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DECARBONISATION OPTIONS FOR EXXONMOBIL CHEMICALS ROTTERDAM

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MIDDEN

Manufacturing Industry Decarbonisation Data Exchange Network

Decarbonisation options for ExxonMobil Chemicals Rotterdam
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ExxonMobil provided comments on specific items of this document. PBL and TNO remain responsible for the content.

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Summary

ExxonMobil Chemicals in the Netherlands operates the Rotterdam Aromatics Plant (RAP), Rotterdam Oxo-Alcohol Plant (ROP) and the Rotterdam Plasticizers Plant (RPP). The RAP and RPP are located in Botlek, forming a network of shared utilities and raw materials with the Esso refinery. The main products, CO_2 emissions, thermal energy and electricity use for the RAP, ROP and RPP are summarized in the table below. The direct CO_2 emissions are attributed to production activities such as use of boilers and furnaces, production of heat and electricity and production of hydrogen (on-site and external). Most of the processes other than the ones mentioned previously are based on novel technology that ExxonMobil developed. It is, therefore, not possible to know, for example, the efficiencies of each process. This report uses publicly available literature to estimate such parameters.

Table 1 Overview of the RAP, ROP and RPP production, final energy use and emissions

Products	Production capacity (kilotonnes per year, kt/y)	Elec-tricity use (PJ/y)	Steam use (PJ/y)	Gas use (PJ/y)	Plant name	Direct CO_2 emissions 2017 (kt CO_2/y)
Benzene (partly intermediate)	832	1	10	3	RAP	473
Toluene (intermediate)	301				RAP	
Ortho-Xylene	149				RAP	
Para-Xylene	775				RAP	
Cyclohexane	282				RAP	
Oxo alcohols	340	0.1	1	-	ROP	60
Phthalic Anhydride (intermediate for plasticisers)	70	0.27	-0.4	0.1	RPP	43
Plasticizers	400	0.1	0.4		RPP	
Total	2,951	1.5	11	3.1		576

The on-site decarbonization options include carbon neutral fuels, such as (blue and green) hydrogen for feedstock and heat supply, and carbon capture and storage (CCS) for the Botlek site (RAP + refinery). Blue hydrogen based on refinery and fuel gases would require a steam reformer with pre-combustion CCS and revisions of the gases network and burners. Electrification for heating is also an option, but it would require redesign of furnaces. Both direct electrification and green hydrogen would also require redirection of the fuel gases and residual flows presently used. The other options such as CCS have some roadblocks too, the area required to set up a CCS is large and is therefore an issue at the Botlek site. A bio-based option for production of aromatics (RAP) is explored in this report. Although there is theoretical evidence on bio-based aromatics production, there is no real plant that currently operates at a scale approaching the RAP of ExxonMobil.

Introduction

This report describes the current situation of the production of aromatics, plasticisers, intermediates and oxo-alcohols by ExxonMobil in Rotterdam and the options and conditions for its decarbonisation. The study is part of the MIDDEN project (Manufacturing Industry Decarbonization Data Exchange Network). The MIDDEN project aims to support industry, policy makers, analysts and the energy sector in their common efforts to achieve deep decarbonisation. Mapping decarbonisation options is an ongoing process. The MIDDEN project will update and elaborate further on options in the future, in close connection with the industry.

Scope

In the Netherlands, producers include:

- Exxonmobil Chemical Holland Rotterdam Aromatics Plant (RAP), Botlekweg 4060 3197 KA Botlek, Rotterdam.
- Exxonmobil Chemical Holland Rotterdam Plasticizers Plant (RPP), Welplaatweg 2, 3197 KS Botlek, Rotterdam.
- ExxonMobil Chemical Holland Rotterdam Oxo-alcohol Plant (ROP), Merwedeweg 21, 3198 LH Europoort Rotterdam.

For further reference the term ‘Botlek site’ means the RAP and the adjacent refinery known as Esso Nederland B.V. The adjacent RPP and Air Products facility are regarded as separate sites.

Production processes include

- Production of aromatics
- Production of plasticisers and intermediates
- Production of oxo-alcohols.

Products include:

- Benzene;
- Toluene;
- Ortho-xylene;
- Para-xylene;
- Cyclohexane;
- Oxo-alcohols;
- Phthalic anhydride;
- Plasticisers.

Reading guide

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

1 ExxonMobil in the Netherlands

Exxon started a refinery in Rotterdam in 1960 which produced raw materials for aromatics production such as naphtha. Thereafter the Rotterdam Aromatics Plant (RAP) was set up in 1963. Successive improvements in further years added the Rotterdam Oxo-alcohol Plant (ROP) and the Rotterdam Plasticizers Plant (RPP) in the surrounding area.

This report describes the RAP, RPP and the ROP. These plants are located close (distance ROP to refinery is 15 km) to the Esso refinery, which is described in the MIDDEN report on oil refineries (Oliveira & Schure, 2020). The RAP produces the aromatic hydrocarbons benzene, ortho-xylene and para-xylene. In addition, cyclohexane is produced from benzene. The oxo-alcohol plant is located in Europoort. The RPP comprises the Phthalic Anhydride Plant and the Rotterdam Plasticizer plant, both of which are located in Botlek. The facilities are closely integrated: ortho-xylene is used for phthalic anhydride production. Oxo-alcohols and phthalic anhydride are both raw materials for plasticizers.

1.1 Products, capacities and energy supply

Energy supply

The facility of ExxonMobil at Botlek that includes the Aromatics (RAP) and Plasticizers (RPP) plant is located in the area adjacent to the refinery. The facilities i.e. RAP and RPP meet their energy needs by combustion of fuel gas, which is produced in the refinery, and by utilizing steam from the refinery processes. Combustion of fuel gas provides the heat that is necessary to heat process flows in furnaces and for generating steam in steam boilers. The steam from the refinery processes is used to drive turbines and for heating process flows and products in storage tanks. The site has a combined heat and power (CHP) installation that uses low calorific gas from the refinery flexicoker. The Botlek site, combined with the RPP, is highly heat integrated. The ROP site, which is located in Europoort, has steam boilers and is supplied with raw materials from other European sites.

The table below shows the production capacities for each product, the direct greenhouse gas emissions in the year 2017 for the RAP, ROP and RPP.

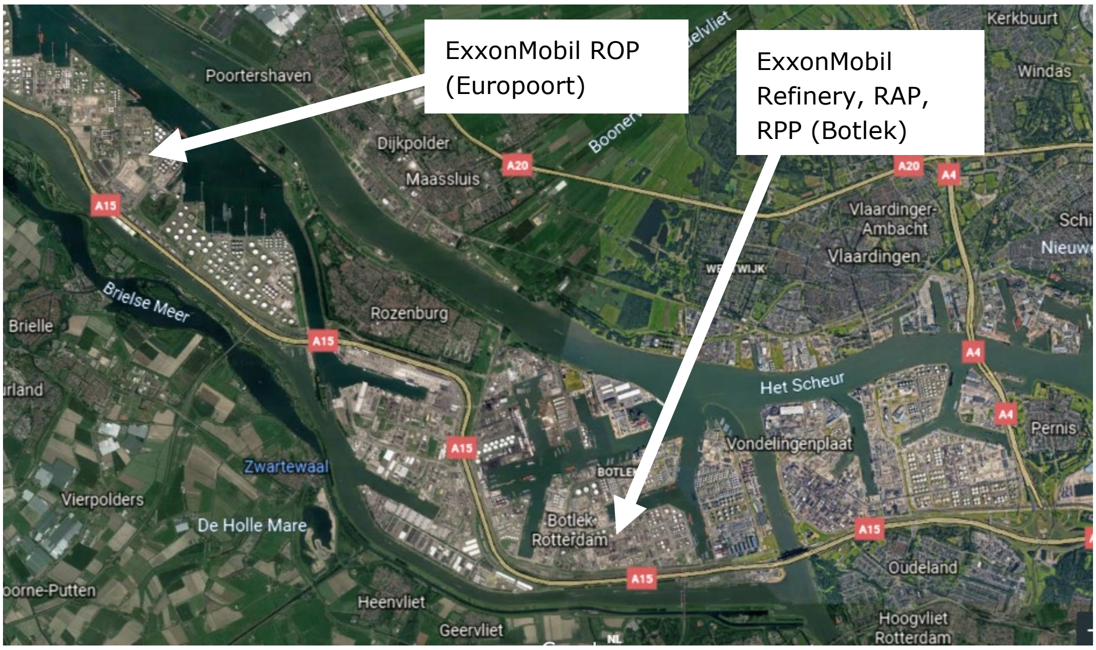
Table 2 Production capacities and direct CO_2 emissions for the RAP, ROP and RPP

Products	Production capacity (kt/year)$^{(1)}$	Plant name	Direct greenhouse gas emissions 2017 (kt CO_2/y)$^{(2)}$
Benzene	832	RAP	473
Toluene$^{(3)}$	301	RAP	
Ortho-Xylene	149	RAP	
Para-Xylene	775	RAP	
Cyclohexane	282	RAP	
Oxo alcohols	340	ROP	60
Phthalic Anhydride	70	RPP	43
Plasticizers	420	RPP	
Total	3,169		576

(1) Source: Permits for RAP, ROP, RPP (ExxonMobil, 2015; ExxonMobil, 2018a; ExxonMobil, 2018b)

(2) Source: Dutch Emissions Authority (NEa, 2018)

(3) The current product range does not contain toluene as a product. This can be produced if desired. The production of benzene and paraxylene then decreases proportionally.



ExxonMobil ROP (Europoort)

ExxonMobil Refinery, RAP, RPP (Botlek)

Figure 1 Location of RAP, ROP and RPP. Source: Google Maps, 30 July 2019

1.2 Greenhouse gas emissions

The refinery and the chemical plants of ExxonMobil participate in the EU Emissions Trading System (ETS). The greenhouse gas emissions over the years 2013-2017 are shown in Table 3 below. Emissions occur at the flare, sulphur recovery plant, steam processing plant, loading operations, and wastewater treatment. This report focusses on CO_2 emissions. Other emissions such as of volatile organic compounds, methane and CO are quite low and therefore will not be described in detail. The table shows that the RAP in the year 2017 produced the highest emissions as compared to ROP and RPP.

Table 3 Greenhouse gas emissions by year in kt/year (NEa)

	2013	2014	2015	2016	2017
ExxonMobil Chemical Holland B.V. (RAP)	426	390	445	389	473
ExxonMobil Chemical Holland B.V. (ROP)	59	53	51	59	60
ExxonMobil Chemical Holland B.V. (RPP)	49	48	32	41	43

1.3 Rotterdam Aromatics Plant (RAP)

The Rotterdam Aromatics Plant (RAP) has been operational from 1963 on the same grounds as the refinery in the Botlek area and is strongly integrated with the refinery. It is one of the largest aromatics manufacturing units in the world. The aromatics plant receives its basic raw materials such as aromatic concentrates from reformers or steam cracked naphtha and hydrogen from the refinery and third-party purchases.

There are three sources of hydrogen for the Botlek facility, such as the Air Products plant connected in 2011, the on-site hydrogen plant and third parties. In the year 2009 the para-xylene production capacity of the RAP was increased by 25%. In addition, the production capacity of benzene in the same plant was increased by 20% (Petrochem, 2007). In 2015, a liquid isoformer unit was installed to increase energy efficiency of paraxylene production (Petrochem, 2015). This so called ParamaX technology suite was used in order to improve environmental performance and decrease in energy consumption per tonne of product by 15%.

1.4 Rotterdam Plasticizers and Intermediates Plant (RPP)

The Phthalic Anhydride Plant and the Rotterdam Plasticizer plant are both located in the Botlek area adjacent to the refinery and closely integrated with it. This plant is the largest producer of plasticizers in Europe (ExxonMobil, 2018b). The plant imports its raw materials directly from the RAP and ROP sites.

The ExxonMobil RPP site in the Botlek area produces plasticizers and is divided into two factory parts. The PAN factory is one part produces phthalic anhydride, the raw material for the plasticiser plant which is the second part.

Oxo-alcohols are supplied by pipeline from the Rotterdam Oxo-alcohol Plant (ROP) in Europoort or from an external tank terminal (ExxonMobil, 2018a). The other additives, such as catalysts, are supplied by trucks. Nitrogen is supplied by third parties via an underground pipeline.

1.5 Rotterdam Oxo-alcohol Plant (ROP)

The ExxonMobil Rotterdam Oxo-alcohol Plant (ROP) is located in Europoort. The ROP came into operation in 1982, after ExxonMobil took this plant over from AKZO and modified it. Before that, it was the AKZO-Zout-Chemie butanol plant. The raw materials for oxo-alcohols are C7 to C10 olefins, which are derived from crude oil (ExxonMobil, 2018a). The oxo-alcohols produced at Europoort (isooctyl alcohol, isononyl alcohol, isodecyl alcohol and undecyl alcohol) are used as raw materials for plasticizer production.

Since investments made in 2016, including for better loading facilities, the raw materials can be supplied by larger ships and the number of sea transport operations has been halved. This has contributed to improvements of the plant's efficiency and environmental performance. The olefins (C7 to C10) are reacted with syngas to form oxo-alcohols. The oxo-alcohols that ExxonMobil produces in the Netherlands are in particular used as raw materials for the plasticiser factory in the Botlek (RPP) and delivered per pipeline (ExxonMobil, 2018a). The remaining part is transported to third parties via pipeline or by ship.

2 Production processes

The three plants (RAP, ROP and RPP) form a complex system comprising of various processes which are described in this chapter. Additionally, a breakdown of the main inputs and outputs and energy consumption of the processes, together with a summary of the CO_2 emissions, is presented in this chapter. This section describes each of the three plants RAP, ROP and RPP and gives an overview of the processes in detail. Each section contains the different elements of the process and their characteristics. The energy calculations in this chapter for all the installations are made based on 24 hours per day operation for a period of one year.

2.1 Processes at the RAP Plant

The aromatics plant produces the aromatic hydrocarbons para-xylene, ortho-xylene and benzene. In addition, cyclohexane is also made from benzene (ExxonMobil, 2015). The entire process is depicted in Figure 1. Table 4 shows a summary of conditions (temperature, pressure and feed) for each process unit (ExxonMobil, 2015). The feed streams for the plant are aromatic concentrates from catalytic reformers (both purchased locally from third parties) and purchased BTX mixes from steam cracked naphtha. The pure, separated aromatics are stored and then shipped. Storage partly takes place in the refinery.

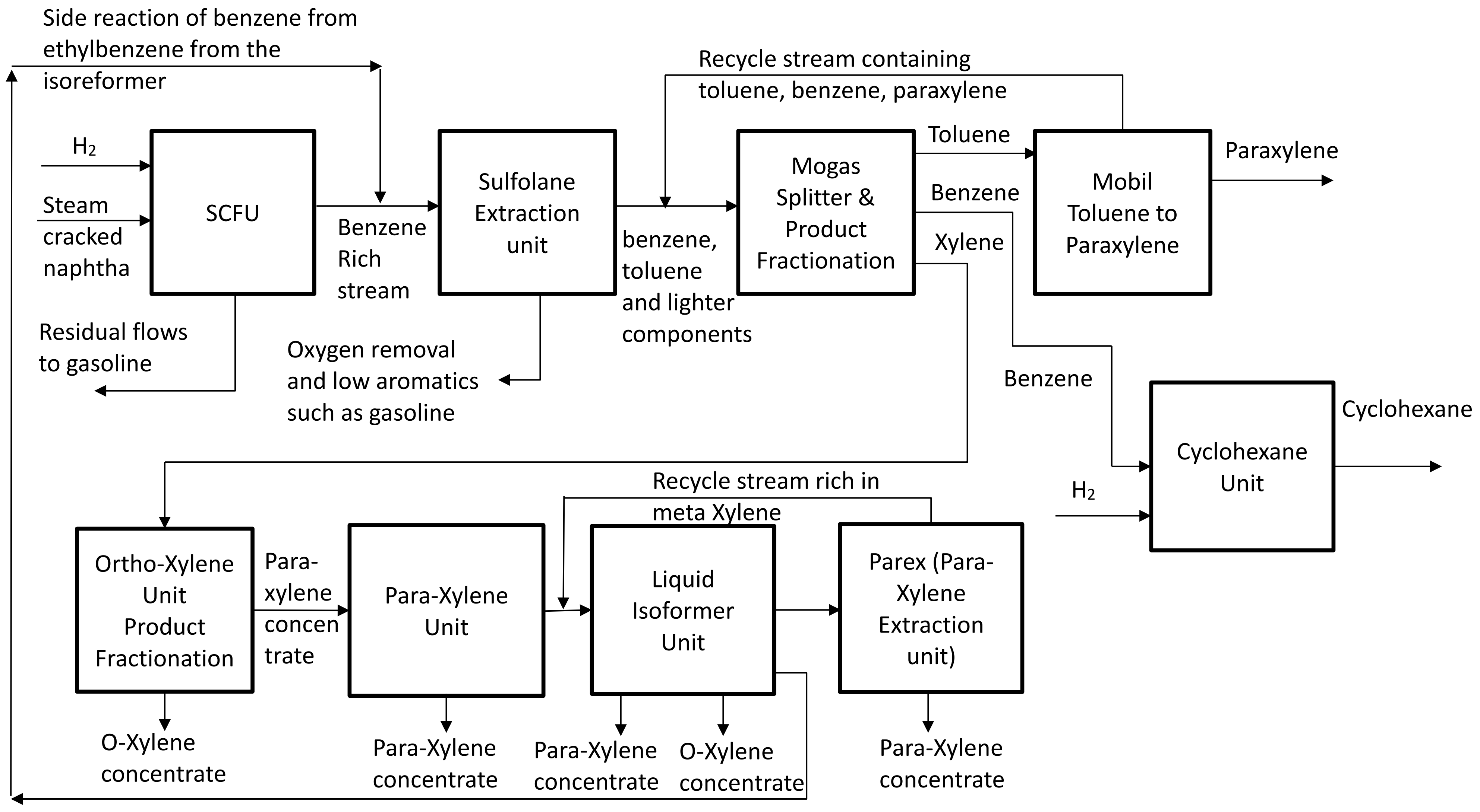


Figure 2 Rotterdam Aromatics Plant process overview (ExxonMobil, 2015)

Table 4 Summary of process units, feeds and process conditions for RAP (ExxonMobil, 2015)

Process unit	Feed	Temperature range	Pressure range
SFHU	SCN, hydrogen	-	-
SEU	Benzene	221-300 °C	2-4 bar
Mogas splitter and fractionation	Benzene, toluene & lighter components	95-108 °C	0.5-0.75 bar
MTPX	Toluene	400-470 °C	20-34 bar
OXU	Mixed xylenes	357 °C	-
PXU	Para-xylene concentrate	343 °C	9.5–16 bar
Liquid Isoformer unit	Naphtha, kerosene, diesel, gasoil	>300 °C	-
Cyclohexane unit	Benzene, Hydrogen	200 °C	40 bar

Capacities

The production capacities for the major raw materials and products are provided in Table 5.

Table 5 Inputs and outputs of the RAP. 'Permit' refers to the permit application (ExxonMobil, 2015)

Input/ Output	Component	Capacity (kt/year)	Comments
Input	Feedstock	1510	Estimate
Input	Hydrogen	pm	
Intermediate/Output	Benzene production	832	Permit
Output	Ortho-xylene production	149	Permit
Output	Para-xylene production	775	Permit
Output	Cyclohexane production	282	Permit
Intermediate	Toluene	301	Permit
Total output	Aromatics	1400	Estimate

SCN Feed Hydrorefiner unit (SCFU)

The Steam Cracked Naphtha (SCN) Feed Hydrofiner unit (SFHU) is where the steam cracked naphtha is converted into benzene by hydrogenation. The stream is fractionated to a benzene concentrate and then sulfur components are removed (Colwell, 2009). The product is fed to the Sulfolane Extraction Unit. The waste products are mixed and sold as a gasoline component.

Sulfolane Extraction Unit (SEU)

In the Sulfolane Extraction Unit (SEU), sulpholane ($C_4H_8SO_2$) is used to extract aromatics selectively as a solvent, using an extractive stripper where the mixture of hydrocarbons is separated based on boiling points (Meindersma & De Haan, 2008). This mixture consists of the benzene-rich stream from the SFHU, an aromatics-rich stream that comes from the refinery and benzene-rich semi-finished products from other refineries. The SEU is equipped with a Feed Deoxygenizer. In this installation the feed is stripped with nitrogen. This removes oxygen from the mixture, because this is an unwanted component in the SEU. The output of this unit is a mix of benzene, toluene and lighter components that is sent to the next unit for fractionation. The low-aromatics residual product is sold as a gasoline component (ExxonMobil, 2015).

Mogas Splitter and Product Fractionation

The output flow of the SEU, which contains benzene, toluene and lighter components, goes to the Mogas Splitter. Here a benzene-rich stream and a toluene-rich stream are produced based on difference in boiling points. The toluene is fed to the MTPX unit. Xylene is fed to the xylenes loop.

Mobil Toluene to Paraxylene unit (MTPX)

In the Mobil Toluene to Para-xylene unit (MTPX), toluene concentrate is converted into benzene. This benzene is then converted via a catalytic process to paraxylene. This is done in a hydrogen-rich environment. The residual flow consisting of benzene, para-xylene and toluene is returned as feed for the Product Fractionation. The primary output of this unit is para-xylene.

The Xylene production loop

The xylene production loop consists of the following units: the ortho-xylene Unit (OXU), the Para-Xylene Unit (PXU) with Refrigeration unit (RFU) the Liquid Isoformer Unit (LIU), the Para-xylene Extraction unit (Parex) and the Isoformer.

The OXU is fed with xylene concentrate streams from tank storage and from the Product Fractionation. In the OXU two products i.e. ortho-xylene and para-xylene are separated by distillation. This para-xylene concentrate is fed to the PXU, where pure para-xylene is obtained by crystallization. This crystallization takes place by strongly cooling the liquid with ethylene from the RFU. The crystals and the liquid are separated by centrifugation (Hongyu Gao, 2019). The residual product is fed to the LIU. The isoformer converts meta-xylene into para-xylene and ortho-xylene and works at high temperatures with gaseous feed in a hydrogen-rich environment. As a side reaction, in the Isoformer ethylbenzene is degraded to benzene (Aransiola, Daramola, & Tunde, 2013). The reaction product of the Isoformer is distilled into a benzene rich concentrate that is fed back to the SEU as a recycle stream (ExxonMobil, 2015).

Cyclohexane unit

Part of the pure benzene produced in the Product Fractionation is sent to the cyclohexane unit and is catalytically converted to cyclohexane with hydrogen. The hydrogen used is produced within the Botlek site (ExxonMobil, 2015). The production of cyclohexane from hydrogenation with benzene and hydrogen is a highly exothermic reaction for which the reactor temperature control is critical (Wenxue Li, 2018).

Utilities for the refinery, RAP and RPP

The RAP, RPP and the refinery are all located in the Botlek and share their utilities. The boilers, the combined heat and power generator (CHP) and connected steam grids are shared by both the RAP, RPP and the refinery. The following sections describe these resources.

Steam generation

Steam from the refinery system is used for process heating and driving turbines. The refinery site has two steam boilers with a total capacity of 350 MW and combined heat and power (CHP) installation of 192 MW thermal input for generation of superheated 40 barg[1] of steam. The output steam is released to lower pressures (1-3 barg[1]) and used for heating. The steam generators of the flexicoker produce superheated steam at 40 and 9 barg[1]. On the site there are more waste heat recovery systems in which low pressure saturated steam (lower than 40 barg[1]) is generated which is used for heating. The steam is injected into various low-pressure steam distribution systems. This distribution system provides steam to the RAP. In addition to steam, the CHP installation also produces electricity that is partly delivered to the 25-kV grid (ExxonMobil, 2015).

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[1] Barg pressure is the pressure, in units of bars, above or below atmospheric pressure. The "g" at the end of the word indicates that the measurement is not absolute pressure, sometimes indicated by bara.

Recent hydrocracker expansion

Since the expansion of the hydrocracker, there is additional energy used in order to produce higher quality products. This additional energy is provided by the fuel gas produced as a result of the expansion. The expansion also allows to reuse as much heat as possible. The design of the new hydrocracker provides for the reuse of more than half of the heat (i.e. 140 MW). Additionally, optimization of the current processes has saved about 30 MW. Potentially about 83 MW low level heat could be used outside the facilities. However currently there are no possibilities for use within the facility (ExxonMobil, 2015).

Fuel gas

Fuel gas that is used for operating the furnaces and the steam boilers comes from the refinery as a residual product. There are two types of fuel gas systems, Low calorific gas (LJG) and High calorific gas (HJG). Since the refinery produces more gas (high calorific) than that is necessary for its own use, the excess gas is also sold to third parties. This is mostly sold to the adjacent Air Products hydrogen production unit as feedstock. The refinery furnaces use a mixture of fuel gas (both LJG and HJG) and a small amount of natural gas.

The RAP emissions according to NEA as described in Table 2 are 473 kilotonnes (kt) (NEa, 2018). This value reflects the part allocated to RAP of the total refinery + RAP emissions, in 2017 amounting to 2540 kt/year. The RAP emissions could not be traced back to separate process steps and utilities. The main source of emissions are furnaces combusting refinery gas, both LJG and HJG. Based on literature values of refineries and aromatics production, fuel and steam use for the RAP is estimated at 13 PJ and electricity use at 1 PJ (Table 6). Another estimation based on the Royal Haskoning report on the hydrocracker expansion gives similar values for RAP energy consumption (Royal HaskoningDHV, 2015) (see Appendix A).

Table 6 RAP final energy use reconstruction from permit (ExxonMobil, 2015) and literature, on annual basis

RAP section	Amount (kt)	Energy (PJ)	Source/Assumptions
Inputs			
BTX, olefins	1510		Estimated
H_2 from refinery/Air products	20		Estimated for cyclohexane
Outputs			
Orthoxylene	149		Exxon permit
Paraxylene	775		Exxon permit
Cyclohexane	282		Exxon permit
Benzene (mostly intermediate)	832		Exxon permit
Toluene (mostly intermediate)	301		Exxon permit
Residuals back to refinery	151		Estimated 10%
CO_2 allocated to RAP	473		NEa, 2018
Energy			
Fuel gas from refinery		3	Estimated (Neelis, Patel, Blok, Haije, & Bach, 2007)
Steam from refinery		10	Estimated (Neelis, Patel, Blok, Haije, & Bach, 2007)
Electricity		1	Estimated (Neelis, Patel, Blok, Haije, & Bach, 2007)

2.2 Processes at the RPP plant

The Rotterdam Plasticizers and Intermediates (RPP) plant produces plasticizers. The entire process is depicted in Figure 3. Table 7 shows the summary of conditions (temperature, pressure and feed) for each process unit of the RPP plant.

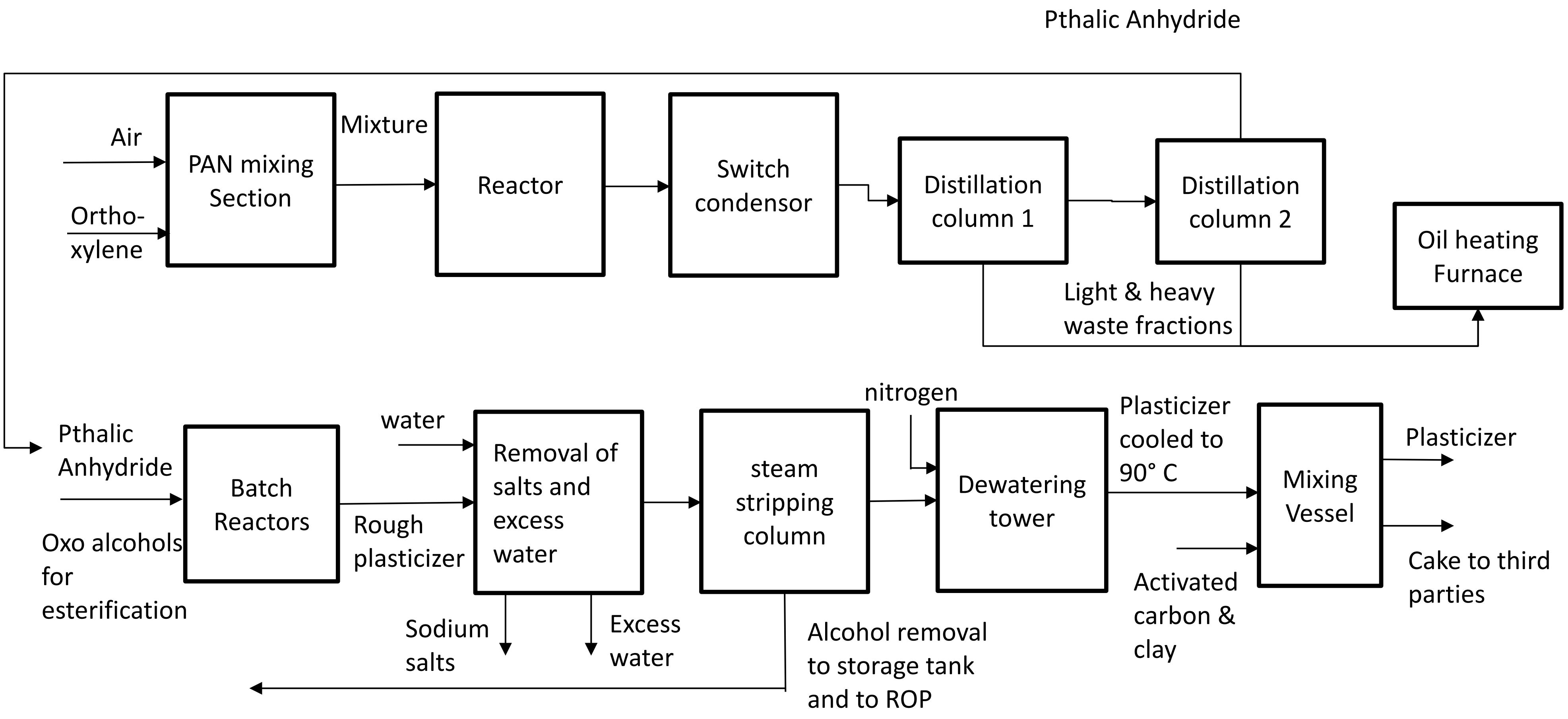


Figure 3 Rotterdam Plasticisers Plant process overview (ExxonMobil, 2015; ExxonMobil, 2018b)

Table 7 Summary of conditions for processes at the RPP plant (ExxonMobil, 2018b)

Process unit	Feed	Temperature range	Pressure range
Batch reaction	Phthalic anhydride, Alcohols	220-230 °C	1-2 bar
Finishing section	Rough plasticizer, water		
Mixing unit	Activated carbon and clay	90 °C	-
PAN section	Ortho-Xylene, compressed Air	190 °C	0.5 bar
PAN section reactor	Mixture of Ortho-Xylene and Para-Xylene	400-460 °C	-

Capacity of the RPP plant

The most important raw materials for the factories in the RPP plant are ortho-xylene, phthalic anhydride and oxo-alcohols. The maximum ortho-xylene feed to the PAN section is 7.6 tonnes per hour. The maximum supply of phthalic anhydride to the RPP amounts to 15 tonnes per hour. The maximum supply of oxo-alcohols to the RPP is 35 tonnes per hour (ExxonMobil, 2018b).

The production capacity of the current PAN plant is around 70,000 tonnes of phthalic anhydride per year. The capacity of the current RPP factory is around 420,000 tonnes of plasticiser per year. The estimated maximum capacities of inputs and outputs are shown in Table 8.

Table 8 Input and output capacities of the RPP plant on annual basis. 'Permit' refers to the permit application (ExxonMobil, 2018b)

	Amount (kt)	Source
PAN section		
Inputs		
Ortho xylene	66	permit
Oxygen (from air)		
Outputs		
Phthalic anhydride	70	permit
Maleic anhydride	minor	
Plasticiser section		
Input		
Phthalic anhydride	70	permit
Oxo alcohols	306	permit
Output		
Plasticisers	420	permit

Table 8 assumes 80% conversion rate for the reaction in RPP. It also shows the inputs and outputs utilised by the RPP.

Phthalic Anhydride (PAN) section

Phthalic anhydride is produced in the Phthalic Anhydride (PAN) plant by the oxidation of ortho-xylene with oxygen. Ortho-xylene is supplied directly with a pipeline from the adjacent ExxonMobil RAP plant (ExxonMobil, 2018b).

The air is heated to a temperature of about 190 °C and pressurized with a compressor to about 0.5 barg and mixed with ortho-xylene by means of misting. The mixture then flows through a set of thousands of pipes filled with a catalyst on a ceramic support. An exothermic reaction takes place in the reactor wherein phthalic anhydride is formed (Akbari & Alavi, 2016).

The temperature in the reactor rises locally to approximately 400-460 °C. This is called the hotspot temperature. Since the reaction mixture is explosive, measures have been taken to prevent ignition. The gaseous phthalic anhydride is passed through a first cooling-and-condensing step to a switch condenser system. In the switch condenser system, the gas is led along pipes, through which cold thermal oil flows. The phthalic anhydride in the gas desublimates (ripens off) as crystals on the pipes (ExxonMobil, 2018b). The thermal oil then flows through the pipes switches to warm oil, causing the crystals to melt. The liquid phthalic anhydride is collected and pumped to an intermediate storage tank as raw PAN. The waste gases consisting of light by-products from the switch condensors and from the distillation jets are burned in an incinerator with a thermal capacity of 3 MW. The resulting unwanted light and heavier fractions are separated into two distillation towers (ExxonMobil, 2018b).

The separated unwanted light and heavy fractions from distillation are fed as liquids to a furnace of 3.3 MW thermal capacity. This furnace heats a hot oil stream used in the process for heating various installation components. The pure phthalic anhydride is taken from the top of the second distillation tower via an intermediate storage pumped to the product tank. From there, the product is pumped to the plasticiser plant (RPP).

The reaction from ortho-xylene with oxygen to phtalic anhydride may have a selectivity in the range of 70%. Further oxidation takes place to maleic anhydride, which is an undesired by-product, or other by-products. These undesired reactions deliver CO_2 as a process emission, representing around 90% of the 43 kt RPP emissions.

Plasticiser section, batch reaction

Plasticizers are formed by esterification (a reaction whereby esters are formed) of C9-13 alcohols with phthalic anhydride. The use of different oxo-alcohols (such as isooctyl alcohol, isononyl alcohol, isodecyl alcohol and undecyl alcohol) leads to the production of various plasticisers. The reaction takes place in batch processes in three parallel reactors, which are operated independently of each other (ExxonMobil, 2018b).

After the raw materials (oxo-alcohol and phthalic anhydride) and a catalyst have been introduced into the reactor, the reactor contents are heated with an internal steam coil. Water that is formed in the reaction is drained by means of a condenser and an alcohol-water separator. During the reaction, the pressure in the reactor varies from 100 to 2000 mbarg. From the reactor vessel the raw plasticizer goes to the finishing section which has a continuous process (ExxonMobil, 2018b).

Plasticiser section, finishing section

The first step in the finishing section is the treatment of the rough plasticiser with water and sodium carbonate (soda). The water ensures the removal of the catalyst. The sodium carbonate reacts with the remaining undesired monoesters (ExxonMobil, 2018b). After the excess water has been removed in a flash vessel (flash drum), the plasticizer is moved to a mixing vessel with perlite filtration material. Catalysts and sodium salts are emitted as a by-product (ECPI, 2015). The filtered stream, consisting of the plasticiser and alcohol, is passed through a steam stripping column. The remaining alcohol is removed from the plasticizer by means of steam and recovered. The recovered alcohol is stored in tanks and reused.

The plasticiser is pumped from the stripper to the dewatering tower. Here the plasticiser is dewatered with nitrogen. After dewatering, the plasticiser is cooled to approximately 90 °C and transferred to a second mixing vessel.

In this mixing vessel, the plasticizer is stirred with activated carbon and clay to remove impurities and improve the electrical properties of the plasticiser. Finally, the mixture of carbon, clay and plasticizers is passed through a set of filters, separating the carbon and clay from the plasticisers. The plasticizer is stored in product tanks. Ultimately, the product is delivered to third parties by trucks or via a pipeline (ExxonMobil, 2018b).

Energy
In the PAN section 40 barg steam is produced with heat from the PAN reaction which is fed in the PAN steam system. This system is connected to the refinery steam system for exchanging surplusses. The RPP used residual liquids and natural gas for the hot oil furnace. Additional to the waste gases, for starting up the incinerator also natural gas is used (ExxonMobil, 2018b). The table 8 shows the energy consumption and the CO_2-emission per year. The CO_2 emissions of the PAN furnace were estimated considering the energy demand shown previously, combined with the emission factor for natural gas of 56.6 kg CO_2/GJ (RVO, 2018). The total installed electric motor capacity is 8 MW (ExxonMobil, 2018b). As shown from the table some further assumptions are made in order to calculate the CO_2 emissions and energy used by the RPP.

Table 9 RPP Utilities and CO_2 emissions on annual basis

Energy	Amount (kt)	Energy (PJ)	Source/Assumptions
PAN section			
Steam export		-0.4	(Neelis, Patel, Blok, Haije, & Bach, 2007)
Electricity use		0.27	(Neelis, Patel, Blok, Haije, & Bach, 2007)
Hot oil furnace/ incinerator		0.1	Natural gas (56.6 kg CO_2/GJ), 10% of RPP NEa emissions
CO_2 process	39		Calculated at 82% conversion rate
CO_2 combustion	4		Based on NEa
Total CO_2	43		(NEa, 2018)
Plasticizers section			
Steam		0.4	LP steam is assumed
Electricity		0.1	Assumption

2.3 Processes at the ROP plant

Oxo-alcohols are produced by reacting C_7 to C_{10} olefins with synthesis gas, a mixture of hydrogen and carbon monoxide. Further purification and separation of alcohol, light and heavy components takes place in distillation columns, hydrogenation units and crackers. Syngas and H_2 are supplied from external sources. The production of syngas and H_2 is not separately described here. Table 10 shows a summary of conditions (temperature, pressure and feed) for each process unit.

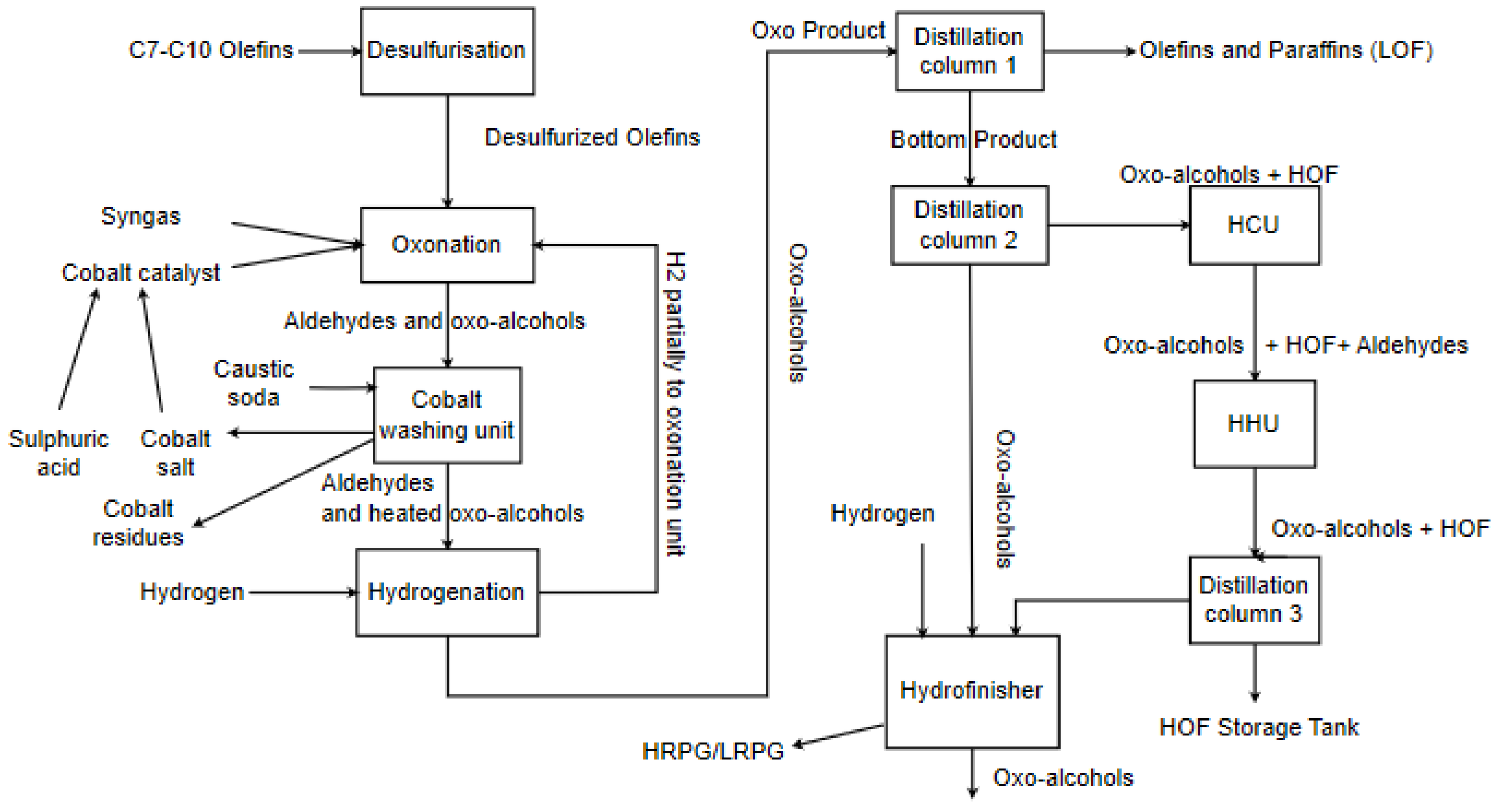


Figure 4 ROP process overview (ExxonMobil, 2018a)

Table 10 Summary of conditions for processes at the ROP plant (ExxonMobil, 2018a)

Process unit	Feed	Temperature range	Pressure range
Olefin desulfurization	Olefins C7-C10, catalyst	150-200 °C	-
Oxonation	Desulfurized olefins	221-300 °C	290 bar
Cobalt washing unit	Aldehydes and oxo-alcohols, cobalt	-	-
Cobalt creation unit	Cobalt oxide	-	-
Hydrogenation unit	Oxo-Products	160-320°C	-
Distillation unit	Oxo-alcohols	-	-
Hydrofinishing	Oxo-alcohols	>300 °C	-
HOF cracking (HCU)	Oxo alcohols, HOF (heavy by-products)	300-350 °C	-
HOF hydrogenation (HHU)	Aldehydes, HOF (heavy by-products) and oxo-alcohols	230-245 ° C	30-60 bar

Capacity

The input and output capacities for the ROP are shown in Table 11.

Table 11 ROP products and throughputs on annual basis (ExxonMobil, 2018a)

	Amount (kt)	Source/Assumptions
Inputs		
Olefins C7-C10	292	Estimated at 90% conversion rate
Syngas	91	Estimated at 90% conversion rate
Outputs		
Oxo alcohols	345	Permit (approximate capacity)
Residuals	38	Estimated based on 90% conversion rate

Olefin desulfurization

Olefin is pumped from storage tanks to the desulphurization reactors. The sulfur is adsorbed on a catalyst in the reactors at a temperature between 150 and 200 °C (ExxonMobil, 2018a). After cooling and filtering the catalyst dust, the desulfurized olefin goes to the Oxonation unit (OXO).

Oxonation (OXO)

In the OXO unit, olefins are converted to aldehydes and oxo-alcohols. The unit has two parallel lines with three pumps each, four reactors placed in series, a cobalt separator and a high-pressure cooler and separator. The reactors are equipped with a water jacket and heat exchanger which controls the temperature of each reactor. The closed water system dissipates the heat with an air cooler. Olefins from the desulfurization unit and return flows from the cobalt washing unit are compressed to about 290 barg after which the active cobalt catalyst and synthesis gas are added. This is fed to the reactors where water is also injected to prevent the formation of by-products. The output flow includes unreacted olefins and paraffins (light oxo fractions (LOF), aldehydes, alcohols, formate esters and heavy by-products (heavy oxo fractions (HOF)) (ExxonMobil, 2018a). The reaction heat is dissipated through a closed water system. The cobalt catalyst is deactivated with caustic soda and converted into a water soluble salt to be separated.

Cobalt Washing Unit

In the cobalt washing unit, the aldehydes, oxo-alcohols mixture is separated by washing the cobalt catalyst. The oxo product is thus stripped of surplus synthesis gas (so-called High-Pressure Residue Gas (HPRG)) which is fired in the boilers. In the aqueous phase, the dissolved catalyst is separated in the form of the deactivated cobalt salt. Most of the soluble deactivated cobalt salt is converted to active cobalt catalyst in a gaseous form using sulfuric acid. The remaining aqueous phase is washed with olefins to get rid of the last active parts of the catalyst and then treated with caustic soda to precipitate residual inactive cobalt catalyst as insoluble cobalt salt in a settling tank. After filtration and neutralization, the virtually cobalt-free flow of water is fed to the water treatment plant (ExxonMobil, 2018a).

Cobalt creation unit

Cobalt recovery has been maximized in the process. To compensate the small amount of cobalt lost, cobalt oxide (Co_3O_4) is added to the mixture. This mixture is brought in contact with oxo-alcohols in batches. This suspension is pressurized by membrane pumps. After addition of synthesis gas in the preforming reactors it is converted to the active catalyst.

Hydrogenation

In the hydrogenation unit, aldehydes are converted into alcohols with hydrogen. This unit consists of four parallel lines of three reactors each. Each reactor is equipped with a water jacket with heat exchanger that controls the temperature of each reactor. The temperature of the water is regulated by either adding cold water or steam (Biradar, Dongare, & Umbarkar, 2009). The water is boiled by keeping it under pressure with nitrogen. The recycled water is cooled by air coolers. The temperature in the hydrogenation unit varies between 160 and 320 °C. The oxo product is first heated as feed to the hydrogenation unit. The feed first passes through a pumice filter to remove contaminants (ExxonMobil, 2018a). The next step is to add hydrogen. The product is cooled by exchanging heat with the feed and by cooling with cooling water. The gas is then separated from the liquid. The gas is partially returned to the oxonation unit and the remainder is discharged to the HPRG network. Finally, the water is separated from the product.

Distillation unit

The oxo product from the hydrogenation unit is distilled to separate alcohols from the by-products. The unit consists of three vacuum distillation towers. The feed for this unit comes from tankage or directly from the hydrogenation unit. It is first preheated via heat exchange with the top product of the second distillation tower. Distillation tower 1 separates the olefins and paraffins (LOF) from the crude alcohol. The LOF top product is then condensed and pumped to tankage after separation of water. The water is extracted from the distillation unit and stored in a methanol-containing water tank. The bottom product is pumped to distillation tower 2 which separates oxo-alcohols from heavy by-products (HOF). The top product oxo-alcohol is condensed by heat exchange and cooled further with cooling water. The oxo-alcohols are then pumped to the hydro-finishing unit. Distillation tower 3 distils the residual product stream from the HHU (HHU-HOF hydrogenation. The top product, consisting of oxo alcohols and aldehydes, after condensation, is sent back to the feed for the distillation tower 1) (ExxonMobil, 2018a).

Hydro-finishing

In this unit, the remaining aldehydes in the oxo-alcohol product are hydrogenated to alcohol. From the distillation unit, the product is pumped to the hydrogenation unit. The heated stream is then passed in series in the two reactors, where aldehydes are converted to alcohol with a catalyst. The reaction product is water cooled and the unused hydrogen gas is separated from the liquid. This gas is referred to as high pressure residual gas (HPRG) or low pressure residual gas (LPRG) and used in steam boilers (ExxonMobil, 2018a).

HOF cracking Unit (HCU)

In addition to oxo-alcohols, the bottom product of distillation tower 2 also contains heavy by-products. This bottom product is pumped to a furnace that is fired at the desired reaction temperature of 300-350 °C. Due to the cracking and hydrolysis reactions, part of the heavy by-products is converted back to oxo-alcohols and aldehydes. This is done in a fixed-bed reactor using steam on a catalyst. Methanol containing water is sprayed into the furnace of the steam boiler to reduce the NO_x emissions. After the cracking reaction, the product is separated from the water. This is largely recycled to the reactor and methanol-containing water is partially discharged into a vessel. Light gases are transported to the LPRG grid for use as fuel for the combustion plants on the site. The bottom drain is pumped to the HOF hydrogenation unit. (ExxonMobil, 2018a).

HOF hydrogenation (HHU)

The bottom drains of the HCU, consisting of HOF, oxo-alcohols and aldehydes, is added to the HOF hydrogenation unit at a temperature of 230-245 °C and a pressure of 30-60 barg using a catalyst. The unit consists of two reactors placed in series. The feed is heated by high-pressure steam. The product is cooled using air coolers. The unused hydrogen is transported to the LPRG network for use as fuel (ExxonMobil, 2018a). The product is then passed to the distillation tower 3 where the oxo-alcohol mix flow is separated.

Energy

The energy used in the ROP consists of natural gas for the steam boilers and electricity. Gas use was estimated with the emission factor for natural gas of 56.6 kg CO_2/GJ (RVO, 2018) combined with NEA emission data. Furnace and process emissions op the ROP are assumed to be of minor importance.

Table 12 ROP Utilities and CO_2 emissions (ExxonMobil, 2018a)

Oxo alcohols	Amount (kt)	Energy (PJ)	Source/Assumptions
Energy			
Net steam use		1.0	Based on 90% boiler efficiency
Electricity use		0.1	(Neelis, Patel, Blok, Haije, & Bach, 2007)
Natural gas for steam		1.1	Based on NEa (2018).
CO_2 combustion	60		
Total CO_2 emission	60		(NEa, 2018)

3 Products and intermediate use

This section will be divided into three subsections, for RAP, ROP and RPP. This will give an overall idea of the products produced along with price indications for the products. Table 13 summarises the products of the RAP and gives an overview of the applications along with the market value in the year 2017-2018.

3.1 RAP products

Table 13 Summary of product price indications and applications

Product	Market Value EUR/tonne	Industrial Applications	Other Applications	Source
Benzene	550-800	Plastics, resins, synthetic fibres, lubricants, dyes, pesticides and gasoline	Glues, adhesives, cleaning products, paint	(Yarns and fibers news, 2018)
Toluene	620-689	Paints, rubber, Plastic, lacquers, glues and adhesives	Nail polish remover, resins, hardeners and lacquers	(ICIS, ICIS Toluene prices, 2017)
Ortho-xylene	600-1,100	Mainly Phthalic anhydride	Coatings and Plastic	
Para-xylene	600-1,100	Terephthalic acid (TPA), dimethyl-terephthalate (DMT)	Polyester fibres, polyethylene terephthalate (PET)/ PET bottles	(ICIS, ICIS Chemical commodities, 2020)
Cyclohexane	800-1,500	Manufacture of cyclohexanone and nitro cyclohexanone, used as a solvent for paints, resins, varnish	Production of nylon6 and nylon6.6	(ICIS, ICIS Chemical commodities prices, 2020a)

3.2 ROP products and PAN

Table 14 gives an overview of the products and their costs and applications. The majority of the oxo-alcohols and phthalic anhydride are used as intermediate products for the production of plasticizers.

Table 14 ROP/RPP summary of product prices and applications (ICIS, ICIS Oxo-alcohols, 2018)

Product	Market Value EUR/tonne	Industrial Applications	Other Applications
Oxo alcohols		Production of plasticizer, acrylates, acetate, resins, solvents, glycol ethers, lubes and blending into gasoline	Solvent and feedstock in manufacturing of printing inks, amino resin, and nitro-cellulose lacquers.
Isooctyl alcohol	922		
Isononyl alcohol	1,600		
Isodecyl alcohol	1,300-1,800		
Undecyl alcohol	1,600		
Phthalic Anhydride	855-900	Preparation of the anthroquinone dye quinizarin, production of plasticizers such as Vestinol 9 DINP (diisononyl Phthalate)	PVC (Vinyl) products, Wire & Cable applications, coated fabrics, roofing membranes and swimming pool liners

3.3 RPP products

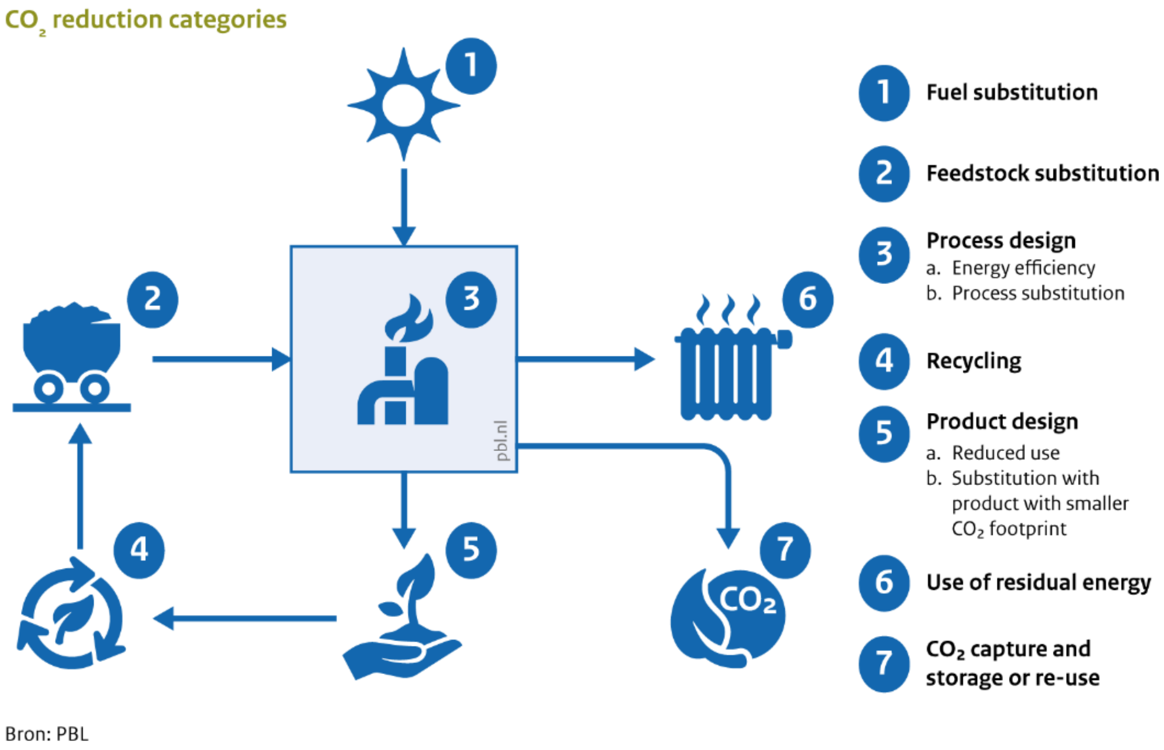
Over 90% of all plasticisers produced in Europe are used in PVC applications (European Plasticizers Information Centre, 2018). The plasticizers that are produced in ExxonMobil are listed in the Table 15 below. Plasticizers are used to improve the plasticity or decrease the viscosity of a material. The percentage of plasticizers in PVC ranges from 18-40 % (European Plasticizers Information Centre, 2018). Therefore, the applications of the different plasticizers are based on the properties they add to the PVC end use products. For example, in applications where high stress environments are present, and the PVC must have good resistance to degradation at high temperatures the DIDP plasticizer will be used.

Table 15 ROP/RPP summary of product prices and applications (ICIS, ICIS Oxo-alcohols, 2018)

Product	Market Value (EUR/tonne)	Applications
Plasticizers	500-900	
Adipate plasticizers		Low-temperature applications, for resistance to UV light and for food contact applications
DINP plasticizer		Plastisol coating, spraying and dipping
DTDP plasticizer		Highest-molecular-weight phthalate plasticizer, automotive cable applications, electrical wire insulation
MB10 plasticizer		Fast-fusing capability, improving PVC processability
DIDP plasticizer		Flexible PVC products that require resistance to degradation due to high temperatures (such as wire and cable), roofing membranes and tarpaulins
DIUP plasticizer		PVC products that require a low contribution to fogging for the automotive industry
Linear plasticizers		Greater low-temperature flexibility, flexible PVC products
Trimellitate plasticizers		Automotive interiors, wire and cable applications, electrical cable insulation and sheathing

4 Options for decarbonisation

Figure 5 shows the different options for decarbonisation as described by PBL. They are split into 7 categories. The focus of this section will be on fuel and feedstock substitution, recycling, the use of residual energy and CO_2 capture and storage. Table 16 summarises the options while considering all the current options and potential options for decarbonisation.



CO_2 reduction categories

Bron: PBL

Figure 5 Decarbonisation options by categories

Table 16 Overview of the decarbonisation options based on the categories in Figure 5

Technology	Relevant to process	Comments
Carbon capture and storage Botlek site process flows and post combustion	Applicable for hydrogen plants, crackers, furnaces, boilers, CHP etc.	For the Botlek site, this would be an integrated approach including the refinery. See Oliveira & Schure, 2020.
Carbon capture and storage ROP post combustion	Applies to steam boilers	Relatively small emission.
Electrification of heat supply	Heat supply for RAP and RPP. Electric boiler for ROP	Steam supply for RAP and RPP is integrated with the refinery. Electrification is relatively unattractive for the Botlek site because currently used refinery gas and fuel gas must be redirected.
Blue hydrogen as fuel for heat supply	Heat supply for RAP and RPP. Hydrogen boiler for ROP	Steam supply for RAP and RPP is integrated with the refinery. Pre combustion capture could be centralised and the fuel gas network could be used for hydrogen. For ROP blue hydrogen could replace natural gas in current boilers.
Green hydrogen as fuel for heat supply	Heat supply for RAP and RPP. Hydrogen boiler for ROP	Steam supply for RAP and RPP is integrated with the refinery. Green hydrogen is relatively unattractive for the Botlek site because currently used refinery gas and fuel gas must be redirected. For ROP this could replace natural gas in current boilers.
Blue hydrogen as feedstock for processes	Hydrogen production	Part of the hydrogen is imported from Air Products. Currently the hydrogen is produced from refinery gases. Air Products could apply CCS.
Green hydrogen as feedstock for processes	Hydrogen production	Part of the hydrogen is imported from Air Products. Currently the hydrogen is produced from refinery gases, these would have to be redirected to other uses.
Bio aromatics feedstock and process	Separate manufacture of BTX input for RAP using a bio based raw material	Since the RAP is fully integrated with the refinery in terms of using refinery feedstocks the bio-aromatics route cannot be directly integrated.
Use of Botlek site waste heat	Low temperature uses in or outside the site	ExxonMobil is studying on further options.

4.1 Carbon Capture and Storage

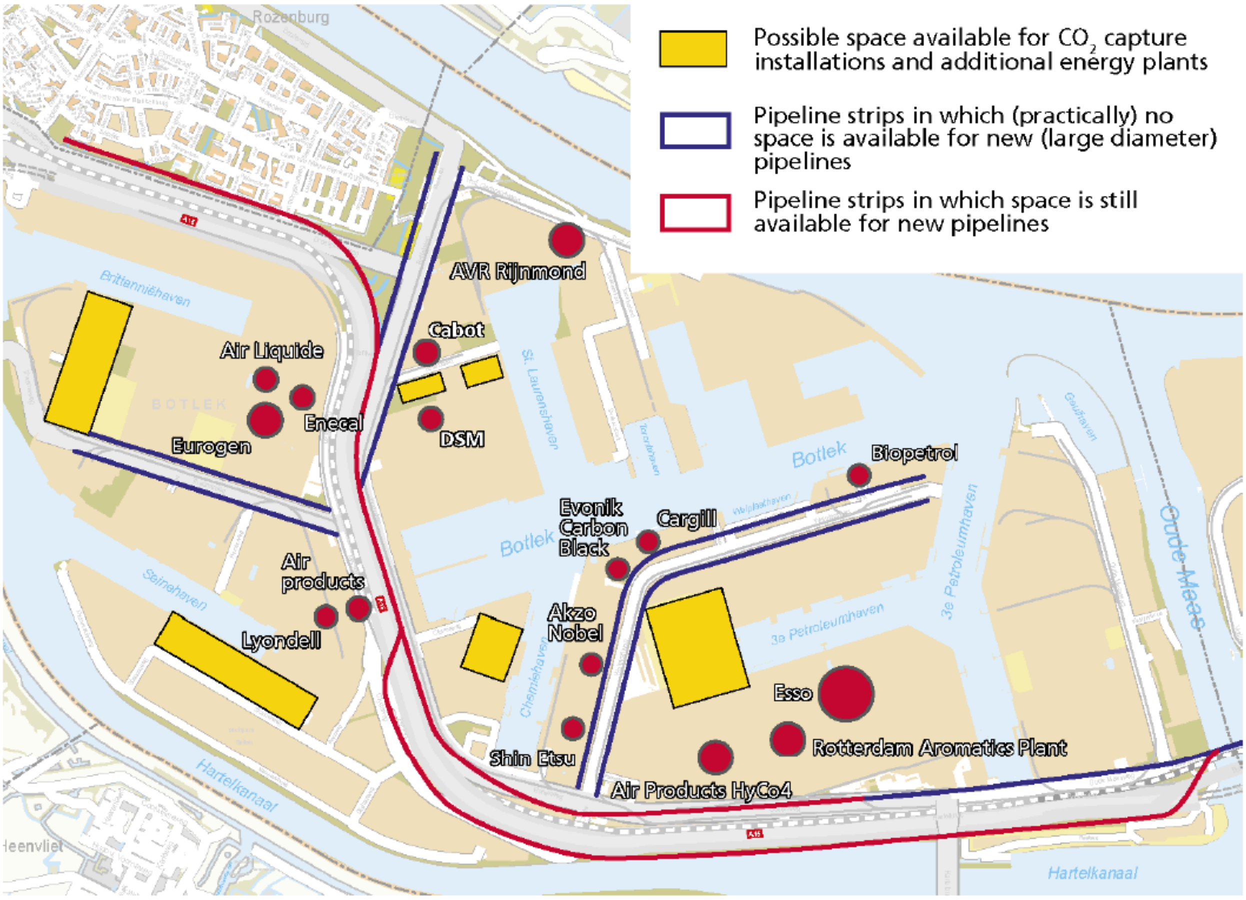


Figure 6 Information regarding pipelines strips is based on Pipeline (Berghout, 2015)

The figure from a 2015 study illustrates the Botlek area with industrial plants emitting CO_2 (red circles). The Esso refinery, RAP and RPP are at the bottom right hand side. The size of the circles reflects the annual amount of CO_2 emissions. The yellow spots are the spaces available for implementing CCS installations in the area. ExxonMobil disagrees with the spatial possibilities illustrated.

Carbon capture and storage (CCS) is a technology that can capture up to 90% of the CO_2 emissions produced from various sources such as burning of fossil fuels. A set of possible CO_2 capture infrastructure configurations was identified based on literature. Three main CO_2 capture routes were selected:

- pre-combustion capture, which is based on the conversion of gases into hydrogen and CO_2 in a steam reformer (SR).
- post-combustion capture based on chemical absorption, for example using an aqueous solvent with a mass fraction of 30% mono-ethanolamine (MEA),
- post combustion combined with oxy-fuel combustion, i.e. fossil fuel combustion with cryogenically produced oxygen.

Table 17 summarises all the three configurations i.e. pre-combustion, post-combustion and oxy-fuel combustion with respect to the RAP, ROP and RPP.

Table 17 Summary of CCS systems and their implications in RAP and RPP, adapted from the MIDDEN report on decarbonisation options for the refineries (Oliveira & Schure, 2020)

Capture technology	Possible applications in the RAP, ROP & RPP	Key points	Comments
Pre-combustion	Any system that can burn H_2 or that allows for burner modification	• Capture equipment does not need to be located close to the firing systems • If the fuel gas network is integrated which it is in case of RAP,ROP, the pre-combustion capture could be centralized and the network could be used to transport H_2 instead of fuel gas • Modification of existent system with burners to allow H_2 firing	All the gases will have to be collected from the refinery, ROP and sent to the steam methane reformer, to produce hydrogen. This hydrogen will then be sent back to the furnace.
Post- combustion	Any combustion-based system	• Since the RAP, and ROP have combustion systems post-combustion can be applied • Each stack would need a dedicated capture equipment to accommodate high flow volumes and connections to a CO_2 grid	Might be unattractive for systems with low CO_2 concentration (below 10% vol.)
Oxy-fuel combustion	Systems that can be sealed to air ingress and that allow operation with pure oxygen such as boilers and fired heaters	• Requires oxygen, which also needs to be produced by an energy-intensive process on- or off-site • Smaller volume equipment when compared to the other capture option	The oxy-fuel combustion will need equipment to separate water from the CO_2.

Results of the comparative study using techno-economic characteristics of all three configurations give a clear indication as to which configurations can be used for the RAP and ROP. In case of CCS, the smaller the utility is, the higher will be the cost of setting up a CCS and therefore RPP is left out of this analysis. (Berghout, 2015, pp. 45-46). Table 18 shows costs and CO_2 reduction ranges for a refinery which is similar to ExxonMobil. Ranges include different technological configurations both long term and short term. Avoided costs only include capture, not transport and storage. The data are not representative for separate boilers or furnaces at RAP, ROP and RPP.

Table 18 Economics of CCS for different technologies for the refinery as a whole (Berghout, 2015)

Capture technology	% CO_2 avoided, different configurations	Annual total costs (capex, opex) M€2010/y	Annual Total costs (capex, opex, energy) M€2010/y	Total costs per ton of CO_2 avoided, €2010
Pre-combustion	82-96%	80-90	160-180	84-90
Post combustion	81-85%	50-60	130-140	69-80
Oxy-fuel combustion	70-86%	40-80	50-110	31-62

A Sintef study (Sintef, 2017) reports CO_2 post-combustion capture costs for oil refinery systems. The values may differ depending on the CO_2 concentration, resulting in an investment (CAPEX) in the range of 31–45 EUR 2017/t CO_2 captured. The OPEX amounts to 14-19 EUR 2017/t CO_2 captured, excluding energy costs (Oliveira & Schure, 2020).

4.2 Options for hydrogen production

In the case of the existing hydrogen plant, two cases that can be considered for post-combustion, capturing HP (High pressure) process gas and a combination of process gas and furnace combustion gas. In the case of only process gas being captured the annualised total costs of CAPEX, OPEX and energy are 60 M€$_{2010}$/year[2], with 54% of the emissions avoided resulting in avoidance costs of 67 €$_{2010}$/ton[3]. In case of capturing both process and furnace gas, the annualised total costs are 120 M€$_{2010}$/year[2], with 84% of emissions avoided, resulting in avoidance costs of 87 €$_{2010}$/ton[3] (Berghout, 2015, pp. 49-51).

In case of replacement of the H_2 plant, Table 19 summarises the decarbonisation options investigated in the MIDDEN report on refineries (Oliveira & Schure, 2020).

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[2] M€$_{2010}$/year – The value of Million Euros in the year 2010.

Table 19 Summary for H_2 production (Oliveira & Schure, 2020)

Option	Description	Investment costs	Energy demand (GJ/t H_2)	Comments
Blue hydrogen production	CO_2 capture and storage either from the syngas, tail gas or flue gas of a SMR process	CAPEX – 90–145 EUR/t CO_2 captured OPEX – 10–15 EUR/t CO_2 captured	2.1 – 4.5 (electricity)	CAPEX value includes capital investments for CO_2 capture plant and CO_2 compression plant. Monetary value updated in 2017 EUROS. OPEX value includes labour and maintenance costs. Monetary value updated in 2014 EUROS.
Hydrogen via electrolysis	Hydrogen production via electrolysis	CAPEX – 3193 EUR/t H_2 OPEX – 1320 EUR/t H2	166.2 (electricity)	CAPEX includes hydrogen production plant, cell stack replacement, land area and installation & engineering costs. Monetary value updated in 2017EUROS OPEX includes maintenance and H_2 production grid connection costs. It represents 41% of the CAPEX index. Monetary value updated in 2017EUROS
H_2 production via biomass	Gasification of biomass with steam and recovery of H_2 (50 to 80g H_2/kg of biomass)	CAPEX – 3344 EUR/t H_2 OPEX – 17 EUR/t H2	11.2 (electricity)	CAPEX includes feedstock costs, gasifier costs and labour costs. Monetary value updated in 2017 EUROS. OPEX represents 0.5% of the CAPEX index. Monetary value updated in 2017 EUROS
H_2 production via thermal decomposition of methane	Methane decomposes thermally to produce hydrogen and carbon black as by-product. No CO_2 is formed.	CAPEX – 500–1300 EUR/t H_2 OPEX – 20–40 EUR/t H_2	54 – 72 (electricity)	CAPEX includes just the equipment costs. Monetary value updated in 2017EUROS OPEX includes just operation and maintenance cost. It represents 2% of the CAPEX index. Monetary value updated in 2017 EUROS

4.3 Heating options

The ExxonMobil refinery and chemical installations are highly integrated and optimised regarding heat. Decarbonising the heating system would involve the entire refinery and not just the chemicals section. Average annual energy efficiency improvements for refineries and chemical plants amount to 0.5-1% (ExxonMobil, 2018) (VNCI, 2018). Additional energy efficiency improvement is still possible but may require investments that compete with other internal projects, or do not pay back sufficiently. These may include the internal or external use of waste heat, possibly including the application of heat pumps. In this section, electrification is explored as heat supply. The use of hydrogen for heating has been dealt with in 4.1, using the available refinery gas applying pre combustion CCS. Biobased energy is not likely to be applied in an integrated fossil fuel based refinery situation, and not further investigated. Biobased options can be found in the MIDDEN report on decarbonisation options for the refineries (Oliveira & Schure, 2020).

Electrification has a lot of potential in terms of GHG emission reductions for the chemical industry (VNCI, 2018). Boilers are present in the refinery and ROP. The furnaces present in the RAP use refinery gases. The HCU at the ROP, the PAN hot oil furnace are smaller units which also co-combust process residues. Electrification of specific furnaces would require further investigation. Alternative heating sources for boilers and furnaces would require new useful applications of the currently used refinery gases and residuals.

In electric boilers, electricity is conducted through a heating element. This heats the water through a heat exchanger. Electric boilers require little equipment to be set up and the initial investment costs are lower than other technologies like CCS. As mentioned in Table 20, electric boilers are an economically difficult option to be implemented in this particular plant because of the available refinery gas and residual fuel gas which are currently used to fire the current boilers.

Table 20 Economic parameters for electric boilers that need to be considered (VNCI, 2018; Scherpbier & Eerens, 2020)

Parameter	Unit	Value
Unit of main output	GJ steam	
Investment per unit main output capacity	€	15,000
Depreciation period	years	15
Refurbishment interval	years	10
Capital expenditure (CAPEX) per unit main output	€/year	1,400
Operation expenditure (OPEX) per unit main output	€/year	6.0
Electricity requirements per unit main output	GJ	1.1
Capacity of single unit (on full utilisation)	TJ/year	20

4.4 Bio-based raw materials

The most sought-after bio-based raw material to produce aromatic compounds in general is lignin. The effective use of lignin is considered as the key in reducing the carbon footprint and being economically profitable (Vural Gursel, Dijkstra, Huijgen, & Ramirez, 2019). Lignin as a feedstock is underutilized. There is only a fraction of lignin that is being used in the form of lignosulfonates, which are used as animal feed additives, binders and adhesives. The potential of lignin lies far beyond these applications.

There are three basic methods to convert lignin into aromatics based on the end use and properties desired (Vural Gursel, Dijkstra, Huijgen, & Ramirez, 2019). They are:

1. Lignin pyrolysis
2. Direct HDO
3. Hydrothermal upgrading

Lignin pyrolysis

Lignin is pyrolyzed in a fluid bed with a temperature of 500°C with sand as the heat carrier. The output of this bed is char and sand. This char and sand are then fed into the bubbling bed to separate lignin from the larger particles. There is a gas stream of CO, CO_2 and CH_4. The gas stream is used for heating and the liquid stream undergoes several separation steps to give an organic products mixture and water. This mixture is separated to give the aromatic compounds (Vural Gursel, Dijkstra, Huijgen, & Ramirez, 2019).

Direct HDO

In this method, feed consisting of lignin and hydrogen gas are reacted in a depolymerisation reactor at a temperature of 400 °C with a pressure of 150 bar, in the presence of the catalyst (NiMo). The liquid product from the reactor is reduced in pressure and the left-over lignin solidifies (Vural Gursel, Dijkstra, Huijgen, & Ramirez, 2019). The liquid product then undergoes various separation steps to obtain the aromatic compounds from the mixture.

Hydrothermal upgrading

In this process lignin is dissolved in an aqueous sodium hydroxide solution. After this the mixture goes to a depolymerisation reactor. The outlet mixture from the reactor is reduced to 30 °C and pressure is reduced to 1 bar from 250 °C and 55 bar in the depolymerisation reactor (Vural Gursel, Dijkstra, Huijgen, & Ramirez, 2019). After a series of reactions with sulphuric acid the remaining lignin is removed as precipitate. After this there are several separation steps that result in the aromatics production.

Table 21 shows the economic performance of (1) Lignin pyrolysis, (2) Direct HDO, (3) Hydrothermal upgrading for setting up a plant.

Table 21 Economic performance of lignin to aromatics production methods (Vural Gursel, Dijkstra, Huijgen, & Ramirez, 2019)

Parameter	Unit	Lignin pyrolysis	Direct HDO	Hydrothermal
Plant size	kt/year	200	200	200
Installed cost of reactor	M€	60	51	34
Installed cost fractionation	M€	15	40	68
Total direct plant cost	M€	75	91	102
Indirect cost	M€	22	27	30
Contingency	M€	20	24	26
Fixed capital investment(FCI)	M€	117	142	158
Working Capital	M€	18	21	24
Total capital investment (TCI)	M€	135	163	182

Table 21 shows the costs of a scaled-up plant which is modelled in ASPEN plus. Here the costs of the reactor and the fractionation give the total direct plant costs. The indirect costs are based on literature. The fixed capital investment costs are the sum of all costs and the contingency costs. The FCI when added to the working capital gives the total capital investment costs.

5 Discussion

Decarbonising the RAP and RPP factories needs to be combined with decarbonisation of the refinery. For the ROP, a separate approach can be taken. Within the scope of the study no alternative configurations for RAP and RPP could be developed. Furthermore, the complexity of the plant and confidentiality did not allow for an accurate analysis of the separate process steps.

The CCS pathway involves relatively few modifications in production processes in the refinery and RAP furnaces and the hydrogen plant. CCS, however, requires a new infrastructure grid for CO_2 transport and storage. Moreover, public acceptance remains a barrier towards the large-scale implementation of CCS. Spatial implementation of the required equipment and pipelines is under study, including considerations on the area required to install the CCS. In the ExxonMobil chemicals plants, there is limited space for a dedicated CCS Plant. There is enough offshore capacity for storage. The Port of Rotterdam CO_2 Transport Hub and Offshore Storage (PORTHOS) project is key because it is planned in the Rotterdam Botlek and Europoort where the refinery, RAP and the ROP are located.

Despite the indications in the previous chapter, made for the decarbonization options for ExxonMobil Chemicals at Rotterdam, there are a series of limitations to these options. The focus of this report is to reduce the direct emissions of CO_2. The effect of reduced electricity consumption on indirect CO_2 emissions is not included in this study, neither is the decarbonisation of materials transport.

An example of a roadblock is the pre-combustion option for hydrogen. It is recognised that this option is difficult to implement because all the gases will have to be collected from the refinery, ROP and sent to a steam methane reformer, to produce hydrogen. This hydrogen will then be sent back to the furnaces and boilers. According to ExxonMobil, the entire process requires large investments and alterations to the current combustion units.

Finally, for the RAP the available options include bio-based raw materials. The use of CCS in combination with hydrogen as a fuel or bio-based production with a combination of hydrogen as a fuel and energy carrier is a long-term option for reducing emissions. This requires further technology development and system analysis.

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Appendix A Energy balance

This section gives an overview of the energy balance of the refinery site at Botlek, including RAP and RPP. It is based on the balances of the 2015 environmental impact report of the hydrocracker installation (Royal HaskoningDHV, 2015), unless otherwise indicated. Utility data are based on the large combustion plants register (LCP) (European Environmental Agency, 2017). Steam is split into high, middle and low pressure: 40, 9 and 3 barg. The numbers include the hydrocracker. The lower section derives the energy demand of the RAP and RPP, based on the MIDDEN refineries report (Oliveira & Schure, 2020).

Table A1 Energy balance Refinery + RAP + RPP

		Elec- tricity	High	Middle	Low	Source
Refinery gases supply	**PJ**	**GWh**	**MW**	**MW**	**MW**	
Unsaturated high joule gas	6.8		227			
Refinery high joule gas	15.7		523			
Total high joule gas	24.7		824			
Low joule gas	14.1		471			
Furnaces						
Fuel input furnaces	19.2		642			
Steam output furnaces	10.0		176	128	29	
CHP						
Fuel gas input CHP	5.2		192			LCP data (European Environmental Agency, 2017)
Steam produced by CHP	3.9		142			
Electricity produced by CHP	1.04	290	38.3			Royal Haskoning DHV Expert TNO data on CHP, 86% load
Boilers						
Fuel input steam boilers	4.8					LCP data (European Environmental Agency, 2017)
Steam output steam boilers	4.0		135			
H_2 production						
Fuel input	2.1		70			
Air Products						
Fuel gas exported	9.9		329			
Steam imported	2.3		76			
Steam system						
Steam supply	20.2		529	128	29	
Steam to turbines	13.8		462			
Steam from turbines	10.3			210	133	
Steam reduced to middle	0.4		15			
Steam reduced to low	0.7			23		
Steam from reduction	1.2			16	25	
Steam to heating processes	18.2		51	358	198	
Electricity						
CHP generation	1.0	290				Royal Haskoning DHV Expert TNO data on CHP, 86% load
Imports	1.0	285				
Total consumption	2.1	575				Calculated

Table A2 Reconstructed energy balance RAP and RPP

		Electr.	High	Middle	Low	Source
Final use Refinery+RAP+RPP	**PJ**	**GWh**	**MW**	**MW**	**MW**	
Steam end use heating	18.2		51	358	198	Sum
Steam end use turbines	3.6		462	-210	-133	Sum
Total steam	21.8		513	148	65	Sum
Fuel gas furnaces input	19.2					Sum
Electricity	2.1					Sum
Final use refinery, literature						
Steam demand process	9					(Oliveira & Schure, 2020)
Fuel gas process (input furnaces)	13.5					(Oliveira & Schure, 2020)
Electricity	1.9	530				(Oliveira & Schure, 2020)
Estimated final use RAP+RPP						
Total steam	9.2					Calculated
Fuel gas furnaces input	5.7					Calculated
Electricity	0.2					Calculated