



PBL Netherlands Environmental Assessment Agency

DECARBONISATION OPTIONS FOR THE DUTCH POLYOLEFINS INDUSTRY

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Manufacturing Industry Decarbonisation Data Exchange Network

Decarbonisation options for the Dutch Polyolefins industry

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MIDDEN project coordination and responsibility

The MIDDEN project (Manufacturing Industry Decarbonisation Data Exchange Network) was initiated and is also coordinated and funded by PBL and TNO EnergieTransitie. The project aims to support industry, policymakers, analysts, and the energy sector in their common efforts to achieve deep decarbonisation. Correspondence regarding the project may be addressed to:

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This report was offered to review to Dow Benelux, SABIC Limburg, Ducor Petrochemicals. Both SABIC Limburg and Dow Benelux gave comments that have been incorporated into this report. PBL and TNO remain responsible for the content. The decarbonisation options and parameters are explicitly not verified by the companies.

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List of abbreviations

BAT	Best Available Technique
CAPEX	Capital Expenditures
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
CHP	Combined Heat and Power
СО	Carbon Monoxide
CO ₂	Carbon Dioxide
EEI	Energy Efficiency Improvement
EFA	Energy Flow Analysis
EU ETS	European Union Emission Trading System
GHG	Greenhouse Gases
GWP	Global Warming Potential
HDPE	High-density Polyethylene
IHP	Industrial Heat Pump
LDPE	Low-density Polyethylene
LLDPE	Linear Low-density Polyethylene
MFA	Material Flow Analysis
MSF	Municipal Solid Waste
МТО	Methanol-to-Olefins
MIDDEN	Manufacturing Industry Decarbonisation Data Exchange Network
NEa	Dutch Emission Authority (Nederlandse Emissieautoriteit)
NOX	Nitrogen Oxides
OPEX	Operating Expenditures
PE	Polyethylene
PP	Polypropylene
PV	Photovoltaic
TRL	Technology Readiness Level
WGS	Water-Gas Shift

FINDINGS

Summary

The Dutch chemical industry is the fourth largest in Europe and tenth in the world, having a turnover of over 50 billion euros. Characterised by a central position in the European market and by the presence of highly integrated clusters such as the Port of Rotterdam and the Chemelot industrial park in Limburg, The Netherlands hosts some of the biggest producers of polyethylene (PE) and polypropylene (PP), the two most common plastic polymers worldwide. Lightweight, cheap, and reliable, these two polyolefins compose about half of the European demand for plastic products, especially for packaging, agriculture, construction, automotive, and household objects.

In the Netherlands, the main producers of PE and PP are Dow in Terneuzen (Zeeland), SABIC in Geleen (Limburg), and Ducor in Rozenburg (Zuid-Holland), for a total yearly production of 2.6 Mt, equal to 4% of the total polyolefins production in Europe. Dow and SABIC are registered with the European Emissions Trading Systems (EU ETS), while Ducor provides an annual environmental report to the Dutch government. Together, the production of PE and PP by these three companies cause the consumption of 5.2 PJ of primary energy and the (declared) emissions of 233 kt of CO₂-eq.

The main processes involved in the production of the polyolefins are naphtha cracking for ethylene and propylene, high-pressure polymerisation for low-density polyethylene (LDPE), solution polymerisation for linear low-density polyethylene (LLDPE), suspension polymerisation for high-density polyethylene (HDPE), and gas phase polymerisation for PP. The electricity, heat, and material consumption of these processes, as well as the emissions of greenhouse gases (GHG) is obtained from available literature together with data from Dow Terneuzen, SABIC Geelen, and Ducor Rozenburg.

As the polymerisation processes do not offer much potential for efficiency improvements and energy demand reduction, the most promising decarbonisation options for the Dutch polyolefins industry involve system-wide changes and the integration of a bio-based supply chain with a plastic-to-plastic circular economy loop based on innovative recycling techniques to recover the plastic waste. The deployment of industrial-scale chemical recycling technologies such as solvent-based purification, pyrolysis, and gasification, coupled with the production of virgin polymer from sugar-based crops, lignocellulosic materials, and biowaste, is most likely the best decarbonisation strategy for the sector.

The economic costs of bio-based PE and PP are currently higher than their fossil-based counterparts, and the pyrolysis and gasification of plastic waste are not yet at a commercial level, but the transition to a greener plastic industry could be facilitated by governmental policies such as an increased carbon tax for fossil-based processes, the creation of subsidies for sustainable technologies, and stricter regulations for the use of plastic products and the design of easy-to-recycle packaging. If all the decarbonisation options described in this report were to become economically feasible on a large-scale, this would be one of the ways for the realisation of its national and European carbon emissions reduction goals.

FULL RESULTS

Introduction

This report describes the current situation of the polyethylene (PE) and polypropylene (PP) production in the Netherlands and the options and preconditions for its decarbonisation. The study is part of the MIDDEN project -Manufacturing Industry Decarbonisation Data Exchange Network-, which aims to support industry, policymakers, analysts, and the energy sector in their common efforts to achieve deep decarbonisation of the Dutch economy (PBL, 2020). The MIDDEN project will update and elaborate further on options in the future, in close connection with the industry.

Problem definition

In the last decades, planet Earth and human society have experienced tremendous changes, with the world population growing by 42% (World Bank, 2020), the final consumption of energy increasing by 51%, and CO₂ emissions rising by 58% (IEA, 2020), in the period from 1990 to 2017. This immense growth of human activity has unequivocal impacts on the climate system, and the observed environmental changes have reached unprecedented magnitudes. Anthropogenic greenhouse gases (GHG) emissions led to increasing temperature of atmosphere and oceans, and the last 30 years have been the warmest of the last 14 centuries, with most projections forecasting an increase of 2-4°C in 2100 (IPCC, 2014). The negative effects of climate change are widespread over all continents and include the rapid increase of heat waves, floods, droughts, hurricanes, ocean acidification, desertification, the melting of the polar ice caps, and the consequent rise of the sea level (NASA, 2020), which is forecasted to grow between 0.3 and 1.0 meters before the end of the century (IPCC, 2014).

The worry for the future of mankind has led to the development of environmental policies and the creation of worldwide treaties like the Kyoto Protocol in 1997 and the Paris Agreement in 2016, when 196 state parties ratified their common determination to reduce GHG emissions and keep the global temperature rise below 2°C (UNFCCC, 2020). According to the EU Climate & Energy framework, in the European Union this effort has been quantified with the target of cutting 40% of GHG emissions by 2030 (European Commission, 2020a), and the new European Green Deal has the goal to make the EU climate neutral by 2050, making energy, buildings, industry and transport sustainable and boosting circular economy (EU Green Deal, 2020). Like many other European countries, The Netherlands has developed a national plan to achieve the targets agreed on in the Paris Agreement, and its *"Klimaatakkoord"* has the ambition of reducing GHG by 49% in 2030 compared to 1990 levels, with the industrial sector alone reducing its emissions by 59% (Klimaatakkoord, 2019). Among the other subsectors, manufacturers of plastic monomers and polymers are thus in the need of improving the energy and material efficiency of their production processes and reduce the associated GHG emissions.

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 specific project is the polymerisation of PE and PP in the Netherlands, starting from respectively ethylene and propylene as feedstocks. When looking at the decarbonisation options, however, the research boundaries will be expanded to cover the end-of-use (i.e. recycling) and feedstock production (e.g. bio-based ethylene) options.

The research question to be answered is: "What is the environmental impact of polyethylene (PE) and polypropylene (PP) production in the Netherlands in terms of energy use and GHG emissions, and what is the potential of the available decarbonisation options to reduce the effect on climate change?"

Producers involved in this project are:

- Dow (Terneuzen, Zeeland)
- SABIC (Geleen, Limburg)
- Ducor (Rozenburg, Zuid-Holland).

Production processes include:

- High-density polymerisation with tubular reactor
- Solution polymerisation with double reactor
- Slurry polymerisation with loop reactor
- Gas phase polymerisation.

Products include:

- Low-density Polyethylene (LDPE)
- Linear Low-density Polyethylene (LLDPE)
- High-density Polyethylene (HDPE)
- Polypropylene (PP).

The main options for decarbonisation are:

- Bio-based polyolefins from the fermentation of sugar-based crops
- Bio-based polyolefins from the gasification of lignocellulosic and biowaste streams
- Mechanical recycling of the polyolefins
- Chemical recycling of the polyolefins with solvent-based purification
- Chemical recycling of the olefin monomers with pyrolysis
- Chemical recycling of the olefin monomers with gasification.

Reading guide

- Chapter 1 gives a general introduction to the PE and PP manufacturing industry in the Netherlands, presenting plastics companies, production sites, and registered CO₂ emission.
- Chapter 2 describes the PE and PP production process schemes adopted by plastics producers in the Netherlands, including the specific energy consumption and specific CO₂ emissions.
- Chapter 3 gives an overview on the relevant products and applications of PE and PP, presenting production volumes, prices, and market shares.
- Chapter 4 systematically quantifies and evaluates the options for decarbonisation, providing economic and environmental indicators.
- Chapter 5 is dedicated to the discussion, including a simplified decarbonisation scenario to 2050, and final conclusion.

1 Polyolefin production in the Netherlands

1.1 Introduction to the Dutch chemical industry

In the past decades the Dutch chemical industry has evolved, making the Netherlands the fourth largest chemical producer in Europe and tenth worldwide, with a sector turnover of 50 billion euros that constitutes 6% of the national GDP (World Bank, 2020) and 13% of the industrial added value, providing employment to more than 43,000 people distributed among more than 800 chemical companies (VNCI, 2018). Compared to other countries, the Dutch industry is characterised by the presence of highly integrated clusters which result in cost-efficient exchange of energy and materials, and other competitive benefits (VNCI, 2018). The industry is home to a wide variety of sectors, such as the petrochemical, fertilizers, chlor-alkali, and polyolefins. Crude oil is processed in petroleum refineries to produce platform chemicals (e.g. propane, gasoil and naphtha) which are then converted into plastic monomers (e.g. ethylene and propylene) and used to manufacture polyolefins such as LDPE, HDPE and PP, but also rubbers, resins, and other chemical products.

The geographical position of the Netherlands in the centre of Europe, coupled with the highly developed seaports and pipelines, helped the country to become a central hub for the other European countries, with yearly imports of oil products exceeding 84,000 ktoe in 2019 and exports over 106,000 ktoe (IEA, 2020). While this industrial activity is beneficial for the Dutch employment and national economy, it is also responsible for a massive amount of GHG emissions. In 2018, the manufacture of refined petroleum products resulted in the emissions of 10 Mton of CO_2 (CBS, 2020), and the chemical industry (including the production of plastics) emitted another 20 Mton, while consuming 295 PJ (IEA, 2020). To put this into perspective, the chemical and oil subsectors used 12% of the Dutch primary energy demand (IEA, 2020) and emitted 18% of the total emissions (CBS, 2020).

1.1.1 Production locations of polyolefins in the Netherlands

In the Netherlands PE and PP are mainly produced by three companies: Dow, SABIC and Ducor. While Dow and SABIC are registered under the EU ETS and their emissions are reported by the Dutch Emissions Authority (NEa), Ducor is below the threshold (25 ktCO₂- eq) for direct emissions and is thus not part of the program (EU ETS, 2015). Ducor, however, declares its emissions to the emission registration department of Dutch government (Emissieregistratie, 2020). The PE and PP production locations of the three companies are shown in Figure 1, while more information about the history, infrastructure, carbon emissions and energy demand of the production sites will be given in the following sections of this chapter.



Figure 1 locations of Dow (Terneuzen, in green), SABIC (Geleen, in blue), and Ducor (Rozenburg, in red) in the Netherlands. (Simplemaps, 2020)

An overview of the producers, including their production capacity and registered CO₂ emissions, is presented in Table 1. The value declared to the NEa by Dow and SABIC is the sum of the emissions caused by all the activities carried out in the production sites and are thus not limited to the production of polyethylene and polypropylene. The other activities of Dow and Sabic (including their decarbonisation options) are described in other MIDDEN reports (Rodriguez, Van Dril, & Gamboa Palacios, 2021); (Oliveira C. & Schure, 2020). More information about the existing infrastructures, the energy demand, and the carbon emissions of these production sites will be given in the specific sections regarding the three companies involved in the project.

Producer	Location (city, province)	Polyolefins produced	Production capacity [kt/yr]	Number of employees	Declared CO ₂ emissions [t/yr]
Dow	Terneuzen, Zeeland	LDPE, LLDPE	1,100	3,600	124,283
SABIC	Geleen, Limburg	LDPE, HDPE, PP	1,290	1,600	96,191
Ducor	Rozenburg, Zuid-Holland	РР	200	80	12,940

Table 1 Overview of PE and PP producers in the Netherlands, made with information from different sources (Dow, 2017, 2020b; Ducor, 2020b; Emissieregistratie, 2020; NEa, 2020; SABIC Limburg, 2020).

1.2 DOW

1.2.1 History of the company

The Dow Chemical Company (from now on, Dow) is the third largest chemical producer in the world (C&EN, 2019), with headquarters in the United States of America. Dow was founded in 1897 by chemist Herbert Henry Dow and always had the tradition of diversifying its product line, ranging from agricultural chemicals and plastics resins, to plutonium during World War II and napalm during the Vietnam War. In 2011, Dow divested its global polypropylene business to Braskem, the largest petrochemical company in Latin America, in order to better focus on improving the performance of its polyethylene production (Business Wire, 2011). In 2017, Dow merged with DuPont, becoming the largest chemical producer in the world, but two years later the company was reorganised and split into three separate publicly traded companies focusing on materials science (Dow Inc.), agriculture (Corteva), and specialty products (DuPont) (C&EN, 2019).

Dow is present in Europe since 1955 and in The Netherlands since 1964, when it opened its first factory in Terneuzen. The industrial cluster in the province of Zeeland also houses other chemical companies, like Yara and Arkema, and good transport connections via land and water (VNCI, 2018). The company expanded in the last decades, and Terneuzen is currently the second largest Dow production site in the world (Dow, 2020b), with a yearly turnover of more than 2 billion euros (Dow, 2017). For what concerns polyethylene production, the site hosts a production line for LDPE, built between 1968 and 1975, and three production lines for LLDPE, built in 1980, 1986 and 2000, as seen in Figure 2 (*Internal communication with Dow Terneuzen, 2020*).



Figure 2 Aerial view of Dow chemical plants in the Terneuzen site with the locations of the LLDPE and LDPE production and the crackers where the Low Hydro Carbons (LHC) are produced (Dow, 2020b).

1.2.2 Registered emissions and energy consumption

Dow Terneuzen has ten permit numbers registered with the Dutch Emissions Authority (NEa) and the EU ETS. The production sites relative to PE production are shown in Table 2. The large difference between 2017 and 2018 for the production site Dow BKG 07 is the result of a maintenance stop in 2017.

Permit number	Production site	Activity	CO ₂ emissions [t/yr] in 2017	CO ₂ emissions [t/yr] in 2018
NL-200400084d	Dow BKG 05	PE production	6,827	6,112
NL-200400084f	Dow BKG 07	Energy for PE	36,199	54,314
NL-200400084g	Dow BKG 08	Energy for PE	61,675	63,857

Table 2 Registered direct carbon emissions for Dow Terneuzen (NEa, 2020).

The nominal capacity and energy demand of each product is shown in Table 3. A production line for HDPE was being planned, but the project has been recently cancelled (*Internal communication with Dow Terneuzen, 2020*).

Table 3 Nominal capacity and estimated energy consumption for the production ofLDPE and LLDPE in Dow Terneuzen (Internal communication with Dow Terneuzen,2020).

Product	Nominal capacity [kt/y]	Electricity consumption [GWh/y]	Steam consumption [TJ/y]	Total primary energy consumption [TJ/y]
LDPE	300	288	-200	497
LLDPE	800	282	552	1,319

Electricity and steam are supplied to Dow by the "Electricity and Steam Association" (ELSTA) near Terneuzen, which has been owned by Dow since 2018. The cogeneration facility is equipped with one steam turbine and three gas-fired turbines with a connected heat recovery boiler, and is able to generate a total of 460 MW of electricity and 850 tonnes/hour of steam at a pressure of 90 bar, supplying to Dow and, for electricity, also to the public grid (ELSTA, 2020).

1.3 SABIC

1.3.1 History of the company

SABIC is the fourth largest chemical producer in the world (C&EN, 2019), and the second largest public company in the Middle East and in Saudi Arabia, where its headquarters are based. SABIC was founded in 1976 under the will of the Saudi government to covert the oil into polymers and other chemicals, and later expanded in the fertilizers and metals subsectors. In 2019, 70% of SABIC's shares were acquired by Saudi Aramco, the state-owned energy company of Saudi Arabia (SUSTG, 2019). In 2002, SABIC acquired several

factories from the Dutch petrochemical company DSM, officially starting operations in Europe (Kapner, 2002). The company is present in The Netherlands through its subsidiaries SABIC Europe, SABIC Limburg B.V., SABIC Petrochemicals B.V., and SABIC Innovative Plastics B.V. (SABIC Limburg, 2020).

1.3.2 Registered emissions and energy consumption

SABIC is part of the Chemelot cluster in Geleen, an industrial area characterized by strong integration of utilities and services, grouping together more than 50 factories and R&D facilities (VNCI, 2018). SABIC infrastructures constitute about half of the space at Chemelot, including two naphtha crackers (NAK3 and NAK4) for the production of plastic monomers, three LDPE production lines (Id-PE), two HDPE production lines (hd-PE), and two PP reactors (*Internal communication with SABIC, 2020*), as shown in Figure 3.



Figure 3 Aerial view of SABIC chemical plants at Chemelot industrial park, showing the naphta crackers NAK3 and NAK4, and the production lines of PP, HDPE and LDPE (SABIC Limburg, 2020).

The companies within the Chemelot industrial cluster are grouped together and registered to the Dutch Emissions Authority (NEa) under the name of "Chemelot BKG", for a total of 14 permits. However, starting from the next year the companies will be treated as a single entity and their emissions will be merged together in one NEa permit number (*Internal communication with SABIC, 2020*). At the moment, the emissions caused by SABIC production of PE and PP fall under the "Chemelot BKG 012" permit, which also include other production activities, as shown in Table 4.

Table 4 Registered carbon emissions in 2018 and 2019 for PE and PP production bySABIC Limburg (NEa, 2020) and (Internal communication with SABIC, 2020).

Permit number	Production site	Activity	CO ₂ emissions [t/yr] in 2018	CO2 emissions [t/yr] in 2019
NL-200400161k ¹	Chemelot BKG 012	PE, PP, others	78,068	96,191
NL-200400161k ¹	Chemelot BKG 012	Only PE and PP	34,823 ²	34,497 ²

¹ Including emission of some Utility Support Group (USG) Industrial Utilities units.

² Only direct emissions and heat-related emissions, no power emissions.

Table 5 shows the nominal capacity of the PE and PP production lines and the correspondent electricity and steam demand for 2019.

Table 5 Nominal capacity and energy consumption for the production of LDPE,HDPE, and PP in SABIC Geleen for 2019 (Internal communication with SABIC,2020).

Product	Nominal capacity [kt/y]	Electricity consumption [GWh/y]	Steam consumption [TJ/y]	Gas consumption [TJ/y]	Total primary energy consumption [TJ/y]
LDPE	430	383	-428	0	950
HDPE	310	112	468	11	882
PP	550	178	168	0	810

Electricity, steam and technical gases are supplied by Utility Support Group (USG), a joint venture between SABIC and Sitech Utility Holding CV with approximately 200 employees (USG, 2020a). USG supplies many companies within the Chemelot industrial park thanks to its 150 MW cogeneration plant, plus other 90 MW purchased externally. USG also collects around 620 tonnes/hour of waste steam produced by the factories and produces itself an additional 330 tonnes/hour to satisfy the steam demand of the companies (USG, 2020b).

1.4 DUCOR

1.4.1 History of the company

The polypropylene manufacturing facilities in Rozenburg were built in 1979 by Basell, but in 2007 the company merged with Lyondell and the agreement involved some capacity divestment requirement (ChemEurope, 2001). The Rozenburg plant was acquired by DOMO, a joint venture between the Belgian Domo Group and Carmel Olefins, a subsidiary of BAZAN Group, the biggest petrochemical company of Israel. The joint venture changed name in 2011, becoming Ducor Petrochemicals (PlastEurope, 2011).

The manufacturing site in Rozenburg operates within the boundaries of Rotterdam-Rijnmond, the largest chemical and petrochemical cluster in the Netherlands, which is characterised by excellent infrastructures and connections, i.e. roads, pipelines and railways (VNCI, 2018). Ducor is also part of "CIRCLE", a consortium of international plastic companies and academia aiming to reduce industrial waste and increase the amount of recycled material in plastic products (Ducor, 2020b).

1.4.2 Registered emissions and energy consumption

Ducor Rozenburg has 80 employees (Port of Rotterdam, 2016) and three production lines that can produce different PP resins at the same time or be combined together to bear big production loads in a short time. The strategic location into the logistic hub of the Rotterdam port also means that Ducor is connected with an efficient system of pipelines for the supply of utilities and feedstock (Ducor, 2018). Part of the infrastructures of Ducor Rozenburg can be seen in Figure 4.



Figure 4 View of Ducor chemical plants in the Rozenburg site (Ducor, 2020b).

As previously mentioned, Ducor is not registered with the NEa, but in its environmental report to the Dutch government, it declares 12,940 tonnes of CO_2 -eq for 2017 (Emissieregistratie, 2020). The nominal capacity and energy demand for the production of PP in 2019 is shown in Table 6.

Table 6 Nominal capacity and energy consumption for the production of PP in DucorRezenburg (Internal communication with Ducor).

Nominal capacity	Electricity	Steam	Total primary energy
of the product	consumption	consumption	consumption
[kt/y]	[GWh/y]	[TJ/y]	[TJ/y]
200 (PP)	68	131	725

Utilities such as electricity, steam and industrial gases are supplied to Ducor by Air Liquide, which is also part of the Rotterdam Port industrial cluster and adopts gas-fired cogeneration turbines.

2 Polyolefins production processes

2.1 General overview

This chapter is dedicated to the description of the current processes applied in The Netherlands and utilities with all relevant physical inputs, outputs, and efficiencies. Polyolefins are based on crude oil or, more specifically, on raw materials like ethene and propene. During the chain polymerisation process, the chemical bonds of thousands of monomers are forced to open and link to each other, creating a saturated chain macromolecule whose properties can vary depending on the polymerisation process and technique (European Commission, 2007). The first section will provide a quick overview of the production of ethylene and propylene, the precursors required as feedstock to produce polyolefins, while the following sections will be dedicated to LDPE, HDPE, LLDPE, and PP. For each product, the flow scheme will be shown, including chemical structures, temperature and pressure levels, the usable catalysts, initiators, co-monomers, and solvents. The CO₂ emissions and energy demand of each process will also be compared to available benchmarks from international literature and verified by the company involved in the study or by other appointed sector representatives.

POLYMERISATION PROCESS	LDPE	LLDPE	HDPE	РР	Explained in
High-pressure	Х				Section 2.3
Solution		Х	Х		Section 2.4
Suspension/slurry			Х	Х	Section 2.5
Gas phase		Х	Х	Х	Section 2.6

Table 7 Most common processes applied in polyethylene and polypropyleneproduction. Made with information from (European Commission, 2007;PlasticsEurope, 2014a, 2014b).

As seen in Table 7, four main polymerisation process technologies are applied in the production of polyolefins, and all of them will be described and analysed in the following sections. At Dow, LLDPE is produced under the brand name of Dowlex with a double reactor solution process (Townsend Solutions, 2017), while HDPE is produced under the brand name of Continuum with UNIPOL II process technology, which corresponds to a double reactor gas phase process (Dow, 2020a). At SABIC, LDPE is produced by a high-pressure, 240 MPa, tubular reactor, HDPE is produced using a slurry process with loop reactor, while PP is produced using a gas phase polymerisation process (*Internal communication with SABIC, 2020*). At Ducor, PP is produced under the brand names DuPure and DuClear using Novolen technology (Ducor, 2020a), which employs a stirred gas phase polymerisation reactor and a nitrogen degassing vessel (McDermott, 2020).

2.2 Ethylene and propylene

The monomers necessary for polyolefin production, namely ethylene (also called ethene, chemical formula: C_2H_4) and propylene (also called propene, chemical formula: C_3H_6), are produced by steam crackers. In the European Union, around 63% of the cracker feedstock is made up by naphtha coming from petroleum refineries, with the remaining share being liquified petroleum gas (LPG) and other natural gas liquids (Petrochemicals Europe, 2020). In The Netherlands, between 5,000 and 6,000 ktoe of naphtha are produced every year (IEA, 2020), accounting for around 10% of the cracker feedstock in the European Union (Petrochemicals Europe, 2020).

Steam cracking units have a generic universal design, with only little modifications implemented to adapt to local conditions and optimize the plant performance. The energy and environmental performance of the steam crackers is assessed in (Oliveira C. & Schure, 2020; Wong & Van Dril, 2020), and this section only provides a summarized overview of the production steps, shown in Figure 5.



Figure 5 Schematic diagram showing ethylene and propylene production in a naphtha-based steam cracking plant. Made with information from (*PlasticsEurope*, 2012).

The hydrocarbon feedstock is vaporised with superheated steam and sent to the furnace to be cracked into smaller molecules. The temperature inside the furnace ranges from 750 to 875°C, and the steam is injected with a pressure of 1 MPa and a temperature of 180-200°C, so the process only takes the fraction of a second. After exiting the furnace, the cracked gases enter the transfer line exchanger, which cools them down to block further reactions and recovers heat for internal use. In the quench tower the gases are de-superheated by a water/oil stream and then condensed by a multi-stage gas compression. Carbon dioxide and acid gases are removed, then the cracked gases are cooled down and dried. The product fractionation consists of four progressive stages of chilling, extracting hydrogen, methane, ethylene, propylene, and pyrolysis gasoline. Selective catalytic hydrogenation or extractive distillation is used to remove the undesired acetylene, while the remaining ethane and propane are recycled back into the steam cracker (PlasticsEurope, 2012).

Table 8 Energy demand and Greenhouse gasses emissions (GHG) relative to the production of 1 kg ethylene and propylene. Made with information from the Ecoprofiles report (*PlasticsEurope, 2012*).

Product	Electricity demand [MJ]	Steam demand [MJ]	GHG [kg CO ₂ -eq]
Ethylene (1kg)	0.76	12.60	1.44
Propylene (1kg)	0.76	12.60	1.44

The values shown in Table 8 refer to the useful energy consumed by foreground processes (i.e. steam cracking) for 1 kg of product (PlasticsEurope, 2012). When considering also the extraction of resources, production processes and transportation, the total primary energy demand for 1 kg of product is equal to 22.4 MJ for ethylene and 23.8 MJ for propylene (PlasticsEurope, 2012). As it will be showed in the next sections, the production of ethylene and propylene from steam cracking is significantly more energy-intense and carbon-intense than the polymerization process. More information can be found in the MIDDEN reports about steam cracking processes and the relative decarbonisation options (Wong & Van Dril, 2020).

2.3 Low-Density Polyethylene

Low-Density Polyethylene (LDPE) is a low crystalline and high amorphous polymer with an average density of 0.91-0.94 g/cm³ and a melting point of 105-115°C. It is composed by 4,000-40,000 carbon atoms with a high degree of short and long side-chain branching (Omnexus, 2020a), as shown in Figure 6.





2.3.1 High-pressure polymerisation process

LDPE is produced through high-pressure polymerisation, which is a very standardized process following the steps shown in Figure 7.



Figure 7 LDPE high-pressure polymerisation process scheme. Made with information from (*European Commission, 2007; PlasticsEurope, 2014a; SABIC Limburg, 2020*).

After compressing the gaseous ethylene to 20-30 MPa together with the unreacted gas of previous cycles, the polymerisation take place in an autoclave reactor, operating with a temperature of 180-300°C and pressure of 100-250 MPa, or in a tubular reactor as is used by SABIC Limburg, operating with a temperature of 140-340°C and a pressure of 200-350 MPa (European Commission, 2007). The specific figures for Sabic are 250 °C and 240 MPa. LDPE polymerisation usually requires the use of initiators, namely oxygen or organic peroxides with a mass fraction concentration of 0.1-0.5%, and sometimes the use of polar modifiers (e.g. ketones) or aliphatic hydrocarbons to influence the molecular weight distribution (PlasticsEurope, 2014a). The resulting polymer and unreacted gases are then separated in a high-pressure separator (15-30 MPa) and low-pressure separator (0.15 MPa), where the unreacted gases are recycled back into the process and part of the residual heat is recovered and used to produce steam (European Commission, 2007). As the polymerisation of ethylene is a highly exothermic process (3,300-3,600 J/g), the manufacture of LDPE is a net steam producer (Burdett & Eisinger, 2016). If required by the application of the product, specific additives (e.g. stabilizers or fire retardants) are added to the polymer melt to obtain the desired properties, and the polyethylene is then extruded into granules. Finally, the LDPE is dried, blended, and degassed to remove the residual ethylene before being transported to storage silos or packed and sent to the costumers (European Commission, 2007).

2.3.2 Energy and material demand

In 1999, the European average energy demand for LDPE production was equal to 3.9 MJ/kg of direct energy, or 9.4 MJ/kg of primary energy (assuming an efficiency of 40% for electricity and 90% for steam), while the average of the top 50% companies was equal to 2.6 MJ/kg of direct energy, or 7.5 MJ/kg of primary energy (European Commission, 2007). More than one decade later, the values are not so different, as in 2014 the production of LDPE still required an average of 7.9 MJ/kg of primary energy (assuming an efficiency of 40% for electricity and 90% for steam). As shown in Table 9, the polymerisation of 1 kg of

LDPE causes the emission of 0.32 kg of CO_2 -eq, considering the Global Warming Potential (GWP) for 100 years.

Table 9 Energy demand and global warming potential (GWP) for the polymerisation of 1 kg of LDPE. Average values from literature (*PlasticsEurope, 2014a*) and internal communication with the companies involved.

Product	Electricity demand	Steam demand	GWP
[1 kg]	[MJ]	[MJ]	[kg CO ₂ -eq]
LDPE	3.43	-0.29	0.32

As explained in the previous section, the value for steam demand is negative because LDPE polymerisation is a net producer of heat, which is recovered and used for other processes (European Commission, 2007). If the boundaries of the life-cycle analysis are extended to the extraction of fossil and mineral resources, the production of raw materials (e.g. monomers and solvent), and the production of electricity, the primary energy demand for the production of 1 kg LDPE is equal to 82.9 MJ and the emissions are equal to 1.87 kg of CO_2 -eq (PlasticsEurope, 2014a). Regarding the input materials, 1 kg of LDPE required 1.02 kg of monomer in 1999 (European Commission, 2007), and the value was unchanged in 2014 (PlasticsEurope, 2014a), showing no improvement in the efficiency of the process.

2.4 Linear Low-Density Polyethylene

Low-Density Polyethylene (LDPE) is a semi-crystalline polymer with an average density of 0.91-0.94 g/cm³ and a melting point of 105-115°C. It has a linear structure with short and uniform side-chain branches (Omnexus, 2020a), as shown in Figure 8:





2.4.1 Solution polymerisation process

LLDP can be produced through a solution process (which is also used to produce HDPE) or a gas phase process (which is also used to produce HDPE and PP). In the solution process, the ethylene is diluted with the co-monomer (such as hexene-1 and octene-1) and a hydrocarbon solvent in the range of C6 to C9, which are all purified by passing throughout beds of absorbent material (European Commission, 2007). As catalyst, both Zieglar-Natta and Metallocene-types can be applied (PlasticsEurope, 2014a). The solution is then sent to the polymerisation reactor, which operates at a temperature higher than 100°C and with pressure up to 20 MPa (European Commission, 2007). The unreacted ethylene and the residual solvent are separated by the evaporator, then the polymer passes through the standard steps of extrusion (including the addition of additives), drying, blending, degasification, and storage (European Commission, 2007), as shown in Figure 9.



Figure 9 LLDPE solution polymerisation process scheme. Made with information from (European Commission, 2007; PlasticsEurope, 2014a; SABIC Limburg, 2020).

2.4.2 Energy and material demand

In 1999, the European average energy demand for LLDPE production was equal to 2.4 MJ/kg of direct energy, or 4.1 MJ/kg of primary energy (assuming an efficiency of 40% for electricity and 90% for steam), while the average of the top 50% companies was equal to 2.1 MJ/kg of direct energy, or 2.9 MJ/kg of primary energy (European Commission, 2007). More than one decade later, the values are not so different, as in 2014 the production of LLDPE still required an average of 3.9 MJ/kg of primary energy (assuming an efficiency of 40% for electricity and 90% for steam). As shown in Table 10, the polymerisation of 1 kg of LLDPE causes the emission of 0.27 kg of CO₂-eq, considering the Global Warming Potential (GWP) for 100 years.

Table 10 Energy demand and global warming potential for the polymerisation of 1 kg of LLDPE. Average values from literature (*PlasticsEurope, 2014a*) and internal communication with the companies involved.

Product	Electricity demand	Heat demand	GWP
	[MJ]	[MJ]	[kg CO ₂ -eq]
LLDPE (1 kg)	1.27	0.69	0.23

If the boundaries of the life-cycle analysis are extended to the extraction of fossil and mineral resources, the production of raw materials (e.g. monomers and solvent), and the production of electricity, the primary energy demand for the production of 1 kg LLDPE is equal to 79.2 MJ and the emissions are equal to 1.87 kg of CO_2 -eq (PlasticsEurope, 2014a). Regarding the input materials, 1 kg of LLDPE required 1.03 kg of monomer in 1999 (European Commission, 2007) and 1.02 kg of monomer in 2014 (PlasticsEurope, 2014a), showing a small improvement in the efficiency of the process.

2.5 High-Density Polyethylene

High-Density Polyethylene (HDPE) is a high crystalline and low amorphous polymer with an average density of 0.94-0.97 g/cm³ and a melting point of 120-140°C. It has a linear structure with a low degree of short side-chain branches (Omnexus, 2020a), as shown in Figure 10.



Figure 10 HDPE structure with the main carbon chain in black and the side branches in blue (*Graziano et al., 2019*)

2.5.1 Suspension/slurry polymerisation process

HDPE is mainly produced through a suspension/slurry process (which is also used to produce PP), but also through a solution process (which is also used to produce LLDPE) or a gas phase process (which is also used to produce LLDPE and PP). Moreover, two different reactors can be applied in the suspension/slurry process: a stirred tank reactor (STR) or a loop reactor (PlasticsEurope, 2014a). The flow diagram for HDPE production using a suspension process and a STR is shown in Figure 11.



Figure 11 HDPE suspension/slurry polymerisation process scheme. Made with information from (*European Commission, 2007; PlasticsEurope, 2014a; SABIC Limburg, 2020*).

The process starts with the purification and the mixing of the reagents: beside the ethylene as main feedstock, HDPE also requires a co-monomer (such as butene-1 or hexene-1), a catalyst (usually Ziegler-Natta organo-metallic compounds), and a solvent in the C5-C8 hydrocarbon group (PlasticsEurope, 2014a). If the loop reactor is used, Philips and Metallocene catalysts can also be applied, coupled with isobutane as solvent (European Commission, 2007). The mixture is fed to the reactor, which operates under 80-90°C and 0.5-1 MPa conditions. The resulting polymer is insoluble and precipitates in a fine suspension that can be separated from the solvent by centrifugation (PlasticsEurope, 2014a). The concentration of HDPE in the slurry is dependent on many process parameters, but generally it ranges between 30 and 45% by weight (European Commission, 2007). After the centrifuge, the polymer faces the standard steps of extrusion in granules (including the addition of additives to obtain the desired properties), drying, blending, degasification of residual monomer, and storage in silos (PlasticsEurope, 2014a; SABIC Limburg, 2020).

2.5.2 Energy and material demand

In 1999, the European average energy demand for HDPE production was equal to 2.5 MJ/kg of direct energy, or 5.1 MJ/kg of primary energy (assuming an efficiency of 40% for electricity and 90% for steam), while the average of the top 50% companies was equal to 2.1 MJ/kg of direct energy, or 4.2 MJ/kg of primary energy (European Commission, 2007). More than one decade later, the values are not so different, as in 2014 the production of HDPE still required an average of 5.4 MJ/kg of primary energy (assuming an efficiency of 40% for electricity and 90% for steam). As shown in Table 11, the polymerisation of 1 kg of HDPE causes the emission of 0.27 kg of CO₂-eq, considering the Global Warming Potential (GWP) for 100 years.

Table 11 Energy demand and global warming potential for the polymerisation of 1
kg of HDPE. Average values from literature (PlasticsEurope, 2014a) and internal
communication with the companies involved.

Product	Electricity demand	Heat demand	GWP
	[MJ]	[MJ]	[kg CO ₂ -eq]
HDPE (1 kg)	1.55	1.34	0.27

If the boundaries of the life-cycle analysis are extended to the extraction of fossil and mineral resources, the production of raw materials (e.g. monomers and solvent), and the production of electricity, the primary energy demand for the production of 1 kg HDPE is equal to 80.2 MJ and the emissions are equal to 1.80 kg of CO₂-eq (PlasticsEurope, 2014a). Regarding the input materials, 1 kg of HDPE required 1.03 kg of monomer in 1999 (European Commission, 2007) and 1.02 kg of monomer in 2014 (PlasticsEurope, 2014a), showing a small improvement in the efficiency of the process.

2.6 Polypropylene

Polypropylene (PP) is a semi-crystalline and low amorphous polymer with an average density of 0.90-0.91 g/cm³ and a melting point of 210-290°C (BPF, 2020). It has a linear structure with a low degree of unsaturation, and thus of short side-chain branches, as shown in Figure 12.



Figure 12 PP structure with the main hydrocarbon chain in white and the methyl groups in black (*BPF, 2020*).

2.6.1 Gas phase polymerisation process

PP can be produced with a gas phase process (which is also used to produce LLDPE and HDPE) or with a suspension/slurry process (which is also used to produce HDPE). In the gas phase process, the first step is to mix and compress the gaseous propylene, co-monomer, hydrogen and catalyst together before sending them in a steady flow to the polymerisation reactor under 2-4 MPa and 70-90°C conditions (European Commission, 2007). For many

companies adopting the Borstar loop-reactor or Unipol II fluidised bed reactor technologies, it has become common to have a setup of two or more reactor in sequence. This so-called multistage configuration increases the capital cost of the production line, but adds flexibility and widens the portfolio of produced polyolefins (Kanellopoulos & Kiparissides, 2019). For PP production, catalysts based on titanium and aluminium are usually chosen, including Ziegler-Natta, Phillips-types, and Metallocene-types (PlasticsEurope, 2014b). The resulting polymer powder is extracted at the bottom of the reactor and moved to a degassing vessel to deactivate the catalyst and remove the residual feedstock, which is cooled and recycled back into the cycle (PlasticsEurope, 2014b), as seen in Figure 13.



Figure 13 PP gas phase polymerisation process scheme. Made with information from (*European Commission, 2007; PlasticsEurope, 2014b; SABIC Limburg, 2020*).

The resulting PP is sent to the granule extruder, where the necessary additives are also added to the polymer mix. Finally, the product faces the standard steps of drying, blending, degasification of the residual monomer and storage in silos (European Commission, 2007).

2.6.2 Energy and material demand

The European average energy demand for PP production was not reported in 1999, but it could be considered equivalent to comparable HDPE processes, which had an average consumption of 5.1 MJ/kg of primary energy (European Commission, 2007). More than one decade later, the value seems to have improved, as in 2014 the production of PP required an average of 3.8 MJ/kg of primary energy (assuming an efficiency of 40% for electricity and 90% for steam). As shown in Table 12, the polymerisation of 1 kg of PP causes the emission of 0.20 kg of CO₂-eq, considering the Global Warming Potential (GWP) for 100 years, making PP more environmentally friendly than LDPE, LLDPE, and HDPE.

Product	Electricity demand	Heat demand	GWP
	[MJ]	[MJ]	[kg CO ₂ -eq]
PP (1 kg)	1.29	0.59	0.20

Table 12 Energy demand and global warming potential for the polymerisation of PP. Average values from literature (*PlasticsEurope, 2014b*) and internal communication with the companies involved.

If the boundaries of the life-cycle analysis are extended to the extraction of fossil and mineral resources, the production of raw materials (e.g. monomers and solvent), and the production of electricity, the primary energy demand for the production of 1 kg PP is equal to 77.9 MJ and the emissions are equal to 1.63 of CO₂-eq (PlasticsEurope, 2014b). Regarding the input materials, 1 kg of PP required 1.03 kg of monomer in 1999 (European Commission, 2007) and 1.02 kg of monomer in 2014 (PlasticsEurope, 2014b), showing a small improvement in the efficiency of the process.

2.7 Recap of energy demand and carbon emissions

Considering only the energy demand relative to the polymerisation of the polyolefins (LDPE, LLDPE, HDPE, and PP), the primary energy demand and greenhouse gases emissions are shown in Table 13. The energy and the emissions of CO_2 -eq relative to the production of the input monomers and other raw materials are thus excluded from the analysis, as explained in the previous sections of this chapter.

Table 13 Energy demand and GHG emissions for the polymerisation of 1 kg of LDPE,LLDPE, HDPE, and PP. Average from PlasticsEurope EcoProfiles (*PlasticsEurope,*2014a, 2014b) and internal communication with SABIC, Dow and Ducor.

Product	Polymerisation process	Electricity demand [MJ]	Heat demand [MJ]	GHG emissions [kg CO2-eq]
LDPE (1 kg)	High pressure	3.43	-0.29	0.32
LLDPE (1 kg)	Solution	1.27	0.69	0.23
HDPE (1 kg)	Suspension/slurry	1.55	1.34	0.27
PP (1kg)	Gas phase	1.29	0.59	0.20

As seen in the table, LDPE has the highest energy requirements and GHG emissions, while PP is the product with the smallest environmental impact.

3 Polyolefins products and application

3.1 General overview

In 2018, plastic production reached 360 million tonnes globally and 60 million tonnes in Europe, of which almost 80% was consumed by the six largest European countries (Germany, Italy, France, Spain, United Kingdom, and Poland) and the Benelux countries (Belgium, Netherlands, and Luxembourg) (PlasticsEurope, 2019). Despite the existence of dozens of plastic types, Figure 14 shows how almost half of the European consumptions consists just of PE and PP, which are used especially for packaging, building and construction, and the automotive industry.



Figure 14 Distribution of European plastic demand in 2018, based on data from *(PlasticsEurope, 2019)*.

In The Netherlands, the annual demand for plastics is equal to 2.2 million tonnes, and around 32% of the post-consumer plastic waste is recycled, while the remaining part is burned in energy recovery plants (PlasticsEurope, 2019).

Packaging is the biggest sector overall, and although plastics account for only 18% of all packaging materials (by weight) in The Netherlands, it makes up 43% of the total revenue, which was over 6 billion euros in 2016 (ABN AMRO, 2017).

In the following sections the properties and applications of the different polyolefins will be discussed. The main physical properties that determine the field of application of these plastics are:

- **Density**: the ratio between the mass and the volume of the material, it is measured in g/cm³ or in kg/m³.
- **Tensile yield strength**: the stress a material can withstand without permanent deformation, it is measured in MPa or in N/mm².
- **Shore hardness (D scale)**: it measures the resistance of a material to be penetrated by an indenter, it goes from 0 (softest) to 100 (hardest).
- **Continuous service temperature**: the maximum temperature (measured in Celsius) above which the mechanical properties of the material degrade significantly.

3.2 Low-Density Polyethylene

3.2.1 Product characteristics

Low-Density Polyethylene (LDPE) is a flexible and translucent plastic with good resistance to electricity and chemicals like alcohols, acids, and dilute alkalis (Omnexus, 2020a). Table 14 shows an overview of the physical properties of LDPE.

Table 14 Density, tensile yield strength, shore hardness and maximum continuousservice temperature (CST) of low-density polyethylene (Omnexus, 2020b).

Density	Tensile yield	Shore hardness	Max CST
(g/cm³)	strength (MPa)	(D scale)	(°C)
0.92-0.94	10-20	40-50	80-100

Although it is susceptible to stress cracking and it cannot sustain high temperatures, its low cost, light weight and transparency make LDPE a very good material to manufacture containers and bags by using extrusion or injection moulding (Omnexus, 2020a). A practical application of LDPE is shown in Figure 15:



Figure 15 Blown film extruded low-density polyethylene bags (LDPE Bags, 2020).

3.2.2 Main applications

LDPE and LLDPE together make 17.5% of the plastics demand in Europe, for a total of 8.96 million tonnes (PlasticsEurope, 2019). Assuming the ratio is the same in The Netherlands, the volume of LDPE and LLDPE would be equal to 385,000 tonnes. Considering a price between 0.98 and 1.08 \in /kg for LDPE (PlasticPortal, 2020), the Dutch market would be worth 375-515 million euros per year.

LDPE is used especially in the packaging sector (single use food film, reusable bags and containers), agriculture sector (single use agricultural film), building and construction sector, and it is marginally used in the electrical and automotive sectors (PlasticsEurope, 2019). The shares of low-density polyethylene in each sector in The Netherlands are shown in Figure 16.



Figure 16 Thousands of LDPE/LLDPE tons used by the main economic sectors in The Netherlands. Made with estimates from European data extracted from (*PlasticsEurope, 2019*).

3.3 Linear Low-Density Polyethylene

3.3.1 Product characteristics

Linear low-Density Polyethylene (LLDPE) is a flexible and translucent plastic with high impact strength resistance and good resistance to water and chemicals such as alcohols (Omnexus, 2020a). Table 15 shows the main physical properties of LLDPE.

Table 15 Density, tensile yield strength, shore hardness and maximum continuous service temperature (CST) of linear low-density polyethylene (*Omnexus*, 2020b).

Density	Tensile yield	Shore hardness	Max CST
(g/cm³)	strength (MPa)	(D scale)	(°C)
0.92-0.95	10-30	55-65	90-110

Just like LDPE, LLDPE has light weight and low production cost. The most common manufacturing process in extrusion (e.g. for blow and cast films), but injection and roto-moulding can also be used (Omnexus, 2020a). Moreover, LLDPE sheets are physiologically harmless, making it the perfect material for food packaging and agricultural film, as shown in Figure 17.



Figure 17 Linear low-density polyethylene agricultural film (Mulch Film, 2020).

3.3.2 Main applications

LDPE and LLDPE together make 17.5% of the plastics demand in Europe, for a total of 8.96 million tonnes (PlasticsEurope, 2019). Assuming the ratio is the same in The Netherlands, the volume of LDPE and LLDPE would be equal to 385,000 tonnes. Considering a price of 1.01 \notin /kg for LLDPE (PlasticPortal, 2020), the Dutch market would be worth around 390 million euros per year.

LLDPE is used especially in the packaging sector (single use food film, reusable bags and containers) and agriculture sector (single use agricultural film), with marginal use in the building and construction sector (PlasticsEurope, 2019). The shares of LLDPE in each sector are shown in Figure 18.



Figure 18 Thousands of LDPE/LLDPE tons used by the main economic sectors in The Netherlands. Made with estimates from European data extracted from *(PlasticsEurope, 2019)*.

3.4 High-Density Polyethylene

3.4.1 Product characteristics

High-density polyethylene (HDPE) is a flexible and translucent plastic with excellent resistance to electricity and solvents, and good resistance to heat, alcohols, dilute acids and alkalis (Omnexus, 2020a). Table 16 shows an overview the main physical properties.

Table 16 Density, tensile yield strength, shore hardness and maximum continuousservice temperature (CST) of high-density polyethylene (Omnexus, 2020b).

Density	Tensile yield	Shore hardness	Max CST
(g/cm³)	strength (MPa)	(D scale)	(°C)
0.94-0.97	25-30	60-70	100-120

HDPE is usually processed by injection moulding, extrusion, roto-moulding, and blow moulding. This grade of PE is heavier, sturdier, harder and can resist to higher temperatures than both LDPE and LLDPE, making it suitable for rigid packaging, household and consumer goods, fibres, textiles, pipes and fittings (Omnexus, 2020a). Practical applications of HDPE are shown in Figure 19 and Figure 20.



Figure 19 Example of blow moulded high-density polyethylene bottles (*Indiamart, 2020*).



Figure 20 Example of high-density polyethylene corrosion resistant pipes (*Acme Plastics, 2020***).**

3.4.2 Main applications

HDPE makes 12.2% of the plastics demand in Europe, for a total of 6.25 million tonnes (PlasticsEurope, 2019). Assuming the ratio is the same in The Netherlands, the volume of HDPE would be equal to 268,400 tonnes. Considering a price range between 1.05 and 1.08 €/kg (PlasticPortal, 2020), the Dutch market would be worth 280-290 million euros per year.

HDPE is used especially in the packaging sector (milk bottles and shampoo bottles), for houseware and toys, and in the building and construction sector to make pipes (PlasticsEurope, 2019). The shares of HDPE in each sector are shown in Figure 21.



Figure 21 Thousands of HDPE tons used by the main economic sectors in The Netherlands. Made with estimates from European data extracted from (PlasticsEurope, 2019).

3.5 Polypropylene

3.5.1 Product characteristics

Polypropylene (PP) is a semi-rigid and translucent plastic with high resistance to heat, fatigue, electricity and chemicals like alcohols, acids, alkalis and oils (BPF, 2020). These properties can be altered by adding additives or by changing the share of co-monomers during the polymerisation process, making PP a very versatile material with a vast range of applications. The PP homopolymer contains only propylene and is a general purpose grade plastic, while the PP Random Copolymer features ethene units (up to 6% by mass) randomly incorporated into the polymer chain, making it very flexible and optically clear, and the PP Block Copolymer incorporates ethene (5-15% by mass) arranged in a regular pattern, making the polymer less brittle. Finally, the PP Impact Copolymer also incorporates randomly ethylene, reaching a share of 45-65% and thus making it lighter while providing a good resistance to impact (Omnexus, 2020c). Table 17 gives the overview of the main physical properties of PP.

Table 17 Density, tensile yield strength, shore hardness and maximum continuousservice temperature (CST) of polypropylene (Omnexus, 2020b).

Grade	Density (g/cm³)	Tensile yield strength (MPa)	Shore hardness (D scale)	Max CST (°C)
Homopolymer	0.90-0.91	35-40	70-83	100-130
Copolymer	0.90-0.91	20-35	70-80	100-130
Impact modified	0.88-0.91	11-28	45-55	90-115

Polypropylene is harder and more resistant to heat than most of polyethylene compounds. Moreover, the tensile strength of PP makes it the perfect material to manufacture living hinges, i.e. thin and flexible connections between two relatively rigid section, potentially being able to be flexed more than 900,000 times without breaking (MIT-Edu, 2020). A practical application of a PP living hinge can be seen in Figure 22.



Figure 22 Example of a polypropylene butterfly living hinge used on the dispensing cap of a ketchup bottle (*Davis, 2015*).

3.5.2 Main applications

PP makes 19.3% of the plastics demand in Europe, for a total of 9.88 million tonnes (PlasticsEurope, 2019). Assuming the ratio is the same in The Netherlands, the volume of PP would be equal to 424,600 tonnes. Considering a price range between 1.08 and 1.21 \in /kg (PlasticPortal, 2020), the Dutch market would be worth 450-510 million euros per year.

PP is used especially in the packaging sector for flexible packaging (e.g. snack wrappers, thin films for clothing and tobacco) and rigid packaging (e.g. stackable crates, detergent and condiments bottles), in the household sector for reusable items (e.g. microwave food containers, toys, and gardening tools), in the building and construction sector (e.g. pipes), and has many applications in the automotive sector (e.g. interiors and bumpers) (BPF, 2020; PlasticsEurope, 2019). The shares of PP in each sector are shown in Figure 23.



Figure 23 Thousands of PP tons used by the main economic sectors in The Netherlands. Made with estimates from European data extracted from *(PlasticsEurope, 2019)*.

4 Decarbonisation options for polyolefins

The plastics industry aims to reduce its emissions while maintaining economic growth, in line with the targets of the Dutch "*Klimaatakkoord*", which has the ambition of reducing the national GHG emissions by 49% in 2030 compared to 1990 levels, with the industrial sector alone reducing its emissions by 59% (Klimaat-akkoord, 2019). Naturally, many stakeholders have already investigated some of the possible solutions, and some of the problems have also been analysed in other countries with similar issues. Thus, this chapter include a review of reports from public and private organisations and research institutes, as well as scientific literature. Some of the current scenarios for the chemical industry are presented in the following list:

- VNCI, the Dutch association of chemical industry, analysed four possible decarbonisation pathways to 2050, each with a different focus: bio-based materials and circular economy, electrification and renewable energy, "clean" fossil with carbon capture and storage (CCS). Although the scope of the report is quite broad and not specific for the production of polyolefins such as PE and PP, it provides a good overview of the possible strategies to achieve deep decarbonisation in The Netherlands. The research also shows that it is technically possible to achieve a reduction of GHG emissions while keeping an annual growth rate of added value (VNCI, 2018).
- McKinsey, an international consultancy company, published a report on decarbonisation options for the industrial sectors, focusing on the sub-sectors of cement, iron and steel, ammonia, and ethylene. Although the research boundaries of the MIDDEN project are different and McKinsey's report is not specific for The Netherlands, the part regarding ethylene can provide some useful insights, with biobased feedstocks, zero-carbon fuel sources and CCS as the most suggested solutions (McKinsey&Company, 2018).
- JRC, the European Commission's institute for science and knowledge, analysed costeffective technological improvements and perspective scenarios for the European chemical and petrochemical industries. Even though polyolefins are not among the products analysed, the methodology and models present in the report can serve as inspiration when dealing with decarbonisation options for PE and PP. Moreover, the research suggests combined heat and power (CHP) and CCS as the most viable cross-cutting technologies (Boulamanti & Moya Rivera, 2018).

This chapter is structured according to the MIDDEN framework for decarbonisation options shown in Figure 24. The next sections follow the same order and describe the options one by one.



Figure 24 MIDDEN project framework for decarbonisation options.

In order, the measures analysed are:

- Fuel substitution, i.e. the substitution of the currently fossil energy supply with more sustainable sources such as biogas, renewable electricity, hydrogen, geothermal heat, and recycled heat.
- 2) **Feedstock substitution**, i.e. the substitution of the currently fossil raw materials with more sustainable options such as biomass, and other upstream material substitution.
- 3) Process design, e.g. energy efficiency improvements of the current production processes (on top of the baseline efficiency improvement, which is around 0.5% annually), and substitution production processes based on different fuel, feedstock, or innovative technologies.
- 4) **Recycling,** i.e. mechanical and/or chemical treatment of the plastic waste in order to reintroduce the materials in the feedstock mix.
- 5) **Product design,** e.g. measures to reduce the use of the product and/or to replace with a more sustainable product requiring less energy and materials.
- 6) **Use of residual energy,** i.e. the recovery of the waste heat resulted from the production processes, both inside the company or from external sources.
- Carbon Capture and Storage (CCS) or re-Use (CCU): capture of the CO₂ emissions and storage processes, or alternative uses of the captured carbon.

Considering the scope and research boundaries of this MIDDEN project (as seen in the Introduction section of the report), only the decarbonisation options in the **(2) Feedstock substitution** (i.e. bio-based polyolefins) and **(4) Recycling** (i.e. circular material flows) categories will be described in detail and analysed quantitively, while options **(1)**, **(3)**, **(5)**, **(6)**, and **(7)** will be only described and discussed briefly.

4.1 Fuel substitution

The key concept of this category of decarbonisation options is to produce the same amount of electricity and heat energy while emitting less GHGs than the current processes. However, the production of these utilities is not within the scope of this MIDDEN report, so the decarbonisation options in this category will only be discussed briefly and without performing a detailed quantitative analysis. For more information on e.g. electrification of the Dutch refinery sector see (Oliveira C. & Schure, 2020).

4.1.1 Biomass fuel for cogeneration (CHP)

As seen in Chapter 1, the electricity and steam required to produce polyolefins are usually generated by combined-heat-power (CHP) plants, which normally consist in natural gas-fired turbines paired with a steam boiler. To reduce the GHG emissions caused by the combustion of natural gas, the producers could choose to use bio-based fuels. As the amount of CO_2 absorbed by the vegetation during its growth is almost equal to the amount that is emitted when burning it, biomass is usually considered carbon neutral if the areas harvested are reforested (Sebastián, Royo, & Gómez, 2011). Direct-fired systems use wood chips or pellets with moisture content lower than 15% as direct fuel, while gasification systems adopt lowoxygen processes to convert the biomass into syngas, which is then burnt to activate the turbines (US EPA, 2007). Some case studies suggest that the payback period of bio-CHP is in the 5-11 years range (Ciric & Kuzmanovic, 2014), while the actual environmental performance depends on the supply chain, the type of biomass and the competition for soil with edible crops. However, in the best-case scenario the overall emissions can be ten times lower than when using natural gas (US EPA, 2007). Another option is the use of biogas produced from the anaerobic decomposition of organic wastes, such as domestic sewage or animal manure (Akbaş, Bilgen, & Turhan, 2015; Khanal, Tirta Nindhia, & Nitayavardhana, 2019). Generally speaking, cogeneration systems using biogas and natural gas have the same global efficiency (around 63%), while the financial performance depends on the local economy and national energy prices (Brizi et al., 2014). Provided that the biogas is precleaned to remove the hydrogen sulphide (H_2S) , which is corrosive for the thermal engine, biogas can be used without specific modifications of the cogeneration system (Ochoa Villa, Campos, Charamba Dutra, & Henriquez Guerrero, 2014). A possibility would also be to just mix the biogas with the natural gas, thus guaranteeing flexibility and stable supply of the fuel, but still reducing to some extent the CO_2 emissions from the power plant (Nikpey, Assadi, & Breuhaus, 2013).

4.1.2 Industrial Heat Pumps (IHPs) powered by renewable electricity

Heat pumps are active devices able to recover heat energy from a lower temperature reservoir and transfer it to a higher temperature space. The process is made possible by compressing and expanding a refrigerant substance similar to the ones used by fridges and air conditioners. The efficiency of a heat pump is indicated by the coefficient of performance (COP), which is the ratio between the thermal energy moved and the electricity used by the compressor (Bundschuh & Chen, 2014; HPT TCP, 2019). Currently, temperatures above 140 °C are only in special cases reached (IEA, IETS, & HPP, 2014), and this limits the applicability in the polyolefins production. Potential improvements include the combination of photovoltaic (PV) solar panels with the heat pump, in which the PV cells are laminated on the evaporator-collector plate. The solar energy is converted into both electricity and heat, which is absorbed by the refrigerant and carried over to the heat pump condenser. In this way, the PV efficiency is increased due to the lower temperature, and the COP of the heat pump is increased thanks to the absorption of the thermal energy (Pei, Ji, Han, & Fan, 2008). IHPs commonly have a COP ranging between 3 and 6, depending on design, application, weather, and coupling with PV systems (Chua, Chou, & Yang, 2010; Dikici & Akbulut, 2008; IETS TCP, 2014). Industrial Heat Pumps (IHPs) can recover the waste heat of an industrial process and increase its temperature to make it useful for an adjacent process, thus reducing the overall energy consumption and relative GHG emissions (J. Zhang, Zhang, He, & Tao, 2016). Although many heat pumps for residential and district heating can only reach temperatures around the 50-90°C range, there are now IHP systems able to supply heat at temperatures higher than 100°C (IETS TCP, 2014). Within polyolefins production, IHPs could be used to prepare the feedstock for polymerisation and to dry the resulting polymer. Especially for the

drying process, IHPs could be convenient thanks to their ability to control the gas temperature and humidity while extracting the latent heat of condensation (Chua et al., 2010), potentially consuming between 30 and 50% less energy than conventional steam drying cycles and adopting low GWP refrigerants like R-1234yf and R-744 (IETS TCP, 2014). The electricity required by IHPs could be supplied by PV systems installed on the rooftop of the industrial infrastructures and warehouses, which is considered a technically and economically feasible project by many studies (Anwari, Rashid, Hui, Yee, & Wee, 2011; Mao, Jin, Zhao, Chen, & Chang, 2013; Subrahmanyam, Sahoo, & Reddy, 2012), or be provided by utilities suppliers adopting renewable sources like wind power, which in 2018 generated more than 10 TWh of electricity in The Netherlands (IEA, 2020).

4.1.3 Hydrogen fuel (H₂)

Hydrogen has the potential to be a clean and renewable fuel used for transportation, industries, heating, and power generation, and in the last decades the industry has been rapidly growing (Gupta, 2008). Hydrogen is mainly produced through reformation of natural gas and coal, or from water splitting using electrolysis, thermolysis, or photo-electrolysis, and there are many other processes under development, although not all of them are economically competitive (Holladay, Hu, King, & Wang, 2009). For hydrogen to be a decarbonisation option it should be produced by using renewable energy sources. The rapid development of a hydrogen network is also in line with the national strategy of The Netherlands, since using hydrogen as energy carrier would allow the country to integrate more solar and wind in the national energy mix. The policy agenda is based on four main pillars: legislation and regulation, cost reduction and scaling up of green hydrogen, sustainability of final consumption, international partnerships and focus on research (Government of the Netherlands, 2020). The current market is currently equal to 0.8 Mt/year, but has the potential to grow tenfold by 2030, leading to a yearly emission reduction of 5 Mt of CO_2 (CE Delft, 2018). Looking at current and future projects in The Netherlands, the Port of Rotterdam is planning to invest 2 billion euros in the development of production infrastructures and related value chain to produce hydrogen to use as fuel, carrier, or raw material in industrial processes. The estimated production will be able to supply up to 20% of the heat and power required by the industries part of the Rotterdam Port, leading to a CO_2 emission reduction of 16% (Port of Rotterdam, 2020).

4.1.4 Recap of fuel substitution options

Table 18 summarises the most important characteristics of the decarbonisation options described in this section.

Table 18 Recap of fuel substitution decarbonisation options, namely biomass for cogeneration of heat and power, industrial heat pumps powered with renewable energy, and hydrogen fuel.

Indicator	Biomass for CHP	PV-powered IHPs	H ₂ fuel
Description	Cogeneration plant powered by biomass or biogas to produce heat and electricity for the industrial processes	Heat pumps powered by renewable electricity to convert waste heat and into high temperature heat	Hydrogen used as energy carrier, fuel, or raw material for the industrial processes
Potential emissions avoided	Biomass (with reforestation) technically causes net- zero emissions	IHPs and renewable sources (e.g. PV) can substitute natural gas for energy production	Hydrogen produced using renewable energy (e.g. wind) and from natural gas combined with CCS is a carbon-free fuel
Main	No change to	Self-sufficient system,	Versatile energy
advantages	infrastructures	zero emissions	carrier, it can use the existing gas network
Main flaws	Competition with other solutions requiring biomass	High initial investment Temperatures at polyolefins polymerisation process not reached yet	Economic cost of production process

4.2 Feedstock substitution to bio-based materials

The key concept of this category of decarbonisation options is to produce the same amount and quality of polyolefins while using more sustainable feedstock materials (e.g. bio-based ethylene and propylene), thus reducing the fossil-dependency and GHG emissions of the overall production. The share of bio-based polymers is growing at a faster rate than the overall polymer market, showing the interest of consumers and the increasing economic feasibility for producers (Aeschelmann & Carus, 2015). Although this category of options does not directly involve the polymerisation process, it is considered one of the most interesting ways to decarbonise the polyolefins industry and it will thus be investigated thoroughly, including a quantitative analysis of the economic indicators and the potential environmental benefits.

4.2.1 The difference between bio-based and biodegradable

Among the general public there is often confusion regarding the definition of bio-plastics, so before describing the available bio-based options for feedstock substitution it is useful to clarify the meaning of the terms. "Bio-based" means that the plastic product is made of raw materials that are directly or indirectly derived from plants, such as corn or cellulose. "Biodegradable" means that the material can be degraded by microorganisms into natural substances, such as water, carbon dioxide and compost (European Bioplastics, 2020; Molenveld, van den Oever, & Bos, 2015). The potential for biodegradation is linked to the chemical structure of the plastic product and not to the source of the material, so a fossil-based plastic may be biodegradable, and a bio-based plastic may be not.

Table 19 Biodegradation property of fossil-based and bio-based plastics. Made withinformation from (European Bioplastics, 2020; Molenveld et al., 2015).

	Fossil-based	Partly bio-based	Bio-based
Biodegradable	PBS(A), PBAT, PCL	Starch blends	PLA, PHA, PBS, cellophane
Not biodegradable	PE, PP, PET, PS, PVC	Bio-PET, Bio-PA	Bio-PE, Bio-PP

As seen in Table 19, even though bio-based PE and PP are not biodegradable, their characteristic of saving fossil resources, thus providing the potential for carbon neutrality, is enough to make them a very interesting solution for plastic producers looking for decarbonisation options.

4.2.2 Sugar-based bio-ethanol to bio-ethylene

The most established way to produce ethylene (and to some extent, propylene) from biobased sources is by dehydrating ethanol obtained through the fermentation of sugar-rich crops. The typical plant is the sugarcane, which grows mostly in Brazil (39% of the global production), India (20%), China, Thailand, Pakistan and Mexico (FAOSTAT, 2018). Braskem, the biggest chemical company in Brazil and the global leader of bio-ethanol and bio-plastics production, collects sugarcane from 65,000 hectares (about 0.2% of the total arable land in Brazil) to produce 200 kilo tonnes of bio-PE every year (Braskem, 2020). As seen in Figure 25, the typical first-generation biorefinery involves the extraction of the sugarcane juice and its fermentation using microorganisms (e.g. yeast, bacteria or moulds), followed by a distillation process to separate the ethanol. The leftover fibrous residue of the sugarcane, which is called bagasse, is burned in a cogeneration plant to supply the biorefinery processes and possibly produce surplus electricity (Braskem, 2020; Gotro, 2013).



Figure 25 Process steps of bio-ethylene production, including the amounts of sugarcane necessary to produce 1 kg of final product. Made with information from (*Braskem, 2017, 2020; Gotro, 2013; Machado, Walter, & Cunha, 2016*).

The dehydration process is an endothermic chemical reaction, and it is usually carried out by heating the ethanol to 300-500°C together with a catalyst (e.g. concentrated sulfuric acid or activated alumina) in a fluidised bed reactor, causing the separation of bio-ethylene and water (Mohsenzadeh, Zamani, & Taherzadeh, 2017; M. Zhang & Yu, 2013). Figure 26 shows the dehydration process, while the chemical reaction happening inside the reactor is $C_2H_5OH \rightarrow C_2H_4 + H_2O$.



4.2.3 Environmental performance of bio-PE

Although the production of bio-ethanol and the de-hydration into ethylene have an energy consumption comparable to the production of ethylene from naphtha cracking (Ghanta, Fahey, & Subramaniam, 2014), the absorption of CO_2 during the growth of the crops makes bio-based polyethylene (bio-PE) significantly better than his fossil counterpart when fighting climate change. Moreover, most of the energy necessary for the fermentation and distillation of the bio-ethanol can be produced through on-site cogeneration using the sugarcane bagasse as fuel, thus making the production process less reliant on fossil fuels (Machado et al., 2016). The cradle-to-gate life-cycle analysis (LCA) of bio-ethylene, starting from the cultivation of sugarcane and ending after the polymerisation process, shows that the overall process is a net-absorber of greenhouse gases, removing 3.09 kg of CO₂-eg for every kg of PE produced (Braskem, 2017). As the LCA does not cover that gate-to-grave cycle of the plastics, the CO₂ released when the plastic waste is burned for energy recovery (a common process in many European countries), is not considered. Would that be included, then 3.14 kg of CO₂- would be released in the atmosphere for every kg of PE incinerated, thus yielding an almost net zero carbon balance. Another LCA presents a significantly smaller value, having calculated that every kg of PE produced from bio-based sources causes the net absorption of 0.75 kg of CO_2 -eq from the atmosphere (Tsiropoulos et al., 2015). Even though the exact carbon balance of bio-PE varies from case to case, the benefit is still clear, especially when considering that each kg of fossil-based PE causes the emission of around 1.86 kg of CO₂-eq from cradle to gate (PlasticsEurope, 2014b).

Finally, one study shows that when considering the whole cradle-to-grave life cycle, each kg of bio-ethanol used as precursor for bio-PE has a net positive emission (1.3-2.0 kg of CO₂-eq), which in any case is around half of the emissions caused by its fossil-based counterpart (3.7 kg of CO₂-eq) (Muñoz et al., 2014). Seeing how great the impact of the materials end-life on GHG emissions is, it is extremely important to establish a circular economy system, which will be discussed in Section 4.4. Lastly, bio-PE has some major downsides compared to fossil-PE, namely high values of ozone and water depletion, land use, and terrestrial and aquatic eutrophication (Braskem, 2017), making necessary to evaluate the sustainability of each case and to carry out a multi-criteria environmental analysis assigning a weight to the different impacts on the local ecosystem and society. A comparison of fossil-based PE and bio-PE from sugarcane can be observed in Figure 27.



Figure 27 Comparison of the cradle-to-gate environmental impact of fossil-based PE and sugarcane-based PE. Normalised values extracted from (*Braskem, 2017***)**.

4.2.4 Conversion of bio-ethylene in bio-propylene

The bio-based ethylene can also undergo a commercial process involving dimerization and metathesis, in which the double bonds between carbon atoms are broken down and rearranged to form propylene (Chemical Engineering, 2013; Davie, Whan, & Kemball, 1972). The process is well established and requires low investments, resulting economically attractive whenever the price ration between propylene and ethylene is above 1.08, and allowing companies to balance the production of the two bio-based olefins according to the market demand (McDermott, 2020).

The chemical steps of dimerization, isomerization, and metathesis from ethylene to propylene are shown in Figure 28.



Figure 28 Dimerization and metathesis process to convert ethylene into propylene.

In 2012, Braskem announced its plan to build a production line able to produce 30 kt/year of bio-based polypropylene (Bio-Based News, 2012), but there is no recent news about the state of the project. Looking at alternative processes, the Japanese group Mitsui Chemical has recently been attempting to commercialize a new production method based on the fermentation of non-edible biomass materials to produce bio-isopropanol, which is then dehydrated to obtain bio-propylene. Compared to the traditional dimerization and metathesis process, this first-of-its-kind approach is said to have a better economic performance (Bio-Based News, 2019).

4.2.5 Competition with biofuels and food production

In Europe, the cultivation of sugarcane is not common, therefore 43% of the European bioethanol is produced from corn, 26% from wheat, 21% from sugar beet, and 10% from other sources like lignocellulosic residues (ePURE, 2020). More than 80% of the European bioethanol is blended with gasoline to produce biofuel (usually with a 5-10% share of ethanol), and the market is expected to rapidly grow in the next years (ePURE, 2020), potentially strongly competing with the bio-ethanol demand for bio-plastics production. A Japanese study calculated that the added value and GHG reduction of using bio-ethanol for bio-plastics production is greater than when bio-ethanol is used as fuel (Kikuchi, Oshita, Mayumi, & Hirao, 2017), while an American study calculated that the GHG reduction achieved are indeed the same, but the economic potential is better when the bio-ethanol is used as a substitute for gasoline (McKechnie, Pourbafrani, Saville, & MacLean, 2015). Finally, according to a European study, the use of sugar beet to produce bio-ethanol and then bio-PE in Europe is considered at least as economically convenient as producing ethylene from fossil sources, with a margin of uncertainty of $\pm 10\%$ due to the price volatility of the feedstocks (Posada et al., 2013). It is thus difficult to clearly evaluate the economic convenience of investing in bio-PE, but all the studies agree that scaling-up the production would have positive effects and make the production of bio-plastics more financially attractive.

In The Netherlands, sugar beet cultivation has a very high yield and it is thus possible to produce 7,200 litres of bio-ethanol for each hectare, which is the same value obtained by Brazilian sugar cane (Langeveld, Van De Ven, De Vries, Van Den Brink, & De Visser, 2014). The energy intensity in The Netherlands, however, is way higher: while sugar cane has a net energy balance ratio of 8, the Dutch sugar beet only reaches 1.3, although it could be improved up to 2.8 by using CHP systems for the distillation and reducing the amount of fertilizers used for the crops (Langeveld et al., 2014). Since the production of bio-ethanol only requires the sugar component of the beet, the remaining part can be used as animal feed: for every litre of bio-ethanol, the fermentation process also produces almost 1 kg of co-products (Dammer et al., 2017). According to this data, it would be possible to produce from one hectare of sugar beet 3 tonnes of bio-PE and 7 tonnes of animal feed. In that sense, bio-ethanol production can make a positive contribution and may not hamper the food and feed security (Dammer et al., 2017). Some research even shows that a fair supply chain for bio-plastics may stabilize food prices and provide an additional income to farmers, thus making food production more profitable (Van Den Oever, Molenveld, Van Der Zee, & Bos, 2017).

If Dow Terneuzen and SABIC Limburg were to completely substitute their current production of 1,840 kt/year of fossil-based PE with its bio-based counterpart, the required bio-ethanol would be equal to 4 billion litres. If all of it was to be produced from sugar beets grown in The Netherlands, that would require around 613,000 hectares of land, which is over 7 times more than the current area and is equal to 59% of the arable land in the country (FAOSTAT, 2018). Apart from being unrealistic about this large claim on agricultural land, many studies show that the import of the required 4 billion litres of bio-ethanol from other countries (e.g. Brazil) would be economically more convenient (Althoff et al., 2013).

4.2.6 Biomass gasification and methanol-to-olefins (MTO) conversion

As an alternative to the biochemical route involving fermentation and distillation, bio-based ethylene and propylene can also be produced with a thermochemical process. As seen in Figure 29, the process starts with the gasification of lignocellulosic biomass (e.g. wood chips) or bio-waste (e.g. forest and agricultural residues, or by-products of the paper industry), although the feedstock may need to be pre-treated to reduce the amount of moisture and increase the energy density (Nouri & Tillman, 2005). Gasification is the incomplete combustion (or partial oxidation) of the biomass feedstock in order to break down the molecules and produce a mix of syngas, char, and tars. If catalysts are used, the reaction takes place at 750-900°C (De-León Almaraz & Azzaro-Pantel, 2017), otherwise the temperature needs to be in the 1200-1500°C range (Ragaert, Delva, & Van Geem, 2017). The unreformed syngas and biomass chars are combusted to supply heat to the gasification reactor, while the tars are reformed into useful syngas using a catalytic reaction (Foust, Aden, Dutta, & Phillips, 2009). The resulting syngas needs to be cleaned and conditioned to remove acid gases and impurities, before being compressed and sent to the methanol synthesis reactor (Brachi et al., 2014). Quite often, the syngas needs to undergo a water-gas shift (WGS) reaction to maximize the hydrogen content (Speight, 2019). The conversion reaction is facilitated by a commercial methanol catalyst, ensuring a selectivity of 99.8% (Xiang et al., 2015).



Figure 29 Steps of the gasification process of biomass into methanol. Made with information from (*Brachi et al., 2014; De-León Almaraz & Azzaro-Pantel, 2017; Ragaert et al., 2017*).

Methanol (CH₃OH) is the simplest chemical in the alcohol category and it can be used as precursor to other chemicals, or as fuel for transportation and energy production (Shamsul, Kamarudin, Rahman, & Kofli, 2014). Methanol-To-Olefins (MTO) is a well-known conversion process, whose chemical reactions have been studied for more than two decades (Nouri & Tillman, 2005). As seen in Figure 30, the bio-methanol faces a catalytic conversion in a fluidised-bed reactor at 350°C and 30 bar (Ragaert et al., 2017), often coupled with a catalyst regenerator. The resulting gaseous product is sent to a purification unit to separate the olefins, with a final yield of 49-55% for ethylene and 25-33% for propylene (Xiang et al., 2015).



Figure 30 Methanol-to-olefins (MTO) process (Xiang et al., 2015).

Overall, the production of 1 kg of light olefins requires the input of 4 kg of biomass feedstock and 8 MJ of energy, which is used mainly for the gasification process (Xiang et al., 2015). In comparison, the production of ethylene and propylene from naphtha cracking consumes around 16 MJ of primary energy (PlasticsEurope, 2012), so it could be assumed that the carbon emissions of bio-based ethylene are also halved compared to fossil-based ethylene. Although gasification and MTO conversion follow a production route that is quite different from the fermentation and dehydration of bio-ethanol, the production of bio-polyolefins using thermochemical and biochemical process seem to have very comparable cost, respectively 1.22 and 1.33 USD/l¹ and environmental impacts (Foust et al., 2009). Considering that they require two different types of biomass feedstock, they complement well each other, and both have the potential to make a positive contribution for the Dutch decarbonization strategy.

4.2.7 Current and future bio-plastics projects in The Netherlands

This section provides a brief overview of the projects regarding bio-based plastics under development in The Netherlands:

- The Chemelot Industrial Park has developed many bio-based chemistry processes, including the production of polymers from lignin (i.e. woody) biomass (Brightlands, 2020). The production of bio-plastics from biomass and bio-waste is an important part of Chemelot decarbonisation strategy for 2050 (Chemelot, 2020).
- Dow Terneuzen announced a partnership with the Finnish biorefinery UPM, which produces renewable naphtha from residues of paper pulp production. The feedstock is called BioVerno and can be used by Dow Terneuzen to produce bio-based LDPE, potentially cutting in half the emissions of CO₂ compared to the standard fossil-based process (Dow, 2019a). The production of bio-ethanol from lignocellulosic materials is made more difficult because the lignin molecules create a barrier around the cellulose, thus making necessary to pre-treat the feedstock with a physicochemical process. The cellulose is then hydrolysed into simple sugars, and finally fermented and distilled just like the bio-ethanol obtained from sugarcane and sugar beet (Mohsenzadeh et al., 2017).
- Borealis, a company with its roots in Scandinavia has been a provider of polyolefins, base chemicals, and fertilizers announced in 2019 a cooperation with the Finnish company Neste, which produces renewable propane from a mix of residue oils and other fat waste streams (Borealis, 2019). The propane will be produced in Neste's

¹ 2007 price level.

facilities in the Rotterdam Port industrial cluster, and then dehydrogenated into propylene in Borealis' Belgian plant of Beringen, where it will be used for the polymerisation of bio-based PP (BioPlastic Magazine, 2019). The production of bio-propanol uses Neste's proprietary technology NEXBTL to process animal fat waste, used cooking oil (UCO), and other fat residues (e.g. from palm oil production), but the company is also looking for ways to use plastic waste as feedstock (Neste, 2020).

 SABIC announced its intention to create a co-continuous blend of PE and thermoplastic starch to obtain a packaging film resistant against both oxygen and water. The inclusion of the bio-polymer, produced from potatoes, improves the carbon balance of the plastics, and is especially suited for printable multilayer films. The company also announced its plan to produce bio-PE and bio-PP with bio-based feedstock produced from waste oils and other biomass not in competition with the food chain (Vachon, 2019).

4.2.8 Economic and environmental indicators

Using data from (Oliveira, Rochedo, Bhardwaj, Worrell, & Szklo, 2020) adjusted for the European market, Table 20 presents a comparison between the standard production of naphtha-based ethylene using steam crackers, the production of sugar-based bio-ethylene through fermentation, and the production of methanol-based ethylene from the gasification of biowaste. As the production of bio-based ethylene is more expensive than when using naphtha crackers, a price on carbon emissions is necessary to make the process convenient. It is assumed that 40% of the PE gets recycled at the end of its life, thus keeping the carbon sequestered from the atmosphere. In The Netherlands, 32% of the plastics is already recycled, and the share will most likely increase in the next years thanks to improvements in mechanical and chemical recycling processes. In addition, the "*cheap feedstock"* case is made using the price of Brazilian ethanol, which is roughly 50% cheaper than the European one (GlobalPetrolPrices, 2020).

Table 20 Economic indicators and break-even carbon price necessary to make the production of bio-ethylene as economically convenient as its naphtha-based counterpart. Based on data from *(Oliveira et al., 2020)* adjusted for the European market.

Indicator	Naphtha steam crackers	Bio-ethanol from sugar beets	Bio-methanol from bio-waste
Levelized costs (k€ ₂₀₁₇ /t ethylene)	1.07	1.67	1.79
GHG emissions (tCO ₂ -eq/t ethylene)	1.02	-1.09	-0.84
Break-even carbon price (\in_{2017} / tCO ₂)	baseline	286	389
Break-even carbon price (\in_{2017} / tCO ₂) cheap feedstock	baseline	126	191

To summarise, the production of bio-PE and bio-PP from ethanol or methanol is certainly one of the most promising options to decarbonise the Dutch plastic sector. The implementation of a large-scale supply chain for bio-based polymers, however, would require a joint effort from both companies and governments. From a technological and logistical point of view, the conversion technology for lignocellulosic materials must improve, and the production of sucrose or starchy crops needs to be expanded without competing with food production

(Broeren, 2013). Furthermore, European and Dutch policies need to change to improve the business case for bio-based alternatives compared to fossil products. Other measures beneficial for bio-plastics would include the incentive schemes and the removal of tariffs on imported bio-ethanol (IRENA, 2013). The combination of all these measures could make bio-based PE and PP as convenient as their fossil-based counterparts, facilitating the development of sustainable production facilities by the chemical companies and the achievement of the national and European decarbonisation targets.

4.3 Process design

Although this category of decarbonisation options fits with the research scope and boundaries, the lack of commercial options and publicly available data led to the choice of shifting the focus to large scale options (namely bio-based polymers and recycling processes). This section will thus only provide a brief description of process design improvements and list a few practical examples.

The key concept of process design improvements is to change the manufacturing process of polymers to reduce the energy consumption and GHG emissions, while at the same time preserving the productivity and quality of the products. Examples of technologies and processes that could help to achieve this goal are:

- Design optimisation (e.g. reduced leakage) and energy efficiency improvements (e.g. power factor) for the industrial compressors used during the polymerisation process (Ekradi & Madadi, 2020; Hu, Wang, & Huang, 2019; Mascarenhas, Chowdhury, Thirugnanasambandam, Chowdhury, & Saidur, 2019).
- Use of better catalysts to lower the temperature and pressure requirements for the polymerization process and increase the copolymerisation performance (Zhu, Guo, Cen, & Mao, 2011).
- Renewal of existing process parts, integration of multi-functional equipment, and superstructure design optimization (Harmsen, 2004).
- Better heat recovery and integration of processes, for example using the Industrial Heat Pumps (IHPs) described in Section 4.1.2.

Even minor improvements in energy efficiency could have significant impacts over time. It is estimated that the total primary energy losses related to the production of polyolefins in Western Europe are exceeding 100 PJ for PE and 50 PJ for PP (Neelis, Patel, Blok, Haije, & Bach, 2007). To have a better understanding of the value, if even only one third of this energy could be used in a productive way, then Dow, SABIC and Ducor could all triplicate their production of polyolefins.

4.4 Recycling

The key concept of this category of decarbonisation options is to produce the same amount of polyolefins while using more sustainable feedstock materials (recovered monomers or polymers), thus reducing the need for virgin materials, and the overall GHG emissions. Although this does not directly involve the polymerisation process, it is considered one of the most interesting ways to decarbonise the polyolefins industry and it will thus be investigated

thoroughly, including a quantitative analysis of the economic indicators and the potential environmental benefits.

As seen in Figure 31, the main technological processes for the end-of-life management of the post-consumer plastic waste are mechanical recycling, feedstock recycling (also called chemical recycling), incineration (possibly with energy recovery), and landfill. After a brief description of mechanical recycling technologies, this section will focus on innovative chemical recycling process able to increase the share of recycled plastic waste.



Figure 31 Possible treatments for plastic waste, in order of priority from highest (mechanical recycling) to lowest (landfill). Made with information from (*Al-Salem, Antelava, Constantinou, Manos, & Dutta, 2017; Rigamonti et al., 2014*).

Mechanical and chemical recycling are the two only options that allow for the recovery of the material and its re-inclusion in the circular economy cycle and are thus the preferable technologies for the treatment of plastic waste. Moreover, other options such as incineration and landfill have a significantly higher environmental impact (Lazarevic, Aoustin, Buclet, & Brandt, 2010; Rigamonti et al., 2014). In The Netherlands, the annual demand for plastics is equal to 2.2 million tonnes, and around 32% of the post-consumer plastic waste is mechanically recycled, while the remaining part is incinerated in energy recovery plants (PlasticsEurope, 2019).

4.4.1 Mechanical recycling

Mechanical recycling is the most common method for the material recovery of plastic waste, although it requires the waste to be sorted and divided in single-polymer plastics (Al-Salem, Lettieri, & Baeyens, 2009). As seen in Figure 32, after the collection of the plastic waste the process starts with the separation of the plastic products based on chemical composition, density, colour, size and shape. The waste is then washed to remove contamination (often organic e.g. food waste, or chemical e.g. glue and labels), grinded into flakes, and finally milled and compounded into pellets and granules (Ragaert et al., 2017; Singh et al., 2017).



Figure 32 Mechanical recycling process. Made with information from (*Al-Salem et al., 2009; Ragaert et al., 2017; Singh et al., 2017*).

Sorting and separating the different polymers are the most delicate steps of the mechanical recycling process, and can be done by a combination of FT-NIR (Fourier Transform Near Infrared), optical colour recognition, a ballistic separator, float-sink techniques, and manual sorting by trained operators (Ragaert et al., 2017). Other possible sorting methods are triboelectric, X-rays, and high-speed separation (Al-Salem et al., 2009). The carbon footprint of mechanical recycling has been assessed to be equal to -0.5 kg of CO₂-eq/kg input waste, compared to the production of virgin plastics for naphtha crackers (Bergsma & Broeren, 2019; Martijn Broeren, Lindgreen, & Bergsma, 2019). From a life cycle perspective, mechanical recycling is thus the preferred option to manage plastic waste, provided that the plastic stream is well defined, there is little organic contamination and the substitution ratio with virgin plastics is close to 1:1. For hard-to-recycle plastic waste, feedstock recycling becomes the preferable option (Lazarevic et al., 2010).

4.4.2 Solvent-based purification

Solvent-based purification, also known as dissolution, is a chemical recycling process able to recover high-quality polymers and separate them from additives and impurities. Although the method could technically be applied to mixed plastic waste, current setups are only able to handle homogeneous flows of polymers (Zero Waste Europe, 2019). When talking about polyolefins, however, an experiment involving the solvent-based purification process of a 50/50 mix of PE and PP has been proved successful, with a recovery rate of 99% for both polymers (Pappa et al., 2001). If the plastic waste contains a mix of LDPE, HDPE, PP, PS, and PVC, a preliminary separation by floatation in water is necessary to separate the polyolefins from the heavier polymers (PS and PVC) before processing them with solvent-based recycling (Pappa et al., 2001). The potential carbon footprint of dissolution for polyolefins can be estimated by taking that for the dissolution of PET-PE packaging materials, there the nett footprint is approximately -1.0 kg CO₂-eq./ton plastic packaging waste (Vollmer et al., 2020).

As seen in Figure 33, the process starts by cutting the polyolefins and cleaning them to remove organic contaminants. The polymers are then dissolved with a solvent (S) and filtrated to remove the unsolved particles (e.g. other polymers or impurities), then precipitated using an anti-solvent (AS), filtered from the A/AS liquid, washed and dried (Pappa et al., 2001). The solvent and anti-solvent are separated by distillation and re-used in the next cycle. For the chemical recycling of PE and PP, the most common selective solvent is xylene, while propanol, ACE or n-hexane can be used as anti-solvent for the precipitation step (Zhao, Lv, & Ni, 2018).



Figure 33 Solvent-based purification process. Made with information from (*Pappa et al., 2001; Zero Waste Europe, 2019; Zhao et al., 2018*).

The main advantage of the solvent-based purification is that it removes all the additives and unsolvable contaminants, resulting in recycled polymers with properties comparable to virgin products. On the long term, however, the stress generated by the process may affect the quality of the polymers, meaning that solvent-based purification cannot be used as perpetual chemical recycling method (Zero Waste Europe, 2019). Other disadvantages are the relatively high technical requirements and costs (Zhao et al., 2018), so improvements in the process could be necessary to facilitate the deployment of this technology on a national-scale level in The Netherlands. One example of solvent-based PE and PP recycling process at the industrial level is the APK chemical recycling plant, located in Germany and active since 2018 (APK AG, 2020). Outside of Europe, Unilever has co-developed a solvent-based process designed to recycle sachets and since 2018, it has been operating a pilot plant in Indonesia with a capacity of 3 tonnes/day, with the ambition of developing a 30 tonnes/day commercial plant as soon as possible (Unilever, 2020). An factor that could make chemical recycling a better choice than mechanical recycling is the thermal-mechanical degradation faced by the polymers during the shearing and melting processes during mechanical recycling (Ragaert et al., 2017).

4.4.3 Thermo-chemical recycling with pyrolysis

Pyrolysis is the thermal conversion process at elevated temperatures in the absence of oxygen that allows the recovery of the monomers from the polymer plastics waste (Ray & Thorpe, 2007). Its advantage is that, unlike mechanical recycling, it can handle highly heterogeneous mixtures of plastics, such as the modern multi-layer packaging materials (Ragaert et al., 2017). A variety of researchers have demonstrated the feasibility of the pyrolysis of plastic waste composed by a mix of PE, PP and PS (Demirbas, 2004; Donaj, Kaminsky, Buzeto, & Yang, 2012; Kaminsky, Schlesselmann, & Simon, 1996), although PET and PVC need to be separated and removed to guarantee the quality of the final product (Sharuddin, Abnisa, Wan Daud, & Aroua, 2016). The usual pyrolysis product is a hydrocarbon liquid called pyrolysis oil, which can be used as a heavy fuel oil substitute (Fivga & Dimitriou, 2018). However, if the process reaches high-temperatures (650-850°C), secondary cracking of the gas phase occurs, resulting in the production of a wide spectrum of smaller hydrocarbons (Ray & Thorpe, 2007). This allows pyrolysis to directly produce ethylene and propylene, thus avoiding the need to run the pyrolysis oil into the steam crackers. Since the pyrolysis process requires high energy, using catalysts to reduce the optimal temperature helps reducing the overall cost, and it also improves the production of olefins. The most common catalysts used in plastic pyrolysis are zeolites, FCC, and silica alumina catalysts (Sharuddin et al., 2016).

As seen in Figure 34, the process starts with the pre-treatment of the mixed plastic waste, which usually consists just in the shredding of the polymers to a size of 1-5 mm (Donaj et al., 2012). As explained before, it is extremely important to use only polyolefins as feedstock, thus excluding PET and PVC (Sharuddin et al., 2016). The pyrolysis reaction takes place in a fluidised bed reactor and the products are then separated, with some of the by-products (e.g. methane) being combusted to supply the heat to the pyrolysis reactor (Fivga & Dimitriou, 2018). The resulting ethylene and propylene can then be sent to the PE and PP polymerisation processes described in Section 2 of this report.



Figure 34 Pyrolysis process. Made with information from (*Donaj et al., 2012; Ray & Thorpe, 2007*).

The pyrolysis of polyethylene to produce lower olefins has been tested since more than two decades: experiments have shown that LDPE can be chemically recycled in a fluidized bed reactor, obtaining a max yield of 27% for ethylene gas and 19% for propylene gas with a temperature of 700°C. When considering also the production of methane and other by-products, the overall yield reached 73% (Williams & Williams, 1999). The pyrolysis of HDPE in a fluidized bed reactor has also been proven successful, obtaining a max yield of 42% for ethylene gas and an overall yield of 86% with a temperature of 780°C and residence time of 1.34 seconds (Mastral, Esperanza, Garciía, & Juste, 2002). Dozens of studies also investigate the pyrolysis of plastic waste in combination with biomass, reporting that the thermal conversion is facilitated, and the yield is higher than the sum of the two independent processes (Xue, Zhou, Brown, Kelkar, & Bai, 2015). Some economic indicators for a commercial pyrolysis plant are given in Table 21.

Table 21 Comparison of the economic indicators for a pyrolysis plant with a
capacity of 100 kg/h, 1,000 kg/h, and 10,000 kg/h (Fivga & Dimitriou, 2018).
Values adjusted for inflation.

Indicator	Capacity of 100 kg/h	Capacity of 1,000 kg/h	Capacity of 10,000 kg/h
CAPEX [M€ ₂₀₂₀]	1.24	3.84	11.7
OPEX [M€ ₂₀₂₀ /year]	0.53	1.50	2.76
Payoff period [years]	Never	3.6	1.2
NPV in 20 years [M€ ₂₀₂₀]	-1.4	13	220
Additional comments	Negative revenue	Economically convenient	Lowest cost per unit

From an environmental point of view, using pyrolysis to recover ethylene and propylene from plastic waste reduces the need to produce them from virgin oil and natural gas, thus reducing the emissions of carbon monoxide and CO₂ (Al-Salem et al., 2017). Recent simulations based on LCA studies estimate a reduction of 0.33 kg of CO₂-eq for each kg of PE and PP recycled through pyrolysis, compared to the reference emissions caused by the production of virgin material from naphtha cracking (*Internal communication with Mark Roelands, TNO*). The result is the same range of another analysis, which found out an emissions reduction up to 0.20 kg of CO₂-eq/kg input waste (Martijn Broeren et al., 2019). Today, pyrolysis is mainly applied to produce crude diesel for power plants or ship fuel, making policy intervention a necessary step to ensure that the technology is used to close the plastic-to-plastic loop instead (Zero Waste Europe, 2019).

4.4.4 Plastic waste gasification and methanol-to-olefins (MTO) conversion

As seen in Section 4.2.6, lignocellulosic materials and biowaste can be gasified into syngas, which is then converted into methanol and then into olefins. The same process can be applied to hard-to-recycle plastic waste and municipal solid waste (MSW), thus increasing the circularity of the polymers supply chain (Arena, Di Gregorio, Amorese, & Mastellone, 2011). As seen in Figure 35, the process starts with the gasification of the plastic waste, although the feedstock may need to be pre-treated to reduce the amount of moisture and increase the energy density (Nouri & Tillman, 2005). Gasification is the incomplete combustion (or partial oxidation) of the feedstock in order to break down the molecules and produce a mix of syngas, char, and tars. If catalysts are used, the reaction takes place at 750-900°C (De-León Almaraz & Azzaro-Pantel, 2017), otherwise the temperature needs to be in the 1200-1500°C range (Ragaert et al., 2017). When MSW is included in the feedstock mix, the optimal temperature for catalytic gasification seems to be 900°C in order to minimize the amount of tars produced (Guan, Luo, Liu, Xiao, & Cai, 2009). The unreformed syngas and carbon chars are combusted to supply heat to the gasification reactor, while the tars are reformed into useful syngas using a catalytic reaction (Foust et al., 2009). The resulting syngas needs to be cleaned and conditioned to remove acid gases and impurities, before being compressed and sent to the methanol synthesis reactor (Brachi et al., 2014). Quite often, the syngas needs to undergo a water-gas shift (WGS) reaction to maximize the hydrogen content (Speight, 2019). The conversion reaction is facilitated by a commercial methanol catalyst, ensuring a selectivity of 99.8% (Xiang et al., 2015).



Figure 35 Gasification of plastic waste into methanol. Made with information from (Brachi et al., 2014; De-León Almaraz & Azzaro-Pantel, 2017; Ragaert et al., 2017).

Methanol (CH₃OH) is the simplest chemical in the alcohol category and it can be used as precursor to other chemicals, or as fuel for transportation and energy production (Shamsul et al., 2014). Methanol-To-Olefins (MTO) is a well-known conversion process, whose chemical reactions have been studied for more than two decades (Nouri & Tillman, 2005). As seen in Figure 36, the bio-methanol faces a catalytic conversion in a fluidised-bed reactor at 350°C and 30 bar (Ragaert et al., 2017), often coupled with a catalyst regenerator. The resulting gaseous product is sent to a purification unit to separate the olefins, with a final yield of 49-55% for ethylene and 25-33% for propylene (Xiang et al., 2015).





Many studies investigate the possibility of combining biomass and plastic waste as feedstock in order to achieve a better performance of the system. When polymeric waste (in quantities exceeding 20% of mass share) is co-processed with biomass, the resulting syngas has such quality that does not require the WGS conditioning to become suitable for methanol synthesis, thus simplifying the system configuration and reducing the projected costs (Brachi et al., 2014). Another successful syngas process managed to achieve 98% of energy conversion when mixing 60% of PE plastic waste with wood waste in the form of pine chips (Pinto et al., 2002). Promising results have been obtained also when using a mix of polyethylene waste and biomass in a 0.3 mass ratio (Moghadam et al., 2014). In conclusion, gasification of plastic waste (potentially in combination with biomass) seems to be the most promising technology to process hard-to-recycle plastic waste, reducing the need for virgin plastics and increasing the share of recovered carbon content, potentially leading to emissions reduction up to -0.25 kg CO₂-eq/kg input (Martijn Broeren et al., 2019).

4.4.5 Current and future recycling projects in The Netherlands

This section provides a brief overview of the projects regarding chemical recycling of plastic waste under development in The Netherlands:

- Recycling is already one of the most interesting options for plastics producers in The Netherlands, and both mechanic and chemical recycling are included in the circular economy strategy of the Rotterdam Port, the biggest industrial cluster of the country (Port of Rotterdam, 2019b).
- Dow Terneuzen announced a partnership with the Dutch company Fuenix Ecogy Group for the supply of pyrolysis oil, which will be used by Dow to produce new polymers. The collaboration will help Dow Terneuzen in its goal to produce at least 100 ktonnes of recycled plastics (around 9% of their current LDPE and PP production) by 2025 (Dow, 2019b).

- SABIC started a collaboration with Renewi and Plastic Energy to realize a chemical recycling plant in the Chemelot site to process low-quality mixed plastic waste to use as feedstock for their steam crackers. The plant will use pyrolysis technology to convert the plastic waste into feedstock, thus reducing both the flow of low-quality waste to incineration and the demand for fossil naphtha. The project is expected to be operational by 2021, helping SABIC in its goal to process 200 kt/year of recycled plastics by 2025 (Chemelot, 2018; Renewi, 2018).
- 'Pyrolyseproeftuin Moerdijk' is a pyrolysis project in the Southern part of The Netherlands supported by various private and public parties. Among other experimental projects, the company Teknow Systems developed a pilot set-up for the recycling of plastic waste (Recycling Netherlands, 2019).

4.4.6 Economic and environmental indicators

The chemical recycling industry is still at its infancy and still needs further research. Most pyrolysis and gasification plants for the treatment of plastic waste are in a pilot stage and the deployment of these technologies on a commercial scale can only be expected after 2025. It is thus very difficult to show precise values regarding the economic and environmental indicators of these recycling technologies. Table 22 shows the available data, collected from multiple sources.

Table 22 Costs of the mechanical (*Gradus, Nillesen, Dijkgraaf, & van Koppen, 2017*) and chemical recycling options (*Fivga & Dimitriou, 2018*) and CO₂ emissions reduction compared to the production of virgin material from naphtha crackers (*Ligthart, Vroonhof, & Horssen, 2019; Martijn Broeren et al., 2019*).

Indicator	Mechanical	Solvent-based	Pyrolysis	Gasification
Costs (€ ₂₀₂₀ /t input waste)	677 ¹	n.a.	330 ²	n.a.
GHG emissions reduction (tCO ₂ -eq/t input waste)	-0.50	≈-1.0.	-0.20	-0.25

¹ For mechanical recycling these costs include collection and transport costs and nettreatment costs.

² For pyrolysis the capital, utilities and operating costs are included.

4.5 Product design

As seen in Section 4.4, the biggest barrier to recycling technologies like mechanical recycling and solvent-based recycling is the sorting of the mixed plastic waste into separated streams of polymers. Product design improvements to make plastic products easier to recycle (e.g. by reducing the use of multi-layer packaging and miscellaneous plastic parts) could thus be a game-changer for the development of a circular economy in the polyolefins sector (Milios et al., 2018). One of the policy instruments that could improve the collection and recycling of plastic streams is the Extended Producer Responsibility (Leal Filho et al., 2019), which is defined as "*an environmental protection strategy that makes the manufacturer of the product responsible for the entire life cycle of the product and especially for the take back, recycling and final disposal of the product"* (Iqbal et al., 2015).

The European Commission is already trying to tackle the issue in the European Strategy for Plastics in a Circular Economy (European Commission, 2020b), and with the proposal for a directive on single-use plastics, which would ban certain products (e.g. plastic straws), reduce others (e.g. drinks cups), and create obligations for the producers to develop less polluting products (European Commission, 2020c).

4.6 Use of residual energy

See Section 4.1.2 regarding the use of Industrial Heat Pumps (IHPs) to produce high-temperature heat by recovering waste heat, and Section 4.3 about other technologies and process aiming to reduce the amount of energy losses and waste heat.

4.7 CO₂ capture, storage, and usage

The key concept of this decarbonisation option is not to reduce the GHG emissions, but to capture the carbon dioxide before it is released into the atmosphere and store it in protected reservoirs. Although it is considered a viable solution by some stakeholders (*Internal communication with the companies*) and in many scenarios regarding the petrochemical industry (Boulamanti & Moya Rivera, 2018; McKinsey&Company, 2018; VNCI, 2018), the process is not within the scope of this MIDDEN report and will thus be discussed briefly.

In short, the term CCS (Carbon Capture and Storage) refers to technologies which capture carbon dioxide from processes such as gasification and power generation. The CO_2 is then pressurised to 100 bar or more, transported, and stored underground (e.g. in a depleted natural gas reservoir) (Boot-Handford et al., 2014). An example of a CCS project in The Netherlands can be found in the Rotterdam Port industrial cluster, where petrochemical companies such as Shell, ExxonMobil and Air Liquide have signed an agreement with the project organisation Porthos for the realisation of a CCS system. The carbon emitted by the companies will be captured, transported, and stored beneath the North Sea by the end of 2023 (Port of Rotterdam, 2019a). More information about CCS as a decarbonisation option for large volume organic chemicals production (such as ethylene and propylene) can be found in MIDDEN reports about Sabic Geleen, Dow Terneuzen and Shell Moerdijk (Oliveira & Van Dril, in prep.; Eerens, in prep.; Wong & Van Dril, 2020). The captured carbon could also be re-valorised in industrial supply chains, such as the production of methane or methanol (Leonzio, Foscolo, Zondervan, & Bogle, 2020). In these cases, the system takes the name of CCU (Carbon Capture and Utilisation). An innovative example of CCU taking place in The Netherlands is the collaboration between the plastic producer RENOLIT and the Dutch company Photanol, which developed a technology based on cyanobacteria to process CO₂ into plastic monomers (Photanol, 2020).

5 Discussion and conclusion

5.1 Discussion

The techno-economic parameters, requirements, impacts, opportunities, and barriers of the main decarbonisation options have been discussed in each section of Chapter 4 and summarised in Table 23. In short, the most promising technologies, besides an increase in the efficiency of mechanical recycling, are:

- The production of bio-polyolefins from sugar-based crops,
- The production of bio-polyolefins from the gasification of biowaste (possibly in combination with plastic waste) and MTO conversion,
- The chemical recycling of plastic waste using solvent-based dissolution,
- The chemical recycling of plastic waste using high-temperature pyrolysis,
- The chemical recycling of plastic waste using gasification (possibly in combination with biomass) and MTO conversion.

Note that also chemical recycling may need a sorting and mechanical recycling step to deliver the raw materials for these processes.

	Biomass fuel for	- availability limited		
5	cogeneration (CHP)	+ drop-in possible		
12	5	+ good decarbonisation		
1. E	Industrial Heat Pumps	- too low temperature for process		
S	(IHPs renewable electricity)	- not available vet		
9	Hvdrogen fuel (H ₂)	- higher price		
<u>w</u>		- needs new infrastructure		
0		↓ decarbonisation when using renewable energy for		
цщ, т		production		
	Cusar based bis sthulens	production		
c	Sugar-based bio-ethylene	- net zero unterence to positive in case plastic waste is		
± .2 ₪		used for energy recovery		
S I S		- competition biorueis, reed & rood		
ä ti st		- nigner price		
bs d	Biomass gasification and	- less competition biofuels, feed & food		
je je	MTO conversion	- higher price		
		+ positive decarbonisation possible		
Process	Energy efficiency	+ increase energy eff by heat recovery		
design				
	Mechanical recycling	 recycling efficiency has to be improved 		
		+ good decarbonisation option		
	Solvent-based purification	- cost balance unknown		
	-	+ good decarbonisation option		
	Thermo-chemical recycling	- pilot plants, further development needed		
	with pyrolysis	- cost balance unknown		
D		+ decarbonisation possible		
	Plastic waste gasification	- pilot plants, further development needed		
<u> </u>	and methanol-to-olefins	- cost balance unknown		
S a	(MTO) conversion	+ combining biomass and plastics waste seems promising		
Ř 📃		+ decarbonisation possible		

Table 23Summary of the decarbonisation options with the drawbacks (-) and
benefits (+).

If 60% of the polyolefins demand were to be satisfied through mechanical and chemical recycling, with the remaining 40% produced from bio-based materials, it is estimated that the emissions related to the production of PE and PP would be less than 2 Mt of CO_2 -eq, which is 67% less than the current value (More information in the Appendix).

When analysing the Dutch polyolefin industry as a whole, the success of the national decarbonisation strategy for the plastic sector could be facilitated by the wide range of available technologies. Universities, knowledge institutes, and R&D departments of many chemical companies are working on innovating and developing commercial-scale designs for a multitude of different bio-based and recycling options, making the discovery of a feasible and convenient solution just a matter of time.

Potential problems could arise by the lack of governmental support (in the form of policies and subsidies) and by the competition of some options with other economic sectors (e.g. the production of biomass for food, power, and biofuels production). Proper regulations and economies of scale are thus required to the realisation of these technologies and processes.

5.2 Conclusion

In conclusion, this report has succeeded in its goal of analysing the current state of the Dutch polyolefins industry and identifying the most promising decarbonization technologies (shown in Figure 37), providing techno-economic and environmental indicators whenever possible. The use of renewable energy sources such as green electricity and 'green' hydrogen are options for decarbonisation. Decarbonisation is also possible via the route of feedstock substitution, ethylene and propylene can be made from plant-based sugars and biowaste via, among others, fermentation, gasification and pyrolysis processes. Modified process design can, especially via reducing energy losses also contribute to decarbonisation. The last decarbonisation option to be applied is recycling. The efficiency of the current recycling of polyolefins has room for improvement and so, potentially, the demand for virgin polymers is reduced. Novel ways of recycling based on solvent-based purification, pyrolysis or gasification can further close the need for the production of virgin plastics or their feedstocks.



Figure 37 Combination of decarbonisation options for the Dutch polyolefins industry. The blocks connected with dotted lines (energy efficiency and renewable energy supply) are the improvements that could potentially be applied on every other industrial process.

Overall, it is thought that only a combination of these decarbonisation options (plus an increase in renewable energy production, changes in policies, and large-scale CCS projects) will allow The Netherlands to reach its decarbonisation goals for the plastics industry.

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Appendix: Simplified scenario for the polyolefins industry

A1 Introduction

To understand the potential environmental impact of the most promising decarbonisation options described in this report, a simplified scenario for the polyolefins industry has been modelled for the Netherlands, with the following assumptions:

- The initial production of virgin polyolefins is equal to the sum of the polyolefins produced by Dow Terneuzen, SABIC Limburg and Ducor Rozenburg. In the worst-case scenario, the value increases by 1.75% from 2020 to 2035 and by 1% from 2036 to 2050, while in the best-case scenario it stays stable through the whole period thanks to policies and changes in the product design.
- An additional input of polymers is given by the stream of mechanically recycled waste, which in the worst-case scenarios is equal to 30% of the virgin polyolefins production through the whole period, while in the best-case scenario starts as 30% in 2020 and reaches 35% in 2020.
- In the best-case scenario, the share of sugar-based and biowaste-based polyolefins starts as 0.1% in 2020 and reaches 2.5% in 2030 (pilot phase), 10% in 2040 (commercial phase), and 20% in 2050 (full effort phase).
- The share of polyolefins produced through chemical recycling with pyrolysis and gasification starts as 0.1% in 2020 and reaches 1% in 2030 (pilot phase), 5% in 2040 (commercial phase), and 12.5% in 2050 (full effort phase).
- In both scenarios, the characteristics of the technologies do not change over time.

A.2 Results

The result of this simulation is shown in Figure 38: in 2050, 60% of the polyolefins are produced from mechanical and chemical recycling flows (plastic-to-plastic loop), while the remaining 40% comes from virgin bio-based plastics (from both sugar crops and biowaste).



Figure 38 Shares of polyolefins production from fossil-based, bio-based, and recycling flows in the best-case scenario.



As seen in Figure 38, in 2050 the best-case scenario emissions are less than 2 Mt of CO_2 -eq, 67% less than the current emissions and 78% less than in the worst-case scenario.

Figure 39 Comparison between a fossil-based scenario and a decarbonisation scenario for polyolefins production in the Netherlands.

This scenario is based on arbitrary assumptions, it oversimplifies the dynamics of the polyolefins supply chain, and it does not consider the economic effort necessary to the realization of such large-scale decarbonisation options, but it could still serve as indication of the potential environmental benefits represented by the technologies described in this MIDDEN report.