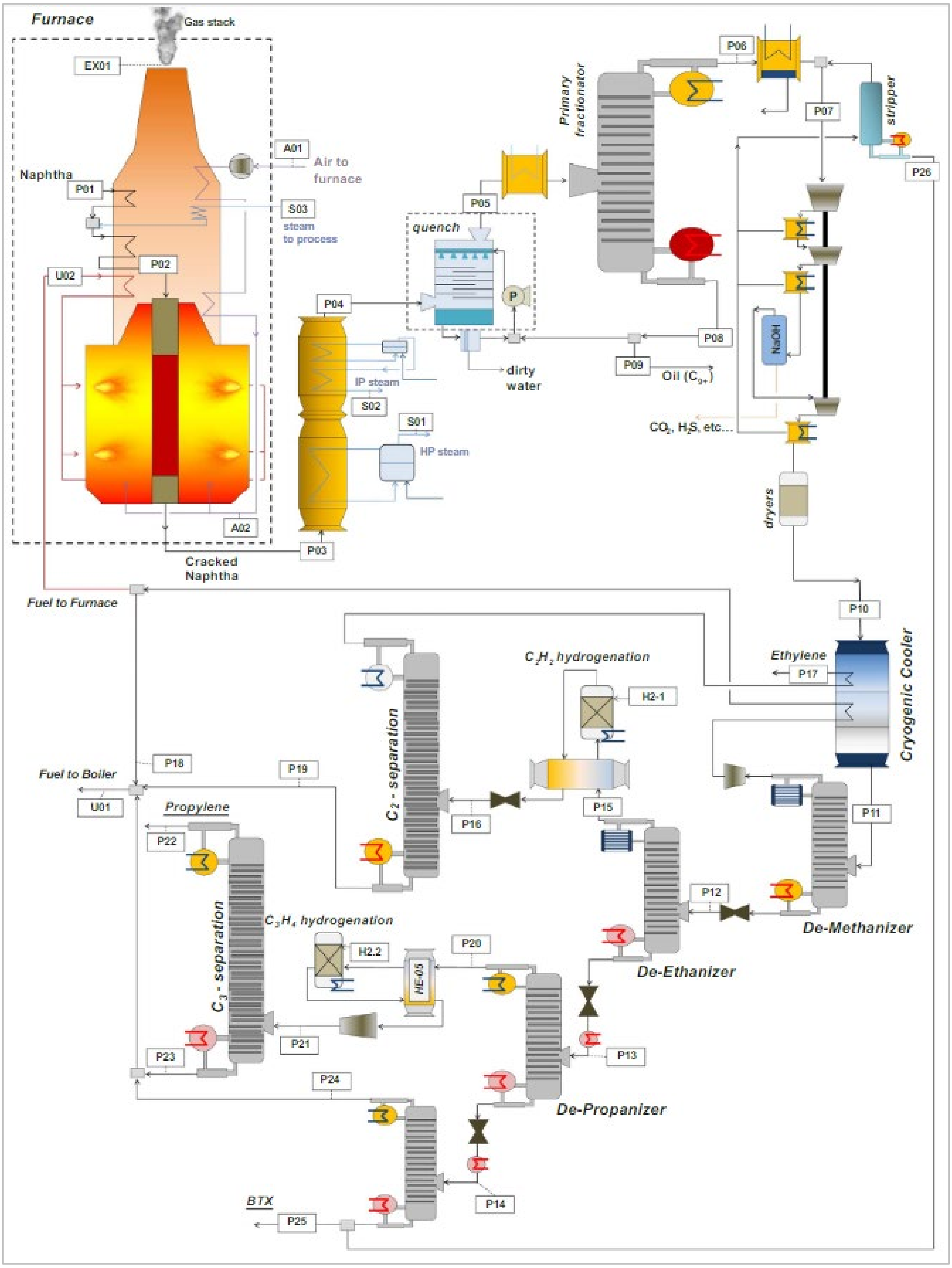

Figure 2.1 Flow diagram of naphtha steam cracking process (Spallina, et al., 2017)

2.2.4 C_4 hydrocarbons separation

The crude C_4 stream from the steam cracking process can be upgraded to obtain more valuable chemicals. Butadiene is recovered by extractive distillation. The required steam and electricity for this step is 6.4 and 0.9 GJ/tonne of product respectively, based on (Neelis, Patel, Blok, Haije, & Bach, 2007). Alternatively, mixed C_4's can undergo selective hydrogenation of butadiene to produce butenes. For this extraction and hydrogenation, the same energy requirement is assumed per tonne of product. In Figure 2.2 (Morgan, 2018) the several routes are illustrated, taken as representative for Shell Moerdijk. Butane that is produced is recycled to the cracker as feedstock.

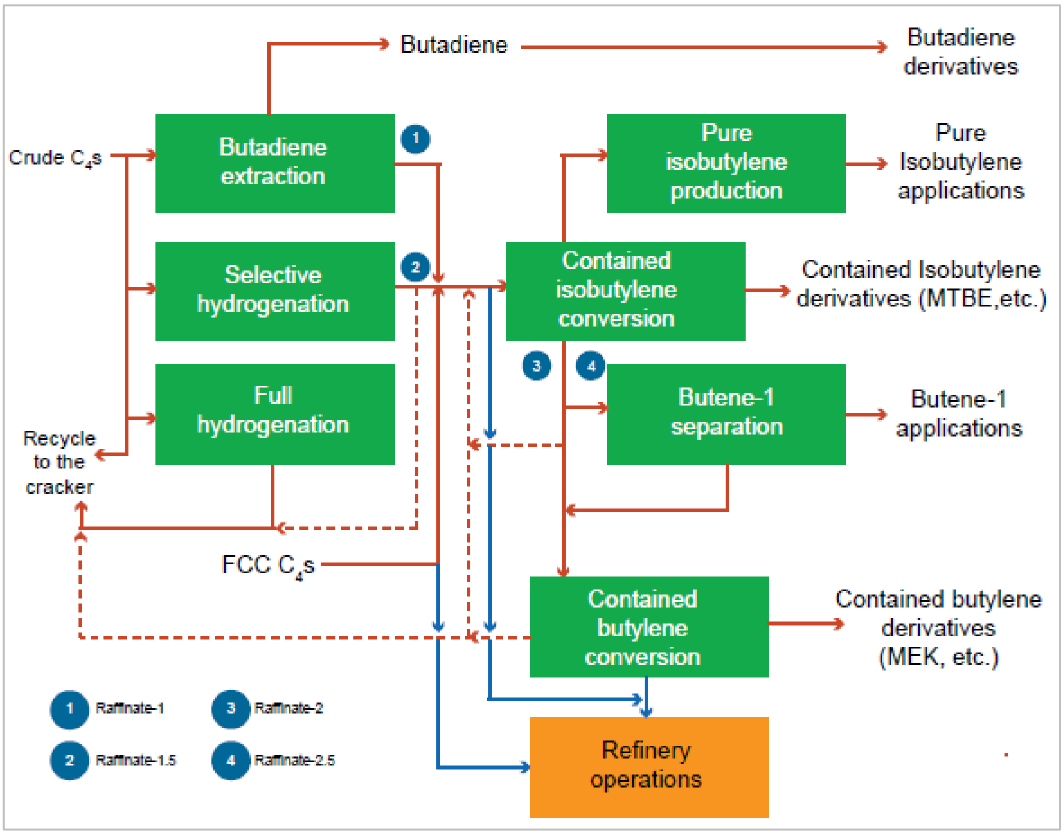

Figure 2.2 Processing of crude C_4 hydrocarbons (Morgan, 2018)

2.2.5 Benzene extraction

Heavy components are sent to the BTX recovery section (P25) where for Shell Moerdijk, benzene is recovered in a separate benzene extraction unit. The distillates (P24) are mixed with the other incondensable gases (chemical waste gases) and used as fuel in the boiler. After a selective hydrogenation reaction in the pygas hydrotreater, benzene is extracted via the Morphylane Extractive Distillation Process from Thyssen Krupp (Figure 2.3). Benzene concentration in the feed is approximately 65 wt %, where the feed capacity of Shell is reported to be 850 kt/year and a nameplate capacity of 550 kt/year (Thyssen-Krupp, 2014).

The first step involves selective hydrogenation so that the diolefins are not polymerized. The stream enters the de-pentanizer where the C_5 fraction can be removed and sent to the fuel network. Olefins and the impurities, such as nitrogen and sulfur are then fully hydrogenated and the off gases containing H_2S are sent to the steam cracker. After the de-heptanizer, the aromatics are extracted using an extraction distillation technology and enters the benzene/toluene (B/T) column. The blue section in Figure 2.3 demonstrates how C7+ aromatics can be converted into benzene, where a thermal hydrodealkylation unit is used to dealkylate extracted toluene from the B/T column into benzene (Thyssen-Krupp, 2014).

From literature, energy consumption of benzene extraction from pygas amounts to 7.01 GJ steam, 2.67 GJ fuel and 0.92 GJe electricity per tonne of benzene (Neelis, Patel, Blok, Haije, & Bach, 2007). Capital costs for the new extraction unit at Shell Moerdijk were reported to be 25 million dollars (27 million euros) in 2001 (Oil and Gas Journal, 2001).

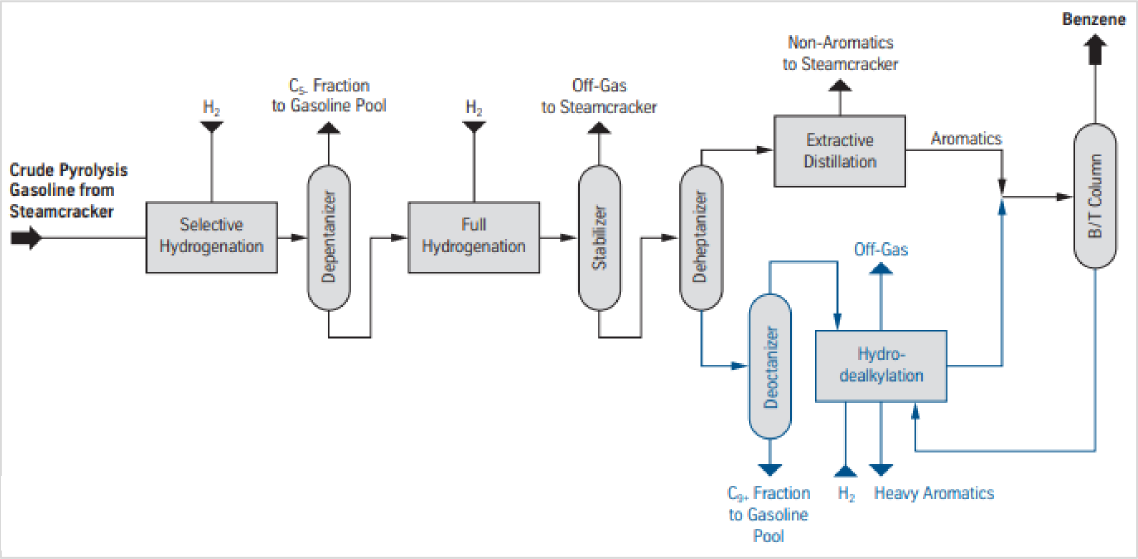

Figure 2.3 Benzene extraction from crude pyrolysis gasoline of the steam cracker (Thyssen-Krupp, 2014)

Table 2.2 Estimated energy and material flows: HVCs, including C4 and benzene extraction

Inputs	Capacity (kt/year)	Energy (PJ/y)	Source
Naphtha	3,000	132	Calculated from JRC (Falcke, et al., 2017), based on ethylene capacity
HP Steam for cracking	1,500	5.1	Hydrocarbon to steam ratio 0.5, based on JRC
(imported Pygas for benzene)	175		Estimate, assuming 60% benzene yield from Pygas
Outputs			**Mostly based on JRC (Falcke, et al., 2017)**
Hydrogen-rich gas	26		Calculated, based on JRC
Methane-rich gas	567	25.6	Estimate based on NEa (NEa, 2020) and EEA's Large Combustion Plants (LCP) list (European Environmental Agency, 2019)
Ethylene	910		Capacity from Shell's website for 2017
Acetylene	12		Indicated by Shell
Propylene	500		Capacity from Shell's website for 2017
Butadiene	138		Calculated, based on JRC
Butenes/Butanes	231		Calculated, based on JRC, corrected
Pyrolysis gasoline (intermediate)	658		Calculated, imports excluded
Fuel oil	77	3.2	Calculated, based on JRC
Benzene	500		Capacity from Shell's website for 2017

Other Pygas fractions (toluene, C_{8+})	333	14.0	Calculated, based on JRC
Total high value chemicals	2,318		Hydrogen, ethylene, propylene, acetylene, butadiene, butenes, benzene

Inputs	Kt/year	Energy PJ/y	Source
Energy			
HP Steam for cracking	1,500	5.1	Hydrocarbon to steam ratio 0.5, based on JRC (Falcke, et al., 2017)
Generated steam HP	2,000	-6.1	Estimate 2.000 kt/y
Steam for compression/separation		6.1	Estimate 2.000 kt/y
Steam for C_4		1.4	Calculated, based on Neelis et al. (Neelis, Patel, Blok, Haije, & Bach, 2007)
Steam for benzene		3.5	Calculated, based on Neelis et al. (Neelis, Patel, Blok, Haije, & Bach, 2007)
Fuel gas to cracking furnaces	424	19.2	Estimate based on NEa/LCP, emission factor 62.4 kg/GJ (Zijlema, 2018)
Direct CO_2 emissions cracking	1,196		NEa, total for cracking 2017
Electricity for cracking		0.7	Assumption
Electricity for C_4		0.2	(Neelis, Patel, Blok, Haije, & Bach, 2007)
Electricity for benzene		0.46	(Neelis, Patel, Blok, Haije, & Bach, 2007)

Table 2.3 includes some literature values that are relevant for HVC production. Exact values for Shell are not calculated because comparison can be inaccurate due to methodological differences. The load factor for Shell Moerdijk is estimated to be substantially higher than the EU average.

Table 2.3 Some energy and material flows literature values on HVCs

	Value	Unit	Source/comment
Naphta cracking Load factor EU-28	83	%	(Boulamanti & Moya Rivera, 2017)
HVC yield Naphtha use	1.56 – 1.88	t/t HVC	(Boulamanti & Moya Rivera, 2017) HVCs here excluding benzene (Saygin, Patel, Tam, & Gielen, 2009)
Feedstock energy content	44 - 45	GJ/t	(Zijlema, 2018)
Naphtha flow rate	350	t/h	(Spallina, et al., 2017). For production of 1000 kt ethylene per year
Steam-to-naphtha ratio	0.5	t/t	(Spallina, et al., 2017) wt. basis
Electricity use	0.3 – 0.55	GJ/t HVC	(Ren, Patel, & Blok, 2006); (Saygin, Patel, Tam, & Gielen, 2009)

Steam	-1.4 - 0	GJ/t HVC	(Dechema, 2017), (Ren, Patel, & Blok, 2006) net steam exporting process
Specific energy consumption	14-17 (typical for existing units)	GJ/t HVC	(Ren, Patel, & Blok, 2006) 11-14 GJ/t HVC for new state-of-the-art crackers

2.2.6 Breakdown of energy consumption and losses

The typical energy demand of existing naphtha steam crackers is within the range of 14-17 GJ/t HVC, while new state of the art crackers use 11-14 GJ/t HVC. The pyrolysis section requires the most energy input, with 55-65% of the total energy demand allocated to this section. 13-22% of the total energy is required for the primary fractionation step, and 20-30% is used for the product separation step. The pyrolysis section exhibits exergy losses of approximately 75% since the total temperature drop can be up to 1100°C, with a total pressure drop of nearly 70 bar. The remaining exergy losses of nearly 25% can be attributed to electricity use in the compression and separation section, where cryogenic temperatures are required (-150°C), and pressures of up to 30 bar. 1-2% of energy is required for decoking, shutdowns/restarts, and other maintenance (Ren, Patel, & Blok, 2006).

As discussed earlier, fuel grade by-products are generated from the cracker which are reused in the fuel network. Gaseous and/or fuel oil production amounts to approximately 20-25% of the energy content of naphtha. Since the energy content of the naphtha feedstock is 44-45 GJ/t naphtha, it equates to 9-11 GJ/t naphtha of fuel by-products (Chauvel & Lefebvre, 1989; Ren, Patel, & Blok, 2006).

2.3 Ethylene oxide and ethylene glycol production

The integrated MEOD unit produces both high purity ethylene oxide (EO) and mono-, di-, tri-ethylene glycols (MEG/DEG/TEG). The EO reaction is exothermic while the EG reaction is endothermic, therefore producing both chemicals allow for efficient heat integration of the two processes (Boulamanti & Moya Rivera, 2017; Falcke, et al., 2017). EO and EGs production are described in the section 2.3.1 and 2.3.2, followed by Table 2.4 detailing main energy and material flows.

2.3.1 Ethylene oxide

Figure 2.4 shows EO production divided into four sections, as described by Boulamanti & Moya Rivera (Boulamanti & Moya Rivera, 2017).

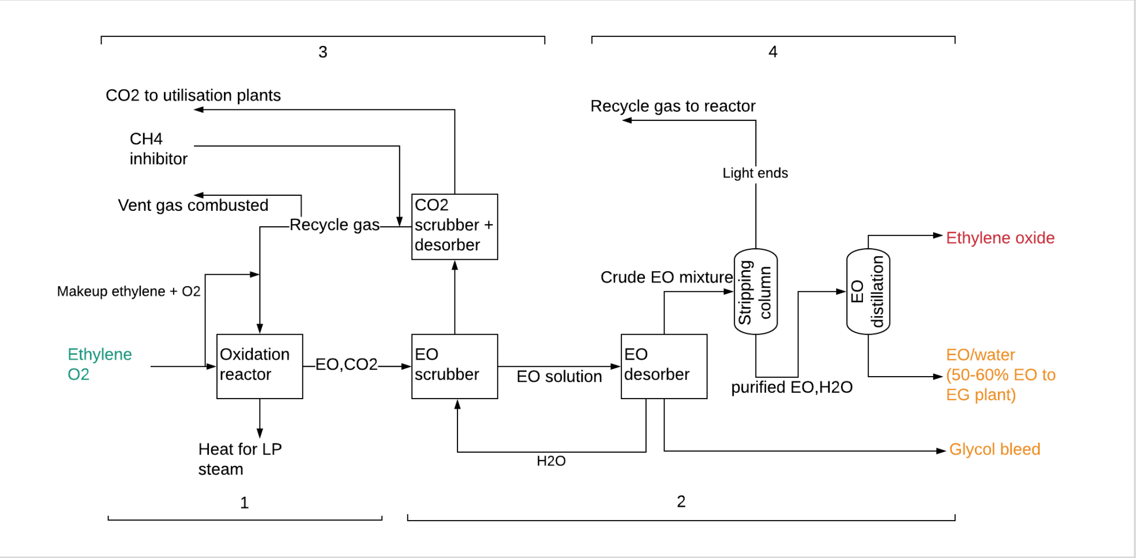

Figure 2.4 EO production process from ethylene

1. Direct oxidation of ethylene

Ethylene is partially oxidized over a silver oxide catalyst to produce EO according to the following reaction

$$C_2H_4 + ½\ O_2 \rightarrow C_2H_4O$$

Oxygen is supplied from an oxygen separation unit. The exothermic reaction is carried out under temperatures of 200-300°C, at a pressure of 15-25 bar and a residence time of 1 second. The excess heat is used to produce steam for the process. Another exothermic reaction that takes place is the complete oxidation of ethylene,

$$C_2H_4 + 3\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$$

As the temperature increases the complete oxidation reaction is favored and the selectivity for the EO process decreases. Therefore, it is important to control the temperature so that complete oxidation is minimized. Selectivity to EO reaches 80-90% if the ethylene conversion is at 7-15% (Boulamanti & Moya Rivera, 2017). The excess heat is recovered with coolant for low pressure steam production and is used to offset the later energy demand for dewatering and separation of ethylene glycols.

2. EO recovery

The gas from the reactor (containing EO and other constituents) is routed to the EO scrubber and is dissolved in water. The EO solution is concentrated in the desorber and the top stream sent for further purification. The bottom water stream is cooled and returned to EO scrubber. The glycol bleed stream from the EO scrubber is further processed.

3. CO_2 removal

Off gas from the EO scrubber is sent to the CO_2 scrubber and desorber, where CO_2 is stripped from the stream and transported via pipelines for utilization. Approximately two-thirds of CO_2 produced in the EO process is routed to OMYA B.V., and used to produce calcium carbonate from quicklime for paper whitening. For the 2005-2008 period, Shell obtained an opt-out for this emission under the ETS (Harmelink & Coenraads, 2005). Currently however, for the EU-ETS this remains a process emission attributed to Shell. The rest of the recycle gas is returned to the oxidation reactor with an addition of the required amounts of O_2 and ethylene. Some of the recycle gas (0.1 – 0.2 vol%) which contains approximately 70% hydrocarbons (mostly ethylene/methane), is vented and combusted.

4. Non-condensables removal and EO purification
The crude EO mixture from the desorber enters the stripping column and traces of CO_2, nitrogen, methane, ethylene, and aldehydes are removed and join the recycle gas loop to the reactor. Since the recycled gases are rich in ethylene, the process yield and economics can be improved by their recycling. The purified stream containing EO and water enters a distillation column where EO is obtained in the top stream. EO is used as a raw material for further processing into specialty chemicals.

2.3.2 Ethylene glycols (EG)

This section describes EG production as shown in Figure 2.5. Ethylene oxide undergoes thermal hydrolysis without a catalyst to produce an EG mixture. The reaction takes place at a temperature of 200ºC, a pressure of 12.5 bar and a residence time of one hour. The crude glycol mixture contains 75-92 wt% MEG, and all the EO is converted. The main product is MEG, but heavier di- and tri- ethylene glycols (DEG & TEG) are also produced from the consequent reactions of EO with the lighter EGs,

$$C_2H_4O + H_2O \rightarrow OH\text{–} C_2H_4\text{–}OH \text{ (MEG)}$$

$$OH\text{–} C_2H_4\text{–}OH + C_2H_4O \rightarrow OH\text{–} C_2H_4\text{–}O\text{–} C_2H_4\text{–}OH \text{ (DEG)}$$

$$DEG + C_2H_4O \rightarrow OH\text{–} C_2H_4\text{–}O\text{–} C_2H_4\text{–}O\text{–} C_2H_4\text{–}OH \text{ (TEG)}$$

Heavier glycol formation is inevitable since EO reacts more readily with MEG than water, therefore excess water is used to minimize the reactions. Water is separated from the EG mixture via evaporation and distillation and recycled. Low pressure steam that is generated is used for heat in other parts of the plant.

After drying, the crude glycol mixture undergoes successive distillations where heavier glycols are recovered in decreasing yields. The glycols cooled and routed to storage. MEG emission factors are based on the stochiometric reaction and assuming a yield of 90%.

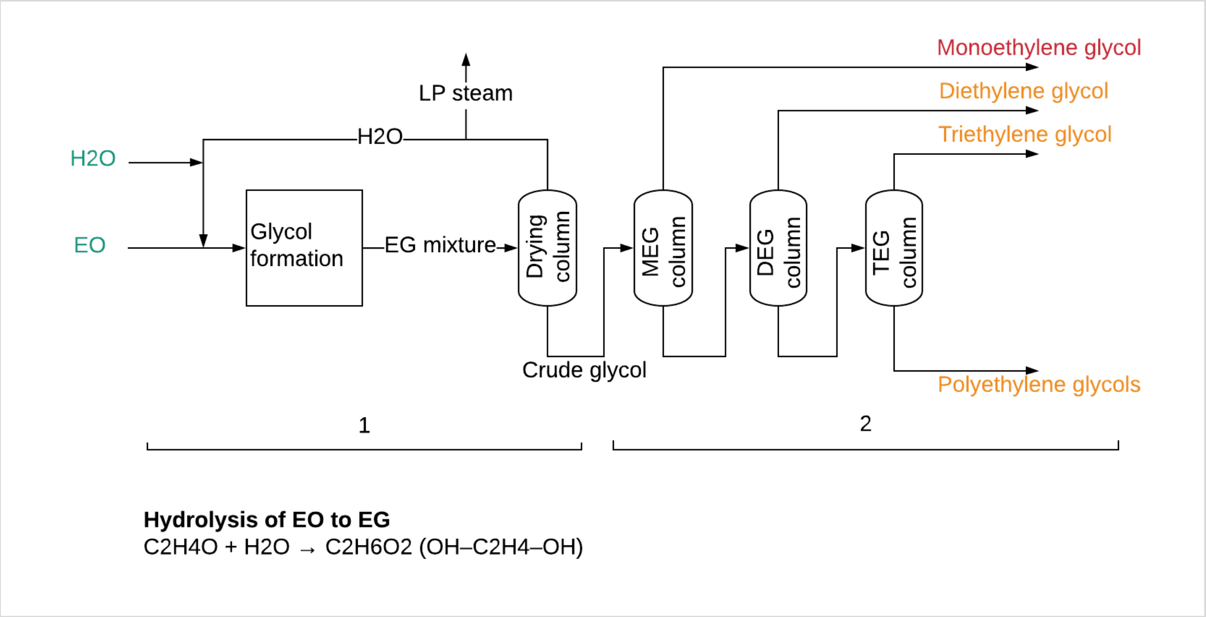

Figure 2.5 MEG, DEG, TEG, and polyethylene glycols production from ethylene oxide

Table 2.4 Energy and material flows: EO and MEG

EO	Kt/year	Energy pJ/y	Source
Inputs			
Ethylene	218		calculated, estimated 89% conversion
Oxygen	276		calculated
Outputs			
Ethylene oxide	305		Shell's website capacity for 2017 (Shell, 2018a)
CO_2 (partly exported)	75		calculated process emission at 89% conversion rate
Energy			
Steam	net export	-1.5	estimate based on Neelis et al. (Neelis, Patel, Blok, Haije, & Bach, 2007)
Electricity		0.31	(Neelis, Patel, Blok, Haije, & Bach, 2007), calculated
MEG			
Inputs			
Ethylene oxide	122		calculated, 90% conversion
Outputs			
Ethylene glycols	155		Shell's website capacity for 2017 (Shell, 2018a)
Energy			
steam		0.7	(Neelis, Patel, Blok, Haije, & Bach, 2007)
electricity		0.04	(Neelis, Patel, Blok, Haije, & Bach, 2007)
fuel gas	3	0.1	(Neelis, Patel, Blok, Haije, & Bach, 2007)
CO_2	9		calculated
Total CO_2	85		NEA total for EO and EG 2017

Table 2.5 Some energy and material flows literature values on EO and MEG production

Product	Unit	Ethylene oxide (EO)	Monoethylene glycol (MEG)	Source/comment
Load factor EU-28	%	86	83	(Boulamanti & Moya Rivera, 2017)
Inputs				(Falcke, et al., 2017)
Ethylene	t/t EO	0.70 - 0.85		
O_2	t/t EO	0.75 - 1.1		
EO	t/t MEG		0.789	0.51 t ethylene/t MEG
Energy consumption				(Boulamanti & Moya Rivera, 2017)
Electricity	GJ/t	1.2	0.2 – 0.3	
Fuel	GJ/t		0.75 - 1.1	
Steam	GJ/t		3.6 - 8	EO production is exothermal

2.4 Ethylbenzene and Styrene Monomer/Propylene Oxide co-production

For ethylbenzene (EB), styrene monomer (SM), and propylene oxide (PO) production, Shell Moerdijk applies its proprietary SMPO process technology. The technology is a fourth-generation process that has incorporated improvements in the catalytic steps and increases the yield of both PO and SM. There are four major steps in the process which occurs under a closed system, therefore waste products and heat can be reused. The process is reported to reduce energy consumption by around 20% and is 5–10% cheaper to run than previous processes (Buijink, Lange, Bos, Horton, & Niele, 2008).

2.4.1 Alkylation of ethyl benzene

Shell has a reported production capacity of 640 kt ethyl benzene (chapter 1). Ethylbenzene is produced by combining benzene and ethylene in an acid-catalyzed chemical reaction:

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5CH_2CH_3$$

Shell operates the Mobil Badger process, using a zeolite catalyst, since 1991 (Elzenga, 1993). Benzene is evaporated with and then superheated in a process furnace, then mixed with ethylene and fed into a reactor at 350-450 ^{o}C and 15-25 bar. After reaction, the product is separated in distillation columns. Excess benzene is separated and recycled, other aromatic residuals are used as fuel and fed in the fuel gas grid or incinerated. The process is described in detail in (Falcke, et al., 2017).

From literature, the process requires fuel 2.51 GJ fuel and 0.07 GJ electricity per tonne of ethyl benzene (Neelis, Patel, Blok, Haije, & Bach, 2007). From the excess heat of the reactor, steam is produced which is used for preheating feedstock and other adjacent processes.

2.4.2 Co-production of styrene monomer and propylene oxide

The following section explains the co-production process in Figure 2.6 and 2.7, as described by Falcke et al. (Falcke, et al., 2017) and Buijink et al. (2008). The black and red arrows represent the raw material inputs and outputs respectively, while blue arrows show the sources of emissions to air from the process.

Oxidation unit

1. In the hydroperoxidation reactor, EB is reacted with oxygen to form ethylbenzene hydroperoxide (EBHP) (Figure 2.6, reaction A), along with small amounts of alpha-methylbenzyl alcohol (ɑ-MBA) and acetophenone (ACP). The reaction occurs in a liquid phase at a pressure of 2 bar, and at a temperature of 140 – 150 ^{o}C. Emissions to air from the reactor contain inert gas and a mixture of organic vapours. The stream is cooled, and aromatics are recovered, while the remaining gases are sent to end-of-pipe-abatement.
2. The stream enters an evaporation system, where unreacted EB and low-boiling contaminates are removed. Recovered EB from the condensing column is recycled back to the recovery section for further purification. The concentrated EBHP solution is sent to the epoxidation reactor. Main pollutants in the off-gas stream from this unit are CO, CO_2, EB, methanol, some ACP, and a-MBA).

Epoxidation unit

3. EBHP is mixed with propylene and undergoes a liquid phase epoxidation reaction over a heterogenous titanium-on-silica catalyst to produce crude PO and ACP (Figure 2.6, reaction B). This reaction occurs at a high pressure of 35-40 bar and 100ºC.
4. The distillation column extracts both unreacted propylene to be recycled back to the epoxidation reactor, and light hydrocarbons such as ethane and propane to be used in the plant fuel gas network.
5. The stream undergoes a caustic and water wash to remove acidic impurities and/or dissolved catalyst.
6. The washed stream is further distilled to purify the PO which is the principal co-product and sent to storage. Again, propylene is recovered and recycled to (3), while wash water is recycled back to (5), and tars/heavy liquid impurities are used as fuel or disposed.
7. After PO is removed the remaining organic layer enters the central EB/ α-MBA recovery section. The layer is washed and EB is recovered via distillation, where along with fresh EB and EB recycled from other steps, is used in the initial step (1). Tars/heavy liquid impurities are used as fuel or disposed.
8. The α-MBA (and small amounts of ACP) from the EB/ α-MBA recovery section is dehydrated over a solid catalyst (mixture of zinc and copper oxide) to produce styrene (Figure 2.6, reaction D). The residual catalyst is separated and disposed.
9. The crude styrene is refined through a series of distillation columns where ACP is removed and sent to the hydrogenation unit. The pure SM product is obtained and sold.

Hydrogenation unit

10. The removed crude ACP is hydrogenated with hydrogen gas under pressure (Figure 2.6, reaction C). The resulting emissions containing hydrogen and some organic vapours are either used for hydrogen recovery or used in the plant fuel network.
11. α-MBA from the hydrogenation reaction is routed back to the EB/ α-MBA recovery unit to join the dehydration stream.

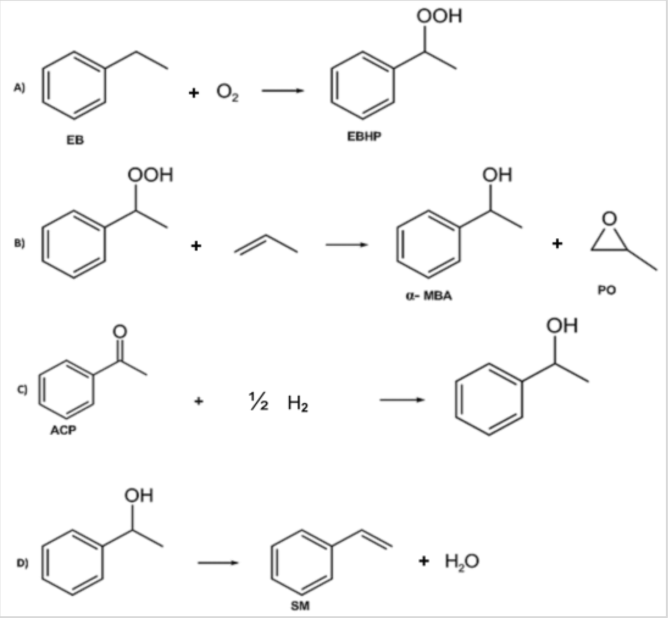

Figure 2.6 Four main reactions in the SM/PO co-production process (Buijink, Lange, Bos, Horton, & Niele, 2008)

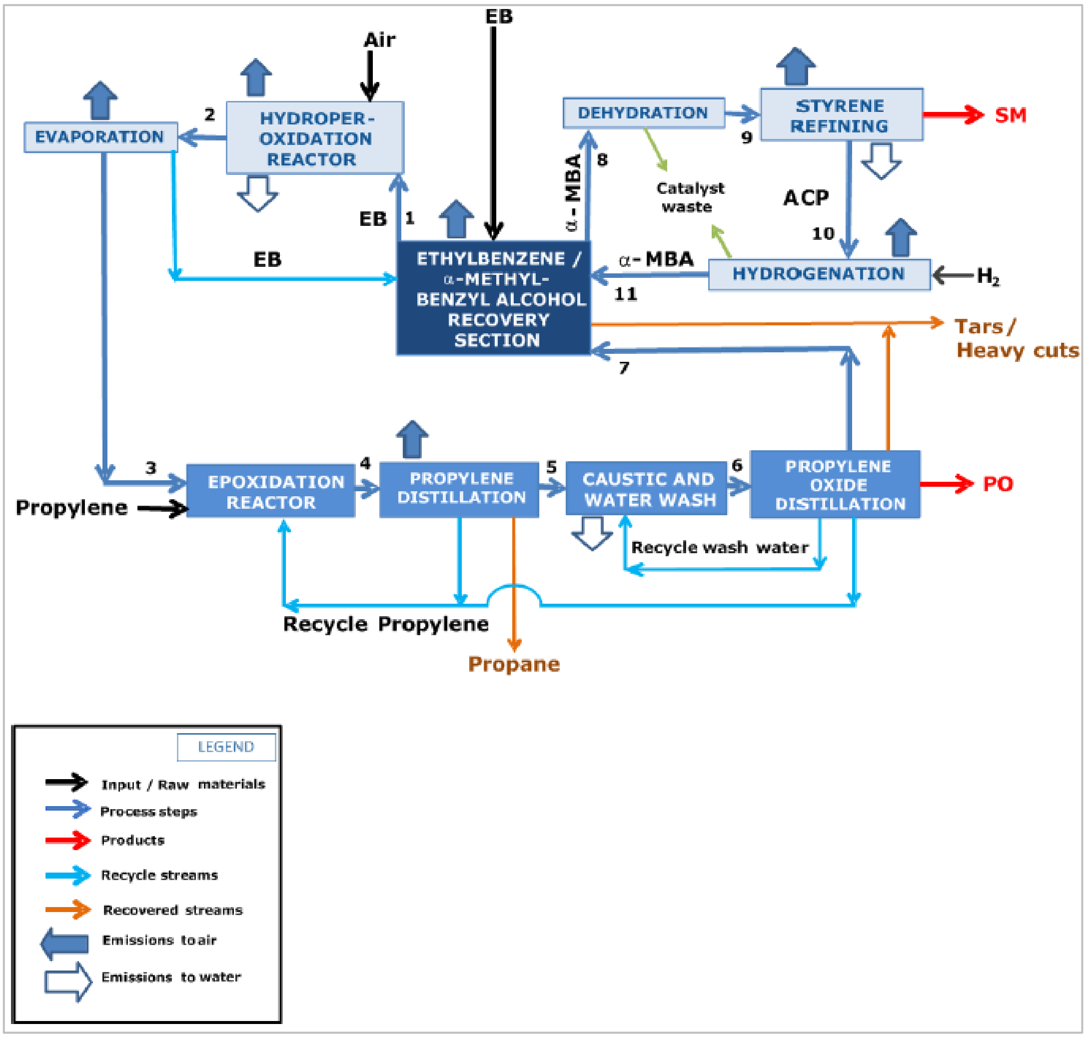

Figure 2.7 Flow diagram of EB peroxidation process to co-produce SM and PO, numbers represent steps of the reaction (Falcke, et al., 2017)

Table 2.6 Energy and material flows: Ethyl benzene and SMPO

EB	Kt/year	Energy pJ/y	Source
Inputs			
Ethylene	175		Calculated
Benzene	488		Calculated
Output			
Ethyl benzene	640		Shell's website capacity for 2017 (Shell, 2018a)
Energy			
Fuel gas	36	1.61	(Neelis, Patel, Blok, Haije, & Bach, 2007)
Steam	Net export	-2.0	(Neelis, Patel, Blok, Haije, & Bach, 2007)
Electricity		0.04	(Neelis, Patel, Blok, Haije, & Bach, 2007)
CO_2 from fuel gas	100		Calculated

SMPO			
Inputs			
Ethyl benzene	640		Shell's website capacity for 2017 (Shell, 2018a)
Ethyl benzene imported	500		Estimate, based on smpo output
Oxygen	344		Calculated
Propylene	438		
Output			
Styrene	1,000		Shell's website capacity for 2017 (Shell, 2018a)
Propyleneoxide	460		Shell's website capacity for 2017 (Shell, 2018a)
Other residues, for fuel purposes	110	3.8	Indicated by Shell, 85% recovery efficiency estimate
Energy			
Steam		4.0	Estimated
Fuel gas for furnaces	55	2.5	(European Environmental Agency, 2019)
Other residues for furnaces	73	2.9	(European Environmental Agency, 2019)
Electricity		0.6	(Falcke, et al., 2017)
CO_2 from fuel gas	156		Calculated
CO_2 from other residues	214		Calculated
Total CO_2	456		Total for EB and SMPO 1+2 (NEa, 2020)

Table 2.7 Some literature values on energy and material flows: SMPO (from Boulamanti & Moya (2017) unless otherwise specified)

Product	Unit		Source/comment
Load factor	%	83	General utilization rate for Dutch chemical industry (Neelis, Patel, Blok, Haije, & Bach, 2007)
Capacity SMPO 1+2	(kt PO/SM)	1,000/460	Shell (Table 1.2)
Inputs			
Benzene	(t/t PO)	2.11	
Ethylene	(t/t PO)	0.76	
Propylene	(t/t PO)	0.88	
Outputs			
Propylene oxide	(t/t PO)	1	
Styrene	(t/t PO)	2.2 – 2.5	

2.5 Utilities

The complex contains a utilities facility (MLO-U) which supplies steam, electricity, air and water (NEa, 2014). The MLO Utility Centre (1973) has a total maximum thermal input capacity of 1,055 MW, consisting of three high pressure steam boilers, one middle pressure steam boiler and a gas turbine. The boilers are fired with mostly natural gas and fuel gas, residual oils and tar. The gas turbine has a 38 MWe capacity and is fired with natural gas, exhaust gases are heating up the boilers (Provincie Noord Brabant, 2003; European Environmental Agency, 2019). Assumed efficiencies of the turbine are 19% electric and 63% thermal. Thermal input to MLO-U in 2017 amounted to 15 PJ, but the total capacity of 1,055 MW would allow for double this input (European Environmental Agency, 2019; ECN, 2019). The facility mainly delivers the high pressure 105 bar steam for cracking, for driving the main cracked gas compressor as well as for compressor turbines in the refrigeration section. High pressure steam is also generated by quenching the cracker output flows. Medium pressure steam is extracted to provide heat to separation processes. Other steam is provided by heat recovery from fired heaters and from exothermic reactions.

Until 2018, additional electricity and steam for the Moerdijk site is provided by a nearby cogeneration of heat and power (CHP) plant owned by RWE. The unit uses natural gas while also utilizing steam from the nearby waste incineration plant. The rated electrical output is reported as 339 MW and generates 200 tonnes of medium pressure steam (25 bar) per hour, of which a maximum of 150 tonnes per hour is sent to Shell (Chemicals Technology, 2016); RWE, 2018) (RVO, 2015) (DWA, 2008). In 2018, it was reported that 2 PJ of steam was delivered from the CHP to Moerdijk, and 0.120 PJ is returned as condensate. As of 2018, a new 123 MWe steam turbine at the Attero waste incineration plant (AEC Moerdijk) supplies steam to the Shell site, replacing the steam that was previously supplied by the CHP. 30 to 150 tonnes of steam are provided per hour, depending on the requirements of Shell (Attero, 2018).

Shell supplies also steam to LyondellBasell Benelux B.V. and Solvay Solutions Nederland B.V. LyondellBasell Benelux B.V. produces polymers based on propylene and also supplies off-gases to Moerdijk for the steam boiler (DWA, 2008) (Havenschap Moerdijk, 2014).

Due to the combustion of different fuels of varying emission factors, flue gas with a wide-ranging CO_2 composition is produced. Combustion of fuels produce a large share of the site's CO_2 emissions and according the ETS emissions in Table 2.1, the heaters and boilers do not necessarily share the same emissions point (European Environmental Agency, 2019). In Table 2.8 an overview of energy inputs and outputs is given.

Table 2.8 Estimated overview of energy balance and utilities

Utilities			
Inputs	kt/year	PJ/y	
Natural gas		8.1	LCP list (European Environmental Agency, 2019)
Fuel gas	86	3.9	LCP list (European Environmental Agency, 2019)
Other residues	79	3.2	LCP list (European Environmental Agency, 2019)
Output			
Steam		11.6	calculated based on 85% efficiency
Electricity		1.1	calculated output based on 94% load
CO_2	946		NEA, utilities incl HP steam for aromatics
Imports steam		1.35	Attero/WKC Moerdijk: 90 MWth, 50% load
Exports steam		0.5	estimated exports to Lyondell, Solvay, e.o.
Imports electricity		1.3	calculated

Totals			
	kt/year	energy PJ/y	
Total net steam demand processes		11.2	calculated
Total steam supply		12.5	calculated
Total fuel (gas & oil) inputs		41.5	calculated
>Fuel for final energy use		26.3	calculated
>Fuel for utilities		15.1	calculated
Total fuel (gas & oil) produced		32.6	cracker and SMPO output, excl imports
Total electricity demand		2.4	
Total electricity produced		1.1	
Total CO_2 emission	2,683		(NEa, 2020)
Total end use		39.9	

2.6 LVOC production economics

This section provides some insight in the costs structure of current LVOC production, specifying costs for greenfield investment and operations. These costs reflect the competitive conditions in the global market where Shell Moerdijk is operating. It does not refer to the historic costs or current costs situation of the Moerdijk site. From the historic costs, relevant information includes the large refurbishment and expansion completed in 2000. The Moerdijk ethylene cracker had its capacity increased from 650,000 t/year to 900,000 t/year. The cost was estimated to be 136 million euros (Chemicals Technology, 2016).

2.6.1 Lower olefin production costs

A general assessment of costs associated with LVOC manufacture is based on techno-economic assessments of olefin production from (Spallina, et al., 2017), and (Boulamanti & Moya, 2017a). Focus is placed on costs associated with the steam cracker unit to produce ethylene, propylene and high value chemical by-products such as benzene, as production of these base chemicals are central to the site. Cost assessments for intermediates and monomer production typically include costs for base chemical production as the units are largely integrated.

Spallina et al. addresses the production of olefins and aromatics via conventional naphtha steam cracking for a plant with a 1,000 kt/y ethylene capacity, which is in the order of magnitude of the cracker at Shell Moerdijk. The study follows the cost estimation methodology from the National Energy Technology Laboratory (NETL), which provides guidelines for cost assessments of power plants. Exponential scaling law is applied to calculate costs as a function of scaling parameters. The costs are then adapted to the equipment capacity size (for a 1,000 kt ethylene capacity plant), and the costs are actualized according to the chemical engineering cost index (Spallina, et al., 2017). The costs are expressed in base-year euros. A more detailed explanation of the cost estimation methodology and assumptions can be found in the NETL report (DOE NETL, 2011)

Plant components
The bare equipment cost (BEC) is the sum of plant component costs, on site facilities and infrastructure supporting the plant (e.g. piping, civil works, instrumentation, steel structure etc.). The plant component costs and are categorized in Figure 2.8 and Table 2.9. The costs for naphtha steam cracking plant components are reported as a percentage of the BEC. On

top of that, the total installation cost is defined as 80% of the BEC which represent the labor costs associated with the construction and installation of these plant components and infrastructure. The total direct plant cost (TDPC) is the sum of the BEC and the total installation costs (TIC).

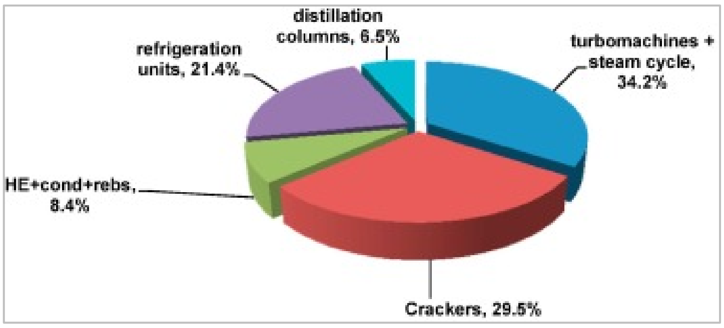

Figure 2.8 BEC for plant components, as a percentage of total BEC. HE = heat exchanger, cond = condenser, rebs = reboiler (Spallina, et al., 2017)

In Figure 2.8, the costs of the plant components are divided as a percentage of the total BEC specified in Table 2.9. The single component with the highest cost for a conventional naphtha steam cracker is the cracker itself, followed by the combined turbomachines and steam cycle.

Table 2.9 Estimated costs for plant components (Spallina, et al., 2017)

Plant component	Cost (Meuro)	Comment
Turbomachines & steam cycle	140.2	Include blowers, pumps, compressors, expanders and steam turbines.
Cracker	120.9	
Refrigeration units	87.7	
Heat exchangers, condensers & reboiler	34.4	
Distillation columns	26.6	Costs depend on the weight of the column and the material chosen
Total BEC	409.9	

Engineering procurement and construction costs (EPC)
Indirect costs (IC) are defined as 14% on top of the TDPC, which are the costs of services provided by the engineering, procurement, and construction contractor. This may include project and construction management, design, and contract permit costs. The total engineering procurement and construction costs (EPC) are defined as the sum of the TDPC and the IC.

Contingencies and owner’s costs (COC)
The project contingency costs account for unknown costs that may be excluded or unforeseen due to incomplete project planning. This is included because it has been shown from practice that these costs are likely to occur and cannot be predetermined prior to the cost estimations. The amount allocated for process contingency is determined by the maturity level of the technology, and for a process that is commercially applied such as a steam cracker, is set at 10% on top of the EPC. The owner’s cost estimation includes pre-production and start-up costs, inventory capital (e.g., spare chemicals and catalysts), and financing costs. Owner’s costs may also include costs associated with delayed startup,

equipment cost fluctuations, and legal fees. The owner's cost is estimated to be 5% of the EPC which results in the total COC to be 15% on top of EPC. This results in the total overnight costs (TOC).

CAPEX

The CAPEX for ethylene production is determined from the total overnight cost (TOC) and capital charge rate factor (CCF). The TOC is the sum of the EPC and COC. The CCF accounts for expenditures occurring in different time periods on a common value basis and defines the characteristic unit cost of the plant over its lifetime. It has been calculated based on financial assumptions (Table 2.10) and determined to be 0.10 for a conventional naphtha steam cracker (Spallina, et al., 2017).

$$CAPEX_{C_2H_4} = TOC * CCF$$

OPEX

The operating costs consider the feedstock costs, credits due to production of additional chemical co-products (e.g., benzene), variable O & M costs, and the import/export of electricity. The OPEX for ethylene production (Meuro/year) is therefore determined by,

$$OPEX_{C_2H_4} = \left(OPEX_{feedstock} + \sum \pm OPEX_{chem} + OPEX_{el} + OPEX_{O\&M}\right)$$

Assumptions for fixed and variable costs are listed in Table 2.10, and the calculated costs are summarized in Table 2.11.

Table 2.10 Assumptions for fixed/variable costs calculations as used by Spallina et al., 2017

Fixed/variable cost	Unit	Value
Inflation	%	3
Taxation rate	%	35
Depreciation (Year)	years	20
Debt interest rate	%	5
Revenue interest rate	%	15
Revenue fraction	%	40
Debt fraction	%	60
Construction Payment Years	years	3
→payment 1st year	%	40
→payment 2nd year	%	30
→payment 3rd year	%	30
Life time	years	25
Construction years	years	3
Labor costs	Meuro	5
Maintenance cost	% TOC	2.5
Insurance	% TOC	2

Table 2.11 Costs associated with a naphtha steam cracking plant (Spallina, et al., 2017)

Cost	Unit	Value	Source/comment
Bare equipment cost (BEC)	410	Meuro	Breakdown detailed in Table 2.12
Total installation cost (TIC)	328	Meuro	80% BEC; the corresponding installation costs of the equipment such as piping and assembly.

Total direct plant cost (TDPC)	738	Meuro	(BEC+TIC)
Indirect costs (IC)	103	Meuro	14% of TDPC
Engineering procurement and construction (EPC)	841	Meuro	(TDPC + IC)
Contingencies and owners costs (COC)	126	Meuro	(15% of EPC)
Total Overnight Cost	967	Meuro	(EPC + COC)
CAPEX	96.7	Meuro/y	(TOC*CCF)
OPEX (excluding feedstock and energy)	48.5	Meuro/y	Labour + maintenance + insurance costs

Shell considers the costs in this green field based calculation as too low. This can be substantiated by recent news on the investment in a less complex ethane cracker by INEOS in Antwerp. The cracker part investment amounted to 1.7 billion euro (De Tijd, 2019).

2.6.2 Other chemical production unit costs

This section reports the costs for other chemical production plants associated with Shell Moerdijk. Less specific data are available compared to steam cracking installations, therefore only the investment costs are summarized in Table 2.12. Reference investment cost data come from various literature sources and are adjusted to different capacities according to the following formula,

$$Investment\ cost = Investment\ cost_{ref} * \left(\frac{Capacity}{Capacity_{ref}}\right)^{n}$$

The exponent n can be in the range of 0.4 to 0.9, but for chemical equipment the Figure is averaged at 0.6 (Perry, Green, & Maloney, 1997).

Table 2.12 Investment costs for other chemical facilities associated with Moerdijk, reference capacity adjusted (Boulamanti & Moya Rivera, 2017)

Product	Capacity (kt/y)	Investment cost (MEUR$_{2013}$)
Aromatics[1]	1,070	54.8
Ethylene oxide	305	75.9
Mono-ethylene glycol	155	120.2
Ethylbenzene[2]	640	58.3
Styrene[2]	450	114.5

[1] Aromatics complex with production capacity of 655 kt/y paraxylene, 355 kt/y benzene, and 60 kt/y of toluene, Shell Moerdijk focuses on benzene production.

[2] For separate ethylbenzene and styrene units, Shell Moerdijk produces ethylbenzene which is exclusively used for the co-production of styrene monomer and propylene oxide.

3 LVOC production and use

The LVOC production chain is outlined to contextualize its position in the global and Dutch chemical industry. Raw materials such as natural gas and crude oil are refined into chemical feedstocks such as naphtha, which are transported by pipeline to Moerdijk where the reported processes in Chapter 2 transform them into several downstream products. Shell Moerdijk manufactures chemicals associated with several steps of the chain, from short chain building blocks, to more complex final products such as butadiene and styrene (EPCA, 2007). The following sections will describe in more detail the feedstocks and products handled at Moerdijk, including production volume/markets, applications and their chemical and physical properties.

3.1 Feedstock

In Europe, liquid feedstocks are more prominent than gaseous feedstocks and steam crackers are designed to facilitate a range, from lighter propanes/butanes to heavier gas oils (Koottungal, 2015). Heavier feedstocks produce higher percentages of co-products (e.g. butadiene, aromatic hydrocarbons), than lighter feedstocks such as ethane. The feedstock used will depend on market conditions and the availability of supplies (Falcke, et al., 2017; Zimmerman & Walzl, 2012). Since the prices of fuels are higher in Europe than in North America and/or the Middle East, the prices of co-products are also high and are thus more favorable to obtain (Boulamanti & Moya, 2017a). The main feedstocks in Europe comprise of naphtha, natural gas condensate, liquid petroleum gas (LPG), and gas oil (Figure 3.1), with naphtha holding the largest share. Furthermore, reaction conditions such as temperature, pressure, and steam requirements are dependent on the feedstock input. Therefore, the choice of feedstock not only impacts the product ratios but also the total process energy consumption and associated emissions (Falcke, et al., 2017; Zimmerman & Walzl, 2012).

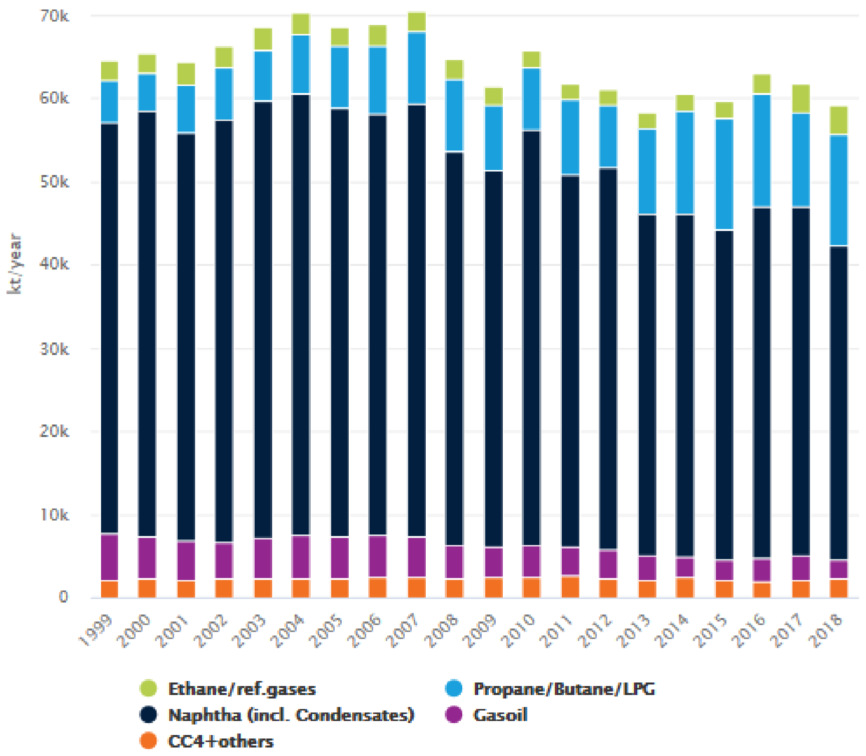

Figure 3.1 Cracker Feedstocks in EU15 + Norway for 1999-2018 (Petrochemicals Europe, 2020)

National statistics for the Netherlands indicate that naphtha represents approximately 50% the energy used as a feedstock, gas condensate for about 30%, and the remainder is mostly LPG (Figure 3.2). Rotterdam has a large market for gas condensates, which are mostly imported from Russia. The predominant feedstock used at Shell Moerdijk is naphtha (~80%) and LPG (~20%) (Saygin, Patel, Tam, & Gielen, 2009). This is comparable with feedstock mixes reported for the Benelux region where naphtha constitutes 81% of the feedstock mix, and the remainder being ethane, propane, and butane (~19%).

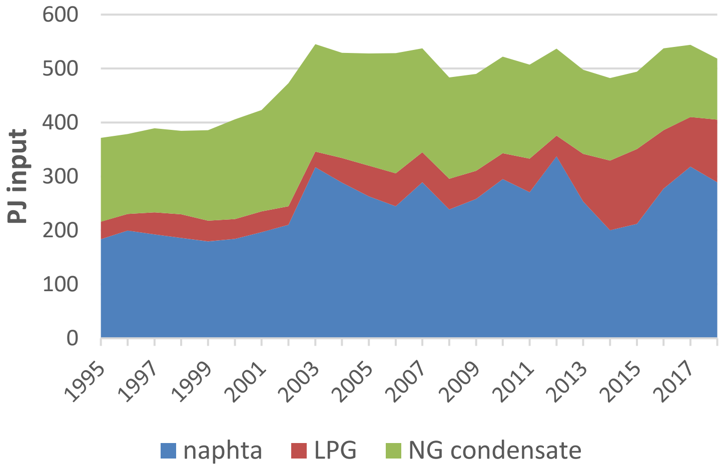

Figure 3.2 Feedstock input to Dutch crackers from 1995 – 2018 (CBS, 2020)

Table 3.1 shows the typical product yields (kt) for different feedstocks for a plant with an ethylene capacity of 453.6 kt/y (ACC, 2004). The cracking severity is assumed to be medium to high and depends on the desired product ratios. It indicates the conditions used for cracking and is a function of the temperature and residence time of the feedstock in the furnace (Boulamanti & Moya Rivera, 2017). Yields in Table 3.1 are representative of one feedstock entering the cracker, and with ethane and propane produced being recycled as a feedstock to extinction. Hydrogen is recovered and usually used in downstream hydrogenation reactions or hydrotreating of heavier products. The methane-rich gas is used as fuel gas internally.

Table 3.1 Typical yield of co-products from feedstocks for steam cracking process (ACC, 2004)

Product	**Feedstock**		
(kt)	**Propane (LPG)**	**Naphtha**	**Gasoil**
Ethylene	453.6	453.6	453.6
Propylene	166 – 296.5	199 - 222	183 - 196
Butadiene	18 – 32	56 – 77	76 – 82
Butenes/Butanes	13 – 22	60 – 128	78 – 88.5
Pyrolysis gasoline	47 – 71	183 – 494	294 – 342.5
Benzene	17 – 26.5	51 – 84	96 – 109
Toluene	5 – 5.5	19.5 – 71.5	51 – 54.4
C_8 aromatics	0	26.5 – 43	20 – 43
Other	25 – 39	86 – 295	127 - 136
Fuel oil	4.5 – 10	29.5 – 51	289 – 376.5
Methane-rich gas	263 – 296.5	199 – 222	183 – 196
Hydrogen-rich gas	17 – 21	11 – 14	12 – 26.5
Total	982 – 1,200	1,173 – 1,670	1,614 – 1,822
Ethylene yield (%)	38 – 46	27 – 39	25 - 28

Naphtha is a refinery fraction comprised of a combination of C_5 – C_{11} aliphatic hydrocarbons and has a boiling range between 35 – 190 °C. It is a colourless aromatic liquid and obtained as the raffinate from a solvent extraction process, therefore can also be referred to as "solvent-refined naphtha" or C_6 raffinate. Depending on refinery conditions and source, it can vary in composition and is typically processed as light naphthas (boiling range 35 – 90 °C), heavy naphtha's (90 – 180 °C), and full range naphthas (35 – 180 °C) (Zimmerman & Walzl, 2012).

Table 3.2 Chemical components of naphtha produced at Shell (Shell, 2020a)

Chemical name	**Concentration (%)**
n-Hexane	≥ 10 - ≤ 30
Cyclohexane	≥ 5 - ≤ 10
Pentane	≥ 0 - ≤ 5
Benzene	≤ 1

Liquid Petroleum Gas (LPG) is defined as a group of hydrocarbon gases derived from crude oil or natural gas refining, which can be compressed into liquid form at low pressures. It can be a mixture of ethane, ethylene, propane, propylene, butane and butylenes (ACC, 2017). In Europe, LPG is generally a blend of propane, and the exact composition varies depending on the country and time of year. It is reported to be comprised of 60:40 to 70:30 propane to butane for Belgium and Denmark, respectively (myLPG, 2018). Besides its use as a petrochemical feedstock, it is also used as a fuel in heating or cooking, in refrigerants, or in aerosols (Elgas, 2018).

Gas condensates and natural gas liquids (NGLs) are liquid mixes of mostly ethane, propane, butanes and pentanes (Keller, 2012). They are separated from natural gas production by lowering pressure and temperature during or after production. They differ in composition, depending the specific gas field situation and subsequent degassing, stabilizing and purification steps. There are not only gas fields but also gas condensate fields in the subsurface. As a rule, gas condensate is a transparent fluid, but the color can change from straw to almond due to oil admixtures depending on the depth from which it was extracted. Gas condensate is sometimes called "white oil" and can be used as fuel or feedstock for chemicals. In 2016, 2017 and 2018, the Gazprom Group produced 15.9 million tonnes of gas condensate. Reserves of gas condensate owned by Gazprom amount to 1.3 billion tonnes (Gazprom).

Table 3.3 Physical and chemical properties of naphtha and LPG

Feedstock Physical/chemical properties	Naphtha (Shell, 2020a)	LPG (propane) (Elgas, 2018)
Appearance	Liquid	Liquid
Colour	Colourless	Colourless
Odour	Aromatic	Odorless
Melting/freezing point (°C)	N/A	-188
Boiling point/range (°C)	Approx. 35 – 180	-42
Molecular weight (g/mol)	N/A	44.1
Reactivity	Reacts with strong oxidising agents.	Reacts with strong oxidising agents.
Conditions/materials to avoid	Avoid heat, sparks, open flames and other ignition sources. In certain circumstances product can ignite due to static electricity.	Avoid heat, sparks, open flames and other ignition sources. In certain circumstances product can ignite due to static electricity.

3.2 Products

The chemicals produced at Shell Moerdijk can be classed as "Bulk Petrochemicals and Organic Intermediates". They are derived from hydrocarbon feedstocks and therefore characteristically feature a carbon molecule. Bulk petrochemicals include olefins (short chain hydrocarbons), aromatics (molecules with a six-carbon ring structure) and methanol, and are associated with over 90% of all organic chemical production (ACC, 2017). After World War II, the demand for olefins accelerated as their contribution to gasoline quality, and use as a chemical precursor to polymers were discovered (Weissermel & H-J., 2008). Favorable properties include their high reactivity and their numerous uses as chemical building blocks in downstream processes. It is estimated that over 85% of olefins produced are used in polymer production (Wesseling & Deng, 2009). Other co-products such as aromatics, fuel gases and hydrogen are of value as they can be sold, recycled, or used in other reactions (Falcke, et al., 2017).

3.2.1 Ethylene

Ethylene is one of the largest volume commodity chemicals produced globally. It is predicted that by the end of 2018, approximately 20 Mt of ethylene will be produced by Western Europe. Its various applications include the packaging, construction, agrochemical, textile, and automotive industries (Figure 3.3) (ACC, 2017). The single largest use of ethylene (~60%) produced in Western Europe is for production of different types of low-, linear low- and high-density polyethylene. From 2011-2016, global ethylene consumption increased at an average rate of 3% per year and the global capacity grew at around 2%, which therefore led to higher utilization rates of steam crackers. Growth is expected to continue for the next five years. The recent ban on waste material imports into mainland China is bound to further support incremental demand growth for virgin plastic material such as polyethylene (IHS Markit, 2015-2020).

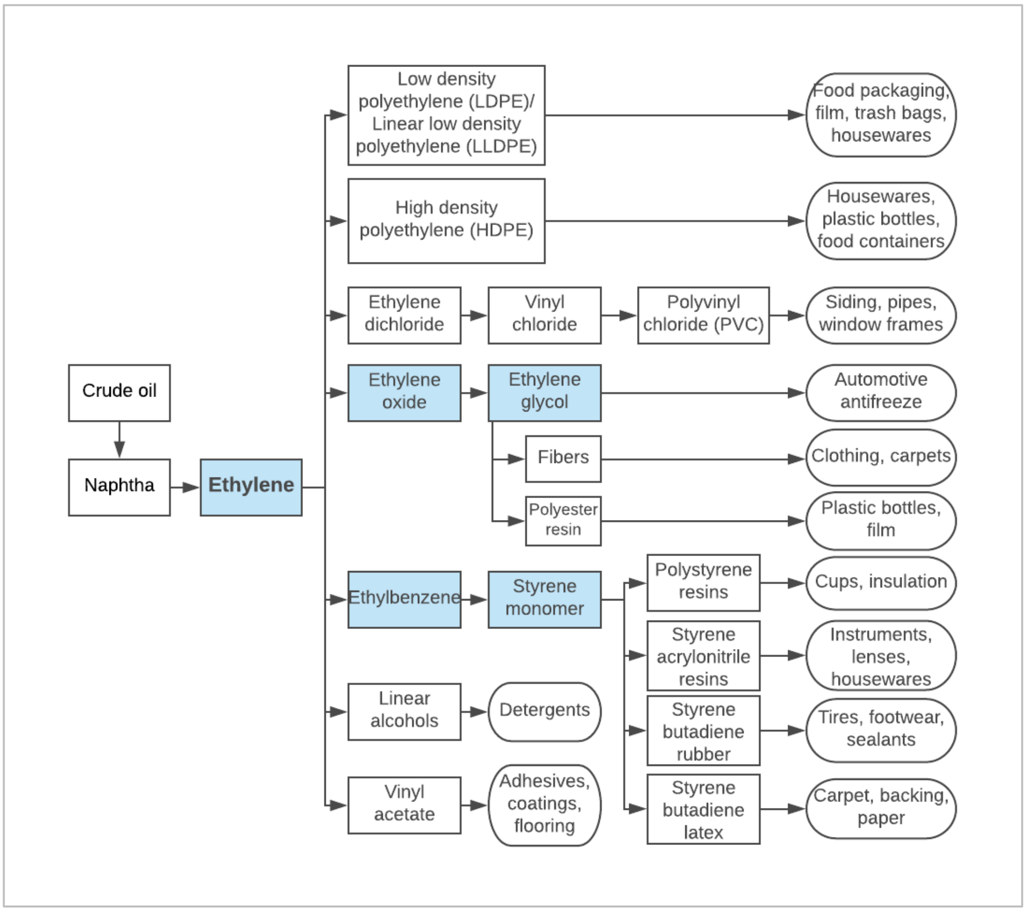

Figure 3.3 Production chain for ethylene, blue boxes indicate chemicals produced at Shell Moerdijk (adapted from ACC, 2017)

3.2.2 Propylene

After ethylene, propylene is the second most-produced building block in the chemical industry. Historically, it is obtained as a co-product from steam cracking for ethylene, however in recent years industry has even turned to “on-purpose” propylene technologies in order to satisfy demand (IHS Markit, 2015-2020). Its production is largely driven by polypropylene and propylene oxide demand, which are used in resins and fibers and found in important materials such as textiles, packaging, and pipes. As seen in Figure 3.4, is also used extensively to produce other specialized chemicals with the most prominent being; propylene oxide, acrylonitrile, cumene, and various alcohols (ACC, 2017; IHS Markit, 2015-2020). In Western Europe, 70% of propylene is obtained from steam crackers with a total nameplate capacity of 12,140 kt/year in 2014 (Falcke, et al., 2017; Boulamanti & Moya Rivera, 2017).

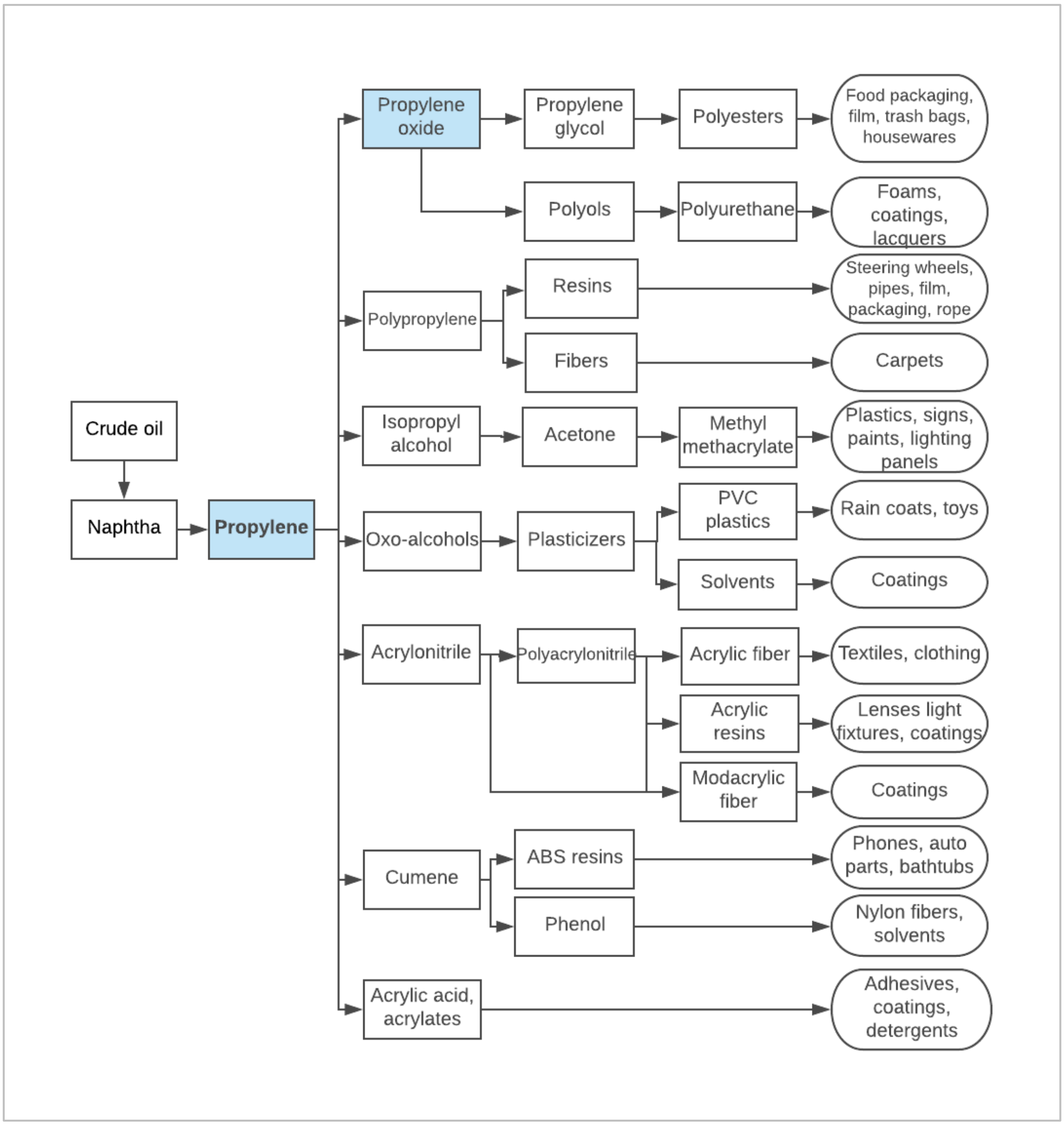

Figure 3.4 Production chain for propylene, blue boxes indicate chemicals produced at Shell Moerdijk (adapted from ACC, 2017)

3.2.3 C_4 hydrocarbons

The C_4 hydrocarbon chain is complex, given the multiple uses and process routes of its respective components. Around 90% of butadiene extracted is used for production of synthetic rubbers, which are highly flexible materials with many uses. The automotive and construction sectors are the primary consumers, using C_4 derivatives to make tires, auto parts, and pipes (ACC, 2017). Furthermore, C_4s such as butane can be recycled from the cracked stream and be reused as feedstock, or fuel to produce ethylene (Figure 3.5).

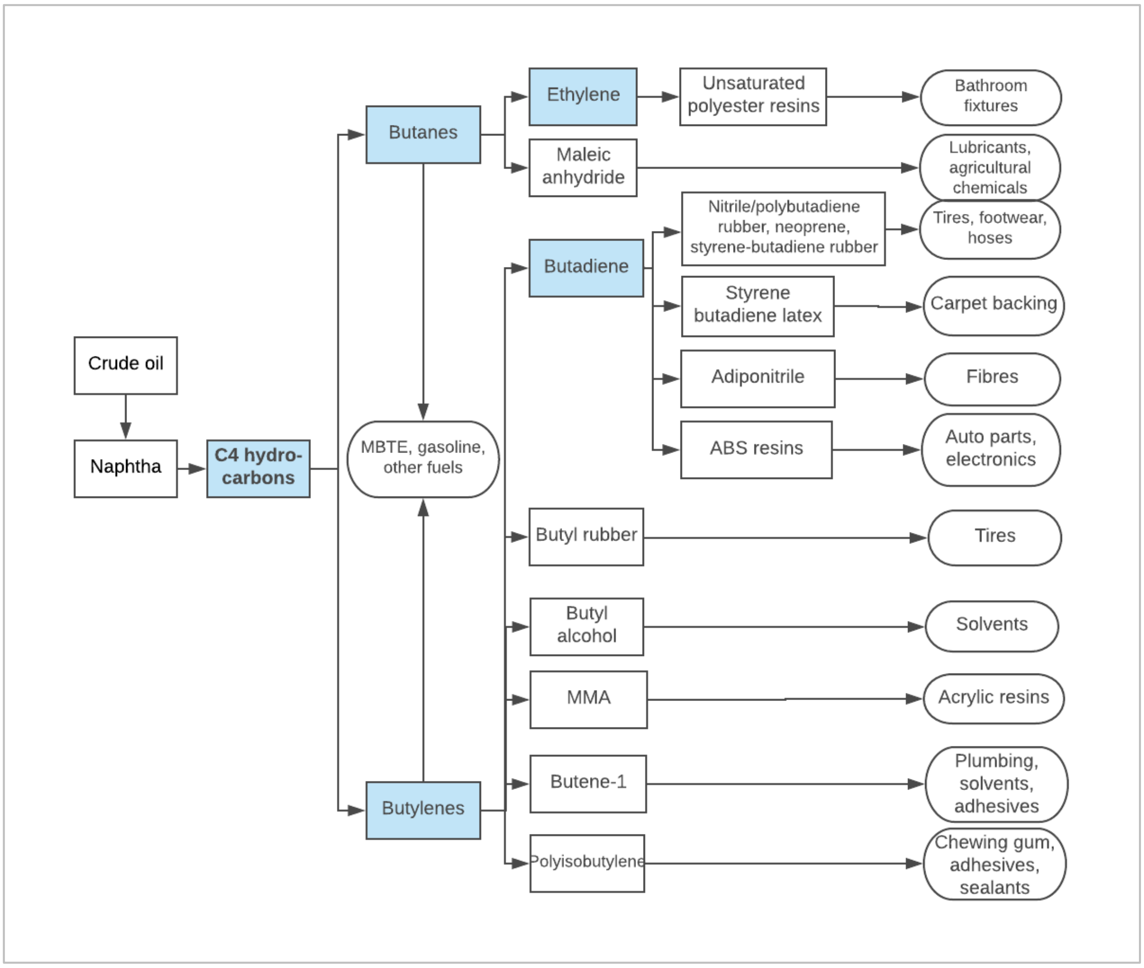

Figure 3.5 Production chain for C4 hydrocarbons, blue boxes indicate chemicals produced at Shell Moerdijk adapted from (ACC, 2017)

3.2.4 Aromatics (Benzene)

In the chemical industry, the term “aromatics” is predominantly used to describe benzene, toluene, and xylenes, otherwise known as “BTX” chemicals. They have the common characteristic of an aromatic six carbon ring, which gives them a specific odor. One of their main uses are in the production of polymers, and multiple consumer products including, solvents, paints and polishes. BTX chemicals are often obtained together from different fractions of oil distillation, therefore referred to as a group. In the Netherlands, the capacities for benzene, toluene, and xylene were 2.5 Mt, 0.3 Mt, and 1.1 Mt respectively in 2013 (Boulamanti & Moya Rivera, 2017). Shell Moerdijk concentrates on benzene extraction; therefore, this section will describe its production chain only (Shell, 2018a).

Benzene is produced in the largest volumes out of the aromatic chemicals. In 2013, global production reached 42.7 million tonnes, with Western Europe, China, and the US responsible for about half the total world consumption (IHS Markit, 2015-2020). Previously, it was added to gasoline to increase the quality, however due to its toxicity it has since been regulated. The maximum amount of benzene in petrol is limited to 1% v/v (EU, 2009). It is mainly consumed as a chemical feedstock, where 70-75% of the produced benzene is applied in ethylbenzene and cumene production (IHS Markit, 2015-2020), and it is also an important feedstock for cyclohexane and aniline production. Ethylbenzene is used to produce styrene and consequently polystyrene, while cumene is used to produce phenol and acetone.

Therefore, the demand for aromatics like benzene is strongly linked to consumer demand for plastics. It is reported that the rate of benzene consumption is expected to grow annually by 2.9% until 2023 (IHS Markit, 2015-2020). The full production chain for benzene is shown in Figure 3.6.

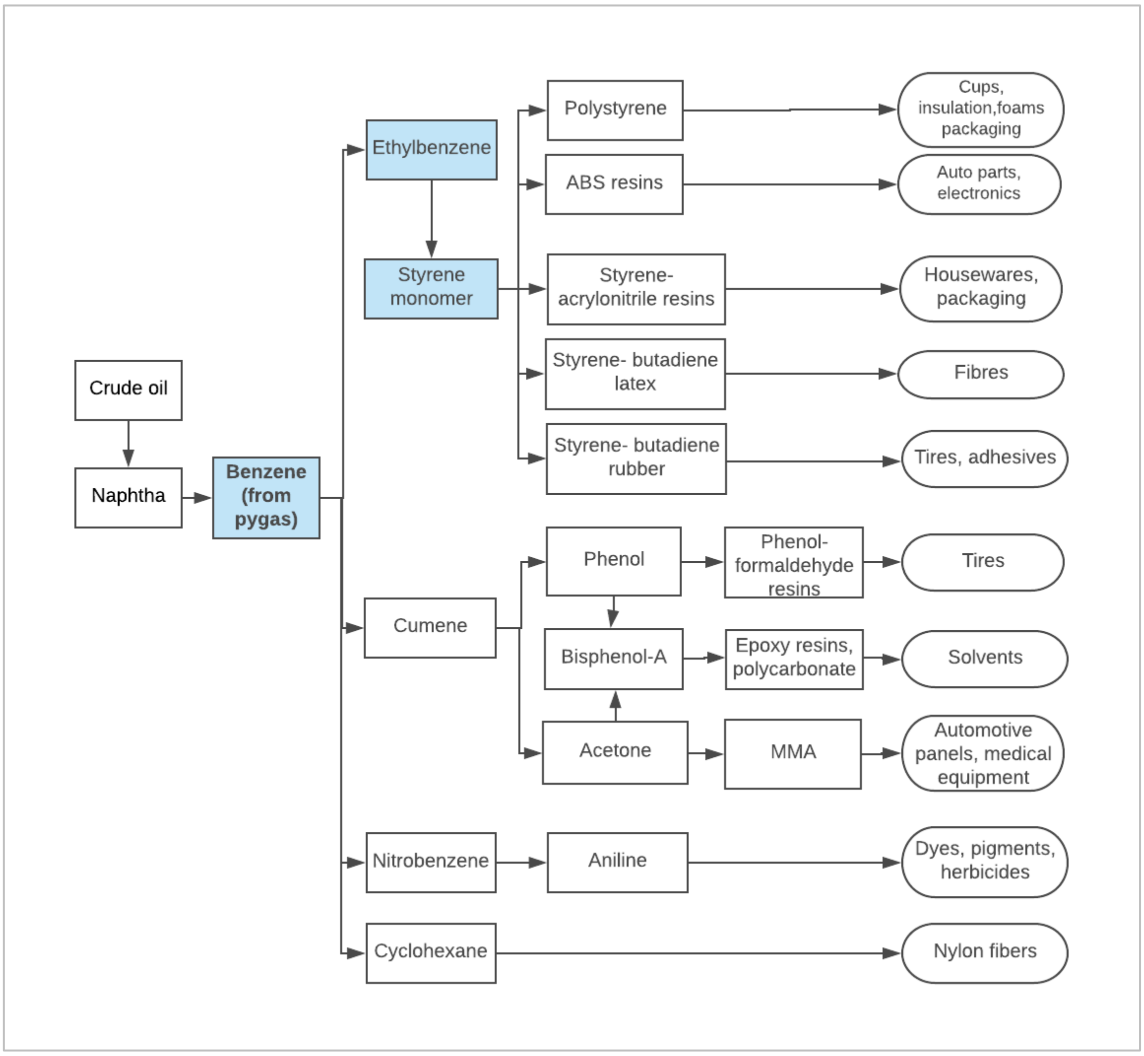

Figure 3.6. Production chain for benzene, blue boxes indicate chemicals produced at Shell Moerdijk (adapted from ACC, 2017)

Historically benzene was obtained as a by-product from coal during coke production for the steel industry. New production methods were established in the 1930s, and presently the two main feedstocks for aromatic production are pyrolysis gasoline (pygas) and reformate from reformers (Ecofys; Fraunhofer ISI; Oeko-Institut, 2009). Most of aromatics originate from refinery reformate and pyrolysis gasoline from steam cracking, and less than 4% from coke oven plants. BTX extraction units are usually built in close proximity to or inside a refinery. At Shell Moerdijk the unit is linked to the steam cracker, from which the aromatic-rich pyrolysis gasoline can be sourced easily. Pyrolysis gasoline typically contains high amounts of benzene and toluene, and the aromatic yield depends on the feedstock. It contains still high amounts of olefins, but low amounts of xylenes, making it more suitable for benzene or benzene/toluene extraction (Table 3.4).

Table 3.4 Typical composition of raw pyrolysis gasoline (Thyssen-Krupp, 2014)

Component (% w/w)	Pygas
Benzene	30
Toluene	20
Xylenes	4
Ethylbenzene	3
C_{9+} aromatics	3
Naphthenes	High
Olefins	High
Paraffins	Low
Sulphur	Up to 1,000 ppm

Table 3.5 summarizes the physical and chemical properties of the lower olefins and benzene produced at Shell Moerdijk, as listed in material safety data sheets.

Table 3.5 Physical and chemical properties of lower olefins and benzene (Shell, 2020a)

Product				
Physical/chemical properties	**Ethylene**	**Propylene**	**Butadiene**	**Benzene**
Appearance	Gas at standard temperature and pressure	Liquid under pressure	Liquid under pressure	Liquid
Colour	Colourless	Colourless	Colourless	Colourless
Odour	N/A	Faint	Mild aromatic	Aromatic
Melting/freezing point (°C)	-169.2	-185.2	-108.9	5.5
Boiling point (°C)	-103.7	-47.7	-4.4	80.1
Molecular weight (g/mol)	28	42	54.1	78.11
Reactivity	Reacts violently with strong oxidising agents, hydrochloric acid, hydrogen bromide and nitrogen oxides.	Reacts violently with strong oxidising agents. Polymerisation may occur at elevated temperatures.	Oxidises on contact with air to form unstable peroxides. Unstable at elevated temperatures	Stable under normal conditions of use.

3.2.5 Ethylene oxide and glycol derivatives

Ethylene oxide (EO) is one of the most important raw materials used in large-scale chemical production. As of 2016, there were 12 production sites for EO in the EU-28, with two of the sites located in the Netherlands equaling a total capacity of 470 kt/y (ICIS, 2013). It contains a strained epoxy group (C-C bond triangulated with oxygen) which is very reactive, and therefore commonly used as an intermediate in chemical production. It can be used as a disinfectant, sterilizing agent, or as a fumigant. However, most ethylene oxide is used for synthesis of mono-ethylene glycol (MEG), and its by-products; di-ethylene glycol (DEG) and tri-ethylene glycol (TEG), together accounting for up to 75% of global consumption. At Moerdijk, Shell delivers also ethylene oxide to Solvay Solutions Nederland B.V., which produces a large range of specialty chemicals, including surfactants and polymers (Solvay Solutions, 2018).

Ethylene glycol production is driven by demand for resins for PET products, polyester fibres and films. Its properties make it also useful in textiles treatment, adhesives, inks and cellophane. A large part of MEG produced is used for PET production, which is converted into plastic bottles. Another large market for MEG is in anti-freeze applications including coolants, aircraft anti-icer, and de-icers (IHS Markit, 2015-2020). EG is a derivative of EO therefore the EO and EG production plants are typically located close together. The EO process is a net energy producer while the MEG process is a net energy consumer, therefore plants are generally integrated to improve efficiency (Boulamanti & Moya Rivera, 2017). The EO/EG product chain is included in that for ethylene (Figure 3.3). Table 3.6 summarizes the physical and chemical properties of the EO and EG, as listed in material safety data sheets from Shell.

Table 3.6 Physical and chemical properties of ethylene oxide and ethylene glycol

Product Physical/chemical properties	Ethylene oxide (Shell, 2020a)	Ethylene glycol (Shell, 2020a)
Appearance	Liquid under pressure	Slightly viscous liquid
Colour	Clear	Colourless
Odour	Ethereal, sweet	Mild
Melting/freezing point (ºC)	-112	-13
Boiling point/range (ºC)	10.6	196 - 200
Molecular weight (g/mol)	44	62
Reactivity	Pure EO or EO vapour mixed with air or inert gases can decompose explosively. Reacts exothermically with bases, alcohols, water and acids	Oxidises on contact with air.
Conditions/materials to avoid	Heat, flames, and sparks. Temperatures above 30 °C / 86 °F. Prevent vapour accumulation.	Extremes of temperature and direct sunlight. Strong oxidising agents. Strong acids and bases.

3.2.6 Ethylbenzene, styrene monomer and propylene oxide

Globally, nearly all ethylbenzene (EB) (> 98%) is consumed as an intermediate for styrene monomer (SM) production, and therefore its demand is driven by demand for SM. SM is the main feedstock in the manufacture of styrene-based polymers. These include polystyrene (PS), expandable polystyrene (EPS), styrene copolymers such as acrylonitrile-butadiene-styrene (ABS) resins, styrene-acrylonitrile (SAN), acrylonitrile-styrene-acrylate (ASA), styrene-butadiene (SB) latexes, styrene-butadiene rubber (SBR) and unsaturated polyester resins. Around half of styrene consumption globally is used in PS manufacture (ICIS, 2011). Global demand for both EB and SM are projected to increase at a rate of 2% per year up to 2022 (IHS Markit, 2015-2020).

Consumer articles derived from PS include food packaging, plastic cutlery, and hot beverage cups. Expandable PS is extensively used in the building and construction sector as thermal insulation panels (Ecofys; Fraunhofer ISI; Oeko-Institut, 2009) and for packaging. In the Netherlands, there are 12 manufacturers of expandable PS products equating an annual production of 210 kt. Plastics derived from PS (general purpose PS and high-impact PS) are produced at approximately 180 kt/y, while co-polymers such as acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile are produced annually at 163 and 30 kt respectively. Styrene-butadiene rubber is also produce in large volumes (170 kt/y) and is the precursor for tire manufacture. It is also used in other automotive parts such as drive belts. Styrene production is closely linked to ethylene and benzene production, therefore its product chain (including ethylbenzene) is incorporated into that for ethylene (Figure 3.3) and benzene (Figure 3.6). The PO product chain is included in that of propylene (Figure 3.4).

Commercially there are two principal production pathways to produce SM; dehydrogenation of ethylbenzene, and via the co-production of propylene oxide (PO). Both processes are employed in the Netherlands, with Trinseo operating the dehydrogenation process, and Shell and Lyondell Basell using the co-production method (Table 3.7). The co-production route involves large capital investment and higher production costs, however it has the benefit that both the SM and PO product can be sold (Boulamanti & Moya Rivera, 2017).

Table 3.7 Capacity and production routes for Dutch producers of EB and SM (Falcke, et al., 2017; Yong Min Feng & Keys, 2020)

Company	Location	Ethylbenzene (kt/y)	Styrene via EB dehydrogenation (kt/y)	Styrene via co-production with PO (kt/y)
Lyondell Basell	Maasvlakte	994	NA	864
Trinseo	Terneuzen	550	250	NA
Shell	Moerdijk	640	NA	990

As listed in Table 3.7, there are two plants at Shell Moerdijk (SM/PO 1 & SM/PO 2) that follow the co-production route. SM and PO have been produced for over three decades at Shell, using its proprietary SM/PO process. The benzene production on site in Moerdijk can largely cover the required input for both units. The physical and chemical properties of EB, SM, and PO are listed in Table 3.8.

Table 3.8 Physical and chemical properties of SM and PO

Physical/chemical properties	Product		
	Ethylbenzene (CDH, 2020)	**Styrene monomer (Shell, 2020a)**	**Propylene oxide (Shell, 2020a)**
Appearance		Oily liquid	Oily liquid
Colour	Colourless	Colourless to yellowish	Colourless to yellowish
Odour	Aromatic	Aromatic hydrocarbon	Ethereal
Melting/freezing point (°C)	-95	-31	-112
Boiling point/range (°C)	136	145	35
Molecular weight (g/mol)	106.17	104.15	58.01
Reactivity	Highly flammable. Reacts with strong oxidising agents.	Polymerises with risk of fire and explosion. Reacts with strong oxidising agents.	Will polymerise at elevated temperatures (50 ºC) or if contaminated with water. Reacts violently with strong oxidising agents and acids.
Conditions/materials to avoid	Heat, flames, sparks, strong oxidizing agents	Heat, flames, and sparks. Exposure to sunlight and/or air. In certain circumstances product can ignite due to static electricity.	Heat, flames, and sparks. Prevent vapour accumulation.

4 Options for decarbonisation

The following are proposed as potential options for reduction of energy use and/or CO_2 emissions for LVOC production at Shell Moerdijk. Table 4.1 shows the options applied to processes which are described in Chapter 2. The options are focused on the MLO unit, given that it is the largest source of emissions on the site, and the products from this unit are the main input sources for the MEOD and MSPO units.

Table 4.1 Main potential decarbonisation options for units/sections at Shell Moerdijk

	MLO	MEOD	MSPO	Utilities
Energy efficiency				
Coalesce-filtration systems furnace	x			
Heat integration in distillation columns and heat pumps	x	x	x	
Membranes	x			
Heat recovery and use	x	x	x	x
Improved process control	x	x	x	
Omega process		x		
Electrification				
Electrification furnaces	x		x	
Electrification compressors	x			
Hydrogen as fuel				
Hydrogen-fired furnaces	x			
Feedstock and process substitution				
Biomass to bio-ethylene	x			
Methanol to olefins	x			
Hydro pyrolysis of naphtha	x			
Carbon capture, storage, utilisation				
CCS, post combustion	x		x	x
CCS-U high concentration		x		

4.1 Energy efficiency

Autonomous energy efficiency improvements are expected to contribute to an annual yearly increase of 0.5 – 1% (Ecofys; Berenschot, 2018). The options detailed in this section are in addition to this yearly increase. CEFIC, the European Chemical Industry Council, gives an overview in its 2013 roadmap. For existing cracker sites, the energy efficiency is expected to improve by 14-21% (2030) and by 23–34% (2050) compared to 2010 (CEFIC, 2013). The recently announced plans for replacing the 16 oldest furnaces built in 1972 with 8 new ones is said to reduce CO_2 emissions by 10% (Petrochem, 2020). The options described below may be part of the energy efficiency improvement.

Due its large share of energy consumption in the process, many efforts are concentrated on improving heat transfer and severity in the MLO pyrolysis section. Options related to increasing energy efficiency or reducing emissions in the pyrolysis section are described below.

4.1.1 Coalesce-filtration systems

Contaminants in the inlet hydrocarbon stream may promote coke formation and reduce efficiency. Frequent decoking cycles decreases furnace tube lifetime, cause particulate emissions to air, lowers ethylene production, and increase maintenance costs. Novel high efficiency coalesce-filtration systems can be installed to extend the run length of the furnaces by reducing coking (Brayden, Wines, & Del Guidice, 2006). Due to less decoking operations throughout the year, lifespan of the tubes increases, while particle and GHG emissions are avoided. Total investment costs including installation costs for installing the system was estimated at 1,5 M$\$_{2004}$. Annual operating costs were determined to be >10% of the capital plus installed cost. The coalescers have a lifetime of 2 years, and the pay-back period was estimated to be less than 10 months. Overall, improvements to the pyrolysis section are estimated to provide energy savings on the current SEC of approximately 10%, or 2-3 GJ/t ethylene (Nieuwlaar, 2001).

4.1.2 Heat recovery

Based on literature, heat recovery via heat exchangers can capture and reuse heat to improve efficiency of the process. Improved designs with higher temperature and pressure tolerances may lead to energy savings. At a process level, heat recovery may deliver up to 4% savings in fuel use (or 1,1 GJ/t ethylene savings). Indicative investment costs are 1.7 EUR/t ethylene which equals a total investment cost of 1.5 Meuro (Worrell, Phylipsen, Einstein, & Martin, 2000). Shell doubts if this potential would still apply to the optimized Moerdijk site.

4.1.3 Heat pumps

Heat pump technologies such as Heat Integration in Distillation Columns (HIDiC) can be used in units which employ distillation columns. In the case of Shell Moerdijk, distillation columns are used after pyrolysis in the separation section of the MLO unit (as described in chapter 2). Furthermore this option could be considered for the MEOD and MSPO unit where distillation is used to separate the desired products.

The technology involves placing heat exchangers between the rectifying and stripping sections to improve heat transfer, and can be applied to the de-ethanizer and the de-propanizer sections (Ren, 2009). As a result, the number of distillation columns required is reduced and the quality of the final ethylene product is not altered. Energy savings for this section are in the range of 60-90%, or 0.1-0.3 GJ/t ethylene. The primary energy usage is as measured at 0.59 MW compared to 2.49 MW in conventional columns (Nakaiwa, et al., 2003). A further 0.15 GJ/t ethylene can be saved if upgraded with a heat pump on a modern installation (Ren, 2009). The CAPEX and OPEX are 1,393 kEUR and 104 kEUR/y, compared to 468 kEUR and 536 kEUR/y for conventional columns. It is expected that process integrated heat pumps will be in the pilot stage for medium-scale distillation processes by 2025, and high temperature heat pumps being demonstrated by 2030 (ECN, 2018). Mechanical vapor recompression was also suggested as an alternative for the propylene/propane splitter (Ren, 2009). According to Shell, the site is already largely integrated, so this potential may not exist at Moerdijk.

4.1.4 Adsorption heat pumps

Waste heat can be used in an adsorption heat pump (AHP) to generate cooling water for the process. Currently, heat pump options are expected to be feasible for low and medium temperature heat processes, therefore could be applied to compression and separation sections. They can be stand-alone, delivering heat to a process, but also process integrated. Their applications are expected to steadily grow until 2050, at which time commercial deployment is achieved. An AHP designed by Mitsubishi Plastics Inc. is reported to give energy savings of up to 12% in the compression section by replacing the propylene refrigerant. The investment costs which include equipment costs and installation costs for retrofitting a steam cracking plant, are estimated at 7.4 $M\$_{2011}$ (Hirata & Kakiuchi, 2011).

4.1.5 Membranes

Membranes made of polymer or inorganic materials can be applied to the C_2 and C_3 separation section to separate olefin/paraffin, gases and coke/water. Currently their application is limited to hydrogen recovery from cracked gas (Staudt-Bickel & Koros, 2000) (Al-Rabiah, 2001). However, it is a relatively immature technology that is unable to endure severe operating conditions, therefore regular replacement is needed. 8% energy savings or 1.5 GJ/t ethylene are estimated (Ren, Patel, & Blok, 2006). Furthermore, net power savings are around 9.3 MW which translates to 2.9 $M\$_{2001}$/year, and it requires a capital investment of 13.5 $M\$_{2001}$.

4.1.6 Process control sensors (overall process)

Process control systems and sensor technology can be implemented to not only improve energy efficiency but also can reduce downtime, maintenance costs, processing time, and improve emissions control. They can lead to final energy savings of 3% and investment costs are in the range of 1 to 13 EUR/t ethylene (Worrell, Phylipsen, Einstein, & Martin, 2000).

4.1.7 OMEGA process (EO/EG production)

Shell applies two processes for EO and EG production: the Shell MASTER process and the Shell OMEGA process (ICIS, 2008). The former is based on a high-selectivity EO catalyst and thermal conversion of EO to ethylene glycols. The latter is also based on a catalyst but an only-MEG producing technology. The MASTER process is a traditional process, the OMEGA process is more innovative. It is designed to use the CO_2 produced during the EO reaction, so as to convert EO into ethylene carbonate, which is then treated with water to produce MEG, without the presence of higher glycols (Chemicals Technology, 2009). At Moerdijk, EO is produced by the conventional Shell technology, using a proprietary silver-based catalyst. This process is expected to have a selectivity of 90 % with ethylene conversion of 10-15 %, while the yield of MEG is as high as 99 %. Ethylene consumption is estimated to be 0.51

t/tMEG, (Chemicals Technology, 2009) compared to 0.63 t/tMEG of the conventional method. Capital investment is estimated to be 15 % less than for the conventional process for a 400 kt MEG plant (Naqvi, 2009) and in 2004 it was estimated to be at USD 120-160 million for a 600 kt/y MEG plant, corresponding to 135 million EUR_{2013}. The process consumes 20% less steam than the conventional thermal conversion, but 10 % more electricity compared to the standard process. This process is fully commercialised with a 400 kt/y plant in Korea, a 600 kt/y plant in Saudi Arabia and a 750 kt/y plant in Singapore (Boulamanti & Moya Rivera, 2017).

4.1.8 Summary

Table 4.2 summarises various energy efficiency options for MLO from literature. Numbers are indicative and are site specific for existing plants. Also the recently announced furnace replacement is included for comparison.

Table 4.2 Summary of technologies with energy/CO_2 savings potential for LVOC production

Technology	Energy savings (GJ/t ethylene)	CO_2 savings (tCO_2 avoided/t ethylene)[1]	Investment costs mln (EUR)	O&M costs (EUR)[2]	Lifetime (years)	Source
HiDiC (+ heat pump)	0.15	0.007	3	0.3	20	(Ren, Patel, & Blok, 2006); (Nakaiwa, et al., 2003)
Heat recovery	1.12	0.054	1.6	NA	10	(Worrell, Phylipsen, Einstein, & Martin, 2000)
Process control sensors	0.84	0.041	6.4	0.6	20	(Worrell, Phylipsen, Einstein, & Martin, 2000)
Coalesce-filtration	2.50	0.122	1.5	0.15	2	(Boulamanti & Moya Rivera, 2017)
Mechanical vapor recompression PP splitter	1.00	0.048	0.5	0.05	20	(Ren, 2009; Boulamanti & Moya Rivera, 2017);
Membranes	1.50	0.073	13.5	1.3	2	(Ren, Patel, & Blok, 2006)
Adsorption heat pumps	0.50	0.025	7.4	0.7	20	(Boulamanti & Moya Rivera, 2017)
Shell furnace replacement plans[3]	4.7	0.3	200 to 400		40	(Petrochem, 2020) Data are not checked.

[1] Based on an emission factor of 48.7 kg/GJ for the chemical industry.

[2] O&M costs are assumed to be 10% of investment costs if data was unavailable.

[3] Several hundred mln euro was announced. The 10% CO_2 reduction referred to the entire site.

4.2 Electrification

Electric furnaces have the potential to significantly reduce the energy consumption of the process, while eliminating energy related emissions, provided that the required electricity is renewable (Ecofys; Berenschot, 2018). Heating technologies with relatively low CAPEX, such as resistance and electric arc heating, can be operated flexibly to utilize periodic low electricity prices. High temperature (above 500 °C) electric heating is currently in the research phase, with the first applications being expected by 2030. A pilot project initiated by several major chemical companies will be started at the Chemelot site (VNCI, 2019). Shell and DOW have recently set up cooperation on electric cracking technology development (Shell, 2020). Industrial-scale electric furnaces are not commercially available, but key processes such as cracking are expected to deploy electric heating by 2050 (Roelofsen, Speelman, Pee, & Witteveen, 2017; Van Kranenburg, et al., 2016). As in the case for Shell Moerdijk, commercial production sites are highly integrated, therefore changes to one part of the process results in modifications needed in other parts of the process. For example, electrifying a steam cracking furnace will require the amount of methane produced by the cracker to find other applications. Moreover, further research should be carried out to determine whether the grid can support the large increases in demand for renewable electricity.

The steam driven compressors in the separation section may also be replaced by electric compressors. Currently, steam for these compressors is generated from quenching the main cracked gas flow. Similarly, this would require a redesign of the steam system in the MLO to reduce steam production in the utilities plant. In 2019, a steam driven motor was replaced in the MSPO-1 section. This project is said to reduce CO_2 emissions by 13 kt (Shell, 2019). This would be equivalent to around 0.2 PJ avoided steam use. Extra electricity consumption is in the range of 0.1 PJ with around 3 MW motor capacity.

4.3 Hydrogen as fuel

In order to reduce GHG emissions at Shell Moerdijk, the natural gas used as fuel could (at least partially) be replaced by low-carbon hydrogen. Steam methane reforming or autothermal reforming of natural gas, combined with CO_2 capture and storage (blue hydrogen) is a promising candidate for this. The possibility of producing blue hydrogen for at least four large steam cracker furnaces at Shell Moerdijk (360 MW combined) is discussed in the feasibility report of the H-vision initiative in the Rotterdam area (H-vision, 2019). The conversion costs of these furnaces is estimated to be similar to the costs of converting the refinery furnaces (Oliveira & Schure, 2020), which is about 150 kEUR/MW. Another pipeline between the Rotterdam blue hydrogen plant and Shell Moerdijk would be necessary, which is not included in these costs. Additional 650-700 MW of furnaces could be fueled by hydrogen, but this requires more complex furnace modifications (H-vision, 2019). In the longer term, hydrogen based on electrolysis of water with renewable electricity (green hydrogen) can replace blue hydrogen.

4.4 Feedstock/process substitution

This section describes options which involve the substitution of the feedstock or entire process to obtain olefins. They are differentiated from the above options since they require major rebuilds or replacement of the entire process. The previous options can be more generally regarded as retrofits to the existing processes and may be more attractive for investment decisions. It is worth mentioning them as potential routes to obtain the desired olefin products while incurring lower emissions and/or energy use. Below is a selection of alternative processes. Waste based processes are included in the MIDDEN report about decarbonisation options for LVOC production at Sabic Geleen (Oliveira & van Dril, 2020) and on PE and PP production (Negri & Ligthart, 2020).

4.4.1 Biomass to bio-ethylene

Biomass can be used to produce ethylene, but the feedstock requires several intermediate transformations. Sugar- or starch-rich biomass can be fermented to a bioethanol feedstock which is then dehydrated over an alumina/silica-alumina catalyst to produce bio-ethylene (Figure 4.2). One tonne of bio-ethylene produced requires 1,74 tonne of ethanol and significantly higher energy requirements compared to conventional naphtha steam cracking (IEA, 2013). Moreover, to determine the amount of CO_2 saved requires a specific analysis on the type of biomass used and the local production logistics and infrastructure. Assuming wood is used, the bioethanol synthesis step is estimated to produce around 1 t CO_2eq/t ethylene, and the following conversion to ethylene emits approximately 0.2 t CO_2eq/t ethylene. Considering the biogenic carbon sequestered in the process results in negative emissions of 3.14 t CO_2eq/t ethylene, the difference amounts to 1.95 t CO_2eq/t ethylene avoided, compared to the fossil-based process (Dechema, 2017). Direct and indirect land use change is not accounted for in these calculations, and bio-based material production is subject to upstream emissions from fossil energy use or land cultivation (Benner, van Lieshout, & Croezen, 2011; Ecofys; Berenschot, 2018).

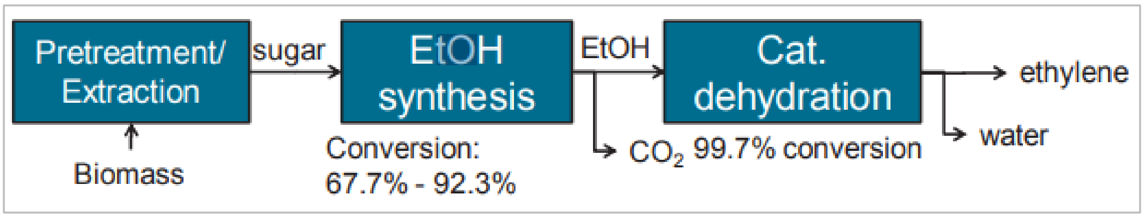

Figure 4.2 Ethylene production from bioethanol (Dechema, 2017).

4.4.2 Methanol to olefin process

The methanol-to-olefin (MTO) process has a TRL of 8-9 and is currently used in several locations in China, but so far not commercially deployed in Europe (Dechema, 2017). Figure 4.3 describes the process where methanol is first synthesized from hydrogen and CO_2, then followed by a MTO or methanol-to-propylene (MTP) conversion. Licensed processes include UOP/Hydro MTO technology, and Lurgi’s MTP process-based on a proprietary ZSM-5 catalyst. Since the reaction is highly exothermic, the temperature increase is controlled by using a two-step dehydration of methanol to DME and water, followed by the conversion to olefins. The total energy consumption of the MTO technology equals 5-8 GJ/t HVC, however the energy needed to produce the methanol feedstock requires an additional 23 GJ/t HVC. This is approximately double the state-of-the-art value for conventional steam cracking (11-14 GJ/t HVC). It has been estimated that production cost using the MTO process amounts to 816 euro/t HVC while considering an economic gap of a least a factor of two (Dechema, 2017)

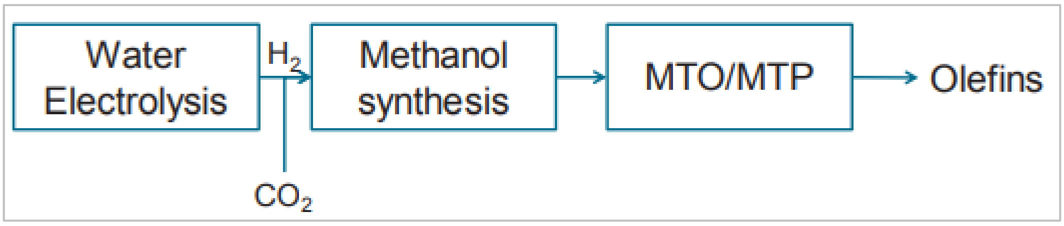

Figure 4.3 Ethylene/propylene production from methanol (Dechema, 2017)

4.4.3 Hydro-pyrolysis of naphtha

Hydro-pyrolysis of naphtha uses reactors which incorporate a hydrogen co-feed and less steam is required (Ren, Patel, & Blok, 2006). This technology is used on a commercial scale but not offered by major licensors. An average of 20% increase of ethylene yield and 30% less energy use is reported. Total energy use is 10-13 GJ/t HVC (or 16-20 GJ/t ethylene) compared to 11-14 GJ/t HVC in state-of-the-art technologies. These values are assuming the compression and separation sections are similar to that of conventional steam cracking installations, and technology only differs in the pyrolysis section.

4.4.4 Biobased ethylene glycol

Ethylene glycol can also be based on ethanol, which can be obtained from sugar, molasses or also from lignocellulosic biomass. New shorter routes are now developed (Gómez-Jiménez-Aberasturi & Ochoa-Gómez, 2016) (Pang, et al., 2015). Haldor Topsoe and Braskem have developed a demonstration factory in Denmark. The route uses pyrolysis to break down sugars into mixed oxygenates. A Topsoe catalyst then hydrogenates the oxygenates into ethylene glycol and co-product propylene glycol. Topsoe’s shorter route may prove cheaper than the ethanol-based route in the long run.

The Dutch process technology firm Avantium has started up a 10-metric-tonnes-per-year demonstration facility in Chemie Park Delfzijl, the Netherlands for ethylene glycol. Avantium’s claims its Ray Technology™ is an alternative for fossil MEG, producing it in a single-step hydrogenolysis process from plant-based sugars (Bioplastics News, 2019).

4.5 Carbon capture and storage (CCS)

In an integrated plant configuration such as Shell Moerdijk, thermal energy is required in various processes in the units, such as cracking, distillation reactions, flaring of off-gases, and other conversion reactions. Accordingly, the CO_2 emission sources from heat provisions are distributed and may be of different concentrations. The major CO_2 emission sources at the Moerdijk site are from combustion derived emissions of the fired process heaters, the on-site utilities for power and steam generation, and process derived CO_2 emissions from the ethylene oxide process. At the MLO unit, CO_2 emissions are largely from the furnaces and boilers that provide heat and steam for the pyrolysis section. The ethylene oxide reaction in the MEOD unit results in a stream of high concentration CO_2 (described in 2.3). These emissions sources present opportunities for implementation of carbon capture and storage, or usage in other processes and sectors.

Most of the emissions are from combustion processes and typically are low in CO_2 concentration and at low pressures, which subsequently drive up the cost of capture. The CO_2 concentration in the off-gas flow from process furnaces range from 8-10% (vol.), and from 4-15% (vol.) for steam boilers (Markewitz & Bongartz, 2015). Furthermore, the type of carbon capture technology implemented will depend on whether the CO_2 is stored or utilized. There may be certain specifications required in CO_2 concentration or purity which will essentially affect the energy used for capture, or from an economic perspective, costs of a specific capture technology. In both furnaces and steam boilers, chemical absorption and physical absorption techniques are theoretically feasible, however the low CO_2 concentrations may limit the capture efficiency.

In Shell's energy transition report (Shell, 2018), it is mentioned that although CCS is not feasible at current prices, potential retrofit is considered in the design of some new projects. While carbon-capture technology has been developed, it has not been widely applied, largely because of its cost. If the captured carbon can be used instead of being stored, it could replace fossil-based feedstocks, further reducing resource needs and possibly making this route more economical. CCS would be retrofitted to the existing facility, therefore post-combustion capture (e.g., via chemical absorption) is considered to be a feasible technology for CO_2 capture at steam cracker furnaces (Kuramochi, Ramirez, Turkenburg, & Faaij, 2012). For carbon capture, the CO_2 concentration in the flue gas is dependent on the fuel mix. If excess heat is available, and oxyfuel combustion can be applied, the costs in the long term are reported to be in the range of 30–60 euro/t CO_2 avoided (Kuramochi, Ramirez, Turkenburg, & Faaij, 2012). CCS post combustion projects in current situations for waste incineration and at refineries are estimated at a cost of 91-139 euros per tonne of CO_2 avoided (PBL, 2019), although the uncertainties are large (PBL, 2020). This range could apply to the MLO-U, and possibly to the naphtha cracker. These costs include a surcharge for transport and offshore storage and variable energy and O&M costs.

Implementation of an amine carbon capture process for 0.31 Mt would require a 70 mln euro investment, with additional fixed O&M of 3.2 mln euro annually. There are no direct estimates available for upscaling these costs to around 2 Mt for both MLO-U and cracker. Further, for Shell Moerdijk, a connection to a CO_2 transport system would be required. Currently, in the Rotterdam area such a system is planned (Ministry of Economic Affairs and Climate, 2019). The Shell refinery is already participating in this initiative. For Moerdijk an extension would be necessary, and costs would depend on available or further required infrastructure to connect to Rotterdam.

A CO_2 stream (40,000 tonnes in 2004) of high purity from ethylene oxide production is currently routed to OMYA B.V., which produces industrial minerals for paper whitening from calcium carbonate. Under the ETS, these emissions currently still fall under the process emissions of Shell. Due to the energy intensive CO_2 separation step not being necessary, the costs of CCS for this specific flow are lower. The costs are basically limited to the costs for routing the CO_2 to a transportation and storage facility and the surcharge to use of this facility.

5 Discussion

The optimal portfolio of decarbonisation options for chemical production companies depends on several factors and will differ greatly from one facility to another. Based on the results, several observations can be made.

The furnace section of the steam cracking process presents the most opportunities for CO_2 savings. Bulk chemical processes such as steam cracking are long-running, mature technologies, therefore industrial decarbonisation efforts appear to focus on incremental energy efficiency improvements rather than major retrofits or entire process substitutions. These include optimizing the furnace operations through heat recovery options or advanced process control systems. The announced replacement of the oldest cracking furnaces would reduce the SNC Moerdijk emissions by a substantial 10%. However, these improvements alone are not sufficient in achieving deep decarbonisation in 2050. Electrification, biomass routes, and CCS, are among the other discussed decarbonisation options for the chemical industry, and in this study some barriers relating to their implementation at Moerdijk and general bulk chemical production processes were highlighted. Excess fuel gas as a by-product of the cracking process is one of the key issues for decarbonising current state of the art crackers.

If future electricity prices are low and CO_2 prices high, it may be favorable to implement electrification options, however technologies such as high temperature electric furnaces currently require more development in order to be successfully implemented on an industrial scale. Furthermore, as in the case for Shell Moerdijk, commercial production sites are highly integrated, therefore changes to one part of the process results in modifications needed in other parts of the process. For example, replacing a steam turbine by an electric motor will reduce the production of steam from the utilities, but also the amount of exhaust heat available downstream. Adjustments to other parts of the process are then required to keep the steam cycle in equilibrium and reduce losses.

Using hydrogen as a fuel in the furnaces also represents an option for achieving reduced emissions. However, this likely depends on whether a large blue hydrogen plant will be installed in the Rotterdam industrial area.

CCS/CCU is another decarbonisation option that requires technical solutions and business models that cross sectoral boundaries. Under current conditions the technological challenges of retrofitting plants with CCS/CCU results in costly rebuilds or retrofits. The local infrastructure will need to be assessed for suitability, and support is needed from local regulations and public opinion (Roelofsen, Speelman, Pee, & Witteveen, 2017). If breakthrough innovative technologies are explored, CCS/CCU may become cost competitive in the long term (Ecofys; Berenschot, 2018). In terms of the long-term outlook, if future electricity prices are low, it may be more economically attractive to implement electrification options for olefin production rather than decarbonising with CCS/CCU.

Although biomass routes are generally more energy intensive, high GHG savings downstream can be achieved compared to conventional steam cracking. The discussion of bio-fuels or bio-based feedstock use for bulk chemical production is not limited to the boundary of the plant. The successful implementation of this option is also dependent on the bio-refining cluster in the surrounding area, which includes facilities for importing the biomass, co-firing facilities, and bio-fuel conversion plants. Furthermore, a substantial amount of biomass is required, with different types having varying carbon footprints; therefore, the availability of sufficiently sustainable biomass needs to be considered. Using only biomass as the feedstock for ethylene production in the Netherlands is estimated to require 600 PJ of energy from biomass or the equivalent of 16 Mt of biofuel (Roelofsen, Speelman, Pee, & Witteveen, 2017). These are some of the many factors that need to be considered when analyzing the feasibility of biomass routes for the chemical industry.

It is worth mentioning that this study includes currently available decarbonisation options, and strategies which are implemented on the shorter term may present barriers for further innovation. Investments in infrastructure and downstream processing that depend on waste flows from processes (e.g. heat, CO_2), may hinder investments in innovation of the core process.

References

ACC. (2004). *Ethylene: product stwardship guidance manual.* American Chemical Council. Opgehaald van https://docplayer.net/37044200-Ethylene-product-stewardship-guidance-manual.html

ACC. (2017). *Elements of the Business of Chemistry.* American Chemistry Council.

Al-Rabiah, A. (2001). *Membrane Technology for Hydrogen Separation in Ethylene Plants.* Riyadh.

Attero. (2018). *Warmte ontwikkeling.* Opgehaald van https://www.attero.nl/nl/nieuwsbrieven/nieuwsbrieven-september-2018/warmte-ontwikkeling/

Benner, J., van Lieshout, M., & Croezen, H. (2011). *Identifying breakthrough technologies for the production of basic chemicals.* CE Delft.

Bioplastics News. (2019). *Avantium Ray Technology To Disrupt Mono-Ethylene Glycol Market*. Opgehaald van Bioplastics News: https://bioplasticsnews.com/2019/11/07/avantium-ray-technology-mono-ethylene-glycol-meg-market/

Boulamanti, A., & Moya Rivera, J. (2017). *Energy efficiency and GHG emissions: Prospective scenarios for the Chemical and Petrochemical Industry.* European Commission / JRC.

Boulamanti, A., & Moya, J. (2017a). Production costs of the chemical industry in the EU and other countries: Ammonia, methanol and light olefins. *Renewable and Sustainable Energy Reviews*, 68 (2), 1205-1212.

Brayden, M., Wines, T., & Del Guidice, K. (2006). Improve Steam Cracking Furnace Productivity and Emissions Control through Filtration and Coalescence. *American Institute of Chemical Engineers (AIChE) Spring National Meeting, Ethylene Producers' Conference (EPC).*

Buijink, J. K., Lange, J. P., Bos, A. N., Horton, A. D., & Niele, F. G. (2008). Propylene Epoxidation Via Shell's Smpo Process: 30 Years of Research and Operation. In S. Ted Oyama, *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis* (pp. 355–371). doi:https://doi.org/10.1016/B978-0-444-53188-9.00013-4

CBS. (2018). *Energy balance 20-21 Chemistry and pharmaceuticals.* Opgehaald van https://opendata.cbs.nl/statline/#/CBS/en/dataset/83989ENG/table?ts=1582715085299 ; https://opendata.cbs.nl/statline/#/CBS/en/dataset/83300ENG/table?ts=1582731175444

CBS. (2020). *Statline, Energiebalans; aanbod en verbruik, sector organische basischemie.* Opgehaald van https://opendata.cbs.nl/statline/#/CBS/nl/dataset/83989NED/table?ts=1583839584341

CDH. (2020). *Product specification Ethyl Benzene.* Central drug house. Opgehaald van https://www.cdhfinechemical.com/images/product/specs/37_1092830057_ETHYLBENZENE_CASNO-100-41-4_028320.pdf

CEFIC. (2013). *European chemistry for growth. Unlocking a competitive, low carbon and energy efficient future.* Brussels.

Chauvel, A., & Lefebvre, G. (1989). *Petrochemical processes.* Gulf.

Chemicals Technology. (2009). *Shell Mono-ethylene Glycol Plant*. Opgehaald van https://www.chemicals-technology.com/projects/shell-monoethylene/

Chemicals Technology. (2016). *Moerdijk ethylene cracker and plant expansion*. Opgehaald van Chemicals Technology: https://www.chemicals-technology.com/projects/moerdijk/

Chemicals Technology. (2020). *Air Liquide to build air separation unit in Netherlands*. Opgehaald van Chemicals Technology: https://www.chemicals-technology.com/news/air-liquide-air-separation-unit-netherlands/

De Tijd. (2019). *Investering van Ineos in Antwerpen 300 miljoen hoger dan verwacht*. Opgehaald van https://www.tijd.be/ondernemen/chemie/investering-van-ineos-in-antwerpen-300-miljoen-hoger-dan-verwacht/10087315.html

Dechema. (2017). *Low carbon energy and feedstock for the European chemical industry.*

DOE NETL. (2011). *Cost and Performance Baseline for Fossil Energy Plants Volume 2: Coal to Synthetic Natural Gas and Ammonia.* National Energy Technology Laboratory.

DWA. (2008). *Inventarisatie reststromen West-Brabant.* DWA installatie- en energieadvies.

ECN. (2018). *A first order roadmap for electrification of the Dutch Industry.* Commissioned by RVO (under number TSE1706004) on behalf of the TKI E&I.

ECN. (2019). *Basislijst WKK.* Amsterdam.

Ecofys; Berenschot. (2018). *Chemistry for Climate: Acting on the need for speed; Roadmap for the Dutch Chemical Industry towards 2050.*

Ecofys; Fraunhofer ISI; Oeko-Institut. (2009). *Methodology for the free allocation of emission allowances in the EU ETS post 2012, Sector report for the chemical industry.*

Elgas. (2018). *Properties of LPG.* Opgehaald van https://www.elgas.com.au/blog/453-the-science-a-properties-of-lpg

Elzenga, H. (1993). *SPIN Samenwerkingsproject Procesbeschrijvingen Industrie Nederland, Shell Chemie Nederland.* Opgehaald van http://publicaties.minienm.nl/documenten/samenwerkingsproject-procesbeschrijvingen-industrie-nederland-sp

EPCA. (2007). *A Paradigm Shift : Supply Chain Collaboration and Competition in and between Europe's Chemical Clusters-Results of the EPCA Think Tank Sessions organized and sponsored by EPCA.* European Petrochemical Association.

ESCPP. (2010). *Chemical Parks in Europe: An Overview of the Pipeline Networks of Europe.* European Chemical Site Promotion Platform. Opgehaald van https://chemicalparks.eu/europe/pipeline-networks

EU. (2009). *DIRECTIVE 2009/30/EC .*

European Environmental Agency. (2019). *Large combustion plants database, version 5.2v*. Opgehaald van EEA: https://www.eea.europa.eu/data-and-maps/data/lcp-9/plant-by-plant-emissions-lcp

Falcke, H., Holbrook, S., Clenahan, I., Lopez Carretero, A., Sanalan, T., Brinkmann, T., . . . Delgado Sancho, L. (2017). *Best Available Techniques (BAT) Reference Document for the production of large volume organic chemicals.* JRC.

Gazprom. (sd). *informatorium.* Opgehaald van http://www.gazprominfo.com/articles/condenced-gas; https://www.gazprom.com/about/production/extraction/

Gómez-Jiménez-Aberasturi, O., & Ochoa-Gómez, J. (2016). New approaches to producing polyols from biomass. *Journal of Chemical Technology and Biotechnology*, 92(4), 705-711.

Harmelink, M., & Coenraads, R. (2005). *Transfers of CO2 under the EU emissions trading scheme.* Ecofys.

Havenschap Moerdijk. (2014). *Port Environmental Review System Port of Moerdijk.* Opgehaald van https://www.portofmoerdijk.nl/media/1222/20140820_pers_rapport_2014.pdf

Hirata, K., & Kakiuchi, H. (2011). Energy saving for ethylene process by Adsorption Heat Pump. *Applied Thermal Engineering*, 31(13), 2115-2122.

H-vision. (2019). *Blue hydrogen as accelerator and pioneer for energy transition in the industry.*

ICIS. (2008). *Shell's Omega MEG process kicks off in South Korea.* Opgehaald van https://web.archive.org/web/20081023133948/http://www.icis.com/Articles/2008/08/18/9148176/shells-omega-meg-process-kicks-off-in-south-korea.html

ICIS. (2011). *Styrene Uses and Market Data.* Opgehaald van https://www.icis.com/explore/resources/news/2007/11/06/9076472/styrene-uses-and-market-data/

ICIS. (2013). *Chemical Profile: Europe ethylene oxide.* Opgehaald van https://www.icis.com/explore/resources/news/2013/04/13/9658385/chemical-profile-europe-ethylene-oxide/

IEA. (2013). *Technology Roadmap Energy and GHG Reductions in the Chemical Industry via Catalytic Processes.* International Energy Agency.

IHS Markit. (2015-2020). *Chemicals economics handbook*. Opgehaald van https://ihsmarkit.com/products/chemical-economics-handbooks.html

Keller, A. (2012). *NGL 101 the basics.* Opgehaald van EIA: https://www.eia.gov/conference/ngl_virtual/eia-ngl_workshop-anne-keller.pdf

Koottungal, L. (2015). *International Survey of Ethylene from Steam Crackers - 2015.* Oil & Gas Journal. doi:https://doi.org/10.3109/J058v03n02_09

Kuramochi, T., Ramirez, A., Turkenburg, W., & Faaij, A. (2012). Comparative assessment of CO2 capture technologies for carbon-intensive industrial processes. *Progress in Energy and Combustion Science*, 38(1), 87-112.

Markewitz, P., & Bongartz, R. (2015). Carbon Capture Technologies. In W. Kuckshinrichs, & J. Hake, *Carbon Capture, Storage and Use.* Springer.

Ministry of Economic Affairs and Climate. (2019). *Notitie Reikwijdte en Detailniveau voor het milieueffectrapport Rotterdam CCUS project Porthos.* Den Haag.

Morgan, M. (2018). *Cracker dynamics and the impact of feedstock developments*. Opgehaald van IHS Markit: https://ihsmarkit.com/research-analysis/cracker-dynamics-and-impact-of-feedstock-developments.html

myLPG. (2018). *Propane/butane mixture in countries around Europe.* Opgehaald van https://www.mylpg.eu/useful/lpg-mixture

Nakaiwa, M., Huang, K., Endo, A., Ohmori, T., Akiya, T., & Takamatsu, T. (2003, 1 1). Internally Heat-Integrated Distillation Columns: A Review. *Chemical Engineering Research and Design, 81*(1), 162-177.

Naqvi, S. (2009). *Ethylene Glycol Process Economics Program Report 2I*. Opgehaald van IHS Markit: https://ihsmarkit.com/products/chemical-technology-pep-ethylene-glycol-2009.html

NEa. (2014). *Ambtshalve wijziging emissievergunning/goedkeuring bemonsteringplan.* Dutch Emissions Authority.

NEa. (2020). *ETS emission figures.* Dutch Emissions Authority. Opgehaald van https://www.emissieautoriteit.nl/documenten/publicatie/2019/04/04/emissiecijfers-2013-2018

Neelis, M., Patel, M., Blok, K., Haije, W., & Bach, P. (2007). Approximation of theoretical energy-saving potentials for the petrochemical industry using energy balances for 68 key processes. *Energy*, 32(7), 1104-1123.

Nieuwlaar, E. (2001). *Icarus 4: Sector study for the chemical industry.* Utrecht University.

Oil and Gas Journal. (2001). *Shell Nederland to build benzene unit*. Opgehaald van https://www.ogj.com/refining-processing/article/17261777/shell-nederland-to-build-benzene-unit

Oliveira, C., & van Dril, A. (2020). *Decarbonisation options for large volume organic chemicals production, Sabic Geleen.* PBL and TNO.

Pang, J., Zheng, M., Sun, R., Song, L., Wang, A., Wang, X., & Zhang, T. (2015). Catalytic conversion of cellulosic biomass to ethylene glycol: Effects of inorganic impurities in biomass. *Bioresource Technology*, 175, 424-429.

PBL. (2019). *Conceptadvies SDE++ CO2-reducerende opties: CO2 afvang en opslag (CCS).* Den Haag: PBL.

PBL. (2020). *Eindadvies basisbedragen SDE++ 2020.* Den Haag: PBL.

Perry, R., Green, D., & Maloney, J. (1997). Gasification. In R. Perry, *Perry's Chemical Engineers' Handbook, 7th ed.* McGraw-Hill New York. doi:https://doi.org/10.1021/ed027p533.1

Petrochem. (2020). *Project Skyline moderniseert Shell Moerdijk.* Opgehaald van https://petrochem.nl/project-skyline-moderniseert-shell-moerdijk/

Petrochemicals Europe. (2020). *Facts and figures: Cracker capacity, cracker inputs.* doi:https://www.petrochemistry.eu/about-petrochemistry/petrochemicals-facts-and-figures/european-market-overview/

Port of Rotterdam. (2010). *Facts and figures Rotterdam Energy Port and Petrochemical Cluster.*

Provincie Noord Brabant. (2003). *Beschikking van Gedeputeerde Staten Wm vergunning Shell Nederland Chemie.*

Ren, T. (2009). *Petrochemicals from Oil, Natural Gas, Coal and Biomass: Energy Use, Economics and Innovation.* Utrecht University.

Ren, T., Patel, M., & Blok, K. (2006). Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes. *Energy*, 31(4), 425-451.

Roelofsen, O., Speelman, E., Pee, A. d., & Witteveen, M. (2017). *Energy transition: mission (im)possible for industry? A Dutch example for decarbonization.* McKinsey&Company.

RVO. (2015). *Restwarmtekoppeling Moerdijk.* Rijksdienst voor ondernemend Nederland.

Samadi, S., Lechtenböhmer, S., Schneider, C., Arnold, K., Fischedick, M., Schüwer, D., & Pastowski, A. (2016). *Decarbonization Pathways for the Industrial Cluster of the Port of Rotterdam.* Wuppertal Institut.

Saygin, D., Patel, M., Tam, C., & Gielen, D. (2009). *Chemical and Petrochemical Sector: Potential of best practice technology and other measures for improving energy efficiency.* IEA Information Paper.

Shell. (2016). *Shell starts new aromatics unit at Pernis refinery in the Netherlands.* doi:https://www.shell.nl/media/persberichten/2016-media-releases/shell-pernis-starts-building-major-factory-for-more-flexibility.html

Shell. (2018). *Energy transition report.* Opgehaald van https://www.shell.com/energy-and-innovation/the-energy-future/shell-energy-transition-report.html

Shell. (2018a). *Shell Manufacturing locations. Retrieved August 7, 2018, from.* Opgehaald van https://www.shell.com/business-customers/chemicals/manufacturing-locations.html#EU

Shell. (2018b). *Shell Moerdijk: About Us. Retrieved June 3, 2018, from.* Opgehaald van https://www.shell.nl/over-ons/shell-moerdijk/over-shell-moerdijk.html

Shell. (2019). *Onderhoudsstop Shell Moerdijk, stappen in de energietransitie.* Opgehaald van https://www.shell.nl/over-ons/shell-moerdijk/nieuwsberichten-shell-moerdijk/archief/nieuwsberichten-2019/onderhoudsstop-shell-moerdijk-stappen-in-de-energietransitie.html

Shell. (2020). *Dow and Shell team up to develop electric cracking technology*. Opgehaald van Shell: https://www.shell.com/business-customers/chemicals/media-releases/2020-media-releases/dow-and-shell-team-up-to-develop-electric-cracking-technology.html

Shell. (2020a). *Materials safety data sheets: C6 raffinate; ethylene; propylene; butadiene; benzene; ethylene glycol; styrene monomer; ethylene oxide; propylene oxide.* Opgehaald van https://www.shell.com/business-customers/chemicals/safe-product-handling-and-transportation/chemicals-safety-data-sheets.html

Spallina, V., Velarde, I. C., Jimenez, J. A., Godini, H. R., Gallucci, F., & Van Sint Annaland, M. (2017). Techno-economic assessment of different routes for olefins production through the oxidative coupling of methane (OCM): Advances in benchmark technologies. *Energy Conversion and Management*, 154, 244-261.

Staudt-Bickel, C., & Koros, W. (2000). Olefin/paraffin gas separations with 6FDA-based polyimide membranes. *Journal of Membrane Science*, 170(2), 205-214.

Thyssen-Krupp. (2014). *World Market Leader in Aromatics Extraction.*

Van Kranenburg, K., Schols, E., Gelevert, H., De Kler, R., Van Delft, Y., & Weeda, M. (2016). *Empowering the chemical industry - Opportunities for electrification.* TNO/ECN. TNO and ECN.

VNCI. (2019). *Elektrische kraker komt in beeld*. Opgehaald van VNCI: https://www.vnci.nl/nieuws/nieuwsbericht?newsitemid=4677402624

Weissermel, K., & H-J., A. (2008). *Industrial Organic Chemistry.* Wiley.

Wesseling, B., & Deng, Y. (2009). *Sectoral Emission Reduction Potentials and Economic Costs for Climate Change (SERPEC-CC).*

Worrell, E., Phylipsen, D., Einstein, D., & Martin, N. (2000). *Energy use and energy intensity of the U.S. chemical industry.*

Yong Min Feng, C., & Keys, A. (2020). *Decarbonisation options for LyondellBasell Rotterdam.* PBL and TNO.

Zijlema, P. (2018). *List of fuels and standard CO2 emission factors, (January).* RVO, Netherlands.

Zimmerman, & Walzl. (2012). *Ethylene.* Ullman's Encyclopedia of Industrial Chemistry. Wiley VCH.