

PBL Netherlands Environmental Assessment Agency

# DECARBONISATION OPTIONS FOR THE DUTCH REFINERY SECTOR

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Manufacturing Industry Decarbonisation Data Exchange Network

#### Decarbonisation options for the Dutch refinery sector

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#### MIDDEN project coordination and responsibility

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## FINDINGS

### Summary

This report describes the current situation of the Dutch refinery sector, which is composed of 6 industrial sites owned by 6 different companies: BP, Esso, Gunvor, Shell, Vitol (VPR Energy) and Zeeland Refinery (owned by Total and Lukoil). The total nameplate capacity for the entire sector is over 67 million tonnes (Mt) of crude oil processing. In 2019, the total production of LPG, naphtha, gasoline, kerosene, gasoil/diesel and fuel oil was more than 55 million tonnes.

In the past three years, the average energy consumption of the refinery sector was around 130 PJ/yr and the  $CO_2$  emissions were 10 Mt/yr. The main energy carrier for the refineries sites is fuel gas, which is a by-product from several process units and responsible for around 55% of the sector's total energy consumption. The main sources for emissions are the gas fired furnaces, hydrogen production (steam methane reforming and gasification) and fluidised catalytic cracking (FCC) units. The emissions from the latter two present high concentration of  $CO_2$  (above 15% vol).

The report also explores the options and preconditions for decarbonisation of the refinery sites considering a 2050 horizon. The options studied include post combustion carbon capture and storage, furnace electrification, hydrogen as fuel substitute, hydrogen production decarbonisation, co-processing of bio-oil in an FCC unit, biofuels production via biomass gasification followed by Fischer Tropsch (FT) and waste heat usage. All the covered options present benefits and challenges related to its implementation, which are further discussed in this report.

Carbon capture (and storage) is an interesting option, mainly for the hydrogen production and fluidised catalytic cracking units, because of the higher CO<sub>2</sub> concentration. However, significant infrastructural changes are needed to capture all CO<sub>2</sub>. Nevertheless, hydrogen production and FCC systems are responsible for 30% of direct CO<sub>2</sub> emissions. Furnace electrification requires reliable renewable electricity supply and significant infrastructural changes on site. Additionally, the extra fuel gas as a by-product from the process units may represent a burden and increase the costs. However, if implemented, this option has the potential to reduce around 51% of direct CO<sub>2</sub> emissions. Regarding the alternative feedstocks, bio-oil co-processing in refinery units presents potential, but this is still going through technical development and there is public debate on the use of biomass and its sustainability. Residual heat utilisation is a prominent option given the fact that it allows an estimate of over 22% of the total energy consumption of a refinery to be reutilised. Medium and high temperature waste heat can be applied for district heating, if the required infrastructure is in place. For the low temperature streams, technologies that can upgrade its heat quality may be needed, such as heat pump systems.

# FULL RESULTS

# Introduction

This report describes the current situation of the Dutch refinery sector 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

The aim of the MIDDEN project is to compile a database of material and energy uses of industrial processes at a plant level for the Dutch manufacturing industry. The scope of this research will focus on the 6 refinery sites present in The Netherlands.

Production locations include:

- BP Refinery Rotterdam BV: Darcyweg 76, 3198 NA Europoort Rotterdam
- Esso Nederland B.V.: Botlekweg 121, 3197 KA Botlek Rotterdam (port number 4060)
- Gunvor Petroleum Rotterdam BV: Moezelweg 255, 3198 LS Europoort Rotterdam
- Shell Nederland Raffinaderij: Vondelingenweg 601, 3196 KK Vondelingenplaat
- Vitol B.V. Netherlands: Neckarweg 5, 3198 LJ, Europoort Rotterdam
- Zeeland Refinery N.V.: Luxemburgweg 1, 4455 TM Nieuwdorp.

Processes include: Atmospheric distillation, vacuum distillation, alkylation, reforming, isomerisation, catalytic cracking, thermal cracking, visbreaking, hydrocracking, flexcoking, solvent deasphalting, hydrotreating processes and gasification.

Main products include: Liquified Petroleum Gas (LPG), propane, butane, gasoline, naphtha, kerosene, benzene, xylenes, fuel oil, gasoil, lube oils, bitumen and hydrogen.

The main decarbonisation options are: carbon capture and storage (CCS), electrification, hydrogen as fuel for furnaces, co-processing of bio-based feedstocks and waste heat utilization.

#### Reading guide

Chapter 1 introduces the Refinery sector in the Netherlands. Chapter 2 describes the current situation for refinery production processes in the Netherlands, and Chapter 3 describes the relevant products of these processes, while options for decarbonisation are systematically quantified and evaluated in Chapter 4. The feasibility of and requirements for those decarbonisation options are discussed in Chapter 5.

# 1 The refinery sector in the Netherlands

#### 1.1 The Dutch refinery sector

In recent years, the Dutch refinery sector energy consumption was over 131-152 PJ of energy commodities and around 2,444-2,496 PJ of crude oil (CBS, 2020a). The sector was responsible for over 10 million tonnes (Mt) of  $CO_2$  direct emissions for the past 3 years (NEa, 2020). Table 1 summarizes the crude oil capacities and  $CO_2$  direct emissions in 2016-2019 for each refinery site in The Netherlands. The ratio between  $CO_2$  emissions and crude oil intake (source: CBS (2020c)) is also present in Table 1.

Refinery site	Crude oil nameplat e capacity [kt/yr] <sup>1)</sup>	Crude oil nameplate capacity [PJ/yr] <sup>2)</sup>	Direct CO <sub>2</sub> emissions 2016 [kt/yr] <sup>3)</sup>	Direct CO <sub>2</sub> emissions 2017 [kt/yr] <sup>3)</sup>	Direct CO <sub>2</sub> emissions 2018 [kt/yr] <sup>3)</sup>	Direct CO <sub>2</sub> emissions 2019 [kt/yr] <sup>3)</sup>
BP Refinery Rotterdam B.V.	20,000	854	2,292	2,074	2,254	2,151
ESSO Refinery Rotterdam	9,100	389	2,106	2,068	1,583	2,376
Gunvor Petroleum Rotterdam B.V.	4,500	192	420	448	397	421
Shell Nederland Raffinaderij B.V.	21,000	897	4,254	3,831	4,211	4,357
Vitol B.V.	3,500 <sup>4)</sup>	149	74	115	102	109
Zeeland Refinery N.V.	8,907 <sup>4)</sup>	380	1,552	1,601	1,633	1,588
Total	67,007	2,861	10,699	10,137	10,180	11,002
Direct CO <sub>2</sub> emissions/ crude oil intake			0.197	0.189	0.185	0.194

Table 1 D	utch ref	ineries n	ameplate	capacities	and	CO <sub>2</sub>	emissions
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1) Data source: Facts & Figures on the Rotterdam Energy port and Petrochemical cluster (Port of Rotterdam, 2017)

 Calculated based on average crude oil daily capacity and heating value of 42.7 MJ/kg for crude oil (RVO, 2018)

3) Nederlandse Emissieautoriteit (NEa, 2020)

4) Private communication with company, 2019

### 1.2 Refinery characteristics

#### 1.2.1 Location and infrastructure

#### Regarding location,

Figure 1 shows that all sites, except for Zeeland refinery, can be found in the Rotterdam port industrial complex, which occupies around 12,000 hectares. The complex contains around 1,500 km of pipelines (Port of Rotterdam, 2017), which are connected to other industrial clusters including Zeeland's site, as illustrated in Figure 2 and Figure 3.



**Figure 1** Locations of refineries sites in the Netherlands (extracted from Google Maps, 2019)







Figure 3 Industrial gas pipelines (Port of Rotterdam 2017)

#### 1.2.2 Main activities

The Dutch refinery plays an important role in the national industrial sector, delivering around 36 billion euros as net turnover in 2018 and employing more than 6,000 people in the country (Table 2). The Netherlands is also the house of the biggest refinery in Europe (i.e. Shell Nederland Refinery) and the sites locations allow broad access to different crude oil types. The port of Rotterdam, for example, receives crude oil from distinct areas, including the North Sea region, Russia and the Middle East. Also, the flexibility in terms of products is

significant, 85% of the total products are fuels, such as diesel, gasoline, gas oil and LPG; the remaining 15% consists of naphtha, base oils and bitumen (VNPI, 2020).

Торіс	Unit	2016	2017	2018
Labour volume persons employed	x 1,000 employed persons	5.2	5.6	6.4
Total operating returns	x mln euro	26,166	29,867	36,772
Total operating costs	x mln euro	25,559	29,278	36,777
Operating result	x mln euro	607	589	-4

Table 2 Labour and economics figures for the Dutch refinery sector for the pastyears (CBS, 2020b)

A refinery is generally composed of physical separation processes (distillation, extraction, etc), catalytic conversion processes (reforming, hydrotreating, hydrocracking, etc) and thermal conversion processes (thermal cracking, visbreaking, delayed coking, etc). Each site differs in configuration and levels of integration, this will be further explored on Chapter 2. The summary of the main units present in each site is shown in Table 3.

Regarding the products portfolio, the shares and total production from 2018 for Dutch refineries are present in Table 4. The products with highest shares are gasoil/diesel and naphtha, the latest is an important feedstock for the petrochemical sector, which is highly integrated with refineries in the country. The production of gasoil/diesel is high due to demand by the transportation sector.

Table 3	Overview of refining processes allocated to each refinery site (based on
Facts an	d figures Port of Rotterdam, 2017)

Process unit	BP	ESSO	Gunvor	Shell	Vitol	Zeeland
Atmospheric distillation	х	х	х	х	х	х
Vacuum distillation	х	х	х	х		х
Catalytic reforming	х	х	х	х		х
Alkylation	х			х		
Fluidised bed catalytic cracking	х			х		
Hydrocracker		х		х		х
Hydrotreating	х	х	х	х		х
Thermal cracker			х	х		
Visbreaker	х		х	х		
Flexicoker		х				
Solvent Deasphalting				x		
Gasification				x		

#### Table 4 Output of Dutch refining industry per product for 2018 (CBS, 2020c)

Product	Production 2018 [PJ]	Share [%]
LPG	66.9	3
Naphtha	416.5	17
Gasoline	171.5	7

Product	Production 2018 [PJ]	Share [%]
Kerosene	393.8	16
Gasoil/diesel	796.0	33
Fuel oil	338.6	14
Other oil products	207.2	9
Total	2,390	

# 2 Refinery processes

A refinery site is a complex system composed of different processes, which are briefly described in this chapter. A breakdown of the main inputs and outputs and energy consumption of the processes, together with a summary of the  $CO_2$  emissions, are also presented in this Chapter.

#### 2.1 Process descriptions

On a refinery site, crude oil is processed into smaller carbon-chain components, of which some fractions are converted into valuable substances. These products can be used as fuels, both for heat generation and for mobility purposes. Additionally, some oil outputs serve as feedstocks for the petrochemical and chemical industries (i.e. naphtha, lubricating oils, bitumen and paraffins/waxes). A refinery can also produce, as by-product, steam and power (JRC, 2015).

Figure 4 shows a simplified schematic of a possible configuration that contains the full range of processes that may exist on a refinery. As illustrated in this Figure, a refinery may constitute separation, thermal and catalytic conversions, deasphalting processes, and, finally, treatment and upgrading processes. The following paragraphs give a brief explanation of these units and point out their most relevant aspects. Feeds from each process and their respective operating conditions are summarized in Table 5.

Process unit	Feed	Temperature range	Pressure range
Atmospheric distillation	Crude oil	315-425 °C	1.4-2.4 bar
Vacuum distillation	Vacuum gasoil	400-415 °C	0.03-0.07 bar
Catalytic reforming/ Platforming	Desulphurised naphtha	477-550 °C	3.4-42 bar
Alkylation	C3-C4 rich stream	21-38 °C	<30 bar
Fluidised bed catalytic cracking	Vacuum gasoil	205–750 °C	2.7–1.1 bar
Hydrocracker	Vacuum gasoil and heavy gasoil	350-450 °C	95-160 bar
Hydrotreating	Naphtha, kerosene, diesel, gasoil	290-455 °C	18-104 bar
Thermal cracker	Residual oil- and short residue	315-538 °C	8-22 bar
Visbreaker	Atmospheric or vacuum residue	455-510 °C <sup>5)</sup>	3.5–21 bar <sup>5)</sup>
Flexicoker®	Vacuum residue	454-510 °C <sup>6)</sup>	1-5.5 bar <sup>6)</sup>

#### Table 5 Summary of general process conditions for several refinery technologies (Meyers, 2004)

6) ExxonMobil, 2015



Figure 4 General refinery process flow diagram

#### Separation processes

<u>Crude distillation</u>: This involves the first separation step of desalted crude oil into fractions composed of shorter carbon chains. The separation takes place at atmospheric pressure through a distillation process. In such systems, the main equipment is the distillation column, in which both operating temperature and pressure, together with differences in boiling point of the various fractions, determine which substances are recovered in specific sections of the column. The fractions in a crude distiller usually are: fuel gas, LPG, naphtha, kerosene, light gasoil, heavy gasoil and long residue. This last one is further separated in the vacuum distillation. In order to reach the right temperature for separation, the crude oil is pre-heated by gas-fired heaters.

<u>Vacuum distillation</u>: This unit processes the long residue that comes out of the crude distiller. Since increasing the temperature of this vacuum feed (long residue) would lead to its thermal decomposition, this separation step is done under vacuum pressure to allow fractionation within mild conditions. Similar to the atmospheric separation, the vacuum distillation system is composed of a distillation column and gas-fired heaters. Additionally, an ejector is needed to reach vacuum pressures. The main fractions of this unit are called: vacuum gasoil (which feeds into catalytic conversion processes) and vacuum residue (which serves as feed for thermal conversion and the deasphalting units).

#### Thermal conversions

<u>Thermal cracking or Visbreaking</u>: Visbreaking stands for viscosity breaking and is a mild form of thermal cracking. The thermal reactions are not allowed to complete and are interrupted by quenching (direct contact cooling). The main process goal is to reduce the length of the carbon chains and thereby the viscosity of residue, to produce fuel oil that meets the required specifications. Other product streams are: fuel gas, naphtha, light gasoil and heavy gasoil.

<u>Flexicoking</u> This process was developed by ExxonMobil. It is characterised as low-pressure thermal conversion that takes place in a continuous fluidised bed environment. It is capable of converting heavy feeds into a full range of gas- and liquid products and coke.

<u>Solvent deasphalting process (SDA</u>): The SDA process separates the vacuum residual oil with a high metal content into a deasphalted oil (DAO) of relatively low metal content and a highly viscous substance. The SDA process uses a light paraffin solvent to extract the residue's heavier components, this fraction is called bitumen and usually is used in the manufacturing of asphalts and cement and as a blending component in refinery fuel oil pools. If the metal content of the DAO is sufficiently low, it can be fed directly into catalytic conversion units.

#### Catalytic conversions

<u>Fluidised catalytic cracking (FCC)</u>: The process is used to convert higher-molecular-weight hydrocarbons into lighter, more valuable products through contact with a powdered catalyst at appropriate conditions. The system is in constant fluidisation, which occurs when a gas or liquid flow passes through a granular solid material and converts it from a static solid-like state into a dynamic fluid-like state. For the FCC, the granular material is the catalyst and the feedstock is the liquid flow. The primary purpose of the FCC process is usually to process straight-run atmospheric gasoil, vacuum gasoil, certain atmospheric long residues, and heavy substances from other refinery operations. The products usually are: high-octane gasoline, light fuel oils, and olefin-rich light gases. The catalyst is regenerated after use by

burning the coke layer formed due to the cracking reactions. The coke burning provides the energy necessary for the cracking step. For this reason, the FCC flue gases present high concentration of  $CO_2$ .

<u>Hydrocracking</u>: This is a catalytic conversion process in the presence of hydrogen. Hydrocracking aims to produce a wide range of products that contain molecular weights lower than the feed. It normally presents fixed-bed reactors and its feedstock options are similar to the FCC's. Contrary to the thermal cracking processes that present random bond rupture, the hydrocracking breaks the chains in an ordered and selective way. Simultaneously to the molecular cracking, impurities removal, such as sulphur, nitrogen, and oxygen, takes place. The production yields depend on the operating conditions and can vary significantly, but in general, the main products from a hydrocracker are: naphtha, kerosene and diesel.

#### Treatment and upgrading processes

<u>Hydrotreating</u>: This process uses hydrogen in order to reduce the sulphur (among other impurities such as nitrogen and oxygen) content of the feed in a catalytic hydrogenation process. Some refineries produce all hydrogen on site (see more details below), some obtain (part of) it from a supplier.

<u>Catalytic reforming</u>: This process aims to improve the octane number in naphtha by increasing the aromatics content. Generally, the feedstock is brought into contact with a catalyst at elevated temperatures and hydrogen pressures. The resulting product is a high-octane liquid that is rich in aromatic compounds, which is usually added to the gasoline pool for upgrading purposes. Besides this application, this product can be further processed to recover aromatics such as xylenes and benzene. Other reforming products are: hydrogen, light gas, and LPG (Meyers, 2004).

<u>Alkylation</u>: The hydrofluoric (HF) alkylation process catalytically combines light olefins, which are usually mixtures of propylene and butylene, with isobutane to produce branched-chain components. The alkylation reaction takes place in the presence of hydrofluoric acid. The alkylate product possesses valuable properties for fuel upgrading. Therefore, the alkylate is usually a gasoline blending component.

*Isomerisation*: This is a process that converts C5 and C6 paraffinic compounds to their branched isomers. The isomerisation product normally is used to increase motor fuels' octane number. It is a catalytic process and, depending on the technology, it may include hydrogen consumption.

<u>Aromatics recovery</u>: An aromatics complex is a combination of process units that can be used to produce the basic petrochemical intermediates: benzene, toluene, and xylenes (BTX) from reformed naphtha. Usually, the recovery occurs via an extraction process, either with solvent utilisation or through adsorption.

#### Hydrogen

<u>Hydrogen production</u>: In a refinery, hydrogen is an important feedstock that is used in several processes (e.g. hydrocracking, hydrodesulfurization). Depending on its demand, hydrogen is produced on site. It can be obtained via steam methane reforming (SMR), by gasification of residue oil, via recovery from gaseous streams in a PSA (pressure swing adsorption) or even as a by-product of the catalytic reforming process. More details about hydrogen production are given in the MIDDEN report 'Decarbonisation options for the Production of Industrial Gases in The Netherlands' (Cioli et al., in prep.).

#### 2.2 Process diagrams of the Dutch refineries

This section includes the simplified process schemes of each refinery site located in the Netherlands. Quantities are included in the next section.



Figure 5 BP refinery process diagram







Figure 7 Gunvor Refinery process diagram



Figure 8 Shell Refinery process diagram







Figure 10 Zeeland Refinery process diagram

## 2.3 Energy and material flows

Since refinery sites are usually complex, some processes were grouped in order to keep the process analysis simpler. The main criteria used to group the units was their relevance for evaluating decarbonisation options.

Following this approach, the grouped units are:

- Thermal cracking/visbreaking: these two processes are considered in one group due to similar characteristics.
- Hydrotreating includes all hydrodesulphurisation and similar processes, even with different feedstocks, e.g. kerosene and diesel treating are considered in the same group.

		Companie	s				
Process units	unit	BP <sup>7)</sup>	Esso <sup>8)</sup>	Gunvor 7)	Shell 7)	Vitol 7)	Zeeland <sup>9)</sup>
Atmospheric distillation	kt feed/yr	20,000	10,512	4,500	21,000	3,500	9,267
Vacuum distillation	kt feed/yr	4,900	5,256	2,400	8,000	-	3,985
Hydrocracking	kt feed/yr	-	3,635	-	3,900	-	4,210
Thermal cracking	kt feed/yr	-	-	530	2,700	-	-
Visbreaking	kt feed/yr	2,100	-	480	-	-	-
Catalytic cracking	kt feed/yr	3,500	-	-	2,600	-	-
Hydrotreating	kt feed/yr	16,500 <sup>10)</sup>	5,430	3,860 <sup>10)</sup>	15,400 <sup>10)</sup>	-	3,707
Lube oils	kt feed/yr	-	-	260	-	-	-
Catalytic reforming unit/ Platforming	kt feed/yr	1,200	1,577	1,000	1,800	-	1,320
Alkylation unit	kt feed/yr	330	-	-	300	-	-
Solvent deasphalting unit	kt feed/yr	-	-	-	84011)	-	-
Flexicoker ®	kt feed/yr	-	2,628	-	-	-	-
Hydrogen via SMR	kt H₂/yr	-	26	-	<b>49</b> <sup>11)</sup>	-	92
Hydrogen as byproduct	kt H <sub>2</sub> /yr						
from catalytic		52	68	43	77	-	38
reforming/Platforming <sup>12)</sup>							
Hydrogen production via	kt H <sub>2</sub> /yr	-	-	-	104 <sup>13)</sup>	-	-

#### Table 6 Nameplate Capacity per process unit

7) Facts & Figures on the Rotterdam Energy port and Petrochemical cluster (Port of Rotterdam, 2017)

8) Milieueffectrapport hydrocrackerinstallatie Uitbreiding van de ExxonMobil Rotterdam hydrocrackerinstallatie (Royal Haskoning DHV, 2015)

9) Internal communication with company, 2019

10) Based on capacity values for several hydrotreating processes found at Worldwide refining survey 2017 (Oil & Gas Journal Research, 2017)

 Based on hydrogen production capacity found at environmental application permit Aanvraag Wm/Wvo-(revisie) vergunning Shell Nederland Raffinaderij B.V. – Pernis (DCMR, 2008)

(revise) verguining Shell Nederland Ramaderij B.v. - Perns (DCMR, 2008)
 Assumed that hydrogen production is 4.3 wt% of catalytic reforming unit capacity

13) Initial Operation of the Shell Pernis Residue Gasification Project (Zuideveld et al., 1998)

#### 2.3.1 Energy consumption

The refinery sector presented around 134 PJ of energy commodities intakes in 2018 (disregarding feedstock use) (CBS,2020a). Figure 11 presents the energy shares among the



commodities. Fuel gas and natural gas hold the highest shares, which is due to the fact that most of the refinery units have gas-fired equipment that runs on either one or the other fuel.

# Figure 11 Energy use shares for the Dutch Refining sector for 2018. Based on CBS (2020a)

The fuel gas consists of a methane-rich gas which is a by-product of most of the refinery processes. It is usually consumed on site as fuel for furnaces and boilers. In 2018, the total fuel gas production from the sector was around 87.8 PJ (CBS, 2020a) and the total input for energy use was around 81.8 PJ, leaving 6 PJ for exporting to third parties (CBS, 2020a). The composition of this gas can vary depending on the site, however, for simplicity, the emission factor from natural gas of 56.6 CO<sub>2</sub> kg/GJ (RVO, 2018) was considered also for fuel gas in this report. Regarding natural gas, the total amount imported by the refineries in 2018 was 50.4 PJ (CBS, 2020a).

Some refinery sites have CHP (combined heat and power) units and boilers that use natural gas and/or fuel gas as energy commodities. The input of natural gas and fuel gas for the steam and electricity generation via CHP on site was around 13.7 PJ (CBS, 2020a) and 6.8 PJ (CBS, 2020a) in 2018, respectively. For boilers, the values were 1.1 PJ (EEA, 2019) and 8.7 PJ (EEA,2019). Natural gas is also used as feedstock for hydrogen production (i.e. steam methane reforming), the amount used for this purpose in 2018 was 16.1 PJ (CBC, 2020a). Thus, the energy use by other combustion processes could be derived by subtracting the inputs for boilers, CHPs and the use of natural gas as feedstock from the total production of fuel gas and the amount of natural gas imported. Table 7 and Table 8 include detailed information on the use of natural gas and fuel gas by the refinery sector.

# Table 7 Summary of fuel gas use by the Dutch refinery sector in 2018 (CBS, 2020a& EEA, 2019)

Торіс	Fuel gas ( <i>Residual gas</i> at CBS) [PJ]
Total fuel gas produced by the sector (CBS, 2020a)	87.8
Energy input for CHPs (CBS, 2020a)	6.8
Energy input for boilers (EEA,2019)	8.7
Fuel gas export to third parties (CBS, 2020a)	6
Total fuel gas used for combustion except boilers and CHPs (calculated)	66.3
Total fuel gas used by the sector for energy (calculated)	81.8

Table 8 Summary of natural gas use by the Dutch refinery sector in 2018 (CBS,2020a & EEA, 2019)

Торіс	Natural gas [PJ]
Total natural gas imported by the sector (CBS, 2020a)	50.4
Energy input for CHPs (CBS, 2020a)	13.7
Energy input for boilers (EEA,2019)	1.1
Natural gas use as feedstock (CBS, 2020a)	16.1
Total natural gas used for combustion except boilers and CHPs (calculated)	19.5
Total natural gas used by the sector for energy (calculated)	34.3

Besides natural gas and fuel gas, the CBS (2020a) energy balance for the refinery sector also indicates the use of LPG and of so-called *other petroleum products*, together their consumption summed 11.4 PJ in 2018 (Figure 11). It was assumed that these two fuels are used as fuel for furnaces. Regarding electricity, the total consumption by the refinery sites was and 9.3 PJ (CBS,2020a) in 2018, however, around 6.1 PJ (CB2, 2020a) of electricity was delivered by the CHPs, leaving 3.2 PJ to be provided by the grid.

Table 9 summarises the energy intake considered as baseline per energy carrier for each process unit mentioned in this chapter. Negative values represent generation of steam via heat recovery from a certain process unit. It is important to highlight that the specific energy input (per tonne of feedstock) is very dependent on which crude oil is processed in the refinery. This is due to the density difference between distinct crude oils. The calculations are based in three types of crude oils: Brent blend (833 kg/m<sup>3</sup>), Arabian heavy (886 kg/m<sup>3</sup>) and Iranian light (847 kg/m<sup>3</sup>).

#### Table 9 Energy demand per process unit for the refinery sector

Process unit	Fuel gas/ natural gas [MJ/t feed] <sup>14)</sup>	Steam [MJ/t feed] <sup>14)</sup>	Electricity [kWh <sub>e</sub> /t feed] <sup>14)</sup>
Atmospheric distillation	506 - 538	316 - 336	4.8 - 5.1
Vacuum distillation	322 - 350	350 - 380	2.2-2.4
Hydrocracking	970 - 993	523 - 535	76 - 78
Thermal cracking/ Visbreaking	737 - 830	(-92) – (-103)	37 - 42
Catalytic cracking (FCC)	0 15)	2	26
Hydrotreating	555 - 577	217 - 225	32 - 33
Lube oils	9,268 - 9,485	265 - 271	125 - 128
Catalytic reforming/ Platforming	1,500 - 1,590	737 - 781	23 - 25
Alkylation	400	3,720	77
Solvent deasphalting	910 - 1,024	17 - 19	11 - 13
Flexicoker® <sup>16)</sup>	0 <sup>17)</sup>	19	23 <sup>18)</sup>
Hydrogen via SMR <sup>19)</sup> (per t H <sub>2</sub> )	<b>30,000-80,000</b> <sup>20)</sup>	(-10,000) - (-20,000)	200-400
Hydrogen via gasification $^{21)}$ (per t H <sub>2</sub> )	0	-18,000	not known

 Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas (JRC, 2015) and Energy Efficiency Improvement and Cost Saving Opportunities for Petroleum Refineries (Energy star, 2016)

15) Catalytic cracking energetic input is provided by coke burning during catalyst regeneration, this coke layer is formed due to the cracking reactions. The energy demand was estimated to be around 410-420 MJ coke/t feed (Meyers, 2004)

16) Values for this process calculated based on ExxonMobil (2015)

17) Similar to the catalytic cracking process, the Flexicoker® partly burns the coke produced to provide the necessary heat for the reaction step. The coke demand was estimated to be around 5,100 MJ/t feed based on Methodology for the free allocation of emission allowances in the EU ETS post 2012 (Ecofys et al, 2009)

18) Based on electricity demand for conventional delayed coking process extracted from Meyers (2004)19) Best Available Techniques for the co-production of hydrogen, carbon monoxide and their mixtures by

steam reforming (EIGA, 2013) 20) This value corresponds to the natural gas intake as feedstock to be converted into hydrogen and CO2

Based on Initial Operation of the Shell Pernis Residue Gasification Project (Zuideveld et al., 1998)

In Table 10 we combine the average energy consumption numbers with the throughputs of the units of the refineries to arrive at an approximate value for their total energy input per

energy carrier. A utilisation factor of 90% was assumed for the calculation of the yearly energy intake.

Table 10 Estimated energy consumption based on unit throughputs (Table 6) andgeneric energy consumption numbers (Table 9) [PJ/yr]

Commodity	ВР	Esso	Gunvor	Shell	Vitol	Zeeland
Total fuel gas/natural gas as energy use in processes [PJ/yr]	23 - 25	14 - 15	9 - 10	29 - 31	2	14 - 15
Total fuel gas/natural gas demand for hydrogen production via SMR [PJ/yr] <sup>22)</sup>	-	1 – 2	-	2 - 4	-	3 - 7
Steam use in processes [PJ/yr]	12 - 13	8	3 - 4	15	1	7
Total electricity use in processes [PJ/yr]	2.8	1.8	0.8	3	0.1	1.4

22) The fuel gas/natural gas intake encompasses both energy use (combustion in reforming furnaces) and feedstock use (conversion to hydrogen via reforming reaction)

The atmospheric and vacuum distillation systems are responsible for the highest energy consumption share because they have the highest throughput. The lube oils and catalytic reforming/platforming have the highest energy demand per unit of feed, however, these systems usually have smaller capacities. As expected, fuel gas and natural gas are the energy commodities with highest demand for all systems, except for alkylation. It is important to note that the numbers above do not consider differences in terms of energy efficiency and downtime per refinery site.

Steam used on site can be provided via waste heat from furnaces, as indicated via the negative figures on Table 9. Thermal cracking, visbreaking, catalytic reforming and hydrogen production units are, therefore, relevant for the overall energy integration in the refineries. It is important to highlight that Table 8 does not offer a complete overview of the steam balance of each site because it doesn't contain information about all existent heat flows exchanged between process units.

#### 2.3.2 CHPs and auxiliary boilers

Some of the companies discussed in this report have CHP units on site, which is the case for BP, Esso and Shell. Those units provide both steam and electricity for the respective sites. In all cases, the refinery still needs internal or external steam provision, and backup facilities. Shell Pernis, for instance, imports about 4.9 PJ/yr of steam from Pergen facility, which is located on the refinery site itself, but owned by Air Liquide (Cioli et al., in prep). It is also possible that the site is able to sell a surplus of both steam and electricity. Table 11 includes the (derived) main characterises of the cogeneration and boiler systems present at the refineries.

Site/ process unit	Thermal capacity [MW <sub>th</sub> ]	Fuel gas demand [PJ/yr]	Natural gas demand [PJ/yr]	Steam generated <sup>23)</sup> (calculated) [PJ/yr]	Electricity generated <sup>24)</sup> (calculated) [PJ/yr]
BP - CHP	292	1.3	2.8	1.7	1.2
BP - boilers	166	1.5	-	1.3	-
Esso - CHP	192	4.2	0.8	2.1	1.5
Esso - boilers	349	4.6	-	4.1	-
Gunvor - boilers	403	1.4	0.6	1.8	-
Shell – CHP	502	1.3	10.1	4.7	3,4
Shell – gas turbine connected to crude distillation	e 59	-	0.9	-	-
Zeeland – boilers	152	1.2	0.5	1.5	-
Total (CHPs)	986	6.8	13.7	8.5	6.1
Total (boilers)	1,070	8.7	1.1	8.9	-

Table 11 Main power and steam plants capacities (EEA, 2019) and derived energycharacteristics in 2018

23) Steam production calculated based on thermal efficiency of 41% for CHPs, the efficiency value was derived from the Energy balance sheet for the refinery sector from CBS (2020a). For boilers, the thermal efficiency assumed to be 90%

24) Electrical efficiency for CHPs used was 30%. The efficiency value was calculated based on the Energy balance sheet for the refinery sector from CBS (2020a)

Shell presents a gas turbine that provides heat directly to the crude distillation system; for this reason, the table shows no steam or electricity production related to this specific gas turbine. However, its energy intake is quite significant and, for this reason, it was also included in Table 11.

#### 2.3.3 Hydrogen production

As mentioned in section 2.1, hydrogen in the refinery sector can be produced via steam methane reforming and from gasification of heavy oil. Besides these sources, hydrogen is also available as by-product from the catalytic reforming/platforming process. The estimates of the hydrogen production from these three processes are present at Table 12. Regarding the Esso refinery site, part of the Flexicoker® gas is exported to the connected Air Products unit as feedstock for hydrogen manufacturing. This Air Products unit sells hydrogen and steam back to Esso (ExxonMobil, 2019).

Company	SMR production [kt/yr]	Gasification [kt/yr]	Hydrogen by-product from naphtha reforming [kt/yr] <sup>29)</sup>
ВР	-	-	38
Esso	26 <sup>25)</sup>	-	50
Gunvor	-	-	32
Shell	49 <sup>26)</sup>	104 <sup>28)</sup>	58
Zeeland	92 <sup>27)</sup>	-	38
Total	167	104	216

#### Table 12 Hydrogen production nameplate capacity in the Dutch refinery sector

25) Value extracted from Uitbreiding van de hydrocrackerinstallatie ExxonMobil Raffinaderij Rotterdam – 3 t H<sub>2</sub>/h (Commissie MER, 2015)

26) Aanvraag Wm/Wvo-(revisie)vergunning Shell Nederland Raffinaderij B.V. Pernis (DCMR, 2008)

27) Internal communication with company, 2019

28) Initial Operation of the Shell Pernis Residue Gasification Project (Zuideveld et al., 1998)

29) Based on the ratio 51.27 Nm<sup>3</sup>/bbl naphtha feed (Meyers, R. A., 2004).

#### 2.3.4 CO<sub>2</sub> emissions

The  $CO_2$  emissions were grouped into the main sources of the refinery sector. Information on unit capacities, energy consumption per energy carrier and their respective emission factors were used to estimate the values presented at Table 13. Additionally, a utilization factor of 90% was assumed for the operating facilities. As expected, emissions originated from combustion from furnaces present the biggest share.

Shell Pernis delivers around 400 kt/y of  $CO_2$  to the OCAP (Organic  $CO_2$  for Assimilation by Plants) pipeline to supply greenhouse horticulture, but these emissions are still accounted to Shell under the ETS, and included in Table 13.

Sources	CO <sub>2</sub> emissions [Mt/yr]	Share [%]
Furnaces <sup>30)</sup>	5.5	51
CHPs and boilers <sup>30)</sup>	1.9	10
FCC units <sup>31)</sup>	1.0	9
Hydrogen production (SMR + gasification) <sup>32)</sup>	2.3	21
TOTAL	10.7	

#### Table 13 Scope 1 CO2 emissions estimates for the Dutch refinery sector

30) Based on energy values from CBS (2020a). The emission factor for both fuel gas and natural gas were considered to be 56.5 kg CO<sub>2</sub>/GJ.

31) Based on emission factor for FCC units of 0.17 t CO<sub>2</sub>/ t feedstock. These emissions are related to coke burning.

32) SMR emission factor: 9 t CO<sub>2</sub>/t H<sub>2</sub> (EIGA, 2013). Gasification unit emissions:1 Mt CO<sub>2</sub>/yr (internal communication with company, 2019).

# 3 Refinery products and application

This chapter describes briefly the refinery products, production volume, applications, product markets, trade and prices relevant for the Dutch situation.

#### 3.1 Products volumes and its applications

A typical refinery presents a wide range of fossil-based products, which may serve to meet both petrochemical and fuel demands. The main products of a refinery normally are LPG, naphtha, gasoline, kerosene, gasoil/diesel and fuel oil. Table 14 presents the production volumes of the mentioned products by the Dutch refinery sector for the last four years and Figure 12 shows the progressions of these products since 2000.

Product	2016 [kt/yr]	2017 [kt/yr]	2018 [kt/yr]	2019 [kt/yr]
LPG	1,650	1,560	1,480	1,570
Naphtha	7,728	8,131	9,583	8,454
Gasoline	3,981	3,026	3,988	4,061
Kerosene (Aviation fuel)	8,220	7,988	9,099	9,064
Diesel/gasoil	19,162	19,272	18,599	20,753
Fuel oil	11,963	11,684	11,077	8,909

Table 14 Annual production volumes for the Dutch refinery sector (CBS, 2020c)



Figure 12 Production volumes for the Dutch refinery sector. Based on CBS (2020c)

In the past three years, gasoline production has dropped while naphtha, kerosene and fuel oil increased. LPG production has kept relatively constant along the years and diesel has decreased slightly. In order to understand such behaviour, the paragraphs below give an overview of the main properties and applications of the refinery products. The next section will explore the market performance.

#### LPG and other Gaseous products

Gaseous refinery products include hydrogen, fuel gas, ethane, propane, and butane. Most of the hydrogen is consumed in refinery desulphurisation facilities, as mentioned in Chapter 2. Refinery fuel gas varies in composition, but presents a significant amount of methane, therefore, it has a heating value similar to natural gas. As described previously, the fuel gas is consumed in plant operations. Ethane may be recovered from the refinery fuel system for use as a petrochemical feedstock. Propane and butane make up the LPG, which is used as transport fuel and also used as feedstock for the petrochemical sector.

#### <u>Naphtha</u>

Naphtha is a liquid product mainly composed by hydrocarbons with 5-12 carbons atoms (5-6 carbons is light naphtha and 7-12 carbons is heavy naphtha). The mixture mainly consists of straight-chained and cyclic molecules. Naphtha can be sold to the petrochemical sector, to be used as feedstock for steam crackers. It can also be processed internally in the refinery (via catalytic reforming), to increase its octane number and, therefore, be blended into the gasoline pool.

#### <u>Gasoline</u>

It is a liquid product composed by a mixture of paraffins (straight chains), olefins (doubled bonds) and cycloalkanes (cyclic with single bonds), containing molecules with 4-12 carbon atoms. Gasoline is mainly used in the transport sector as a fuel. There are several categories of gasoline depending on its blending characteristics. As mentioned before, gasoline can be blended with reformatted naphtha, but also with alkylate product and with butane; with the purpose to increase its octane number and reach certain quality requirements.

#### <u>Kerosene</u>

Kerosene is a liquid product, constituted by molecules with 10-16 carbon atoms. The main components are paraffins, cycloalkanes and aromatics. It is the primary fuel for modern jet engines. Jet fuels may have strict requirements, such as being free from wax particles or suspended water to ensure safety for its application under sub-zero temperatures.

#### Gasoil/Diesel

Petroleum derived diesel is a liquid product also composed by paraffinic, cyclic and aromatics hydrocarbons. The molecules can have from 10 to 15 carbon atoms. Similarly to gasoline, the principal end use for diesel is as a fuel powering automobile, truck, bus, and railway engines. It is also increasingly used as marine transport fuel because of stricter environmental regulations (Dieselnet, 2020). Until the early 1990s, standards for diesel fuel quality were not particularly stringent for passenger transport. Currently, the European Union restricted the sulphur content between 10 to 15 ppm and there are also regulations limiting aromatic content, which reduces its applicability in automobiles.

#### <u>Fuel oil</u>

Fuel oil is also a liquid product and consists largely of residues from several process units from a refinery. Its composition can vary depending on the application, but normally it contains paraffins, cycloalkanes and aromatics, in long hydrocarbon chains. This product can be blended with other suitable gasoil fractions to achieve the viscosity and density required.

The sulphur levels in the fuel oil can vary significantly because it is highly dependent on the crude oil processed in the refinery (Oiltanking, 2020). To reduce air pollution, regulations regarding the sulphur content are in place in Europe. From 2015, the maximum allowed sulphur content in fuel used on board ships decreased from 1.0 to 0.10 % within the Emission Control Area (ECA) in the North of Europe. The maximum sulphur content of fuel outside the ECA was 3.50% until the January 2020. Currently, the maximum sulphur content in fuel used outside the ECA is 0.50% (ILT,2020).

Table 15 summarises the national consumption distribution in 2019 of the main petroleum products. This table does not include the use of the products for conversion into other petroleum products.

Table	15	Shares	of final	consumption	of petroleum	products	in The	Netherlands	for
2019	(CB	S, 2020	c)	-	-	-			

Consumption	Refinery own use as fuel	Petrochemical use as fuel	Petrochemical use as feedstock	Transportation, fishing industry and other	Total consumed volume (kt/year)
LPG	2%	0%	82%	16%	1,867
Naphtha	0%	0%	100%	0%	3,100
Gasoline	0%	0%	0%	100%	4,329
Kerosene (jet fuel and other)	0%	0%	48%	52%	92
Diesel/gasoil	0%	0%	0%	100%	6,910
Fuel oil	0%	0%	0%	100%	19

#### 3.2 Products markets

The European market faces a growing demand for petrochemicals, kerosene and diesel, and a declining demand for gasoline, light heating oil and heavy fuel oil (JRC, 2015). The increasing production capacity of the Middle East and Asia markets and their ability to trade diverse petroleum products globally are relevant competition factors for refineries in the EU. The European Union has 85 refineries spread across 22 member states, Norway and Switzerland, resulting in a throughput capacity of around 14.5 Mb/d (millions of barrels per day); which accounted for over 14% of global refining capacity in 2015 (CIEP, 2017). Some of the largest refineries in the world (>250 kb/d) are located in The Netherlands (around 8% of global refining capacity) and the Rotterdam port is one of the largest trading harbours (JRC, 2015).

On a European level, the total production of refinery products is relatively balanced with the demand volumes. However, specific policies and regulations (e.g. increase of gasoil/diesel in vehicles and sulphur levels in marine fuel) have motivated the demand for middle distillates (kerosene, gasoil/diesel). Also, the growing market of petrochemicals worldwide increases directly the demand for naphtha in the continent. The European market lacks on middle distillates products and present a significant surplus in gasoline and heavier products. Therefore, considerable import flows of diesel, kerosene and naphtha are needed to fulfill the demand. In contrast, ample export of gasoline and fuel oils results from the surplus production of these products (CIEP, 2017).

Regarding market prices, Figure 14 gives the average price for crude oil imports in Europe for the recent months and Figure 14 presents the average end-use price for some fossil-

based products in the same period. The figures indicate, as expected, that the prices for the selected fuels have similar fluctuation as crude oil imports prices, showing that they are similarly dependent on the refinery feedstock costs.



Figure 13 – Average import prices for crude oil in Europe (IEA,2020)



## Figure 14 - Average end-use prices for gasoline, diesel and LPG in The Netherlands (CBS, 2020) and average end-use prices for fuel oil in Europe (IEA, 2020)

Oil products are among the largest volumes of commodities which are imported and exported in the Dutch economy (JRC, 2015). Figure 15 to Figure 20 show the imported and exported volumes for the past 20 years for the main refinery products (LPG, naphtha, gasoline, kerosene, diesel/gasoil and fuel oil). It is possible to notice that the difference between imported and exported volumes grew significantly for both LPG and naphtha for the past 5-8 years. This is a reflection from the petrochemical sector, which use LPG and naphtha as feedstock (see Table 15). Regarding gasoline, kerosene, diesel/gasoil the exports are historically higher than the imports. For the fuel oil, the flows are balanced.



Figure 15 LPG imports and exports. Based on CBS (2020)



Figure 16 Naphtha imports and exports. Based on CBS, (2020)



Figure 17 Kerosene imports and exports. Based on CBS (2020)



Figure 18 Gasoline imports and exports. Based on CBS (2020)



Figure 19 Diesel/Gasoil imports and exports. Based on CBS (2020)



Figure 20 Fuel oil imports and exports. Based on CBS (2020)

# 4 Options for decarbonisation

This chapter presents potential options for reduction of energy use and/or  $CO_2$  emissions for the Dutch refinery sector. Figure 21 illustrates the framework considered when looking at options. This analysis goes beyond direct emissions and may include upstream and downstream measures to reduce indirect emissions. Each element that is relevant for the industrial sites is taken into consideration in order to have a good idea of the possibilities for decarbonisation. Table 16 summarises the decarbonisation options investigated for the sites discussed in this report. The selection of technologies was based on the process units/equipment contribution to the energy consumption and  $CO_2$  emissions at the refinery sites. Options that are considered to have low impact or very low development level are not explored in this report, yet may be relevant. Therefore, this is not an exhaustive list, and many options are (still) under development.



Figure 21 Schematics for decarbonisation options investigation (PBL, 2018)

#### Table 16 Summary of decarbonisation options for the refinery sector

Category	Technology	Relevant to process	
Carbon capture	Carbon capture and storage	Applicable mainly for hydrogen production, FCC and for gasification units	
		Possibly applicable to all current stacks, but limited by space requirements	
	Electric furnaces	Possibly applicable to all processes that present gas-fired equipment (e.g. atmospheric distillation, cracking processes, reforming)	
Fuel	Electric boilers	Steam boilers	
substitution	Electric shaft equipment	Steam turbines replacement	
	Blue/green hydrogen as fuel	Possibly applicable to all processes that present gas-fired equipment (e.g. atmospheric distillation, cracking processes, reforming)	
Feedstock	Co-processing (5-10%) pyrolysis bio-oil from biomass in FCC unit	Co-feed for FCC	
substitution	Blue/green hydrogen as feedstock for processes	All hydrotreating and hydrocracking processes	
Process design	Stand-alone plant for biofuels production via pyrolysis bio-oil upgrading	Process alternative for production of LPG, gasoline, kerosene and gasoil/diesel	
	Biomass gasification and Fischer Tropsch for fuels production	Process alternative for production of LPG, gasoline, kerosene and gasoil/diesel	
Residual heat usage	Use of process heat, internally or externally	All processes with excess heat	

#### 4.1 Carbon capture and storage

In a complex configuration such as a refinery, many different processes exist, such as cracking, distillation, reactions and flaring of off-gases, that result in  $CO_2$  emissions. The emission sources are distributed and contain different  $CO_2$  concentrations. The majority of  $CO_2$  emissions in a refinery are related to gas-fired process heaters, the on-site utilities for power and steam generation, gas-fired furnaces and hydrogen production.

Table 17 presents the  $CO_2$  concentration for the different processes that may exist on a refinery. These numbers were estimated by the IEA Greenhouse Gas R&D Program (SINTEF, 2017). Hydrogen production via SMR, the fluidised catalytic cracking (FCC) unit and both atmospheric and vacuum distillations are responsible for the highest post-combustion  $CO_2$  concentrations. However, in practice, some of the refinery processes may share the same stack and the  $CO_2$  concentrations may differ from values present in Table 17.

# Table 17 $CO_2$ concentration in flue gases per refinery process unit (SINTEF, 2017)

Process unit	CO <sub>2</sub> concentration in flue gases (vol%)
Atmospheric distillation	11.3
Vacuum distillation	11.3
Visbreaking / Thermal cracking	8.1
Reforming	8.1
Hydrotreating	8.1
FCC	16.6
Hydrogen production via SMR	24.2
Delayed coking	8.1
Hydrocracking	8.1
Solvent deasphalting (SDA)	8.1
Gas turbines	3.2
Steam boilers	8.1

There are currently two options for carbon capture that are relevant for refinery sites: precombustion capture and post-combustion capture. More details are given in the next paragraphs.

#### Pre-combustion capture

In this process, a hydrocarbon-rich stream is fed to a reformer or gasifier in order to produce  $CO_2$  and  $H_2$  (syngas). In a subsequent shift-reactor, the concentration of syngas is increased, after which it is cooled and  $CO_2$  is captured via solvent absorption. An almost pure  $H_2$  stream results from the absorption and the  $CO_2$  is released through solvent regeneration. This  $CO_2$  can then be compressed and exported. The outputs of this option include mainly the production of  $H_2$  and the possibility of steam generation after syngas cooling. Figure 22 illustrates a pre-combustion system.



# Figure 22 Pre-combustion capture system<sup>33,34)</sup> (Ferguson. S. and Stockle, M., 2012)

33) ASU refers to air separation unit 34) AGR refers to acid gas removal

In a refinery site, the pre-combustion system could be connected to any process that can burn hydrogen or that allows burner modification. A promising application could be for gas turbines and boilers with hydrogen combustion. Some of the advantages of this technology are: the capture equipment does not need to be located close to the firing systems and if the fuel gas network is integrated, the pre-combustion capture could be centralized and the network could be used to transport hydrogen instead. Hydrogen burning leads to higher NOx emissions, therefore, equipment for reducing those emissions are required for this option.

#### Post-combustion capture

In this system, the flue gas resulting from a combustion process is cooled and compressed, followed by solvent absorption. Around 90% of the total  $CO_2$  can be absorbed by the solvent (Ferguson. S. and Stockle, M., 2012). The cleaned gas is released to the atmosphere and the mixture solvent/ $CO_2$  is heated and the solvent recovered in order to be reused in the absorption process. If the sulphur concentration in the flue gas is high, pre desulphurisation is necessary. Figure 23 illustrates the post combustion capture system. The most common option for a chemical absorption solvent is Monoethanolamine (MEA).



#### Figure 23 Post-combustion capture system (Ferguson. S. and Stockle, M., 2012)

This capture unit is flexible and can be combined to most of the existent combustion systems (Ferguson. S. and Stockle, M., 2012). In principle, this technology could be applied to any combustion-based system in a refinery site, however, it is economically less attractive for flue gases with low  $CO_2$  concentration (below 10% vol.). Also, each stack would need a dedicated capture equipment due to high flow volumes.

The SINTEF study (2017) reports  $CO_2$  post-combustion capture costs for oil refinery systems. The values may differ depending on the  $CO_2$  concentration, resulting in the range of 31–47 EUR<sub>2019</sub>/t  $CO_2$  captured. Both CAPEX and OPEX values in Table 18 include only the capture and the interconnecting costs, however, the latter is very site dependent. No utilities costs are represented in the values below and they do not include CCS on hydrogen manufacturing because this topic is further explored on section 4.4.

	Low CO <sub>2</sub> concentration (5 %vol)	Medium CO <sub>2</sub> concentration (8-10 %vol)	High CO <sub>2</sub> concentration (10-18%vol)
CAPEX [EUR 2017/t CO <sub>2</sub> captured]	45 <sup>35)</sup>	31 <sup>36)</sup> -39 <sup>37)</sup>	28 <sup>38)</sup> -31 <sup>39)</sup>
Fixed OPEX <sup>40)</sup> [EUR 2017/ t CO <sub>2</sub> captured/yr]	19 <sup>35)</sup>	15 <sup>36)</sup> -18 <sup>37)</sup>	14 <sup>38)</sup> -15 <sup>39)</sup>
Steam consumption [GJ/ t CO <sub>2</sub> captured]	2.5	2.5	2.5
Electricity consumed [kWh/ t CO <sub>2</sub> captured]	183	149-185	162-166
CO <sub>2</sub> avoided/CO <sub>2</sub> captured <sup>41)</sup>	0.65	0.67	0.67

# Table 18 Post-combustion capture systems costs for different $CO_2$ concentrations (SINTEF, 2017)

35) Capture nominal capacity: 750 kt CO<sub>2</sub>/y

36) Capture nominal capacity: 697 kt CO<sub>2</sub>/y

37) Capture nominal capacity: 765 kt CO<sub>2</sub>/y

38) Capture nominal capacity: 2,777 kt CO<sub>2</sub>/y

39) Capture nominal capacity: 1,681 kt  $CO_2/y$ 

40) No electricity or fuels costs are included

41) Considering emission factors of 0.183 kg CO\_2/kWh for electricity and of 56.6 kg CO\_2/GJ\_{LHV} for natural gas

## 4.2 Electrification

Electrification of the heat supply seems to be an interesting solution in the refinery sector, since a large part of its emissions is due to thermal processes (around 70%). Gas-fired furnaces and steam generation systems are the main targets for this option. Considering energy flows presented in section 2.3, it was estimated that the amount of energy used by furnaces in the entire refinery sector is around 97.1 PJ (Table 7 and Table 8) and around 17.4 PJ (Table 11) of steam is provided by CHPs and boilers.

In order to substitute both the thermal demand of the furnaces and the steam supply, nearly 32 TWh of renewable electricity would be required to allow  $CO_2$ -free electrification of the sector. To meet this demand, around 1,900 wind turbines (with capacity of 4 MW and 4,000 full load hours) would be necessary. Another relevant factor is the surplus of fuel gas that the electrification would bring, since this is a by-product from several process units. An alternative use that presents zero or low  $CO_2$  emissions would be necessary. The total electricity demand was calculated assuming 90% efficiency for both conventional and electrical furnaces and 99% efficiency for electrical boilers, further details are given in the next sections.

#### Furnace electrification

Electric furnaces present significant potential to reduce energy related emissions (Ecofys and Berenschot, 2018). Electricity-based processes 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 target without the need for a heat transfer medium, whereas indirect heating takes place outside the heating target and with the aid of a heat transfer medium (Schuwer, D. and Schneider, C. 2018).

Electric heating is already widely used in industry, however none of the known technologies has been applied yet on refinery processes. The technologies for electrical industrial heating

that were identified with significant potential application in refinery processes are direct and indirect resistance heating and arc heating (communication with specialists from TNO, 2019).

Direct resistance heating is composed by an electric current driven through a material, which heats up due to its electrical resistivity. Indirect resistance heating, instead, is defined by an electric current driven through a resistor, which heats up, and, through convection and radiation it heats up a surrounding fluid or gas. Electric arc systems heat up materials with the generation of a high-density electric current between two electrodes (electric arc). The heated materials can be solids, gases and liquids. This technology is more commonly used in the steelmaking industry; however, it could be applied to the refinery sector in hydrocarbon cracking systems via the Plasma Arc Heating technology (communication with specialists from TNO, 2019).

Considering the technology characteristics of each option and expert consultation, the most relevant one to gas-fired furnaces would be indirect resistance heating. This technology is not available yet on an industrial scale for refinery furnaces, but currently under development (TRL 3). One of the possibilities to overcome the technology limitation could be a hybrid system with both gas-fired and electric furnaces. Post-combustion capture could be included in this option as well in order to avoid emissions from the furnaces fed with fuel gas.

Regarding the process units explained in section 2.1, those that use gas-fired furnaces are:

- Atmospheric distillation
- Vacuum distillation
- Naphtha reforming (Platforming)
- Hydrogen production via steam methane reforming
- Hydrocracking
- Thermal cracking/Visbreaking.

#### Steam generation electrification

Some refineries in the Netherlands produce steam on site via CHP systems and/or auxiliary gas-fired boilers. Similar to gas-fired furnaces, natural gas and fuel gas are employed for the steam production.

Boilers powered by electric resistance are an alternative option to produce steam. Current technologies are able to provide steam up to 350 °C (Berenschot et al., 2017). Electric boilers allow flexible operation and they are available in the market for several design capacities (up to 100 MW) (BZE, 2018). The technology is well established (TRL 9), however, similar to electric furnaces, its economic feasibility and decarbonisation potential tie together with the electricity price and the availability of renewable sources for electricity (Berenschot et al., 2017).

The refineries that produce steam on site are: BP (boilers and CHP), Esso (boilers and CHP), Gunvor (boilers), Shell (CHP) and Zeeland (boilers) (see Table 11). Considering the process units mentioned above, the thermal demand for furnaces and steam generation systems were estimated as presented in Table 7. The potential for thermal demand replacement is around 127.5 PJ for the entire sector. However, more than 64% (81.8 PJ) of this demand is met by fuel gas, for which another application should be considered without bringing additional  $CO_2$  emissions.

Table 19 Summa	ry of fuels use in fu	urnaces, CHPs a	and boilers for the	refinery sector
in 2018 (CBS, 20	20a)			

	Total fuels [PJ]	Fuel gas [PJ]	Natural gas [PJ]	LPG and other petroleum products [PJ]
Furnaces fuel use	97.1	66.3	19.5	11.4
CHPs and boilers fuel use	30.4	15.5	14.8	-
Total	127.5	81.8	34.3	0.8

Assuming 90% of thermal efficiency for the conventional furnaces, the heat provided to the processes was calculated, then the electricity demand for the electrical furnace was derived. For the electrical boilers, the total steam produced by CHPs and boilers from Table 11 was used to calculated the electricity needed if electrical boilers substitute the current steam generation systems. A thermal efficiency of 99% (Berenschot et al., 2017) for the electrical boilers was considered.

#### Table 20 Electricity demand for electrical furnaces and boilers

	Efficiency	Heat/ steam delivered [PJ]	Electricity demand [TWh]
Electrical furnaces	90%	87.4	27.0
Electrical boilers	99%	17.4	4.9

Regarding investment costs for both electric furnaces and electric boilers, estimates are provided in Table 21. For the electrical furnace, the CAPEX value relates to equipment, substation and cabling costs are related to the equipment costs and the CAPEX for the electric boiler corresponds to equipment costs only.

# Table 21 Estimates on electrification investment costs for electric furnaces andelectric boilers (2018)

Costs	Electric furnace (10 MWe) <sup>42)</sup>	Electric boiler (70 MWe) <sup>43)</sup>
CAPEX [MEUR2018]	35 - 50	10 - 13
OPEX [MEUR2018/yr] <sup>44)</sup>	0.7 – 1	0.08

42) 90% efficiency. CO<sub>2</sub> Reductie Roadmap van de Nederlandse raffinaderijen (DNV-GL, 2018)

43) 99-99.9% efficiency. Electrification in the Dutch process industry (Berenschot et al., 2017)

44) Excluding energy costs.

Since the technology for both electrical furnaces and boilers are still under development, it is expected that shaft equipment, such as steam turbines, will be firstly electrified at the refinery sector. This option can reduce the steam demand on site, which may allow some of the current boilers to close and reduce emissions from these installations. Because each refinery differs, the type and number of shaft equipment can vary significantly between the sites, therefore, it is difficult to assess the electrification potential for this equipment without site-specific information. For this reason, no electricity demand for this option was calculated, however, the VNPI roadmap report (VNPI, 2018) indicated an investment range for an electrical turbine of 10 MWe capacity. The CAPEX value includes equipment, substation and cabling costs and the OPEX figure does not include energy costs.

 Table 22 Estimates on electrification costs for electric turbines (VNPI,2018)

Costs	Electric turbine (10 MWe)
CAPEX [MEUR2018]	20 - 40
OPEX [MEUR2018/yr]	0.4 - 0.8

#### 4.3 Hydrogen as fuel

The aim of this option is to replace fossil-based gas by hydrogen as fuel for furnaces. Since the combustion of hydrogen generates water, the substitution of natural gas and/or fuel gas in fired processes by hydrogen results in the reduction of  $CO_2$  emissions. However, hydrogen should be produced via low  $CO_2$  processes, further discussed in section 4.4.

In principle, the utilisation of hydrogen as a fuel requires changes in the operating conditions for combustion and adaptation of furnaces burners in order to allow hydrogen use. The same application was discussed in more detail in the MIDDEN reports for both PVC and large organic chemicals manufacturing in Geleen (Semeijn & Schure, 2020; Oliveira & van Dril, in prep.). Although a hydrogen combustion flame presents lower radiation heat transfer than the resulted flame from natural gas, the ratio between the calorific value of hydrogen and its density is similar to the one from natural gas. This fact brings an advantage in the case of installing flexible burners that are able to use both fuels. Furthermore, hydrogen combustion leads to higher  $NO_x$  emissions, hence an  $NO_x$  abatement device would be necessary for the application of this option.

Similar to furnace electrification, the use of hydrogen as fuel replacement would leave a surplus of fuel gas in the refineries. Therefore, finding other applications for the fuel gas is also a relevant aspect for this option. The increase on hydrogen demand in the refinery sector if fuel gas and/or natural gas were to be fully substituted by hydrogen in furnaces is estimated at 1,063 kt. This was based on the lower heating value of hydrogen (120 MJ/kg) and the furnaces/CHP/boilers energy demand values from Table 19. If only natural gas is substituted, around 286 kt per year would be required, considering that both natural gas/fuel gas furnaces and hydrogen furnaces present the same efficiency.

It is expected that the wind energy supply will increase from 13.5 GW to 35 GW by 2028, of which 5 GW from offshore wind (PBL, 2019). This could give an opportunity to produce green hydrogen at a lower cost than at the moment. Another important aspect is storage, there is a potential to store hydrogen in salt caverns, which are currently being used in the Netherlands to store natural gas. The projection is that the salt caverns from Zuidwending will be able to store hydrogen by 2024 (Gasunie, 2020). Regarding 2050, the outlook study developed by TenneT and Gasunie mentions that 3 to 9 storage caverns will be developed, which would be sufficient to meet the projected demand for sustainable hydrogen in 2050.

The Gasunie Backbone initiative claims to deliver by 2030 a network grid with around 15 GW hydrogen capacity connected with the 5 main industrial clusters in The Netherlands (Eemshaven, Noordzeekanaal, Rotterdam, Zeeland and Limburg). The network would be based on the current natural gas grid, which would require few modifications (Gasunie, 2020). Figure 24 illustrates the Backbone grid and shows the connection with the Limburg area.



Figure 24 – Hydrogen Backbone infrastructure (Gasunie, 2020). Blue is existing gas pipeline, yellow is to-be-built hydrogen pipeline. The yellow symbols represent adaptations to existing compressor stations, the blue symbols are industry clusters and the light-blue symbol in the Northeast represents a hydrogen storage site.

Table 23 summarizes the costs for the use of hydrogen as fuel in gas-fired processes in refineries.

Table 23	Investment	costs for	the use	of hydrog	en as fuel	for a	$10 \; \text{MW}_{\text{th}}$	furnace in
the refine	ery sector (D	NV-GL, 2	018)					

Costs	Value	Comment
CAPEX (EUR <sub>2018</sub> /kW)	400-1,200	Estimation includes costs for the infrastructure for hydrogen transport, hydrogen compressor, and replacement of natural gas burners. It does not include NO <sub>x</sub> emission reduction technology.
OPEX (EUR <sub>2018</sub> /kW/yr)	4-12	1% of CAPEX. It does not contain utilities and hydrogen costs.

#### 4.4 Decarbonisation of hydrogen production

This section presents the relevant aspects for the refinery sector regarding the decarbonisation of hydrogen production. However, the technology options for decarbonisation of hydrogen manufacturing processes are described in detail by the MIDDEN report for industrial gases production in The Netherlands (Cioli et al., in prep.).

#### <u>Blue hydrogen</u>

Steam methane reforming (SMR) with CCS is an option that would be suitable for Esso, Shell and Zeeland since these refineries present SMR units. Also, the carbon capture could be applied to the gasification unit present at Shell. The challenges mentioned for the carbon capture option (section 4.1) also apply for the blue hydrogen production.

The H-vision initiative in Rotterdam investigates the possibility to produce blue hydrogen in a newly-built autothermal reforming (ATR) plant. This plant would use mostly refinery gas from the Shell and BP refineries as feedstock and supply blue hydrogen for use as fuel to the refineries (H-Vision, 2019).

#### <u>Green hydrogen</u>

The production of hydrogen via water electrolysis is also a potential technology for providing hydrogen to refineries. The technology efficiency, the renewable electricity availability and prices are very relevant for this option. The infrastructure for electricity supply is also a determinant factor, since the production of hydrogen via electrolysis demands a significant amount of electricity. The electricity demand is in average 58 kWh/kg H<sub>2</sub> (Elzenga, H. and Lensink, S., 2020).

#### Hydrogen production via biomass

Hydrogen can be produced from biomass gasification. The mentioned yields in literature are around 0.05-0.08 t H<sub>2</sub>/t biomass (Cioli et al., in prep.). Besides biomass availability, another challenge of applying this option is the gasification process itself, since the current commercial technologies present relativity low hydrogen yields. However, the electricity intake is relatively low (3.06 kWh/ kg H<sub>2</sub>) and steam can be recovered in this process.

#### Hydrogen production via thermal decomposition of methane

Methane decomposes thermally to produce hydrogen and carbon black as by-product. No  $CO_2$  is formed. This process produces a marketable product as carbon black instead of  $CO_2$ , as illustrated by the reaction below (Cioli et al., in prep.).

$$CH_4 \rightarrow C + 2H_2$$
  
 $\Delta H = 74.5 \ kJ \ / \ mol \ CH$ 

This technology is still under development for large-scale production (TRL 3-4) (Schneider, S et al, 2020). The high-temperature required (around  $1500^{\circ}$ C) is one of the challenges for its application to a large scale.

As shown at Table 12, around 221 kt/yr of  $H_2$  (nameplate capacity) is provided by the catalytic reformer (Platforming) unit as a by-product. Therefore, the decarbonisation options mentioned in this section would apply only to the 271 kt/yr  $H_2$  produced via SMR and gasification (nameplate capacity).

# Table 24 Summary of decarbonisation options for hydrogen production(based on Cioli et al., in prep.)

Option	САРЕХ	OPEX <sup>45)</sup>
Blue hydrogen production	90–145 EUR2017/t CO2 captured	10–15 EUR2017/t CO <sub>2</sub> captured
Green hydrogen	3,193 EUR2017/t H <sub>2</sub>	159 EUR2017/t H <sub>2</sub>
H <sub>2</sub> production via biomass	3,344 EUR2017/t H <sub>2</sub>	17 EUR2017/t H <sub>2</sub>
H <sub>2</sub> production via thermal decomposition of methane	500–1,300 EUR2017/t H <sub>2</sub>	20-40 EUR2017/t H <sub>2</sub>

45) The OPEX values include labor and maintenance costs and excludes feedstock and energy costs.

### 4.5 Biomass options

This section describes options which involve the substitution of feedstock or processes to obtain refinery products via bio-based technologies. Detailed information about biofuels production in The Netherlands can be found in the MIDDEN report *Decarbonisation Options for the Dutch Biofuels Industry* (Khandelwal, M. & van Dril, T., 2020).

#### 4.5.1 Co-processing pyrolysis bio-oil and full upgrade to biofuels

The options investigated are: co-processing of pyrolysis bio-oil together with fossil feedstock in an FCC unit (fluidised catalytic cracking) in a refinery and full upgrade of pyrolysis bio-oil to biofuels in a standalone unit.

The pyrolysis bio-oil is produced via pyrolysis of solid biomass in an environment free of oxygen. The process scheme includes pre-treatment, reaction and oil recovery. The pre-treatment basically consists of moisture content reduction and biomass milling into smaller particles. The pyrolysis occurs at around 500°C (JRC, 2019) and produces bio-oil, non-condensable gas and char. The gas and char are separated from the bio-oil and the char can be used to produce heat to run the pyrolysis reactor. The non-condensable gas can be used in a CHP to generate electricity and steam. Both steam and electricity are enough to meet the pyrolysis system demand and to export. Figure 25 illustrates a pyrolysis bio-oil plant integrated with a CHP. In The Netherlands, there is an industrial unit similar to the scheme representation. This site is located in Hengelo, owned by Empyro-Twence and the process technology was developed by BTG Bioliquids. Currently, Empyro sells the oil as fuel for boilers for steam production. In addition, there are other two fast pyrolysis plants under construction, one in Finland and another one in Sweden. The unit in Sweden is expected in 2021 to supply pyrolysis bio-oil from wood products company Setra for co-processing in the refinery Preem (Bioenergy International, 2019).



# Figure 25 Pyrolysis bio-oil from wood chips process (adapted from Lammens, 2018)

The produced resulted from the pyrolysis is acidic, high in oxygen and moderate in water content. Therefore, the raw bio-oil is not suitable for direct mixing with fossil oils and cannot be used for engines without further upgrading, which allows the oil to obtain similar properties as more conventional liquid fuels (JRC, 2019). However, the bio-oil has the potential to either be co-processed in an FCC unit in a refinery or, if upgraded, the bio-oil can be distilled to recover products such as naphtha, kerosene and diesel directly. BTG tested their raw bio-oil in a pilot co-processing set-up and verified that up to 5%wt co-feeding no significant changes occur in the current FCC process. With 10%wt co-feeding, small changes in the yields are verified.

Pinho et al. (2015) reported a demo plant in Brazil owned by Petrobras that co-processed 5 and 10%wt of pyrolysis bio-oil together with vacuum gasoil in an FCC unit (200 kg/h capacity). They observed that the gasoline production yields reached for both 5 and 10%wt co-feeding were very similar to those from the original configuration with vacuum gasoil as unique feed (see Figure 26).



Figure 26 Data: Petrobras 2015 & 2017, using fast pyrolysis bio-oil from both BTG & Ensyn in a 200 kg/h FCC demo unit (extracted from Lammens, T., 2018)

Pyrolysis bio-oil processing upgrading routes are currently being developed, some in an earlier stage and others in a more advanced stage of development. The raw bio-oil can be directly upgraded in a hydrodeoxygenation unit integrated with the pyrolysis plant facility. The hydrodeoxygenation process aims to reduce or eliminate the oxygen content in the bio-oil, with the use of hydrogen. These treatments involve putting the bio-oil in contact with a large excess of hydrogen in the presence of a catalyst. The resulting streams of this process are a gas, rich in light hydrocarbons and carbon dioxide, an aqueous phase and the deoxygenated bio-oil (PNNL, 2013).

The hydroprocessing systems normally present in the refineries (fixed bed reactors) could be potential candidates for the bio-oil hydrodeoxygenation. However, new process configurations and equipment are being studied, most of those still in the lab phase. Total deoxygenation of the bio-oil could lead to a product with oxygen levels below 2%wt (Internal communication with BTG-BTL, 2018). The upgraded oil can be directly processed in a distillation column in order to recover fuels such as gasoline and diesel (PNNL, 2016).



#### Figure 27 Pyrolysis bio-oil upgrade stand-alone unit (adapted from PNNL, 2016)

There is the possibility to partially deoxygenate the raw pyrolysis bio-oil with one-step mild hydrotreatment, leading to a stabilised and partially deoxygenated oil (SPDO). BTG-BTL believes that the co-processing of this oil in the FCC unit would be possible up to 20%wt without causing significant changes in the original products yields (internal communication with BTG-BTL, 2019).

In summary, three ways were identified as potential options of incorporating pyrolysis bio-oil in the refinery sector:

- 1. Co-processing up to 10%wt the raw pyrolysis bio-oil in an FCC unit together with vacuum gasoil. Currently this option is into demo scale (TRL 6).
- Upgrading the raw pyrolysis oil via partial hydrotreating process (deoxygenation) and co-feeding the stabilised oil (SDPO) up to 20%wt in an FCC unit. Option studied in pilot plant scale (TRL 5).
- 3. Completely separated unit for further hydrotreating of raw bio-oil to complete deoxygenated upgraded oil and recovery of fuel fractions via distillation. Option under development in pilot plant scale (TRL 5).

Option 3 could be implemented as a stand-alone plant (green field project) and the recovered products could be used in existent fuel blending facilities on refineries sites.

Regarding investment costs, Table 25 summarizes the main findings. Option 1 does not require major engineering changes in the FCC unit. The CAPEX would be related mainly with extra feed nozzles in the FCC reactor and with a stainless-steel tank (due to the acid nature of the oil) and feedline dedicated to the pyrolysis bio-oil, which are elements that normally do not represent major sums. The exact values for the CAPEX and OPEX of this option are generally not available and are very site dependent, therefore, generic figures are difficult to find. (SGAB, 2017).

Table 25	Costs	regarding	pyrolysis	oil in	the	refinery	sector	

Option	CAPEX [EUR <sub>2016</sub> /t pyrolysis bio-oil/yr]	OPEX <sup>46)</sup> [EUR <sub>2016</sub> /t pyrolysis oil/yr]
Pyrolysis raw bio-oil co-processing in an FCC unit <sup>47)</sup>	4.4	22
Pyrolysis bio-oil production with upgrading (stand-alone plant) <sup>48)</sup>	1,752	166

46) OPEX does not include both energy and feedstock costs.

47) Based on estimated costs from SGAB report (2017) for modifications in a refinery for co-processing in an FCC unit. Original values: CAPEX 1 EUR/MWh and OPEX 5 EUR/MWh. Utilization capacity considered: 7,500 h/y. The OPEX related to the bio-oil fraction in co-processing is not readily available for estimation, however, the SGAB report based its values on opinion from experts in the field. The basic numbers were used to arrive at a Rough Order of Magnitude (ROM) figure.

48) Based on pyrolysis bio-oil production costs (Venderbosch, 2017) and upgrading unit costs (PNNL, 2016) for a 25 MW pyrolysis bio-oil capacity. The OPEX figures also considers hydrogen demand and catalyst replacement for hydrotreating unit. Utilization capacity considered: 7,500 h/y.

For the Dutch refinery sector, only two refineries have FCC units on site: Shell and BP. For those sites, all the three options listed above could be studied for future implementation. For the other refineries, only option 3 (i.e. total hydrodeoxygenation of the bio-oil and subsequent production of biofuels via distillation) could be a possibility. However, it is important to point out that the supply of sustainable biomass in substantial amounts to maintain the supply chain of pyrolysis oil is crucial for this application. Infrastructural and spatial limitations and the debate around the sustainable use of biomass are also relevant aspects.

#### 4.5.2 Gasification of biomass and biofuels production via Fischer Tropsch

This decarbonisation option is an alternative for the traditional refinery to produce biofuels such as bio-diesel, bio-gasoline and bio-kerosene via biomass gasification and Fischer Tropsch conversion.

The biomass gasification process breaks the feedstock into simpler molecules, in which the main ones are hydrogen, carbon monoxide,  $CO_2$ , water and methane. The process temperature is usually between 800-1300°C and presents products both in gas and solid phases. The raw gas is composed by the substances already mentioned and the solid products are char, ashes and impurities.

In summary, the entire process includes: biomass size reduction, gasification, solids removal, reforming, water-shift reaction, gas cleaning, synthesis gas conversion and upgrading (Figure 28).



Figure 28 Conceptual Flow Diagram of Gasification based Biomass-to-Fuel System (PNNL, 2011). WWT: waste water treatment

<u>Gasification</u>: in the gasification step, the choice of the gasification agent depends on the desired composition for the raw gas, oxygen is typically used together with water either in liquid or vapour phase. For example, high temperature and steam as gasification agent normally leads to high hydrogen (H<sub>2</sub>) and carbon monoxide (CO) content in the gas product. High pressure causes the opposite effect (EBTP, 2016). For biofuels production via Fischer Tropsch, synthesis gas is needed; therefore, high content of hydrogen and CO is preferable. There are several types of biomass gasifiers and, depending on which technology is employed, the reaction temperature can vary. For this reason, the gasifiers temperatures range is  $800-1300^{\circ}$ C.

<u>Solids removal</u>: solids particles such as char and tar are removed from the gas product to avoid equipment and piping erosion. This separation can be done via cyclones.

<u>Reforming</u>: the reforming process converts organic compounds, such as methane and aromatics, into CO and  $H_2$ . This step normally operates between 800-900°C and can be exemplified by the following reaction (PNNL, 2011):

 $CH_4 + H_2O \rightarrow CO + 3H_2$ .

<u>Water gas shift reaction</u>: normally, the resulted gas from the reformer has a small  $H_2/CO$  ratio. The water gas shift step aims to adjust this ratio to the optimal value (usually between 1 and 2) for subsequent use in the Fischer Tropsch process (EBTP, 2016). This step can be described by the reaction:

$$CO + H_2O -> CO_2 + H_2$$

<u>Gas cleaning</u>: The gas cleaning step depends on which type of biomass is employed because the impurities content in the raw gas is influenced by the feedstock. The main substances usually are: alkali compounds, sulphur, nitrogen and chloride. The last three are considered as poisonous for the Fischer Tropsch catalyst. The gas often passes through a washing process to remove sulphur and nitrogen substances such as carbonyl sulphide (COS), hydrogen sulphide ( $H_2S$ ),  $CO_2$ , hydrogen cyanide (HCN) and ammonia ( $NH_3$ ). The washing process can occur via absorption and amine and methanol, among others, can be used as the solvent agent. Other absorption methods can be based on temperature and pressure variation. Finally, the clean synthesis gas is compressed to the required pressure for the Fischer Tropsch conversion.

#### Fischer Tropsch conversion:

Fischer Tropsch (FT) is a thermochemical catalytic process that converts cleaned synthesis gas into alkanes (organic compounds with simple bounds). Depending on the operation conditions of the Fischer Tropsch reactor, the products may differ. For example, temperatures around 300–350°C and pressure between 20–40 bar result in basic petrochemical materials and gasoline while milder conditions, a temperature range of 200–220°C and pressure below 20 bar result in diesel and waxes production (EBTP, 2016).

After the reaction itself, the products need further separation and upgrade. Units normally present in refinery sites, such as reforming and hydrocracking, are possible processes that can be applied to upgrade the raw product into the desired fuels (i.e. diesel, gasoline and kerosene). Table 26 gives an idea of how different the production shares can be in the Fischer Tropsch process when the products pass through upgrading.

# Table 26 Different products yields in the upgrading process. Extracted from SGAB report (2017)

Products (%wt)	FT total output before upgrading	T total output FT liquid output fore upgrading before upgrading	
Methane	5	-	6
LPG	5	-	6
Gasoline	25	28	30
Diesel and kerosene	25	28	58
Heavy oil waxes	40	44	0

Regarding the investment costs for a new gasification and FT unit for biofuels production, the choice of the gasification technology and the upgrading processes influence significantly the total CAPEX of the new installation. Table 27 presents the relevant figures for the costs ranges for this option and the CAPEX figures reflects the equipment costs of a green field project.

# Table 27 Costs regarding production of biofuels via biomass gasification + FT conversion (SGAB, 2017)<sup>49)</sup>

CAPEX	OPEX
[EUR <sub>2015</sub> /GJ products/yr]	[EUR <sub>2015</sub> /GJ products/yr] <sup>50)</sup>
10-17	5-8

49) CAPEX and OPEX are based on a unit with 200 MW output capacity. Original values in EUR/MWh, 3.6 GJ/MWh was used for conversion

50) OPEX values do not consider feedstock costs

#### 4.6 Residual heat usage

In general, refinery processes generate a large amount of residual heat at different temperature levels, which can be utilised for several purposes, such as district heating and electricity generation (Johansson et al., 2012).

In Table 28, the waste heat potential for the Dutch refineries is estimated, based on some considerations. For the waste heat at T> 100°C, the lower limit considered is from Davidse (2012), which considers the residual heat amounts to be approximately 22% of energy consumption in the Dutch refinery sector. Therefore, 22% of the energy consumption at the refinery, as presented in section 2.3, is taken. The upper limit comes from the Johansson (Johansson et al., 2012), which presents that the waste heat potential at T>100°C in refinery processes is approximately 18.8 W/t crude oil capacity, assuming 90% utilisation factor. It should be noted that for Table 28, the energy consumption numbers on which the lower limit are based were from own calculations and may not represent each refinery site exactly. Additionally, the fraction of residual heat per refinery may be different because of different processes and different levels of heat integration on the various sites.

For waste heat below 100°C, a different approach is used. From literature, ranges for the production of heat yield approximately 42–51% of waste heat (Cullen & Allwood, 2010; Forman et al., 2016). It is assumed that residual heat at temperatures below 100°C was not included in the 22% of heat mentioned in the study form Davidse (2012) because this heat has little to no application on site. However, it is expected that there is additional residual heat at T<100°C available, and therefore the estimate from literature is used to assess the entire residual energy potential. Subtracting the amount of heat available at T>100°C, it is expected that the remainder of residual heat is of the form of low temperature residual heat at T<100°C. This corresponds reasonably well with other estimates given in literature about refineries and Dutch refineries (Johansson et al., 2012; Kampman et al., 2010).

Table 28 Waste heat potential in the refinery sector (Johansson et al., 2012;Davidse, 2012; Cullen & Allwood, 2010; Forman et al., 2016)

Heat [PJ/y]	ВР	Esso	Gunvor	Shell	Vitol	Zeeland
T>100 °C	10-11	4-5	2	9-12	1-2	5
T<100 °C	5-12	5-7	3-5	9-15	0	4-7

The waste heat with temperature below 100°C is more difficult to utilise directly. Therefore, it is expected that adding a heat pump to the system might increase the functionality of the waste heat. A heat pump is a thermodynamic device which takes and transfers heat from a heat source to a heat sink using a small amount of energy. A schematic overview of a heat pump is shown in

Figure 29.



Figure 29 Heat pump system (Jouhara, H. et al, 2018)

In short, heat pump systems are suitable to upgrade low temperature waste heat to a higher temperature and quality. The ultimate benefit of heat pump systems in the industry is to generate useful heat that can be directly used on site to reduce the energy intake and improve the overall efficiency of the system. In practice, the waste heat amount available will depend on heat integration on site, and some sites already provide residual heat to third parties, such as the Pernis residual heat initiative by Shell. Currently, heat is supplied that offsets 35,000 tonnes of  $CO_2$  annually in domestic heating. This amounts to 0.6 PJ of natural gas (Port of Rotterdam, 2020). The efficiency of waste heat use is determined by losses in the heat grid and by transport energy (pumping). So, distance (short) and volume (large) are crucial factors when connecting the industry with urban areas.

# 5 Discussion

Due to the European decarbonisation targets (i.e. emission reductions of 90% or more by 2050 vs. 1990), the fossil fuel demand in the transport sector is expected to decrease in the coming decades, which will have an impact on the refinery sector. This makes new investments in the current installations less attractive; however, refineries also provide feedstock for production of base chemicals and fuels for the shipping and aviation sectors. Alternative products for these applications, such biobased and synthetic hydrocarbons, are currently at small scale but this could change over the next decades. A detailed analysis into the alternatives' development is beyond the scope of this report. Due to the importance of their products, the refineries will remain relevant in the following years, emphasising the importance of its decarbonisation assessment for the sector's future.

The decarbonisation options presented in this report for the Dutch refinery sector include the following categories: CCS, alternative energy supply, alternative feedstock, alternative processes, and waste heat usage. The feasibility of these options is heavily dependent on several factors and the main ones are highlighted in this Chapter.

The application of CCS technologies has relevant potential, especially in the Port of Rotterdam where the Porthos initiative is expected to provide in 2024 infrastructure for the transport and storage of captured  $CO_2$  in empty offshore gas fields (Porthos, 2020). In 2019, Porthos signed Joint Development Agreements (JDA) with Air Liquide, Air Products, Esso and Shell (Porthos, 2020). The  $CO_2$  concentration in flue gases from combustion units is determinant for the economic feasibility of this technology, which makes the gases with  $CO_2$ concentration above 10%vol. most suitable for its application. This characteristic indicates that units such as SMR, gasification and FCC present the highest potential for carbon capture projects.

The discussed energy supply alternatives for gas-fired equipment (i.e. electric furnaces and electric boilers) are not commercially available yet, therefore, innovation developments are required before the actual application of these technologies in the refineries. The deployment of hydrogen-based furnaces is very dependent on hydrogen availability, since the hydrogen should come from a low-CO<sub>2</sub> production method, which has not yet been implemented on a large scale. Other determinant factor for the economics of substitution for both electric furnaces and hydrogen is infrastructure. Currently, there is no available distribution network that could meet the demand of hydrogen to be used as energy carrier. For electricity, the current distribution network of renewable electricity should expand in order to allow electric furnaces in large industrial applications.

Electric furnaces in refineries are a novel technology, no large-scale experience is known and high investment costs are expected (Ecofys and Berenschot, 2018). However, the development curve for this technology is becoming steep and, for this reason, it is expected electric furnaces to advance quickly in terms of technical readiness (TNO personal communication, 2018). About electrical boilers, the technology capacity available currently is much lower when compared to the conventional boilers installed in the refineries. Also, the same challenges mentioned about electricity use and infrastructure apply to this technology. It is expected that the refineries sites will reduce the overall steam demand by electrifying shaft equipment (i.e. steam turbines) before investing in electrical boilers. This is an interesting option because the technology is commercially available. However, its application causes direct impacts in the steam balance on site and may affect other industries that share utilities with the refineries.

Biomass utilization in refinery sites is an interesting option because it could potentially allow negative emissions, if combined with carbon capture and storage. However, it still needs to overcome several challenges. Most importantly, the supply chain of sustainable biomass needs to be capable to provide large volumes of feedstock. Furthermore, for co-processing of pyrolysis bio-oil in current FCC units, the bio-oil is limited to 10%wt in the feedstock mix. To allow higher amounts of the bio-oil, upgrading processes are needed, which consume a significant amount of hydrogen. Yet, no large changes in the FCC units are required, making the system adaptation to the bio feed relatively simple. For a bio-oil stand-alone plant, the conventional refinery product fuels can be produced; however, this option is still in lab scale and it would require entirely new installations. Regarding the biofuels production via the Fischer Tropsch process, the biomass gasification and gas cleaning are the limiting steps. The technology needs to be further developed to become economically feasible and flexible to different sources of biomass.

Considering the waste heat from refineries, the sector has considerable potential to offer heat to surroundings areas. However, the challenges lay on building the infrastructure needed for the heat distribution and finding feasible solutions for the utilization of low-level waste heat (T<100°C). Technologies such as heat pumps can upgrade the low temperature waste heat and this could be used again on site, which may reduce the overall heat demand from boilers and CHPs.

Finally, the Dutch refinery sector is complex and several aspects should be taken into account when the decarbonisation of the sector is discussed. Ideally, a combination of technology options in diverse processes units should be applied, considering the specific aspects from each site. Also, external factors such as carbon transport and storage infrastructure, green electricity and hydrogen supply and biomass availability may play a relevant role in the transition of the refinery sector to a lower CO<sub>2</sub> emissions future. Therefore, holistic assessments of possible pathways for the sector are necessary.

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