PBL Netherlands Environmental
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DECARBONISATION OPTIONS FOR THE DUTCH PVC INDUSTRY

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MIDDEN

Manufacturing Industry Decarbonisation Data Exchange Network

Decarbonisation options for the Dutch PVC 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 ECN part of TNO[a]. 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: K.M. Schure (PBL), Klara.Schure@pbl.nl, A.W.N van Dril (TNO), Ton.vanDril@tno.nl, or D. van Dam (Dick.vanDam@pbl.nl).

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This report is reviewed by Shin-Etsu PVC B.V. PBL and ECN part of TNO remain responsible for the content. The decarbonisation options and parameters are explicitly not verified by Shin-Etsu PVC B.V.

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[a] From 1-1-2020, ECN part of TNO is renamed to 'TNO EnergieTransitie'.

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List of abbreviations

BAT	Best Available Technique
BIS	Buizen Inzamel Systeem
BTX	Benzene Toluene Xylene
CAPEX	Capital Expenditures
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilisation
CHP	Combined Heat and Power
CO	Carbon Monoxide
CO_2	Carbon Dioxide
EDC	1,2-Dichloroethane / 1,2-ethylenedichloride
EEI	Energy Efficiency Improvement
EFA	Energy Flow Analysis
EU ETS	European Union Emission Trading System
H_2	Hydrogen
H_2O	Water
HCl	Hydrogen Chloride
HE	Heavy Ends
HP EDC	High Purity 1,2-Dichloroethane
HP steam	High Pressure steam
HTC	High Temperature Chlorination
kt	Kilotonnes (1000 metric tonnes)
LE	Light Ends
LP steam	Low Pressure steam
LTC	Low Temperature Chlorination
MFA	Mass Flow Analysis
MIDDEN	Manufacturing Industry Decarbonisation Data Exchange Network
MP steam	Medium Pressure steam
NEa	Dutch Emission Authority (Nederlandse Emissieautoriteit)
NO_x	Nitrogen Oxides
OPEX	Operating Expenditures
PVC	Polyvinyl Chloride
TRL	Technology Readiness Level
VCM	Vinyl Chloride Monomer

FINDINGS

Summary

The Dutch chemical industry has evolved into a leading supplier of chemical products and services in Europe. Ethylene, one of the largest volume commodity chemicals produced by the petrochemical sector is the main feedstock for the production of polyvinyl chloride (PVC). Since this polymer is strong, lightweight, resistant to weathering and cost-effective it is widely used for building and construction applications, such as underground pipes, window frames and flooring.

In the Netherlands there are two EU ETS registered PVC manufacturing companies: Shin-Etsu PVC B.V. and Vynova Beek. It is estimated in this report that the sites together are responsible for around 94 kilotonne (kt) direct CO_2 emissions. Shin-Etsu PVC B.V. is located in the Port of Rotterdam and is built up of two production sites: Botlek and Pernis. Vinyl chloride monomer (VCM) is produced in Botlek which is then transported to Pernis where PVC is manufactured. Vynova Beek in Chemelot Industrial Site is only responsible for the production of PVC out of imported VCM from Vynova Tessenderlo in Belgium.

PVC is produced by polymerisation of VCM, which is obtained by thermal cracking (pyrolysis) of 1,2-ethylenedichloride (EDC). In the Netherlands EDC is produced by a combination of (i) direct chlorination and (ii) oxychlorination. The main feedstocks required are ethylene, chlorine, oxygen and hydrogen chloride. Furthermore, natural gas, steam (low-pressure, medium-pressure, high-pressure), hydrogen and electricity are consumed in the process.

Most of the energy in the process is consumed during cracking of VCM. Natural gas is burned to pre-heat the cracking reactants and provide the endothermic reaction process with heat. This goes hand in hand with high CO_2 emissions: from calculations it is found that the cracking furnaces emit 80.6 kt CO_2/year, and are responsible for 86% of the direct emissions reported by the NEa.

In general, decarbonisation options for the PVC manufacturing industry in this report focus on feedstock substitution, fuel substitution, recycling (circularity) and carbon capture and storage (CCS), each with its own advantages and disadvantages. In terms of its chemical composition PVC is only partly based on carbon-containing feedstocks. The mass of chlorine in PVC determines 57% of its weight. In the Netherlands chlorine is obtained in large amounts from the chlor-alkali industry, which is already party fuelled by renewable electricity, indirectly reducing the CO_2 footprint of PVC.

The cracking furnace, as mentioned before, is the main source of CO_2 emissions in the PVC production process. Three main options exist to reduce emissions from the cracking furnace. Firstly, fully replacing natural gas burners with hydrogen burners in the cracking furnace has the potential to remove all CO_2 emissions from the cracking furnace, since burning hydrogen only emits water. Prerequisites for successful implementation of hydrogen burners would be the availability of green or blue hydrogen for a price which is competitive with natural gas and more research into the optimal distribution of burners inside the cracking furnace. It is expected that the technology will be available around 2030.

Alternatively, the cracking furnaces could be fully electrified by applying electric heat technologies. Implementing electric cracking furnaces would require demolition of the existing furnaces and will come most likely with high investment costs (Engelenburg, 2019). In order to avoid indirect emissions, availability of cheap renewable electricity is a prerequisite and the power grid will have to be able to deal with the increased electricity demand. According to TNO experts, electrification does not come with large technological barriers (Zondag, 2019).

Thirdly, carbon capture and storage (CCS) technology could be used in the VCM production process at Shin-Etsu to separate CO_2 from the flue gas coming from the natural gas burners which are currently installed in the cracking furnaces. The Porthos project in the Port of Rotterdam opens up the opportunity for industrial sites in the Botlek area, such as Shin-Etsu, to invest in CCS technology since the transport infrastructure for captured CO_2 will be made available by the Port. Besides that and the capture installation, CCS would not require any major modifications to the existing production process.

During the whole PVC production process, steam is consumed in several steps. Shin-Etsu Botlek imports steam from Nouryon (previously AkzoNobel), Shin-Etsu Pernis from Shell, and Vynova Geleen is dependent on a steam boiler operated by EdeA. Technology which generates steam from renewable energy sources such as renewable electricity, or biomass has the potential to reduce the indirect emissions arising from steam consumption. Both direct-fired bio-CHP or gasification bio-CHP plants are discussed in this report.

The petrochemical industry in Rotterdam produces ethylene by steam cracking naphtha which is an energy intensive process. The total indirect emissions released from the production of ethylene for Shin-Etsu add up to 390 kt CO_2/year[b], which is more than three times the total direct emissions in 2017. Bio-ethylene produced from bio-based sources has the potential to avoid a large part of these emissions. However, this report did not address the absolute total avoided emissions of the entire chain, as it is highly dependent on factors such as the type of biomass used and methods of cultivation and transportation deployed. Bio-ethylene could be directly injected in the already existing ethylene pipeline infrastructure that connects the Port of Rotterdam with Belgium and Germany, which makes integration of bio-ethylene straightforward once the production technology is ready.

Decreasing waste streams by reusing and recycling products is gaining momentum in a wide range of sectors, including plastics. PVC can be recycled in different ways. Post-consumer PVC waste is often difficult to recycle mechanically due to contamination. Moreover, the mixed waste streams only contain marginal amounts of PVC. Therefore the focus lies on specific PVC products that are more easily recyclable. Examples are large volume applications for rigid PVC, such as piping and window frames, which can be mechanically recycled to acceptable quality PVC material up to eight times (Shin-Etsu, personal communication). Pre-consumer waste such as cutting losses or other process losses are recycled by producers at high rates. The future of chemical recycling of PVC to VCM is highly uncertain (Shin-Etsu, personal communication). According to the industry it would be more attractive to look at chemical recycling of PVC to ethene or hydrogen chloride. Alternatively, syngas can be produced by pyrolysis or gasification of PVC waste.

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[b] The specific consumption of ethylene by the production process was estimated at approximately 0.45 tonne ethylene/tonne VCM. Assuming a yearly production capacity of 620 ktonne VCM this would lead to a yearly demand of 279 ktonne ethylene/year. Emission factor of ethylene = 1.4 tonne CO_2/tonne ethylene.

FULL RESULTS

Introduction

This report describes the current situation of the Dutch PVC manufacturing production and the options and conditions for its decarbonisation. It is part of the MIDDEN project: the Manufacturing Industry Decarbonisation Data Exchange Network. MIDDEN aims to support industry, policy makers, analysts and the energy sector in their common efforts to achieve deep decarbonisation.

Scope

The aim of the MIDDEN project is to compile a database of material and energy uses of industrial processes at a plant level for the Dutch manufacturing industry. The scope of this research will focus specifically on the manufacturing of polyvinyl chloride in the Netherlands, starting from ethylene and chloride as feedstocks.

Production locations include:

- Shin-Etsu PVC B.V. in the Port of Rotterdam; Rotterdam, Zuid-Holland.
- Vynova Group in Chemical Site Chemelot; Geleen, Limburg.

Processes include:

- Direct Chlorination
- Oxychlorination
- Thermal Cracking
- Suspension Polymerisation
- Several distillation and drying processes.

Products include:

- Vinyl chloride monomer (VCM)
- High-purity 1,2-dichloroethane (EDC)
- Polyvinyl chloride (PVC).

The main decarbonisation options are:

- Hydrogen as fuel
- Electric furnaces
- Carbon Capture and Storage (CCS)
- Bio-ethylene as feedstock
- Biomass to steam
- Mechanical and chemical recycling of PVC.

Reading guide

Section 1 gives a general introduction to the PVC manufacturing industry in the Netherlands and describes the employed methodology. In Section 2 we describe the current situation of PVC production processes in the Netherlands and in Section 3 we describe the relevant products to these processes. Options for decarbonisation are systematically quantified and evaluated in Section 4. The feasibility and requirements of those decarbonisation options are discussed in Section 5. Finally the Appendices give more background information used in the research.

1 PVC production in the Netherlands

1.1 Introduction to the Dutch chemical industry

1.1.1 The importance of the Dutch chemical industry

In the past decades the Dutch chemical industry has evolved into one of Europe's leading suppliers of chemical products and services. The geographical position of the Netherlands in Europe, the excellent available infrastructure such as the Rotterdam harbour – which is one of the largest in the world – and the abundance of well-educated citizens (32% of the Dutch 25–64 year-olds hold a university degree (OECD, 2014)) allowed the industry to grow to the scale it is nowadays (VNCI, 2018). In total the chemical industry provides employment to 44,000 people, distributed among more than 400 companies, and generates a total turnover of 50 billion euro (VNCI, 2018). The strong international position that the Netherlands holds is emphasised by the fact that 80% of the chemicals produced in the Netherlands are exported to countries all over the world (VNCI, 2018).

The industry is home to a wide variety of chemical sectors, such as the petrochemical, fertiliser, and chlor-alkali sectors. The petrochemical sector produces platform chemicals such as ethylene, propylene and BTX by steam cracking a range of feedstocks e.g. propane, naphtha or gasoil (VNCI, 2018). These compounds form the starting point for a wide variety of products, such as different types of polymers, rubbers, fibre raw materials, natural gas and other organic intermediate products. This is valuable to the Netherlands, but, on the other side of the coin, goes hand in hand with high greenhouse gas emissions. For example in 2018, the petrochemical industry emitted a total of ~10 Mtonnes of carbon dioxide (CO_2) during the production of these chemicals. To put this into perspective, this is ~5 % of the total greenhouse gas emissions of the Netherlands.

1.1.2 Role of ethylene and chlorine in the Dutch PVC manufacturing industry

One of the largest volume commodity chemicals produced by the petrochemical sector is ethylene. The total production in 2013 was estimated at 25 Mtonnes of ethylene in EU-28 countries alone. The Netherlands is the second-largest contributor in Europe, after Germany, with an overall production capacity of almost 4 Mtonnes of ethylene per year in 2013 (Boulamanti & Moya, 2017). The main use for ethylene is the production of different types of polymers. In 2018, approximately 60% was consumed for the production of low-, linear low and high-density polymers, such as HDPE, LLDPE and LDPE[c] (IHS Markit, 2019). Another 9% was used for the manufacturing of 1,2-dichloroethane (EDC) which is the precursor for the polymer polyvinyl chloride (PVC) (IHS Markit, 2019). Other ethylene uses include the

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[c] HDPE: High Density Poly Ethylene, LLDPE: Linear Low Density Poly Ethylene, LDPE: Low Density Poly Ethylene.

production of ethylene oxide, ethylbenzene, alpha-olefins and vinyl acetate (IHS Markit, 2019). These compounds have a wide range of applications.

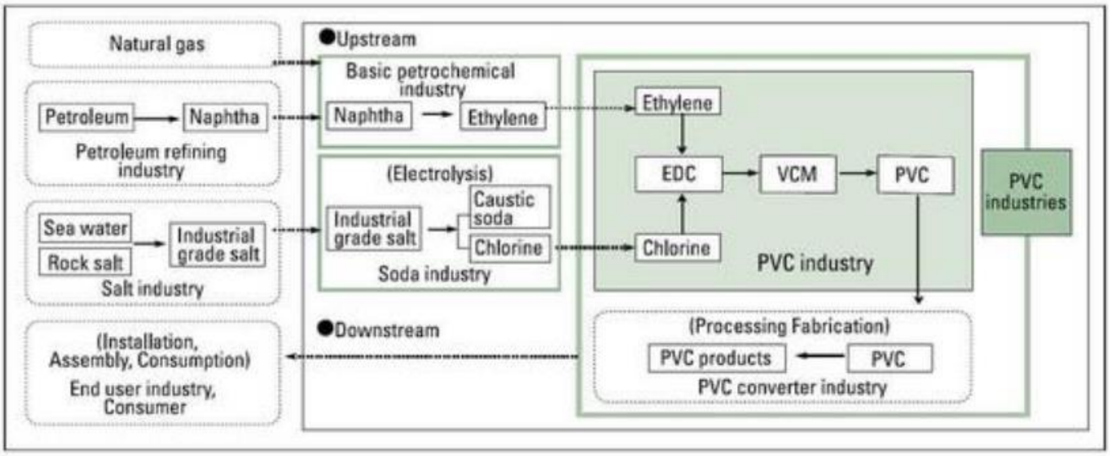

Figure 1 Block scheme of the entire supply chain from crude feedstocks, such as natural gas and petroleum, to PVC products.

The PVC industry is not only dependent on the petrochemical industry for the supply of ethylene, but also on the the chlor-alkali industry to supply chlorine, which is another primary feedstock for the PVC production process (see Figure 1). EuroChlor (2016) reported that the Dutch chlor-alkali industry produces approximately 850 kt chlorine per year. In Europe about one third of chlorine is used for the production of PVC (EuroChlor, 2018). This shows just how interconnected the PVC industry and the petrochemical and chlor-alkali industry are.

1.2 Production locations of PVC in the Netherlands

In the Netherlands PVC is obtained at two production locations: Shin-Etsu PVC B.V. in Rotterdam and Vynova Beek in Geleen. The location of both producers is visualized in Figure 2. Their main activities and emissions in 2017 are presented in Table 1. It is important to note that Shin-Etsu PVC B.V. location Pernis and Vynova Beek have no ETS registered emissions. The production process of PVC only requires steam and electricity, and those are imported in the cases of these PVC producers, which is why the company has no direct emissions. All emissions reported by the Dutch Emission Authority (NEa) for Shin-Etsu PVC B.V. are related to location Botlek.

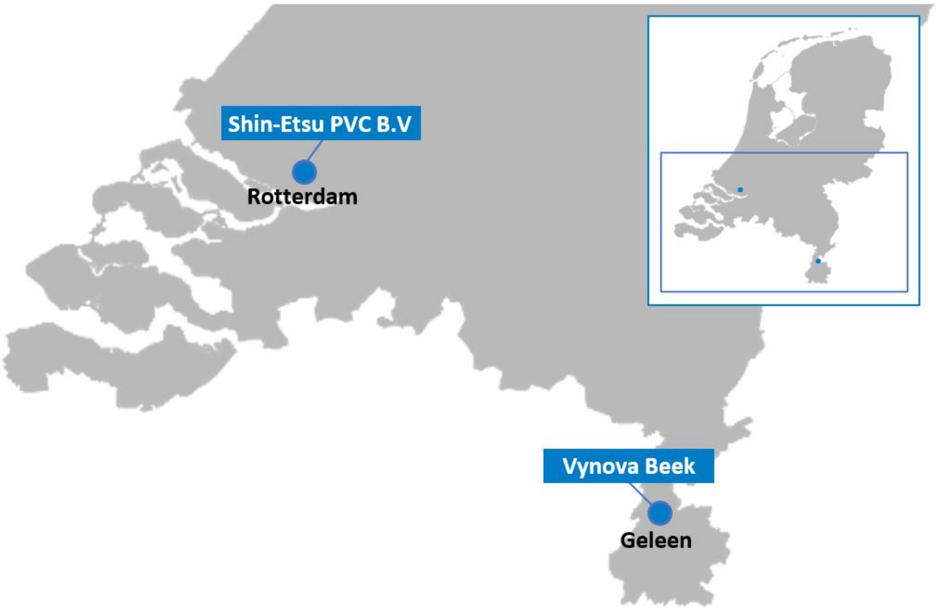

Figure 2 Production locations of the two main PVC producers in the Netherlands.

Table 1 Overview of PVC producers in the Netherlands.

Producer / ETS registration	Location	Main activity	Nameplate production capacity⁶⁾ [kt/yr]	Number of employees	Direct CO_2 emissions in 2017 registered at NEa [tonne/yr]
Shin-Etsu PVC B.V., location Botlek	Rotterdam	Production of vinyl chloride monomer and high purity 1,2-dichloroethane	VCM: 670 HP EDC: 80	110¹⁾	93,615²⁾
Shin-Etsu PVC B.V., location Pernis	Rotterdam	Production of polyvinyl chloride	PVC: 520	75¹⁾	0
Vynova Beek	Geleen	Production of polyvinyl chloride	PVC: 225	100³⁾	0⁴⁾
Chemelot BKG08**⁵⁾**	-	-	-	-	83,369²⁾

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1) (Port of Rotterdam, 2016).
2) The emissions as reported by (NEa, 2018). The emissions of Vynova Beek are reported under Chemelot BKG08, the value in the table is the total emissions from Chemelot BKG08 and thus not specifically for Vynova Beek.
3) ("Over Vynova Beek", 2019).
4) It was estimated that Vynova Beek does not emit direct CO_2 emissions, see Section 1.5 and Appendix A.2 for more information.
5) Chemelot BKG08 includes a group of emissions points owned by several companies at Chemelot Industrial site. In the NEa EU ETS database these are grouped under the same registration. Together this group emitted around 83 kton CO_2 in 2017.
6) In this report nameplate production capacity refers directly to the permitted production capacity, not necessarily the actual production capacity. Actual (realisable) capacity closer to 90% of nameplate capacity.

1.3 Shin-Etsu PVC B.V.

1.3.1 History of Shin-Etsu

Shin-Etsu PVC B.V. is a subsidiary of the Japanese giant Shin-Etsu Chemical Co., Ltd., which is the largest chemical company in Japan (Shin-Etsu Chemical Co., Ltd., 2018). In 1999 Shin-Etsu Chemical Co., Ltd. bought a VCM plant and a PVC plant in the Port of Rotterdam, both of which were operated as part of a Shell/AkzoNobel joint venture. This was part of the Japanese company's strategy to increase their PVC production capacity in Europe and strengthen their position in the European PVC market. Initially in 2000, the yearly nameplate production capacity was 500 kt VCM, 80 kt HP (High Purity) EDC and 400 kt PVC. Quickly Shin-Etsu expanded their permitted capacity at Botlek in 2003 to 620 kt VCM and at Pernis in 2006 to 450 kt PVC (Shin-Etsu Chemical Co., Ltd., 2005). The realisable production potential is assumed to be around 90% of the nameplate capacity.

Over the recent decades both production sites have experienced multiple revamps, as summarised in Appendix A.1. The most notable revamps at location Botlek are the addition of the third and fourth cracking furnaces in 1977 and 2003, the addition of the oxychlorination reactor in 1997 and the replacement of the original two cracking furnaces, which dated from 1971, in 2004. Pernis expanded their PVC production capacity by adding two reactors in 1993 and 2006. Improvements to the polymerisation process in recent years increased the capacity at Pernis to its current size of 520 kt of PVC.

1.3.2 Existing infrastructure in the Port of Rotterdam

As already mentioned, Shin-Etsu has two production sites: Botlek and Pernis. Vinyl chloride monomer (VCM), which is the building block for PVC (see Section 2.3), is produced at Botlek, and PVC is produced at Pernis. VCM is transported by a pipeline connection, called the Multicore pipeline system (Port of Rotterdam, 2016) from Botlek to Pernis. Figure 3 shows the location of production site Botlek and Pernis relative to each other and the pipeline connecting the two sites. The distance between the two production locations is approximately 9 km (Shin-Etsu, personal communication).

As will be shown later in Section 2.2, chlorine is one of the feedstocks for the oxychlorination process, which produces VCM. For the last few decades Shin-Etsu has been a key part of an integrated chlorine chain with several other companies: AkzoNobel MEB (Membraan Electrolyse Bedrijf), Hexion and Huntsman (Shin-Etsu PVC B.V., 2018c). This collaboration reduces chlorine losses to the environment and realises circular and thus effective use of feedstock resources. AkzoNobel produces chlorine and caustic from salt, which are then transported to Shin-Etsu and used as feedstock for oxychlorination and caustic washing, respectively. Hexion and Huntsman produce hydrogen chloride as a by-product during the production of epoxy resins and polyurethanes, respectively, which are also used for oxychlorination.

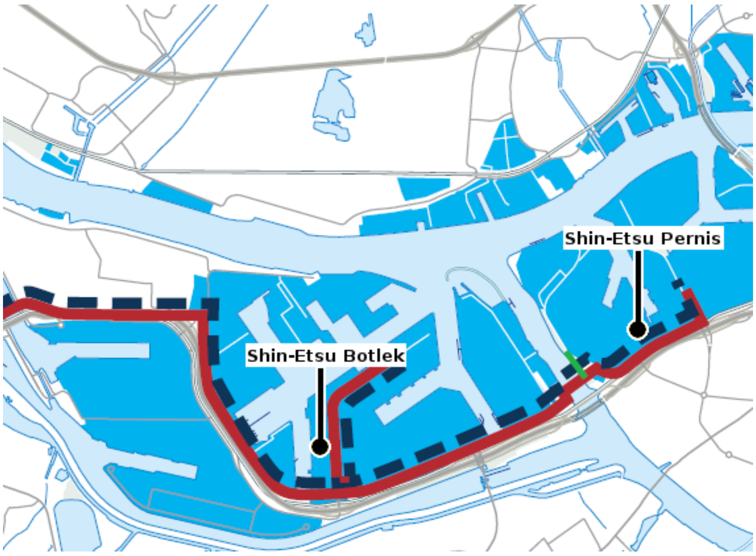

Figure 3 Location of Shin-Etsu Botlek and Shin-Etsu Pernis relative to each other. The red line represents the Multicore pipeline system (Port of Rotterdam, 2016).

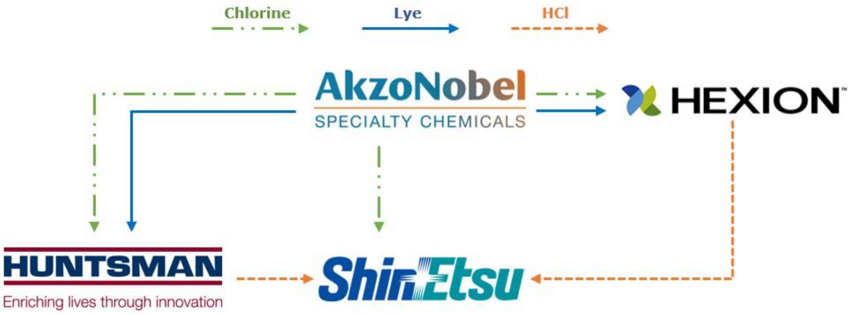

Figure 4 Overview of the integrated chlorine chain at industrial site Botlek (Shin-Etsu PVC B.V., 2018c). AkzoNobel is now Nouryon.

1.4 Vynova Beek

1.4.1 History of Vynova

Vynova Beek is located at Chemelot Industrial park, which is another large industrial cluster in the south of the Netherlands, and part of the larger chlor-vinyls platform Vynova Group (“About Vynova”, 2019). Although Vynova was founded only recently in 2015, the PVC production site at Chemelot has existed for multiple decades. In 1972 the Belgian company Tessenderlo Group, in collaboration with DSM, produced the first batch of PVC in Beek (“Over Vynova Beek”, 2019). In 2011 INEOS ChlorVinyls bought all PVC related activities including the PVC production facilities from Tessenderlo Group (“Over Vynova Beek”, 2019). Finally, in 2015 the International Chemical Investors Group (ICIG) became owner of the site and founded Vynova Beek in Chemelot (“Over Vynova Beek”, 2019). The production capacity of Vynova Beek was estimated based on 2013 data from Boulamanti & Moya (2017) to be approximately 225 kt PVC/year[d].

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[d] Information on the production capacity of Vynova Beek was not found in public sources. Boulamanti & Moya (2017) reported that the Netherlands had a total PVC production capacity of 675 kton in 2013, divided over two production sites. It is assumed that these two sites are Shin-Etsu Pernis and Vynova Beek, as this is not clear from the report. From Appendix A.1 it is known that the production capacity of Shin-Etsu Pernis in 2013

1.5 CO_2 emissions

1.5.1 Scope of this report

In order to effectively allocate CO_2 emissions in any process or system it is important to define direct and indirect emissions. The widely used GHG Protocol published by the World Resource Institute (WRI) formulates direct GHG emissions as *"emissions from sources that are owned and controlled by the company"* (WRI, 2015; p.25). In other words, any emissions that are generated by on-site activities are attributed to direct emissions, which is also often referred to as scope 1 emissions.

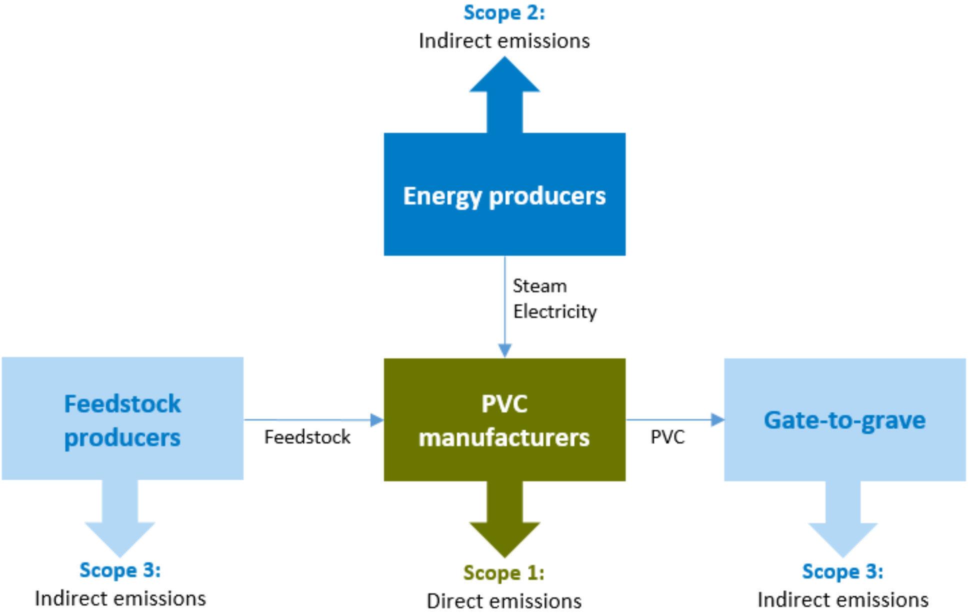

Figure 5 Overview of the definition of scope 1, 2 and 3 emissions in this report.

Indirect emissions are according to the WRI *"emissions that are a consequence of the activities of the company but occur at sources owned or controlled by another company"* (WRI, 2015; p.25). These are further categorized in two scopes: scope 2 and scope 3 (WRI, 2015). Scope 2 indirect emissions are emissions resulting from consumption of purchased steam or electricity. Scope 3 includes all other indirect emissions that are not covered in scope 2, such as transport-related activities, waste disposal or feedstock production. This is visualised in Figure 5 from the perspective of the PVC manufacturing industry.

Within the context of this study scope 1 and scope 2 emissions will be included. From scope 3, only the emissions emitted by other companies for the production of the feedstock will be included.

1.5.2 Shin-Etsu PVC B.V.

In the NEa EU ETS database only emissions from Shin-Etsu Botlek are reported. The scope 1 direct emissions of Shin-Etsu Botlek are displayed in Figure 6. The CO_2 emissions of the VCM plant have been fluctuating over time, which could be due to fluctuating yearly production rates. Between 2010—2017 the average yearly emissions were 99 kt CO_2/year. This is more than 10% higher compared to the period 2005–2009 when the average yearly emissions were 83 kt CO_2/year. This could be explained by the fact that Shin-Etsu might have

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was 450 kton PVC. Therefore, it was estimated that Vynova Beek produced 225 kton PVC in 2013. Since no further details are known, it is assumed that this is still the current production capacity at Vynova Beek.

increased their yearly production rate and thus their emissions. However, this cannot be stated with any certainty as the yearly production rates are unknown. In 2017 the whole production plant was down for a period of time for a planned turn-around (Shin-Etsu PVC B.V., 2018d), which could explain the relative decrease of yearly emissions in 2017 compared to 2016.

As already mentioned in the beginning of this subsection, Shin-Etsu Pernis is not registered in the NEa EU ETS database. As shown later in Section 2.3, the energy consumption of Shin-Etsu Pernis is strictly limited to steam and electricity. Both of these are purchased from a third party (Shin-Etsu, personal communication), meaning that the scope 1 direct emissions are little to none.

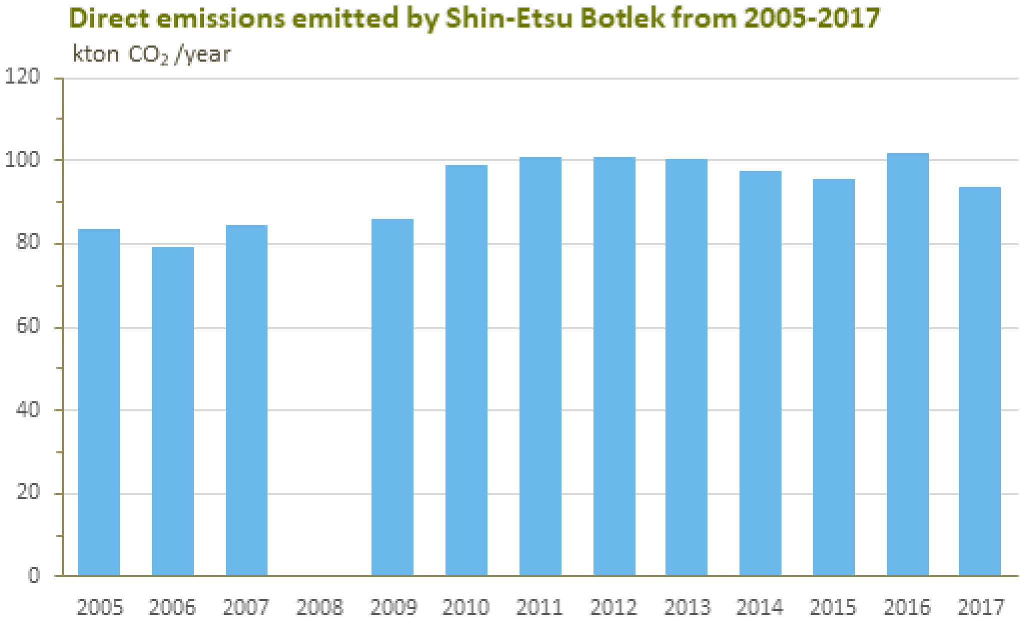

Figure 6 Direct carbon dioxide emissions in kt/yr emitted by Shin-Etsu Botlek from 2005-2017. Unfortunately, data from 2008 is unknown. Data for 2005—2007 from NEa (2014); for 2013—2017 from NEa (2018); for 2009—2012 from Shin-Etsu PVC B.V. (2013), p.12.

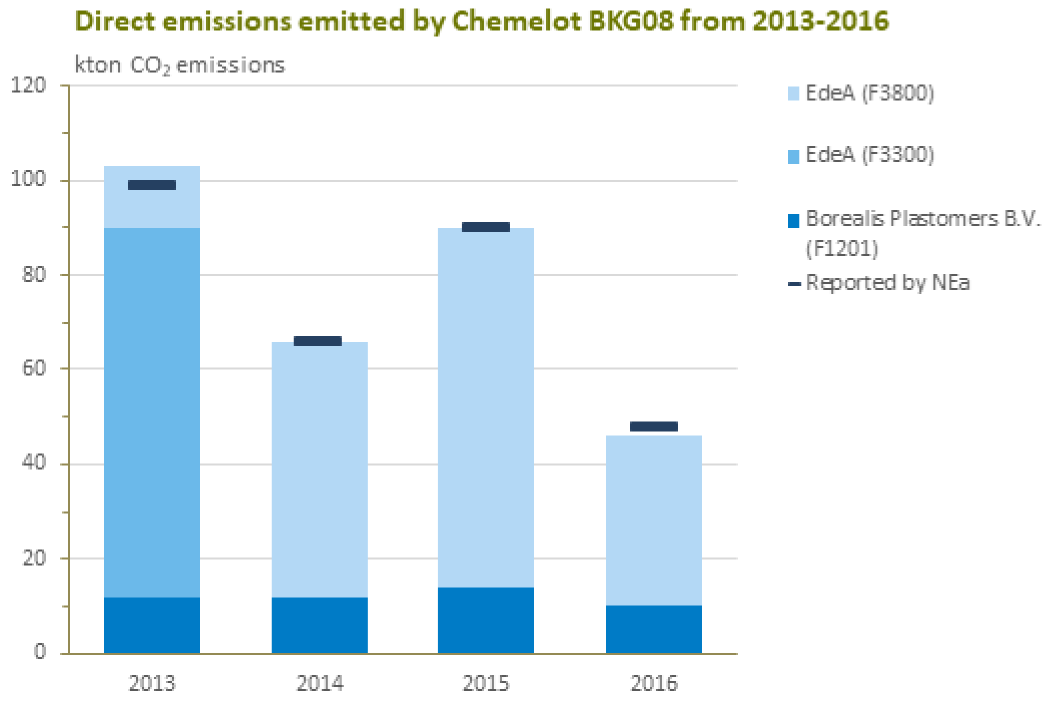

Figure 7 Direct carbon dioxide emissions in kt/year emitted by Chemelot BKG08 from 2013—2016 (NEa, 2018; calculations from Appendix A.2).

1.5.3 Vynova Beek

In the NEa EU ETS database the emissions of Chemelot Industrial Site are not reported per company, but per industrial area 1 to 14 which are referred to as BKGs. According to personal communication with NEa, emissions of Vynova Beek are reported under the name Chemelot BKG08 in the NEa EU ETS database. It is known that Vynova Beek, one steam boiler from EdeA and a furnace from Borealis Plastomers B.V. are included in Chemelot BKG08. However, from the NEa registration alone it is not possible to attribute the emissions among these companies as the NEa reports overall emissions of the BKG. Therefore, the direct emissions of the individual emission sources on BKG08 were calculated using emission registrations from Chemelot themselves, see Appendix A.2. From the calculations it was found that the direct emissions from EdeA (F3300/F3800) and Borealis Plastomers B.V. (F1201) match the yearly emissions as registered under Chemelot BKG08. This leads to the conclusion that the PVC production line of Vynova Beek, similar to Shin-Etsu Pernis, has no direct emissions.

The results are presented in Figure 7. From this graph it can be seen that Vynova Beek, similar to Shin-Etsu Pernis, has no direct emissions as all direct emissions from Chemelot BKG08 can be assigned to EdeA and Borealis Plastomers B.V.. In 2013, EdeA replaced their F3300 steam boiler with a new steam boiler (F3800). This is the reason that after 2014 no emissions from the old F3300 were reported.

1.5.4 Energy efficiency of Shin-Etsu PVC B.V.

The development of energy efficiency of both Shin-Etsu Botlek and Pernis relative to 2006 for the period 2010 to 2017 is displayed below. The target of Shin-Etsu for 2020 is to achieve an Energy Efficiency Index (EEI) of 80% relative to 2006. The EEI of Botlek shows overall a decreasing trend between 2010 and 2017. However, between 2012 and 2014 the EEI increased. There was no explanation found for this. In 2017 the EEI increased relative to 2016 due to a temporary factory shutdown (Shin-Etsu, 2018d). The EEI of Pernis has not improved over the past few years. According to Shin-Etsu, the EEI in 2015 increased significantly due to lower PVC production due to external circumstances (Shin-Etsu, 2018d). The temporary factory shutdown in 2017 also caused the EEI of Pernis to increase in that year (Shin-Etsu, 2018d). Unfortunately, no statistics about the energy efficiency of Vynova Beek were found.

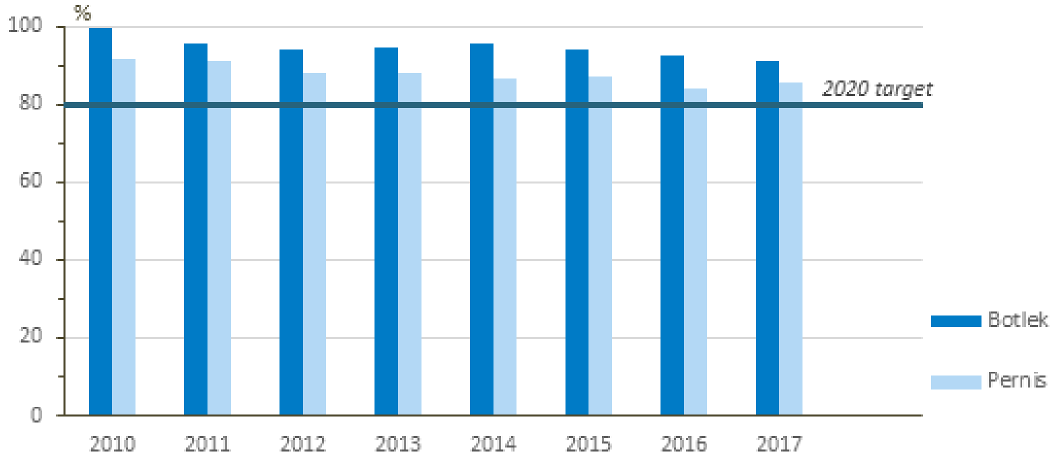

Figure 8 Overview of the Energy Efficiency Index (EEI) of Shin-Etsu Botlek and Pernis from 2010 to 2017 with respect to 2006. The lower the EEI, the more energy efficient the plant is relative to 2006. Data is collected from Shin-Etsu PVC B.V. (2015; 2016; 2018d).

2 PVC production processes

2.1 Overview

PVC is produced by polymerisation of the chemical vinyl chloride monomer (VCM). This chemical is obtained by thermal cracking (pyrolysis) of 1,2-ethylenedichloride (EDC). In the Netherlands EDC is produced by a combination of (i) direct chlorination and (ii) oxychlorination of ethylene. In general, the total PVC process can be divided in two main parts, each consisting of several subprocesses as indicated in Table 2. These subprocesses are selected based on descriptions of the PVC production process in literature (Dimian & Bildea, 2008; EEA, 2006; Falcke et al., 2017). This chapter will describe the total production process using the grouping in Table 2.

Table 2 Primary energy demand of the PVC production process from ethylene via VCM to PVC at Shin-Etsu and Vynova Beek. The assumed production capacities are 620 kt VCM/yr and 470 kt PVC/yr for Shin-Etsu. The assumed production capacity for Vynova Beek is 225 kt PVC/yr, as estimated in Section 1.4.

Production step	Primary energy demand [GJ/tonne product]
Shin-Etsu	
EDC production	1.9[1)]
EDC purification	0.7[1)]
EDC cracking	3.4[1)]
VCM purification	0.9[1)]
PVC production	4.1[2)]
Vynova Beek	
PVC production	4.0[3)]

[1)] Calculated from the EFA (Appendix A.4)

[2)] Provided by Shin-Etsu. Only the aggregate number is known.

[3)] As no information was known about Vynova Beek, the energy demand was assumed to be the same as reported in the most recent BAT document (EU, 2007).

2.2 VCM production

A general overview of the VCM production process is shown in figure 9. The main inputs for VCM are chlorine, ethylene and oxygen. There are several recycling streams, namely the uncracked EDC to the EDC purification step and the produced hydrogen chloride (HCl).

2.2.1 EDC production

In total, there can be four sources of EDC for the VCM production process. Direct chlorination and oxychlorination are two separate processes that are performed in tandem to produce EDC. Thirdly, EDC is recycled back from the VCM purification to EDC purification. Fourthly, an option would be to feed external EDC in case this is necessary, but this practice has not been observed in the Dutch PVC manufacturing industry.

Direct chlorination

The first step in the production of VCM is the formation of 1,2-ethylenedichloride (EDC). During direct chlorination, ethylene and chlorine react to form EDC. Both low-temperature chlorination (LTC) and high-temperature chlorination (HTC) can be performed (Falcke et al, 2017).

LTC is performed in a gas-liquid contact column at operating temperatures between 50-70°C. This process has the advantage of achieving high ethylene selectivity up to 99%, but requires extra processing costs due to catalyst removal (Dimian & Bildea, 2008). The chemical reaction of LTC is the following equation:

$$C_2H_4\,(g) + Cl_2(g) \xleftrightarrow{FeCl_3} C_2H_4Cl_2(l) \qquad \text{(eq. 2.1)}$$

The overall chemical reaction is exothermic with a heat of reaction of approximately -218 kJ/mol (Dimian & Bildea, 2008). The temperature in the reactor has to remain constant since higher temperatures promote the formation of by-products. Therefore, an indirect cooling system has to be used, which can either be positioned inside or outside the reactor. Since the reaction temperatures are relatively low, the transfer of heat is highly inefficient due to the low temperature difference.

In HTC, a chemical reactor is operating at a temperature between 90-150°C and a pressure between 1.5-5 bar (Dimian & Bildea, 2008). HTC has the advantage that the heat of reaction, which is sevenfold higher compared to the heat of evaporation of EDC, can be used for EDC purification later in the process. However, HTC suffers from lower selectivity. It is known that Shin-Etsu applies LTC (Shin-Etsu PVC B.V., 2004).

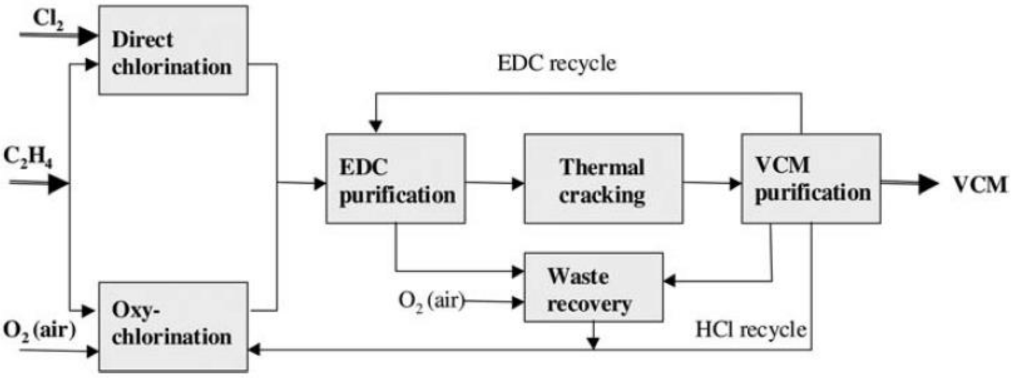

Figure 9 Block scheme of the VCM production process (Dimian & Bildea, 2008).

In most cases ferric chloride, $FeCl_3$, acts as a catalyst. In order to ensure complete ethylene conversion, an excess of chlorine is used. It is preferred to reduce formation of chlorinated by-products, such as 1,1,2-trichlorethane, by adding oxygen as an inhibitor. If the chlorine is produced by means of electrolysis, small amounts of oxygen are usually already present.

Akzo-Nobel produces chlorine during salt production and offers it as input for Shin-Etsu Botlek (Shin-Etsu PVC B.V. 2018c).

Oxychlorination

In oxychlorination, ethylene, hydrogen chloride and oxygen react to produce EDC and water. The reaction can be carried out in either a fluid-bed reactor or a fixed-bed reactor. Fluid-bed reactors generally operate at a temperature between 220-235°C and a pressure between 250-600 kPa (EEA, 2006). The operating temperature of fixed-bed reactors is between 230-300°C, with an operating pressure between 250-1500 kPa (EEA, 2006). Fluid-bed reactors are generally preferred due to more intensive heat transfer, reduced occurrence of hot spots and more efficient catalyst regeneration (Dimian & Bildea, 2008). Indeed, Shin-Etsu Botlek operates a total of three fluid-bed reactors (Shin-Etsu PVC B.V., 2012). The chemical reaction of oxychlorination follows the following equation:

$$C_2H_4(g) + 2HCl(g) + \frac{1}{2}O_2(g) \xleftrightarrow{CuCl_2} C_2H_4Cl_2(g) + H_2O(g) \qquad \text{(eq. 2.2)}$$

Oxychlorination is - similarly to direct chlorination - a highly exothermic reaction with a heat of reaction of approximately -238 kJ/mol (Dimian & Bildea, 2008). Due to the higher reaction temperature in the reactor it is possible to produce steam as a side product using external heat exchangers. This is generally used during the distillation steps in EDC purification.

Copper(III)chloride, $CuCl_2$, impregnated on alumina is widely used as catalyst, also at Shin-Etsu Botlek. During oxychlorination a wide spectrum of impurities can be formed, such as 1,1,2-trichlorethane and chloral. It is important to remove these impurities, since some impurities formed in one reactor might promote the formation of impurities in other reactors (Dimian & Bildea, 2008). E.g. chloral has the tendency to polymerize, which is why it is washed out immediately after oxychlorination.

Oxychlorination acts as a sink for hydrogen chloride, produced in large amounts during thermal cracking, which realizes the balanced process (PlasticsEurope, 2015). Hydrogen chloride from external sources, such as the production of chloroform, can be used as well if it is of suitable purity (PlasticsEurope, 2015). In the case of Shin-Etsu, hydrogen chloride is imported from Hexion and Huntsman. The oxygen source for the chemical reaction can be both ambient air or a pure oxygen stream. Air fed systems have the disadvantage of increased formation of chlorinated by-products and larger waste streams (PlasticsEurope, 2015). Although oxygen fed systems do not suffer from this, they require a larger excess of ethylene in the feed stream and additional energy for the production of oxygen (PlasticsEurope, 2015). At Shin-Etsu Botlek, two of the newly replaced reactors are air fed systems (operating temperatures: 210-240°C), while the third is an oxygen fed system.

2.2.2 EDC purification

EDC produced by direct chlorination, oxychlorination or any unreacted EDC from VCM production requires additional treatments in order to obtain the required purity for thermal cracking. The purity of the feed for the cracker has to be at least 99.5 wt% in order to reduce coke formation and fouling of the pyrolysis reactor (PlasticsEurope, 2015).

Since the operating temperature of LTC (50-70°C) is below the boiling point of EDC (which is 84°C), EDC leaves the direct chlorination reactor as a liquid. The $FeCl_3$ catalyst is still diluted in the outflow stream and has to be removed first. By washing EDC with water the catalyst is separated and recycled back to the reactor.

Because of the high operating temperatures of oxychlorination, EDC leaves this process as a gas mixture with water. Generally, the gas mixture is quenched with water vapor and condensed at successively decreasing temperatures (PlasticsEurope, 2015). Finally, water and EDC will naturally separate from one another by decantation, due to a difference in solubility (EEA, 2006).

The two EDC streams are combined and be fed to an EDC dryer. This is generally a cyclone dryer which will remove a large part of the water. Next the EDC is supplied to the light ends azeotropic distillation column, which will remove water and chlorinated organic by-products with a boiling point lower than EDC (Falcke et al., 2017). Afterwards, the stream is fed to a high ends distillation column, which removes by-products and tars with a boiling point higher than EDC (Falcke et al., 2017). The light ends and heavy ends waste are fed to a chlorine-recycling plant, where the chlorine contained in the compounds can be recovered by oxidation to hydrogen chloride (Falcke et al., 2017). This can in turn be reused in the oxychlorination process.

2.2.3 EDC cracking

In a large cabin-type furnace, EDC is decomposed at high temperatures into VCM and hydrogen chloride (see equation 2.3). The process operates typically at temperatures between 425-550°C and pressures between 1-4 MPa, with mean residence times of 10-20 seconds (Falcke et al., 2017). The reported conversion rate is 50-65% per pass (PlasticsEurope, 2015; Falcke et al., 2017), which means that not all EDC will be reacted in one cycle.

$$\mathrm{C_2H_4Cl_2(g) \rightarrow C_2H_3Cl(g) + HCl(g)} \qquad \text{(eq. 2.3)}$$

The process gas stream containing VCM, hydrogen chloride, EDC and by-products, is immediately quenched in order to reduce the formation of tar and heavy by-products (Falcke et al., 2017). This can be done directly with downstream liquid EDC or indirectly using heat exchangers.

The cracking process is an endothermic reaction with a heat of reaction of +71 kJ/mol (Dimian & Bildea, 2008) and thus requires energy to continue the process reaction. This energy is typically provided by burning natural gas. Also, it is expected that natural gas is burned in gas burners to reach the higher operating temperature of approximately 500°C. This would mean that this step is the main source of CO_2 emissions in the production process.

2.2.4 VCM purification

The final step involves separation of hydrogen chloride, EDC and other by-products from the VCM stream by two-stage distillation. The first distillation column separates hydrogen chloride, together with low-boiling side products, which is then recycled back to the oxychlorination process (Falcke et al., 2017). A hydrogenation step is optional to remove any traces of acetylene in hydrogen chloride. VCM is separated in a second distillation column, neutralized with NaOH to remove any traces of hydrogen chloride, and transferred in liquid form to VCM storage (Falcke et al., 2017). Any leftover EDC is recycled back to the cracking furnace after purification.

2.2.5 Overall VCM production process

When combining the three reaction equations for direct chlorination, oxychlorination and thermal cracking, it becomes clear that the overall balanced equation is highly exothermic. Several sources state that a VCM plant should be able to cover a large part of its energy needs by cleverly upgrading and reusing the energy from heat (Falcke et al., 2017; PlasticsEurope, 2015). It is known that Shin-Etsu is already doing this by installing heat exchangers in their direct chlorination units and their oxychlorination units. The internal heat flows are not known.

Overview of the main process reactions	
Direct chlorination ΔH^o= -218 kJ/mol	$\mathrm{C_2H_4\ (g) + Cl_2(g) \xleftrightarrow{FeCl_3} C_2H_4Cl_2(l)}$
Thermal cracking ΔH^o = +71 kJ/mol	$\mathrm{C_2H_4Cl_2(g) \rightarrow C_2H_3Cl(g) + HCl(g)}$
Oxychlorination ΔH^o = -238 kJ/mol	$\mathrm{C_2H_4(g) + 2HCl(g) + \frac{1}{2}O_2(g) \xleftrightarrow{CuCl_2} C_2H_4Cl_2(g) + H_2O(g)}$
Overall reaction ΔH^o = -192.5 kJ/mol	$\mathrm{C_2H_4 + \frac{1}{2}Cl_2 + \frac{1}{4}O_2 \rightarrow C_2H_3Cl + \frac{1}{2}H_2O}$

2.2.6 Mass and energy flows

In order to gain an understanding of the mass and energy flows in the production process, a mass flow analysis (MFA) and energy flow analysis (EFA) were performed. For the details, see Appendix A.3 and A.4. The results from the MFA are compared to Falcke et al. (2017), Wilkes et al. (2005) and ThyssenKrupp (2012) in Table 3. It can be seen that the results from the MFA are very close to the data that is presented in the literature.

Table 3 Raw material consumption for the VCM production process.

Raw materials	Specific consumption			
Ethylene [t/t VCM]	0.47	0.46-0.47	0.46	0.45
Chlorine [t/t VCM]	0.59	0.59	0.58	0.57
Air [t/t VCM]	0.73	0.73	-	-
Oxygen [t/t VCM]	-	-	0.14	0.13
Reference	Wilkes et al., 2005	Falcke et al., 2017	ThyssenKrupp, 2012	MFA (Appendix A.3)

The result of the EFA (A.4) are presented in Table 4. Unfortunately, literature reported no specific breakdown of the specific energy usage of the VCM process.

Table 4 Energy consumption per process step for the VCM production process.

	EDC production	EDC purification	EDC cracking	VCM purification	Total
Final energy demand [GJ/t VCM]	0.69	0.64	2.83	0.85	5.01

It can be found from the results in Table 4 that the EDC cracking process is the most energy intensive part of the process. This should not come as a surprise as the compounds have to be heated and pressurized heavily prior to cracking. Furthermore, the cracking process itself is endothermic, meaning that a constant flow of heat has to be added to the cracking furnace. The total calculated specific energy demand was calculated to be 5.01 GJ/t VCM.

The required energy consumed during the VCM production process is compared with values from literature in Table 5. Energy is provided in the form of steam, natural gas or electricity. For comparability, we report the numbers in both primary and final form, with conversion factors for 2019 (RVO, 2019). Cooling water is not included as it extracts energy from the system. Ideally, the total the sum of the utilities should add up to fit the total energy demand of the VCM plant (as summarized in Table 4).

Table 5 Comparison of the required energy carriers, steam, natural gas and electricity, for the VCM production process from different sources. The relative difference between the numbers from the EFA and the data communicated by Shin-Etsu (2019) are displayed in the final column.

Energy carrier	**Final energy**			
Steam [GJ/t VCM]	0.3-1.7	2.2	1.4-1.8	2.1
Natural gas [GJ/t VCM]	3.4-4.2	3.1	3.0-3.1	2.2
Electricity [GJ/t VCM]	0.4-0.8[1]	0.8	0.68-0.72	0.7
Energy carrier	**Primary energy[2]**			**Comparison EFA**
Steam [GJ_p/t VCM]	0.3-1.8	2.4	1.5-2.0	2.3
Natural gas [GJ_p/t VCM]	3.4-4.2	3.1	3.0-3.1	2.2
Electricity [GJ_p/t VCM]	1.0-2.0	2.0	1.7-1.8	1.8
Total primary energy required for utilities (GJ_p/t VCM)	4.7-8.0	7.5	6.2-6.9	6.3
Reference	Falcke et al., 2017	Shin-Etsu PVC B.V., 2007	Shin-Etsu, personal communication (2019)	EFA (Appendix A.4)

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[1] Falcke et al. (2017) reports an electricity demand of 0.11-0.21 MWh/t VCM. This range was converted to GJ/t VCM using a conversion factor of 1 MWh = 3.6 GJ.

[2] Conversion factors to primary energy are: 1 GJ steam = 1.11 GJ_p; 1 GJ natural gas = 1 GJ_p; 1 GJ electricity = 2.5 GJ_p (RVO, 2019)

The natural gas demand as calculated with the EFA is lower than reported in the literature. On the other hand, the steam demand is higher than in literature. The offset in steam and natural gas demand could be explained by the fact that the assumptions made in the model related to steam and natural gas use are incorrect. It could for example be that in certain parts where steam use is assumed in the model, in the actual plant natural gas is required and/or steam is produced on site using natural gas. Falcke et al. (2017) based their data on a questionnaire which was conducted with VCM producers in Europe, which could explain why the numbers show such a wide range. The total primary energy consumption from the EFA lies within the range as reported by Falcke et al. (2017). Figure 10 visually summarize the main findings from the EFA.

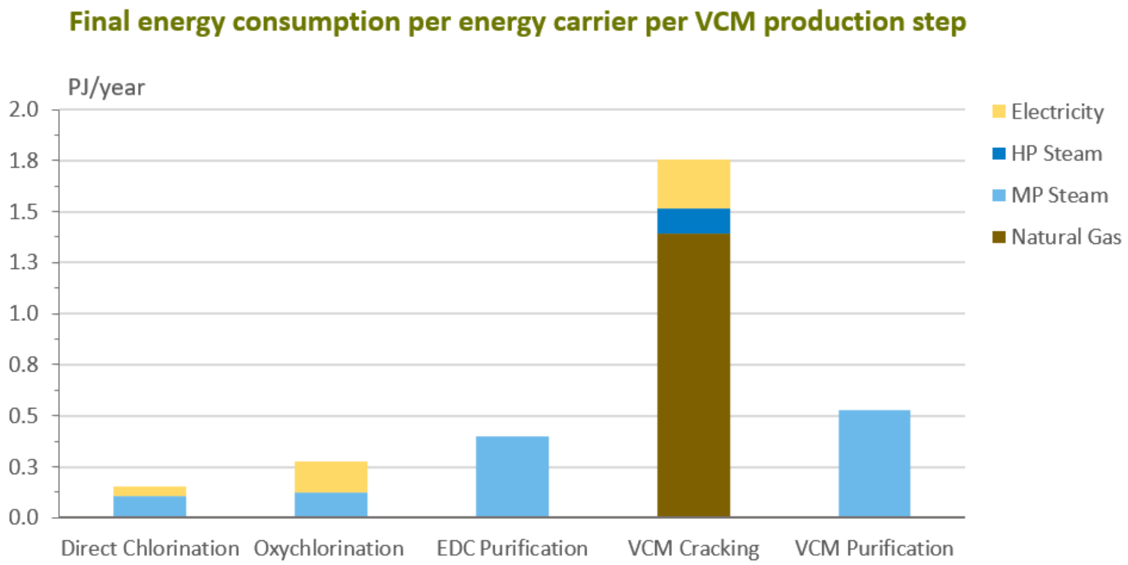

Figure 10 Overview of the final energy consumption of the VCM production process as calculated in the EFA in this report, see Appendix A.4.

2.3 PVC production

A general overview of the PVC production process is shown in Figure 11. The production process is rather linear and only requires VCM and water as the main raw input. Furthermore, it will be shown in this chapter that the process generally does not require natural gas for the heat demand. Steam and electricity are therefore the only sources of energy that are required in this part of the process. Assuming that the steam and electricity are imported, this part of the process emits little or no amounts of greenhouse gases on site. In fact, the PVC production plant of Shin-Etsu is not registered in the NEa emission database. The PVC production process will be described according to the structure presented in Table 2.

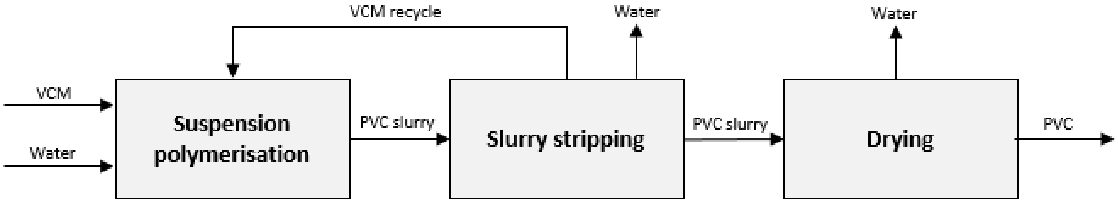

Figure 11 Block scheme of the PVC production process

2.3.1 PVC polymerization

Three different processes for the manufacturing of PVC can be distinguished (EU, 2007: Wilkes et al., 2005):

- Suspension polymerization (S-PVC)
- Emulsion polymerization (E-PVC)
- Mass (or bulk) polymerization (M-PVC).

Suspension polymerization is the most widely used polymerization technique since it performs economically and environmentally better than the other techniques, due to good temperature and viscosity control and relatively simple PVC purification (Wilkes et al., 2005). The produced grain is on average 100-180 μm in diameter, and this method is suited for large volume production applications (EU, 2007). Mass polymerization has lost importance since it cannot be operated in closed-polymerization reactors and because the PVC purification is energy intensive for several technical reasons, which will not be explained here (Wilkes et al., 2005). Emulsion polymerization is the second most used polymerization technique and it produces PVC grains which are one hundred times smaller (0.1-3.0 μm) than suspension PVC grain (EU, 2007). The small particles size makes the resins particularly useful for small specialized applications, such as wall coverings (EU, 2007).

VCM polymerizes via the free radical method and in the liquid state to form PVC (Wilkes et al., 2005). The overall reaction can be simplified to equation 2.4, where n stands for the number of VCM molecules forming the polymer. The length of the polymer can vary between 750-1500 monomer units depending on the operating temperature. The polymerization reaction is exothermic with a heat of reaction of -1540 kJ/mol, and typically operates at a temperature between 35-70°C and a pressure between 4-12 bar (EU, 2007). The overall conversion of VCM is limited to 85-95% (EU, 2007).

$n\,\mathrm{CH_2=CHCl} \rightarrow (-\mathrm{CH_2\text{-}CHCl}-)_n$ +heat (eq. 2.4)

At the start of the reaction, water, VCM and additional compounds such as dispersants and initiators are loaded in the reactor (Wilkes et al., 2005). Unlike most polymers that are soluble in their respective liquid monomer, PVC is highly insoluble in VCM (Wilkes et al., 2005). This characteristic allows industry to produce PVC as porous granules. During polymerization the PVC precipitates as tiny particles, which agglomerate to form a porous internal structure in the resin particles (Wilkes et al., 2005). The polymerization reaction is started by the initiator, after which the length of the polymerization chain is controlled using the polymerization temperature. After the desired conversion has been reached, a stopping agent can be used to terminate the reaction. The reactor is depressurised by venting off unreacted VCM which is recycled back to the reactor for polymerization. The contents of the reactor are removed and the resulting sludge is transported to a blowdown vessel where part of the remaining unreacted VCM is vented off and recycled back to the polymerization reactor. The product stream consists of an aqueous slurry, containing PVC and a small amount of unreacted VCM (2-3%).

2.3.2 VCM recovery

It is common practice to remove any leftover VCM from the PVC down to concentrations well below 1 ppm (Wilkes et al., 2005). This is generally done by means of a steam stripping column. The slurry is blown down into a stripping column from the top recovered down to atmospheric pressure.

Next, steam of approximately 100°C (between 100-120°C) is fed from the bottom of the column, which will evaporate VCM and part of the water from the slurry. The stripped slurry leaves the column from the bottom while the recovered VCM/water gas mixture is captured at the top. The VCM is recovered and recycled back to the polymerization reactor. The PVC slurry, still containing 50-60% water, is processed further in the next part of the process.

2.3.3 PVC drying

The final processing step is the removal of the large fraction of water which is still present in the PVC slurry. This is generally done by a mechanical drying step and a thermal drying step (Wilkes, 2005; ThyssenKrupp, 2012).

After stripping, the slurry enters a centrifuge, which will separate a large fraction of the water from the slurry mechanically and produces a wet-cake with 20-30% moisture content (Allsopp & Vianello, 2002; EU, 2007). The water extracted after centrifuging is transported to a water treatment plant and reused partly. Next, several techniques can be used to further dry the produced PVC. Shin-Etsu implements two drying techniques (Shin-Etsu PVC B.V., 2018a): Fluidized bed drying and flash drying.

Fluidized bed drying is widely used in the chemical industry to reduce the moisture content of powders and granules. Hot air at a temperature of up to 95°C is injected at high pressure through a bed of moist PVC particles (Chan et al., 2008). Due to the hot air, the particles are lifted and suspended in a stream of air. Liquid is vaporized as a result of the heat transfer between the wet solids and the hot air and removed (Law & Mujumdar, 2007).

Flash drying is a technique, similar to fluidized bed drying, where hot air is used to treat powders and granules. The wet particles are fed into a hot gas stream and transported down the drying tube. As the name implies, the thermal contact between the gas stream and the particles is usually short. This means that this technique is most useful for removing surface moisture from particles (Borde & Levy, 2007). Both drying techniques are followed by sieving to remove any coarse particles (EU, 2007). Finally the PVC material is bagged and /or transported.

2.3.4 Mass and energy flows

The inputs for the PVC production process were based on data provided by Shin-Etsu. It is compared in Table 6 with ThyssenKrupp (2012) and EU (2007).

Table 6 Raw material consumption for the PVC production process.

Raw materials	Specific consumption		
VCM [t/t PVC]	1.001 1)	1.001 1)	1.000 2)
Water [t/t PVC]	2.3	3.1	1.5 2)
Reference	ThyssenKrupp, 2012	EU, 2007 3)	Shin-Etsu, personal communication (2019)

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1) Both ThyssenKrupp (2012) and EU (2007) report overall VCM losses to waste water of 10kg VCM/t PVC

2) Both numbers were obtained after personal communication with Shin-Etsu (2019). According to Shin-Etsu VCM losses are negligible (<0.1%) and the water consumption is half of what is reported in EU (2007).

3) EU (2007) base their numbers on data from 2003, which should be taken into consideration when comparing the data.

Similarly to Section 2.2, the energy of the PVC production process, as reported by different sources, are compared. As the approximate steam and electricity demand of Shin-Etsu Pernis are known from recent personal communication by the company itself, that data is considered the most reliable source in Table 7.

Table 7 Comparison of the required energy for the PVC production processes from different sources.

Energy carrier	Final Energy		
Steam [GJ/t PVC]	2.4[1]	3.2	2.1
Electricity [GJ/t PVC]	0.5[2]	0.6	0.7
Energy carrier	**Primary Energy**		
Steam [GJ_p/t PVC]	2.7	3.6	2.3[3]
Electricity [GJ_p/t PVC]	1.3	1.4	1.7[4]
Total primary energy required for utilities [GJ_p/t VCM][5]	4.0	5.0	4.1
Reference	EU, 2007	DCMR, 2004	Shin-Etsu, personal communication (2019)

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[1] EU (2007) reports a steam demand of 879 kg/t PVC. Using an energy density for saturated steam (1 bar, 100°C) of 2675 kJ/kg (Engineering Toolbox, 2003) results in 2.4 GJ/t PVC.

[2] EU (2007) reports an electricity demand of 0.14 MWh/t VCM. This was converted to GJ/t VCM using a conversion factor of 1 MWh=3.6 GJ.

[3] Shin-Etsu shared that Pernis consumes 1.1 PJ steam/year. Considering a production capacity of 470 kton PVC/yr results in a specific steam consumption of 2.34 GJ/t PVC.

[4] Shin-Etsu shared that Pernis consumes 0.8 PJ electricity/year. Considering a production capacity of 470 kton PVC/yr results in a specific electricity consumption of 1.7 GJ/t PVC.

[5] Conversion factors to primary energy are: 1 GJ steam = 1.11 GJ_p; 1 GJ natural gas = 1 GJ_p; 1 GJ electricity = 2.5 GJ_p (RVO, 2019).

3 PVC products and application

Plastic material is widely appreciated due to its unique combination of light-weight, durable and other intrinsic properties. The worldwide production of plastics reached 348 million tons in 2017 of which 64.4 million tons (18.5%) originated from Europe (PlasticsEurope, 2018a). To put this in perspective, in 2002 the worldwide production of plastics was 200 million tons, which shows that in the past 16 years the global supply increased by 74% (PlasticsEurope, 2008). This chapter will present the facts about the applications, market value, and recycling rates of PVC in Europe and the Netherlands.

3.1 PVC in the Netherlands

First of all, it is important to note that it remains difficult to gain quantitative insight in the separate plastic streams in the Netherlands for a couple of reasons (CPB, 2017). Firstly, the amount of plastic in products which are partly consisting of plastic material is not tracked. Secondly, the amount of plastic material which is currently littered in the environment is unknown. And thirdly, the definitions of plastic material and its respective subtypes differ between organizations. A lack of this overview makes it difficult for the government to set waste-and recycling goals and, more importantly, verify if new regulations are sufficient of not (CPB, 2017). In terms of recycling, it is important to note that PVC resin is more often than not used in combination with other materials. Composite products which combine PVC with all types of plastics and other materials, such as metal, require extra treatment before recycling, as will be discussed later.

3.1.1 Grades of PVC resin

There are several grades of PVC resins that can be produced by PVC manufacturers, which is specified by the K-value (Allsopp & Vianello, 2002; Schellerer et al., 2016). Manufacturers are able to control the K-value by changing the polymerisation temperature during production. The K-value of the resin determines its flexibility and therefore the application area of the PVC (see Table 8).

Table 8 Different PVC K-values and the representative applications (Allsopp & Vianello, 2002)

K-Value	Application
55-60	Formulations for injection moulding of pipe and conduit fittings, blow moulding of bottles.
66-68	Rigid formulations, such as pipes, conduit, sheet
65-71	Flexible formulations, such as flexible sheet, flooring, tubing

Shin-Etsu currently produces PVC using suspension polymerisation with 4 different K-values, as can be seen in Table 9. Vynova Beek has a larger PVC grade portfolio, offering a total of 11 grades with 6 different K-values (Vynova Group, 2019b).

Table 9 Overview of the four types of PVC resin that Shin-Etsu produces (Shin-Etsu PVC B.V., 2018b). The first number of the code indicates the K-value. E.g. the K-value of S58-02 is 58.

Shin-Etsu PVC grade	Application
S58-02	Injection moulding of rigid articles, such as pipe fittings. Production of foamed products.
S60-12	Production of thin profiles, foamed boards, film/sheet and boards.
S67-04	Production of window profiles and both pressure or non-pressure pipes.
S70-16	Production of transparent and non-transparent film/sheet, and extrusion of cables.

3.1.2 Production of PVC

The overall plastics production in the Netherlands is known and has been following the global trend and increased therefore slightly in the past years (Euromap, 2016). According to Euromap, in 2018 the total plastics production was about 4 Mton. The plastics consumption per capita has been increasing slightly as well and reached about 87 kg per capita in 2017. As mentioned at the beginning of Section 3.1 there is no specific data available about the volumes per plastic types. However, according to PlasticsEurope (2018a), approximately 10% of the plastic demand in Europe was reserved for PVC. CPB (2017) reports a market share in the Netherlands of 11-12%, however this number is again based on European market statistics.

In order to make an estimate of the total volumetric PVC production demand in the Netherlands it is possible to assume 10% of 4 Mton, which is approximately 0.4 Mton. Comparing this with the total production capacity of Shin-Etsu and Vynova, which sums up to 0.75 Mton, shows that this is a correct estimation. Export of PVC to other countries could explain why the actual production capacity is higher than the demand for PVC in the Netherlands. According to Shin-Etsu their main market is Europe, of which Germany and Italy are the largest importers of PVC (Shin-Etsu, personal communication).

3.1.3 Application of PVC

Again, the applications for PVC in the Netherlands specifically are not reported. However, data for Europe can be used to give some insight in this matter. In Europe, PVC is used mostly used in construction applications, such as window frames and profiles, pipes and fittings, cables and flooring (PlasticsEurope, 2018a). PVC is strong, lightweight, easy to install, resistant to weathering, cost-effective and therefore widely applied (PVC.org, 2018). Furthermore there are more niche applications such as garden hoses and inflatable pools. It can be assumed that these applications will be similar in the Netherlands. Figure 11 shows the distribution of PVC for its different applications.

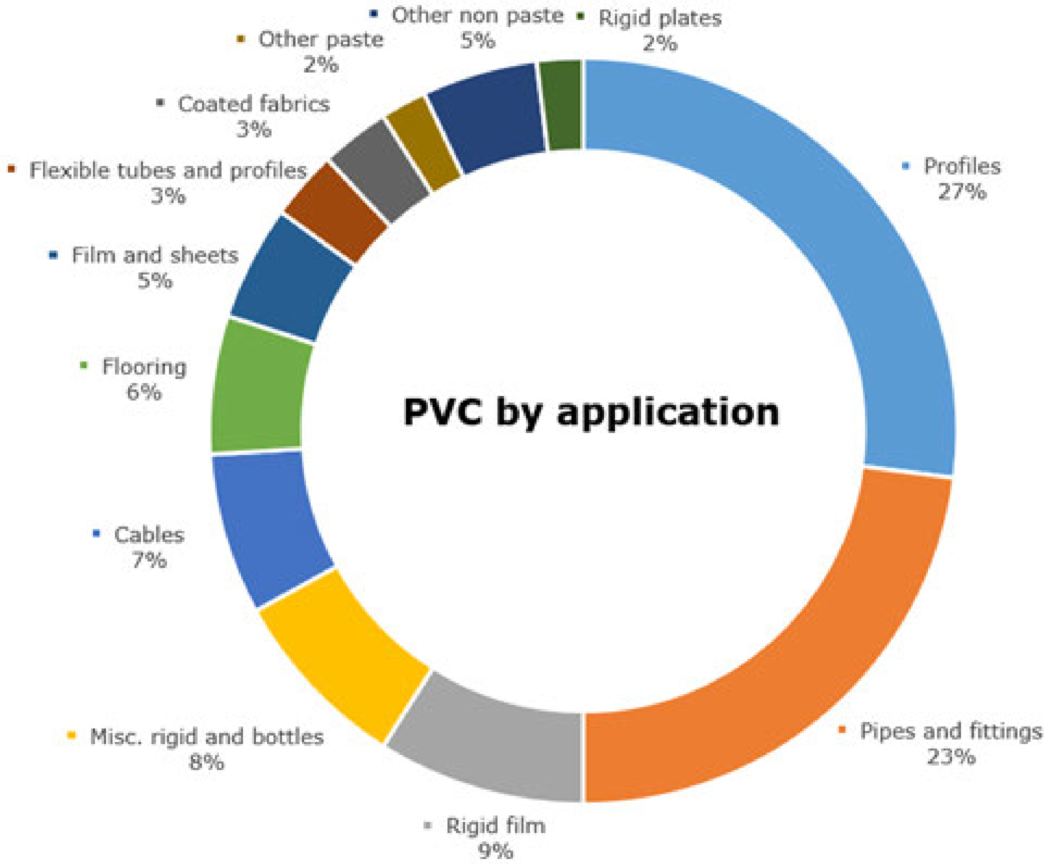


Figure 12 PVC is widely used in a variety of applications. Source: VinylPlus, 2011

3.1.4 Market price

The market price in the Netherlands for PVC has been fluctuating in 2018. As seen from Figure 12, the price for virgin PVC was 970 euro/ton PVC at the beginning of the year and has since then fluctuated to end up at a current price of 950 euro/ton PVC (K&R, 2018). The price of PVC is only partly influenced by the price of oil, because firstly PVC can also be produced using other feedstocks and secondly because the price of oil is only part of the costs to produce PVC (CPB, 2017).

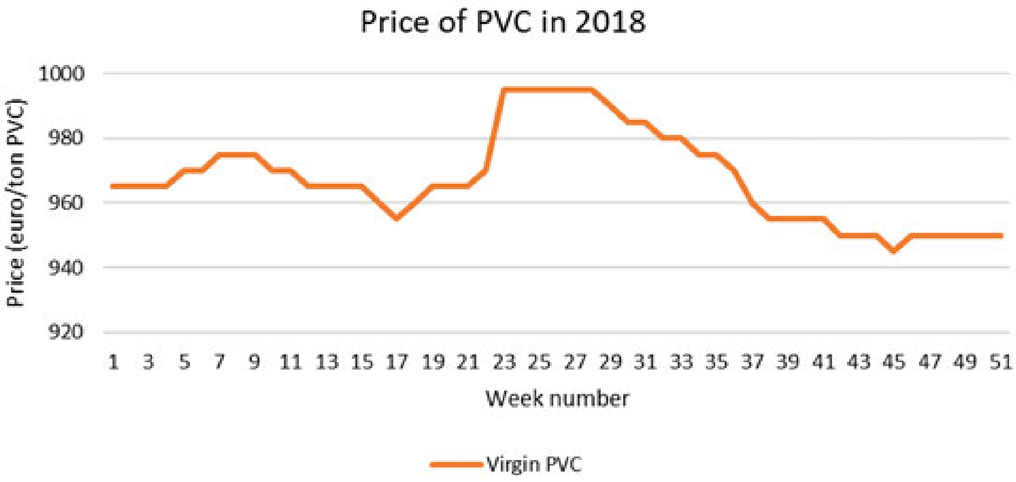


Figure 13 Graph showing the price of virgin PVC in EUR/ton PVC in 2018. It has remained relatively constant and is at the time of writing 950 EUR/ton. The price concerns the Dutch target price for PVC (K&R, 2018).

3.2 Recycling of PVC

3.2.1 Recycling of plastics in the Netherlands in general

Besides the decarbonisation options that will be discussed later in this report, another effective method to indirectly reduce greenhouse gas emissions in the PVC manufacturing industry is to simply reuse PVC that has already been produced. By re-circulating PVC back into the supply chain the industry could on one hand reduce their greenhouse gas emissions because less PVC has to be manufactured to supply the same demand, and on the other hand reduce costs since less feedstock (specifically ethylene) is needed.

The general process of recycling of plastics can be divided in different steps:

1. Collection: plastics have to be collected and transported to the sorter.
2. Sorting: plastics are manually and automatically sorted in their respective mono streams (PP, PE, PVC, etc…) to obtain the purest possible plastic streams. The plastics are then pressed to bales for further processing.
3. Recycling: mechanical recycling or chemical recycling to produce recycle plastic granulates.

In the Netherlands this whole process can be characterised as an ‘open’ organisation (Berenschot, 2017). This means that the producer or importer who brings the plastic product to the consumer market is not involved in the collection, sorting or recycling or their respective product. The collection of plastic is generally done by consumers of the product, and in the case of mixed consumer waste is controlled by the municipalities. The sorting and recycling is then done by another group of sorters and recyclers. Having such a large group of actors involved in this process has proven to slow down innovation and optimisation (Berenschot, 2017).

3.2.2 Where PVC waste occurs

Two major groups of PVC waste can be defined: pre-consumer waste and post-consumer waste (EU, 2000). Pre-consumer waste is PVC material which is leftover before the usage of the product by the consumer. This group can be further divided in 1) production waste and 2) installation waste. Production waste is generated during the manufacturing of the intermediate and final PVC products. An example of production waste is PVC cut-offs when shaping the PVC product. Installation waste is generated during the installation of the PVC products. An example of installation waste is cutting losses during the installation of flooring. Pre-consumer waste is valuable waste as it is a pure PVC stream and can be directly recycled into the process.

Post-consumer waste is PVC material which occurs from products at its end-of-life phase in mixed waste streams or as part of composite materials. Post-consumer waste can occur as a relatively pure mono fraction as a result of sorting from the mixed waste stream or separate collection, such as is the case for PVC pipes. Alternatively, PVC can be processed into composite products in combination with other materials. To recover this PVC the products will have to be disassembled, mechanically grinded and sorted. An example are cables, which are mainly made of PVC and copper.

Table 10 PVC waste classified based on source of origin (EU, 2000).

Group	Subcategory	Example
Pre-consumer waste	Production waste	Cut-offs
	Installation waste	Cutting losses
Post-consumer waste	Mono fraction	Pipes
	Composite fraction	Cables

Currently the quantity of PVC items entering the waste stream is relatively small as the majority of PVC products have long lifetimes averaging 50-100 years. It is expected that this situation will change as more and more PVC products will approach their end of economic lives and will add to the PVC waste stream (Pieter Bruijnincx, personal communication; PVC.org, 2018). Since PVC consumption took off in the 1970s it is expected that due to this time-lag considerable amounts of PVC will be available for recycling in 2020 (EU, 2000).

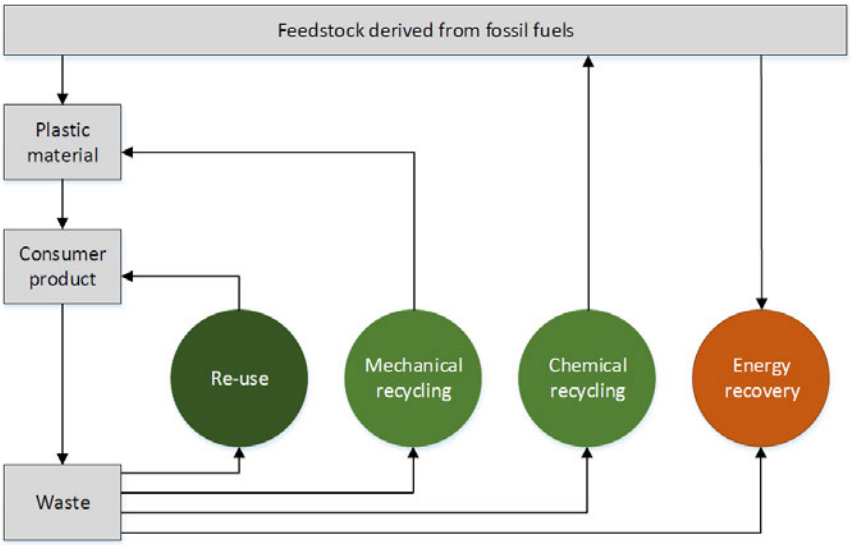
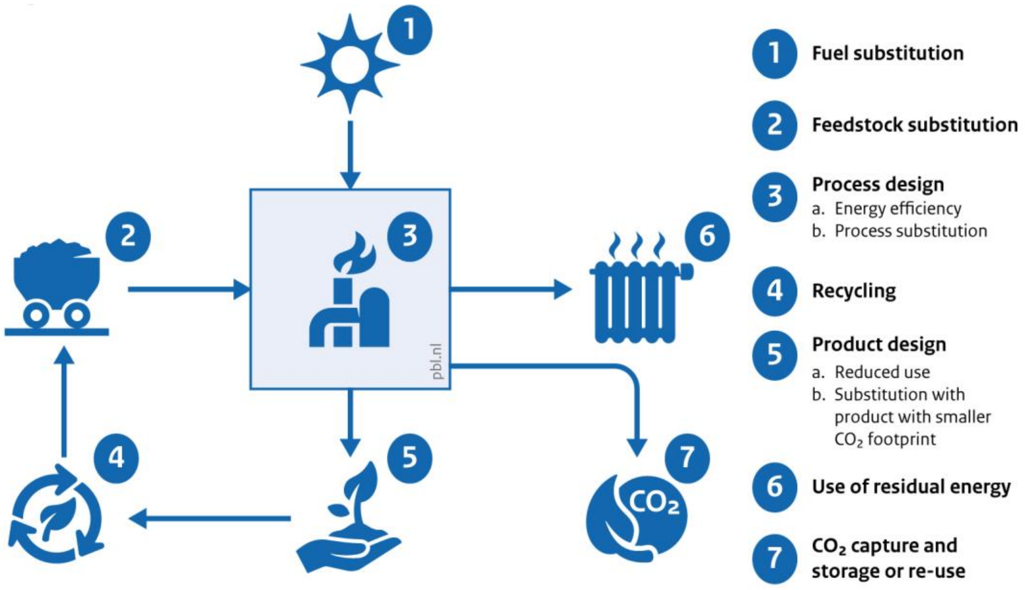


Figure 14 Simplified scheme of the recycling options for PVC waste treatment. Directly re-use of PVC products is most valuable. Alternatively, waste can be recycled mechanically or chemically. Finally, the least valuable method of PVC waste treatment is energy recovery (Berenschot, 2017).

4 Options for decarbonisation

This chapter will describe the proposed options to achieve a reduction of energy use and/or CO_2 emissions for the manufacturing of PVC at Shin-Etsu PVC B.V., Rotterdam and Vynova Beek, Geleen. Figure 14 visualises seven categories that can be distinguished when addressing decarbonisation. A full overview, based on what we could find in literature and from conversations with industry, of possible decarbonisation options for the manufacturing of PVC is shown in Table 11.



Source: PBL

Figure 15 Seven possible categories of decarbonisation measures that can be applied in the full production chain (PBL, 2019).

Table 11 Full overview of all the decarbonisation options for the PVC manufacturing industry, the ones highlighted in green will be discussed further in this chapter.

	Category	Description	Options
1	Fuel substitution	Substitution of the (currently fossil) energy supply: e.g. biogas, electrification, hydrogen, geothermal heat, recycled heat	- Production of steam by syngas-CHP plants - Heat generation by replacing natural gas burners in the cracking furnaces with hydrogen burners - Production of steam by combustion biomass (e.g. wood chips) - Production of steam by combustion of biogas and syngas

	Category	Description	Options
			- Production of steam using an heat pump - Steam upgrading by mechanical vapour recompression (MVR). - Electric cracking furnaces - Electric boilers
2	Feedstock substitution	Feedstock substitution, e.g. with biomass, recycled flows, other upstream material substitution	- Replacement of ethylene from naphtha by bio-ethylene from bio-ethanol
3	Process design	Substitution production processes based on different fuel, feedstock, or entirely different process, for creating the same product or products with the same or similar application, e.g. innovative processes with membrane separation process instead of thermal process	- Substitution of balanced production process by ethane-to-VCM over copper ZSM-5 catalyst process
4	Recycling	Recycling of products or by-products	- Improved mechanical recycling of PVC, especially the post-consumer waste stream - Innovative non-conventional mechanical recycling of PVC - Chemical recycling of PVC to the main chemical building blocks
5	Product design	Reduction of the total product demand or substitution with other product with the same properties but lower CO_2 footprint	- Alternative to PVC - Use alternative polymers for short life cycle applications
6	Use of residual energy	Reuse of waste heat either within the process itself, or other useful applications outside of the process	- Heat integration in the PVC plant
7	CO_2 capture and storage or re-use	Carbon capture and storage processes or alternative uses of the potentially emitted CO_2	- CCS of CO_2 stream from natural gas burners

Figure 15 visualises the decarbonisation options in the total production chain. As part of the MEE-covenant[e] Shin-Etsu aims to maintain an annual yearly increase in energy efficiency of ~2%.

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[e] MEE = Meerjarenafspraak Energie-efficiency Ets-ondernemingen, which is an agreement between ETS registered companies and focuses on continuous energy efficiency improvements.

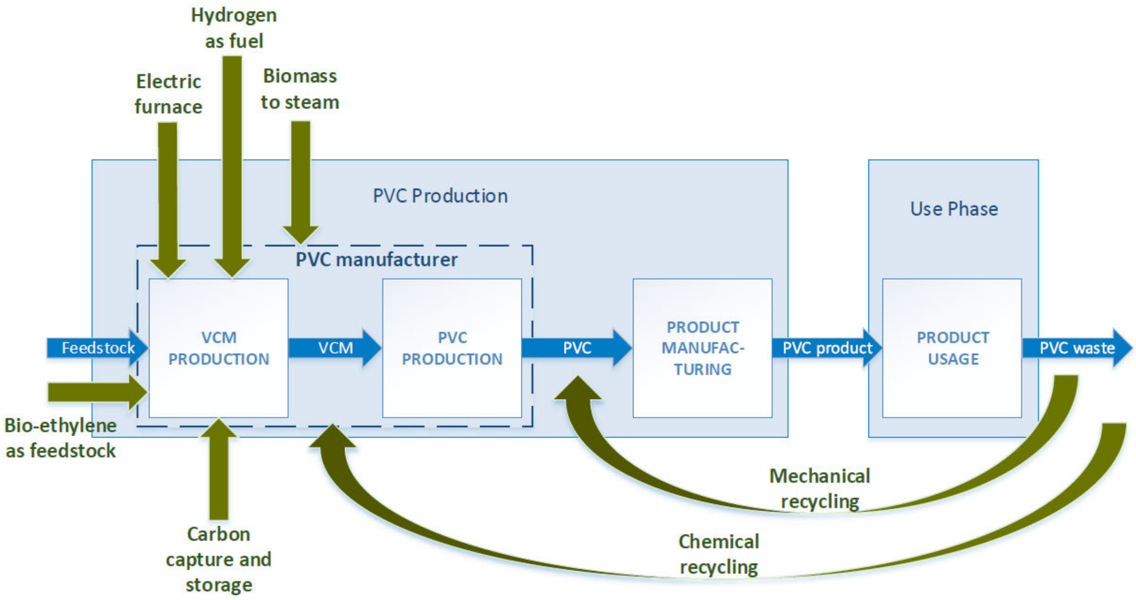

Figure 16 Overview of the proposed decarbonisation options for PVC production.

4.1 Cracking furnace with hydrogen burners

4.1.1 Technology description

Utilising hydrogen as fuel instead of natural gas has the potential to directly avoid a large part of the emissions of any production plant using conventional natural gas burners (Gigler and Weeda, 2018; Stafell et al., 2018). It can be produced from renewable energy sources, such as wind, solar power or biomass (green hydrogen), from fossil fuels in combination with CCS (blue hydrogen), and hydrogen is sometimes a by-product of other processes. The interchangeability of hydrogen versus natural gas can be judged by means of the Wobbe index. This index is a function of the higher calorific value and the specific gravity of the fuel gas. Low-calorific natural gas from Groningen has a Wobbe index of approximately 44 MJ/m^3 (Zachariah-Wolff et al., 2007), which is very similar to that of hydrogen which is typically 45 MJ/m^3, see Table 12 (McGilp & Livermore, 2018). However, as the other gas characteristics are not similar, existing burners will most probably have to be modified (VNP, 2018). The temperature, length, speed and oxygen to fuel ratio of hydrogen flames are different than natural gas flames, see Table 12, which is seen by some stakeholders as a potential barrier for implementation (CE Delft, 2017).

Moreover, a larger challenge is reducing the NO_x emissions from hydrogen burners in order to adhere to the same regulations as natural gas since NO_x emissions from hydrogen burners are significantly higher (CE Delft, 2017; McGilp & Livermore, 2018). Ongoing efforts have been made to tackle this issue and exhaust gas recirculation (EGR) seems to be a feasible solution (CE Delft, 2017). Furthermore, when implementing hydrogen burners the overall primary energy demand of the process will increase, as the hydrogen production chain suffers from lower efficiencies. For example, production of hydrogen from electricity only has an approximate efficiency of 70% (Ros & Daniëls, 2017).

Stafell et al. (2018) stress that flexible burning technology will be required to make the transition to 100% hydrogen burners, as especially in the early stages hydrogen might not always be available. With support of the SBIR project of RVO, DNV GL has developed flexible burners, which can both utilise conventional natural gas and up to 30% hydrogen in natural gas (Stafell et al., 2018). These burners were tested on industrial scale (4MW), but the results of this are unknown. In their most recent project "Varigas" DNV GL are developing burners which are fully flexible and can accept up to 100% hydrogen (Stafell et al. 2018; RVO, 2016). The hydrogen fraction in the fuel is monitored by a sensor after which the oxygen to fuel ratio and geometric of the burner are adjusted accordingly (RVO, 2016).

In literature there are mixed reports about the readiness level of the technology. CE Delft (2017) reports that industry have already built multiple large-scale hydrogen burners of 3-50 MW with state-of-the-art technology, without mentioning any specifics. Also Toyota claims that they have developed the world's first general purpose hydrogen burner for industrial use in their forging line in their Honsha Plant in Japan at the end of 2018 (Toyota, 2018). On the other hand, in the most recent hydrogen roadmap (Gigler & Weeda, 2018) it is expected that high-temperature industrial heating using hydrogen fuel will take at least 10 more years before this will be a realistic option, as the authors report a TRL of 1-3. Since Gigler & Weeda (2018) refer to hydrogen use on industrial scale, a TRL of 3 for hydrogen burners in cracking furnaces is assumed here.

Table 12 Physical characteristics of natural gas and hydrogen. As natural gas consists mainly of methane, it was assumed that those characteristics are representative for natural gas.

Characteristic	Methane (main component of natural gas)	Hydrogen
Density (at 1 bar and 15 C)	0.65 kg/m^3	0.084 kg/m^3
Wobbe index	51 MJ/m^3 (44 MJ/m^3 for LC natural gas)	45 MJ/m^3
Flame Colour	Visible/blue	Invisible/light blue
Flame temperature	Lower flame temperature but higher thermal radiation heat transfer	Higher flame temperature but lower thermal radiation heat transfer
Flammability range	5-15%	4-75%
Flame speed	0.42 m/s	2.37 m/s
Minimum ignition energy	0.29 mJ	0.02 mJ

4.1.2 Techno-economic parameters

Natural gas is burned at a high rate to maintain the endothermic cracking reaction at operating temperatures. According to calculations[f] the annual natural gas demand is equal to 1.2 PJ, which amounts to a total emission of CO_2 of 68.4 kt annually (73% of Shin-Etsu's 2018 direct emissions). Assuming that hydrogen from renewable sources is used, switching to hydrogen burners has the potential to significantly reduce, or even eliminate, the CO_2 emissions from the cracking section. Considering a LHV for hydrogen of 120 MJ/kg, it can be found that the total amount of hydrogen required to fully cover the natural gas demand in the burners is roughly 14 kt/yr, or approximately 1.7 PJ.

Vereniging Nederlandse Petroleum Industrie (VNPI) estimated the costs for several decarbonisation options, including the utilisation of hydrogen fuel in cracking furnaces. According to a recent report the capital costs (CAPEX) for retrofitting a 10MW cracker

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[f] Calculated using an annual production rate of 620 kton VCM/yr and an emission factor for natural gas of 56.6 kg CO_2/GJ.

furnace with hydrogen burners would be in the range of 5–15 MEUR (VNPI, 2018), of which 1% can be used as an estimate for the operational costs (OPEX).

Table 13 Techno-economic characteristics of decarbonisation option 'cracking furnace with hydrogen burners'.

Characteristic	Value	Comment	Source
CO_2 emissions [kt CO_2/PJ]	-	Assuming that green hydrogen is used, burning the fuel leads to zero-emissions.	-
Theoretical specific amount of hydrogen required [kt H_2/PJ]	8.3 1)	Derived using the LHV of hydrogen, which is 120 MJ/kg H_2	-
CAPEX [EUR/kW]	400-1200 2)	Estimation includes costs for the infrastructure for hydrogen transport, hydrogen compressor, replacement of natural gas burners. Does not include NO_x emission reduction technology.	VNPI (2018)
OPEX [EUR/kW/yr]	4-12	1% of CAPEX	VNPI (2018)

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1) The LHV of hydrogen is 120 MJ/kg H_2. This is equivalent to 0.12 PJ/kton H_2. Calculating the inverse of this number yields 8.3 kton H_2/PJ.

2) VNPI (2018) reports the investment costs for a 10MW cracking furnace: 5-15 M€. The CAPEX has been recalculated for a 20 MW cracking furnace using the parametric cost estimation method suggested by Remer & Chin (2015): $C_b = C_a * (S_b/S_a)^{\alpha}$; where C_b and C_a are the investment costs for the scaled installation *b* and the reference installation *a*, S_b and S_a are the sizes of scaled installation *b* and the reference installation *a*, and α is the R factor which indicates an economy of scale. Remer & Chin (2015) report an average R factor of 0.67. Since Shin-Etsu operates cracking furnaces at 20 MW (Shin-Etsu, personal communication) the investment costs from VNPI (2018) have been scaled to 20 MW.

4.2 Electric furnace

4.2.1 Technology description

The heat required for the continuous cracking reaction as described in the previous section can be delivered by fuels, such as natural gas or hydrogen, but also through electricity or electromagnetic fields. This type of heat generation is in literature referred to as electrification of the cracker furnaces and is addressed by several roadmaps as a promising future decarbonisation pathway. For example, de Pee et al. (2018) focused on decarbonisation of the four most polluting industrial sectors (cement, steel, ammonia and ethylene production) and found that replacement of steam-cracking furnaces by electric furnaces for ethylene production should be considered for future decarbonisation. The development of electric furnaces is still in test phase and industrial sized electric furnaces are not commercially available yet (de Pee et al., 2018; VNCI, 2018). Moreover, the success rate of electric furnaces for decarbonisation is heavily dependent on the availability of cheap, renewable electricity (de Pee et al., 2018) and a stable electricity network (VNPI, 2018).

Electrification of electric furnaces can be categorized in two main groups: direct and indirect heating technologies. Direct heating technologies include inductive and dielectric heating; indirect heating technologies include resistance, arc and infrared heating.

Table 14 depicts the characteristics of each technology. Judging on the temperature ranges, indirect resistance heating and dielectric heating are most suitable for the replacement of EDC cracking furnaces, as the temperature in the furnace is typically 500°C. Especially indirect resistance heating is interesting for the PVC manufacturing industry, as it delivers heat in a similar way as gas-fired heating systems (BZE, 2018).

Table 14 Overview of all electric furnace technologies (Energypedia, 2018)

Technology	Brief description	Temperature range (°C)	Common application
Resistance heating	Direct: An electric current is driven through a material, which heats up due to its electrical resistivity. Indirect: An electric current is driven through a resistor, which heats up, and through convection and radiation, heats up a surrounding fluid or gas.	200-1800	Food, metallurgy and glass industries
Arc heating	A metal is placed between two graphite electrodes which are charged to generate an electric arc between them. The high current goes through the metal and heats it.	1200-3000	Steel industry
Infrared heating	A heat source at high temperature emits infrared waves that are subsequently absorbed by a colder object.	300-2600	Metallurgy industry
Dielectric heating	When a changing electrical field is applied to an electrical non-conducting material with an asymmetrical molecule structure, friction will occur between the vibrating molecules as they attempt to align with this field, leading to internal heat development.	100-1300	Plastic molding, drying veneer, and the vulcanization of rubber are typical applications
Induction heating	A solenoid is used to generate an alternating magnetic field. If a conductor is placed inside this field, an alternating electric current is induced in this conductor that opposes the alternating magnetic field. This dynamics heats up the conductor.		Typical applications are the melting, brazing or hardening of metals

4.2.2 Techno-economic parameters

As was the case for the previous decarbonisation option, full electrification of the cracking furnace would lead to a significant decrease in CO_2 emissions, assuming that the electricity is generated using a renewable, zero emission technology, such as solar panels.

VNPI reports a CAPEX of EUR 35–50 million, of which 2% can be used as an estimate for the OPEX. The CAPEX for this decarbonisation is significantly higher than for the retrofitting of hydrogen burners, as seen in Section 4.1. Electrification requires the demolition and rebuilding of an entirely new furnace, which is estimated by VNPI (2018) to require an investment of approximately EUR 30 million. This could be different dependent on the type and capacity of furnace installed. Cost estimation regarding electric furnaces are highly uncertain as the technology is still in an early stage of development.

Table 15 Techno-economic parameters of decarbonisation option 'electric furnace'.

Characteristic	Value	Comment	Source
CO_2 emissions [kt CO_2/PJ]	-	Assuming that green electricity is used, electrification leads to zero-emissions.	-
Theoretical specific amount of electricity required [TWh_e/PJ]	0.3[1)]	Derived using that 1 MWh_e = 3.6 GJ	-
CAPEX [EUR/kW]	2800-4000[2)]	Estimation includes costs for infrastructure, installation of a new electric furnace and additional project costs.	VNPI (2018)
OPEX [EUR/kW/yr]	56-80	2% of CAPEX	VNPI (2018)

[1)] 1 MWh_e = 3.6 GJ, which means that 1 TWh_e = 3.6 PJ. Normalising to 1 PJ gives 1/3.6 ≈ 0.3 TWh_e/PJ.

[2)] The CAPEX has been scaled for a 20 MW cracking furnace using the using the parametric cost estimation method suggested by Remer & Chin (2015), as was explained in the footnotes of Table 13.

4.3 Carbon capture and storage (CCS)

4.3.1 Technology description

Carbon capture and storage (CCS) has the potential to significantly reduce CO_2 emissions from large point emission sources (Leung et al., 2014). Generally, CCS technology is based on the separation of CO_2 from (industrial) gases followed by compression, transport and storage. There are three methods for CCS, which are categorized based on the different combustion processes: post-combustion, pre-combustion and oxyfuel combustion (Leung et al., 2014). As the name implies, during post-combustion CCS CO_2 is captured from flue gas after combustion has taken place. Post-combustion CCS can in principle be retrofitted into existing plants. However, CO_2 levels in combustion flue gas are generally low (4% for gas-fired turbines, 10% for gas-fired furnaces and boilers), which means that the energy usage and costs to reach the required concentration of CO_2 of >95.5% are driven up significantly by large equipment sizes and high capital costs (Leung et al., 2014; Olajire, 2010).

In the case of natural gas, pre-combustion CCS first reforms the fuel gas to syngas (mixture of CO and H_2). Next, the H_2 content of the fuel gas is increased by means of performing the water-gas-shift reaction. Here, CO and H_2O react to form a mixture of H_2 and CO_2. This series of reactions results in a fuel gas with higher CO_2 concentrations and enables efficient CO_2 removal before the remaining H_2 can then subsequently be used as a fuel for the furnace (see Section 4.1).

During oxyfuel combustion the fuel is burned in the presence of pure oxygen, instead of air. This method has the main advantage of producing a flue gas with a nitrogen concentration close to zero and a high CO_2 concentration of up to 80% (Olajire, 2010). The resulting flue gas will be a mixture of mainly CO_2 and steam, which allows for easy CO_2 capture after condensation of the steam to H_2O.

The separation of CO_2 can be performed by a wide range of technologies (Leung et al. 2014). Absorption technology uses a liquid sorbent, such as monoethanolamine (MEA), to separate the CO_2 from the gas, after which the sorbent is recovered through a stripping or regenerative process. Adsorption technology captures CO_2 by means of a solid sorbent, such as activated carbon, and afterwards recovers the CO_2 by swinging the pressure (PSA) or temperature (TSA) of the system containing the CO_2. Other technologies include membrane separation technology where the CO_2 containing gas passes through a selective membrane, hydrate-based separation during which CO_2 forms hydrates in high pressurized water and cryogenic distillation where under low temperature and high pressure components from a gaseous mixture can be separated based on their individual boiling points.

Storage of the captured CO_2 in geological formations is considered to be the most viable option (Leung et al., 2014). In the Netherlands empty gas fields offer the largest CO_2 storage capacity. It is estimated that the Dutch onshore and offshore gas fields have a storage capacity of approximately 1500-2000 and 1200 Mton CO_2, respectively (Ministry of I&E, 2015). This is not counting any additional storage capacity of 9000 Mton CO_2 in Groningen gas fields, although these will most probably not be available until 2050 (Ministry of I&E, 2015).

In the Port of Rotterdam, the Port Authority, Gasunie and EBN are developing large-scale CCS in the Porthos project. The goal is to develop a functional pipeline connection to offshore gas fields in 2022/2023 with a total storage capacity of 37 Mton CO_2, which will be capable of storing 2-3 Mton CO_2/yr (Holleman, 2019). The idea is that industrial sites assess for themselves which CCS method is most effective for their process and deliver to the CO_2 infrastructure.

Alternatively, when CO_2 is utilised as feedstock in the chemical industry or other industries the concept is referred to as carbon capture and utilisation (CCU). Examples are the production of urea and methanol from CO_2 or the supply of CO_2 to greenhouses in the Westland region where it is used to speed up crop growth. The demand for CO_2 is growing, but still not high enough to build profitable business cases. According to (Pérez-Fortes & Tzimas, 2016) the CO_2 utilisation potential in Europe could reach 55 Mton/yr for a selected group of processes, assuming optimistic penetration rates for methanol and hydrogen economies.

4.3.2 Techno-economic parameters

The costs of CCS are highly varying and dependent on the chosen method of CCS, CO_2 separation technique and proximity of geographical storage capacity. Therefore, it is difficult to state costs with any degree of certainty. CE Delft (2018b) estimated that that the costs of the capture of CO_2 from gas-fired furnaces using post-combustion CCS with a CO_2 vol% of 10–15% could be between 80 and over 150 EUR/ton CO_2. This is excluding the costs for transport and storage which would be another 10 EUR/ton CO_2 (CE Delft, 2018b). However, as mentioned this infrastructure will be provided through project Porthos. It is not known what the price will be that companies will have to pay to be connected to this network. Berghout et al. (2015) performed a techno-economic analysis of several large scale CO_2

capture configurations in the Botlek area and reported that the average CO_2 concentration in the flue gas from Shin-Etsu is 10%.

Table 16 Techno-economic parameters of decarbonisation option 'CCS'.

Characteristic	Value	Comment	Source
CO_2 emissions [kt CO_2/PJ]	14	Energy penalty causes extra natural gas consumption and CO_2 capture efficiency approx. 85%	-
Theoretical specific amount of electricity required [GWh_e/PJ]	11-14[1)]	Post-combustion; both capture, treatment and compression	Berghout et al. (2015)
CAPEX [EUR/t CO_2 captured]	80– >150[2)]	Including capture of CO_2, excluding storage and transport.	CE Delft (2018b)
OPEX [EUR/t CO_2 captured/yr]	3– >8[3)]	4% of CAPEX	Own estimate

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[1)] The report indicates 0.7-0.9 GJ_e/tCO_2. Since 1 tCO_2 corresponds to burning 17.6 GJ natural gas, 40-51 TJ_e is needed for 1 PJ natural gas. This corresponds to about 11-14 GWh_e.

[2)] The report indicates a minimum of 80 EUR/ton CO_2, but the maximum costs could be 150 EUR/ton CO_2 or higher. This is in the same order of magnitude as other sources. In 2016, CE Delft (2016) estimated that the costs for capture of CO_2 in natural gas fired cracking furnaces would be 60–80 EUR/ton CO_2. IEA (2013a) reported 80 EUR/ton CO_2 for post-combustion CO_2 capture in a natural gas combined cycle power plant. The additional costs for transport and storage are varying: 10 EUR/ton CO_2 (CE Delft, 2018; Gasunie, 2017); 35–60 EUR/ton CO_2 (ZEP, 2011).

[3)] It was assumed that the OPEX is 4% of the CAPEX.

4.4 Bio-ethylene as feedstock

4.4.1 Technology description

Replacement of petroleum by bio-based feedstock is named by many sources as an important decarbonisation option for the petrochemical industry and is often included in national roadmaps (Posada et al, 2013; Wyns & Axelson, 2016; Dechema, 2017; Fiorentino, 2018). In practice, ethylene can be directly replaced by bio-ethylene as these are chemically identical, even though the initial feedstock and the production processes are different. This opens the opportunity to avoid considerable amounts of CO_2 emissions, provided that the bio-ethylene production process and the origin of the biomass is sustainable. This should be accessed case by case using life cycle assessments (LCA) in order to verify the sustainability of the process (Fiorentino, 2018).
Bio-ethylene can be produced from bio-ethanol, which can be obtained by a series of processes from several types of biomass feedstock, such as sugars in sugar beet or lignocellulosic waste. The sugars are fermented, followed by distillation, to obtain bio-ethanol. Finally, bio-ethanol is dehydrogenated over an alumina or silica-alumina catalyst to produce bio-ethylene.

Although bio-ethylene from sugar beet has high potential in terms of production (1 hectare of sugar beet can produce 2.5 tonnes of bio-ethylene), it competes with the food chain, which limits the overall potential for decarbonisation (Wyns & Axelson, 2016). Alternatively, lignocellulosic waste, such as agricultural and forestry residues, would be an interesting option as bio-ethylene production would not interfere with the food chain (Wyns & Axelson, 2016). The only disadvantage is that this so called second generation feedstock requires extra pre-treatment steps, which could increase the overall energy demand of the process.

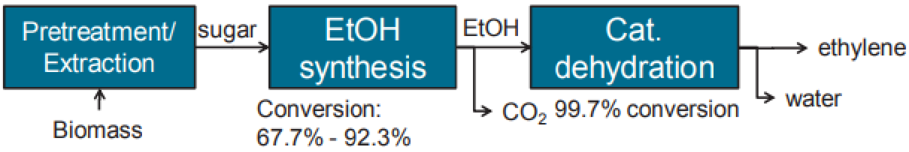

Figure 17 | Block scheme of the production of ethylene using biomass. Adapted from Dechema, 2017.

Until now, the technology used to produce the bio-ethanol is only demonstrated on a large scale in Brazil and the USA, which are responsible for 83% of the world production of bio-ethanol (Mohsenzadeh, 2017). These countries benefit from the abundance of cheap biomass, sugar cane and corn for Brazil and the USA respectively, which reduces the overall production costs of bio-ethanol to competitive prices as the price of feedstock determines 60% of the production costs for bio-ethanol (IRENA, 2013). In turn the cost of bio-ethanol determines, on average, 65% of the production costs for bio-ethylene (IRENA, 2013), meaning that indirectly an estimated 39%[g] of the production costs of bio-ethylene are determined by the price of the biomass feedstock.

In the Netherlands, the bio-ethanol that is available is mainly used as substitute for fuel in vehicles, instead of being used as feedstock for chemical production. A major barrier for the bio-ethanol industry is the high import tariffs on biomass (Accenture, 2009). Therefore, importing bio-ethanol from countries like Brazil and the USA would offer a solution. However, at the moment 30% of the price of imported bio-ethanol is due to high import taxes (Bex & Blank, 2013). Removal of these high import taxes could create a level playing field for bio-ethanol to the point where it can compete with fossil-based ethylene (Bex & Blank, 2013).

There is potential for bio-based chemicals in the Netherlands. The chemical sector in the Netherlands aims to substitute 15% of their feedstock by bio-based alternatives by 2030 and 35% by 2050 (Krebbekx et al. 2013), As far as infrastructure is concerned, the port of Rotterdam is connected to a large network of ethylene pipelines which extends to Belgium and the south part of Germany (Strengers et al., 2018). Injection of bio-ethylene into this network would not involve any large modifications and would make utilisation of bio-ethylene relatively easy.

4.4.2 Techno-economic parameters

There is no general consensus in the literature on the statement that bio-based plastics produced from bio-ethylene will always result in CO_2 savings. The carbon footprint is highly dependent on upstream factors, such as the type of biomass and the local production logistics and infrastructure used (Dechema, 2017). As calculating CO_2 emissions for the entire production chain from biomass to bio-ethylene would require making highly uncertain assumptions regarding these topics, this report will only present the CO_2 emissions produced during the production of bio-ethylene from bio-ethanol. During the production of 1 kg of bio-ethylene 0.7 kg CO_2-eq is emitted[h] (McKechnie et al., 2015) and the displacement of the fossil-based ethylene production process saves -1.8 kg CO_2-eq / kg ethylene (McKechnie et

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[g] Based on the simple calculation where 0.60 is multiplied by 0.65.

[h] This is primarily due to the consumption of natural gas (approximately 88% of the emissions), while electricity and caustic soda inputs are responsible for 8% and 4% of the emissions, respectively (McKechnie et al, 2015).

al., 2015). This would mean that substituting ethylene with bio-ethylene at Shin-Etsu will avoid 0.34 Mtonnes of CO_2-eq per year[i], which is 3 times the yearly emissions of Shin-Etsu. Obviously these do not concern the direct emissions, and this number also does not include the emissions that are generated during the cultivation and transport of the biomass, the production of bio-ethanol, the transport of the bio-ethanol to the Netherlands and the CO_2 savings found in the carbon which is sequestered within the bio-ethylene. For these reasons, it is expected that the actual avoided emissions will be significantly lower. However, it is not within the scope of this report to deal with the avoided emissions of the production of bio-ethanol.

As PVC manufacturers in the Netherlands buy ethylene as feedstock for their process the switch to bio-ethylene would not involve any capital investments for themselves, only operational costs. The market price of fossil-based ethylene in 2016 was 950 EUR_{2016}/tonne ethylene (Mohsenzadeh et al., 2017). The production costs of bio-ethylene from bio-ethanol in Europe are approximately 1740 EUR_{2013}/tonne ethylene (Haro et al. 2013), nearly twice the market price of fossil-based ethylene. Also, to the best of the author's knowledge, there is no bio-ethylene production plant in the Netherlands yet, which means that there will have to be one constructed first. The total investment cost for such a plant is estimated at USD_{2017} 51–190 million, equivalent to EUR_{2017}[j] 45–168 million (Mohsenzadeh et al., 2017).

A final consideration, which is applicable for all biomass decarbonisation options, is whether or not there will be enough sustainable biomass available in the Netherlands. According to Strengers et al. (2018) the total potential of biomass in the Netherlands in terms of energy is currently around 270 PJ, of which 153 PJ is still unused. Strengers et al. estimated that the total demand for biomass in 2030 and 2050 will rise to 430–600 PJ and 670–1470 PJ, respectively. This implies that import of biomass will be almost surely required to meet the future demand (Strengers, personal communication). The availability of sustainable biomass from other countries is highly uncertain (Strengers et al., 2018).

Table 17 Techno-economic parameters of decarbonisation option 'bio-ethylene as feedstock'.

Characteristic	Value	Comment	Source
CO_2 emissions (ton CO_2/ton bio-ethylene)	0.7[h]	CO_2 emissions for the production of bio-ethylene through dehydration of bio-ethanol.	McKechnie et al. (2015)
Production cost bio-ethylene (EUR_{2013}/ton bio-ethylene)	1740	Based on the dehydration of bio-ethylene in the EU. The reported range is 1724–1762, depending on the capacity utilisation of the production plant.	Haro et al. (2013)
Market price bio-ethylene (EUR_{2017}/ton bio-ethylene)	Unknown	-	-

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[i] The feedstock usage of ethylene is approximately 0.5 ton ethylene / ton VCM (see Chapter 2). Assuming the yearly production rate of VCM of 620 kton/yr, the savings will be -1.1 kg CO_2/kg ethylene x 0.5 kg ethylene/kg VCM x 620E6 = 0.34 Mton of CO_2.

[j] Assuming the EUR to USD annual average exchange rate in 2017 of 1.13 (Statista, 2019).

4.5 Steam from biomass

4.5.1 Technology description

Steam for the sector is typically provided by combined-heat-power (CHP) plants burning natural gas. These gas-fired CHP plants have CO_2 emissions of around 275 kg CO_2/MWh (Sims et al, 2007). An alternative is the bio-CHP plant, which either directly combusts biomass, such as wood chips, or biomass derived gases, such as biogas, to produce electricity and steam. These systems are often referred to as direct-fired and gasification systems, respectively (US EPA, 2007). Direct-fired systems combust biomass in a stoker of fluidized bed boiler to produce high pressure steam, which is then passed through a steam turbine generator to produce additional electricity. Gasification systems heat biomass in an oxygen-starved environment to produce syngas, a mixture of mainly CO and H_2, which is then cleaned, filtered and can be burned in a wide variety of technologies to produce electricity and heat, such as gas turbines or fuel cells (US EPA, 2007).

Direct-fired systems are less sensitive to contamination in the fuel source, which means that they can accept a wider range of biomass types. However, they are more polluting than gasification systems, as the syngas in gasification systems is cleaned of contaminants. Gasification systems generally require a clean biomass feedstock, such as wood chips, in order to reduce clean-up costs later in the process (US EPA, 2007).

Both CHP systems have the advantage of higher overall efficiencies compared to conventional systems where steam and electricity are generated independently. The share of bio-fuels in CHP plants in the Netherlands was estimated at 3.9% in 2009, which is relatively low compared to other countries in the EU (Cogeneration Observatory and Dissemination Europe [CODE2], 2013). It is expected that this share can potentially increase to 15.6% in 2030. The main bottleneck limiting this growth is the limited availability of biomass in the Netherlands. To illustrate this, Scandinavian countries with access to large amounts of forests, such as Finland and Sweden, already reached shares of bio-fuels in CHP plants in 2009 of 42.6% and 74.9% respectively (CODE2, 2013).

An example in the Netherlands is a collaboration of AkzoNobel, Eneco and Groningen Seaports who have converted Eneco's biomass plant into a bio-CHP, producing bio-steam and saving 100 ktonnes of CO_2 each year (AkzoNobel, 2017). The refurbishment required a joint investment of 40 MEUR and consumes approximately 300 kt of recycled wood chips per year.

4.5.2 Techno-economic parameters

Cherubini et al (2009) estimated the CO_2 emissions for heat and electricity generation using different feedstocks. Since there are many uncertainties involved, such as the type of biomass consumed and the agronomic practices used, these emissions are presented as ranges. The authors found that electricity and cogeneration using wood chips emits 15–30 kg CO_2eq/GJ and using biogas emits 15–65 kg CO_2eq/GJ, including chain emissions and excluding biogenic CO_2. This is considerably less compared to electricity and cogeneration using natural gas which emits 100–200 kg CO_2eq/GJ.

IRENA estimated the typical costs of several biomass power technologies in 2012 and found that the CAPEX for direct-fired CHP and gasification CHP are 3550–6820 USD_{2010}/kW (3.1-6.0 $kEUR_{2017}$/kW) and 5570–6545 USD_{2010}/kW (4.9-5.8 $kEUR_{2017}$/kW) respectively. The fixed OPEX is generally between 2–7% of CAPEX, with variable OPEX of 0.005 USD_{2010}/kWh (0.004 EUR_{2017}/kW) (IRENA, 2012).

4.6 Circularity

By enabling plastic waste to re-enter the system as a feedstock, material- and energy-savings can be achieved by reducing the need for virgin raw materials (Nielsen, 2018). Here, three types of recycling will be discussed: mechanical, non-conventional mechanical and chemical recycling.

4.6.1 Mechanical recycling

Technology description
Mechanical recycling involves the shredding, cleaning and remoulding of PVC products from used PVC. The mechanical recycling potential of PVC – and plastics in general – is mostly determined by the degree of contamination of the plastic stream (EU, 2000). The lower the contamination, the higher the purity of the stream at consideration and the higher the quality of the recycled PVC. The purity of the stream is affected by:

- The degree to which the PVC is mixed with other materials
- Differences in composition of the collected PVC material itself.

It is important to stress that the quality of the recyclate determines its final application as there are two types of mechanical recycling:

- High-quality recycling: when recyclate directly substitutes PVC from fossil fuels in its original application, e.g. pre-consumer PVC from piping recycled into new PVC pipes. This is obviously the most preferable option.
- Downcycling (low-quality recycling): when recyclate is downgraded to a lower value application due to poor quality, e.g. post-consumer PVC from bottles recycled into PVC plant pots.

In 2000, the EU reported the recycling potential for both high-quality and low-quality recycling of PVC. The report covers a wide range of PVC product groups and also differentiates between pre-consumer and post-consumer waste, as discussed in Section 3.2. Table 18 and Table 19 show a summary of the recycling potential for both high-quality recycling and low-quality recycling. Refer to EU (2000; p.78, p.84) for the full tables.

Table 18 Range (and average) of potential mechanical recycling rates for high-quality recyclate for 7 different PVC waste groups. Full data is available from p.125-127 of EU (2000).

Waste group	Potential recycling rate (%)	
	Pre-consumer waste[1]	Post-consumer waste[1]
Construction products	40–90 (64)	20–65 (40)
Packaging products	70–90 (80)	35–45 (40)
Furniture components	10–35 (20)	-
Other consumer and commercial products	25–90 (72)	10–35 (23)
Electric/electronics	15–90 (60)	-
Automotive	15–90 (55)	-
Other products	65–75 (70)	-

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1) In brackets = average rate of all product groups in the respective waste group

High-quality recycling

Generally the major part of PVC from **pre-consumer** waste has high potential for high-quality recycling. Product groups where the major part of pre-consumer waste is production waste are expected to have recycling rates of more than 70%. Those products groups where installation waste is most dominant generally have recycling rates lower than 70% as the PVC is contaminated and mixed with other waste. This is the case for the major part of building products. Table 18 shows that on average the most promising pre-consumer waste groups for high quality recycling are consumer/commercial products and packaging products.

On the other hand, **post-consumer** waste has on average a lower recycling potential as it is generally more contaminated with other plastics types and consists of a mix of PVC with different compositions. The highest recycling potentials in this stream are expected from the mono fractions from construction project that are collected separately, such as pipes and fittings, which can potentially reach recycling rates of 60–80%. E.g., in the Netherlands Bureauleiding collects PVC pipes, as well as PE and PE pipes, in their BIS (Buizen Inzamel System [Pipe Collection System]) program for high-quality recycling (Bureauleiding, 2019). Window profiles have potential recycling rates of 60–70%. The remaining products from the waste groups are limited for high quality recycling.

Low-quality recycling

When recycling to high-quality PVC recyclate is not feasible, but systems for collection and recycling with other plastic waste are available, downcycling can be done to still recycle the PVC material to low-value products. PVC waste streams that are downcycled are typically mixed plastic waste fractions that consists of many different types of PVC with different compositions.

Similar to high-quality recycling, the achievable mechanical recycling rate to low-quality recyclate from **pre-consumer** waste depends on its origin. Production waste is easier to collect and has a potential recycling rate up 70%, such as cables in the waste group electronics. Installation waste separation takes more effort and the EU estimates an potential recycling rate up to 50%. Installation waste in applications of PVC coatings are not suitable for mechanical recycling.

In the group **post-consumer** waste feasible potential mechanical recycling rates for low-quality recycling are limited to just a few PVC products in three waste groups. Low-quality recycling of cables is the major area of PVC recycling. Together with PVC cut-offs during installation, cable waste is used for extrusion of piles and traffic cones. Since a large part of PVC packaging films generally end up in mixed waste fractions after sorting and end up being incinerated, the recycling potential is limited to 15–25%. On average recycling of PVC products from consumer and commercial waste is limited to 18%. Incineration of difficult-to-recycle PVC combined with chlorine recovery would be an acceptable option according to industry, when combined with the use of a representative amount of bio-based ethylene feedstock.

Table 19 Range (and average) of potential mechanical recycling rates for low-quality recyclate for 7 different PVC waste groups. Full data is available from p.128–130 of EU (2000).

Waste group	Potential recycling rate (%) Pre-consumer waste$^{1)}$	 Post-consumer waste$^{1)}$
Construction products	20–60 (45)	70–90 (80)$^{2)}$
Packaging products	25$^{2)}$	15–25 (20)
Furniture components	60$^{2)}$	-
Other consumer and commercial products	15–90 (55)	15–25 (18)
Electric/electronics	15–70 (39)	40
Automotive	60–90 (68)	-
Other products	30$^{2)}$	-

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1) In brackets = average rate of all product groups in the respective waste group
2) Available data consists of a limited amount of PVC products and thus might not reflect the correct recycling rate for the waste group as a whole

Techno-economic parameters

If virgin PVC is substituted with recycled PVC the overall PVC production chain can reduce its demand for virgin PVC and thus reduce their greenhouse gas emissions significantly. An example is the recycling of old PVC pipes into new PVC pipes. According to PVC recycler Pipelife the company currently uses 50% PVC recyclate in their PVC pipes. Their ambition is to increase this share to 100% by 2030.

According to Brown et al. (2000) mechanical recycling of PVC typically requires between 10–15 MJ/kg PVC. Assuming that all energy is consumed as electricity (Boulamanti & Moya, 2017; Brown et al, 2000) this is equivalent to 2.7–4.2 MWh/t recycled PVC. Assuming an emission factor of Dutch electricity from the grid of 0.5 kg/kWh (World Energy Council Netherlands, 2018) the current indirect emissions related to PVC recycling is 1.35–2.1 t CO_2/t recycled PVC. This might seem a lot as the emission factor of Shin-Etsu is 0.18 t CO_2/t PVC[k], however this is not the case. If indirect emissions for steam and electricity are accounted for the reported emission factors of PVC can increase up to 2.8 t CO_2/t PVC (Boulamanti & Moya, 2017). The uncertainty of this estimation is high, but it shows that recycling of PVC might be able to save CO_2 emissions along the production chain, especially if the emission factor for electricity is reduced in the future.

Mechanical recycling does not directly impact the production process of Shin-Etsu, it only reduces the demand for virgin PVC. Depending on the market evolution this might have an impact on the production capacity of Shin-Etsu, however it is outside of the scope of this report to make any estimations about this.

4.6.2 Non-conventional mechanical recycling

Technology description

Material streams which are not suitable for conventional mechanical recycling as described in the previous sector could potentially be treated using non-conventional mechanical recycling methods (this section) or chemically recycled (next section).

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[k] 94 kton CO_2 / 520 kton PVC = 0.18 t CO_2 / t PVC. This number is so low since it only includes the direct emissions as reported in the NEa database.

VinyLoop is the most well-known and developed example technology of the first mentioned method (VinylPlus, 2017). This process is categorised as mechanical recycling method since it in effect does not break down the polymer, as is done with chemical recycling. VinyLoop is capable of accepting composite streams with up to 70% PVC content (Boulamanti & Moya, 2017). PVC is selectively dissolved in a solvent, which makes it possible to simply filter out PVC material from a composite stream of different materials. The polymer is then recovered using precipitation and dried. The recycled PVC can then be used for applications such as shoe soles, hoses and PVC sheets (VinylPlus, 2017).

Techno-economic parameters
A study carried out in 2017 reported the environmental footprint of the VinyLoop process compared to the conventional production of PVC (including incineration) (Inovyn, 2017). According to Inovyn (2017) VinyLoop has a 47% lower primary energy demand compared to the conventional PVC production process method.

The final investment of the largest VinyLoop plant, which is located in Italy with a total capacity of 10kt PVC/year, was 7.95 million EUR$_{2013}$. However, due to a collapse in the demand for the recycled PVC, the plant was forced to shut down in 2018.

4.6.3 Chemical recycling

Technology description
Chemical recycling is seen as a complementary technology to mechanical recycling because the technologies in place are less sensitive to unsorted or contaminated waste products. Furthermore, addition of chemical recycling to the overall portfolio of recycling technologies will increase the overall capacity of plastics in the future (PVC.org, 2018). As discussed in the previous section, there are a number of streams of mixed plastics which are not suitable for high- or low-quality recycling because the contamination of these streams is high. These streams are currently incinerated. Chemical recycling could offer a solution to process these PVC streams for higher valued use. No cost data on this process could currently be found in literature.

Chemical recycling is in essence a way to recover carbon in PVC by producing useful chemical compounds from PVC waste that can again be used as feedstock in the industry (VinylPlus, 2017). A CE Delft study describes the potentials of chemical recycling technologies for plastic recycling, although it does not specifically focus on PVC (CE Delft, 2018a). The ones which mentions PVC material as input is described here and in Table 20.

Conventional pyrolysis involves the anaerobic heating of the plastic stream to temperatures between 400–600 ºC until it breaks down in pyrolysis oil, low-value fuels and syngas. Integrated hydro pyrolysis is similar to conventional pyrolysis, however, in this case the process is carried out in the presence of water. The operating temperatures are approximately 300–600 ºC. This type of pyrolysis is often referred to as third generation pyrolysis and is more suitable for heterogeneous input streams containing PVC. Gasification involves the heating of the material in the presence of oxygen and breaks down the stream to the smallest molecular building blocks: H_2 and CO (syngas). Both low-temperature (800–1000 ºC) and medium-temperature (900–1650 ºC) gasification technologies are currently being developed. Although low-temperature gasification is currently used for biomass streams, limited amount of plants are researching the potential for processing of mixed consumer streams. Medium-temperature gasification produces a higher quality syngas and the potential to accept mixed consumer streams is currently being investigated.

Table 20 Overview of several chemical technologies (CE Delft, 2018a).

Technique	Usability of PVC as Input (suitable/limited/unsuitable/unknown)	Output	TRL*
Conventional pyrolysis	Limited	Pyrolysis oil, low-value fuels, syngas.	8
Integrated hydro pyrolysis	Limited (although better than conventional pyrolysis)	High-value pyrolysis oil, syngas.	5–7
Low-temperature gasification	Unknown	Syngas	5–7
Medium-temperature gasification	Unknown	Syngas	8

5 Discussion

It was found that possible decarbonisation options for the PVC manufacturing industry include the categories feedstock substitution, fuel substitution, recycling/circularity and carbon capture and storage (CCS). The feasibility of the options that were discussed are heavily dependent on several factors that will be discussed here.

First of all, the discussed alternatives for the cracking furnace are not readily available yet, which implies that innovation will be required before application of these technologies is possible. The TRL of hydrogen-based cracking furnaces is currently only 3, which means that it is expected that it will take at least 10 more years before this becomes a viable option (Gigler & Weeda, 2018). Electric cracking furnaces are an even more novel technology, currently suffering from little hand-on large scale practice and high investment costs (VNCI, 2018; de Pee et al., 2018). However, it is expected that electric furnaces can advance quickly on the technology end (Zondag, 2019). Finally, availability of cheap, renewable electricity is a requisite for successful implementation. CCS technology shows potential, especially in the Port of Rotterdam where the Porthos project will provide the infrastructure for the transport and storage of captured CO_2 in empty offshore gas fields. It is expected that this project will finish in 2022 or 2023 (Holleman, 2019). However, flue gas from natural gas burners have generally low CO_2 concentrations compared to other CO_2 sources (<10%), making CCS of CO_2 emissions from the furnace still relatively expensive (Berghout et al., 2015; CE Delft, 2018).

Secondly, realisation of the other discussed decarbonisation options related to feedstock replacement and recycling are dependent on the choices of the feedstock producers and recycling companies, respectively. As long as the production of fossil-based ethylene will be cheaper than bio-ethylene it might be unlikely that ethylene production will make the switch to renewables. However, if a market is created for bio-based PVC by other parties, such as for example the government promoting construction with sustainable bio-based materials, there could be potential for bio-based PVC. This could be found out by conducting more research in this area. In terms of circularity, high-quality recycling of PVC is necessary in order to significantly replace virgin PVC in products, such as piping and cables. Although efforts are being made in the Netherlands to recycle large volume PVC products, such as pipes in the BIS[I] BureauLeiding, PVC recycling from the post-consumer mixed waste stream could still be significantly improved. The role of PVC manufacturers in both these decarbonisation categories is expected to be limited as developments of these options are happening outside their fence. The degree of action undertaken by bio-refineries and plastic collectors and recyclers will determine to what extend these decarbonisation options will be successful.

Thirdly, electrification of high-temperature heating or the use of hydrogen as fuel could potentially be beneficial for the Dutch industry as a whole, not just the PVC manufacturing sector. The infrastructure for both these resources will have to be capable of dealing with the increased demand. At the moment, the Port of Rotterdam and Industrial Site Chemelot are connected to the same network of hydrogen pipelines stretching out to several industrial sites in Belgium, which could be beneficial in the future (Port of Rotterdam, 2016).

[I] BIS=Buizen Inzamel Systeem (https://www.bureauleiding.nl/bis-buizeninzamelsysteem/)

Being in close proximity of the North Sea opens up the opportunity to exploit renewable electricity from off-shore wind farms in the Port of Rotterdam. In fact, several parties from the port are currently investigating the potential of large scale green hydrogen production using this renewable electricity (Port of Rotterdam, 2017). This could make the use of hydrogen burners more attractive for the PVC manufacturing industry in the future due to these opportunities to produce abundant hydrogen.

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Appendix

A.1 Notable revamps of Shin-Etsu Botlek and Pernis

Table 21 Overview of notable revamps at Shin-Etsu Botlek including year of revamp, description of revamp and respective VCM capacity (+relative increase). Source: Shin-Etsu PVC B.V., 2003, p.16; Shin-Etsu PVC B.V., 2007; Shin-Etsu PVC B.V., 2012.

Year	Revamp at Botlek site	VCM capacity (kt/yr)
1971	Initial production site with two cracking furnaces	300
1977	Expansion with third cracking furnace including quench column	370 (+*70*)
1979	Debottlenecking Botlek site: incremental system changes	500 (+*130*)
1991	Installation waste gas incinerator	500
1997	Expansion with oxychlorination (third) reactor (enabled shift to oxychlorination using HCl)	500
2000	Shin-Etsu buys Rovin from Shell and Akzo	-
2003	Expansion with fourth cracking furnace	620 (+*120*)
2004	Replacement first and second cracking furnaces	620
2009	Debottlenecking Botlek site: incremental system changes	670 (+*50*)
2014	Replacement two air-fed oxychlorination reactors	670

Table 22 Overview of notable revamps at Shin-Etsu Pernis including year of revamp, description of revamp and respective PVC capacity (+relative increase). Source: Shin-Etsu PVC B.V., 2002, p.4–5.

Year	Revamp at Pernis site	PVC capacity (kt/yr)
1966	Initial production site	unknown
1972	Expansion with second production site	unknown
1980	Implementation closed reactor technology	unknown
1992	Replacement of existing technology with Shin-Etsu licensed PVC production technology, installation of six reactors	unknown
1993	Expansion with seventh reactor	250
1997	Incremental system changes	295 (+*45*)
2000	Shin-Etsu buys Rovin from Shell and Akzo	-
	Incremental system changes	325 (+*30*)
	Replacement of centrifuge dryer, expansion with third compressor on VC recovery	350 (+*25*)
2006	Expansion with eighth reactor	450 (+*100*)
2013	Faster initiators	520 (+*70*)

A.2 Calculations on Chemelot BKG08 emissions

Chemelot Industrial site is registered in the NEa EU ETS database under 14 BKGs. The units which are registered under Chemelot BKG08 are presented in Table 23.

Table 23 Information about Chemelot BKG08.

Company	Description	Source of emission in BKG08	Comments
Vynova Beek	Producer of polyvinyl chloride	Unknown	No specifics are known
EdeA	Producer of utilities, such as steam, for the production sites on Chemelot. Part of Utility Support Group (USG) B.V.	F3800 (steam boiler) F3300 (steam boiler)	F3300 was decommissioned in 2013 and replaced by F3800 (USG, 2014)
Borealis Plastomers B.V.	Producer of polyolefins	F1201 (furnace)	No other specific are known

In order to find the share of direct emissions of Vynova Beek in Chemelot BKG08 the following assumption was made: F3800, F3300, F1201 together with emissions from Vynova Beek are responsible for the total emissions registered under Chemelot BKG08 in the NEa EU ETS dataset. In the form of an equation:

$$E_{BKG08} = E_{Vynova} + E_{F3800} + E_{F3300} + E_{F1201},$$

where *E* is the total emissions of the subscripted unit in kt/year. Under this assumption, calculating the emissions of F3800, F3300 and F1201 would give the emissions of Vynova. Environmental reports of Chemelot from 2013—2016 provided the information presented in Table 24.

Table 24 Overview of the collected data from Chemelot (2013; 2014; 2015; 2016).

Unit		2013	2014	2015	2016
F3300	Fuel	Tail gas	-	-	-
	Consumption (ton)	30646	-	-	-
	Calorific value (GJ/ton)	48.37	-	-	-
	CO_2 emission factor (kg CO_2/GJ)	52.35	-	-	-
	Operating hours (hours)	3794	-	-	-
F3800	Fuel	Tail gas	Tail gas	Tail gas	Tail gas
	Consumption (ton)	5082	21150	29387	13842
	Calorific value (GJ/ton)	48.37	48.35	48.22	48.61
	CO_2 emission factor (kg CO_2/GJ)	52.35	53.1	53.84	53.38
	Operating hours (hours)	457	2173	3003	1623
F1201	Fuel	Natural gas	Natural gas	Natural gas	Natural gas
	Consumption (Nm^3)	6064764	6719138	7937605	6985000
	Calorific value (GJ/Nm^3)	0.03165	0.03165	0.03165	0.03165
	CO_2 emission factor (kg CO_2/GJ)	56.5	56.4	56.5	46.3
	Operating hours (hours)	3829	8760	8760	6496

Generally, the emissions for unit i can be found using the following equation:

$$E_i = C_i * CV_i * EF_i,$$

where C is the fuel consumption of unit i in ton or Nm^3, CV is the calorific value of the fuel in unit i in GJ/ton or GJ/Nm^3 and EF is the emission factor of the fuel in unit i in kg CO_2/GJ. Using the information from Table 24 it is now possible to find the total emissions for the three units. As an example the total emission for F3300 in 2013 is calculated below:

$$E_{F3300} = 30646\,[ton] * 48.37\left[\frac{GJ}{ton}\right] * 52.35\left[\frac{kg\ CO_2}{GJ}\right] = 77.6 * 10^6\,[kg\ CO_2] = 78\,[kton\ CO_2]$$

Doing this for all units from 2013—2016 gives the results presented in Table 25 and Figure 17. The sum of the emissions from the three units are compared with the NEa registered BKG08 emissions for each given year. It is concluded that, although there is a small difference in 2013 and 2016, only F3300, F3800 and F1201 contribute to the Chemelot BKG08 emissions. Therefore the direct emissions of Vynova Beek are considered zero.

Table 25 Total emissions for F3300, F3800 and F1201 on Chemelot BKG from 2013–2016.

	CO_2 emissions (kt/year)			
	2013	2014	2015	2016
F3300	78	0	0	0
F3800	13	54	76	36
F1201	12	12	14	10
Total	103	66	90	46
NEa registered	99	66	90	48
Difference	+4	0	0	-2

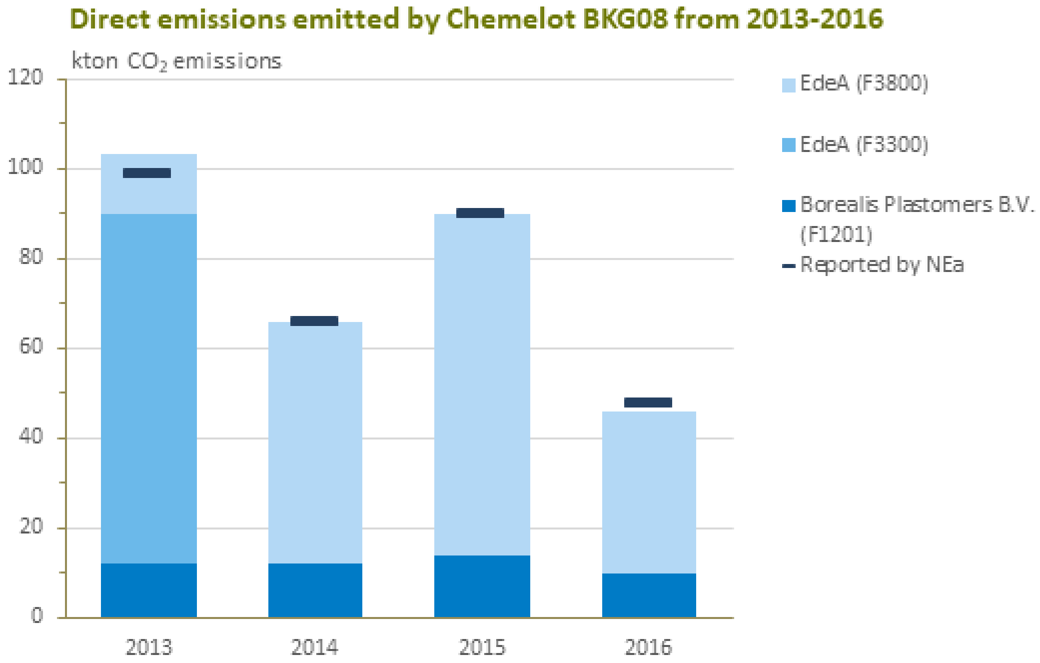

Figure 18 Overview of the contribution of each unit to the total emissions of Chemelot BKG08.

A.3 Mass Flow Analysis (MFA)

The mass flows in the process were calculated for a PVC production plant with the following production rates:

- 70 kt HP EDC/yr for export
- 620 kt VCM/yr, of which 150 VCM/yr is for export
- 470 kt PVC/yr.

Figure 18 shows the flow chart which is used during this MFA. In total the flow chart consists of 8 black boxes, which will be treated in the MFA as 8 separate control volumes. The MFA is carried out backwards, meaning that the calculations start from the final product and follow the flow chart in the reverse direction of the flows to, in the end, calculate the inputs. The description here will be strictly about the calculations as Chapter 2 already discussed in detail what happens within each control volume.

PVC production

PVC Drying
The first control volume to be discussed is the PVC drying. The following assumptions were made:

- The PVC-sludge consists only of PVC and water. All remaining VCM has been effectively removed in the purification step.
- The moisture content of the PVC sludge is 50% (Wilkes, 2005).
- All moisture if effectively removed during the drying process.

This results in the following mass balance:

$$\dot{m}_{PVC-sludge_{pur}} = \dot{m}_{water_{out,3}} + \dot{m}_{PVC}.$$

PVC Purification
At the PVC purification step any remaining VCM in the PVC-sludge is removed together with a fraction of the water using steam stripping. The following assumptions were made:

- The PVC-sludge still contains 3% VCM, which is effectively recovered using steam stripping. This is recycled back to the polymerisation reactor.
- 50% of the water is removed during steam stripping.

This results in the following mass balance:

$$\dot{m}_{PVC-sludge} = \dot{m}_{water_{out,2}} + \dot{m}_{VCM_{recycle}} + \dot{m}_{PVC-sludge_{pur}}.$$

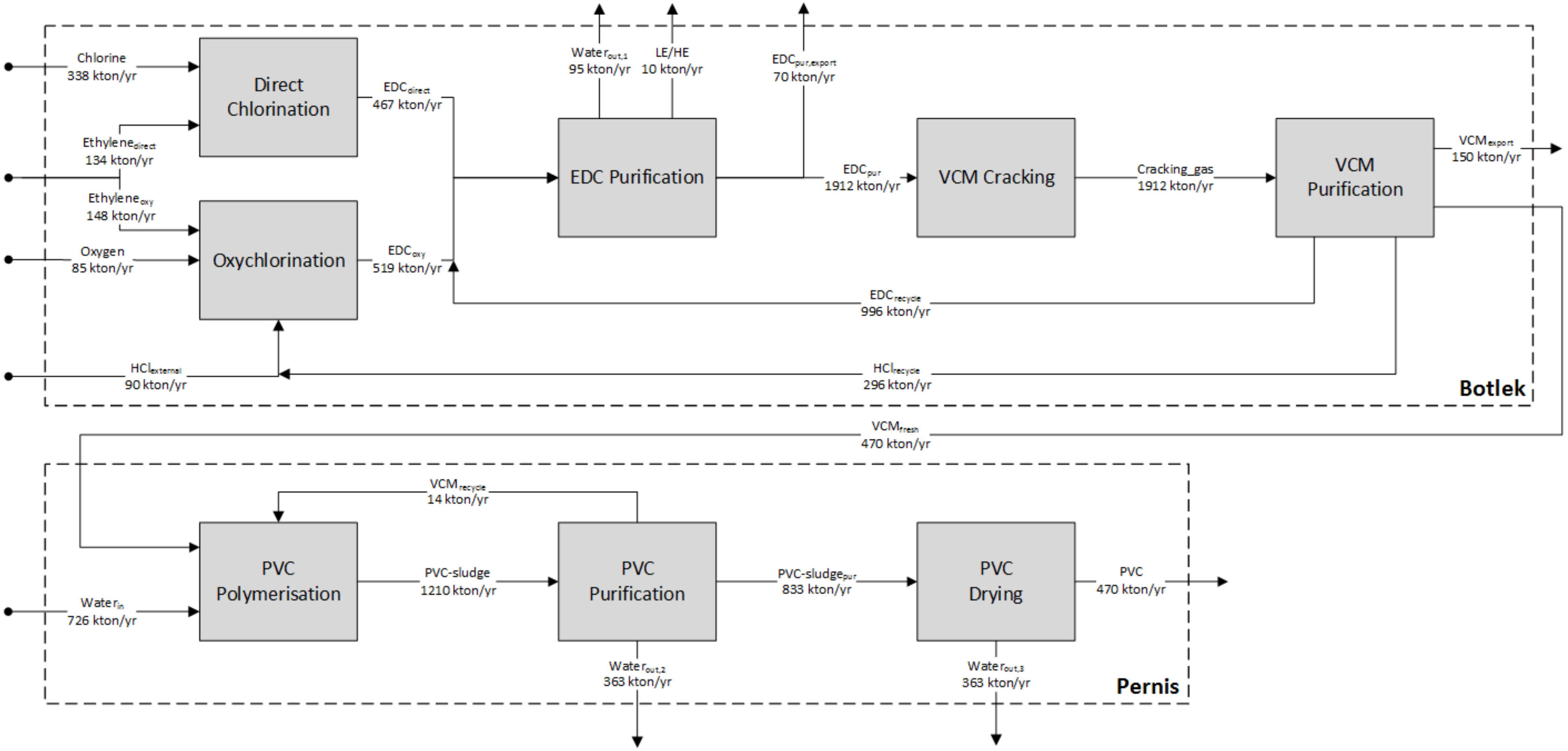

Figure 19 The scope of the MFA.

PVC Polymerisation

In the polymerisation reactor, the VCM which is produced at Botlek is mixed with water and chemicals to form PVC. The following assumptions were made:

- Per ton of PVC 1.5 ton of water is required (Shin-Etsu, personal communication).
- 85–95% of VCM is converted in PVC (EU, 2007). The calculations assume 85%. Of the 15% remaining VCM, 12% is directly captured using vents and recycled to the polymerisation reactor (Wilkes, 2005). The remaining 3% leaves in the PVC sludge (Wilkes, 2005).
- The VCM losses during the overall conversion of VCM to PVC are <0.001% (Shin-Etsu, personal communication). The conversion is therefore assumed to be 100% in the calculations, implying no losses in the production.

This results in the following mass balance:

$\dot{m}_{VCM_{fresh}} + \dot{m}_{water_{in}} + \dot{m}_{VCM_{recycle}} = \dot{m}_{PVC-sludge}$.

The MFA of PVC production is summarised in Table 26.

Table 26 Summary of the MFA of PVC production

	Input		Output	
Control volume	Label	Mass flow (kt/yr)	Label	Mass flow (kt/yr)
PVC polymerisation	VCM_{fresh}	470	PVC-sludge$^{1)}$	1210
	$Water_{in}$	726		
	$VCM_{recycle}$	14		
PVC purification	PVC-sludge$^{1)}$	1210	PVC-sludge$_{pur}$$^{2)}$	883
			$Water_{out,2}$	363
PVC drying	PVC-sludge$_{pur}$$^{2)}$	883	PVC	470
			$Water_{out,3}$	363

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1) Composition of the PVC-sludge exiting the polymerisation section is: 39 wt% PVC, 60 wt% water, 1 wt% unreacted VCM.

2) Composition of the PVC-sludge exiting the purification section is: 56 wt% PVC and 44 wt% water.

VCM production

VCM Purification

In the VCM purification section two distillation columns are used to separate HCl, EDC and VCM. The first column separates HCl from the EDC/VCM flow. The second column separates VCM from the EDC flow. The following assumptions were made:

- In literature studies, the purity of the HCl flow, EDC flow and VCM flow are 99.99%, 99.3% and 99.8% respectively (Chong, 2017). These purities were chosen as well for the mass balance of the distillation unit, except for the purity of the HCl flow, which was set to 100%.

This results in the following mass balance:

$\dot{m}_{cracking\_gas} = \dot{m}_{HCl_{recycle}} + \dot{m}_{EDC_{recycle}} + \dot{m}_{VCM_{fresh}}$.

Box I : Solving the mass balance of the VCM purification section

The molar composition of the cracking gas was derived from the chemical reaction in the cracking furnace, assuming that the conversion of EDC to VCM is 55% (as mentioned in Section 2.2):

$1\,EDC = 0.55\,VCM + 0.55\,HCl + 0.45\,EDC$.

In general terms, the molar fraction of species i (x_i) can be found using:

$$x_i = \frac{n_i}{n_{total}} ,$$

where n_i is the amount of moles of species i, and n_{total} is the total amount of moles in the mixture. For the cracking gas it can then be found that the molar fractions of VCM, HCl and EDC are 0.354, 0.291 and 0.354 respectively.

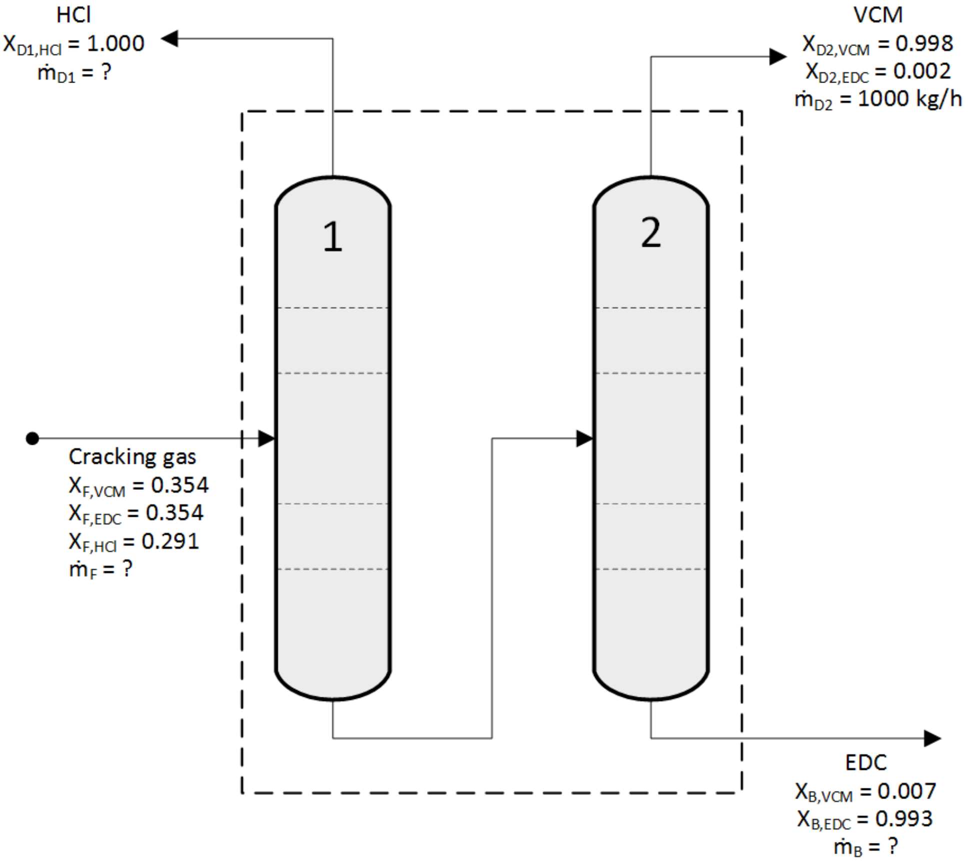

Figure 20 Overview of the control volume (dotted area) over the two distillation columns. All known parameters are given.

Initially for simplicity, the mass flows were solved for an output of 1000 kg/h VCM by using the overall molar balance and the individual species molar balances as a starting point:

Overall molar balance	$\dot{n}_F = \dot{n}_{D1} + \dot{n}_B + \dot{n}_{D2}$
Species molar balance	
HCl	$x_{F,HCl} \cdot \dot{n}_F = x_{D1,HCl} \cdot \dot{n}_{D1}$
EDC	$x_{F,EDC} \cdot \dot{n}_F = x_{D2,EDC} \cdot \dot{n}_{D2} + x_{B,EDC} \cdot \dot{n}_B$
VCM	$x_{F,VCM} \cdot \dot{n}_F = x_{D2,VCM} \cdot \dot{n}_{D2} + x_{B,VCM} \cdot \dot{n}_B$

This is a system with 4 equations and 3 variables, which can be easily solved. Knowing the molar mass of HCl, EDC and VCM from literature, it is possible to now convert the molar flows to mass flows.

The molar flows of the separate streams were modelled in an Excel spreadsheet using the equations mentioned here. The conversion of molar flows to mass flows was also included. Using the solver tool the mass flows of the cracking gas, EDC and HCl were calculated by optimising for a VCM outflow of 620 kton/yr. The output of the solver was:

Species	Mass flow (kton/yr)
Cracking gas	1912
VCM	620
EDC	996
HCl	296

EDC Cracking

In the cracking furnace, EDC is thermally cracked to form VCM and HCl. The conversion of EDC to VCM is 55%, which means that the cracking gas will also contain 45% unreacted EDC. This can summarized by the following reaction:

$$1\,EDC \rightarrow 0.55\,VCM + 0.55\,HCl + 0.45\,EDC.$$

Some of the other assumptions that were made include:

- There is no loss of EDC in the cracking furnace. All EDC is broken down in either VCM or HCl, or does not react at all.

This results in the following mass balance:

$$\dot{m}_{EDC_{pur}} = \dot{m}_{cracking\_gas}.$$

EDC Purification

In the EDC purification section water and LE are first separated from EDC and HE in an azeotropic distillation process. Then the HE are separated from EDC with regular. In order to simplify the calculations for this part of the process, the following is assumed:

- The EDC purification results in an outflow of EDC with close to 100% purity (Dimian & Bildea (2008), use 99.9%).
- LE/HE, water and EDC are effectively separated.

This results in the following mass balance:

$$\dot{m}_{EDC_{oxy}} + \dot{m}_{EDC_{direct}} + \dot{m}_{EDC_{recycle}} = \dot{m}_{EDC_{pur}} + \dot{m}_{EDC_{pur,export}} + \dot{m}_{water_{out,1}} + \dot{m}_{LE/HE}.$$

Oxychlorination

In the oxychlorination reactor ethylene, oxygen and hydrogen chloride are converted in EDC and water, which is represented by the following stoichiometric reaction:

$$1\,C_2H_4 + 0.5O_2 + 2HCl \rightarrow 1EDC + 1H_2O.$$

The total amount of EDC produced is limited by the amount of HCl that is available at the plant. The inflow of HCl is the sum of the following two streams:

- The HCl recycled from the VCM purification section: $\dot{m}_{HCl_{recycle}}$
- The HCl purchased from external partners: $\dot{m}_{HCl_{external}}$

Other assumptions are:

- 1% of the produced EDC is lost due to the production of LE/HE (Falcke et al., 2017).
- From communication with Shin-Etsu $\dot{m}_{HCl_{external}}$ can vary between 60–120 kt/year. For the calculation an average import of 90 kt/year of HCl was used.

The mass balance looks like this:

$$\dot{m}_{ethylene_{oxy}} + \dot{m}_{oxygen} + \dot{m}_{HCl_{recycle}} + \dot{m}_{HCl_{external}} = \dot{m}_{EDC_{oxy}}.$$

Direct Chlorination

In the direct chlorination reactor ethylene and chlorine are converted in EDC. In a 1:1:1 molar ratio:

$$1\,C_2H_4 + 1Cl_2 \rightarrow 1EDC.$$

The total amount of EDC that has to be produced by the direct chlorination section to close the mass balance is determined by:

$$\dot{m}_{EDC_{direct}} = \dot{m}_{EDC_{pur}} - \dot{m}_{EDC_{recycle}} - \dot{m}_{EDC_{oxy}}.$$

Knowing the EDC demand from the direct chlorination and the stoichiometry of the reaction the mass flows for each stream can be calculated. Other assumptions made here are:

- 1% of the produced EDC is lost due to the production of LE/HE (Falcke et al., 2017).

The mass balance of the direct chlorination section is:

$$\dot{m}_{ethylene_{direct}} + \dot{m}_{chlorine} = \dot{m}_{EDC_{direct}}.$$

Summary of the MFA of VCM production

Table 27 Summary of the MFA for VCM production.

	In		Out	
Control volume	**Stream**	**Mass flow (kt/yr)**	**Stream**	**Mass flow (kt/yr)**
VCM purification	Cracking gas1)	1912	VCM$_{fresh}$	470
			VCM$_{export}$	150
			EDC$_{recycle}$	996
			HCl$_{recycle}$	296
EDC cracking	EDC$_{pur}$	1912	Cracking gas1)	1912
EDC purification	EDC$_{direct}$	467	Water$_{out,1}$	95
	EDC$_{oxy}$	519	LE/HE	10
	EDC$_{recycle}$	996	EDC$_{pur,export}$	70
			EDC$_{pur}$	1912
Oxychlorination	Ethylene$_{oxy}$	148	EDC$_{oxy}$	519
	Oxygen	85		
	HCl$_{external}$	90		
Direct chlorination	Ethylene$_{direct}$	134	EDC$_{direct}$	467
	Chlorine	338		

---

1) Composition of the cracking gas exiting the cracking furnaces is: 32 wt% VCM, 16 wt% HCl, 52 wt% unreacted EDC.

A.4 Energy Flow Analysis (EFA)

The energy flows in the process were calculated using the mass balances presented in the previous appendix for an output of PVC of 1 ton/h. In this way the energy for any production capacity can be easily calculated.

Figure 18 and the 5 black boxes from the VCM production part are included in this EFA. As no direct emissions occur in the PVC production part, the total energy demand of the entire section was simply taken from literature and from personal communication with Shin-Etsu.

The internal heat of a compounds under constant pressure is described with the following equation:

$$\Delta\dot{H}_{internal} = \dot{m}c_{p,ave}(T)\Delta T \qquad (7.4.1)$$

Where $\dot{m}$ is the mass flow in kg/hr, $c_{p,ave}(T)$ is the average specific heat dependent on temperature in kJ/kgK and ΔT is the temperature difference between the final and initial temperature in K. The mass flow is found from the MFA. The average specific heat is found using:

$$c_{p,ave}(T) = \frac{1}{2}\left[c_{p,T_2}(T) + c_{p,T1}(T)\right] \qquad (7.4.2)$$

Where $c_{p,T_2}(T)$ and $c_{p,T1}(T)$ is the specific heat of the compound at the final and initial temperature, respectively.

As the specific heat of a compound is dependent on its temperature the following relation is used to calculate this:

$$c_{p,T}(T) = C_1 + C_2T + C_3T^2 + C_4T^3 + C_5T^4 \qquad (7.4.3)$$

Where C_1, C_2, C_3, C_4 and C_5 empirically derived constants reported in literature, see Table 28, and T is the temperature in K.

	C_2H_4 (g)	Cl_2 (g)	O_2 (g)	HCl (g)	$C_2H_4Cl_2$ (g)	Cl_2 (l)
C_1	32.083	27.213	127.601	29.526	29.244	37.275
C_2	-1.48E-02	3.04E-02	-6.02E-01	-8.90E-03	-1.26E-03	1.44E-01
C_3	2.48E-04	-3.34E-05	1.58E-03	3.81E-05	1.12E-06	1.04E-05
C_4	-2.3766E-07	1.60E-08	-5.31E-07	-3.26E-08	4.97E-09	-7.83E-08
C_5	6.8274E-11	-2.70E-12	0	8.86E-12	-2.50E-12	2.89E-11
T_{min} (K)	60	60	50	50	200	172
T_{max} (K)	1500	1500	1500	1500	1500	396

Table 28 Values of the empirically derived constants C_1 to C_5. For each compound the minimum and maximum temperature for which these values hold are given as well.

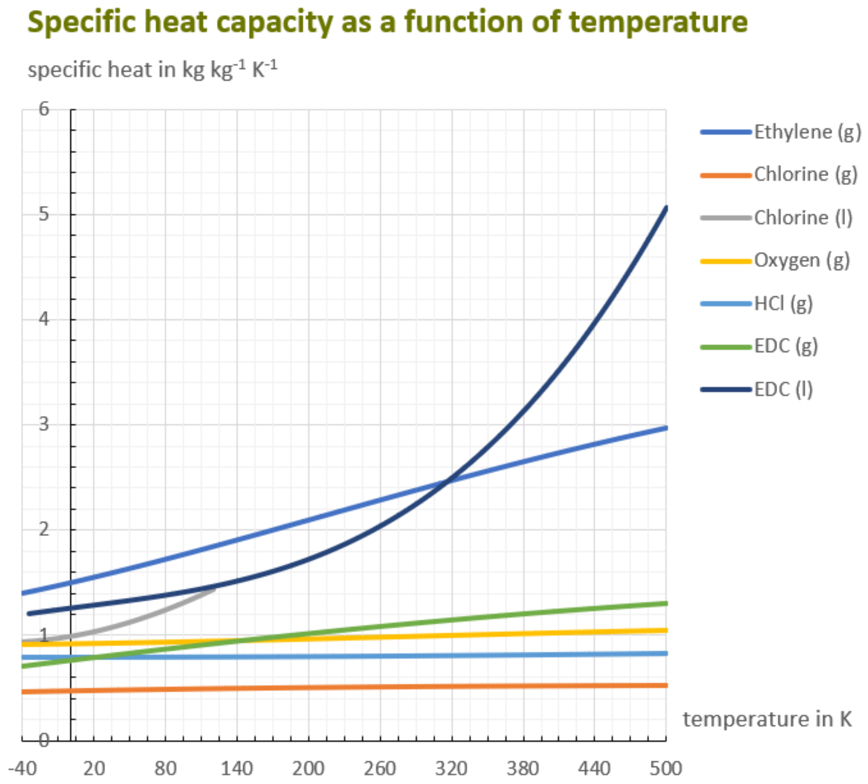

Figure 21 The specific heat capacity for several compounds calculated using equation 7.4.3 with the data from Table 28 for a temperature range of -40 to 500 ºC.

In order to calculate the work of compressing a gas this model has made two simplifications:

1. In reality, when the pressure of a gas increases, its temperature will increase as well. However, here only isothermal (constant temperature) compression is considered.
2. All gases in the system are considered to behave as an ideal gas.

The work required to compress a gas is described with the following equation:

$$\dot{W} = \dot{n}RTln\left(\frac{P_2}{P_1}\right) \qquad (7.4.4)$$

Where $\dot{n}$ is the molar flow in mol/hr, R is the gas constant (8.341 J/molK), T is the temperature of the gas in K and P_2 and P_1 are the final and initial pressure of the gas, respectively. Finally, it is assumed that the compressors used have an overall efficiency of 80%.

Direct chlorination

In Chapter 2 typical operating conditions of the direct chlorination reactor were explained. For this model it is assumed that the reactor operates at a constant temperature of 60ºC and a constant pressure of 5 bar. This means that the feed will have to be pre-heated and pressurized to the correct conditions before entering the reactor.

Chlorine evaporator

The chlorine feed is supplied as a liquid (T=-40ºC, P=1bar) and vaporised in an evaporator after heating it up to its boiling point of -34ºC. The total energy flow required is the sum of the internal enthalpy and the heat of evaporation:

$\dot{E}_{evap} = \dot{m}c_{p,ave}(T_2 - T_1) + \dot{m}\Delta H_{vap}$ (7.4.5)

$$\dot{E}_{evap} = 705.7\left[\frac{kg}{h}\right] * 0.936\left[\frac{kJ}{kgK}\right] * 6[K] + 705.7\left[\frac{kg}{h}\right] * 286\left[\frac{kJ}{kg}\right] = 206\left[\frac{MJ}{h}\right]$$

Feed pre-heating

Now that chorine (T=-34ºC, P=1bar) is in its gaseous phase it is fed into a pre-heater together with the ethylene feed (T=25ºC, P=1bar). The two gases mix and the temperature of the gas mixture is calculated by:

$T_{mix} = \frac{\dot{m}_{Cl_2}c_{p,Cl_2}T_{Cl_2}+\dot{m}_{C_2H_4}c_{p,C_2H_4}T_{C_2H_4}}{\dot{m}_{Cl_2}c_{p,Cl_2}+\dot{m}_{C_2H_4}c_{p,C_2H_4}}$ (7.4.6)

T_{mix} was found to be -0.2ºC. The individual average specific heat capacity of chlorine and ethylene were found using equation 7.4.2 and 7.4.3 and the information from Table 28. Now the average specific heat capacity of the gas mixture can be found using the mass flows:

$$c_{p,ave,mixture} = \frac{\dot{m}_{C_2H_4}}{\dot{m}_{mixture}}c_{p,ave,C_2H_4} + \frac{\dot{m}_{Cl_2}}{\dot{m}_{mixture}}c_{p,ave,Cl_2}$$

This was found to be 0.790 kJ/kgK. Finally the total energy flow to heat up the energy mixture from T_{mix} to the reactor operating temperature of 60ºC is equal to the increase of internal enthalpy of the gas mixture:

$$\dot{E}_{pre-heater} = \dot{m}c_{p,ave}(T_2 - T_1)$$

$$\dot{E}_{pre-heater} = 984.9\left[\frac{kg}{h}\right] * 0.790\left[\frac{kJ}{kgK}\right] * 60.2[K] = 46.8\left[\frac{MJ}{h}\right]$$

Feed compression

Next, the work required to compress the gas mixture from 1 bar to 5 bar is:

$$\dot{W}_{compress} = \dot{n}RTln\left(\frac{P_2}{P_1}\right)$$

$$\dot{W}_{compress} = 19906\left[\frac{mol}{h}\right] * 8.314 * 10^{-6}\left[\frac{MJ}{molK}\right] * 333[K] * \ln\left(\frac{5}{1}\right)[-] = 88.7\left[\frac{MJ}{h}\right]$$

Considering the efficiency of the compressor the actual work required will be 20% higher: 106.4 MJ/h.

In the end, the total energy required for the pre-treatment of the feed for the direct-chlorination reactor is:

$$\dot{E}_{total,DC} = \dot{E}_{evap} + \dot{E}_{pre-heater} + \dot{W}_{compress} = 360\left[\frac{MJ}{h}\right]$$

Reactor

Finally, the reactants (T=60ºC, P=5bar) are fed to the direct chlorination reactor, which is a gas-liquid contact column. Since the reaction is exothermic heat is produced within the reactor. It is assumed that all reaction heat is removed in order to allow the reaction to occur at a constant temperature of 60ºC. From Section 2.2 it is known that the enthalpy of formation is -218 kJ/mol EDC produced. This means that the energy extracted from the reactor is:

$$\dot{E}_{DC,extracted} = -218\left[\frac{kJ}{mol}\right] * 9952\left[\frac{mol}{h}\right] = -2.2\left[\frac{GJ}{h}\right]$$

Oxychlorination

The chosen conditions for the oxychlorination reactor are an operating temperature of 200ºC and an operating pressure of 5 bar, as reported in Section 2.2. This means that, similarly to the previous section, the feed will have to be pre-heated and pressurized to the correct conditions before entering the reactor.

Feed pre-heating

Ethylene (T=25ºC, P=1bar), oxygen (T=25ºC, P=1bar) and HCl (T=25ºC, P=1bar) are fed in the pre-heater. Here, the gases are mixed and heated to 200ºC. Using equation 7.4.2 and 7.4.3, the average specific heat of ethylene, oxygen and HCl was calculated as 1.83 kJ/kgK, 0.94 kJ/kgK and 0.80 kJ/kgK, respectively. Using the equation below it was found that the average specific heat of the gas mixture is:

$$c_{p,ave,mixture} = \frac{\dot{m}_{C_2H_4}}{\dot{m}_{mixture}} c_{p,ave,C_2H_4} + \frac{\dot{m}_{O_2}}{\dot{m}_{mixture}} c_{p,ave,O_2} + \frac{\dot{m}_{HCl}}{\dot{m}_{mixture}} c_{p,ave,HCl}$$

$$c_{p,ave,mixture} = \frac{281\left[\frac{kg}{h}\right]}{1171\left[\frac{kg}{h}\right]} * 1.83\left[\frac{kJ}{kgK}\right] + \frac{160\left[\frac{kg}{h}\right]}{1171\left[\frac{kg}{h}\right]} * 0.94\left[\frac{kJ}{kgK}\right] + \frac{730\left[\frac{kg}{h}\right]}{1171\left[\frac{kg}{h}\right]} * 0.80\left[\frac{kJ}{kgK}\right] = 1.066\left[\frac{kJ}{kgK}\right]$$

Finally the total energy flow to heat up the energy mixture from 25ºC to the reactor operating temperature of 200ºC is equal to the increase of internal enthalpy of the gas mixture:

$$\dot{E}_{pre-heater} = \dot{m} c_{p,ave}(T_2 - T_1)$$

$$\dot{E}_{pre-heater} = 1171\left[\frac{kg}{h}\right] * 1.066\left[\frac{kJ}{kgK}\right] * 175[K] = 218.5\left[\frac{MJ}{h}\right]$$

Feed compression

Next, the work required to compress the gas mixture from 1 bar to 5 bar is:

$$\dot{W}_{compress} = \dot{n} RT ln\left(\frac{P_2}{P_1}\right)$$

$$\dot{W}_{compress} = 35038\left[\frac{mol}{h}\right] * 8.314 * 10^{-6}\left[\frac{MJ}{molK}\right] * 473[K] * \ln\left(\frac{5}{1}\right)[-] = 221.8\left[\frac{MJ}{h}\right]$$

Considering the efficiency of the compressor the actual work required will be 20% higher: 266.1 MJ/h.

In the end, the total energy required for the pre-treatment of the feed for the direct-chlorination reactor is:

$$\dot{E}_{total,oxy} = \dot{E}_{pre-heater} + \dot{W}_{compress} = 485\left[\frac{MJ}{h}\right]$$

Reactor

The reactants (T=200ºC, P=5 bar) are fed to the oxychlorination fluid-bed reactor where, similarly to direct chlorination, an exothermic reaction is carried out. This time, the heat of reaction is -238 kJ/mol EDC produced (see Section 2.2). This means that the energy extracted from the reactor is:

$$\dot{E}_{oxy,extracted} = -238\left[\frac{kJ}{mol}\right] * 9911\left[\frac{mol}{h}\right] = -2.4\left[\frac{GJ}{h}\right]$$

Since the temperature of the heat released is approximately 200ºC it opens up the opportunity to produce MP steam (Shin-Etsu, personal communication). Water with a temperature of 25ºC is assumed to heated and vaporised in an heat exchanger. Assuming the properties of the produced MP steam in Table 29, it can be found that approximately 720 kg MP steam/hr can be produced.

Table 29 Properties of MP steam at a temperature of 198ºC and a pressure of 15 bar (Engineering Toolbox, 2019)

Properties of MP steam	Value
Pressure (bar)	15
Temperature (ºC)	198
Specific heat capacity (kJ/kgK)	2.8197
$\Delta H_{vaporation}$ (kJ/kg)	2789

$$\left|\dot{E}_{oxy,extracted}\right| = \dot{m}_{MPsteam}c_{p,MPsteam}\Delta T + \dot{m}_{MPsteam}\Delta H_{vap} \text{ ,}$$

$$\dot{m}_{MPsteam} = \frac{\left|\dot{E}_{oxy,extracted}\right|}{c_{p,MPsteam}\Delta T+\Delta H_{vap}} = \frac{2.4*10^{6}\left[\frac{kJ}{h}\right]}{2.8\left[\frac{kJ}{kgK}\right]*173[K]+2789\left[\frac{kJ}{kg}\right]} = 720\ \left[\frac{kg}{h}\right] .$$

EDC Purification

For the separation of EDC from impurities and water two distillation columns are used. In the light ends column, water and LE are captured as overhead product. In the heavy ends column, EDC is captured as overhead product. The light ends column will be referred to as C101, the heavy ends column as C102, see the setup described by Dimian & Bildea (2008).

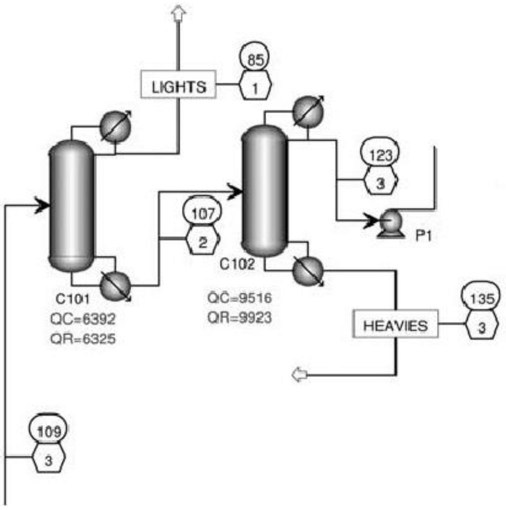

Figure 22 Overview of the C101 and C102 distillation columns (Dimian & Bildea, 2008).

The mass flows of the distillate (D) and bottoms (W), obtained from the MFA, are presented in the Table 30. The reflux ratio of C101 and C102 condensers are assumed to be 3 (Dry et al., 2003) and 0.94, respectively (Koren et all, 1998; Dry et al., 2003). The boil up ratios for both columns are assumed to be 0.6 (Dimian & Bildea, 2008). The top and bottom reflux can now be calculated using the following two equations (Coulson & Richardson, 2005):

$$\dot{L}_{C10X} = R_X * \dot{D}_{C10X} \text{ ,}$$

$$\dot{V}_{C10X} = S_X * \dot{W}_{C10X} \ ,$$

where L_{C10X} and V_{C10X} are the top and bottom reflux rates of column X (X=1,2) in kg/h, R_x and S_x are the reflux and boil up ratios of column X, and D_{C10X} and W_{C10X} are the distillate and bottom flow rates in kg/h of column X. For example, the top reflux rate of C102 is:

$$\dot{L}_{C102} = 0.94\,[-] * 3952 \left[\frac{kg}{h}\right] = 3715 \left[\frac{kg}{h}\right] .$$

The other reflux rates can be calculated similarly using the equations above, the results are also included in Table 30.

Table 30 Model parameters used for the calculation on the C101 and C102 columns.

Column	Model parameter	Mass flow (kg/h)
C101	D_{C101}	190
	W_{C101}	3962
	L_{C101}	570
	V_{C101}	2377
C102	D_{C102}	3952
	W_{C102}	10
	L_{C102}	3715
	V_{C102}	6

The latent heat of the condenser ($L_{C,C10X}$) and reboiler ($L_{W,C10X}$) feed of column X are a function of the mass fractions of the compounds in the stream (w) and their respective heat of evaporation (ΔH_{vap}) (Coulson & Richardson, 2005):

$$L_{C,C10X} = w_i * \Delta H_{vap,i} + w_j * \Delta H_{vap,j} \ ,$$

$$L_{W,C10X} = w_i * \Delta H_{vap,i} + w_j * \Delta H_{vap,j} \ .$$

Knowing the composition of the streams gives the latent heat of the condenser and reboiler feeds of column C101 and C102, as shown in Table 31.

Table 31 Details of the compositions of the distillation and bottom streams of C101 and C102. The calculated latent heat of the condenser and reboiler feeds are also given.

Column	Composition D (wt%)	Composition W (wt%)	Latent heat condenser feed$^{1)}$ (kJ/kg)	Latent heat reboiler feed$^{1)}$ (kJ/kg)
C101	95% water, 5% light ends	99% EDC, 1% heavy ends	2124$^{2)}$	333
C102	100% EDC (<1% heavy ends)	100% heavy ends (<1% EDC)	333	301

The total duty of the condenser for both columns can now be calculated using the calculated parameters from Table 30 and Table 31:

$$\dot{Q}_C = (\dot{D}_{C10X} + \dot{L}_{C10X}) * L_{C,C10X} \ .$$

Similarly, the total duty of the reboiler for both columns is calculated:

$$\dot{Q}_W = (\dot{W}_{C10X} + \dot{V}_{C10X}) * L_{W,C10X} \ .$$

The results are presented in Table 32.

Table 32 Total calculated duty of the condensers and reboilers of C101 and C102.

Column	Duty condenser (GJ/h)	Duty reboiler (GJ/h)
C101	1.61	0.79
C102	2.56	1.77E-03
Total	4.17	0.79

The specific enthalpy of MP steam is, using the characteristics from Table 29:

$$\Delta H_{MP,steam} = c_p(T_{steam} - T_{sat}) + \Delta H_{cond} = 2794 \left[\frac{kJ}{kg}\right] .$$

Table 33 Summary of the characteristics of the cooling water used in the condensers.

	Cooling water for condenser (1 bar, 18°C)
ΔH_{vap} (kJ/kg)	2256
C_p (kJ/kgK)	4.184
T_{in} (°C)	18
T_b (°C)	100

The specific enthalpy of cooling water is, using the characteristics from Table 33:

$$\Delta H_{water} = c_p(T_b - T_{in}) + \Delta H_{vap} = 2600 \left[\frac{kJ}{kg}\right] .$$

Now the amount of MP steam and cooling water consumed in the reboilers and condensers, respectively, can be calculated:

$$\dot{m}_{MP\ steam} = \frac{\dot{Q}_{W,total}}{\Delta H_{MP\ steam}} = \frac{0.79*10^6\left[\frac{kJ}{h}\right]}{2794\left[\frac{kJ}{kg}\right]} = 283 \left[\frac{kg}{h}\right] = 0.28 \left[\frac{ton}{h}\right] ,$$

$$\dot{m}_{cooling\ water} = \frac{\dot{Q}_{C,total}}{\Delta H_{water}} = \frac{4{,}17*10^6\left[\frac{kJ}{h}\right]}{2600\left[\frac{kJ}{kg}\right]} = 1604 \left[\frac{kg}{h}\right] = 1.6 \left[\frac{ton}{h}\right] .$$

EDC cracking

The pure EDC leaving the second distillation column has a temperature of 123°C and a pressure of 3 bar. The cracking furnace requires an input with a temperature of 400°C and a pressure of 20 bar. Similarly to the pre-treatment for the direct chlorination and oxychlorination reactors, pre-heating and pressurising is necessary.

Feed pre-heating

Generally, EDC is party pre-heated to 190°C using HP steam (Shin-Etsu, personal communication). This requires the following energy flow:

$$\dot{E}_{pre-heater,1} = \dot{m}_{EDC} c_{p,ave}(T_2 - T_1) ,$$

where the average specific heat, with T1=123°C and T2=190°C, is:

$$c_{p,ave}(T) = \frac{1}{2}\left[c_{p,T_2}(T) + c_{p,T1}(T)\right] = 0.964 \left[\frac{kJ}{kgK}\right] ,$$

$$\dot{E}_{pre-heater,1} = 3830 \left[\frac{kg}{h}\right] * 0.964 \left[\frac{kJ}{kgK}\right] * (190 - 123)[K] = 247 \left[\frac{MJ}{h}\right] .$$

Natural gas is assumed to be burned to pre-heat the EDC to 400ºC, which requires an energy flow of:

$$\dot{E}_{pre-heater,2} = \dot{m}_{EDC} c_{p,ave}(T_2 - T_1) \text{ ,}$$

where the average specific heat, with T1=190ºC and T2=400ºC, is:

$$c_{p,ave}(T) = \frac{1}{2}\left[c_{p,T_2}(T) + c_{p,T1}(T)\right] = 1.11 \left[\frac{kJ}{kgK}\right] \text{ ,}$$

$$\dot{E}_{pre-heater,2} = 3830 \left[\frac{kg}{h}\right] * 1.11 \left[\frac{kJ}{kgK}\right] * (400 - 190)[K] = 895 \left[\frac{MJ}{h}\right] \text{ .}$$

Feed compression
The feed is isothermally compressed from 3 bar to 20 bar:

$$\dot{W}_{compress} = \dot{n}_{EDC} R T_{EDC} ln\left(\frac{P_2}{P_1}\right) \text{ ,}$$

$$\dot{W}_{compress} = 38703 \left[\frac{mol}{h}\right] * 8.314 * 10^{-6} \left[\frac{MJ}{molK}\right] * 673[K] * \ln\left(\frac{20}{3}\right)[-] = 411 \left[\frac{MJ}{h}\right] \text{ .}$$

Considering the efficiency of the compressor to be 80%, this becomes 493 MJ/h.

Reactor
The pyrolysis furnace is composed of two main area: the convection zone and the reaction zone. In the convection zone natural gas is burned to bring the feed to the temperature where it starts to crack into VCM, which is 500ºC. In the reaction zone, natural gas is burned to fuel the endothermic cracking reaction. The energy flow to the convection zone is calculated first:

$$\dot{E}_{furnace,conv} = \dot{m}_{EDC} c_{p,ave}(T_2 - T_1) \text{ ,}$$

where the average specific heat, with T1=400ºC and T2=500ºC, is:

$$c_{p,ave}(T) = \frac{1}{2}\left[c_{p,T_2}(T) + c_{p,T1}(T)\right] = 1.26 \left[\frac{kJ}{kgK}\right] \text{ ,}$$

$$\dot{E}_{furnace,conv} = \dot{m}_{EDC} c_{p,ave}(T_2 - T_1) \text{ ,}$$

$$\dot{E}_{furnace,conv} = 3830 \left[\frac{kg}{h}\right] * 1.26 \left[\frac{kJ}{kgK}\right] * (500 - 400)[K] = 482 \left[\frac{MJ}{h}\right] \text{ .}$$

The heat of reaction of the cracking reaction is 71 kJ/mol VCM (see Section 2.2).

$$\dot{E}_{furnace,react} = \dot{n}_{VCM} * \Delta H_{reaction} \text{ ,}$$

$$\dot{E}_{furnace,react} = 19872 \left[\frac{mol}{h}\right] * 71 \left[\frac{kJ}{mol}\right] = 1.4 \left[\frac{GJ}{h}\right] \text{ .}$$

The total energy demand for the cracking section, including pre-heating and compression is:

$$\dot{E}_{cracking} = \dot{E}_{pre-heater,1} + \dot{E}_{pre-heater,2} + \dot{W}_{compress} + \dot{E}_{furnace,conv} + \dot{E}_{furnace,react} = 3.5 \left[\frac{GJ}{h}\right] \text{ .}$$

VCM purification

Since the output of the cracking furnace is a mixture of VCM, EDC and HCl the three substances have to be separated using two distillation columns. In the first distillation column HCl leaves as overhead product, in the second distillation column VCM is captured from the top. The methodology used here is very similar to the section EDC purification and will therefore not be fully explained again. The first distillation column is referred to as C201, the second distillation column as C202, see the figure by Dimian & Bildea (2008) below.

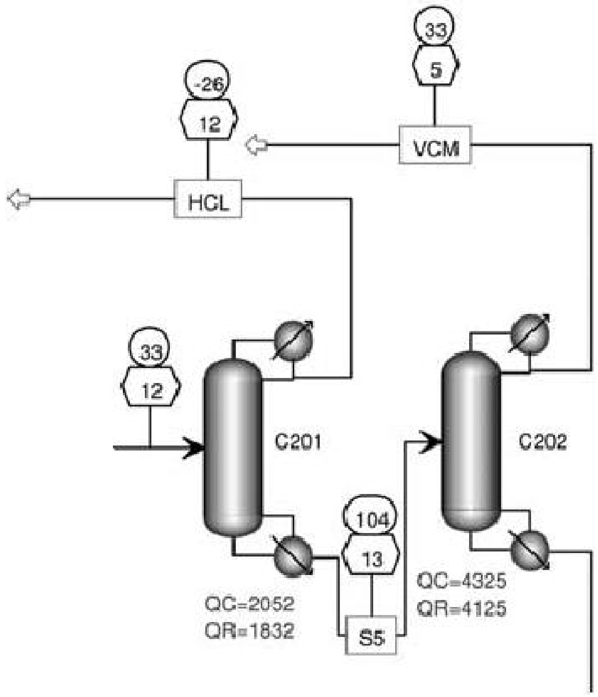

Figure 23 Overview of the C201 and C202 distillation columns (Dimian & Bildea, 2008)

C201 and C202 were modelled with a reflux ratio of 0.8 and 0.9, respectively (Karasek et al., 2016). For both columns a boil up ratio of 0.6 was assumed (Dimian & Bildea, 2008). Using this information and the mass flows for the distillate and the bottoms, as presented in Table 34, the top and bottom reflux rates for C201 and C202 were calculated.

Table 34 Model parameters used for the calculation on the C201 and C202 columns.

Column	Model parameter	Mass flow (kg/h)
C201	D_{C201}	592
	W_{C201}	3238
	L_{C201}	474
	V_{C201}	1943
C202	D_{C202}	1242
	W_{C202}	1996
	L_{C202}	1118
	V_{C202}	1198

The latent heat of the condenser and reboiler feed for C201 and C202 were calculated in a similar way as for C101 and C102, see Table 35.

Table 35 Details of the compositions of the distillation and bottom streams of C201 and C202. The calculated latent heat of the condenser and reboiler feeds are also given.

Column	Composition D (wt%)	Composition W (wt%)	Latent heat condenser feed[3)] (kJ/kg)	Latent heat reboiler feed[3)] (kJ/kg)
C201	100% HCl	39% VCM, 61% EDC	466	348
C202	100% VCM (<1% EDC)	100% EDC (<1% VCM)	368	323

Again, using the same equation during the section EDC purification, the total duty of the condenser and reboilers of the columns is calculated. The results are presented in Table 36.

Table 36 Total calculated duty of the condensers and reboilers of C201 and C202.

Column	Duty condenser (GJ/h)	Duty reboiler (GJ/h)
C201	0.50	0.68
C202	0.87	0.39
Total	1.37	1.07

The flow rate of MP steam required for the reboilers is 0.38 ton/h and the flow rate of cooling water required for the condensers is 0.53 ton/h.

Summary of the EFA

Table 37 EFA summary

Control volume	Energy flow (MJ/h)
Direct chlorination	360
Oxychlorination	485
EDC purification	4960
EDC cracking	3500
VCM purification	2440

The energy can be carried by different sources: natural gas, steam (MP/HP), electricity or cooling water. Below the energy flow of each control volume is broken down per carrier.

Table 38 Energy flow per energy carrier per process step

Control volume	Natural gas (MJ/h)	MP Steam (MJ/h)	HP Steam (MJ/h)	Cooling water (MJ/h)	Electricity (MJ/h)	Total (MJ/h)
Direct chlorination	-	253	-	-	107	360
Oxychlorination	-	219	-	-	266	485
EDC purification	-	790	-	4170	-	4170
EDC cracking	2788	-	247		493	3528
VCM purification	-	1370	-	1070	-	1370
						9913

From this it can be seen that natural gas is exclusively used in the EDC cracking section. MP steam is used in large amounts as well for several distillation and pre-heating steps.

Electricity is used for compression in several parts of the process. HP steam is only used in EDC cracking to pre-heat EDC to 190ºC. Cooling water is used in all four distillation towers.

The PVC production step requires 2.1 GJ/t PVC steam (2.3 GJ_p/t PVC) and 0.7 GJ/t PVC electricity (1.7 GJ_p/t PVC) (Shin-Etsu, personal communication). As was shown in Table 7 this is a total of 4.0 GJ/t PVC primary energy demand.

A.5 CO_2 emission calculation

Overview

The direct and indirect emissions were calculated by using emission factors (EF) for utilities such as natural gas and electricity, or for feedstock, such as the production of ethylene. The following emission factors are considered here:

Table 39 Emission factors of the energy sources and feedstock considered in this report.

Utility	Emission factor (kg CO_2/unit of energy)	Reference
Natural gas	56.6 kg CO_2/GJ_{NG}	RVO, 2017
Steam (LP/MP/HP)	63 kg CO_2/GJ_{steam}	RVO, 2019
Electricity	139 kg CO_2/GJ_e	RVO, 2018
Feedstock	**Emission factor (kg CO_2/kg feedstock)**	
Ethylene	1.4	RVO, 2018
Chlorine	1.3	RVO, 2018
Oxygen	0.42	RVO, 2018
HCl	0.88	PlasticsEurope, 2015

Calculation EF for steam and electricity

Steam

It is assumed that the steam is produced by using natural gas as fuel. Assuming the specific enthalpy of LP, MP and HP steam of 2748 kJ/kg, 2789 kJ/kg and 2794 kJ/kg (taken from the MIDDEN database), a conversion factor to primary energy of 1 GJ_{steam} = 1.11 GJ_p (RVO, 2019) and the emission factor of natural gas from Table 37, the emissions per ton of LP/MP/HP steam are calculated:

$$EF_{steam}\left[\frac{kg\ CO_2}{ton\ steam}\right] = h_{steam}\left[\frac{GJ_{steam}}{ton\ steam}\right] * 1.11\left[\frac{GJ_p}{GJ_{steam}}\right] * 56.6\left[\frac{kg\ CO_2}{GJ_p}\right]$$

Converting the emission factors in kg CO_2/GJ_{steam} yields the same value for all three types of steam (see Table 38)

$$EF_{steam}\left[\frac{kg\ CO_2}{GJ_{steam}}\right] = \frac{EF\left[\frac{kg\ CO_2}{ton\ steam}\right]}{h_{steam}\left[\frac{GJ_{steam}}{ton\ steam}\right]}$$

Table 40 Emission factor of LP, MP, HP steam.

Type of steam	Specific enthalpy (GJ_{steam}/ton steam)	Emission factor (kg CO_2/ton steam)	Emission factor (kg CO_2/GJ_{steam})
LP	2.748	172.6	63
MP	2.789	175.2	63
HP	2.794	175.5	63

Electricity

RVO (2018) reports an emission factor of electricity from the Dutch electricity grid mix of 0.53 kg CO_2/kWh. Considering a conversion factor of 1 kWh = 0.0036 GJ_e, this can be converted to:

$$EF_{electricty} = \frac{0.53\left[\frac{kg\ CO_2}{kWh}\right]}{0.0036\left[\frac{GJ_e}{kWh}\right]} = 139\ \left[\frac{kg\ CO_2}{GJ_e}\right]$$

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1) Data for the heat of evaporation at standard conditions was taken: LE, 35 kJ/mol; Water, 40 kJ/mol; EDC, 32 kJ/mol; HE, 40 kJ/mol. Using the molar mass of each compounds this could be recalculated to kJ/kg. LE, 0.099 kg/mol; Water, 0.018 kg/mol; EDC, 0.096 kg/mol; HE, 0.133 kg/mol.
2) Example calculation: 0.05 * (35/0.099) + 0.95 * (40/0.018) = 2124 kJ/kg.
3) Data for the heat of evaporation at standard conditions was taken: HCl, 17 kJ/mol; VCM, 23 kJ/mol; EDC, 32 kJ/mol. Using the molar mass of each compounds this could be recalculated to kJ/kg. HCl, 0.036 kg/mol; VCM, 0.063 kg/mol; EDC, 0.096 kg/mol.