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DECARBONISATION OPTIONS FOR LARGE VOLUME ORGANIC CHEMICALS PRODUCTION, SABIC GELEEN

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MIDDEN

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Decarbonisation options for Large Volume Organic Chemicals production, SABIC Geleen

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PBL and TNO are responsible for the content. The decarbonisation options and parameters are explicitly not verified by the companies.

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Summary

This report describes the current situation for SABIC's large volume organic chemicals (LVOC) production at Chemelot industrial complex, in Geleen, The Netherlands. The report also explores the options and conditions for its decarbonisation. There are two steam crackers (OLEFINS 3 and OLEFINS 4) owned by SABIC at the Chemelot cluster. The total high value chemicals (HVC) production in 2018 was around 2.2 million tonnes (Mt), of which 1.1 million concerned to ethylene production only. The production volumes for the HVCs are:

Product	Production volumes (kilotonnes, kt)	Main process unit
Hydrogen	35	Steam cracking
Acetylene	4	Steam cracking
Ethylene	1,150	Steam cracking
Propylene	680	Steam cracking
Butadiene	110	Separation from C_4 fraction of steam cracker
Benzene	280	Extraction from pyrolysis gasoline of steam cracker

In 2018, the estimated final energy consumption by OLEFINS 3 and OLEFINS 4 was 33.5 PJ, of which 29 PJ relates to the pyrolysis (cracking) furnaces. Since the cracking section is the most energy intensive step, the decarbonisation options mostly focus on decreasing the CO_2 emissions from this process. In 2018, the CO_2 emissions from the pyrolysis furnaces amounted to 1.5 Mt CO_2 (EEA, 2020).

The decarbonisation options studied include furnaces and steam generation electrification, hydrogen as fuel substitute, plastic waste oil and bio-based naphtha as co-processed feedstock and alternative olefins production via methanol to olefins process. All the options present benefits and challenges related to its implementation, which are further explored in this report. The pyrolysis furnaces could be electrified in the long term, which would avoid the largest part of the emissions. However, electrification needs reliable renewable electricity supply and finding a CO_2-free utilization for the fuel gas from the crackers may also be a limitation. Regarding the alternative feedstocks, plastic oil upgrade is still going through technical development and the supply of plastic waste can be a limitation, nevertheless, the option presents potential for growth and includes the circular economy aspect.

SABIC announced in 2021 the company will start building the first commercial plant in The Netherlands to refine and upgrade an alternative feedstock for the crackers, known as TACOIL, patented by Plastic Energy. This product will be produced from the recycling of mixed plastic waste otherwise destined for incineration or landfill. The plant is anticipated to enter commercial production in the second half of 2022.

FULL RESULTS

Introduction

This report describes the current situation of SABIC's petrochemical site production in Geleen and the options and conditions for its decarbonisation. It is part of the MIDDEN project: the Manufacturing Industry Decarbonisation Data Exchange Network. MIDDEN aims to support industry, policy makers, 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 the plant level for the Dutch manufacturing industry. The scope of this research will focus on the manufacturing of large volume organic chemicals at the Chemelot complex owned by SABIC, address Koolwaterstofstraat 1, 6161 RA, Geleen.

The processes include lower olefin production via steam cracking, butadiene recovery, benzene extraction, pyrolysis gasoline stabilisation and recovery and Methyl tert-butyl ether (MTBE) production.

The products include ethylene, propylene, butadiene, benzene, hydrogen, MTBE, pyrolysis gasoline, acetylene, and fuel oil.

The main decarbonisation options are steam cracker furnace electrification, steam provision via electrical boilers, waste plastic oil as feedstock for steam cracker, bio-naphtha as feedstock, hydrogen as fuel for furnaces and olefins production via methanol.

Reading guide

Section 1 gives a general introduction to the large volume organic chemicals (LVOC) industry in the Netherlands. In Section 2, we describe the current situation of LVOC production processes in the Netherlands, and in Section 3, we present the relevant products from these processes. Options for decarbonisation are systematically quantified and evaluated in Section 4. The feasibility and barriers of those decarbonisation options are briefly discussed in Section 5.

1 Large Volume Organic Chemicals production in the Netherlands

1.1 The Dutch chemical industry

In 2019, the Dutch chemical sector (which excludes refineries) consumed over 805 PJ of energy and feedstock and was responsible for over 18 Mt CO_2eq GHG emissions (CBS, 2021a & CBS, 2021b).

Table 1 shows the role of key chemical processes in terms of share percentage of total CO_2 equivalent (CO_2eq) emissions for the EU chemical industry in 2015. The highest share of GHG emissions in this group belongs to the steam cracking process for olefin production.

Table 1 - GHG emissions intensive chemical processes (Boulamanti and Moya, 2017)

Processes	GHG emissions share [%]
Steam cracking (olefin production)	25.5
Ammonia	19.6
Chlorine	10.6
Hydrogen/Syngas (incl. methanol)	9.2
Aromatics	4.8
Nitric acid	3.8
Carbon black	3.4
Ethylbenzene/Styrene	2.9
Ethylene oxide/ Monoethylene Glycol	2.6
Ethylene Chloride/Vinyl Chloride/PVC	2.6
Soda Ash	1.5
Adipic Acid	0.4

In the Netherlands, the six operating steam crackers had a total ethylene nameplate capacity of over 4,000 kt/year in 2019 (Table 2). The SABIC site in Geleen presents a total production capacity of nearly 1,310 kt/year for ethylene, which corresponds to more than 32% of the total capacity in the country. Ethylene is one of the main products from steam crackers due to the polymer industry, but also other important chemicals are part of the total product portfolio of these sites.

Table 2 - Steam cracking installations and capacities in The Netherlands in 2019 (Petrochemicals Europe, 2021). Other than SABIC, the steam crackers are described in MIDDEN reports by Wong et al. (2020) and Eerens et al. (in preparation).

Steam cracker site	Nameplate capacity ethylene [kt/yr]	Number of steam crackers	Share [%]
Dow Chemical Co. Terneuzen	1,825	3	45
SABIC Europe Geleen	1,310	2	32
Shell Nederland Chemie Moerdijk	910	1	22
Total	4,045	6	100

Most steam cracking installations are located on large chemical sites in relative proximity to a refinery site. Figure 1 shows the Dutch petrochemical cluster where an extensive network of pipelines ensures secure supply of products to and from refineries, steam crackers and olefin consumers within the Netherlands and in the Benelux and Rhine-Ruhr region.

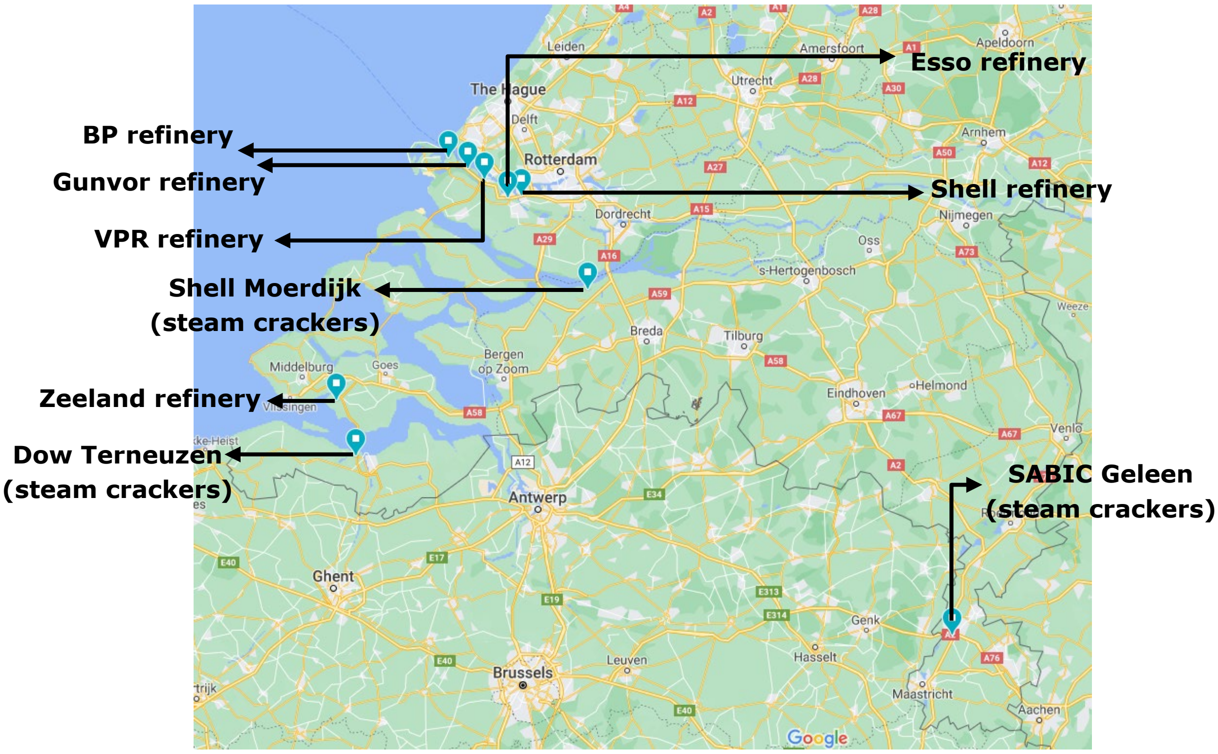

Figure 1 - Locations of refineries and steam crackers in The Netherlands

1.2 SABIC Geleen

1.2.1 Location and infrastructure

SABIC's steam crackers are located at the industrial complex Chemelot, which occupies around 800 hectares in the South of Limburg. The site presents a large number of factories that complement each other, as well as research centres and pilot plants. The cluster is integrated and shares environmental permits and services, such as utilities, fire brigade and maintenance.

The site contains around 800 km of pipeline above ground, 60 industrial units, 60 km of rail road connection and 50 km of roads (Chemelot, 2018a). The pipelines are very well connected with other industrial clusters, as illustrated in figures 2 to 4. Pipelines owned by the Äthylen Rohrleitungsgesellschaft (ARG) cover a distance of approximately 500 km and transport ethylene between producers and consumers in the Netherlands, Germany, and Belgium (ARG, 2018). SABIC's steam cracker is one of the sites connected to the ethylene ARG pipeline.

SABIC's site has also connections with the Port of Antwerp (Figure 5), they can receive naphtha and export ethylene to/from this port.

Figure 2 - Crude oil and oil products pipeline (Port of Rotterdam, 2016)

Figure 3 - Ethylene and propylene pipelines (Port of Rotterdam, 2016)

Figure 4 - Industrial gases pipelines (Port of Rotterdam, 2016)

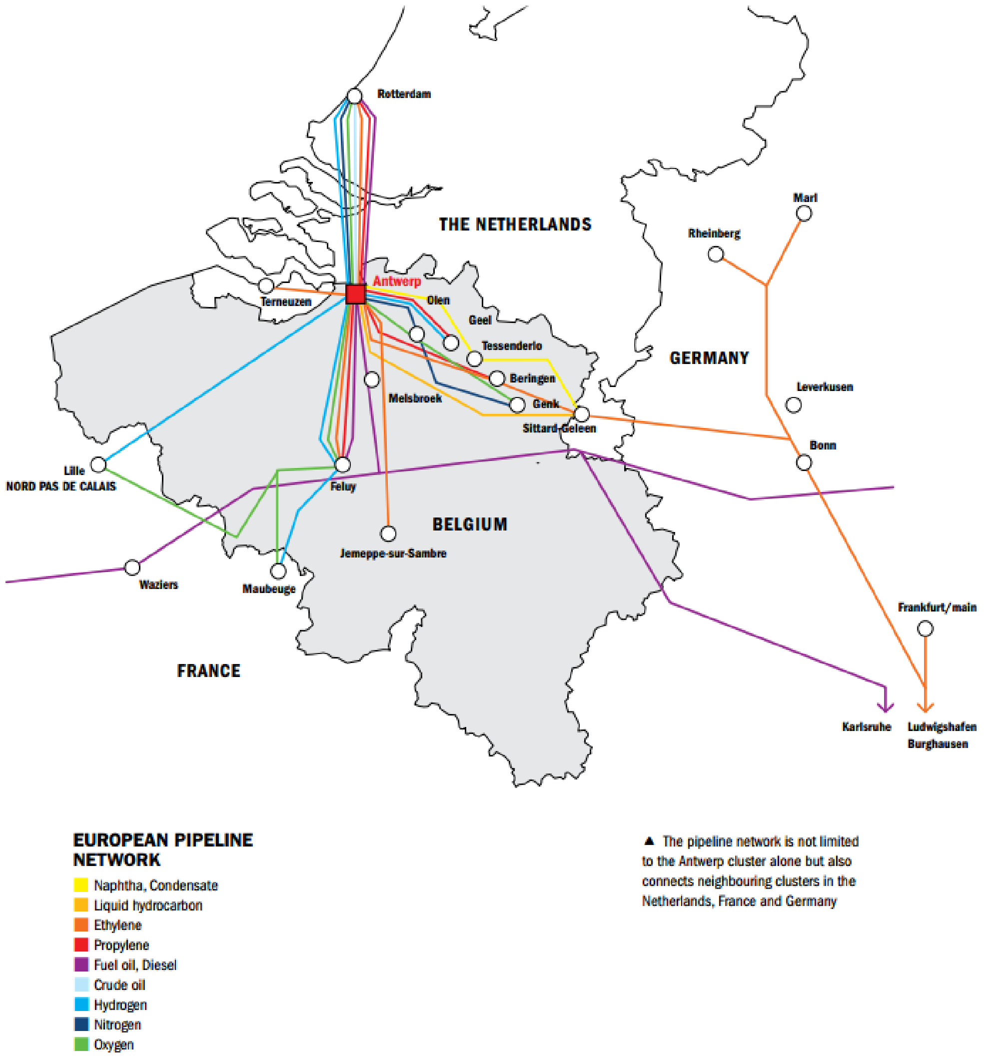

Figure 5 - Naphtha and ethylene pipelines connected with Port of Antwerp (Port of Antwerp website, accessed 2019)

1.2.2 History

Several companies from Germany and Belgium started coal production in South Limburg in the end of 1800’s. For this reason, the Dutch government established the State Mines (later DSM) in 1902. State Mines opened three coal mines in the Eastern Mining Region. After a decade, State Mines also got interested in the Geleen area.

Around 1960, the Dutch mining business faced instability, mainly because of the rise of petroleum and natural gas. In 1965, State Mines decided to stop the mining activities. In 1967 the last coal mine was closed. Already in the 1930s the polyethylene process became popular and State Mines produced ethylene from coke oven gas. About the same period that the mining business was facing difficulties, the company management decided to develop both the high and low pressure polyethene processes, prioritizing LDPE (low density polyethylene), as the LDPE market in the 1950s was booming.

Due to increasing demand, the amount of ethylene from coke oven gas was not enough and a naphtha cracker was put into operation in 1961. The next year, a HDPE (high density polyethylene) plant started operations. At the same time, State Mines developed new technologies for LDPE and HDPE production and applications. This knowledge extended to synthetic rubbers and other polymers.

From 1970, the emphasis gradually shifted from bulk chemistry to food ingredients, pharmaceuticals and agrochemicals. States Mines, since 1973 called Dutch State Mines (DSM), invested in laboratories and factory installations focused on specialized products. Due to the transformation process that DSM was passing through, the steam crackers and directly connected downstream petrochemical activities from DSM in Geleen were transferred to the Saudi Arabian company SABIC in 2002. From this year on, the site was named Chemelot, a combination of 'chemo' (chemical) and 'lot' (place) and also a reference to the mythical castle Camelot of King Arthur. Headquartered in Sittard, Netherlands, SABIC Europe has other petrochemical production sites in the continent: Bergen op Zoom (NL), Teesside (United Kingdom), Cartagena (Spain) and Gelsenkirchen (Germany) (Chemelot, 2018b).

1.2.3 Main Activities

The industrial site in Geleen owned by SABIC is composed by:
- 2 steam crackers units (OLEFINS 3 and OLEFINS 4), including butadiene extraction, benzene extraction, MTBE production and pyrolysis gasoline hydrogenation and separation
- 5 polyethylene units (2 high density and 3 low density polyethylene)
- 2 polypropylene units

Figure 6 shows the geographical position of the installations mentioned above and Table 3 presents the annual production of OLEFINS 3 and OLEFINS 4, which are the focus of this report. The polyethylene and polypropylene production units are described in the MIDDEN report by Negri and Ligthart (2021).

Figure 6 - SABIC steam crackers location, Chemelot site in Geleen (adapted from Google maps, 2019)

Table 3 - Main products at the SABIC Geleen site for the OLEFINS 3 and OLEFINS 4 units

Product	Production volumes [kt/yr]$^{1)}$	Process/reaction description	Comment
Ethylene	1,150	Steam cracking	Feedstock for the HDPE and LDPE plants and sold to third parties
Propylene	680	Steam cracking	Feedstock for Polypropylene (PP) plant and sold to third parties
Hydrogen	35	Steam cracking	Feedstock for Methylacetylene and Propadiene (MAPD) hydrogenation and pyrolysis gasoline stabilisation
Acetylene	4	Acetylene recovery	Sold as final product
Butadiene	110	Separation of butadiene from C_4 fraction	Sold as feedstock to third parties
MTBE	150	Reaction of isobutylene with methanol to produce methyl – tert-butyl ether	Sold to third parties
Benzene	280	Extraction from pyrolysis gasoline fraction of steam cracker	Sold to third parties
Pyrolysis gasoline	1,020	Separation of C5-C9 and hydrogenation for product stabilisation	Intermediary input for pyrolysis gasoline processing system
Total HVC production$^{2)}$	**2,259**		

$^{1)}$ Values based on data gathered via interviews with SABIC Geleen. Base year is 2018.

$^{2)}$ High values chemicals considered in this report are: hydrogen, acetylene, ethylene, propylene, butadiene and benzene.

2 LVOC production processes

The process descriptions for each of the major plants (OLEFINS 3, OLEFINS 4), are described in the following sections, as well as the main inputs and outputs, specific energy consumption and emissions. This is followed by a description of the utilities production on site. The information is mainly based on environmental permit documents and interviews with the company.

2.1 ETS Emissions

Table 4 lists the emissions for selected units on site with SABIC assets reported under the ETS from the Dutch Emissions Authority. These emissions do not correspond only to the SABIC assets. For instance, the allocation Chemelot BKG02 also includes the Swentibold power plant owned by the Utilities Support Group (USG), this plant provides steam and electricity to other units besides SABIC; more details regarding this subject are given in the utilities section of this report.

Table 4 - ETS emissions for plants at Chemelot site for the past years (Dutch Emissions Authority, 2020)

Permit number	Name of ETS allocation	Activity/production unit	ETS emissions 2017 [kt/yr]	ETS emissions 2018 [kt/yr]	ETS emissions 2019 [kt/yr]
NL-200400161	Chemelot BKG 01	Steam cracker OLEFINS 3 MTBE unit Butadiene Flare stacks	594.7	753.7	713.9
NL-200400161a	Chemelot BKG 02	Steam cracker OLEFINS 4 Pygas unit Benzene extraction Swentibold power plant (RWE)	1,771.9	1,602.4	1537.7
		Total emissions	**2,366.7**	**2,356.2**	**2,251.6**

2.2 Steam Cracking process

The OLEFINS 3 and OLEFINS 4 units consist of steam crackers, butadiene and benzene extraction, pyrolysis gasoline stabilisation and recovery systems and MTBE production. The main products are ethylene, propylene, butadiene, benzene, pyrolysis gasoline and MTBE. The steam cracking reaction results in more than one product which makes it difficult to standardise the energy use and emissions accurately for each product. Therefore, benchmarking studies and the Directorate General for Climate Action from the European Commission (DG Clima) consider the term High Value Chemicals (HVCs) which includes hydrogen, acetylene, ethylene, propylene, butadiene and benzene as products for energy efficiency and emissions calculations for steam crackers (European Commission, 2019). Due to the variation in reaction conditions and multiple products formed, grouping these chemicals facilitates the assessment of the overall performance of a site. For this reason, the HVCs approach is also applied in this report to keep the consistency.

2.2.1 Feedstock Preparation and Pyrolysis Furnaces

Olefins are defined by organic chains with double bonds (unsaturated chains). In both OLEFINS 3 and OLEFINS 4, olefins are produced from a variety of raw materials: naphtha, LPG and stabilised natural gas condensates. The choice of raw materials is determined, among other things, by the cost price and the market situation. Naphtha mainly consists of saturated hydrocarbons (called alkanes or paraffins), mostly C5 to C10 carbon chains. LPG is a mixture of different C3 and C4 molecules. The natural gas condensate composition depends on the extraction site, however, it may contain alkanes, cycloalkanes and aromatics. In addition to the fresh feed, by-products are also recycled and used as feedstock. In 2019, the Dutch Manufacturing organic basic chemicals sector consumed around 282.2 PJ of Naphtha, 95.2 PJ of LPG and 94.4 PJ of gas condensate (CBS, 2020b). For SABIC’s crackers, the main feedstock is naphtha.

As mentioned in Section 1.2.1, the raw materials are mainly supplied via pipelines from Rotterdam and/or Antwerp to Geleen. They are stored in tanks of 15,000 to 30,000 m^3. In addition, some of the raw materials are transported by train or by ship (Commissie voor de milieueffectrapportage, 2005).

The fresh feed is pumped from the tanks and heated with warm quench water to about 60°C and then sent to the pyrolysis (steam cracking) furnaces. Pyrolysis (cracking) is a thermal process in which heat is responsible for breaking chemical bonds and, therefore, generates smaller chains, most of them olefins (double bonded compounds). The cracking takes places in tubular furnaces at a temperature of approximately 850°C. The furnaces are heated by combustion of (mainly self-produced) fuel gas and/or limited amounts of natural gas. Next to the liquid feed furnaces there is a furnace fed with gas. In this furnace, recycled ethane and propane are cracked at approximately 850°C.

In the furnaces, the feedstock passes through a "convection section" and a "radiation section". The cracking reactions take place in the radiation section (see Figure 7), where fuel gas combustion provides the required heat of reaction. The cracked gas needs to be cooled just after reaction in order to prevent degradation of certain products that are highly reactive. The hot cracked gas (around 850°C) heats up high pressure (HP) boiler feed water (BFW) in the called transfer line heat exchangers (TLEs) to produce saturated high pressure steam (HPS). Heat recovery also takes place in the convection section of the ovens, in which the flue gases from combustion provide the heat to bring the saturated HPS to superheated steam (SHP) and to heat up the feedstock (from 60 to approximately 600°C). The SHP steam is used by the cracked gas compressor.

Furthermore, low pressure steam is used as dilution to the feed to reduce the vapor pressure of the hydrocarbons, in order to obtain the desired product package and to prevent coke formation in the furnace tubes. Depending on whether naphtha, gas condensate, LPG or ethane is cracked, the weight ratio of the process steam to hydrocarbon feed can vary from 0.35 to 0.7. Figure 7 illustrates a typical cracking furnace and presents the energy shares found in literature (Ullmann, 2002), based on fuel gas intake. The heat losses indicated in the picture refer to the stack losses (5%) and to losses via the furnaces walls (1.5%).

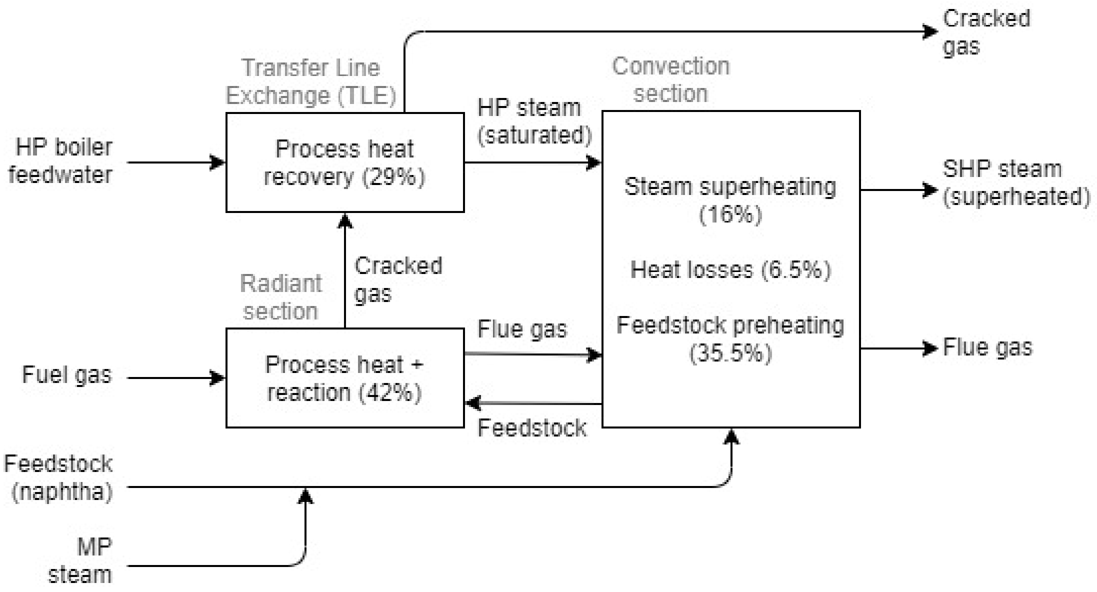

Figure 7 - Pyrolysis furnace thermal distribution overview (based on Ullmann, F., 2002)

2.2.2 Primary fractionation and compression

The hot product gas (cracking gas) that leaves the furnaces must be cooled down quickly in order to prevent unwanted follow-up reactions. This is done in two steps; the first step takes place in the TLEs as previously mentioned. The cracked gas is cooled down to about 450° C in these heat exchangers. The second cooling step takes place in a quench tower and reduces the cracked gas temperature to approximately 200 °C, being responsible for the partial condensation of the cracked gas. This second cooling process happens via direct contact between the cracked gas and a quench oil. In this step, a heavy stream rich in C10+ hydrocarbons is separated from the cracked gas. The C10+ stream is separated from the oil and delivers two products: bunker oil and feedstock for the carbon black industry. A third cooling step of the cracked gas takes place in a water quench column for primary fractionation, cooling down the gas to around 30ºC. In this equipment, the C5-C9 fraction is separated from C4- components and sent to the pyrolysis gasoline/benzene extraction section.

The cracked gas from the top of the water quench column is transported to the cracked gas compressor, which is responsible for building the cracked gas pressure to the desired value in a number of stages. This compressor is driven by a steam turbine that uses SHP steam (110 bar), partially provided by the TLEs as explained in the previous section. Additional SHP steam is supplemented by the combined heat and power plant at the Swentibold location and by auxiliary boilers owned by USG (Utilities Support Group).

Between each compression stage, there are intermediate cooling steps and separation vessels, in which condensate is recovered. Hydrocarbon condensate in the separation vessels in the first compression stages contains mainly cracked gasoline and is transported to the gasoline workup section. Water is also removed from the gas to prevent ice formation in the deep cooling and distillation sections.

2.2.3 Product separation

The dried gas is cooled in a number of steps in a cryogenic refrigeration unit. After each step, condensate is collected. Eventually the cooling temperature can reach approximately minus 165 °C. At this temperature, virtually all hydrocarbons are condensed. The remaining gas from the cryogenic refrigeration unit mainly contains hydrogen (H_2), methane (CH_4) and small amounts of carbon monoxide (CO). The hydrogen gas is used for various catalytic hydrogenations that will be further explained, and the surplus is exported to third parties in the Chemelot campus. Because CO poisons the catalysts, its removal is necessary before the hydrogen can be used. This is done by adsorption. The pure hydrogen stream is used for the conversion processes, while the remaining stream (highly rich in CH_4) is used as fuel gas for the steam cracker furnaces.

The subsequent process route for the condensate basically consists of a series of distillation systems, which are responsible for separating the main products, respecting the quality requirements.

De-ethanizer and demethanizer

The condensate from the first separation vessel of the cryogenic cooling unit (minus 22 °C) goes to the "de-ethanizer" column where lighter components are separated, and propene and heavier components are recovered as bottom stream. The gas consists mainly of C2 hydrocarbons and lighter components and is fed to the acetylene removal unit.

The gas stream from the acetylene unit is cooled in the cryogenic refrigeration unit, with condensate separation. The separated condensate streams contain ethylene, ethane and methane, and are sent to the "demethanizer" column. In this column, methane is recovered as top product and ethylene/ethane as bottom product. The collected gas rich in methane is used as fuel in the pyrolysis furnaces whereas the bottom product of ethylene and ethane is sent to the C2 splitter.

C2 Splitter

In the C2 splitter, ethylene is separated from ethane by distillation. Ethylene is recovered as main product over the top and ethane is collected as bottom product and recycled to the gas furnace to be cracked. Ethylene is vaporised and directly transported via pipes to the LDPE and HDPE unit and also to third parties.

Depropanizer and debutanizer

The depropanizer is fed with the bottom stream of the de-ethanizer. In this column, distillation takes place between C3-hydrocarbons (top) and C4-hydrocarbons and heavier components (bottom). The top product is discharged to the MAPD (methylacetylene and propadiene) hydrogenation reactor, this process is important to allow propylene meet the polymer grade quality requirements. The bottom product is discharged to the debutanizer, which is responsible for separating C4 species (top) from remaining C5-C9 components (bottom). The C4 stream (butenes, butanes and butadienes) goes to further processing into the butadiene and MTBE units and the C5-C9 is sent to the gasoline system and benzene extraction.

C3 Splitter

Following the MAPD hydrogenation, the C3 stream is sent to the C3 splitter. In this column, the last residues of methane and hydrogen go over the top and are returned to the cracking gas compressor. Also, 98-99.5% propylene is obtained as top product and about 90% propane as a bottom product. This pure "polymer grade" propylene is suitable for the production of polypropylene and goes to a storage and / or directly to the PP unit and other buyers. The bottom product goes either to a storage tank or to the feed of the gas crackers. In this process, the propane is cracked together with fresh feedstock (co-fed).

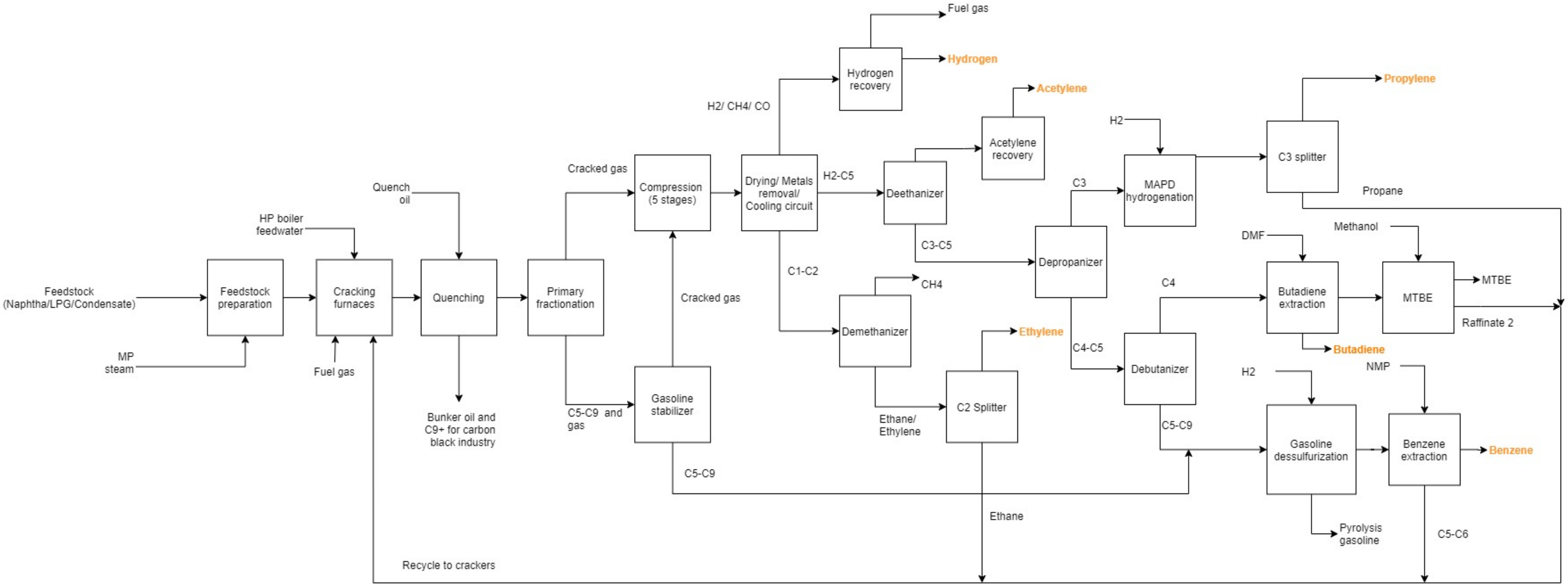

Figure 8 - Steam cracker detailed process flow

2.3 Downstream cracker units

This section describes the process to obtain pyrolysis gasoline, butadiene, MTBE and benzene products.

2.3.1 C_4 hydrocarbons

Butadiene extraction

The butadiene recovery happens via liquid extraction. Normally dimethyl formamide (DMF) is employed as solvent. First, direct contact between the solvent and the C4 rich stream takes place in an extraction column. Following, the solvent and butadiene are separated via distillation. The C4 components separated from the butadiene are called raffinate 1, which is the feedstock for the MTBE unit.

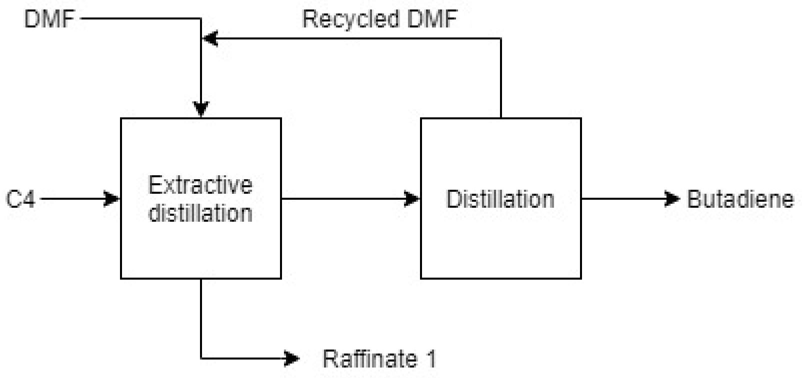

Figure 9 - Butadiene extraction simplified process diagram

MTBE unit

In this unit, the raffinate 1 resulting from the butadiene extraction is fed to the MTBE reactor together with methanol. The catalytic reaction results in methyl tert-butyl-ether (MTBE), which it recovered in a distillation column. The product is sent to proper storage. A second distillation is responsible for separating the remaining methanol from the C4 mix (raffinate 2). The methanol is recycled back to the MTBE converter and the raffinate 2 is sent to the crackers to serve as co-feed.

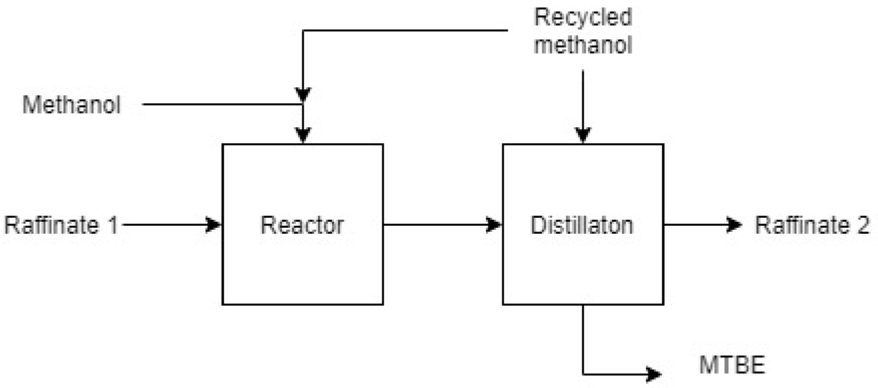

Figure 10 - MTBE simplified production process

2.3.2 Pyrolysis gasoline recovery and benzene extraction

Pyrolysis Gasoline hydrogenation and recovery
The gasoline hydrogenation plant is fed with pyrolysis gasoline (C5-C9) from both crackers OLEFINS 3 and 4 and from the existing buffer storage. The gasoline hydrogenation plant consists of two stages. In the first stage, the di-olefins (two double bonds) present in the gasoline are selectively hydrogenated to mono-olefins, and styrene to ethylbenzene. In the second stage, total hydrogenation of mono-olefins takes place. The hydrogenation step is important to avoid oligomers formation and to, therefore, stabilize the gasoline.

The hydrogenated gasoline is fed to distillation units. From the stabilizer, a bottom product is obtained from distillation which consists in C5 hydrocarbons and heavier components; this stream is sent to the depentanizer. In the depentanizer, a bottom product (C6+) is separated from C5 hydrocarbons, which are sent back to the cracking furnaces as feedstock. The C6+ stream is sent to the dehexanizer column. In the dehexanizer, the top product, rich in C6, is fed to the benzene extraction system and the bottom product (C7-C9) is stored as pyrolysis gasoline.

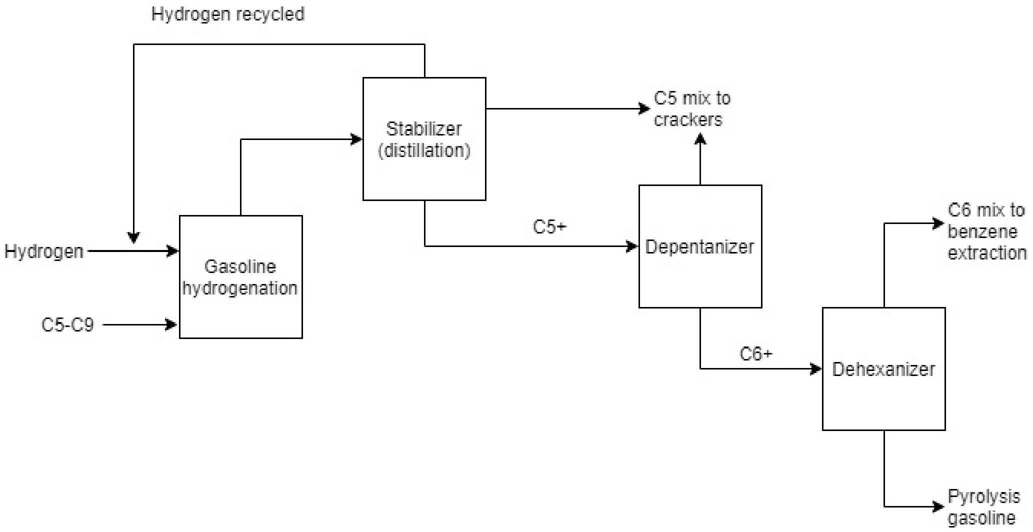

Figure 11 - Pyrolysis gasoline hydrogenation and recovery block diagram

Benzene extraction
The Benzene plant is fed with the distillate from the dehexanizer. This stream is composed by C6 hydrocarbons, which generally consist of 80% benzene. The benzene plant can be divided process-wise in the following parts:

- Extractive distillation plus raffinate separation
- Benzene stripper.

In the extractive distillation column, benzene is absorbed from the gas phase by means of N-methylpyrrolidone (NMP). In the extractive distillation column (at virtually atmospheric pressure) a bottom product obtained from NMP with dissolved benzene is discharged to the benzene stripper. The overhead vapor from the extractive distillation flows to the raffinate column in order to recover NMP. This NMP with some dissolved hydrocarbons is discharged back to the extractive distillation column. The top product from the raffinate column contains C6 hydrocarbons with a limited amount percentage of benzene (about 1%), and is also returned to the crackers together with fresh feeds (co-cracking).

In the benzene stripper, the dissolved benzene is desorbed from the NMP by means of vacuum distillation. The top product consists of benzene and is sent to storage. The bottom product of the stripping column consists of NMP and is returned to the extractive distillation column.

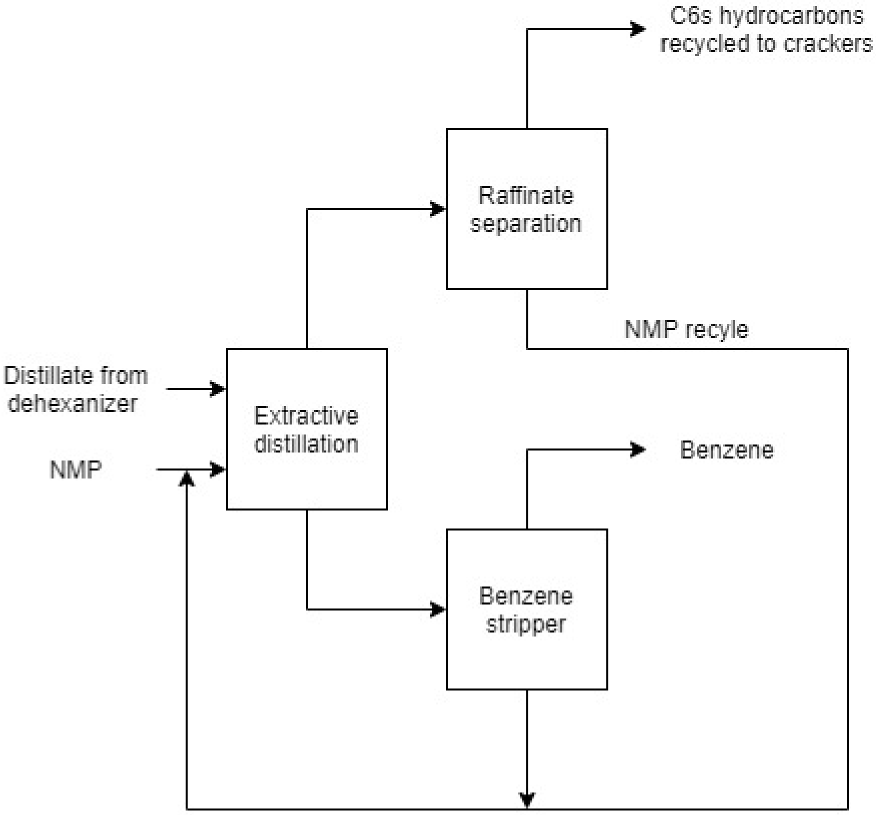

Figure 12 - Benzene extraction from crude pyrolysis gasoline of the steam cracker

2.4 Material and energy flows

Material balance

Considering the processes described above, the main material and energy flows were determined considering literature values for product yields and interviews with the company. Tables 6 to 8 summarize main material flows for each system. Figure 13 illustrates how theses processes interact. These values were based on interviews with SABIC Geleen for 2018 production.

Table 5 - Mass flows Steam cracking units SABIC

CRACKING+COMPRESSION+FRACTIONATION3)					
MATERIAL FLOWS					
Stream nr.	**Inlet**	**[kt/yr]**	**Stream nr.**	**Outlet**	**[kt/yr]**
1	Naphtha	4,000	6	Hydrogen-rich gas	35
2	Steam (HHP)	2,000	7	Fuel gas	576
3	Ethane and propane recycle	284	8	Ethylene	1,150
4	Recycle from C4/MTBE section	110	9	Acetylene	4
5	Recycle from gasoline section	15	10	Propylene	680
			11	C4-C5	360
			12	C5-C9	1,020
			13	Bunker oil	35
			14	Carbon black oil	98
			3	Ethane and propane recycle	284
			15	Steam exported (HP)	1,000
			24	CO_2 emissions from furnaces	1,568

3) The total inputs and total outputs do not reach the same value due to the water content (added via feedstock dilution), which is not balanced in these estimates and due to the coke formation in the furnaces, which it is unknown.

Table 6 - Mass flows C4/MTBE units

BUTADIENE+MTBE					
MATERIAL FLOWS					
Stream nr.	**Inlet**	**[kt/yr]**	**Stream nr.**	**Outlet**	**[kt/yr]**
11	C4-C5	360	17	Butadiene	110
16	Methanol	71	4	Recycle to cracker	110
			18	MTBE	150
			19	Remaining methanol	61

Table 7 - Mass flows gasoline/benzene units

GASOLINE+BENZENE					
MATERIAL FLOWS					
Stream nr.	**Inlet**	**[kt/yr]**	**Stream nr.**	**Outlet**	**[kt/yr]**
12	C5-C9	1,020	21	Gasoline	740
20	H2	15	22	Benzene	280
			5	Recycle to crackers	15

As previously mentioned, the chemicals that constitute the HVC group are hydrogen, acetylene, ethylene, propylene, butadiene and benzene. Considering the mass flows presented above, the total HVC production for SABIC Geleen in 2019 was 2,259 kt/yr.

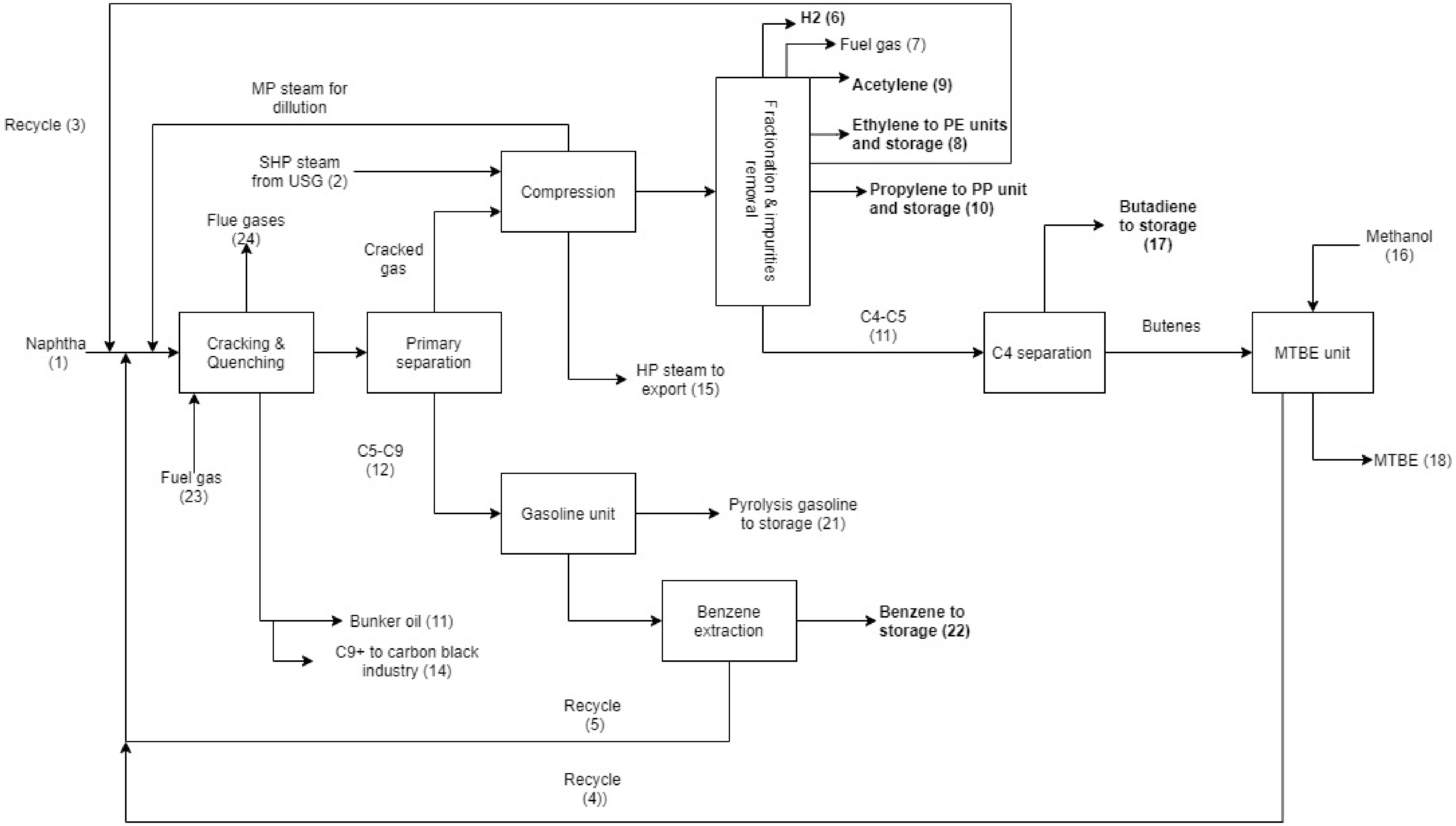

Figure 13 - Simplified process flow scheme from SABIC Geleen Site

Energy balance

Table 8 summarizes the energy flows for the steam cracking system as a whole (OLEFINS 3 and OLEFINS 4 together, considering pyrolysis gasoline, benzene, butadiene and MTBE units). The total energy demand for steam cracking and fractionation on SABIC's sites was around 33.5 PJ/y in 2018 and that is mainly related to fuel gas consumption. All fuel gas that the site produces is combusted to provide the necessary heat amount for the cracking furnaces and steam for the processes.

Table 8 - Overall energy flows SABIC Geleen in 2018

Energy flows			
Inlet	**[PJ/y]**	**Outlet**	**[PJ/y]**
Fuel gas	31 [4]	Steam exported (HP)	5 [7]
Steam from Swentibold (SHP)	7 [5]	Energy losses	0.5 [8]
Electricity	1 [6]		
Net energy **33.5 PJ/y**			

[4] Heating value for fuel gas considered was 50.2 GJ/t (Milieujaarverslag Site Chemelot, 2015)

[5] Heating value for superheated steam at 140 bar was 3.5 GJ/t (TLV, 2020)

[6] Based on interviews with the company, the electricity demand is assumed to be around 3% of the total energy demand

[7] Heating value for steam @18 bar/300 °C was 3 GJ/t (TLV, 2020)

[8] Energy losses considered to be 1.5% of net energy (Ren, T. et al., 2006). Examples of losses in a steam cracker unit is the thermal loss to stack to the walls in the cracking furnaces.

Regarding the processes downstream the crackers, the energy use per energy carrier in 2019 is presented in the table below.

Table 9 - Energy break down chemical plants (internal communication with SABIC, 2019)

System	Fuel gas use [GJ/t]	Fuel gas use [PJ/yr]	Steam use [GJ/t]	Estimated steam use [PJ/y]	Electricity use [GJ/t]	Estimated electricity use [PJ/y]	Total final energy use [PJ/Y]
Benzene	0.74	0.2	3.5	0.9	0.15	0.035	1.13
Butadiene recovery	-		6.4	0.83	0.90	0.1	0.93
MTBE system	-		1.4	0.21	0.08	0.012	0.22

Considering the total net energy of the system (33.5 PJ/y), the following energy breakdown per process unit is derived. The steam for the benzene, butadiene and MTBE systems is assumed to come from the heat recovery and compressions systems of the steam crackers, as mentioned before. Therefore, around 1.9 PJ/y of steam leaves the cracking section to be used in these adjacent units.

Subtracting the total energy consumed by the three downstream processes mentioned above (2.3 PJ/y) from the net energy value from Table 8, the energy consumption related only to the cracking furnaces, compression and fractionation is 31.2 PJ/y. Ren et al. (2006) indicates that 65% of the final energy consumption of a steam cracking process is related to the furnaces, the shares for compression and fractionation are 15% and 20%, respectively.

Applying the percentages from Ren et al. (2006) to the total 31.2 PJ/y, the specific energy consumption for each process unit could be estimated (Table 10).

Table 10 – Estimated final energy use per process unit
(Ren et al., 2006 and internal communication with SABIC, 2019)

System	Energy [PJ/y]	Share [%]
Cracking furnaces	20.3	65
Compression	4.7	15
Fractionation	6.2	20
Total steam cracking system	31.2	

Although nearly 31 PJ/y is given to the cracking furnaces via fuel gas, the pyrolysis section only consumes 20.3 PJ/y. This happens due to the fact that the energy provided by the combustion is not only used in the pyrolysis itself, it is also used to pre-heat the feedstock and to produce super-heated high pressure (SHP) steam (see Figure 14). Essentially high-high pressure (HHP) steam, with pressure around 110 bar, is produced via heat recovering from the furnaces flue gases and from the cooling of cracked gas (see item 2.2.1). This steam is used in the turbine of the cracked gas compressor, which is reduced to high pressure (HP) after use. The HP steam is available for other steam turbines and other equipment such as distillation columns and heat exchangers.

The steam cracking section (pyrolysis + compression+ fractionation) consumes around 31.2 PJ/y and the typical energy demand of current naphtha steam crackers is within the range of 14-17 GJ/t HVC (Ren at al., 2006) and between 11-14 GJ/t HVC (Ren at al., 2006) for world class crackers, for SABIC this value is 13.8 GJ/t HVC. The energy consumption of the remaining process units (benzene, C4 and MTBE systems) is mainly steam (high and medium pressure), which is produced on site.

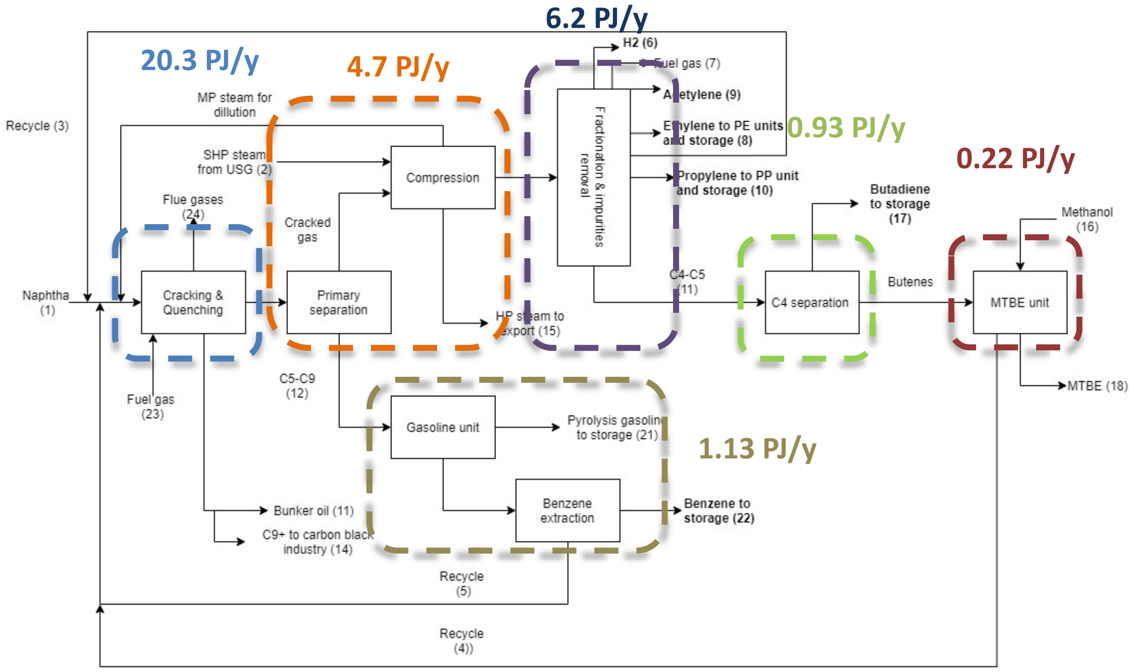

Figure 14 - Schematics of final energy use at SABIC Geleen site.

CO_2 emissions

Table 11 presents the total CO_2 emissions for the steam crackers. The pyrolysis furnaces are responsible for the biggest part of the direct emissions.

Table 11 - Total direct CO_2 emissions SABIC Geleen

CO_2 emissions	Value	Unit
Cracking furnaces emissions (direct)	1,680 [8)]	kt/y
Flaring (direct)	8 [9)]	kt/y
Total emissions	1,688	kt/y
Direct emissions factor	0.75	t CO_2 / t HVC

[8)] The emission factor considered for the fuel gas was 54.2 CO_2 kg/ GJ (Milieujaarverslag Site Chemelot, 2015)

[9)] Flaring emissions extracted from Milieujaarverslag Site Chemelot report (2015)

2.5 Utilities

The Utility Support Group (USG) B.V. is a joint venture between SABIC Petrochemicals B.V. and Sitech Utility Holding C.V. Under the name USG Industrial Utilities, they provide the purchase, production, distribution and sale of electricity, steam, industrial gases, air and water for companies at the Chemelot industrial complex. They support factories from SABIC, OCI Nitrogen, ARLANXEO, Fibrant and AnQore, among others (Chemelot, 2020). USG owns and operates steam boilers producing 140 and 79 bar steam as well as demineralization water plants.

The Swentibold combined heat and power plant in Geleen is in operation since 1999. Currently, this unit is owned by RWE. With gas and steam turbines, the power plant generates electricity with maximum capacity of 210 MWe. The unit also produces steam (140 bar/525 °C and 18 bar/300 °C) by heating demineralized-water with exhausted gases from the gas turbine and by firing natural gas in the waste heat boilers. The maximum generation capacity of steam is 300 t/h (RWE, 2020).

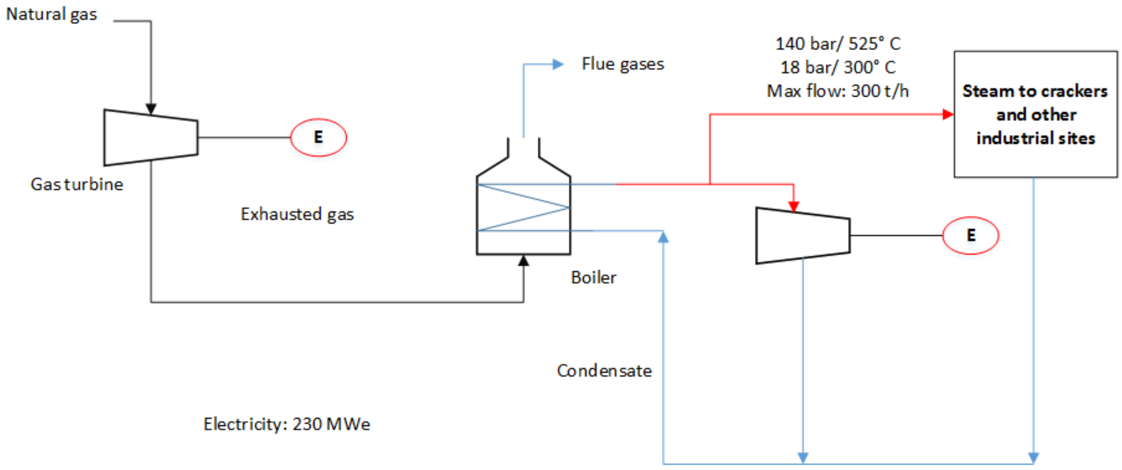

Figure 15 - Schematics of the Swentibold Power Plant

Table 12 presents the main values for energy and emissions related to both the USG auxiliary boilers and the Swentibold power plant.

Table 12 - Overview of Swentibold power plant and USG boilers energy input and emissions

Parameter	Value	Unit	Comment
Swentibold fuel gas intake	10.8	PJ/yr	Based on figures from 2018 from the Large Combustion Plant database (EEA, 2020)
Swentibold steam production	4.8	PJ/yr	Derived assuming 45% of thermal efficiency
Swentibold electricity production	3.2	PJ/yr	Derived assuming 30% of electrical efficiency
Swentibold CO_2 emissions	609	kt/yr	Derived assuming 56.5 kg CO_2/GJ as emission factor (Milieujaarverslag Site Chemelot, 2015)
USG Boilers fuel gas intake	5.6	PJ/yr	Milieujaarverslag Site Chemelot, 2015
USG boilers steam production	4.8	PJ/yr	Milieujaarverslag Site Chemelot, 2015
USG boilers CO_2 emissions	298	kt/yr	Derived assuming 53.9 kg CO_2/GJ as emission factor (Milieujaarverslag Site Chemelot, 2015)

As mentioned previously, SABIC imported around 7 PJ of SHP steam in 2019 from the steam network that connects the industrial sites in Chemelot. This corresponds to 73% of the total estimated steam produced by Swentibold and the USG boilers. Regarding SABIC's electricity consumption (around 1 PJ/yr in 2019), it is unknown how much was provided by the power plant and imported from the grid.

The imported steam is used by the steam turbines that run the compressors on site. The cracked gas compressor is usually driven by a back-pressure turbine, which uses superheated pressure steam (SHP) and exhausts a lower-pressure steam. The energy delivered by the steam is converted to rotational energy by means of rotor blades, which are coupled to the compressor's shaft. This energy is, therefore, used to run the compressor. Additionally to the cracked gas compressor, a steam cracker site normally presents other steam driven compressors that are also quite relevant for the site's steam network. Figure 16 gives an overview of a typical steam network of a steam cracker.

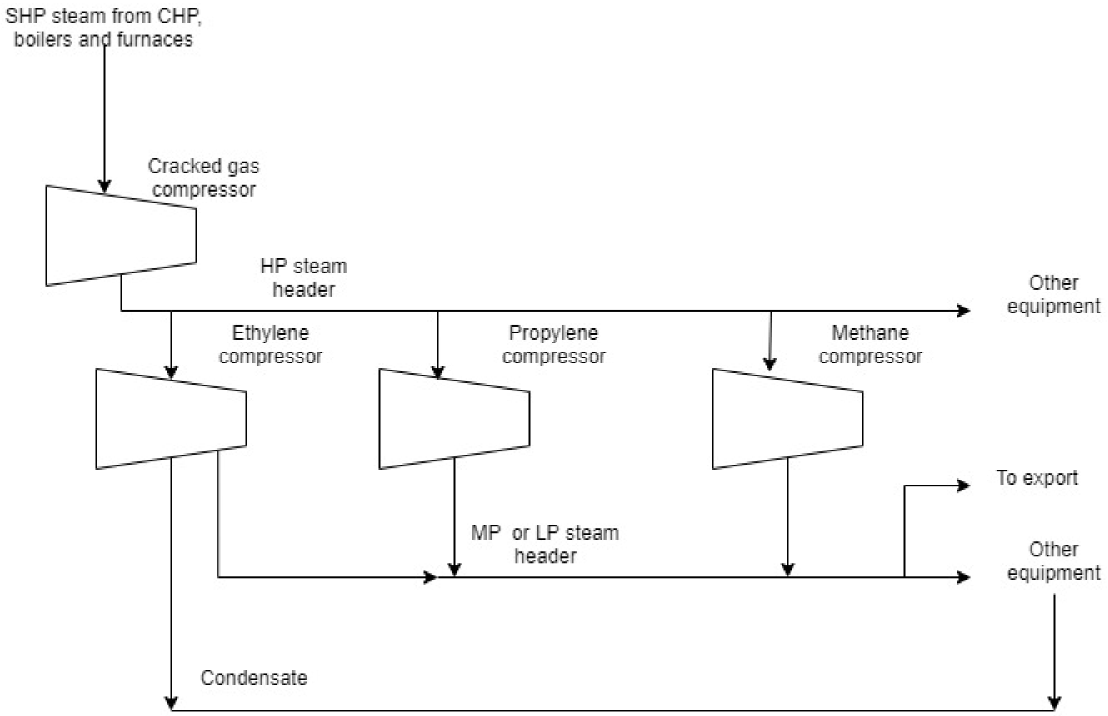

Figure 16 - General schematics of steam network in a steam cracker site

The MIDDEN report 'Decarbonisation options for Large Volume Organic Chemicals production, Shell Moerdijk' (Wong and Van Dril, 2020) presents a complete overview regarding the general economic aspects of a conventional steam cracking facility. For this reason, this report does not include similar section.

3 LVOC products and use

The LVOC production chain is briefly discussed in this chapter 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, LPG and gas condensates transported by pipeline to Chemelot, both from Rotterdam and Antwerp. SABIC's site in Geleen manufactures chemicals from short chain building blocks, such as ethylene and propylene, to more complex final products such as polymers. The following sections will describe in more detail the feedstocks and products handled at SABIC, including production volume/markets, applications and their chemical and physical properties. The scope of this report is limited to the products indicated in Figure 8. SABIC operates other downstream processes at Chemelot for polymers, described in another MIDDEN report 'Decarbonisation options for the Dutch polyolefins production' (Negri & Ligthart, 2020). Further, SABIC supplies products to connected installations for further processing by other companies.

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 such as butadiene and aromatic hydrocarbons, than lighter feedstocks such as ethane. The feedstock used will depend on market conditions and the availability of supplies (EIPPCB, 2014; Zimmermann & Walzl, 2009). The main feedstocks in Europe comprise of naphtha, natural gas condensate, liquid petroleum gas (LPG), and gas oil (Figure 17), with naphtha holding the largest share (CEFIC, 2013; ICIS, 2017). 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; Zimmermann & Walzl, 2009).

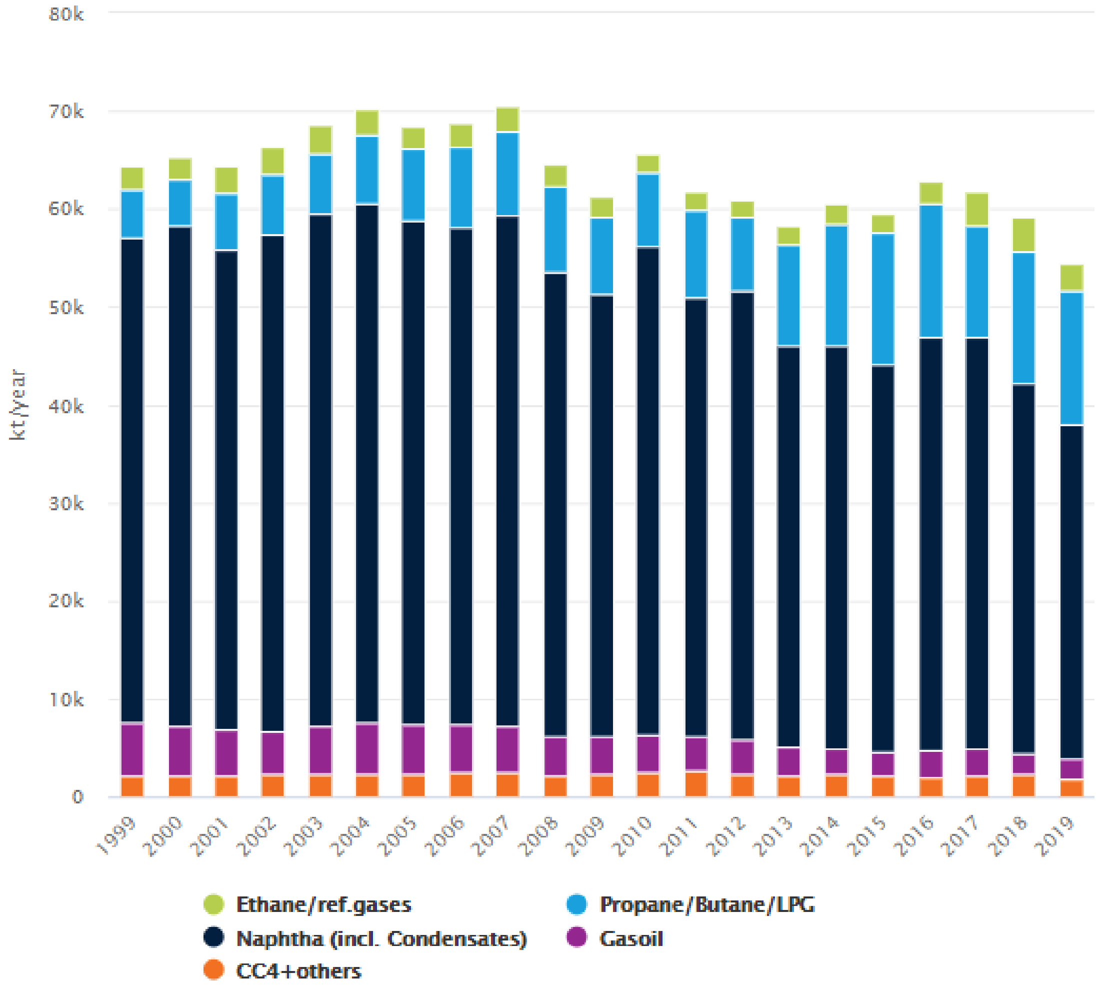

Figure 17 - Feedstock mix for EU15 + Norway between 1999 and 2019 (Extracted from Petrochemicals Europe website, 2020)

National statistics for the Netherlands for the past 10 years indicate that naphtha represents approximately 70% of the fossil feedstock for the petrochemical industry in the country and LPG accounts around 20% (Figure 18). The predominant feedstock used at SABIC is naphtha and gas condensate. This is comparable with feedstock mixes reported for the Benelux region where naphtha constitutes 81% of the feedstock mix, and the remainder is ethane, propane, and butane (~19%) (Saygın et al., 2009).

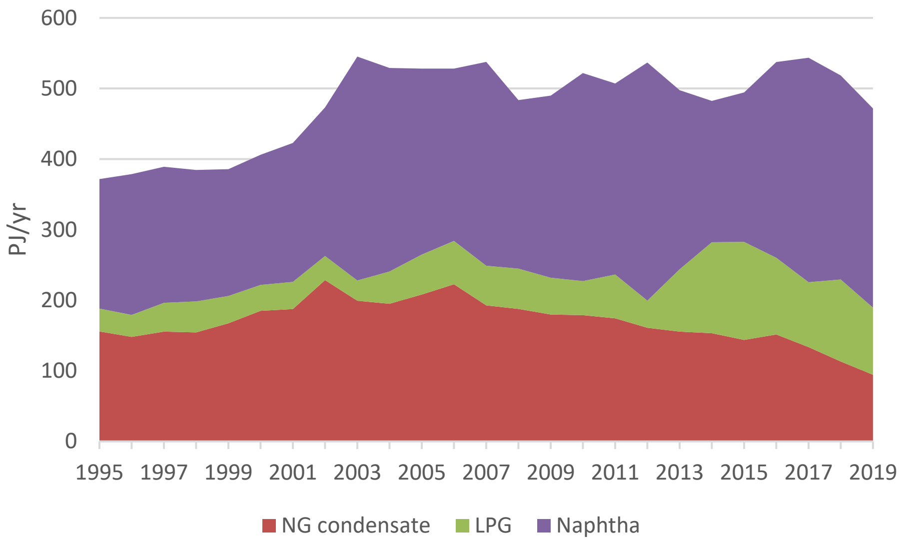

Figure 18 - Feedstock input to Dutch crackers between 1995 and 2019 (CBS, 2020b)

Naphtha is a refinery fraction composed of C5–C11 aliphatic hydrocarbons and has a boiling point range between 35–190 °C. Depending on refinery conditions and source, it can vary in composition and is typically processed as light naphtha (boiling range 35–90 °C), heavy naphtha (90–180 °C), and full range naphtha (35–180 °C) (Zimmermann & Walzl, 2009).

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 butenes (American Chemistry Council, 2017). In Europe, LPG is generally a blend of mainly 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 shares 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 condensate is a hydrocarbon liquid stream separated from natural gas and consists of higher-molecular-weight hydrocarbons that are recovered as liquids in separators in natural gas field facilities or gas-processing plants. Typically, gas condensate contains hydrocarbons to C8 (Speight, J., 2015).

Further details about typical steam cracking feedstocks are present in the MIDDEN report 'Decarbonisation options for Large Volume Organic Chemicals production, Shell Moerdijk' by Wong and Van Dril (2020).

3.2 Products

The chemicals produced at SABIC steam crackers can be classed as "Bulk Petrochemicals and Organic Intermediates". They are derived from hydrocarbon feedstocks and, therefore, characteristically feature a carbon chain. The bulk petrochemicals produced at SABIC include olefins (short chain hydrocarbons), benzene (molecule with an aromatic six-carbon ring structure), butadiene and MTBE. 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 globally are used in polymer production (Wesselink & Deng, 2009). Other co-products such as fuel gases and hydrogen are also valuable as they can be sold or internally used.

3.2.1 Ethylene

Ethylene is the largest volume commodity chemical produced globally. In 2019, approximately 16 Mt of ethylene was sold in the EU28, being The Netherlands responsible for 2.2 Mt (Eurostat, 2020). Its various applications include the packaging, construction, agrochemical, textile, and automotive industries (American Chemistry Council, 2017). The largest use of ethylene (~60%) produced in Western Europe is for production of different types of low-, linear low- and high-density polyethylene (Figure 19) (IHS Markit, 2017). This involves a polymerization reaction where small molecules such as ethylene are repetitively joined together to form larger molecules. From 2011-2016, global ethylene consumption increased at an average rate of 3% per year and the global capacity grew around 2%, which therefore led to higher utilization rates of steam crackers. This trend of 3-4% growth in ethylene consumption is expected to continue for the next five years (IHS Markit, 2017). This trend is mainly due to the polymer industry. Figure 20 presents an overview of the production volumes of products that uses ethylene as feedstock along the years.

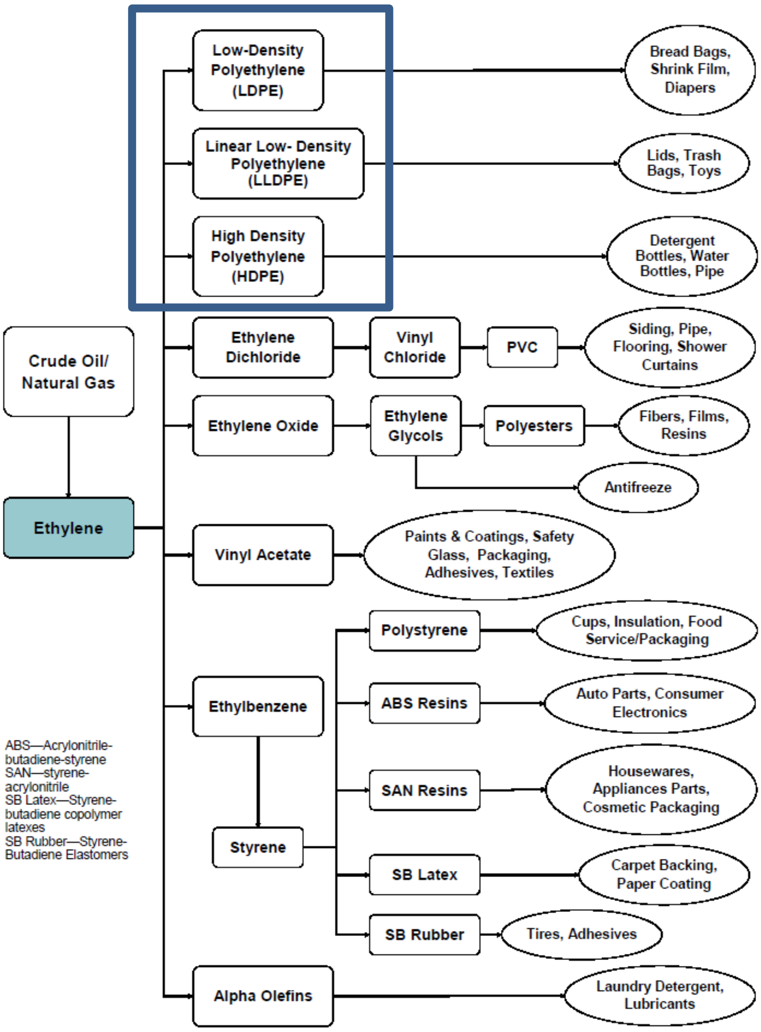

Figure 19 - Production chain for ethylene, blue box indicates chemicals produced at SABIC Geleen (adapted from ACC, 2017)

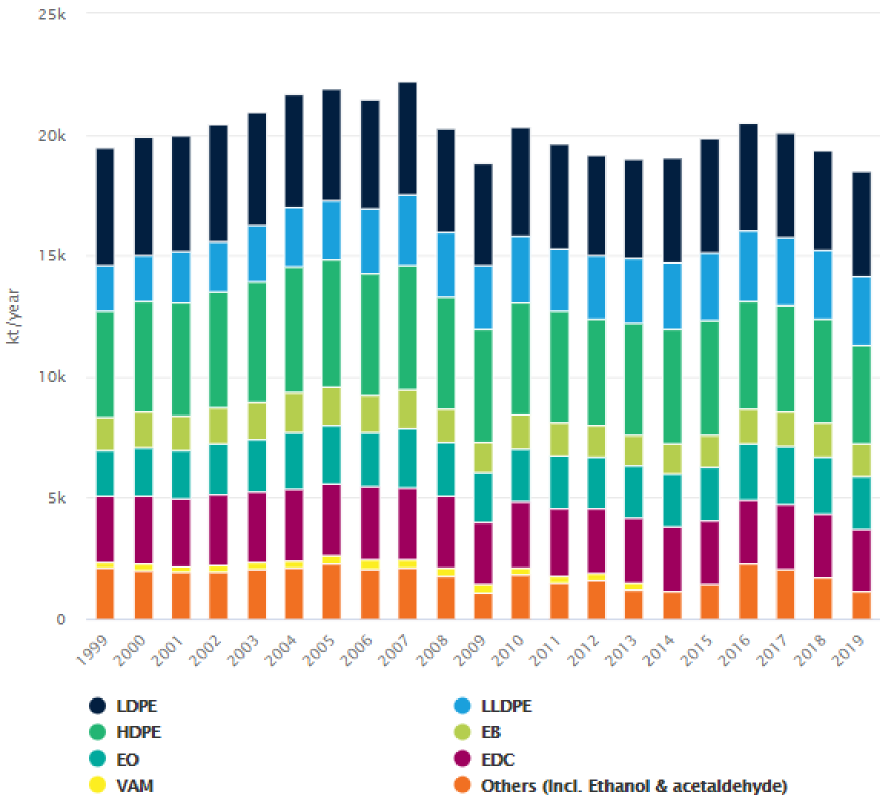

Figure 20 - Ethylene consumption by derivatives in EU15 + Norway (Petrochemicals Europe, 2020). LDPE: low density polyethylene, HDPE: high density polyethylene, LLDPE low-low density polyethylene, EO: ethylene oxide, EB: ethylbenzene, EDC: ethylene dichloride, VAM: vinyl acetate monomer.

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, 2015). Its production is largely driven by demand for polypropylene and propylene oxide, which are used in resins and fibers and found in important materials such as textiles, packaging, and pipes. As seen in Figure 21, it is also used extensively to produce other specialized chemicals with the most prominent being propylene oxide, acrylonitrile, cumene, and various alcohols (ACC, 2015; HIS, 2015). Polypropylene is highlighted in Figure 21 because this product is also produced by SABIC’s site in Chemelot.

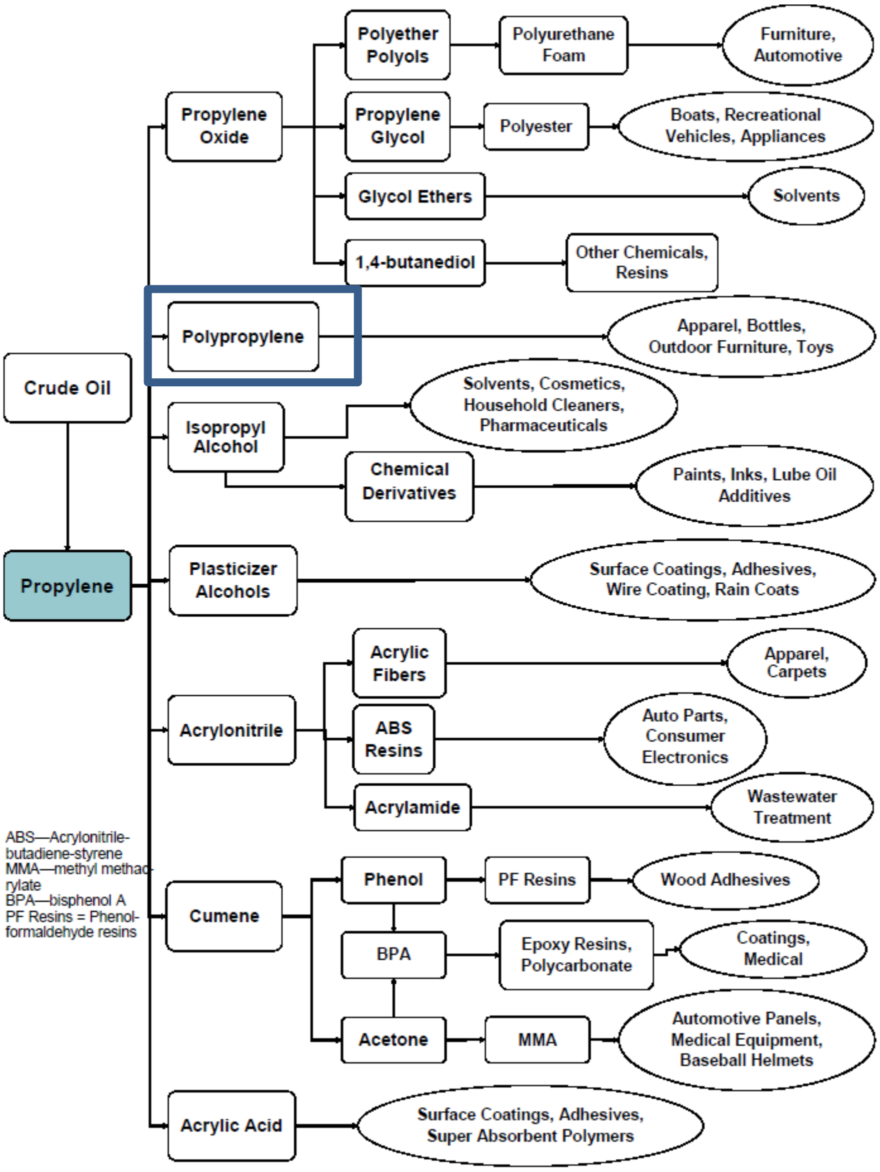

Figure 21 - Production chain for propylene, blue box indicates chemical produced at SABIC Geleen (adapted from ACC, 2017)

In Western Europe, around 70% of propylene is obtained from steam crackers, the remaining 30% is produced via refinery processes, propane dehydrogenation and metathesis (Figure 22). In 2019, the sold production of this chemical in the EU28 was approximately 12 Mt and 1.8 Mt in The Netherlands (Eurostat, 2020).

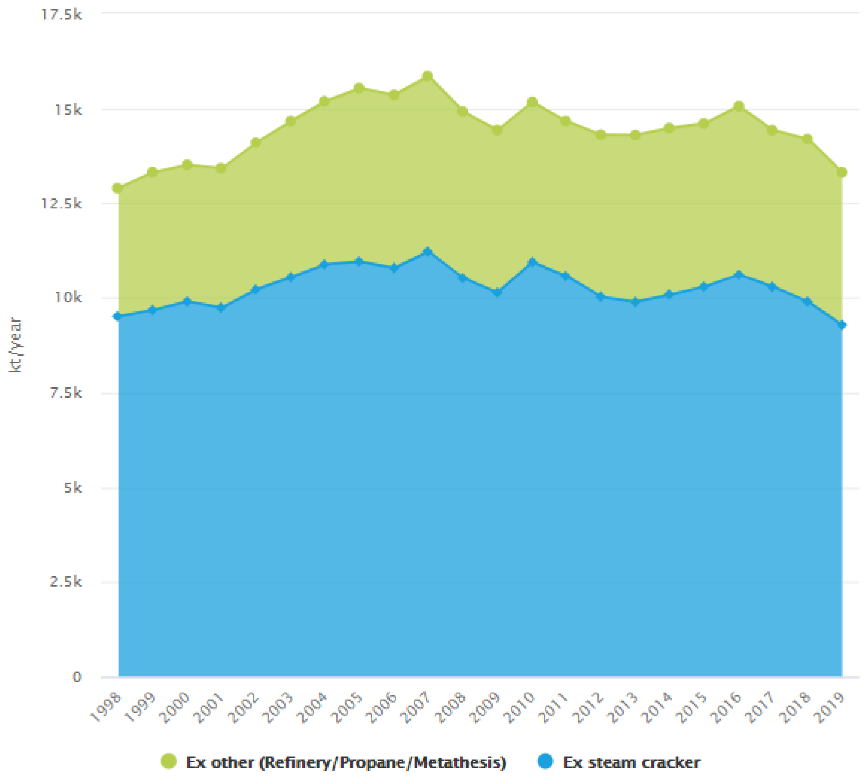

Figure 22 - Propylene production by sources in EU15 + Norway (Petrochemicals Europe, 2020)

3.2.3 C_4 hydrocarbons

The C4 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, and use C4 derivatives to make tires, auto parts, and pipes (ACC, 2017). Furthermore, C4s such as butane can be recycled from the cracked stream and be reused as feedstock, or fuel to produce ethylene (Figure 23). For SABIC's site, the products that are part of the C4 hydrocarbon chain are MTBE and butadiene

Butadiene
Butadiene is used as a chemical intermediate in the manufacture of polymers such as synthetic rubbers or elastomers, including styrene-butadiene rubber (SBR), polybutadiene rubber (PBR), polychloroprene (Neoprene) and nitrile rubber (NR). The largest demand for this chemical is from the tire industry, which uses SBR and PBR. Styrene-butadiene latex is used to produce carpet and paper coatings, neoprene is applied in gloves, wetsuits, waders and foams and products such as hoses, gloves, gaskets and seals can contain nitrile rubber in their compositions (American Chemistry Council, 2020).

The ethylene market influences directly in the butadiene production because butadiene are mainly obtained as a by-product from steam crackers. In 2019, the sold volumes of butadiene in the EU28 and in The Netherlands were 2.8 Mt and 0.2 Mt, respectively (Eurostat, 2020).

MTBE
Methyl tert-butyl ether (MTBE) is a flammable liquid that is commonly used as an additive for unleaded gasoline since the 1980s. MTBE increases octane and oxygen levels in gasoline. This chemical is also used to make high purity isobutylene which is further processed to produce butyl rubber. Additionally, MTBE is employed as a solvent and extractant. Although some pollution regulations limited the addition of MTBE in gasoline in the US, in Europe this chemical is still applied to the fuels. However, some European directives promote the use of biofuels through tax incentives, motivating MTBE production units to convert towards ETBE, in which bioethanol can be used (ICIS, 2010).

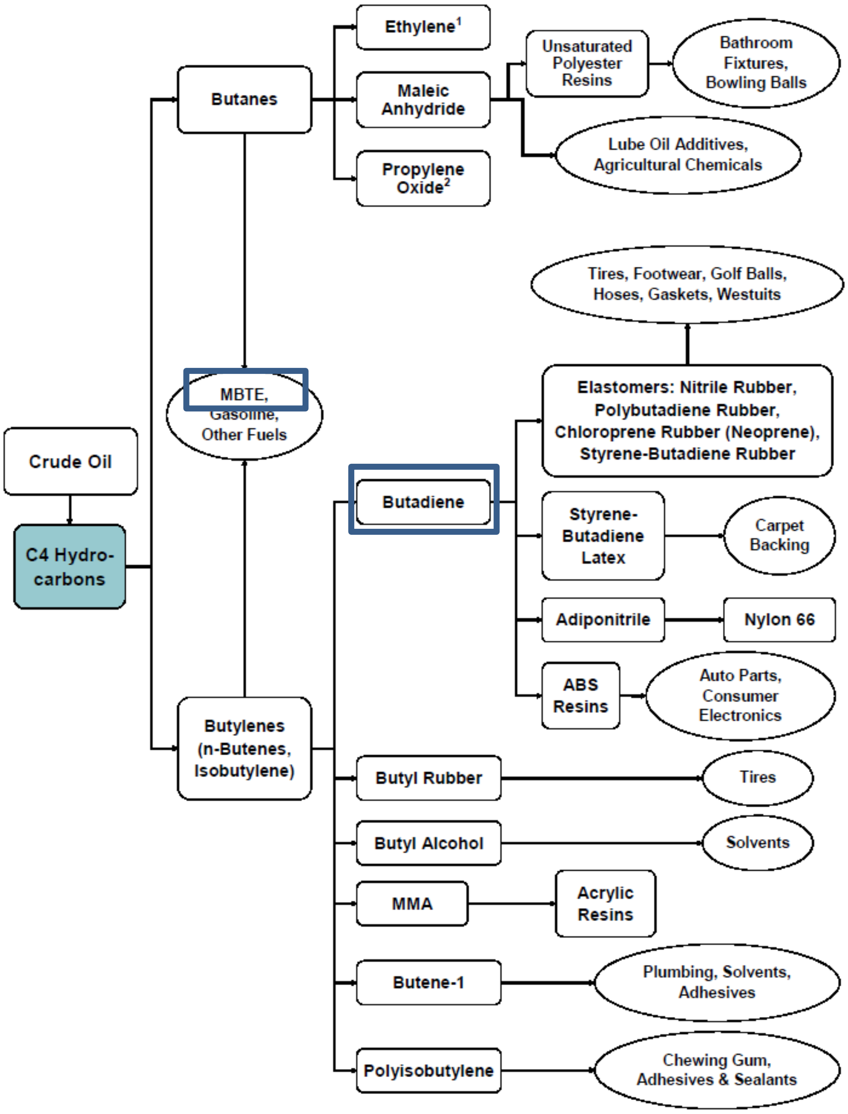

Figure 23 - Production chain for C4 hydrocarbons, blue boxes indicate chemicals produced at SABIC Geleen (adapted from ACC, 2017)

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”. They have the common characteristic of an aromatic six carbon ring, which gives them a specific odor. One of their main uses is in the production of polymers, and further multiple consumer products including solvents, paints and polishes. In Europe, BTX production mainly follows the same pathway as the olefins, i.e.

steam cracking of Naphtha. BTX is extracted from pyrolysis gasoline, one of the by-products from the steam cracking process. An alternative process, commonly present in refineries, is catalytic reforming of Naphtha (also known as Platforming) yielding high-octane gasoline and BTX rich aromatics, which are further extracted (DECHEMA, 2017). SABIC Geleen's aromatics unit concentrates on benzene extraction. Therefore, this section describes the benzene production chain only.

Among the aromatics chemicals, benzene presents the largest production volume globally. In 2019, the production of benzene in the EU28 was 5.7 Mt and 1.1 Mt for The Netherlands (Eurostat, 2020). In the past, this product was added to gasoline to increase the octane number, however, due to its toxicity its use has been regulated (Ullmann, 2002). Benzene is now mainly consumed as a chemical feedstock, where 70-75% of the produced benzene is applied in ethylbenzene and cumene production (IHS, 2020), and it is also an important feedstock for cyclohexane and aniline synthesis. 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. The full production chain for benzene is shown in Figure 24.

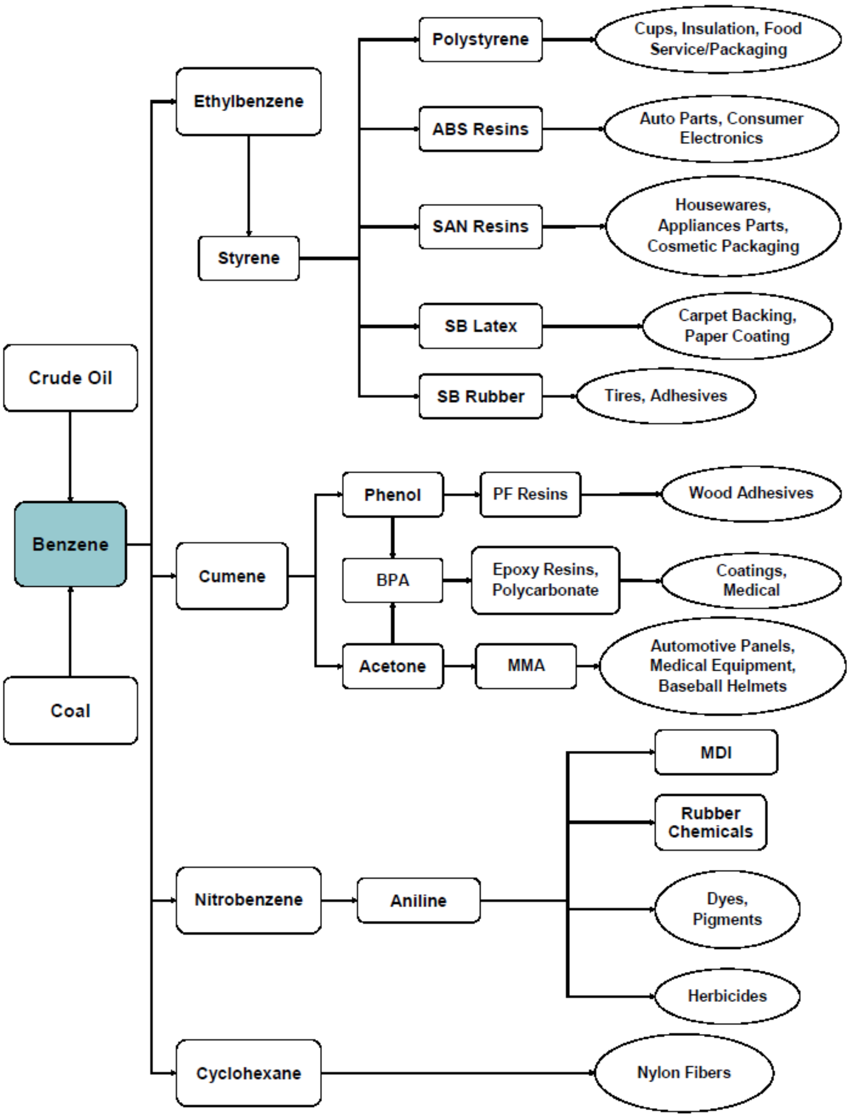

Figure 24 - Production chain for benzene (ACC, 2017)

At SABIC Geleen, 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 high amounts of olefins, and low amounts of xylenes, therefore making it more suitable for benzene or benzene/toluene extraction (Table 13).

Table 13 - Typical composition of raw pyrolysis gasoline (ThyssenKrupp, 2014)

Component	[%wt]
Benzene	30
Toluene	20
Xylenes	4
Ethylbenzene	3
C9+ aromatics	3
Naphthenes	High
Olefins	High
Paraffins	Low
Sulphur	up to 1000 ppm

4 Options for decarbonisation

This chapter presents potential options for reduction of energy use and/or CO_2 emissions for LVOC production at the SABIC site in Geleen. Figure 25 shows the relevant aspects of industrial processes that usually are investigated in MIDDEN.

For SABIC Geleen, the focus is on the pyrolysis section, which is the largest source of direct CO_2 emissions (Table 11), and the products from this unit are the main input sources for other processes, including the pyrolysis gasoline stabilization, benzene extraction, butadiene and MTBE units. Table 14 summarizes the decarbonisation options explored in this report regarding their applicability and relevance to the site.

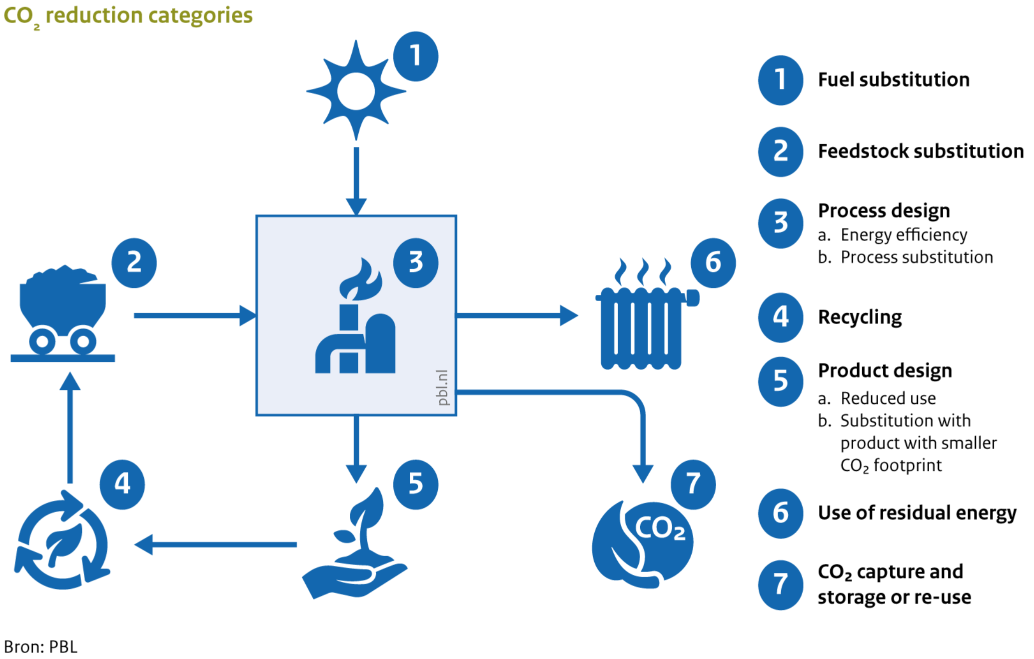

Figure 25 - Schematics for decarbonisation options investigation (PBL, 2018)

Table 14 - Summary of decarbonisation options for SABIC Geleen

Technology	Category	Relevant to process
Carbon capture and storage or utilization	Carbon capture	Might be applicable to all current stacks, limited by space requirements, CO_2 concentration and routes for transport and storage.
Electrification	Alternative energy supply for furnaces	Might be applicable to all processes using gas-fired equipment (e.g. Steam cracking furnaces)
	Alternative energy supply for boilers	Alternative source for SHP steam
Co-processing (5-10%) bio-naphtha in steam cracker furnaces	Alternative feedstock	Possible co-feed for existing steam crackers
Waste plastic oil as feedstock	Alternative feedstock/ Recycling	Possible co-feed for existing steam crackers
Power to methanol +methanol to olefins	Alternative process	Process alternative for olefins production
Blue hydrogen as fuel	Alternative energy supply	Might be applicable to all processes using gas-fired equipment (e.g. steam cracking furnaces)
Green hydrogen as fuel	Alternative energy supply	Might be applicable to all processes using gas-fired equipment (e.g. steam cracking furnaces)

4.1 Carbon capture and storage or utilization (CCS/CCU)

In an integrated plant as SABIC Geleen, fuel combustion occurs mainly in cracking furnaces and in steam production (Swentibold CHP and USG boilers). Accordingly, the CO_2 emissions sources usually are low in CO_2 concentration and present low pressure levels. The CO_2 concentration in the off-gas flow from process furnaces ranges from 8-10% (vol) (Markewitz & Bongartz, 2015). These are relatively low CO_2 concentrations which may limit the capture efficiency (Kuramochi et al., 2012).

Another relevant aspect is the site's location, since its distance to the sea influences the feasibility for the offshore carbon storage in empty gasfields. Offshore storage is preferred because of public perception and available storage volumes. The Chemelot site is more than 100 km from the Rotterdam port and currently not included in the Porthos initiative (infrastructure for carbon capture and storage in the North sea). CO_2 transport infrastructure between Rotterdam and Chemelot could be realized in the future, either in the form of pipelines or by ship. Instead or in addition, utilization of captured carbon is also an option.

There are three CCS technologies currently being studied: pre-combustion capture, post-combustion capture and oxyfuel combustion capture. Among these, the most relevant for steam crackers are post-combustion and pre-combustion capture, therefore, they are the options explored in this study.

Post-combustion capture

As the name indicates, this technology includes CO_2 capture from the flue gas after the combustion process takes place. The CO_2 from the flue gas is chemically absorbed by a suitable solvent, followed by CO_2 desorption due to temperature and pressure changes. The released CO_2 is compressed for further transport and storage or utilisation. The recovered solvent is recycled for another cycle of absorption; literature indicates amines and ammonia as the most suitable solvents for the process. The scrubbed flue gas returns to the combustor stack and is released to the atmosphere.

A positive aspect of this technology is the fact that amine absorption is already extensively used in the chemical industry, also the purity of CO_2 achieved is high (>99.99%) compared to other CCS technologies. Currently, the capturing efficiency reaches around 90%, but researches are exploring new solvents in order to improve this efficiency (Markewitz & Bongartz, 2015).

The integration of the capturing system with the combustion processes is very site dependent, which makes challenging to assess the total costs for its implementation (specially costs related to interconnecting the capturing unit with the present installations). Also, depending on the volume flows captured, each stack on site would need a dedicated capture equipment. Figure 26 illustrates a typical post-combustion system.

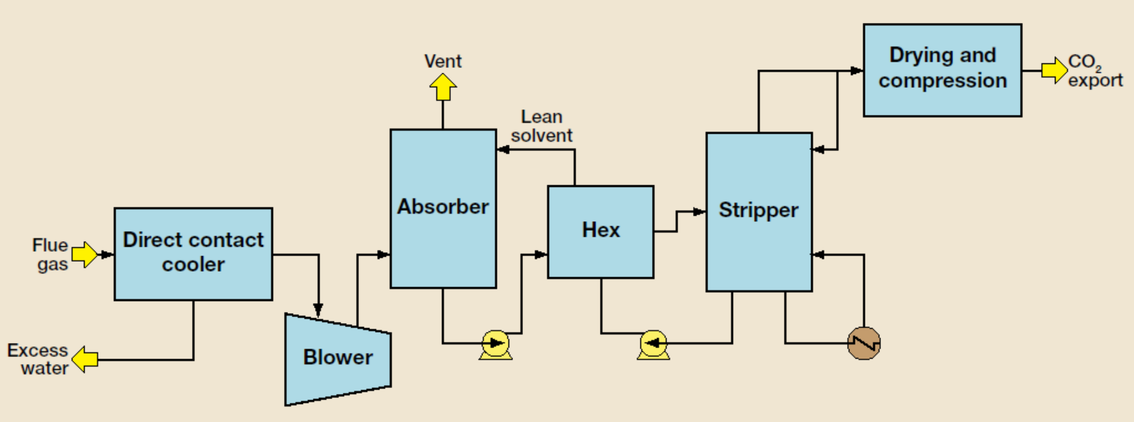

Figure 26 - Post-combustion capture system (Ferguson. S. and Stockle, M., 2012) Hex: heat exchanger

Regarding the investment figures for the post-combustion technology applied to furnaces, a wide range of costs can be found in literature (45-245 EUR_{2017}/ t CO_2 captured) (SINTEF, 2017 & Ho, M.T. et al., 2011). Some of the reasons for this are the different CO_2 concentrations assumed for the flue gas, the distinct combustion systems configurations and the different assumptions considered for the thermal integration between the capturing system and the site in which the new unit is installed. Therefore, an assessment considering the specificness of the site should be done in order to obtain more realistic costs for a CCS installation.

Table 15 includes the investment costs for a retrofit post-combustion system in a steam cracker site with CO_2 concentration of 5% vol. in the flue gas. The CAPEX value refers to the equipment costs for the capture system (absorption, desorption and compression) and the piping for interconnecting with the steam cracking stacks. The fixed OPEX is considered to be 4% of the CAPEX and it does not include energy costs. The site studied by Sherif, A. (2010) differs from SABIC Geleen in some aspects, however, the costs values present in his work may serve as proxy estimate for the application of CCS in a steam cracker.

Table 15 - Investment costs for retrofit post-combustion CCS in steam cracker furnace with 5%vol. CO_2 concentration in the flue gas (Sherif, A., 2010)

Post-combustion using MEA[10)] solvents		
	Value	**Unit**
Capacity	428	kt CO_2 captured/yr
CAPEX	156	EUR_{2010}/t CO_2 captured/yr
Fixed OPEX	6.8	EUR_{2010}/t CO_2 captured

[10)] MEA stands for monoethanolamine, which is a solvent commonly used for absorption of acidic gases

Table 16 summarizes the energy consumption of a typical post-combustion capture system using MEA solvents.

Table 16 - Energy commodities demand for a typical post-combustion capture system

Post-combustion using MEA solvents		
	Value	**Unit**
Steam consumption	2.5[1] – 4.4[11]	GJ/t CO_2 captured
Electricity consumption	156[1] – 172[12]	kWh/t CO_2 captured

[11] SINTEF, 2017
[12] Kuramochi, T. et al, 2012.

Pre-combustion capture

In this process, a hydrocarbon-rich fuel is fed to a reformer or gasifier in order to produce CO_2 and H_2 (syngas). The concentration of syngas is then increased in a shift-reactor, after which it is cooled and CO_2 is captured via solvent absorption. The resulting syngas has a high pressure level, which allows carbon capture to be performed via physical absorption, using methanol (Rectisol wash) or dimethyl ether/polyethylene glycol (Selexol scrubbing). This CO_2 can be further compressed and exported. An almost pure H_2 stream results from the absorption and it would serve as fuel substitute for the cracking furnaces (Oliveira and Schure, 2020; Markewitz & Bongartz, 2015). The hydrogen combustion in steam crackers is explored in more details in Section 4.6. Figure 27 illustrates a typical pre-combustion system.

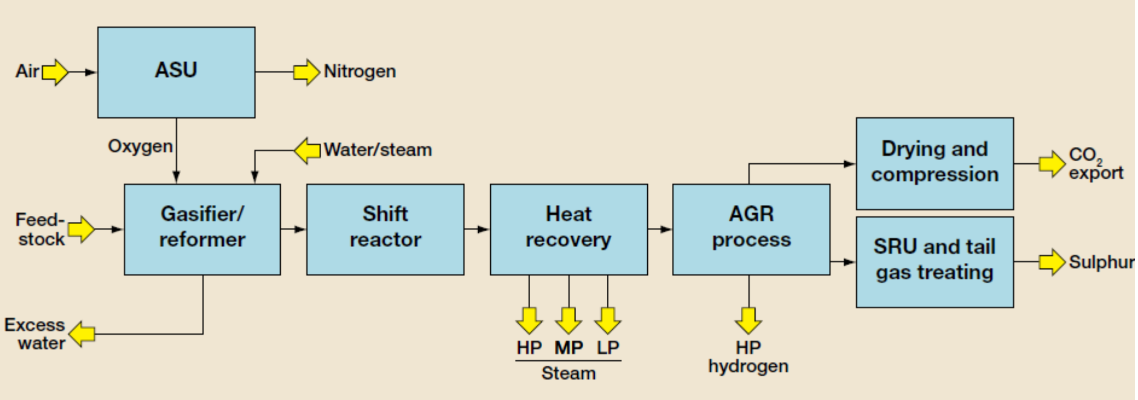

Figure 27 - Pre-combustion capture system (Ferguson. S. and Stockle, M., 2012)
ASU: air separation unit
AGR: acid gas removal
SRU: sulphur recovery unit

Investment data for pre-combustion systems applied specifically to a steam cracker facility was not found in literature reference, however, costs figures and energy flows were estimated by Kuramochi, T. et al. (2012) for both refining and petrochemical sectors. Table 17 summarizes the information gathered regarding expenditures for a retrofit pre-combustion system.

Table 17 – Investment costs for retrofit pre-combustion CCS for petroleum and refining sectors (Kuramochi, T. et al. 2012)

Pre-combustion		
	Value	**Unit**
Capacity	770	kt CO_2 captured/yr
CAPEX	150	EUR_{2011}/t CO_2 captured/yr
Fixed OPEX	7.5	EUR_{2011}/t CO_2 captured

Table 18 presents an overview of the energy consumption of a typical pre-combustion system when connected to petroleum and refining industrial sites. There is the possibility of power production via steam turbines due to steam generation via syngas cooling, however, it is important to point out that these numbers may differ depending on the heat integration with utilities facilities and other units already existent on site.

Table 19 - Energy commodities demand for a typical post-combustion capture system applied to petroleum and refining sectors (Kuramochi, T. et al. 2012)

Pre-combustion		
	Value	**Unit**
Heat consumption	4.8	GJ/t CO_2 captured
Electricity consumption	-0.1	GJ/t CO_2 captured

4.2 Electrification

Electric furnaces present significant potential to reduce energy related emissions (VNCI, 2018). Furnaces and boilers can use electric currents (resistance heating) or electromagnetic fields (induction and dielectric) to heat materials. Most of the electrical heating methods can be subdivided into direct (inductive/dielectric) and indirect (resistance/arc/infrared) heating technologies. Direct technologies generate heat within the material without the need for a heat transfer medium whereas indirect heating takes place outside the material and with the aid of a heat transfer medium (Schuwer, D., Schneider, C., 2013).

Electric heating is already widely used in industry, however, none of the known technologies has been applied yet in large scale for the steam cracking processes. The main existent technologies for electrical industrial heating are: resistance (200-1800 ºC), arc (1200-3000 ºC), infrared (300-2600 ºC), microwave (100-1300 ºC), and induction (100-2500 ºC).

Resistance and electric arc heating, for instance, can be operated flexibly to utilize periodic low electricity prices, although this is not desirable. Arc heating is normally applied to processes in a higher temperature range than the required in the pyrolysis section (850°C). Infrared heating provides high energy densities and is capable of rapid heating when compared to gas furnaces (BZE, 2018). In general, the resistance heating is easily automated and requires low maintenance, it also offers uniform energy supply throughout the processing volume and installation flexibility, once the resistance ovens could be designed in modules (ITP, 2007). Therefore, electrical resistance heating has high potential to offer an alternative to most types of industrial gas-fired furnaces (BZE, 2018).

Considering the general characteristics of each technology and experts consultation, the most relevant option for electric furnaces would be indirect resistance heating. This technology is not available yet on an industrial-scale for steam cracking process mainly because the temperature gradient in a steam cracker furnace is very determinant for the high value chemicals yields, however, it is under development (TRL 1-2) (communication with TNO experts, 2019). A simple illustration of this technology is shown in Figure 28.

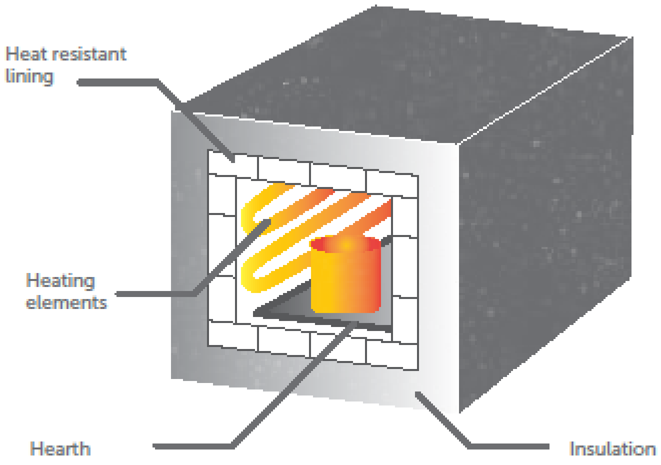

Figure 28 - Overview of indirect electrical resistance heating (BZE, 2018)

Since complex production sites such as steam crackers are highly integrated, changes to one part of the process might require modifications in other parts. For example, electrification of the cracking furnaces would reduce the demand for fuel gas on site. Because the fuel gas is a by-product of the cracking process itself, alternative applications for it needs to be explored. One option could be the use of fuel gas as feedstock for hydrogen production, by methane reforming with CCS (‘blue hydrogen’).

Electric furnace application could also result in a shortage of steam availability for the rest of the site. Without the gas-fired furnaces, the heat recovery from the hot flue gases would no longer take place, affecting directly the plant steam balance. An interesting electrification option is the replacement of steam driven compressors by electricity driven ones. In this way, the total demand of steam on site reduces and the shortage caused by the electrical crackers would be partly addressed.

It is expected that hybrid systems (gas-fired furnaces + electrical furnaces) would take place first coupled with the gradual electrification of other equipment such as steam turbines.

In 2019, six petrochemical companies announced the creation of a consortium to jointly investigate how naphtha or gas steam crackers could be operated using renewable electricity instead of fossil fuels. The Cracker of the Future consortium includes BASF, Borealis, BP, LyondellBasell, SABIC and Total, all located in the trilateral region of The Netherlands, North Rhine-Westphalia and Flanders. The agreement consists on R&D and knowledge sharing as they assess the possibility of transitioning their base chemical production to renewable electricity. Currently, the companies are exploring and screening technical options. Once a potential technical solution is identified, the parties will determine whether to pursue joint development project(s), including R&D activities that could include a demonstration case (Brightlands, 2019).

Electrification potential for the steam cracking-fired furnaces

In order to simplify the analysis, full electrification of both crackers (Olefins 3 and Olefins 4) was considered and this option was evaluated as standalone without compressors electrification. Therefore, the cracked gas compressor turbine would still need SHP steam to run. For this reason, it was considered that the electrical cracking furnaces would keep the same production of SHP steam as the conventional furnaces and the superheating step (previously done by the exhausted gases) would occur via electrical heating. Figure 29 illustrates the proposed thermal distribution in an electrical cracker, in comparison with the conventional technology already presented by see Figure 7. The estimated potential for electrical furnaces at the SABIC Geleen site is presented at Table 20.

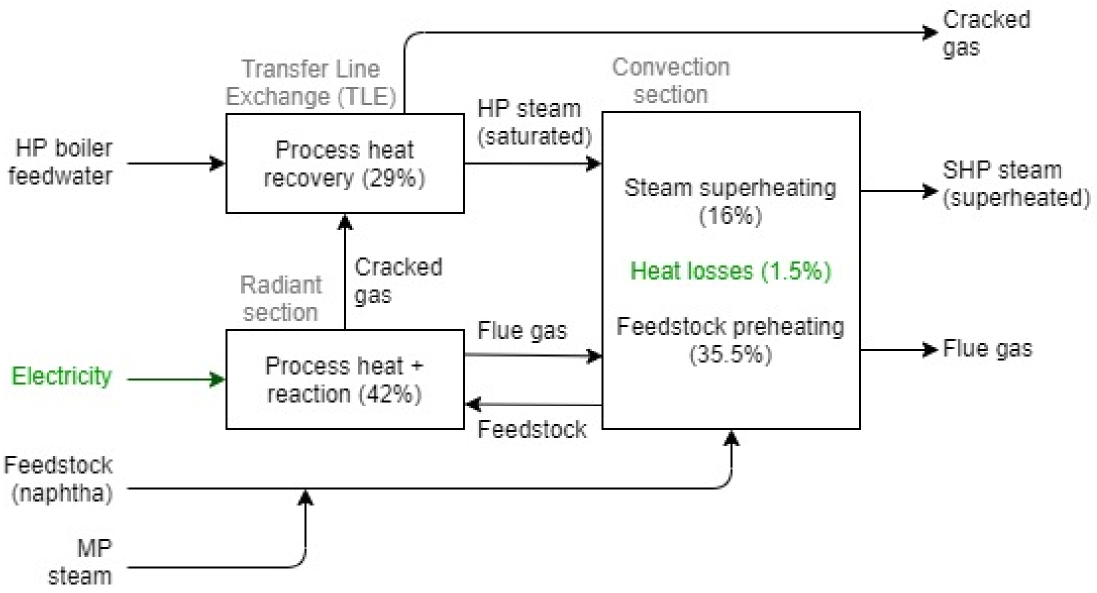

Figure 29 – Assumed thermal energy distribution in an electrical cracking furnaces thermal distribution

Table 19 - Summary of installation capacity, actual thermal demand of conventional cracking furnaces for SABIC Geleen and estimated electrical demand and capacity for electrical crackers

Steam cracker	Installed conventional furnaces capacity [MW_{th}][13]	Current fuel gas demand [PJ/yr][13]	Estimated electrical furnace capacity output [MW_{th}][14]	Estimated electricity demand [PJ/yr][14]
OLEFINS 3	477	13.5	400	12.8
OLEFINS 4	858	17.5	519	16.6
TOTAL	1,335	31	919	29.5

[13] Extracted from the Large Combustion Plant database from 2018 (EEA, 2020)

[14] Regarding thermal efficiency, it was considered that the stack losses do not play a role, reducing the total heat losses from 6.5% to 1.5% in the crackers. Resulting in 93.5% as thermal efficiency for the conventional furnaces and 98.5% for the electrical furnaces.

The electricity price is a determinant factor for the economic feasibility of this technology, as well as reliable supply of renewable electricity is needed for its application to result in CO_2 emissions reduction. Table 21 presents the investment costs found in literature for a generic electric furnace for thermal processes in a refinery site with capacity of 10 MW_{th} (output). The literature values englobes substation, electrical furnaces, cabling adjustment and project handling. The table also contains the estimated costs considering the calculated capacity for electrical furnaces at SABIC's site (919 MW_{th} output and 933 MW_e input), these values were obtained considering a scaling factor of 0.7. The fixed OPEX figures do not include energy costs. Since the expenditures used as reference are not related directly to steam cracking process, the estimative given does not include other factors specific to SABIC's site configuration that might influence in the costs.

Table 20 - Investment costs for electrical steam crackers (DNV-GL, 2018)

Electrical furnaces		
	Value	**Unit**
CAPEX literature	3.5 – 5	$MEUR_{2018}/MW_{th}$
Fixed OPEX literature	2	% CAPEX
CAPEX adjusted to SABIC[1]	800 – 1200	$MEUR_{2018}$
Fixed OPEX adjusted to SABIC	17 – 24	$MEUR_{2018}$/yr

4.2.1 Steam generation electrification

As mentioned in Chapter 2, SABIC Geleen imports altogether around 2,000 kt/y (7 PJ/y) of SHP steam from the Swentibold CHP and from the USG boilers. There is the possibility of obtaining this steam via electrical boilers. For boilers powered by electric resistance, however, current technologies are able to provide steam up to 350°C (Berenschot, 2017). For this reason, further development is still needed to reach the steam quality required (above 500ºC). Literature also indicates that electric boilers have fast response time, which allows flexible operation, and they are available in the market for several design capacities (up to 100 MWe) (BZE, 2018). The technology is well established (TRL 9), however, similar to electric furnaces, its implementation feasibility ties together with the electricity price and the availability of renewable sources for electricity (Berenschot, 2017).

As previously mentioned, the imported steam is used by the steam turbines that run the compressors on site, specially the cracked gas compressor. Because the compressors are key factors in the overall steam network at Chemelot, substituting them for electrical equipment would impact significantly the steam demand and supply on site and it would also affect the exports of HP steam to third parties. This technology option is further explored in the report 'Pathways to industrial decarbonisation in the Netherlands: paper & board and steam cracking' (West, K. et al., in prep.).

Regarding electrical boilers, it was considered that the 7 PJ/yr of SHP could be delivered by this technology, with an efficiency of 99.9% as reference (Berenschot, 2017). Table 22 presents the estimated required capacity of an electrical boiler to substitute the current SHP steam import.

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[1] Rounded to nearest value of 100

Table 21 - Estimated electrical demand and capacity for an electrical boiler at SABIC Geleen site

Electrical boiler		
	Value	**Unit**
SHP steam demand by SABIC's site	7	PJ/yr
E-boiler efficiency	99.9	%
E-boiler estimated capacity	222	MW_e (input)

Table 23 presents the investment costs found in literature for an electrical boiler with 99.9% thermal efficiency and 70 MW_e (input) capacity and the adjusted costs for a capacity of 222 MW_e. Similarly to electrical furnaces, a scaling factor of 0.7 was considered and the fixed OPEX values do not include electricity costs. The CAPEX figures include equipment and electrical connection costs, the later may vary significantly depending on the site, therefore, the estimated figure might not represent the actual situation for the SABIC Geleen site.

Table 22 - Investment costs for electrical steam crackers (Berenschot, 2017)

Electrical boiler		
	Value	**Unit**
CAPEX literature	150 – 190	$kEUR_{2017}/MW_e$
Fixed OPEX literature	1.1	$kEUR_{2017}/MW_e/yr$
CAPEX adjusted to SABIC	24 - 30	$MEUR_{2017}$
Fixed OPEX adjusted to SABIC	0.17	$MEUR_{2017}/yr$

4.3 Mixed plastic waste oil as feedstock

In 2013, 299 million tons of plastic waste was generated globally. The European Union alone generated more than 25.2 million tons of post-consumer plastic waste each year. Of this, around 26% is recycled, 36% is used for energy recovery processes such as incineration, and the remainder is landfilled. Incinerating plastics can cause several environmental issues, such as emissions of dioxins, fly ash, sulphur dioxide, nitrogen oxides, dust and other toxins. Additionally, if not disposed properly, plastics can end up in the environment. Prominently in the media is the pollution of oceans, negatively affecting the marine ecosystems (A. Fivga, I. Dimitriou, 2018).

Plastic solid waste (PSW) can be used as feedstock in steam crackers via thermolysis, a process that converts the waste into a fuel oil that can be upgraded to naphtha level. The thermolysis is the treatment of plastic solid waste in the presence of heat under controlled temperatures, it can be either catalytic or non-catalytic conversion. Thermolysis processes can be divided into advanced thermo-chemical or pyrolysis (thermal cracking in an inert atmosphere), gasification (in the presence of air usually leading to syngas production) and hydrogenation (hydrocracking) (Al-Salem et al, 2009). Figure 30 shows different thermolysis schemes.

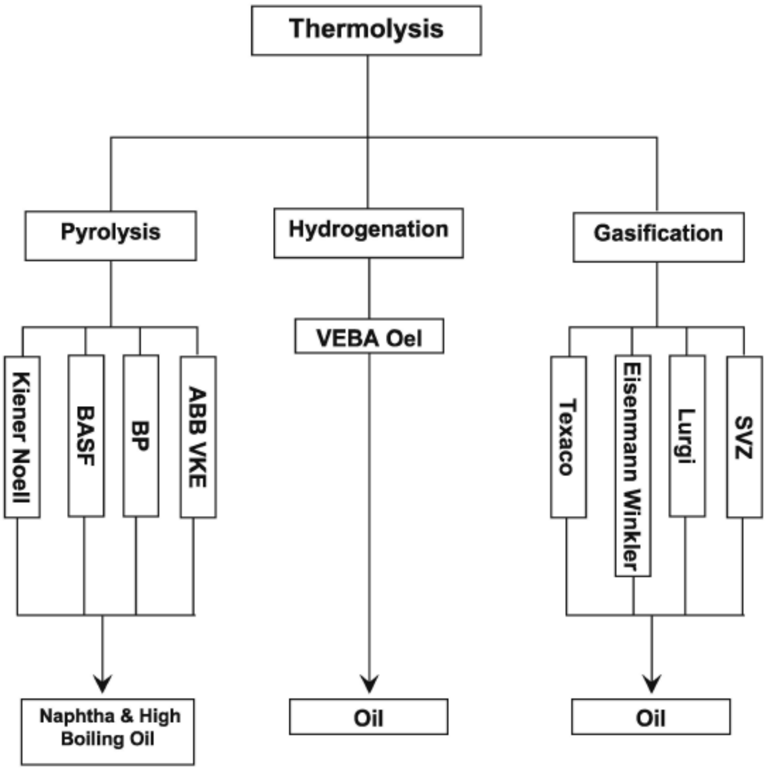

Figure 30 - Thermolysis options for plastic waste (source: Al-Salem et al, 2009)

Among all thermolysis of plastics routes, pyrolysis has shown significant advantages over the others, mainly because it produces less gaseous pollutants due to the absence of oxygen in the process (A. Fivga, I. Dimitriou, 2018). Also, the pyrolysis process main product is a wax/oil that can be used as a heavy fuel substitute or can be upgraded to naphtha. For these reasons, this section is focused on this specific route.

Pyrolysis is a process where plastic is thermally cracked due to rapid heating in the absence of oxygen, reducing the plastics long polymer chains into much shorter hydrocarbons. The process takes place in four stages, which are: initiation, transfer, decomposition and termination, resulting in the production of vapors and char. These pyrolysis vapors include both condensable and non-condensable gases (A. Fivga, I. Dimitriou, 2018).

The condensable vapors deliver the oil product composed of cracked hydrocarbons. Char is a solid product rich in carbon which can be used to produce heat for the pyrolysis reaction (which will produce fossil CO_2 if the plastic was produced from fossil feedstock). Volatile matter and fixed carbon were found to be the main components of the char (>97 wt%), while moisture and ash are minor components. The calorific value of the char is about 18.84 MJ/ kg and it has low sulfur content, characteristics that makes it suitable to be used as fuel (Sharuddin, S.D.A. et al., 2016). The second by-product is a gas which composition depends on the mixture of plastic waste that is pyrolyzed. Some studies report that the main gas components are hydrogen, C1, C2, C3 and C4 hydrocarbons. If PVC is included in the mix, hydrogen chloride is also produced and it requires chlorine removal before this gas can be used.

The gas will typically have a calorific value of 22-30 MJ/m^3 depending on the waste material being processed (Al-Salem, S.M. et al., 2009). Thus, the pyrolysis gas had high potential to be used as heating source in the industrial plant and it can also be used in gas turbines to generate electricity (Sharuddin, S.D.A. et al., 2016).

The general flow scheme for a pyrolysis of plastic waste unit is presented in Figure 31. The process is basically composed of reaction and separation systems. The combustion step is optional if the gas and char by products are produced in significant amounts. A process model from a plant from the UK presented by A. Fivga, I. Dimitriou (2018) shows that the total energy requirement of the pyrolysis step can be met by the combustion of gas and char.

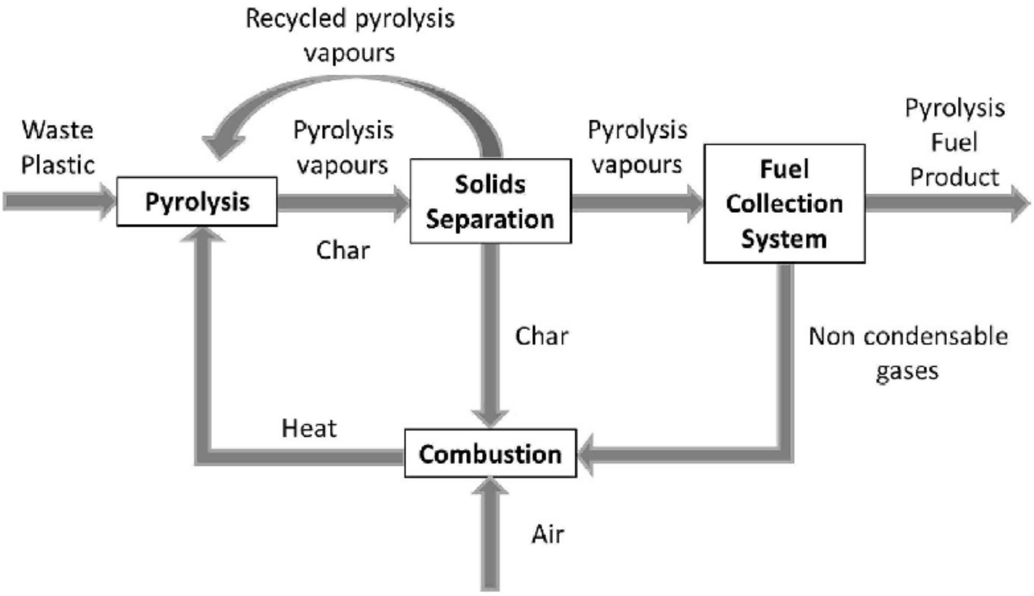

Figure 31 - Overview of a pyrolysis system (A. Fivga, I. Dimitriou, 2018)

Several studies have been done on this topic and different designs of reactors can be applied (fixed bed, fluidized, batch, semi-batch). Although some studies are still on lab scale, there are already some industrial projects for plastic pyrolysis. Some examples are:

BP process

One of the most important pyrolysis processes is the BP polymer cracking process (Al-Salem, S.M. et al., 2009). After a series of pilot trials (between 1994 and 1998), a plant was established in Scotland with a capacity of 25 kt/yr in the refinery complex currently owned by INEOS. Figure 32 illustrates the process, which consists of a fluidized bed reactor (500°C), a lime absorbent column to remove HCl from the gas (in case PVC is part of the feedstock), and cooling and separation sections in which most of the valuable hydrocarbons are distilled and recovered as heavy oil.

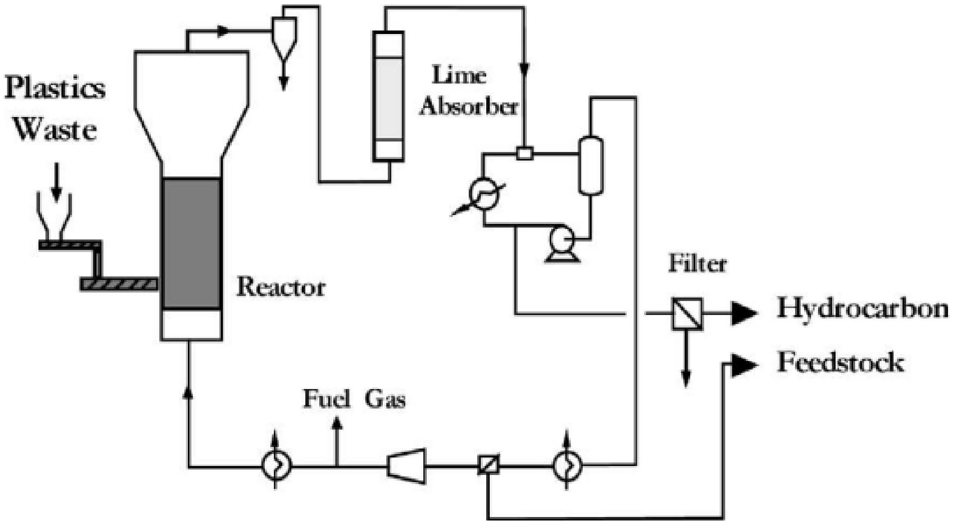

Figure 32 - Overview of the BP pyrolysis process (Al-Salem, S.M. et al., 2009)

BASF process
This process was designed to handle mixed plastic waste, as supplied by the DSD (Duales System Deutschland) green dot packaging collection system. A large pilot plant, with a capacity of 15 kt/yr, started running at Ludwigshafen in 1994. At that time DSD estimated the total volume of mixed packaging plastics available for feedstock recycling to be around 750 kt/yr. BASF offered to erect a full-scale industrial plant with a capacity of 300 kt/yr, but decided in 1996 to shut down the pilot plant since no agreement could be reached on a guaranteed long-term waste supply and a gate fee sufficient to cover the costs (Al-Salem, S.M. et al., 2009).

The BASF process converts plastic waste into petrochemical products in three-stage. As can be seen in Figure 33 the process is constituted by pre-treatment, pyrolysis and separation. In the pre-treatment, non-plastic materials are removed, the plastics are shredded and agglomerated to improve handling and enhance the bulk density. In the first stage, the plastics are melted and liquefied in an agitated tank. The possible gaseous hydrochloric acid is absorbed in a water washer, and further processed to aqueous hydrochloric acid, to be reused in other BASF production plants. The pyrolysis itself occurs in a tubular cracker reactor, heated at over 400°C. The oils and gases obtained are separated in a third stage, resulting in the production of naphtha, aromatic fractions, and high-boiling oils. About 20–30% of gases and 60–70% of oils are produced and subsequently separated in a distillation section.

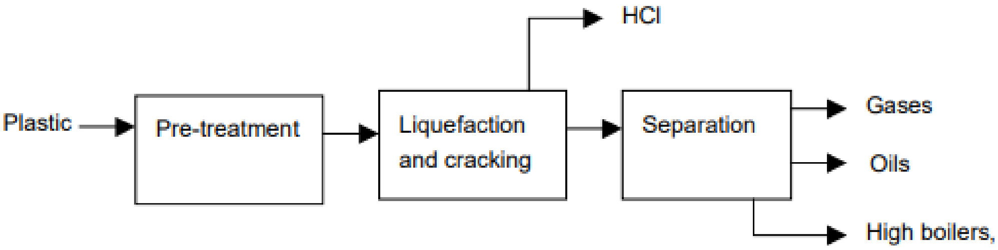

Figure 33 - Overview of the BASF process (adapted from Al-Salem, S.M. et al., 2009).

Literature also mentions the use of waste catalyst from the FCC (fluidized catalytic cracking) process. This is a common process in refineries for the conversion of vacuum gasoil in several products such as LPG, gasoline, diesel and kerosene. Spent FCC catalyst comes with different levels of contamination, yet is still valuable and can be reused in the pyrolysis process. Kyong, H.L. et al. (2002) investigated the effect of spent FCC catalyst on the pyrolysis of HDPE, LDPE, PP and PS. As a result, all plastics produced more than 80%wt liquid oil with PS being the highest (around 90 wt% liquid yield). The liquid yields based on the plastic types were arranged in this order: PS > PP > PE (HDPE, LDPE). The gaseous product yield had a reverse order when compared to the liquids in this following order: PE > PP > PS. This shows that PS was less cracked to the gaseous product since PS contains a benzene ring that creates a more stable structure. Overall, it was concluded that spent catalyst from the FCC refinery process still has high catalytic performance with an obtained liquid yield above 80 wt% for all plastic samples. Additionally, it could be more cost effective since it is a 'reused' catalyst (Sharuddin, S.D.A. et al., 2016).

The costs presented in this report for the mixed plastic oil production are based on the work from Fivga and Dimitriou (2018), which took as an example a technology from a recycling company based in the UK. The costs are related only to the pyrolysis plant that converts mixed plastic waste into oil. The upgrade of this oil to naphtha is not considered. As can be seen by Table 24, the resulting oil has heavier components than the conventional naphtha. One option to upgrade is to feed this oil to the conventional hydrocracking process already existent in refineries. In summary, to get a better understanding on what would be the total costs, the upgrade to naphtha still needs to be added.

Table 23 - Pyrolysis plastic oil composition compared to naphtha

Naphtha			**Plastic oil**		
Compound	**wt%**	**Source**	**Compound**	**wt%**	**Source**
n-octane	21	A. Fivga, I. Dimitriou, 2018	n-Hexane	≥10 - ≤30	Data sheet Shell, 2018
n-c14	37		Cyclohexane	≥5 - ≤10	
n-c18	18		Pentane	≥0 - ≤5	
n-c25	20		Benzene	≤1	
n-c30	4				

The process unit considered by Fivga and Dimitriou (2018) is illustrated at Figure 34, which considers that the combustion of the by-products from the pyrolysis (char and non-condensable gases) provides the total energy required by the process and allows export of excess heat. Table 25 shows the key values for the mass and energy balances for the entire system.

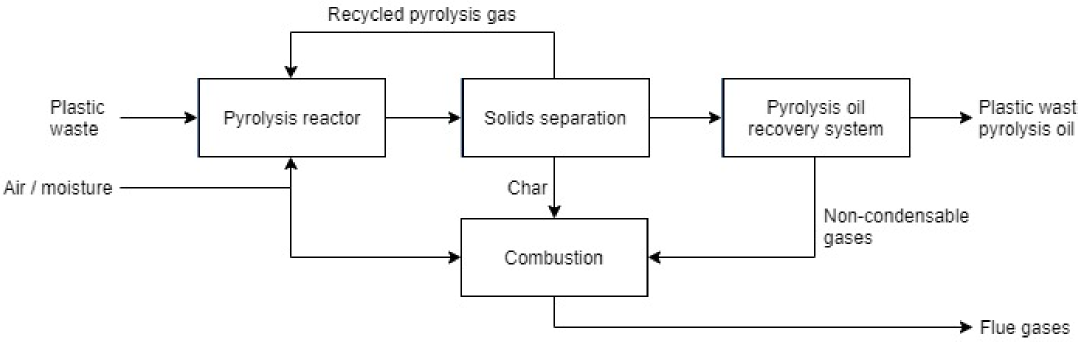

Figure 34 - Plastic waste pyrolysis oil production (adapted from A. Fivga, I. Dimitriou, 2018)

Table 24 - Key figures for the plastic waste process (A. Fivga, I. Dimitriou, 2018)

Pyrolysis reactor + solids separation + pyrolysis oil recovery systems		
Inputs	**Value**	**Unit**
Plastic waste	1	kg/kg plastic
Heat from combustion unit	1.482	MJ/kg plastic
Outputs		
Pyrolysis oil product	0.858	kg/kg plastic
Char	0.07	kg/kg plastic
Non-condensable gases	0.078	kg/kg plastic
Water	0.047	kg/kg plastic

Combustion unit		
Inputs	**Value**	**Unit**
Char	0.07	kg/kg plastic
Non-condensable gases	0.078	kg/kg plastic
Air	2.88	kg/kg plastic
Outputs		
Heat to pyrolysis reactor	1.482	MJ/kg plastic
Heat to export	4.162	MJ/kg plastic
Direct CO_2 emissions	0.346	kg/kg plastic

The investment costs related to this plant for distinct processing plastic waste capacities are summarized in Table 26. The load hours considered by Fivga and Dimitriou (2018) were 7,012 and the OPEX figures do not contain energy and feedstock costs.

Table 25 - Economics for plastic waste pyrolysis technology (A. Fivga, I. Dimitriou, 2018)

Capacity [kt plastic/yr]	CAPEX [$MEUR_{2013}$/kt plastic/yr]	Fixed OPEX [$MEUR_{2013}$/kt plastic]
0.7	1.663	0.706
7	0.514	0.202
70	0.157	0.037
701	0.095	0.017

PLASTIC ENERGY process

SABIC announced in December 2018 that the company has signed a memorandum of understanding (MoU) with UK-based PLASTIC ENERGY Ltd., for plastic-based feedstock for SABIC’s petrochemical operations in Europe. SABIC and PLASTIC ENERGY intend to build the first commercial plant in The Netherlands to refine and upgrade a valuable feedstock, known as TACOIL, a patented PLASTIC ENERGY product, which will be produced from the recycling of mixed plastic waste. The plant is expected to become operational in the second half of 2022 and the project is being supported by a Top Sector Energy Subsidy from the Ministry of Economic Affairs (SABIC website, 2021).

PLASTIC ENERGY has commercialized a patent of thermochemical conversion technology to convert a wide range of end-of-life, dirty and contaminated plastics, hardly recyclable for conventional processes, into usable feedstock. Plastics are melted in an oxygen free environment and then broken down into synthetic oils. The oils need to be refined and upgraded for feedstock use (SABIC website, 2018).

4.4 Second generation bio-naphtha as feedstock

This process bases on co-feeding steam crackers with bio-based naphtha obtained from second generation biomass. The technology routes for bio-naphtha production explored in this study are: solid biomass pyrolysis + upgrading and solid biomass gasification followed by a Fischer Tropsch process. Since naphtha is provided by refinery processes, this topic is further explored in the MIDDEN report for the refinery sector (Oliveira and Schure, 2020)

In general, if the bio-based naphtha reaches the quality specifications of the conventional naphtha via upgrading processes, little changes in the steam crackers itself are expected. For this reason, the related costs are mainly linked to the feedstock price. Table 27 summarizes the investment costs of bio-naphtha for the two technologies options mentioned. The values might be helpful to have an indication of the production costs.

Other bio-based feedstock options for steam crackers are more detailed discussed in the report 'Pathways to industrial decarbonisation in the Netherlands: paper & board and steam cracking' (West, K. et al., in prep.).

Table 26 - Summary of options costs for bio-naphtha production (Jong, S. de, et al., 2015)

Option	Bio-naphtha capacity [kt/yr]	CAPEX [EUR_{2013}]15)	Fixed OPEX [EUR_{2013}]16)
Pyrolysis bio-oil production and full upgrade to naphtha and fuels	82-164	156-482	16-59
Solid biomass gasification and Fischer Tropsch	41-83	327-1,186	8-24

15) These values are based on greenfield facilities.

16) It was assumed 5% of CAPEX and the OPEX range does not consider feedstock and energy costs.

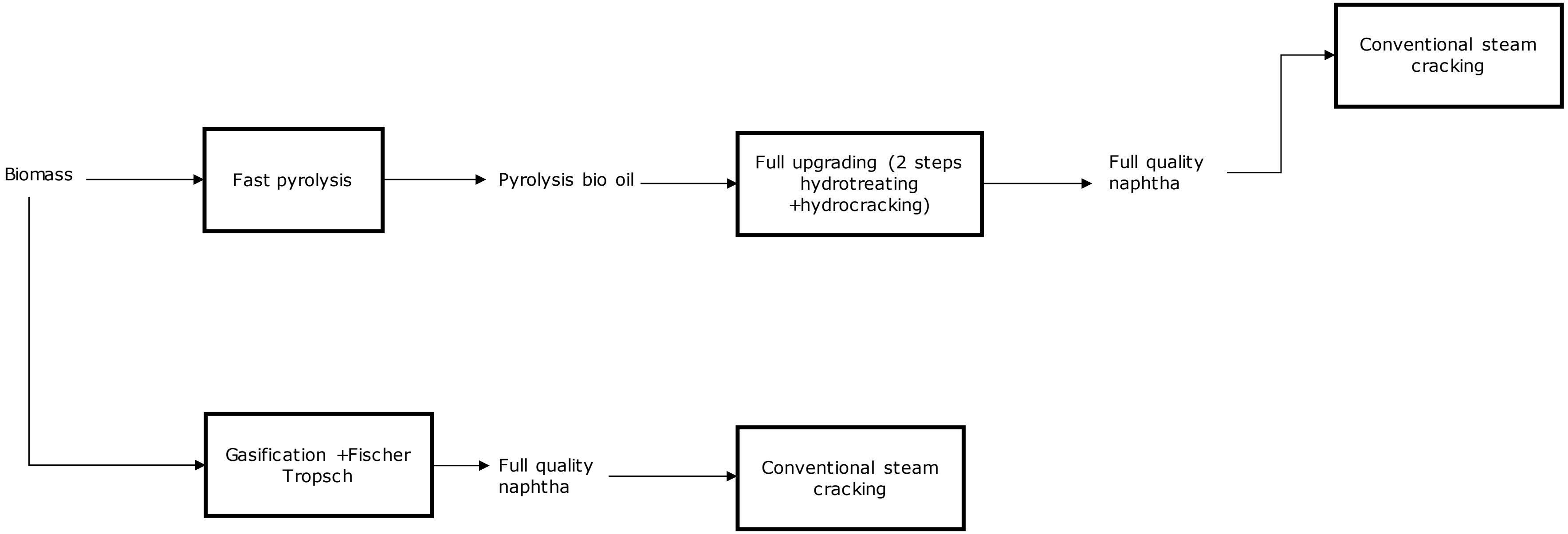

Figure 35 - Options for bio-naphtha production via 2nd generation biomass

4.5 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). The methanol normally used in these units are fossil based, however, this recent researches are exploring more sustainable methods to obtain this feedstock. The technology option explored in this study consists in producing olefins (ethylene and propylene) via methanol synthetized by green hydrogen and captured CO_2. Figure 36 is a simplified block diagram of the system proposed. Hydrogen is obtained via water electrolysis, followed by methanol synthesis and olefins production via MTO.

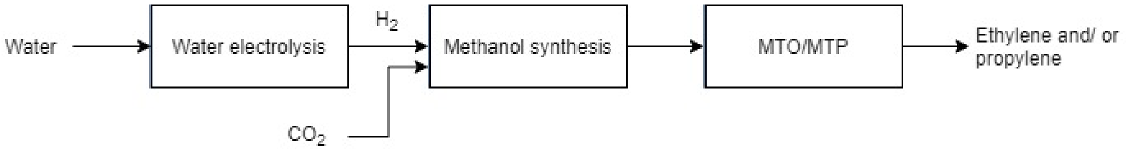

Figure 36 - Olefins production via captured CO_2 and water

The main reaction for the methanol synthesis step the following:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

The reaction for MTO can be described by two steps. The first step is the conversion of methanol to dimethyl ether (DME) and water:

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$$

The second step is the conversion of DME to both ethylene and propylene:

$$CH_3OCH_3 \leftrightarrow C_2H_4 + H_2O$$

$$3CH_3OCH_3 \leftrightarrow 2C_2H_6 + 3H_2O$$

The methanol synthesis process heat demand is fully covered by steam produced internally (M. Pérez-Fortes, E. Tzimas, 2016), being electricity the only energy carrier that is outsourced. However, the MTO unit is not auto sufficient in heat and requires steam import (Jasper, S., El-Halwagi, M. M., 2015). The mass and energy flows for the whole system are presented in Table 28 and Table 29.

Table 27- Mass and energy balance for water electrolysis and methanol synthesis (M. Pérez-Fortes, E. Tzimas, 2016)

Water electrolysis + methanol synthesis (mass and energy)		
Inputs	**Value**	**Unit**
Water	1.99	t/t MeOH
CO_2	1.46	t/t MeOH
Air	0.813	t/t MeOH
Cooling water	92.26	t/t MeOH
Electricity consumption	11.954	MWh_e/t MeOH

Water electrolysis + methanol synthesis (mass and energy)		
Outputs		
Methanol	1	t/t MeOH
Water	0.768	t/t MeOH
Oxygen	1.592	t/t MeOH
Direct CO_2 emissions	0.09	t/t MeOH

Table 28 - Mass and energy balance for methanol to olefins process (Jasper, S., El-Halwagi, M. M., 2015 and Zhao, Z. et al., 2020)

Methanol to olefins process (mass and energy)		
Inputs	**Value**	**Unit**
Methanol	1	t/t MeOH
Steam (5 bar, 160 ˚C)	4.3	GJ/t MeOH
Cooling water	32.2	t/t MeOH
Electricity consumption	17.4	MWh_e/t MeOH
Outputs		
Ethylene	0.14	t/t MeOH
Propylene	0.25	t/t MeOH
Ethane	0.01	t/t MeOH
Propane	0.01	t/t MeOH
C4+ mix	0.25	t/t MeOH
Direct CO_2 emissions	5.3	t/t MeOH

Regarding the investment costs for the processes mentioned, some estimated figures were found in literature (Table 30 and Table 31). The OPEX values considered refer to fixed OPEX and do not include energy and feedstock costs.

Table 29 - Investment costs for water electrolysis and methanol synthesis (M. Pérez-Fortes and E. Tzimas, 2016)

Water electrolysis + methanol synthesis		
	Value	**Unit**
Capacity	440	kt MeOH/yr
CAPEX	1.28	$MEUR_{2016}$/kt MeOH/yr
Fixed OPEX	0.07	$MEUR_{2016}$/kt MeOH

Table 30 - Investment costs for methanol to olefins process (Jasper, S., El-Halwagi, M. M., 2015)

Methanol to olefins process		
	Value	**Unit**
Capacity	1,523	kt MeOH/yr
CAPEX	0.19	$MEUR_{2015}$/kt MeOH/yr
Fixed OPEX[17)]	0.01	$MEUR_{2015}$/kt MeOH

[17)] Calculated assuming that fixed OPEX is 5% of CAPEX.

4.6 Hydrogen as fuel for steam cracking furnaces

The aim of this option is to replace the fuel gas by green hydrogen as energy source for the steam cracking furnaces. Since the combustion of hydrogen generates only water, the substitution of natural gas and/or fuel gas in fired processes by hydrogen results in the reduction of direct CO_2 emissions. However, the hydrogen should be produced through a low CO_2 process, a topic that is covered in detail in the MIDDEN report 'Decarbonisation options for the Dutch production of industrial gases' (Cioli, Schure, and Van Dam, 2021).

In principle, the utilisation of hydrogen as a fuel would require changes in the operating conditions related to the combustion itself and the installation of burners that are capable to burn gas with high concentration of hydrogen. The same application was discussed in more details in the MIDDEN reports on PVC manufacturing (Semeijn and Schure, 2020) and on refinery processes (Oliveira and Schure, 2020). This decarbonisation option still needs to overcome some challenges, such as the electricity costs and low efficiency of hydrogen production via electrolysis (approximately 70%) leading to high green hydrogen costs.

Regarding the differences between the physical properties of hydrogen and natural gas, the hydrogen flame has lower radiation heat transfer, however, the Wobbe index[2] of both methane and hydrogen are close. The latter can lead to an advantage in the case of installing flexible burners that are able to use both fuels (Table 32). Another important aspect is the fact that hydrogen combustion results in higher NOx concentration in the flue gas, making necessary the installation of technologies for NOx abatement.

Table 31 - Main differences in physical properties between methane and hydrogen (table based on Semeijn and Schure, 2020)

Property	Methane (main component of natural gas)	Hydrogen
Density (at 1 bar and 15 °C)	0.65 kg/m^3	0.084 kg/m^3
Wobbe index	53.44 MJ/m^3 (44 MJ/m^3 for Low calorific natural gas)	48.16 MJ/m^3
Flame Colour	Visible/blue	Invisible/light blue
Flame temperature	Lower flame temperature but higher thermal radiation heat transfer	Higher flame temperature but lower thermal radiation heat transfer
Flammability range	5-15%	4-75%
Flame speed	0.42 m/s	2.37 m/s
Minimum ignition energy	0.29 mJ	0.02 mJ
Low heating value (LHV)	47.1 MJ/kg CH_4	120 MJ/kg H_2

Similarly to furnace electrification, the use of hydrogen as fuel replacement would leave a surplus of fuel gas on site. Therefore, finding another (non-fuel) application for the fuel gas is a relevant aspect for this option as well. Considering the LHV of hydrogen and the current heat demand of the pyrolysis furnaces (29 PJ/y), to replace the current 576 kt of fuel gas would require an amount of hydrogen of around 241 kt/y (see Table 33). Steam reforming of the fuel gas, combined with pre-combustion CCS, could supply the required hydrogen. Assuming that the hydrogen production yield via fuel gas reforming is the same as via

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[2] The Wobbe index is a function of the higher calorific value and the specific gravity of the fuel.

methane reforming (0.285 t H_2/t CH_4 based on IEAGHG, 2017), the total hydrogen produced from the 29 PJ (578 kt/y) of fuel gas could be around 165 kt H_2/y.

Table 32 - Estimated hydrogen demand per steam cracking unit at SABIC Geleen site

Steam cracker	Installed conventional furnaces capacity [MW_{th}]18)	Actual fuel gas demand [PJ/yr]18)	Estimated hydrogen demand [kt/yr]19)
OLEFINS 3	477	13.5	113
OLEFINS 4	858	17.5	146
TOTAL	1,335	31	259

18) Extracted from the Large Combustion Plant database from 2018 (EEA, 2020)

19) Based on 120 MJ/kg hydrogen (LHV).

Table 34 presents the estimated costs for a generic heating system using hydrogen combustion as energy source with capacity of 10 MW_{th} (output). Although the indicated investments are not specific for steam crackers, the information can serve as a reference. The investment costs include extra pipeline for hydrogen, hydrogen compressors, adjustment to the furnaces, however, it does not include the costs for the NO_x abatement equipment.

It was assumed that the hydrogen furnaces would present the same thermal efficiency as the conventional furnaces, for this reason, both CAPEX and OPEX were adjusted to the current thermal capacity of the SABIC Geleen crackers (1335 MW_{th}). A scaling factor of 0.7 was considered for the calculation.

Table 33 - Investment costs for hydrogen as fuel for steam crackers

Hydrogen furnaces		
	Value	**Unit**
CAPEX literature	0.5 – 1.5	$MEUR_{2018}/MW_{th}$
Fixed OPEX literature	1	% CAPEX
CAPEX adjusted to SABIC[3]	150 – 460	$MEUR_{2018}$
Fixed OPEX adjusted to SABIC	1.5 – 4.6	$MEUR_{2018}$/yr

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[3] Rounded to nearest value of 10

5 Discussion

The optimal portfolio of decarbonisation options for chemical industries depends on several factors and will differ greatly from one facility to another. The MIDDEN project contributes by focusing on some of the most promising decarbonisation options. Based on the results, several observations can be highlighted.

The furnace section of the steam cracking process presents the most relevant opportunities for CO_2 reduction. Bulk chemical process such as steam cracking are long-running, mature technologies, therefore, current decarbonisation efforts appear to focus on incremental energy efficiency improvements rather than major retrofits or entire process substitutions. Incremental improvements include optimising the furnace operations through heat recovery options or advanced process control systems. However, these improvements alone are not sufficient in achieving deep decarbonisation by 2050. Electrification, alternative process routes, plastic waste as feedstock, hydrogen as a fuel are pertinent technology options for SABIC Geleen. In this study, some benefits and barriers related to their implementation were presented.

The discussed alternatives for gas-fired equipment are not yet available and further innovation is required before the actual application of these technologies to steam crackers. The hydrogen-based furnaces require additional NO_x emissions abatement technology and the hydrogen supply should be either from SMR with CCS (blue) or from electrolysis (green). Although neighboring OCI currently produces hydrogen for ammonia on a large scale, transporting the CO_2 from Chemelot to off-shore storage would need significant infrastructural investment due to the large distance. Similarly, this would apply for transporting green hydrogen from coastal locations. Nevertheless, the fuel gas generated by the cracking process could be a potential feedstock for blue hydrogen production (165 kt H_2/y), if not used anymore as fuel in the furnaces. Electric furnaces are an even more novel technology. No large scale practice is yet in place and high investment costs are foreseen (VNCI, 2018). However, the development for this technology is going fast and SABIC is actively involved via the Cracker of the Future Consortium. It is expected that electric furnaces will advance quickly on the technology end (TNO personal communication, 2018). Still, availability of cheap renewable electricity and the infrastructure for distribution is crucial for its implementation, mainly due to the high demand of green electricity for this alternative (933 MW_e input).

Biomass application in petrochemical industry is an interesting option because it could enable negative emissions if combined with carbon capture, however, it still needs to overcome several challenges. In short, a supply chain of sustainable biomass for big volumes of feedstock is required. Also, for bio-naphtha co-processing via pyrolysis bio-oil upgrading, a substantial amount of hydrogen is needed. However, no significant changes in steam cracker units are expected for the use of biobased feedstocks.

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. More specifically, for steam crackers, the low concentration of CO_2 in the flue gas (5-10%vol.) reduces the economic feasibility of its application. The requirements in Chemelot for CO_2 infrastructure have already been mentioned.

Plastic waste pyrolysis is a promising technology, since it avoids the need for waste incineration, reduces the usage of naphtha in the crackers and it includes the circular economy aspect which may help to improve plastic waste management. The challenges include the supply chain of the plastic waste and the upgrade process of plastic based oil to naphtha level. Since plastics are fossil based, the use of plastic waste oil does not reflect in reduction of direct CO_2 emissions for the steam cracker site, however, it may allow emissions mitigation for the overall production/consumption chain after some cycles of plastic waste utilization.

Finally, the petrochemical sector is complex and several aspects should be taken into account when the decarbonisation of processes such as steam cracking is discussed. The analysis of a combination the technology options explored and other innovative options could help the sector to transition towards a lower CO_2 emissions future. Specific aspects from SABIC Geleen site should be carefully taken into consideration when evaluating the possibilities. Also, external factors such as CO_2 transport and storage infrastructure, green electricity, hydrogen supply and biomass availability may play a relevant role. Therefore, holistic assessments of possible pathways considering the connections beyond the site’s fence are necessary.

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