TNO

PBL Netherlands Environmental
Assessment Agency

DECARBONISATION OPTIONS FOR THE DORDRECHT CHEMICAL CLUSTER

**Marian Alejandra Rodriguez, Ton van Dril,
Silvana Gamboa Palacios**

04 January 2021

MIDDEN

Manufacturing Industry Decarbonisation Data Exchange Network

Decarbonisation options for the Dordrecht chemical cluster
© PBL Netherlands Environmental Assessment Agency; © TNO
The Hague, 2021
PBL publication number: 4558
TNO project no. 060.33956 / TNO 2020 P11629

Authors
M.A. Rodriguez, A.W.N. van Dril and S. Gamboa Palacios

Acknowledgements
The authors kindly acknowledge input and review by Marc Reijmers (Chemours Dordrecht), Ton Knijnenburg (DuPont Dordrecht) and Willem Buitelaar (DuPont Dordrecht).

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 (which is named TNO EnergieTransitie after 1-1-2020). 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:
D. van Dam (PBL), Dick.vanDam@pbl.nl, or S. Gamboa Palacios (TNO), Silvana.Gamboa@tno.nl

This publication is a joint publication by PBL and TNO EnergieTransitie and can be downloaded from: www.pbl.nl/en. Parts of this publication may be reproduced, providing the source is stated, in the form: Rodriguez, M.A., Van Dril, A.W.N., and Gamboa Palacios, S. (2021), Decarbonisation options for the Dordrecht chemical cluster. PBL Netherlands Environmental Assessment Agency and TNO EnergieTransitie, The Hague.

PBL Netherlands Environmental Assessment Agency is the national institute for strategic policy analysis in the fields of the environment, nature and spatial planning. We contribute to improving the quality of political and administrative decision-making by conducting outlook studies, analyses and evaluations in which an integrated approach is considered paramount. Policy relevance is the prime concern in all of our studies. We conduct solicited and unsolicited research that is both independent and scientifically sound.

TNO EnergieTransitie has a twofold mission: to accelerate the energy transition and to strengthen the competitive position of The Netherlands. TNO conducts independent and internationally leading research and we stand for an agenda-setting, initiating and supporting role for government, industry and NGOs.

This report was reviewed by Chemours Dordrecht and DuPont Dordrecht. PBL and TNO remain responsible for the content. The decarbonisation options and parameters are explicitly not verified by the companies.

Contents

FINDINGS

Summary

This report presents the current situation of the Dordrecht chemical cluster, which is composed by production locations of three different companies: Chemours, DuPont, and Dow. Chemours is dedicated to the production of fluoropolymers and fluoroelastomers, DuPont produces polyoxymethylene, and Dow produces copolymers of ethylene.

Table 1 shows the main feedstock, products, main technologies, and an estimation of energy consumption, and greenhouse gas emissions[1] of the three companies.

Table 1 Overview of the three companies (Elektronisch Milieujaarverslag, 2018)

Company	Chemours	DuPont	Dow	Total Dordrecht Site
Main Feedstock	• Chloroform • Hydrofluoric acid	• Methanol	• Polyethylene • Acrylic acid • Maleic anhydride	
Product	• Polytetrafluoroethylene (PTFE) Teflon™ • Fluorinated ethylene-propylene (FEP) Teflon™ • Chlorotrifluoroethylenevinylidene fluoride (FPM/FKM) Viton™	• Polyoxymethylene (POM) Delrin®	• Ionomer of ethylene acid copolymer Surlyn™ • Resin Adhesives Bynel™ • Modified polymers Fusabond™	
Technology	• Fluorination of Chloroform to produce Chlorodifluoromethane (HCFC-22) • Pyrolysis of HCFC-22 to produce Tetrafluoroethylene (TFE) and pyrolysis of TFE to produce Hexafluoropropylene • Homopolymerization and copolymerization of TFE and HFP	• Catalytic oxidation of methanol to produce formaldehyde (Formox process) • Polymerization of formaldehyde to produce polyoxymethylene (POM) • Compounding (melting the polymer and mixing with additives to produce granules)	• Reactive extrusion of polyethylene • Granulation	
Estimated production capacity 2018 (kilotonnes, kt)	15-25	90-100	40-45	
Estimated energy consumption (TJ)	805	1,284	192	2,282
CO_2 emissions (kt/year)	15	42	0	57
CO_2 emissions Percentage[2]	24%	76%	0	100%
F-gases emissions (kt CO_2 eq/year)	491	0	0	491
F-gases emissions percentage	100%	0	0	100%

---

[1] These emissions correspond to scope 1, which implies direct greenhouse gas (GHG) emissions.

[2] The breakdown of the emissions is based on estimations from different sources including NEA, 2018 the eMJV,2018, consultations with the companies, and own calculations.

Currently, the main source of steam of the site is a waste to energy plant, owned by HVC, which is located adjacent to the cluster. HVC provides around 840 TJ of steam per year, converted in a heat exchanger operated by Chemours to supply the different processes in the industrial facility. The steam supply is also connected to the urban heat network of Dordrecht. Natural gas is mainly used to feed furnaces and the two back-up boilers owned by Chemours and DuPont. There is no electricity production on-site, so currently all the electricity supply comes from the grid.

The vast majority of the emissions of greenhouse gases occurs at Chemours, in the form of fluorinated gases (F-gases), which are man-made gases with a large global warming potential. The main methods to reduce F-gases emissions, besides the ongoing strategies, are increasing the efficiency of the current thermal converter and implementing plasma technology to destroy F-gases.

Regarding CO_2 emission reduction, the main opportunities are related to fuel substitution. Around 65% of the CO_2 emissions of the site are from natural gas combustion for boilers and furnaces. Although the steam production related emissions have been reduced in the past years through external supply and heat integration, there are still opportunities by using carbon-free electricity, blue or green hydrogen, and sustainable biomass. Carbon capture and storage is included as an alternative to reduce emissions not only from natural gas combustion, but also from residual gases combustion, which represents around 30% of the total CO_2 emissions. Further alternatives include biobased feedstocks and recycling.

Introduction

This report describes the current situation for Dordrecht Chemical Park in The Netherlands and the options and preconditions for its decarbonisation. Besides, it includes alternatives for reducing fluorinated gases (F-gases) emissions for one of the companies located in this industrial site due to the high global warming potential of these gases. The study is part of the MIDDEN project (Manufacturing Industry Decarbonisation Data Exchange Network). The MIDDEN project aims to support industry, policymakers, analysts, and the energy sector in their joint efforts to achieve deep decarbonisation. The MIDDEN project will update and elaborate further on options in the future, in close connection with the industry.

Scope

The companies located in Dordrecht at the Baanhoekweg industrial chemical park are:

- The Chemours Company
- DuPont Dordrecht
- The Dow Chemical Company.

Production processes include:

Chemours

- Fluorination of chloroform to produce chlorodifluoromethane (HCFC-22)
- Several separation steps, including distillation and drying
- Neutralization
- Gas compression
- Pyrolysis of HCFC-22 to produce tetrafluoroethylene (TFE) and pyrolysis of TFE to produce hexafluoropropylene
- Homopolymerization and copolymerization of TFE and HFP
- Thermal conversion of gases
- Blending of gases.

DuPont

- Catalytic oxidation of methanol to produce formaldehyde (Formox process)
- Polymerization of formaldehyde to produce polyoxymethylene (POM)
- Compounding (melting the polymer and mixing with additives to produce granules)
- Biogas production (Anaerobic water treatment)
- Incineration of by-products and residual process gases.

Dow

- Reactive extrusion of polyethylene
- Granulation
- Drying.

Products include:

Chemours
- Polytetrafluoroethylene (PTFE) Teflon™
- Fluorinated ethylene-propylene (FEP) Teflon™
- Chlorotrifluoroethylenevinylidene fluoride (FPM/FKM) Viton™

DuPont
- Polyoxymethylene (POM) Delrin®

Dow
- Ionomer of ethylene acid copolymer Surlyn™
- Resin Adhesives Bynel™
- Modified polymers Fusabond™

The main options for reducing greenhouse gases emissions and energy consumption are:

Chemours
- F-gases: Plasma technology for F-gases destruction.
- CO_2: energy efficiency, electrification, hydrogen, heat pumps, biomass, recycling, and CCS.

Dupont
- CO_2: electrification, hydrogen, heat pumps, biomass, recycling, CCS/CCU, biobased feedstocks.

Dow
- CO_2: hydrogen, recycling, biobased feedstocks.

The report is elaborated using information and data from 2018 and is presented in separated sections per company for each chapter.

Reading guide

Section 1 introduces the chemical cluster located in Dordrecht, its history, and gives an overview of the site's companies. Section 2 describes the current situation of the production processes of each company, and Section 3 describes the relevant products of these processes and the main market insights; options for decarbonisation are presented and evaluated in Section 4. The timeframe of implementation and main challenges are briefly discussed in Section 5.

1 Dordrecht chemical cluster

1.1 Location, description, and history

This chemical cluster or park is located in Baanhoekweg 22, in Dordrecht, part of the province of South Holland. The location is close to the Merwede river and the populated residential areas De Staart and Sliedrecht-Oost. The residents of Dordrecht, Papendrecht, and Sliedrecht are actively involved in The Neighbours Council of the companies located in this site. This council is an initiative to have a frequent and open dialogue with the community about current affairs, licenses, environment, and funding initiatives. The council involves the management boards of the companies as well (Burenraad DuPont and Chemours, 2020)

Dordrecht chemical cluster was originally a factory complex of DuPont de Nemours, with an area of 55 hectares. DuPont de Nemours was established in The Netherlands in 1959 and started operations in Dordrecht in 1962 with the fiber factories of Orlon™ and Lycra™ (DuPont, 2020a). Around 1967 the Teflon factory™ was put in operation, and then, in the 1970’s, the Delrin® factory was constructed (Dordrecht regional archives, 2020). Years later, other processes of DuPont were added to the industrial complex. However, several business transactions took place over time, including the sale of the DuPont textile segment, including Lycra (INVISTA) to Koch Industries in 2004 (Wilson, 2012). Another change was the closure and the demolition of the Lycra factory located in this industrial site in 2009 (DuPont, 2017). Subsequently, in 2015, the Chemours company was formed and separated as a spin-off of DuPont for the performance chemicals business, including the fluoroproducts segment. Afterwards, in 2017, a merge between DuPont and Dow Chemical was announced, with a further split into three new companies: Corteva, the new DuPont, and the new Dow. As a result of this split, DuPont's ethylene copolymers production facility in Dordrecht was allocated to the new Dow. These business transactions led to the reorganisation of the industrial site, currently owned by Chemours, with three different companies: The Chemours Company, DuPont, and The Dow Chemical Company. Although these companies are independent, they still have a shared environmental permit associated with the entire site. Nevertheless, according to Chemours, DuPont, and Dow information, each company recently applied for a separate permit under evaluation of the South Holland province environmental service (DCMR Milieudienst Rijnmond). Chemours and DuPont participated jointly in the voluntary long-term agreement on Energy Efficiency (MEE covenant), so both companies have an Energy Efficiency Plan (EEP). Once the companies have separate permits, each company will participate separately.

1.2 Local context and relevant projects

Different industrial processes take place in the industrial cluster, which implies high energy consumption. Historically a cogeneration plant operated in this site and was the primary source of carbon dioxide (CO_2) emissions. This plant combusted natural gas to produce the steam and electricity required by the different processes. Nevertheless, the plant was shut down in 2018, and its steam production was replaced by an external supply, thanks to the cooperation project between HVC, DuPont, and Chemours. HVC operates a waste-to-energy plant located adjacent to the industrial cluster, which has supplied steam to the site since 2014. Municipal solid waste is incinerated to produce heat, which required a 1 km steam pipe connecting HVC to the industrial cluster. The amount of steam supplied has increased considerably, reaching to 400 kt/year in 2017. Due to that shift from burning natural gas to HVC steam supply, the site has reduced its CO_2 direct emissions by over 60%.

According to the HVC business manager, one of the main barriers starting the project was the quality of the steam produced by HVC; the steam did not meet the requirements of the processes, so it was necessary to invest in a heat exchanger to convert the steam from 40 bars to 22 bars. The steam from HVC is 55% renewable (Chemours, 2018), a percentage based on the incinerated waste composition. This cooperation agreement with HVC is aligned with Dordrecht municipality's goals of becoming energy-neutral by 2050, with a heat network that also supplies the urban area (Dordt Duurzaam, 2016). Because of the steam system's existing connections on the site, Chemours transfers part of the steam to Dow and Du Pont. Therefore, these companies also benefit from this measure to reduce their CO_2 emissions. Although in 2018 there was a single environmental permit for the complete site, a new independent application has been sent by each company to the South Province environmental agency, and is currently under evaluation. Below, there is an aerial picture of the Dordrecht site, indicating the operations of the three companies (Chemours, Dow Chemical, and DuPont) and the HVC plant's location.

In the next sections, each company is separately described.

Image 1 Dordrecht chemical cluster (adapted from Chemours.com)

1.3 The Chemours Company

The Chemours Company is a multinational American chemical company created as a spin-off from DuPont in 2015. Chemours produces chemical products in three main categories: Titanium Technologies, Fluoroproducts, and Chemical solutions. Chemours Netherlands B.V. Dordrecht site is a complete subsidiary of The Chemours Company. Its focus is on fluoroproducts: manufacturing industrial fluoropolymer resins and blending refrigerants[3]. With more than 500 employees and operating 24-7, Chemours Dordrecht site is the principal private employer in Dordrecht (Burenraad DuPont and Chemours, 2018). Chemours annual production capacity of fluoropolymers is around 15-20 kt, including PTFE, and FEP polymers, under the brand Teflon™ and FKC elastomers, under the brand Viton™ (Elektronisch Milieujaarverslag (EMJV), 2018; own calculations). The main raw materials used for the production of fluoropolymers are chloroform (Trichloromethane) and HF (Hydrofluoric Acid). These materials are used to produce HCFC-22, which is only intended as a feedstock in the subsequent production of monomers[4]; these monomers are then used to produce the final polymers and elastomers.

Different by-products of the fluorination of chloroform are produced, including HFC-23. Due to this gas's high global warming potential[5], this is the main source of GHG emissions. Chemours annual emissions of HFC-23 are around 15 tonne/year (EMJV, 2018), which equals 186 kt CO_2-eq/year. Besides these emissions, there are other diffuse F-gases emissions in two additional steps of the process[6]. First, during the blending of refrigerants, some HFCs are emitted, and second, during the production of the monomers mentioned above TFE and HFP. During the pyrolysis to produce the monomers, low amounts of hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and chlorofluorocarbons (CFCs) are produced; however, due to the high GWP of these gases, the CO_2 equivalents are high (see table 1). Moreover, although their monomers are water-based, they use a solvent during the pelletization of polymers. This solvent can generate some diffuse emissions as well.

Through different projects, Chemours has reduced its GHG emissions to air. These projects include process efficiency to reduce HFC-23 production, the circulation loop system in the monomer plant, and a final thermal treatment of the waste gases from the different processes, for which a thermal converter was installed in 2002. Despite these reduction strategies, there are still significant emissions, mainly when the thermal converter is interrupted. To reduce these diffuse emissions, Chemours is now working on stop protocols and also on increasing the buffer capacity of emissions (increase emissions storage capacity to incinerate later). Although the different processes also use, and in consequence emit, other critical substances such as Gen-X, we do not focus our research on those substances; this study's scope is only on GHG emissions.

As mentioned in section 1.2, the main Chemours CO_2 emissions source was the cogeneration plant. However, the cogeneration plant is no longer in operation. One unit was already withdrawn from the site, and the other one was turned off. Now Chemours receives steam from HVC and DuPont (waste steam) and recently installed two backup boilers, to be used as a backup for the HVC steam supply. The steam supply from HVC and DuPont has led to a significant reduction of CO_2 emissions. The CO_2 emissions related to energy consumption represent less than 4% of the Chemours total GHG emissions per year. In the table below, there is a summary of the main GHG emissions of Chemours, including not only CO_2 but also F-gases:

---

[3] Chemours Dordrecht does not produce refrigerants; the blends are made using imported refrigerants.

[4] In the past Chemours produced HFC-22 also as final product (mainly as a refrigerant), but due to Montreal Protocol this was phased-out. Now its production is only permitted as a feedstock.

[5] HFC-23 global warming potential is 12.400 times than CO_2 (IPCC 5th assessment report).

[6] These emissions will be further described in the section 2 of this report.

Table 2 Chemours GHG Emissions and Main Sources of Emissions (Elektronisch Milieujaarverslag, 2018 and own estimations)

Substance	Amount (tonne)	GWP	CO_2 eq (kt)
CO_2	15,000	**-**	**15**
CFCs	20	8,463	169
HFC-23	15	12,400	186
Other HFCs	24	1,716	41
Total PFCs	11	8,629	95
Total F-gases	**70**		**491**
Total of GHG emissions			**506**

Because the total CO_2 emissions are taken from the NEA report, these do not include the electricity-related (scope 2) emissions. In the case of Chemours, the emissions related to the electricity from the grid are around 29 kt[7]. The analysis of the emissions was carried out using information and numbers from 2018, which, according to Chemours, was a turnaround (TAR) year. Hence, the fugitive emissions of F-gases from the refrigeration machines are expected to be somewhat lower in normal operating conditions.

Regarding energy consumption, all the industrial methods of production of the main fluoropolymers require chlorination/fluorination of hydrocarbons and a further dehydrohalogenation using high temperatures. Due to these processes, the production of fluoropolymers is energy-intensive. As an average, to produce 1 tonne of TFE, the overall energy requirement is more than 10.000 kWh/tonne (Hintzer and Schwertfeger, 2014). In the case of Chemours, 30% of the energy consumption is electricity, 29% natural gas, and 41% steam.

The table below illustrates the energy overview of Chemours in 2018:

Table 3 Chemours Net Energy Consumption (EMJV, 2018; information shared by Chemours)

Energy Carrier	Amount	Unit of Measure	TJ	Percentage (%)
Electricity[8]	68,055	MWh	245	30
Natural Gas	7,341,818	Nm^3	232	29
Steam	117,700	tonne	328	41
Total			805	100

1.4 DuPont Dordrecht

DuPont Dordrecht is part of DuPont de Nemours Inc., an American corporation created after the merge between DuPont and The Dow Chemical Company (DowDuPont) and the subsequent division into three separate companies, one of them DuPont. The predecessor DuPont was established in 1802 in Wilmington, Delaware. The new portfolio of DuPont is based on specialty products, including segments such as safety and construction, transportation, electronics, industrial biosciences, and advanced polymers. Besides the Dordrecht plant, DuPont has four locations in The Netherlands: Landgraaf, Leiden, Ouderkerk aan den IJssel and Zaandam (DuPont, 2020b).

---

[7] According to KEV 2020, the grid electricity emissions in 2018 (integral method) were 0.43 kg CO_2/kWh.

[8] Electricity was converted to TJ using the final energy equivalent 0.0036 TJ/MWh.

The Dordrecht DuPont plant has 250 direct employees, and its production, which operates 24-7, is focused on the advanced polymers segment. According to DuPont, this plant, with an estimated annual production capacity of around 90-100 kt, produces the homopolymer POM (Polyoxymethylene) under the brand Delrin®. The main raw material is methanol, used for the production of formaldehyde; the formed formaldehyde polymerizes to POM in a subsequent step. Later, a compounding process takes place to melt the polymer and mix it with some additives to produce granules.

In terms of CO_2 emissions, according to a recent Life Cycle Assessment (cradle to gate) of the DuPont factory, two-thirds of the carbon load comes from steam, electricity, and methanol used as a raw material. The rest comes mainly from other raw materials. The company has been working on energy efficiency, heat recovery, and steam production as part of its energy efficiency plan 2017-2020 (DuPont, 2020). The main source of CO_2 emissions is the furnace to burn liquid and residual process gases; this furnace operates with natural gas and biogas produced in the anaerobic water treatment plant. The DuPont CO_2 emissions per year are around 35 kt, 35% from burning natural gas, and the rest mainly from burning by-products and residual process gases (DuPont corporate responsibility report, 2019; EMJV, 2018). Table 4 illustrates the main CO_2 emissions, scope 1, from DuPont, and table 5, its energy overview.

Table 4 DuPont CO_2 Emissions and Main Sources of Emissions (EMJV, 2018; information shared by DuPont)

Emission Source	CO_2 (kt)
Process Emissions Emission control system (ECS) unit	1.0
Natural gas combustion	24.0
Combustion of biogas[9]	2.5
Combustion of residual gases[10]	14.5
Total Emissions	42.0

Table 5 DuPont Net Energy Consumption (EMJV, 2018; information shared by DuPont)

Energy Carrier	Amount	Unit of Measure	TJ	Percentage
Electricity[11]	94,000	MWh	338	26%
Natural Gas	13,397,428	Nm^3	424	33%
Steam	186,805	Ton	521	41%
Total			1,283	100%

DuPont emissions related to the electricity from the grid (scope 2 emissions) are around 40 kt[12].

Due to the formaldehyde production reaction's exothermic nature, there is a heat-recovering process to produce steam in a boiler. This steam is used in the Delrin® chemical plant, in which the total energy consumption has decreased, because of different strategies, such as energy integration and insulation. Due to the complexity of the formaldehyde process, heat

---

[9] Biogas is produced from a biological process but does not imply the use of biomass, thus its related emissions are included in the analysis.

[10] These emissions are from the combustion of by-products and residual gases.

[11] Electricity was converted to TJ using the final energy equivalent 0.0036 TJ/MWh

[12] According to KEV 2020, the grid electricity emissions in 2018 (integral method) were 0.43 kg CO_2/kWh

recovery requires a high cooling capacity. Additionally, DuPont receives steam from HVC but also from a backup boiler in case HVC supply is interrupted. Moreover, during the incineration of by-products and residual gases from the process, the heat released is used to produce steam; the steam produced is used in other parts of the process. Residual steam from DuPont processes is sent to Chemours.

Looking into the future, DuPont sees CO_2 reduction opportunities related to bio-based raw materials, green electricity, and steam production from renewables.

1.5 The Dow Chemical Company

The Dow Chemical Company is an American multinational corporation founded in 1897; its headquarters are located in Midland, Michigan, United States. As part of its broad portfolio, Dow has products for consumer care, infrastructure, and packaging industry. In The Netherlands, Dow has been active since 1955, with production sites at Terneuzen and Delfzijl, and also in Dordrecht since 2019 (Dow, 2020). After the merge with DuPont, and the subsequent split, the DuPont ethylene copolymer factory in Dordrecht was transferred to Dow. This factory started operations in Dordrecht in 2011 with two production lines for specialty chemical intermediates, which operates 24-7 and has around 45 employees.

The copolymer factory is focused on the production of the ionomer of ethylene acid copolymer, under the brand Surlyn™, adhesive polymers under the brand Bynel™, and other modified polymers under the brand Fusabond™. The main raw materials are polyethylene, acrylic acid, and maleic anhydride.

Dow's energy sources are mainly electricity and steam from Chemours. The energy is used for the reactors, blenders, and extruders. There are no direct emission sources such as furnaces or boilers.

Table 6 Dow Energy Overview (General information shared by Dow and official information about the whole site from EMJV, 2018)

Energy Carrier	Amount	Unit of Measure	TJ	Percentage (%)
Electricity[13]	53,417	MWh	194	99%
Steam	72	tonne	0.2	1%
Total			194.2	100%

Dow emissions related to the electricity from the grid (scope 2 emissions) are around 23 kt[14].

---

[13] Electricity was converted to TJ using the final energy equivalent 0.0036 TJ/MWh.

[14] According to KEV 2020, the grid electricity emissions in 2018 (integral method) were 0.43 kg CO_2/kWh.

2 Production processes

This chapter describes and quantifies the main processes taking place at Dordrecht chemical cluster. An overview of the main chemical reactions and the energy and materials flows is developed in separate sections on the three companies, based mainly on literature review and information shared directly by the companies.

2.1 Chemours

2.1.1 Fluoropolymers Overview

Chemours produces different fluoropolymer and elastomer grades under two main brands:

Teflon™: Polytetrafluoroethylene (PTFE) and Fluorinated ethylene-propylene (FEP)
Viton™: Chlorotrifluoroethylenevinylidene fluoride (FPM/FKM)

These products are based on the monomer Tetrafluoroethylene (TFE) and other comonomers, such as HFP (Hexafluoropropylene) and VDF (Vinylidene fluoride). TFE, the most common monomer used in the production of fluoropolymers (Drobny, 2009), is produced by the pyrolysis of HCFC-22[15], which in turn, is produced by the fluorination of chloroform with hydrofluoric acid (HF).

The main production processes that take place at Chemours are illustrated in the diagram below:

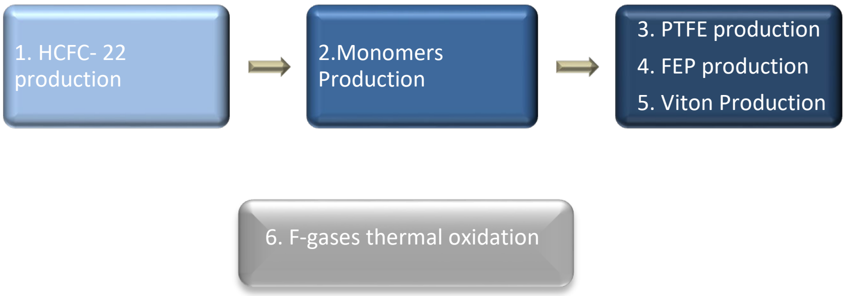


Figure 1 Chemours Main Processes

Besides these processes, an additional blending plant of imported refrigerants is located at the Chemours facility.

There are no descriptions of the Chemours processes publicly available. Thus, sections 2.1.2, 2.1.3, and 2.1.4 illustrate mainly findings from a thorough literature review, including publications and commercial patents, and assumptions about Chemours process configurations. The methods of production subsequently described were selected as the most widely used at the industrial level.

---

[15] In the past HCFC-22 was commercialized as Freon™ 22, when it was produced and sold as a refrigerant

2.1.2 HCFC-22 Production

The next schematic diagram illustrates an overview of the main steps involved in the production of HCFC-22. It includes the ranges of main inputs and outputs of materials and energy requirements per year. The black arrows represent the main raw materials and products; red arrows are GHG emissions and orange arrows energy inputs.

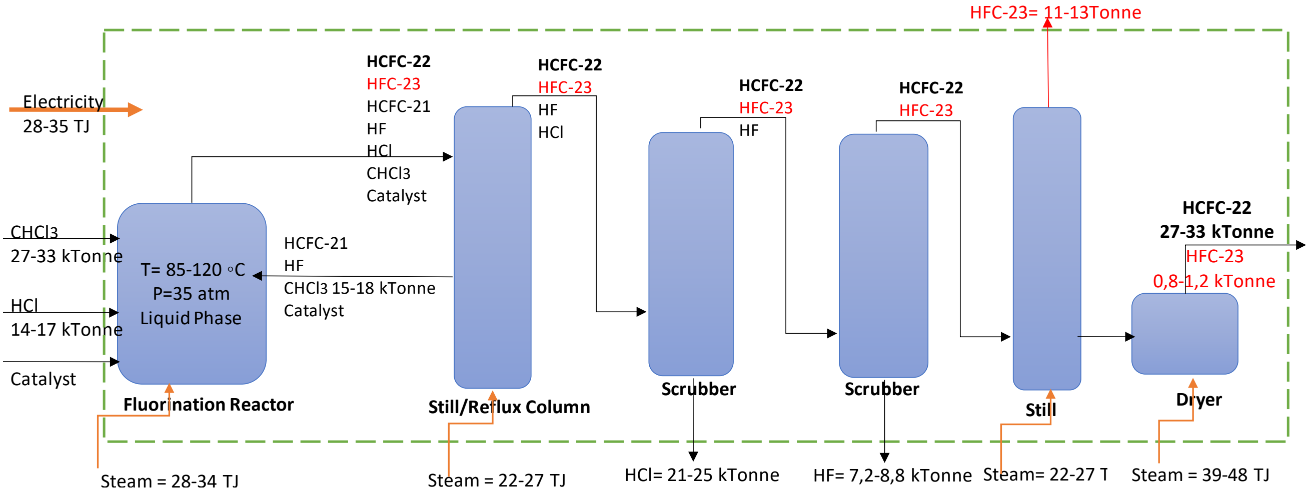


Figure 2 General Production Process of HCFC-22

Chloroform ($CHCl_3$) and hydrofluoric acid (HF) are fed as liquids to a continuous-flow reactor, without mechanical agitation, in a liquid phase mix of antimony catalyst ($SbCl_5$), chloroform, and other compounds that are partially fluorinated. Usually, HF is fed in excess to guarantee a maximum consumption of chloroform. The reaction occurs at high pressures (around 35 atm) and moderate temperatures (85-120°C). Although the reaction is exothermic, some heat can be added to increment the product vapor stream leaving the reactor (Christmas & Dimitratos, 2008). The reaction's main products are HCFC- 22 (Chlorodifluoromethane, $CHClF_2$) and hydrochloric acid (HCl).

$$CHCl_3 + 2HF \xrightarrow{SbCl_5} CHClF_2 + 2HCl \quad \text{(eq. 1)}$$

According to some studies about the kinetics of the reaction (Basile *et al*., 1989), the partially fluorinated intermediates in the reactor are produced from the reaction between the catalyst and the HF, with the subsequent exchange of the halogens Cl and F. (Eq.2).

$$SbCl_{5-x}F_x + HF \leftrightarrow SbCl_{4-x}F_{x+1} + HCl \quad \textit{where } 0 \le x < 4 \quad \text{(eq. 2)}$$

Then, these fluorinated compounds can also react with chloroform to produce some by-products, such as $CHCl_2F$ (HFC-21) and CHF_3 (HFC-23), as represented in equations 3 and 5; the reaction rates depend on the initial concentrations that are also influenced by the liquid-vapor phase equilibrium (Equations 1 and 5) (Mader, 1984).

$$SbCl_{4-x}F_{x+1} + CHCl_3 \leftrightarrow SbCl_{5-x}F_x + CHCl_2F \quad \text{(eq. 3)}$$

$$SbCl_{4-x}F_{x+1} + CHCl_2F \leftrightarrow SbCl_{5-x}F_x + CHClF_2 \quad \text{(eq. 4)}$$

$$SbCl_{4-x}F_{x+1} + CHClF_2 \leftrightarrow SbCl_{5-x}F_x + CHF_3 \quad \text{(eq. 5)}$$

Besides these by-products, unreacted chloroform and HF are part of the output stream. However, through process parameters, the selectivity towards specific products is managed to reduce undesirable by-products, such as the HFC-23, which is the main GHG source of this process. Parameters like temperature, the mix ratio between HF and antimony chlorofluoride, and the contact time between them determine the fluorination degree and the composition of the outputs stream (Mader, 1984).

Because of the composition of the output stream, several separation steps are needed. These include the condensation and return of small amounts of unreacted chloroform and other partially fluorinated substances to the reactor. The separation process is driven initially by the differences in the boiling point. Some separation operations, such as distillation, scrubbing, and drying, are used to withdraw the HF, HCl, and the water remaining in the product stream. The HFC-23 is sent to the monomers plant, where the concentration is kept at a maximum level. The excess of this gas is subsequently sent to the thermal converter for destruction.

2.1.3 Monomers Production

The main monomers produced by Chemours are TFE (Tetrafluoroethylene, C_2F_4) and HFP (Hexafluoropropylene, C_3F_6). TFE is a colourless gas and is the principal building-block for the production of fluoropolymers like PTFE. Although several methods have been developed for the synthesis of TFE, the pyrolysis of HCFC-22 is the most commonly used at the commercial level (Ebnesajjad, 2015). HFP is also a colourless gas and an important monomer, used mainly to produce copolymers or make adjustments to the homopolymer's physical properties (Drobny, 2009). Similarly, HFP can be produced by different chemical routes. One of them is by pyrolysis of TFE and trifluoromethane (HFC-23). The next diagram represents an overview of the production process of monomers TFE and HFP, including the main feedstocks amount, energy inputs, and GHG emissions. The black arrows represent main raw materials and products; red arrows are GHG flows, and orange arrows energy inputs.

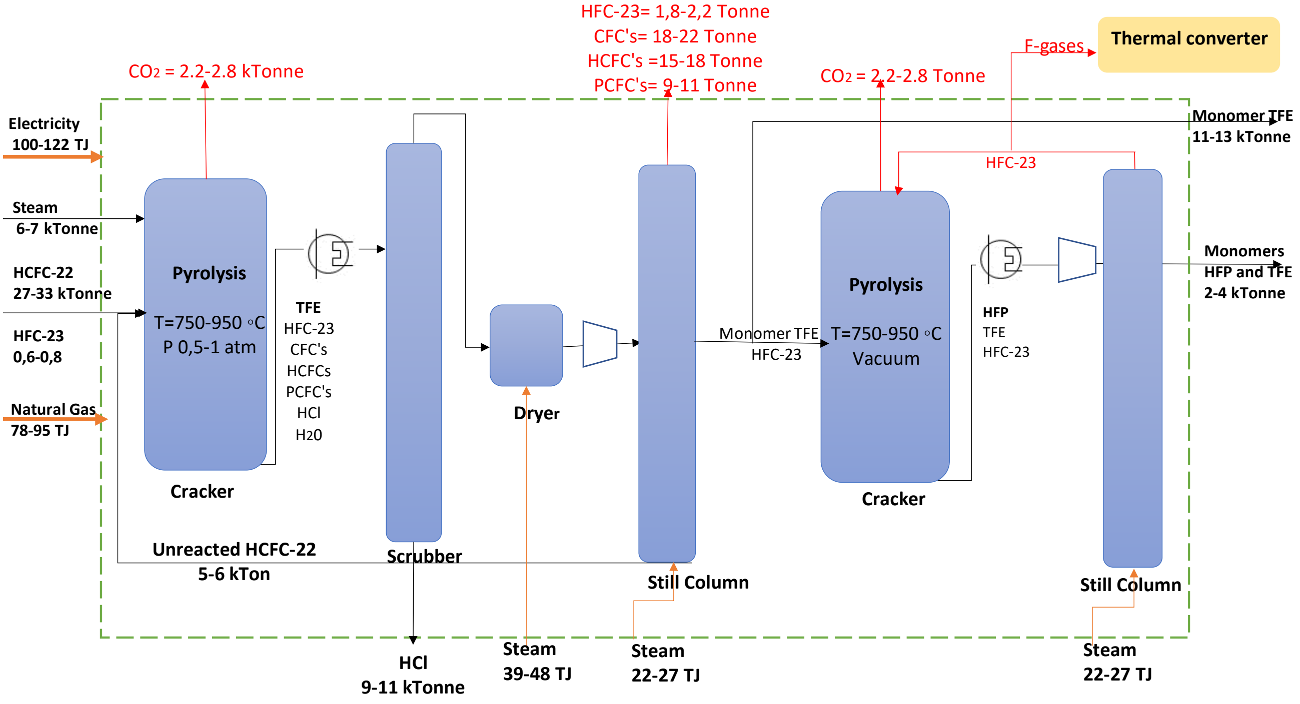


Figure 3 General Production Process of Monomers

TFE (Tetrafluoroethylene)

The pyrolysis of HCFC-22 ($CHClF_2$) is a gas phase process that takes place at high temperatures (around 750-950 °C) and atmospheric or sub-atmospheric pressures (0.5-1.2 atm), in a flow reactor, at very short contact times (2-3 sec.) (Drobny, 2009). Because of HFC-22 pyrolysis's endothermic features, the reaction requires heat supply (Ebnesajjad, 2015). Equation 6 is the pyrolysis's general reaction to produce TFE in which HCl is produced as a by-product. A decrease in the partial pressure of HCFC-22, adding an inert gas or water vapor as a diluent, leads to higher TFE production rates.[16] (Ebnesajjad, 2015). Different by-products are obtained from the pyrolysis, such as HCl and halogenated compounds like HFP (C_3F_6), perfluorocyclobutane, and perfluoroisobutylene (C_4F_8). Process condition adjustments can modify the output composition.

$$2CHClF_2 \leftrightarrow CF_2\ \ CF_2\ + 2HCl \quad \text{(eq. 6)}$$

The output gas stream, composed mainly of TFE, HFP, by-products, and also unreacted HCFC-22, is then cooled and passed through different separation steps to increase the monomers' purity. Separation steps include removing HCl and HF by scrubbing and washing, using water, and basic solutions. Further, a drying process is applied, using a drying agent like calcium chloride and sulphuric acid (Drobny, 2009). The gas stream is then compressed and distilled to recover the unreacted HCFC-22 (Ebnesajjad, 2015).

Strict safety measures are required for the handling of TFE, considering its instability and high flammability. TFE polymerizes spontaneously at ambient temperature, and in contact with air, it produces explosive peroxides. Also, even when air is removed, TFE contact with a hot metal surface or a spark from static electricity can generate explosions; an inhibitor, such as terpene, can help avoid spontaneous reaction (Ferrero and Shenton, 2017). Because of that, Chemours uses dichloromethane (DCM) as a coolant during the production of monomers to maintain a very low temperature (around -35°C).

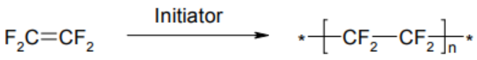
HFP (Hexafluoropropylene)

HFP can be produced through the same pyrolysis reaction of HCFC-22 to produce TFE or through pyrolysis of TFE and HFC-23. This last method takes place at temperatures below 900 °C and longer residence time. Due to the endothermic features of the pyrolysis of HFC-23 and the exothermic dimerization of TFE, a heat balance is achieved through temperature controls to maintain safe reaction conditions (Ebnesajjad, 2015). The output gas stream passes through some separation steps like distillation, and then, the unreacted TFE and HFC-23 are recycled. In the case of Chemours, a closed-loop system of HFC-23 is operating in the monomers plant. HFP is very stable, so it does not autopolymerize and can be stored in a liquid phase without using an inhibitor (Moore, 2006).

2.1.4 Polymers and elastomers production

PTFE (Polytetrafluoroethylene) Production

PTFE, under the brand Teflon™, is a homopolymer of TFE. Homopolymerization takes place in the gaseous state, at moderate temperatures (60-90°C) and elevated pressures (15-35 atm), via free radical polymerization. This exothermic reaction occurs in an aqueous medium using initiators that are soluble in water (Drobny, 2009).



(eq. 7)

---

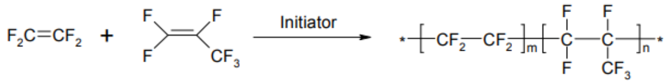
[16] Le Chatelier's principle anticipates that changes in concentration, volume, temperature or partial pressure, lead to a shift of the equilibrium to compensate the change. (Ebnesajjad, 2015)

Chemours has three batch production lines for dispersion and fine powder PTFE and granular PTFE. In the dispersion and fine powder production lines, an aqueous dispersion is formed, with a fluorinated surfactant and moderate agitation of the mixture. The agitation is relevant to remove heat from the reactor. Depending on the finishing steps, the final product can be the dispersion or the fine powder (Ebnesajjad, 2015). In the first case, the concentration of solids is increased by evaporation or thermal concentration. In the second case, a mechanic separation process removes the fine powder from the dispersion, which is later dried.

In the granular production line, a suspension process takes place, with an active agitation system of the mixture and using small amounts or even no surfactant. The reactors need to have an external heating/cooling system to heat the reactor at the beginning of the reaction and remove the heat generated by the exothermic reaction when the polymerization is progressing (Ebnesajjad, 2015). In this process, the formed product is water with unregular polymer particles. The two main finishing operations are the removal of water and the size reduction of particles. Depending on the final resin (pellets, divided resins), grinding and agglomeration can be used. These operations may require the use of fluorinated surfactants.

FEP (Fluorinated Ethylene Propylene) Production

FEP, also branded as Teflon™, is a copolymer of TFE and HFP, which has similar properties to PTFE. The conditions for the copolymerization reaction are comparable to the conditions described for the dispersion production of PTFE. The mix ratio between the comonomers is determinant to control the polymer's composition and its molecular weight. Usually, the FEP composition requires only 5mol% of HFP (Teng, 2012).



(eq. 8)

FKM Elastomers (Chlorotrifluoroethylenevinylidene fluoride) Production

FKM, under the brand Viton™, is a fluorocarbon elastomer produced by the free radical emulsion copolymerization of the monomers vinylidene fluoride (VDF), TEF, and HFP. VDF is a flammable gas at room temperature and can be explosive in contact with air. Fluoroelastomers are copolymers of different monomers; thus, the monomers reactivity ratios determine the polymer's final composition. The polymerization reaction is exothermic and takes place at pressures around 120 atm, using an initiator (Moore, 2006). Chain transfer agents, such as methanol, are used to regulate the molecular weight of the polymer. Typically, suspension polymerization is used for VDF/HFP/TEF polymerization. The product of the reaction is a latex that is coagulated by adding salt or acid. Subsequently, the coagulated latex goes to the filtration, washing, and drying process (Drobny, 2009). Fluorinated surfactants are also used in this process.

The diagrams below represent the three main polymerization processes, including the main energy inputs and the main feedstock amounts. In this step of the process, there are no direct GHG emissions.

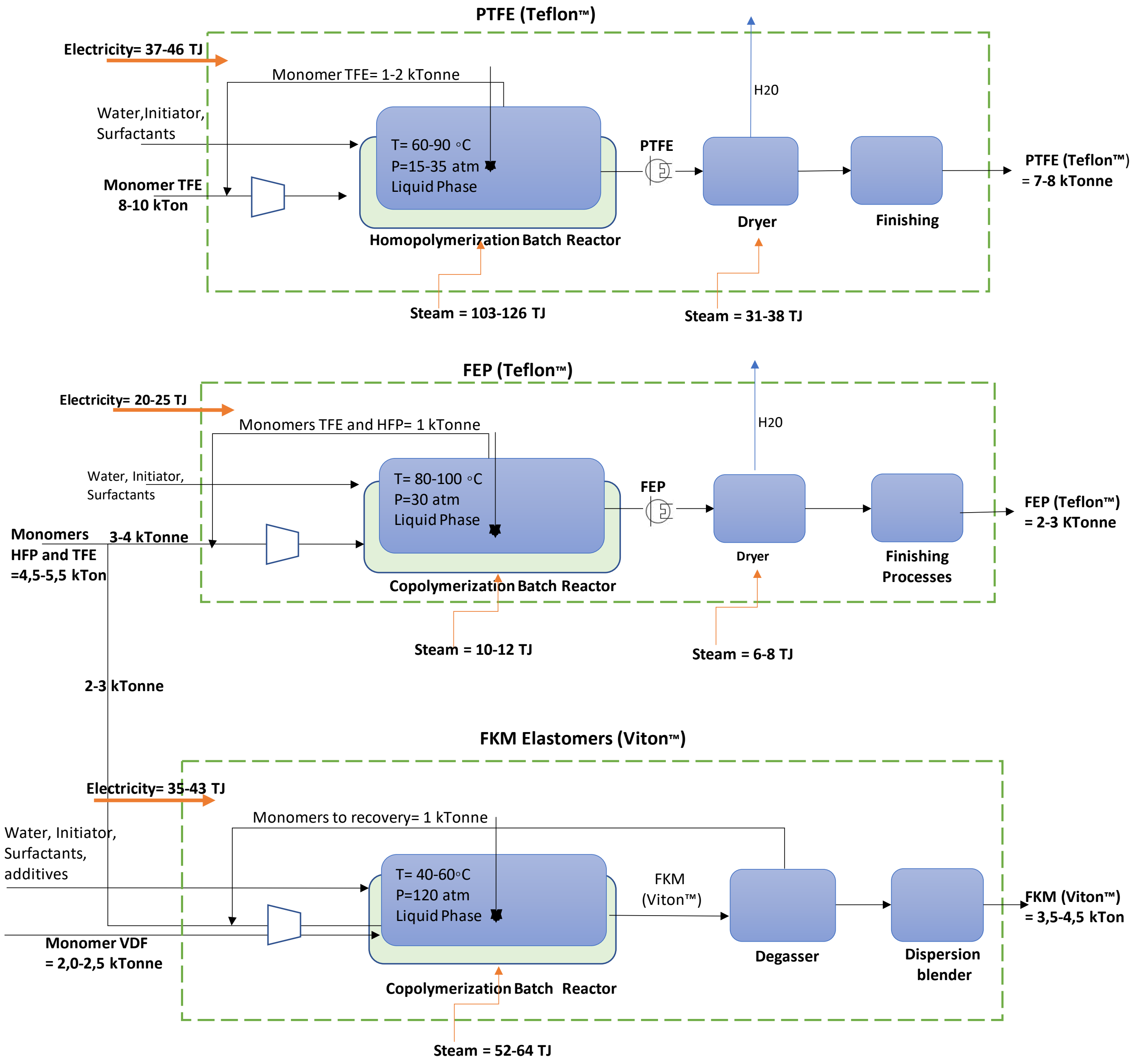


Figure 4 General Production Process of Polymers and Elastomers

2.1.5 Main Material Flows

Material flow estimations are presented in the table below, based on some studies about the kinetics of fluorination of chloroform (Santacesarea et al., 1989), the industrial production of HFC-23 as a by-product during HCFC-22 production (Irving and Branscombe, 2000), and the pyrolysis of HCFC-22 (Chinoy and Sunavala, 1987), in addition to the information shared by Chemours and public information about imports and trading (CBS, 2020).

Table 7 Chemours main mass flows
(CBS,2020; EMJV, 2018; own calculations and estimations)

Section Plant	Main Input	Amount (Kt/year)	Main Output (in bold letters)	Amount (Kt/year)
HCFC- 22 Production Plant- Fluorination Reactor	HF	14-17	**HCFC-22**	**27-33**
	Chloroform	42-51	HFC-23	0.8-1.2
			HF	7.2-8.8
			HCl	21-25
	Total	*56-68*		*56-68*
Monomers Production Plant	HCFC-22	27-33	**Monomers (TFE and HFP)**	**13-17**
			HCFC-22 (to recycle)	5-6
			HCl	9-10
	Total	27-33		27-33
PTFE Production Plant	Monomers (TFE)	8-10	**PTFE**	**7-8**
			Unreacted monomers (to recycle)	1-2
	Total	8-10		8-10
FEP Production Plant	Monomers (TFE+HFP)	3-4	**FEP**	**2-3**
			Unreacted monomers (to recycle)	1
	Total	3-4		3-4
Elastomers Production Plant	Monomers (TFE+HFP)	2-3	**Elastomer Viton™**	**3.5-4.5**
	VFD	2.0-2.5	Unreacted monomers (to recycle)	0.5-1.0
	Total	4.0-5.5		4.0-5.5
Whole Plant	**Total Final Polymers and Elastomers (PTFE, FEP Viton)**			**12.5-15.5**

2.1.6 Main Energy Consumption

Based on the Elektronisch Milieujaarverslag (2018) document and the energy overview 2018, shared directly by Chemours, the main energy consumption discriminated by energy carrier in each step of the process was estimated and is described in the next table.

Table 8 Main Energy Consumption (EMJV, 2018 and Chemours energy overview, 2018)

Section Plant	Electricity (TJ)	Natural Gas (TJ)	Steam (TJ)	Total (TJ)
Input				
Steam imports (HVC and DuPont residual heat)			-328	-328
Total Input			**-328**	**-328**
End-use				
Steam Production	-47[17]	122	-106	-31
HCFC- 22 Production Plant	*32*	*0*	*121*	153
Monomers Production Plant	111	87	91	289
PTFE (Teflon™) Production Plant	42	0	148	190
FEP (Teflon™)Production Plant	23		17	40
FKM elastomers (Viton) Production Plant	39		56	95
Thermal Converter		24		24
Others (CTW circulation pump)	44			44
Net end use/ consumption	**245**	**294**	**328**	**804**
Total balance	245	294	0	538

The greatest demand for electricity comes from two refrigeration machines used to keep a low temperature (-45°C) to guarantee the proper safety conditions to produce and handle TFE. TFE polymerizes spontaneously at ambient temperature due to its instability and high flammability and can generate explosions; thus, it requires strict safety measures (Ferrero and Shenton, 2017). Electricity to operate these refrigeration machines represents around 20% of the total electricity consumption.

The back-up steam boilers are the largest natural gas users, with around 52% of the total consumption. The other main consumption comes from two furnaces used for the pyrolysis process in monomers' production and the thermal oxidizer used in the F-gas thermal treatment.

PTFE plant uses almost 30% of the steam, including dryers, reactors, and heat exchangers; then, the second largest users are the distillation towers for the purification of HCFC-22 and monomers, being around 25%. The third-largest use is from the HCFC-22 plant, including heat exchangers, dryers, and the reactor. Then, there is the consumption of the other plants (monomers and the other polymers).

According to literature, the average energy consumption in the monomer TFE production process is 43 GJ/tonne (Hintzer and Schwertfeger, 2014). Using these numbers and based on an estimation of monomers production between 13 and 17 kt, it could represent an energy consumption around 560-731 TJ/year. Based on the table above, Chemour's energy consumption for monomers production is around 442 TJ/year (HCFC- 22 and monomers process), which means 26-34 GJ/tonne.

---

[17] Electricity produced by the CHP in 2018.

2.2 DuPont

The DuPont process has three main steps: catalytic oxidation of methanol to produce formaldehyde (Formox process), formaldehyde polymerization to POM, and compounding (melting the polymer and mixing with additives to produce granules). Compounding is based mainly on electricity for the extruder and the mixing motor. There are also some heating and cooling steps in this part of the process.The main processes that take place at DuPont are illustrated in the diagram below:

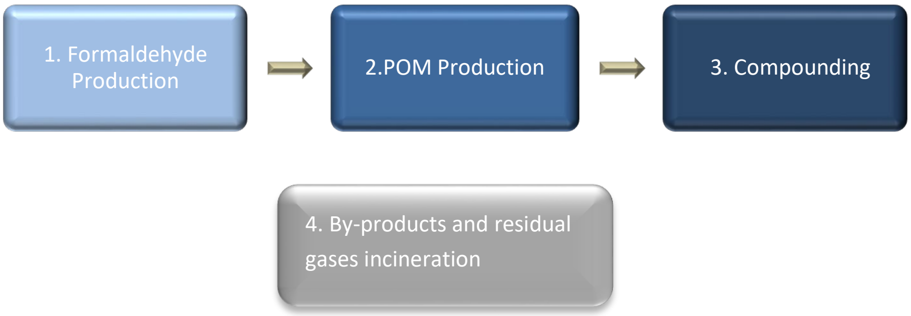


Figure 5 DuPont Main Processes

2.2.1 Formaldehyde Production

Formaldehyde is produced at the industrial level from methanol through two main routes: the air-deficient process or silver contact and the Formox process, which implies an excess of air. DuPont Dordrecht uses the Formox process, which is the partial oxidation of the vapor phase methanol over a metal oxide catalyst. This reaction is highly exothermic, and the heat generated drives the dehydrogenation of methanol (Bahmanpour et al., 2014). DuPont uses the reaction heat to produce steam.

$$CH_3OH+\frac{1}{2}O_2 \rightarrow CH_2O+H_2O \quad \Delta\hat{H}_r^o=\text{-}159 \text{ kJ/mol.}$$

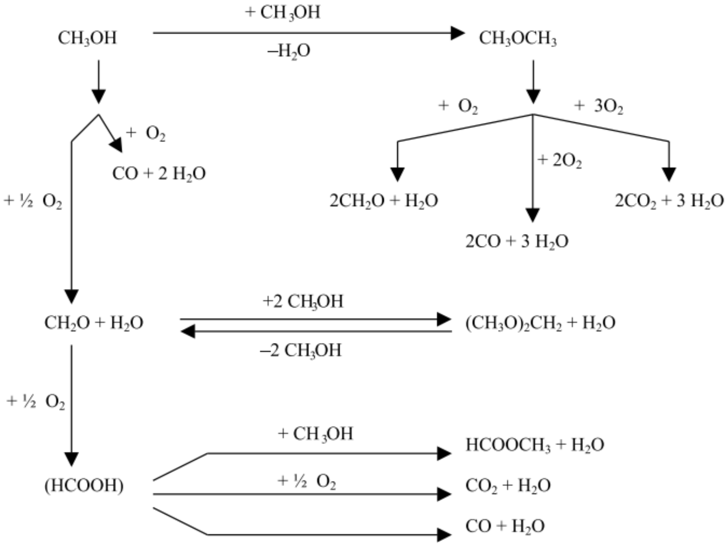
(eq. 11)

Fresh and recycled methanol is combined with an airstream, and the mixture is vaporized at 115°C. Air is used in excess to keep the methanol/air ratio below the explosion limits (Wells, 2020). Then, the gas is mixed with steam, reaching the reaction temperature. The mixture passes through a catalyst bed reactor, where the oxidation of methanol occurs, and formaldehyde is produced (Elliott et al., 1996). Iron/molybdenum or vanadium oxide are the main catalysts used in this process. Methanol is practically totally converted at temperatures around 270 °C – 400 °C and atmospheric pressures. However, oxidation of formaldehyde to carbon monoxide increases at temperatures above 470 °C. Typically, the conversion of methanol is between 97% and 99%, and the total yield is around 88-91% (Bahmanpour et al., 2014).

$$CH_2O+\frac{1}{2}O_2 \leftrightarrow CO+H_2O \quad \Delta\hat{H}_r^o=\text{-}215 \text{ kJ/mol.}$$

(eq. 12)

According to some researches, the reaction could take two different routes, depending on the surface heterogeneity of the molybdenum oxide catalyst. Methanol suffers dehydration and produces dimethyl-ether (DME) on the hexagonal surface; simultaneously, methanol partially oxidizes to produce formaldehyde, which is the main product. Other studies suggested that by using iron oxide as a catalyst, complete oxidation of methanol is achieved, and high amounts of CO_2 are produced (Bahmanpour et al., 2014). According to Ivanov and Dimitrov (2008)., the main source of CO_2 emissions is DME oxidation. The conversion to CO_2 can be approximately 0.2-0.4%. In the following equation scheme, there is a representation of the different oxidation reactions that occur and the main products and by-products.



(eq. 13) Scheme of reactions for the oxidation and dehydration of methanol (Ivanov & Dimitrov, 2009)

The reactor's product stream at around 280 °C is immediately cooled down to about 110 °C in a heat exchanger, and then it is fed to an absorption column (Elliott et al., 1996). The amount of water ad at the top of the column is a control parameter of the formaldehyde concentration (Bahmanpour et al., 2014). An aqueous solution of approximately 55% formaldehyde, known as formalin, is obtained from the absorber's bottom. The gases from the top of the absorber are scrubbed with water and later burned (Wells, 2020). The residual process gases from formaldehyde production require a purification process, which is also exothermic and produces heat (Mursics et al., 2020).

For this purpose, DuPont Dordrecht has an emission control system (ECS) unit. There, the off-gas from the absorber, containing by-products from formaldehyde production, are catalytically oxidized. These by-products are mainly CO, N_2, O_2, methanol, and DME, which are converted to CO_2 in the ECS (Gammelgaard,2018). The ECS unit also generates heat to produce steam (DuPont direct communication, 2020). Steam could also be used to produce electricity.

Over time, important process optimization and improvements have taken place to increase the production yield and the steam production and to reduce the CO selectivity and energy consumption. Pressurization at 0.3-0.5 bar, the prevaporization of methanol, catalyst innovation, and turbocharger use to reduce power consumption are part of the process improvements (Wells, 2020).

According to literature, the amount of methanol required to produce 1 tonne of formaldehyde at the industrial level can be around 1.16 tonnes (Wells, 2020); and the average steam amount produced is about 750-800 kg/tonne, which is driven by the methanol concentration in the inlet stream to the reactor (Andersson et al. 2016).

The next schematic diagram illustrates the main Formox process steps, including the ECS unit.

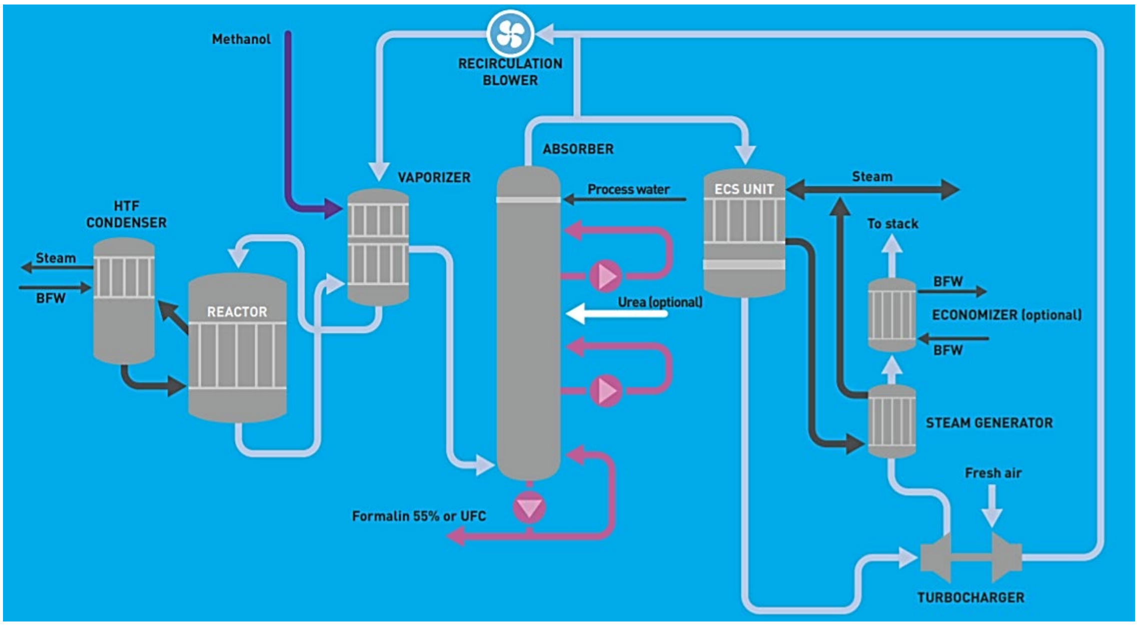


Figure 6 Formox Plant (Jhonson Matthey n.d)

During the formaldehyde industrial process, the main sources of emissions are the ECS unit and some fugitive emissions from tanks and pipelines (Elliott et al., 1996).

DuPont has an up to date energy efficiency plan and a function called the “energy champion” to look for future developments regarding energy consumption reduction and optimization. The role focuses on the analysis of the consumption of energy and flows of residual heat. Heat recovery is an essential aspect of the energy strategy due to the high amounts of heat generated in formaldehyde production and the incineration of by-products and residual process gases. The formaldehyde plant produces steam, which is later used in the Delrin® chemical plant. Besides, the ECS unit generates heat to produce steam as well.
As illustrated in figure 15, a turbocharger uses the ECS gas output energy to supply air to the formaldehyde plant, using around two-third of the energy required using an electric blower (Svensson, 2012).

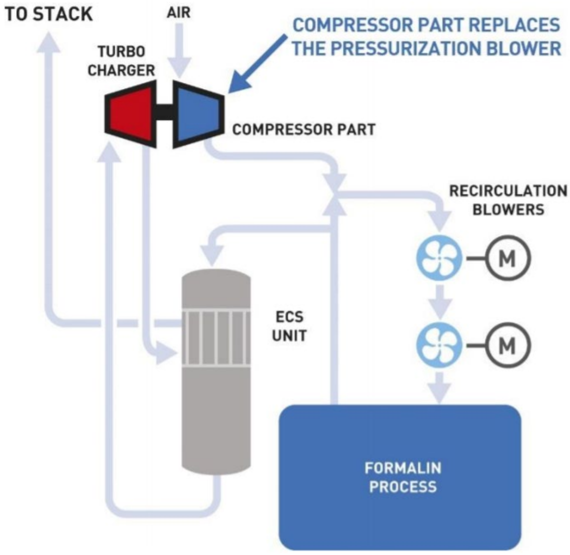


Figure 7 The turbocharger concept (Gammelgaard, 2018)

Consequently, and because of the energy integration and the implementation of different projects, like insulation to avoid heat loss, the formaldehyde factory's heat consumption is negative (DuPont, 2018). Moreover, during the incineration of waste gases from other processes, the heat released is used to produce steam, which is used in other parts of DuPont and Chemours processes. The total steam produced from Formox process and the incineration furnace is around 650-700 TJ (DuPont information and own calculations).

2.2.2 Main Material Flows

The table below shows some general estimations of inputs and outputs for an annual formaldehyde production of 100 kt/year. This analysis elucidates, to some extent, the generation of CO_2 emissions in this part of the process. According to the literature review, CO_2 is produced mainly due to other secondary oxidation reactions, such as dimethyl ether (DME) oxidation.

Table 9 Mass Estimations of Formaldehyde Production-Oxidation Reactor

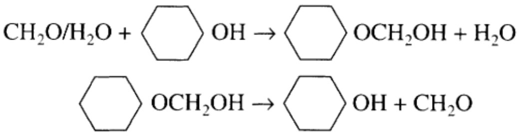
INPUT		OUTPUT	
	kt		**kt**
Methanol	116	Formaldehyde	100
N_2	90	H_20	101
O_2	298	Unreacted methanol	2
Recycled N_2	1,191	CO	5
Recycled O_2	120	N	1,489
Recycled H_20	34	O_2	150
		HCOOH	2
		CO_2	1
Total	1,849		1,849

Table 10 Mass Estimations of Formaldehyde Production-Absorber

INPUT		OUTPUT		
	kt		**kt**	
Formaldehyde HCHO	100	Formaldehyde	100	Bottom
H_20	101	H_20	152	
Unreacted methanol	2	CH_3OH	2	
HCOOH	2	HCOOH	2	
CO	5	CO	5	Top
N	1,489	N	1,489	
O_2	150	O_2	150	
CO_2	1	CO_2	1	
Solvent (Water)	103	H_20	52	
Total	1,951		1,951	

2.2.3 POM Production and Finishing Process

Formaldehyde produced from the formox process described above is the monomer to produce polyoxymethylene (POM). The general production process of POM can be divided into four different steps: monomer purification, polymerization, end-capping, and finishing. The aqueous formaldehyde solution passes through a reactive extraction process, using alcohol to dehydrate the hemiformal/water mixture and form hemiformal (Masamoto et al., 1994). Then, the hemiformal is heated to release the formaldehyde. The following equations illustrate these separation processes:



(eq. 14 and 15)

Next, the formaldehyde gas monomer is polymerized by anionic catalysis; a deactivator, such as an organic or inorganic base, is added to finish the polymerization and suppress other reactions (Lüftl & Chandran, 2014). The resulting polymer (POM) is stabilized using acetic anhydride as a chain transfer or end-capping additive. The stable POM goes to the extrusion plant to produce the Delrin® final product grains.

All the by-products and residual gases from the POM production are sent to incineration in the furnace, where the heat released is used to produce steam.

2.2.4 Main Energy Consumption

Based on Elektronisch Milieujaarverslag (2018) document, literature review, and general information shared by DuPont, some calculations and assumptions were made to determine DuPont's energy consumption. It was then discriminated by energy carrier in each step of the process and described in table 11. The highest energy demand for DuPont is related to steam consumption. This steam is mainly used in the concentrator, the pyrolysis, stabilization, and dehydration processes (polyoxymethylene production), and also in the drying operations (finishing and compounding processes) (DuPont direct communication, 2020). Natural gas is used to operate the furnaces and the back-up boiler. The Delrin® compounding factory uses energy mainly in the form of electricity to run the extruders.

According to the literature review, DuPont information and estimations, steam production from the furnace heat recovery could be around 260-320TJ. This steam is used to supply the process's energy requirements, reducing DuPont's net energy consumption.

Table 11 Main Energy Consumption (Estimations from Elektronisch Milieujaarverslag, 2018 and Dupont direct communication)

Section Plant	Process/Technologies	Electricity (TJ)	Natural Gas (TJ)	Steam (TJ)	Biogas (TJ)	Total (TJ)
Input						
Steam imports (HVC)				-708		-708
Total Input				**-708**		**-708**
End-use						
Steam Production (backup boiler)			350	-280		70
Process residual heat[18]				-700		-700
Water treatment[19]					-31	-31
Formaldehyde Production	Methanol Evaporator Concentrator	67		510		577
POM Production	Dehydration of hemiformal Pyrolizer Stabilizer	51		600		651
Compounding	Centrifuge Dryer Extruder	135		390		525
Process by-products and residual gases incineration	Furnace		74		31	105
Others (cooling)		85				85
Net end use/consumption	**0**	**338**	**424**	**521**[20]	**0**	**1283**
Total balance		338	424	-188 (residual heat sent to Chemours)	0	574

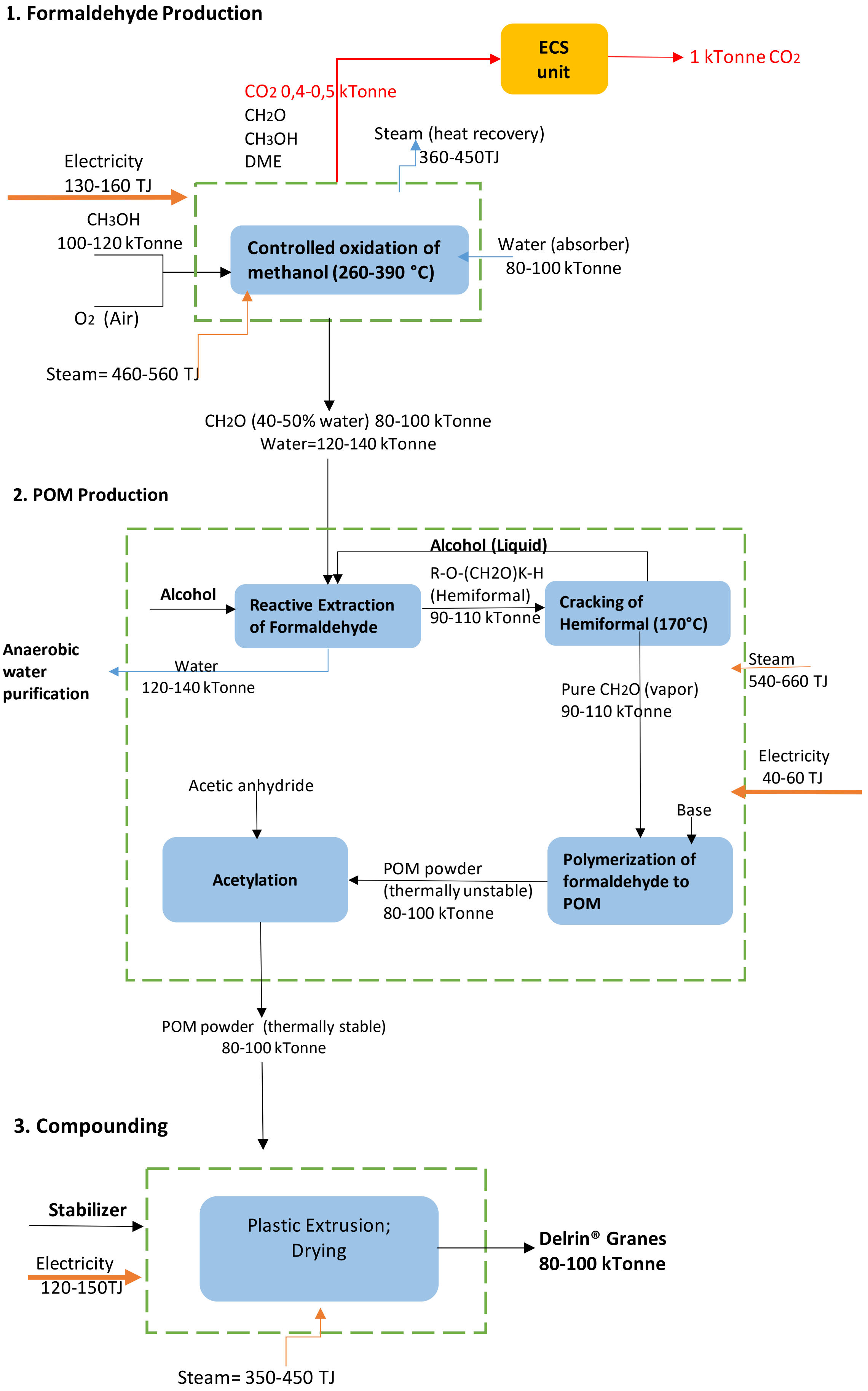
The next schematic diagrams represent DuPont processes, including the main flows of energy (orange arrows) and the main material flows (black arrows). The red color represents the main CO_2 emissions.

---

[18] The calculated steam production from residual heat includes heat recovery from formox process and from the incineration of by-products and residual gases.

[19] Biogas is produced in the water treatment throughout biological processes

[20] Net end use of steam corresponds to the total estimated consumption of steam minus the steam generated by DuPont in the steam boiler or through heat recovery.


1. Formaldehyde Production
ECS unit
1 kTonne CO_2
CO_2 0,4-0,5 kTonne
CH_2O
CH_3OH
DME
Steam (heat recovery)
360-450TJ
Electricity
130-160 TJ
CH_3OH
100-120 kTonne
Controlled oxidation of methanol (260-390 °C)
Water (absorber)
80-100 kTonne
O_2 (Air)
Steam= 460-560 TJ
CH_2O (40-50% water) 80-100 kTonne
Water=120-140 kTonne
2. POM Production
Alcohol (Liquid)
Alcohol
Reactive Extraction of Formaldehyde
R-O-(CH2O)K-H
(Hemiformal)
90-110 kTonne
Cracking of Hemiformal (170°C)
Anaerobic water purification
Water
120-140 kTonne
Steam
540-660 TJ
Pure CH_2O (vapor)
90-110 kTonne
Electricity
40-60 TJ
Acetic anhydride
Base
Acetylation
POM powder
(thermally unstable)
80-100 kTonne
Polymerization of formaldehyde to POM
POM powder (thermally stable)
80-100 kTonne
3. Compounding
Stabilizer
Electricity
120-150TJ
Plastic Extrusion; Drying
Delrin® Granes
80-100 kTonne
Steam= 350-450 TJ

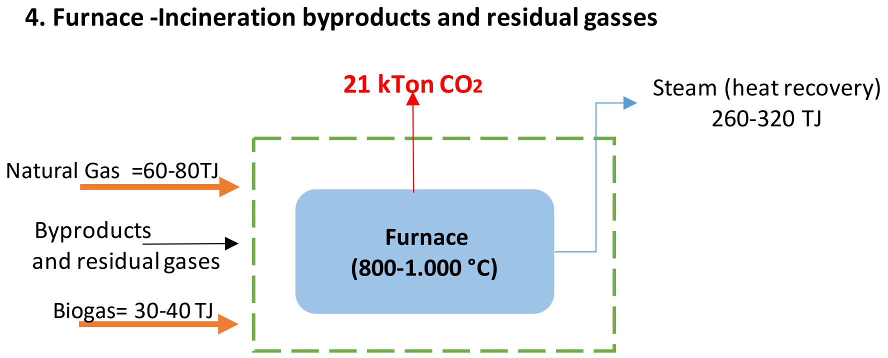


Figure 8 Scheme of DuPont processes and main flows of energy and materials

Regarding CO_2 emissions, besides the emissions from the production reaction of formaldehyde, there are other sources. 21 kt/year are emitted in the incineration process. This amount includes 4 kt from natural gas combustion, 3 kt from biogas combustion, and 14 kt/year from the residual gases and by-products combustion. Additionally, natural gas combustion, mainly for steam production generates approximately 17 kts/year (Estimations from NEA, 2018, and EMJV, 2018). This will be further developed in chapter 4.

During DuPont's processes, there are other emissions than GHG; however, considering the MIDDEN project's scope, the analysis is only focused on GHG emissions.

2.3 Dow

Extrusion is one of the most used techniques to process plastics, and it is also used as a basis for other processing techniques. However, some applications require to modify the polymers, using peroxides, halogens, or grafting techniques, to improve some properties such as thermal or mechanical stability, chemical resistance, and compatibility. Reactive extrusion is used to modify and process a polymer simultaneously (Isac, 2001).

Furthermore, it allows the production of polymers with functional groups, like copolymers with carboxyl groups. The direct polymerization process cannot produce these copolymers. Grafting is the reaction between a molten polymer with a monomer or a mix of monomers to make grafts to the polymer backbone. It means that one polymer grows as branches on another polymer (Rudin and Choi, 2013). The reactivity and molar ratio of the monomer and polymer, the amount of initiator, and the process temperature are some of the parameters that determine the graft chain length. The extruder acts as a pressure vessel, with temperature and residence time control, and venting of unreacted monomer and by-products.

Polyethylene can be grafted with acrylic acid, using a crosslinking peroxide such as DCP (dicumyl peroxide) in an extruder reactor at 180 °C. Also, grafting of maleic anhydride with polyethylene is another example of reactive extrusion, using free-radical initiators, like peroxides. In the Dordrecht plant, Dow uses acrylic acid in one production line to produce resins under the name of Surlyn™, and maleic anhydride in the other one to produce resins under the brands Bynel™ and Fusabond™. The amount of maleic anhydride is around 1-5% of the total polymer, and the amount of DCP can be about 2-6% of the maleic anhydride amount. In the next diagram, there is a schematic representation of Dow processes in Dordrecht, including the main flows of energy and materials:

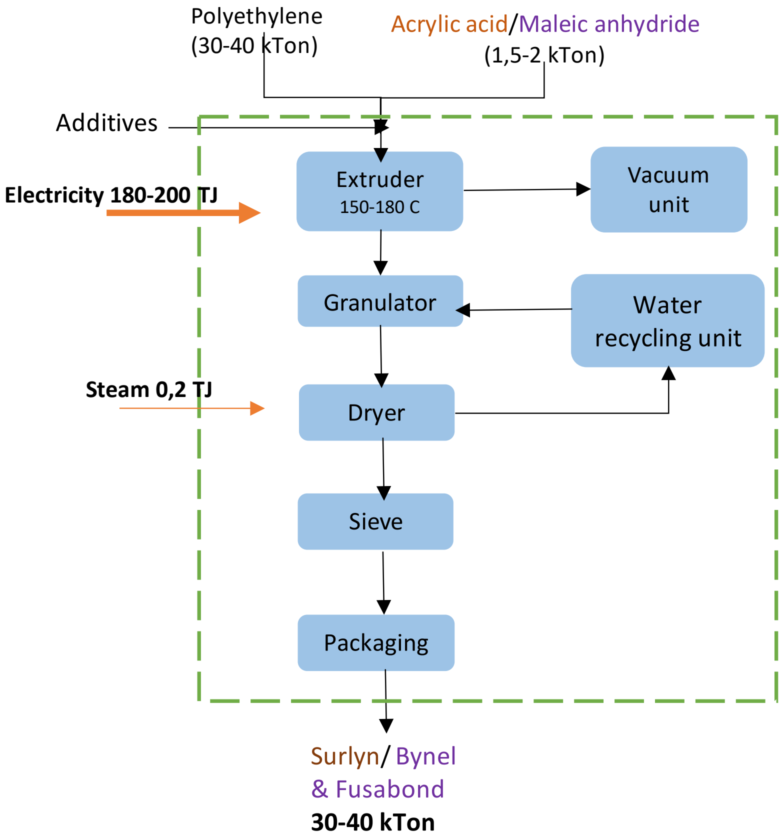


Figure 9 Scheme of Dow processes and main flows of energy and materials (Shared directly by Dow)

2.3.1 Main Energy Consumption

Dow operation at Dordrecht is relatively small, and the main energy demand is electricity to operate the extruders for the two production lines and a small amount of steam, provided by Chemours, for drying operations. In table 6 above (presented on page 15), there is a summary of Dow's main energy consumption in the Dordrecht site.

3 Dordrecht Chemical Cluster products and applications

This section contains information about the products manufactured in Dordrecht by each company, their main raw materials, applications, market insights, and the main sustainability trends.

3.1 Chemours: Fluoroproducts Market Overview

Fluoroproducts are produced from mined fluorite and include fluorocarbons, fluoropolymers, and surfactants. The development of the automotive and electronics industry and the accelerated industrialization have promoted the growth of the fluoroproducts market (Ahuja and Singh, 2018). One of the main segments of fluorocarbons is the refrigerants market, in which the largest amount corresponds to HCFC-22. China leads the production globally, with 418 kt/year produced in 2016, followed by The United States, with a reported amount of 135 kt/year in 2011. In 2015, the European Union had a production of around 120 kt/year, with HCFC-22 being the main gas produced (Abdelaziz, et al., 2020). Because this substance is part of the ozone-depleting substances (ODS) regulated by the Montreal Protocol, its consumption is decreasing, and it is in a phase-out process. Europe prohibited the use of HCFC-22 for emissive applications (refrigerants). However, its use as a feedstock (mainly to produce fluoropolymers) is not restricted.

Furthermore, the emissions of HFC-23, as a by-product of the HCFC-22 production process, are strongly regulated (Abdelaziz et al., 2020). In the case of The Netherlands, HCFC-22 production is only allowed as a feedstock.

3.1.2 Fluoropolymers

In the 1930s, during some investigations about fluorinated refrigerants, by accident a scientist from DuPont in the USA, discovered the polymerization of TFE into PTFE. PTFE's outstanding properties were later recognized to meet the needs of having a polymer able to resist highly corrosive conditions in the fabrication of the first atomic bomb during the second world war. In 1946, DuPont de Nemours started PTFE commercialization under the brand Teflon™ (now owned by Chemours) (Hintzer & Schwertfeger, 2014).

Fluoropolymers are polymers with only carbon and fluorine in the polymer backbone. The strength of the carbon-carbon bond and the high stability of the carbon-fluorine bond explain these polymers' unique properties. The replacement of hydrogen by fluorine in a polymer increases the service temperatures, reduces flammability, and gives low surface energy, which implies nonstick properties, a low coefficient of friction, and a low solubility in hydrocarbons. Furthermore, it offers high electrical and optical properties (Smith *et al*. 2014). The next table summarizes the main applications and properties of fluoropolymers.

Table 12 Fluoropolymers: Key Properties and Main Applications (Ebnesajjad, 2014)

Industry/Application area	Key Properties	Typical uses
Chemical processing	Chemical resistance Good mechanical properties Thermal stability Cryogenic properties	Gaskets, vessel liners, valves, and pipelines
Electrical and communication	Low dielectric constant High volume/surface resistivity High dielectric breakdown voltage Flame resistance, thermal stability Low refractive indices	Wire and cable insulation, connectors, optical fibers
Automotive and office equipment	Low coefficient of friction Good mechanical properties Cryogenic properties Chemical resistance	Seals and rings in automotive power steering, transmission, and air-conditioning. Copier rollers. . Fuel management systems
Houseware	Thermal stability Low surface energy Chemical resistance	Cookware coatings and food processing equipment covering
Medical	Low surface energy Stability Excellent mechanical properties Chemical resistance	Cardiovascular grafts, heart patches, ligament replacement, intravenous infusion membranes
Architectural fabrics/films	Excellent weatherability Flame resistance Low surface energy	Coated fabric and films for building and roofs, front/backside films for solar applications

3.1.3 Fluoropolymers Main Raw Materials

Fluorspar

Fluorspar is one of the main feedstocks for hydrofluoric acid (HF) production, a main input at Chemours Dordrecht. It is a natural mineral, which is mainly found in mines located in China, Mexico, Mongolia, South Africa, and Namibia. Although Europe still has some fluorspar mines, the viable ones have reduced over time (Eurofluor, 2019). Contrary, China has the third position of fluorspar deposits globally and is one of the main exporters, giving this country a critical competitive advantage in the fluoroproducts market (Po, 2017). Fluorspar price, but mostly its availability, drive the prices of fluoropolymers.

Fluorspar has different grades, but the acid grade is the most widely used, i.e., hydrofluoric acid (HF). This grade is produced by the reaction of fluorspar and sulphuric acid. Because of the highly corrosive potential of hydrofluoric acid, there are strong international regulations to meet safety criteria during production, handling, storage, and use of this product, especially related to the materials used for transportation and packaging. Hydrofluoric acid (HF) is transported by rail from Germany. HF prices are around €1,700/tonne (CBS, 2020).

Chloroform

Chloroform, or trichloromethane, is a volatile solvent. Its main use is to produce HCFC-22, which is used to produce mainly fluoropolymers and also refrigerants. As reported by ICIS outlook in 2002, Europe's demand for this product has been reduced by the restriction over HCFC-22 production in the refrigerants industry due to the Montreal Protocol. Nevertheless, the growth of the fluoropolymers market has compensated for that gap in demand. In Europe's case, regulations limit chloroform production only as raw material, or special

solvent, for industrial processes (Nouryon, 2020). In The Netherlands, the company Nouryon produces chloroform in Rotterdam. Chloroform is produced from the chlorination at high temperatures of methane or methyl chloride. Its price is around €800/tonne (CBS, 2020).
Appendix 1 contains a schematic representation of the fluoropolymers value chain.

3.1.4 Fluoropolymers market

The global fluoropolymer demand from diverse markets and applications has been increasing considerably during the last years; end uses are the main drivers of that increase. On the one hand, the expansion of current applications, and on the other hand, the development of new markets. Due to the high mechanical properties, chemical resistance, and high electrical insulation offered by fluoropolymers, the use of these polymers is increasing. In some cases, the use is to replace other petrochemical-based polymers, especially in applications that demand high-quality specifications (Po, 2017). One of the main reasons for the growing use is the demand from the transport industry. The increase in sales of passenger cars in emerging economies like China and India is determinant, and also the need for lower weight materials in this industry (Ebnesajjad, 2014). Apart from transport, fluoropolymers have many other and diverse applications, such as plumbing, wire and cable, lubricants, photovoltaic cells, textiles, and cookware. There is a summary of the main applications and sales in 2015 in the EU in the table below.

Table 13 Fluoropolymers sales in EU, 2015 (PlasticsEurope, 2018)

Key Sectors in the EU	Fluoropolymers Sales	
	tonnes	€ millions
Transport	18,500	300
Chemicals & Power	16,500	220
Cookware	3,500	60
Electronics	3,500	50
Food & Pharma	3,000	40
Textiles and architecture	3,000	40
Medical applications	1,500	20
Photovoltaic	500	5
Other	2,000	30
Total	52,000	765

According to Schmit et al. (2014), the global and European fluoropolymer consumptions were around 233 kt and 45 kt, respectively. Moreover, in 2015, the EU's fluoropolymer sales were approximately 52 kt (PlasticsEurope, 2018). The table below illustrates the EU's production amounts, imports, exports, and local sales.

Table 14 Volume and Revenues in EU, 2015 (PlasticsEurope, 2018)

	Volume (tonnes)	Sales (€ millions)
Produced in the EU	51,000	€ 840
Imports to the EU	21,500	€ 310
Exports from the EU	20,500	€ 380
Sold on the EU market	52,000	€ 765

Globally, the fluoropolymer market can also be segmented by product and region. In terms of product, this market has four main segments: PTFE, PVDF, FEP, and fluoroelastomers. PTFE is the largest segment with a share of more than 50%. The region producing the largest share of fluoropolymers is Asia-Pacific, considering the increasing demand from emerging economies. This growth has reduced production costs during the last years with new production plants in China (Trends market research, 2020). North America is the second region, followed by Europe. However, for consumption, the order is different. The highest demand is in North America, followed by the Asia Pacific and Europe (Ebnesajjad, 2014).

3.1.5 Fluoropolymers prices and competitors

Based on the yearly sales reported by PlasticsEurope in 2015, and as an average, fluoropolymers prices can be around €15.6/kg[21] depending on the grade and the final application. According to the fluoropolymers group of the German Association for Semi-finished Plastics and Consumer Products (2017), PTFE prices should be increasing in the coming years due to the closures of production plants in China and thus resulting in a reduction in global supply. These closures are related to violations of environmental regulations imposed by the Chinese government.

There is a limited amount of producers of fluoropolymers around the world, which has created a highly competitive market in terms of innovation and new developments. The main producers are very much focused on developing alliances with strategic customers to innovate (Zion research analysis, 2017). In the EU, the R&D investment is above 5% of the total revenues (PlasticsEurope, 2018).

3.1.6 Fluoropolymers sustainability trends

There is a rising trend and a strategy of main suppliers to develop recyclable and low toxicity fluoropolymers to capture some key markets such as the healthcare sector. Nevertheless, this is limited by rigorous regulation on the production and use of these products. Compared to China, the higher cost of labor and higher environmental and safety regulations in the US and Europe have been a competition issue (Market research trends, 2020). However, the Chinese government is now applying more stringent environmental regulations to industry, which could also increase their operating costs and reduce the current competitiveness differences (Hong *et al.* 2019). Regulation standards are expected to increase, especially on risks of handling some critical raw materials, such as hydrofluoric acid and TFE (Ebnesajjad, 2014).

The fluoropolymers industry's main research subjects are the alternatives for fluorinated emulsifiers and technologies to reduce their missions. Emulsion polymerization of fluoromonomers usually requires the use of perfluorinated emulsifiers, including ammonium salts of perfluorooctylsulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). These substances are used to stabilize the particles of the polymer and prevent coagulation. Although these substances are not greenhouse gases, they are under strict regulations. These regulations are due to the high toxicity, bioaccumulation, and persistence reported in different studies over the last 25 years (Hintzer and Schwertfeger, 2014). Chemours processes at Dordrecht have never used PFOS. And although PFOA was used years ago, that substance was phased out in 2012.

3.2 DuPont: POM overview

Polyoxymethylene, also known as polyacetal or polyformaldehyde, is an engineering thermoplastic. Its mechanical properties such as strength, impact, stability, and fatigue

---

[21] Euro 2019

resistance make it an excellent alternative to replace metals for applications that require low weight materials. POM developments started in 1859 by the Russian chemist Aleksandr Mikhailovich Butlerov, who began to study polymerization with formaldehyde (Lüftl et al., 2014). Later, beginning in the twentieth century, there was additional research on it without defining processing technologies. Subsequently, in 1940, DuPont started its analysis about the production of formaldehyde and its polymerization, and in 1950 installed the first industrial plant of POM homopolymer under the brand Delrin®, which started production in 1960 (Lüftl et al., 2014). In the next table, there is a summary of the main advantages and disadvantages of this material.

Table 15 Advantages and Disadvantages of POM (Lüftl et al., 2014)

Advantages	Disadvantages
Outstanding short-term mechanical properties (Tensile strength, rigidity, and toughness)	Low thermal stability without adequate stabilizer system
Superior long-term mechanical properties (low tendency to creep and fatigue)	Low resistance to hot water in the presence of chlorine
Good mechanical and electric properties above 140°C (short-term) and 90°C (long-term)	Flammable without flame retardant due to the high oxygen content
Good mechanical properties below -40°C	Low chemical resistance to strong acids, bases, and oxidizing agents
Outstanding chemical resistance to solvents and fuels	Release of toxic gases, such as formaldehyde at high temperatures or during the burning process
Excellent dimensional stability and high hardness in comparison with other thermoplastics	Sensitivity to UV radiation
High resistance to abrasion	For medical and food applications, special grades are needed

3.2.1 POM main raw materials

Methanol

Methanol is also known as methyl-alcohol and is used to produce different chemicals, such as solvents and fuels. It is mainly used in the production of formaldehyde, acetic acid, and MTBE (methyl tertiary butyl ether). Around 35% of methanol's global production is used to produce formaldehyde (Heim et al., 2017). In 2018, methanol prices were between €280-380/tonne in Europe (Ellis, 2019), but later, in the first quarter of 2020, the prices were around €210-260 tonne; however, by the end of March, prices drastically fell to €150/tonne levels[22] due to the global crisis (Chavda, 2020).

Formaldehyde

Formaldehyde is a colorless gas at ambient temperature, and its odor can affect skin and eyes even at low concentrations. Although it is produced in nature when the combustion of organic materials is not complete or through photochemical processes in the atmosphere, it was synthesized and produced for the first time in 1889. Formaldehyde is an important intermediate chemical with a wide range of applications in different industrial processes, such as polymers, adhesives, and paint production (Bahmanpour et al., 2014). Due to its multiple applications, its global demand is around 40 megatons per year (Heim et al., 2017). The international trade of formaldehyde is very low, mainly because most of the production is used at the same production plant to produce other chemicals. Moreover, transportation costs are high because of the amount of water in the formalin, which is the typical aqueous solution of formaldehyde (Mursics et al., 2020).

---

[22] Prices are FOB Rotterdam.

Appendix 2 contains a schematic representation of the POM value chain.

3.2.2 POM market

The European POM market is segmented in homopolymers and copolymers, and depending on the grade mainly into standard, modified grades, special grades, and recycled (Graphical research, 2019). The POM market growth is related mostly to the automotive industry's growing demand to manufacture parts and pieces for the interior and exterior. Besides this, there is a wide range of applications in the electric and electronic market to produce industrial pieces, like gears, pump impellers, and even daily applications such as kitchen drawer bearings and the seatbelt's red button. Medical applications are also expected to grow in a new and specialized market, to manufacture pacemakers, pieces for reconstruction, and traumatology. Nevertheless, the principal use comes from automotive, with around 34,5% of the global POM market. The electric and electronic applications are the second-largest market (Olabisi & Adewale, 2016). Market demand for POM polymer has almost duplicated during the last decade, increasing the production capacity to 1.7 million tons/year in 2015 (Beydoun & Klankermayer, 2020).

Table 16 Applications of POM
(Source: adapted by the authors from Olabisi & Adewale, 2016)

Industry	Applications
Automotive	Door handles, gears, wipers, speedometers, safety belts, seat adjustments, windows lifters.
Electrical Engineering	Gears for washing machines, cabinets for radios
Mechanical Engineering	Gears, brushes, pumps, gaskets, housing for drills
Packaging	Tanks, aerosol cans
Toys and fancy goods	Buckles for belts, zippers, hangers
Sports	Tennis racquet handles, ski bindings, windsurfing boards
Domestic Articles	Kitchen utensils, electronic brushers, shavers
Biomedical	Medical devices such as inhalers, atomizing systems, device components, handles for surgical instruments

Asia-pacific is the leading region producing POM, with 45.6% of global market profits in 2012, followed by Western Europe (Olabisi & Adewale, 2016). In terms of consumption, China leads, and then the U.S. These two countries represent 47.4% of the total global consumption (Markets and markets analysis, 2014).

3.2.3 POM prices and competitors

There are six main players in the POM market, including homopolymer and copolymer production, representing around 58% of the global market in 2012. One of these players is DuPont de Nemours (Olabisi & Adewale, 2016). Regarding prices, it varies considerably depending on the grade. However, as a referent, a standard grade is approximately €1,272/tonne, special grades can be above €89,000/tonne and recycled polymer with a purity close to 94-96% around €795/tonne (Lüftl et al., 2014)[23].

---

[23] All prices were converted to EURO 2019.

Dow: ethylene copolymer overview
More than 25% of the low-density polyethylene (LDPE) contains various copolymers of ethylene. Copolymerization is a strategy applied by LDPE producers to increase or change LDPE resins' properties, such as optical clarity, impact resistance, oil resistance, barrier adhesion, and wettability (Odian, 2004). The modification of these properties is required to adapt and respond to the increasing applications and market needs (Ali *et al*., 2019).

Ethylene polymerizes with different substances, including propylene, vinyl, and ethyl acrylate, to produce copolymers used in diverse applications, such as packaging, lamination, and consumer goods. Because of the number of grades and applications, the ethylene copolymer market is broad and atomized. Furthermore, this market is characterized by some key players with integrated value chains (Grand view research, 2017).

North America is the major shareholder of the ethylene copolymers industry market, serving the production of food and beverages, consumer goods, and the automotive industry. The second region is Europe, and then Asia Pacific (Industryarc,2020). The main driver influencing this market's growth is food packaging demand, derived from food conservation and safety concerns. Moreover, packaging recyclability is a significant trend that will increase the demand for some copolymers used to make compatible recycled plastics (Grand view research, 2017). Ethylene-vinyl acetate (EVA) represented the most significant segment in the global market in 2016, with expectations to keep growing in the coming years. The table below includes the main segments of copolymers by chemistry and some applications and properties.

Table 17 Main Ethylene Copolymers (Spechialchem, 2020)

Main chemistry groups of Ethylene copolymers	Main Applications	Properties
Ethylene acrylic acid (EAA) copolymer Ethylene/methacrylic acid (EMAA) copolymer	Films, blown film, packaging, frozen food packaging, agricultural films, greenhouse films, shrink wrap Flexible packaging and rigid packaging	Good tenacity High flexibility Good weather resistance Puncture resistance Scratch resistance Broad sealing temperature Excellent oil resistance
Ethylene-vinyl acetate (EVA) copolymers	Industrial hot-melt adhesives for packaging and label sticking	High flexibility High cohesive strength and compatibility Outstanding adhesion to diverse substrates High resistance to rupture
Ethylene acrylate copolymers: a. Ethylene butyl acrylate (EBA copolymer) b. Ethylene methyl acrylate (EMA copolymer)	Industrial hot-melt adhesives and hot melt pressure-sensitive adhesives for packaging and disposables	High thermal stability. High adhesion to polyethylene, polystyrene, and polypropylene. Good chemical resistance and elastic properties. Excellent mechanical properties at low temperature
Ethylene acrylic terpolymers: A wide range, depending on the type of acrylic ester (methyl, ethyl or butyl acrylate) and the third monomer used (MAH: maleic anhydride, GMA: glycidyl methacrylate)	Thermo-adhesive films for the interior liners of automobiles. Hot-melts for packaging applications.	High reactivity, crystallinity, and fluidity. Easy to process. Compatible with different types of polymers and additives.
Ethylene-vinyl acetate terpolymers: These are random ethylene vinyl acetate/maleic anhydride terpolymers.	Thermo-adhesive films for the textile and automobile industries Extrudable hot-melt adhesives for coating various materials Many hot-melt formulations for	Maleic anhydride improves the adhesion properties

	packaging and assembly	

Dow's ethylene copolymer portfolio includes Surlyn™ resins, Bynel™ coextrudable adhesives, and Fusabond™ polymer modifiers. These products, which are produced in the Dordrecht plant, are further described in the next sections.

3.2.4 Surlyn™

These resins are ethylene acrylic acid copolymers neutralized to some level with salts of sodium or zinc. The level of neutralization and the acid content determine the mechanical properties. Surlyn is an ethylene/methacrylic acid copolymer (E/MAA) (Sykutera and Czyżewski, 2012).

3.2.5 Surlyn™ market

Ethylene acrylic acid copolymer (EAA) is a common ionomer and thermoplastic material used for diverse applications. These range from flexible packaging, molded rigid packages for cosmetics to golf balls surface coatings, considering its high barrier properties, high clarity, and hardness. These ionomers are also used as adhesive resins, offering important mechanical properties, such as resistance to puncture, abrasion, tear, and good resistance to oil and acids (Ahner *et al.* 2008). The main application of this ionomer resin is for food packaging, which is the main driver of the EAA market growth. Also, medical and pharma applications and cosmetics industry applications are adding value to this market. For example, the line of perfumes packaging, specifically caps, takes advantage of Surlyn characteristics to replace glass. Surlyn™ offers more flexibility for designing, in terms of shapes and colors, and by reducing the costs of traditional packaging in around 30-40% (Sykutera and Czyżewski, 2012). Further, this resin is used in the soles of sports shoes to prevent wear. In 2017, the Asia Pacific region dominated the EAA global market.

3.2.6 Bynel™

Bynel™ is an extrudable adhesive resin produced by Dow Chemical, which is supplied in pellets to be processed in conventional extrusion equipment to process polyethylene. Furthermore, this resin is used as a sealant layer as well. There is a wide range of grades of extrudable adhesives depending on the final application, from polyethylene to vinyl acetate, and copolymers of ethylene, which is the case of Bynel™. Bynel™ resins can be part of the polymer family EVA, Ethylene acrylate copolymer ACR, HDPE, LLDPE, and PP.

Extrudable adhesives, which are generally based on polyolefins, are used to bond different polymer materials that cannot bond under normal conditions. These polyolefin extrudable adhesives are one single layer, commonly referred to as a tie layer, in a multiple layer material. Multilayer materials are formed by coextrusion of various plastics, which are melted and then put in contact with a coextrusion screw. Here, diffusion of molecules occurs, which allows the production of a single multilayer material that combines the specific properties of each material. A good example is packaging films, that bond layers such as an oxygen barrier, an abuse resistance layer, or a heat-sealable layer with adhesive resin (Tanny, 2009).

3.2.7 Bynel™ market

The main market for extrudable adhesive resins is the food packaging industry, for flexible applications, such as processed meats and cheese packaging, rigid plastics, such as high-barrier ketchup bottles, and also for sealing yogurt lids (Tanny, 2009). Globally, there are several extrudable adhesive resins producers, some of them with a small portfolio and others with a complete offer of adhesive resins. Dow Chemical is one of the producers of acid copolymers, such as EAA. In Dordrecht, Dow produces acid and anhydride-modified ethylene acrylate resins, among others. Regarding sealant layers, there are different grades, depending on the needs, from high to standard performance. The table below lists the main sealant layer resins produced around the world:

Table 18 (Marks and Wagner, 2010)

Sealant Layer Resins
Ionomers of acid copolymers
Acid copolymer (EAA or EMAA)
mVLDPE (ultra-low density)
EVA or EMA blends with LLDPE
CoPP/TerPP, EVA, EMA, LLDPE, Mlldpe
LDPE or PP

3.2.3 Fusabond™

Fusabond™ resins are modified polymers used to bond different polymers in mixed compounds, which is key for recycling plastics. In Dordrecht, Dow produces maleic anhydride grafted (MAH) polymer.

The main obstacle to recycle multilayer materials is related to the incompatibility between their different layers (Niaounakis, 2020). Therefore, this resin is highly promoted for recycling applications, to improve the compatibility between different polymers, and to increase the quality of recycled plastics (Dow, 2020b). Moreover, this resin is a coupling agent and an impact modifier, which improves the compounds' performance.

4 Options for decarbonisation

In the next diagram, the main categories of reduction alternatives considered by the MIDDEN project are illustrated.

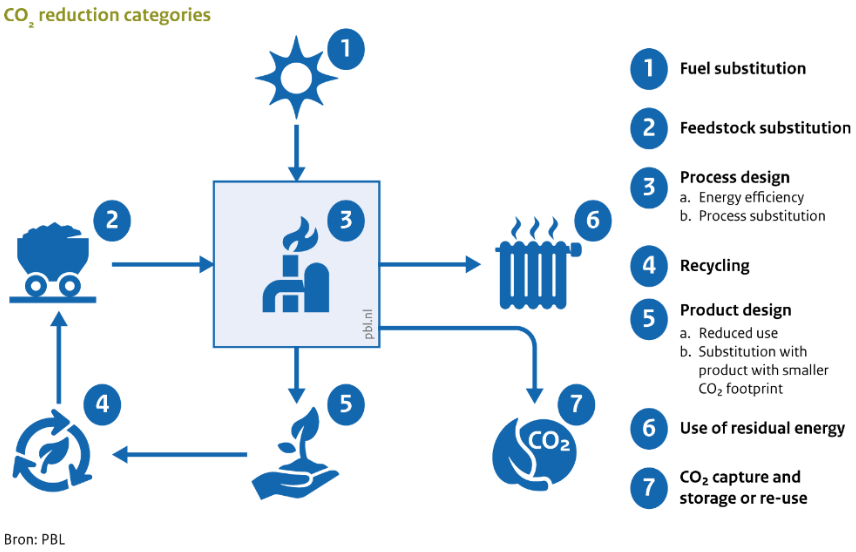


Figure 10 Main categories of CO_2 emissions and energy consumption reduction alternatives

This section contains the main GHG emission and energy consumption reduction alternatives for the Chemours, DuPont, and Dow processes in the Dordrecht site by 2050. Because some alternatives are common for several processes, the first part of this chapter explains the main options for the whole site to be further developed for each company's specific situation and processes in section 4.8. Given that the CHP is no longer in operation since 2018, it will not be included as a source of emissions in the analysis of the potential of the decarbonisation alternatives. The HVC supply and the back-up boiler replaced all the steam production from the CHP.

Table 19 contains a summary of the main decarbonisation alternatives considered for the processes taking place at the Dordrecht industrial cluster.

Table 19 Decarbonisation alternatives Dordrecht cluster

Technology	Relevant to process	Category
Electricity	Natural gas-fired equipment: Furnaces Boilers	Fuel substitution
Hydrogen	Natural gas-fired equipment: Furnaces Boilers	Fuel substitution
Biomass	Steam production: Boilers	Fuel substitution
Heat pumps	To recover heat from processes and supply steam. Furnaces, distillation towers.	Use of residual energy
Gasification of biomass to produce biomethanol	Processes that use methanol as a feedstock (POM)	Feedstock substitution
Carbon capture and storage/utilisation	Applicable for all current stacks. CO_2 can be used to produce methanol, and subsequently, POM	Carbon capture
Chemical, mechanical, and solvent-based recycling	Internal process waste and end-life polymers	Recycling

4.1 Decarbonisation of heat supply

Electricity must be generated from renewable energy sources to consider electrification as a decarbonisation alternative. As illustrated in table 19, for the processes included in this report, electricity applies to furnaces and boilers.

4.1.1 Electrification

Electric Boiler

Electric boilers are one of the alternatives that are already implemented for different industrial processes, especially for small-scale operations (Marsidi, 2018a); thus, its TRL is 9 (Berenschot, 2015).

There are two main systems of industrial electric boilers. The electric boilers that use a heating element as a resistance, heating the water to its boiling point. And the electrode boilers, in which water carries the electric current and produces steam (Marsidi, 2018a).

A conventional industrial boiler has thermal capacities from 10 to 30 MWe. In comparison, an electric boiler has thermal capacities up to 5 MWe. Thus, it would be necessary to use additional electric boilers units to produce the amount of steam generated in a conventional one. Therefore, this alternative would not be suitable for Dordrecht steam demand. The capacity is higher in electrode boilers, from 3MWe to 70MWe (Marsidi,2018), being a better option for the Dordrecht site. Electric and electrode boilers that are commercially available can produce superheated steam at pressures above 70 bar and temperatures from 100 to 350 °C. These alternative boilers have efficiencies from 95 to 99.9% (Berenschot et al., 2017).

Due to the relative low electricity prices in The Netherlands and the relatively low investment costs compared to other sustainable steam production alternatives, electric boilers have received more attention during the last years (Stork et al, 2018). Nevertheless, industry still considers electricity prices too high for a feasible business case. The operational costs are also moderate compared to conventional fuel-heated boilers, which require more frequent maintenance (Element Energy; Jacob. 2018). The next table shows the technical and economic parameters of electrode boilers.

Table 20 Electrode boiler technical parameters

Parameter	Unit	Value	References
Efficiency	%	95 – 99.9	(Berenschot, 2017; Marsidi,2018a)
Technical Lifetime	Years	15	(Element Energy; Jacob, 2018)
TRL		9	(Berenschot, 2017)
Carbon Abatement Potential	%	100 (assuming renewable electricity)	

Table 21 Electrode boiler technical parameters (Reference capacity 70MWe)

Parameter	Unit	Value	References
Investment Cost[24]	$€_{2019}/kW_e$	77.4 – 126.6	(Planbureau voor de Leefomgeving (PBL), 2020; Element Energy; Jacob, 2018)
Fixed O&M Cost	$€_{2019}/kW_e/year$	1.4 – 48	
Variable O&M Cost	$€_{2019}/MWh$	0 - 0.21	
Fuel Cost	-	Electricity price	

Electric Furnace

Electric furnaces are an alternative for natural gas fired furnaces to reduce energy consumption and mitigate CO_2 emissions. Nevertheless, due to the high temperatures requirements of some processes, such as pyrolysis or cracking, the full implementation of electric furnaces is still limited; hence, this technology requires further development (VNCI, 2018). However, electric furnaces for demand up to 1000 ◦C are technologically available for all applications. Some key petrochemical companies in The Netherlands are developing cracking furnaces that can operate at around 850 ◦C and expect to implement them in about five years (VNCI, 2018). For medium and high-temperature applications, electric furnaces require investment costs and efficiencies comparable with conventional alternatives (Roelofsen et al., 2020).

Processes based on electricity can be divided into direct heating (inductive/dielectric), which does not need a heat transfer medium. This heating method implies an electric current moving through a material, which is heated due to its electrical resistivity. Second, indirect heating (resistance/arc/infrared), which requires a heat transfer medium. In this case, an electric current moving through a material, which transfers heat to a fluid or gas through convection and radiation. And third, electric arc systems, which generate a high electric current between two electrodes (electric arc) and then heat up materials. In hydrocarbon cracking systems arc systems are used via the Plasma Arc Heating technology (Oliveira and Schure, 2020).

Considering each technology characteristic and expert consultation, the most relevant alternative for gas-fired furnaces would be indirect resistance heating. This technology is not available yet on an industrial-scale for refinery furnaces. However, they are currently in development (TRL 3). Regarding electric arc systems, they are already applied in processes such as the destruction of F-gases.

---

[24] Refers to the total boiler installed cost (TIC). The cost range is re-estimated based on original reference capacities in (Planbureau voor de Leefomgeving (PBL), 2020; Element Energy; Jacob, 2018), using a scale factor of 0.7.

In Table 22, there is a summary of the economic parameters for electric furnaces.

Table 22 Economic parameters for electric furnaces

Parameter	Unit	Electric furnace (10 MWe)	Reference
CAPEX	mln. €2019 MWth	3.5– 5.0	(VNPI/DNV-GL, 2018)
OPEX	mln. €2019 /MWth	0.07 – 0.1	

4.1.2 Use of residual energy: Heat pumps

Although there is already a highly heat integration in the Dordrecht site, this section offers a general description of heats pumps (HP) to give relevant concepts of this alternative.

Heat pumps use power to transfer heat from a low-temperature source to a higher temperature application. This technology is commonly applied in processes that demand heat at temperatures below 200°C (ECN, 2017). This technology can transform renewable and waste heat from processes into heat for final applications. This alternative allows generating heat to use on-site and even supply heat to third parties (Oliveira and Schure, 2020). Furthermore, electric heat pumps, which have a TRL of 9, could be an option for low-temperature heat (<100°C) applications (de Pee et al., 2018).

High temperature (HT) heat pumps are not commercially applied yet (well-above 130 °C), nonetheless, there are ongoing developments to achieve temperatures close to 140 °C (Marina et al., 2017). The TRL of heat pumps at around 90 °C is 9, and above 160 °C is 4-5 (ECN, 2017).

Furnaces could use a combined-cycle gas turbine (CCGT) power system. As stated by Mursics et al. 2020, the theoretical power produced by an incineration process of waste gases from formaldehyde production (using metal oxide catalyst) in a CCGT is 4,239 kW. In the CCGT system, an electrical generator is driven by a gas turbine, which produces steam by recovering waste heat from the turbine exhaust gas. The steam produced is used to produce electricity. The electrical efficiency is around 50-60%. Because CCGT uses steam extraction from the steam turbine, its power generation efficiency is reduced. According to literature, the efficiency of CCGT can increase by using heat pumps (Tretyakova, 2017). By combining CCGT and HP, steam extraction is not required. In that case, the CCGT flue gas is used as a heat source for the HP (Albul,2014).

Heat pumps could also be applied to distillation processes. This mechanism uses the heat released from the condenser in the reboiler for evaporation. A heat integrated distillation column (HIDiC) is a diabatic process which exchanges heat from the rectifier (high pressure) to the stripper (low pressure). This configuration can decrease the utility cost by 25-35%

and the total annualized costs by around 10-20% compared with the conventional design of a vapour recompression column (VRC) (Bruinsma and Spoelstra, 2010).
The next table illustrates the economical parameters of a 20 MWth heat pump.

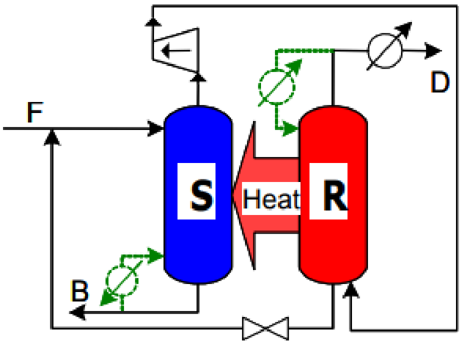


Figure 11 The HIDiC principle (Bruinsma and Spoelstra, 2010)

Table 23 Heat pumps technical parameters (Reference capacity 20 MWth)

Parameter	Unit	Value	References
COPh (Coefficient of performance)	-	3-4	(ECN, 2017) (Berenschot et al., 2017)
Technical Lifetime	Years	15	(Berenschot et al., 2015)
TRL	-	9 (for 90 °C) 4-5 (for 160 °C)	(ECN, 2017)

Table 24 Heat pumps economic parameters (Reference capacity 20 MWth)

Parameter	Unit	Value	Reference
CAPEX	€$_{2019}$/kW$_e$	800-2,000 (up to 90 °C); 2,000-5,000 (up to 140 °C) Including installation cost and grid connection cost	Noothout et al. 2019
OPEX	€$_{2019}$/kW$_e$	60	Marsidi, 2018b

4.1.3 Hydrogen

Hydrogen is an alternative that has significant potential to reduce CO_2 emissions from industry by replacing fuel gas with hydrogen to operate furnaces or boilers. Hydrogen boilers have a TRL of 9 (Hart, et al., 2015), and have capacities between 2 to 50 MW (Navigant, 2019). The burning of hydrogen emits water and heat, so CO_2 emissions are avoided. However, to be a carbon-free technology, hydrogen has to be produced through sustainable processes.

Conventional combustion boilers can use hydrogen to replace natural gas by retrofitting. In that case, the only modification required is to the burner, as it has to be adapted to the hydrogen gas properties, and in consequence, its process conditions change. Retrofitting has a TRL of 7 and is expected to be commercially available around 2025 (Durusut, et al., 2019).

Two sustainable hydrogen production routes are being considered. One is using water-electrolysis powered renewable electricity from wind or solar panels, which results in so-called green hydrogen. The other is from natural gas, but using carbon capture and storage (CCS) to avoid most CO_2 emissions, resulting in so-called blue hydrogen. Although the availability of green and blue hydrogen is still limited, it is expected an increase in the coming years, associated with new hydrogen projects. In the case of green hydrogen, the technology readiness level (TRL) of electrolyzers is around 6-8 (Dechema, 2017). Blue hydrogen production is a mature alternative, with a TRL around 9; however, for industrial applications, it still requires capabilities for underground storage of CO_2 (Evangelopoulou et al., 2019). Nevertheless, it is essential to consider that hydrogen combustion produces higher amounts of NO_x; thus, it is necessary to implement abatement measures to reduce them.

Tables 25 and 26 present the technical and the economic parameters, respectively, for new hydrogen boilers and the retrofitting alternative. Table 27 shows the economic parameters of hydrogen use in furnace.

Table 25 Technical parameters for a newly installed hydrogen boiler and the boiler retrofitting

Parameter	Unit	Value (Range)	References
New hydrogen boiler			
Efficiency	%	90-100[25]	(E4tech, 2015) (Ricardo-AEA, 2015)
Technical Lifetime	Years	25	E4tech, 2015
TRL		9	(Hart, et al., 2015)
Retrofitting of natural gas boiler			
Efficiency	%	90[26]	(Hart, et al., 2015; Navigant, 2019)
Technical Lifetime	Years	Depending on the remaining lifetime of the combustor	(Hart, et al., 2015)
TRL		7	

In terms of economic parameters, the investment information of hydrogen boilers is still limited. Nevertheless, according to Ricardo-AEA, 2015, compared with conventional natural gas boilers, it is expected no increases in capital costs for blends of 30% hydrogen and natural gas. However, for 100% hydrogen with oxyburners, it is expected a capital increase of 30%. This increase is due to the condensation and flue gas recycling costs.

The variable O&M cost depends on the amount of fuel and its related cost, which, in turn, depends on the source of hydrogen. Some projections expect a decrease in green hydrogen cost; however, there is still high uncertainty related to hydrogen prices. According to experts, hydrogen boilers OPEX will be closer to the conventional natural gas boilers, decreasing from 2.8 to 0.4 $€_{2019}/kW_{th}$ (Ecodesign,2014).

---

[25] E4tech (2015) reports an efficiency of 90% but does not specify whether this is based on LHV or HHV. Ricardo-AEA (2012) reports an efficiency of 100%, LHV or HHV not specified.

[26] Due to the lack available information, the efficiency of retrofitted boilers is assumed to be the same as the new hydrogen boilers

Table 26 Economic parameters for a new hydrogen boiler and a retrofitted boiler

Parameter	Unit	Value (Range)	References
New Hydrogen Boiler (Reference Capacity: 50 MW_{th})			
Investment Cost [27]	$€_{2019}/kW_{th}$	128	Rutten, 2020
Fixed O&M Cost	$€_{2019}/kW_{th}$/year	15 – 21	(Navigant, 2019)
Retrofitting natural gas boiler (Reference Capacity 115 MWth)			
Investment Cost [28, 29]	$€_{2019}/kW_{th}$	27	(Durusut, et al., 2019)
Fixed O&M Cost	$€_{2019}$	3% of total investment	(Durusut, et al., 2019)

Table 27 Economic parameters for hydrogen use as fuel for a 10 MWth furnace VNPI, 2018)

Characteristic	Value	Comment
CAPEX ($€_{2019}$/kW)	400-1,200	Estimation includes costs for the infrastructure for hydrogen transport, hydrogen compressor, replacement of natural gas burners. Does not include NO_x emission reduction technology.
OPEX ($€_{2019}$/kW/yr)	4-12	1% of CAPEX; it does not contain utilities and hydrogen costs.

4.1.4 Biomass Boilers

According to studies conducted by DNV GL (DNV,2017) and the Biomass Policies project (Uslu, 2018), waste food, forest residues, fuelwood, nature, and landscape biomass, and lignocelluloses dedicated crops are among the feedstocks included in this category. These studies found a biomass potential of 58.7-72.8 PJ in 2030. Nevertheless, in The Netherlands, the import potential depends on several aspects, including EU policy frameworks (Uslu, 2018).

Although biomass has played an important role in the Dutch energy and climate agenda, it is still under debate whether biomass is a carbon-neutral and renewable energy source. Thus, a clear sustainability framework is required.

Steam boilers using solid biomass are widely applied at the industrial-scale, with a TRL of 9.

Table 28 Technical parameters for a biomass boiler

Parameter	Unit	Value (Range)	References
Efficiency	%	90	(Uslu, 2018; Planbureau voor de Leefomgeving (PBL), 2020)
Technical Lifetime	Years	12 – 15	(Uslu, 2018; Planbureau voor de Leefomgeving (PBL), 2020)
TRL	-	9	(Uslu, 2018)

---

[27] The investment cost is re-estimated based on the original reference capacity in (Navigant, 2019), using a scale factor of 0.7.

[28] The investment cost includes the equipment costs as well as engineering design (5% of total cost), project construction and management (3% of total cost), removal (5% of total cost), labour (10% of total cost), commissioning (2% of total cost) and estimated contingency (12% on top of all other costs).

[29] The investment cost is re-estimated based on the original reference capacity in (Durusut, et al., 2019), using a scale factor of 0.7, scaling up to match the capacities of the existing steam boilers.

Regarding economic parameters, investment costs include wood pellet storage, steam boiler, selective non-catalytic reduction system (SNCR)[30], and the dust filter costs (Uslu, 2018). The operational costs include the warranty and maintenance contracts and insurance policies, and direct personnel costs.

Table 29 Economic parameters for biomass boilers > 5 MWth

Parameter	Unit	Value	References
CAPEX	mln €2019/MWth	0.55	Uslu, 2018
OPEX	mln €2019/MWth	0.04	

4.2 Energy Efficiency

Although energy efficiency is always an appropriate option to be considered, it will not be further elaborated in this report because there are already important ongoing projects in the Dordrecht site to this respect. The cooperation agreement between the Dordrecht site and HVC to supply the heating network and the steam supply between the three companies are clear examples. Integration of processes, heat recovery, and insulation are some of the energy efficiency initiatives taking place at Dordrecht. In section 4.1.3, heat pumps were included as an alternative aligned with energy efficiency. As stated in chapter one, Chemours and DuPont have an up-to-date Energy Efficiency Plan (EEP).

4.3 CCS/CCU

CCS (carbon capture and storage) technology is an alternative to reduce CO_2 emissions from industrial processes. After capturing the CO_2, the gas stream is compressed and then injected underground into reservoirs for long-term storage. According to IPCC (2005), there are three main technologies to capture carbon dioxide for industrial applications: pre-combustion, post-combustion, and oxyfuel combustion.

Capture

In the pre-combustion system, the primary fuel is processed in a reactor to produce hydrogen, CO_2, and water, in different streams. This method is widely applied in the fertilizer and refining industry to produce fuels with lower carbon content (IPCC, 2005); it is also used to produce blue hydrogen (TNO, 2019). The pre-combustion system requires relatively low energy for the separation processes due to the total high pressure and concentrations of the mix of hydrogen and CO_2. The standard separation processes imply capturing the CO_2 by chemical absorption, such as using aqueous solutions of amine or using a membrane; typically, the sorbents' properties determine the capital and investment costs of the processes in which they are used (Bui et al., 2018). Both chemical absorption and polymeric membranes have a TRL of 9 and 7, respectively (Bui et al., 2018). Further, the CO_2 is released in a process known as regeneration, modifying some sorbent conditions, such as pressure. The MIDDEN report about the refineries industry offers additional details about this technology (Oliveira & Schure, 2020).

---

[30] SNRC systems are used to decrease nitrogen oxide emissions.

In the post-combustion process, the separation is applied to the flue gas from the combustion. This process is an appropriate alternative for existing installations (IEAGHG, 2007; Leung et al., 2014). The flue gas contains CO_2, N_2, sulphure-oxides, nitrogen oxides, carbon monoxide, particulate matter, and water. The separation process requires more energy than pre-combustion because the concentration of CO_2 is reduced before releasing into the atmosphere; the reduction of CO_2 concentration is made through scrubbers and other methods. Although the cost of pre-combustion processes is higher than post-combustion, it is applied more often, considering the higher concentrations of CO_2 (IPCC, 2005).

Oxyfuel is a capture method to replace air with oxygen for the combustion process. In this way, the resulting gas composition will be CO_2 and water. Although this technology still requires development, with a TRL of 7 (Bui et al., 2018), the glass industry demonstrated its feasibility (IPCC, 2005).

Transport

According to the IPCC, 2005, after capturing, for a distance up to 1,000 km, carbon can be transported using pipelines, and, for more considerable distances, shipping could be an option. Nevertheless, a particular pipeline infrastructure would be required to avoid important variations in the flow (Berghout, 2015). Both transport alternatives have a TRL of 7 (Bui et al., 2018).

There is an ongoing project in The Netherlands which will use a collective pipeline to transport CO_2 to the compressor station: The Port of Rotterdam CO_2 Transport Hub and Offshore Storage (PORTHOS) project. Companies in the Port of Rotterdam will capture and supply the CO_2 emissions from their production processes to the pipeline (Port of Rotterdam, 2020). The pipeline will connect Vondelingenplaat to a compressor station on the Maasvlakte. From there, the compressed CO_2 will be sent to a platform in the North Sea, using an offshore pipeline, and the CO_2 will be pumped to an empty gas field. It is expected that the PORTHOS project will be operational by 2024 (Porthos, 2020).

Storage

Regarding storage, the more mature and used method is underground CO_2 storage. Many CCS at the commercial-scale level have used the CO_2-enhanced oil recovery (EOR) method, which has a TRL of 9. Moreover, the use of saline formation has been implemented for the storage of CO_2 at commercial-scale levels. Differently, CO_2-enhanced gas recovery (EGR) and its storage in depleted oil fields are still at the demonstration level, with a TRL of 7 (Bui et al., 2018).

The tables 30 and 31 presents the technical and economic parameters of post-combustion carbon capturing, purification and compression.

Table 30 Technical parameters for post-combustion carbon capturing, purification and compression

Parameter	Unit	Value	References
Availability	%	84 – 97	(Berghout, Kuramochi, Broek, & Faaij, 2015)
CO_2 Capture Efficiency	%	90	
Technical Lifetime	Years	15 – 25	
Regeneration heat required for carbon capturing	GJ_{LHV}/tCO_2	3.5 – 4.0[31]	
Electricity for carbon capturing	GJ_e/tCO_2	0.1 – 0.3	
Electricity for CO_2 compression	GJ_e/tCO_2	0.45	

Table 31 Economic parameters for post-combustion carbon capturing, purification and compression (Reference CO_2 Capture Capacity: 800 kt/year)

Parameter	Unit	Value	References
CAPEX			
Stack Modification	$M€_{2018}$/stack	0.1	Berghout et al., 2015
SCR/FGD[32] units	$€_{2018}/(tCO_2/year)$	26	
CO_2 Capturing Equipment	$€_{2018}/(tCO_2/year)$	79	
CO_2 treatment & compression	$€_{2018}/(tCO_2/year)$	12	
OPEX			
Maintenance	-	3% of Total Plant Cost	Berghout et al., 2015
Labour, Taxes & Insurance, Administration & Overhead	$€_{2018}/tCO_2$	2.45	
Connection Cost[33]	$€_{2018}/tCO_2/year$	4.3	(Planbureau voor de Leefomgeving (PBL), 2020)
Others[34]	$€_{2018}/tCO_2$	2.7	Berghout et al., 2015

CCU: Carbon Capture and Utilization

Currently, several facilities are already using CO_2 for different purposes, and the current utilization has a TRL of 9. The main applications of CO_2 are in the food and beverage industry, in horticulture, and the chemical production of important feedstocks such as urea and methanol (Bui et al., 2018). CO_2 utilisation allows to substitute the CO_2 that is produced from natural gas combustion for these specific applications. Also, and according to a recent report of the European Commission (2019) analysing promising carbon capture and utilization technologies, the most favorable CCU routes are fuels and base chemicals (ethanol, methane, methanol, oxymethylene ether; ethylene and propylene, intended for the production of polymers (polyethylene), polyoxymethylene, polypropylene, polycarbonate,

---

[31] Lower carbon concentration, which is the case for oil or gas-fired systems, requires higher regeneration heat and electricity.

[32] SCR: Selective catalytic reduction; FGD: Flue gas desulphurisation.

[33] Assumed 3km connection from the industrial site to the PORTHOS CO_2 grid

[34] Includes water usage and chemical costs (Berghout, Kuramochi, Broek, & Faaij, 2015).

polyols for polyurethane and minerals, such as calcium carbonate and sodium carbonate. Nevertheless, CCU emission reduction potential depends on the period of time in which the CO_2 remains stored in the materials. In the case of fuels it can be weeks, in the case of plastics it can be years (European commission, 2019).

4.4 Bio-based feedstocks

Biomass can replace fossil fuels and reduce CO_2 emissions. This alternative is already used to produce different alcohol fuels, such as ethanol, methanol, liquified biogas, or bio-diesel, or gaseous fuels, such as methane. Although biomass has shown increasing technological development, there are still some drawbacks; first, biomass availability and the potential competition with other biomass applications, such as food production (VNCI, 2018). Second, biomass sustainability (VNCI, 2018). Biobased materials require the use of natural resources, hence defining sustainability criteria is needed. If methanol is produced from green hydrogen and CO_2, the potential reduction of CO_2 emissions is higher.

Different molecules that are conventionally produced from fossil fuels can be derived from biomass to produce specialty chemicals. One of the most relevant alternatives is the carbohydrates from lignocellulose, starch, or sugar (Pramod et al., 2018). Available technologies include the fermentation of sugars, transesterification of fat, and gasification of cellulose (VNCI, 2018).

Although the different feedstocks required for the processes are not produced at the Dordrecht site, biobased feedstocks should be considered part of the alternatives to reduce CO_2 emissions. For Dordrecht processes, these alternatives include the POM production from biomethanol, in the case of DuPont, and the production of copolymers of ethylene from biobased raw materials, including biobased acrylic acid in the case of Dow.

4.5 Chemours specific options

4.5.1 F-gases destruction

The primary method to reduce F-gases emissions is recycling and recovering of gases through the process's optimization. Regarding abatement techniques, there are two main alternatives, thermal oxidation, and plasma technology. Thermal oxidation is the combustion and cracking process, where CFCs, HCFCs and HFCs are broken down into HF, H_2O, HCl, CO_2, and Cl_2 in a reaction chamber at temperatures of about 1000 °C. The gases are then passed through a water scrubber and a caustic scrubber with an alkaline solution to withdraw volatile acid gases. Thus, the process requires a superior design by using specific acid-resistant materials (McCulloch, 2004). The whole system uses propane, methane, natural gas, or hydrogen for the destruction of F-gases. In the case of Chemours, the thermal converter combusts natural gas.

Besides, thermal plasma treatment has become a widely used technology over the past decade because of its excellent efficiency (see table 20). Both technologies are included among the best available techniques (BAT's) (European Commission, 2015).

The plasma system is a proven technology for fluorocarbons abatement. There are different systems using plasma torches to destroy F-gases. PLASCON™ is a system developed in Australia, which uses argon stabilized DC discharge to produce the electric arc. This system has been implemented for HFC-23 destruction, with a high abatement potential. Another system is SPARC™ (Steam Plasma Arc Refrigerant Cracking), developed in Canada, which hydrolyses F-gases into CO_2, HCl, and HF. There have been plants destroying CFCs since the '90s (Lozano, 2008). Several F-gases destruction facilities have been developed in Japan using plasma technology. For example, a commercial plant using this technology started operations in 1995 in Ichikawa City by the Clean Japan Center to destroy CFCs, HCFCs, and HFCs. This plant uses a plasma torch of 90 kW radio frequency induction, with steam plasma at atmospheric pressure (Heberlein and Murphey, 2008).

Another example is a plant in Monterrey, Mexico, which produces refrigerant gases. This plant installed a plasma system to destroy HFC-23 as a by-product of HCFC-22 production in 2004. Because of this technology, the emissions decreased to only 7 tonne CO_2 per tonne of HFC-23, which were basically electricity-related emissions (Heberlein and Murphey, 2008).

In the plasma system, F-gases are fed into the plasma torch and then are mixed with the plasma at 3000°C. The F-gases are degraded by heat and go to a water-cooled reaction chamber, where they are cooled to 1000°C. Later, the gases are quenched to 50°C in an alkaline scrubber to neutralize the acid gases (Lozano, 2008).

The facility destruction in Mexico uses argon as plasma gas. Argon, an inert gas, allows a long durable life to the torch components, which is essential for industrial applications, and due to its thermodynamic properties, this gas is a preferred option. The argon plasma is generated using a direct current discharge between a cathode and anode. The exit enthalpy of the plasma is around 11 MJ/Kg. The torch's radiofrequency induction is 150 kW, and its electrical efficiency is approximately 50% (Lozano, 2008). According to a public monitoring report of that company, the process input (electricity, argon, steam, and sodium), and consequently, the output, is lower than the one required for an equivalent capacity thermal convertor. The output gas is a mix of argon, carbon gases, and water vapour. The liquid effluent is an alkaline aqueous solution of sodium salts. The plant also has a water treatment system to withdraw fluoride using calcium hydroxide (Lozano, 2008).

In the figure below, there is a representation of the thermal plasma abatement system.

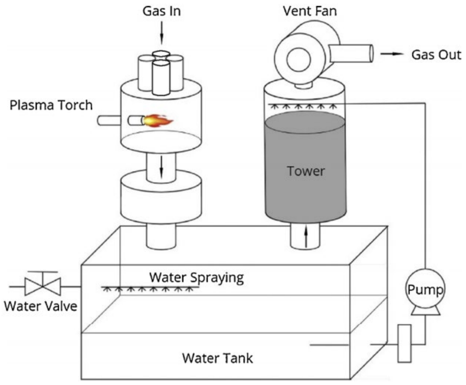


Figure 12 Representation of the thermal plasma abatement system (Chen et al., 2019)

According to the Executive Committee of The Multilateral Fund For The Implementation Of The Montreal Protocol (2018), a thermal converter's operating costs can be around €2.03 /kg, and the investment in capital costs, about €1.44 million to destroy 100 MT of HCF-23 annually. Although this technology has a good efficiency for waste destruction, it produces CO_2 emissions from burning natural gas. Regarding plasma technology, the operating costs can be around €2.5/kg. Moreover, a production plant that destroys annually 100 tonnes would need an investment of approximately €2.11 million in capital costs.

Table 32 Economic parameters and Efficiency of F-gases destruction technologies

Parameter	Unit	Technology		Reference
		Thermal oxidation	Plasma Technology	
TRL	-	9	9	(Heberlein and Murphey, 2008)
Efficiency	%	99	99.9	(Executive Committee Of The Multilateral Fund For The Implementation Of The Montreal Protocol, 2018)
CAPEX	(mln € 2019)	1.44	2.11	
OPEX	(€ 2019 /kg)	2.03	2.53	

4.5.2 Recycling

Wastes from production and processing:

PTFE materials

In the case of PTFE materials, which are unfilled, the main sources of scrap or waste are not during the polymers production process but in processing and manufacturing of final products. In this processing step, the amount of scrap can be around 10-30%, due to the specific processing methods, such as molding, sintering, cutting, etc. (Dams and Hintzer, 2017). There are some alternatives to recycle or reprocess the scrap, including mechanical recycling, in which possible contaminants are withdrawn, and the particle size is reduced. Then, it is re-used for less demanding applications. These alternatives are thermal degradation or high energy radiation. During thermal degradation, high molecular weight PTFE is degraded at temperatures of around 500 °C in ovens or extruders, to reduce the molecular weight, and then to produced micro-powder for specific applications, such as fillers or additives in other production processes. In the case of high energy radiation, some techniques are used, such as x-ray, gamma-ray, or electron beam. Electron bean is actually applied at a commercial scale (Dams and Hintzer, 2017).

PTFE Compounds

Because of the different types and amounts of fillers that are present in PTFE compounds (such as glass fiber, graphite, pigments, metal compounds, among others), there are no commercially established recycling technologies so far. Moreover, due to the growing regulations in Europe, the landfill will not be an option. Thus, chemical recycling is now being considered as an option to convert PTFE compounds into monomers (Dams and Hintzer, 2017).

Partially fluorinated thermoplastics and elastomers

Waste from the production and processing of partially fluorinated thermoplastics can be sent back to their processes to be recycled without modifying the final properties of the products. However, these have to be without contaminants, fillers, and pigments, and additionally, they have to be uncured (Dams and Hintzer, 2017).

Post-Consumer Waste

Used fluoropolymers can be recycled for specific applications in the reprocessed PTFE or micro powder PTFE market. Some polymers can be re-used for applications that do not require such high-quality specifications. Nevertheless, most of the end-of-life fluoropolymers are disposed in landfills, incineration plants, or blast furnaces. Conventional incinerators have restrictions about the amounts of fluoropolymers that can be incinerated due to highly corrosive hydrofluoric acid formation during incineration (Hintzer and Schwertfeger, 2014).

Because the production process of the monomers TFE and HFP is highly energy-intensive, there have been several attempts to produce the monomers from polymers scrap through pyrolysis. Although currently, this alternative has not been implemented, it could be a future option due to the development of high-temperature conversion development (HTC). HTC is a new process for the pyrolysis of all types of perfluoro polymers (Hintzer and Schwertfeger, 2014). Figure 14 illustrates the main alternatives for recycling and closing the loop of fluoropolymers. Around 87% of global fluoropolymers production corresponds to PTFE and compounds.

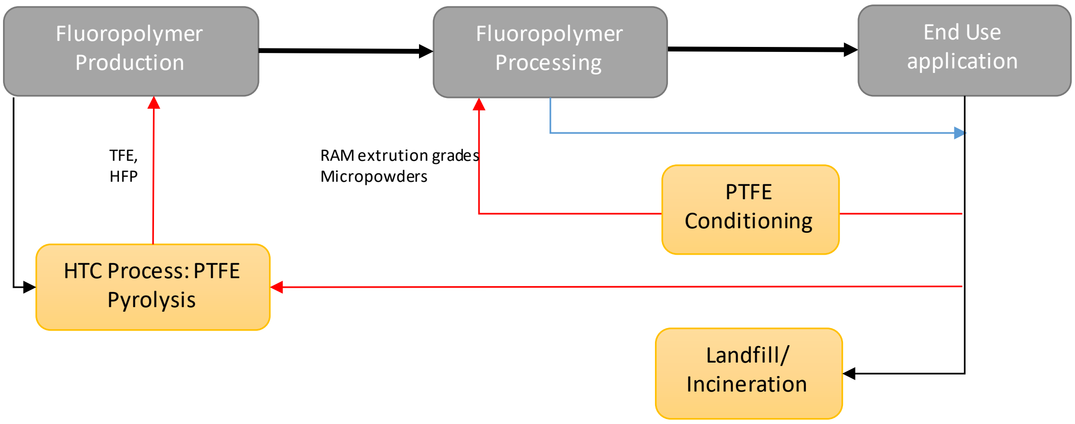


Figure 13 Perfluoropolymer recycling alternatives (Hintzer and Schwertfeger, 2014)

There is already a pilot in Burgkirchen, Germany, dedicated to recycling PTFE. The plant has a capacity to process 1,000 tonne of PTFE /year. It was installed in 2015 by one of the main fluoropolymers manufacturers and has demonstrated significant energy savings (Plasteurope, 2015).

4.6 DuPont specific options

4.6.1 POM Recycling

Regarding recycling, the wide variety of grades and applications of POM makes re-compounding and melting complex. First, some grades are highly fluent in the injection molding process, and others have very low fluency for extrusion processes. Moreover, the different additives and modifiers considerably change the properties of each specific application. Second, compounding and melting can result in formaldehyde release due to the POM decomposition.

Current recycling alternatives include mechanical recycling, which uses wastes of plastics as feedstocks for new products, and re-extrusion, which uses scrap. For re-extrusion, parts of a specific polymer are mixed with a virgin polymer in a standard mix ratio of 1:3, respectively. However, re-extrusion also has limitations related to the further degradation of POM. Chemical recycling, including pyrolysis and solvolysis, can convert POM into different products, using different chemical routes (Olabisi & Adewale, 2016). Although there are few approaches to converting POM into formaldehyde, a recent study by Beydoun and Klankermayer (2020) demonstrates an efficient plastic waste recycling to produce added-value products. For example, cyclic acetals can be used as commercial solvents, fuel additives, and other chemical intermediates for the pharmaceutical industry.

Cyclic acetals are produced by combining polymer waste and biobased diols through depolymerization and catalytic condensation. Besides the biobased diols, it is possible to use diols from recycled plastics, polyethylene terephthalate (PET), and polylactic acid (PLA) to produce ethylene glycol and propylene glycol. The reaction takes place without using solvents. Moreover, this process allows for producing various cyclic products in high yield. Although it is not at the industrial level, there are potential opportunities to explore this alternative (Beydoun & Klankermayer, 2020). This alternative has a TRL of 3-4.

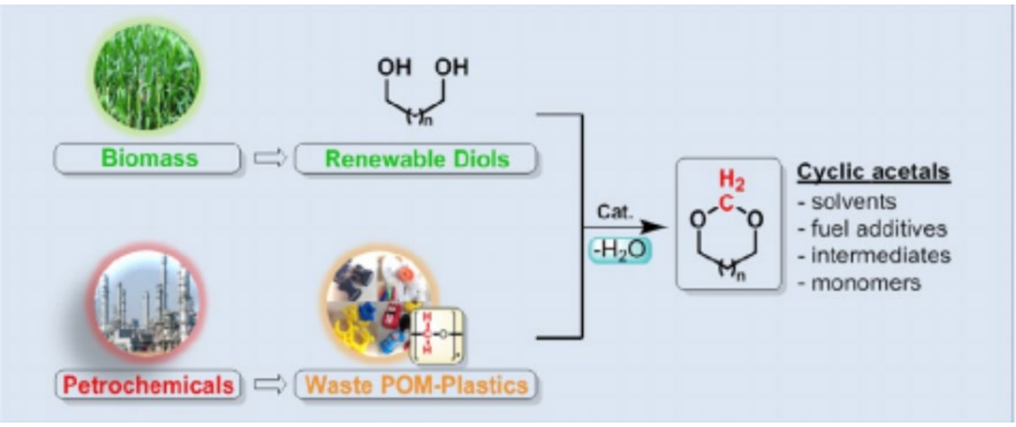


Figure 14 Cyclic acetals production from biobased diols and POM wastes (Beydoun & Klankermayer, 2020)

4.6.2 Biobased POM

In the case of POM, an alternative for a bio-based polymer is the replacement of methanol from natural gas with methanol from biogas or hydrogen and CO_2. Bio-based methanol is chemically identical to methanol; hence, it can also be used as a fuel or as a feedstock for other industrial processes (Block et al., 2020). That is the case of the production of formaldehyde, which is a critical methanol derivative. The gasification of cellulose, such as wood, can produce synthesis gas used as the feedstock to produce methanol (VNCI, 2018). Figure 14 shows the main production processes of methanol from different production processes. More details about bio-methanol production can be found in the report "Decarbonisation options for the Dutch biofuels industry" (Khandelwal & van Dril, 2020).

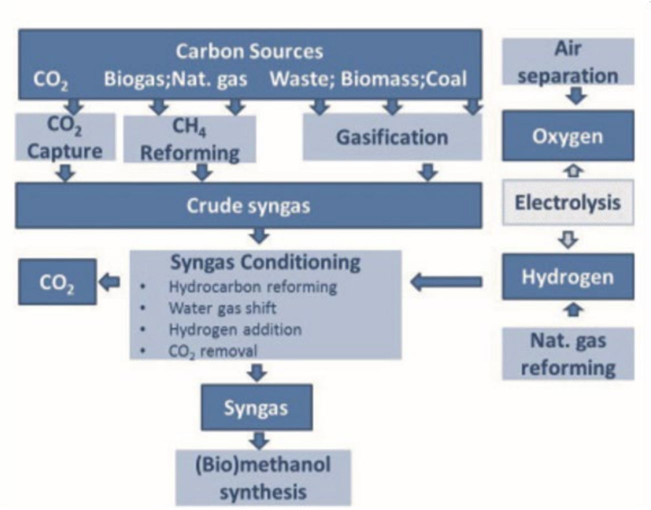


Figure 15 Major methanol production processes from different carbon sources (IRENA & IEA-ETSAP, 2013)

Nevertheless, bio methanol use can be limited by its production costs, which can be in the range of 521-626 EUR2019/tonne, compared to natural gas-based methanol at around 42-417 EUR2019/tonne (Boulamanti et al., 2017). In wind power and CO_2 based methanol, its costs can be from 644- 1,320 EUR2019/tonne, depending on electricity costs (Bozzano et al., 2016).

4.6.3 Carbon Capture and Storage for POM production

POM homopolymer can be produced from CO_2 without using any feedstock from fossil fuels. Its lifecycle is defined as ten years, as an average. This specialty polymer, with advanced properties, could promote the market entry of CO_2-based products. Although reuse or mechanical recycling requires less energy than the recovery of CO_2 through CCU, this polymer offers a high potential value to cover the initial recycling costs for CO_2, due to its high market price (€2,780 per tonne on average) (European Commission, 2019). Figure 16 illustrates the CO_2 based production of POM.

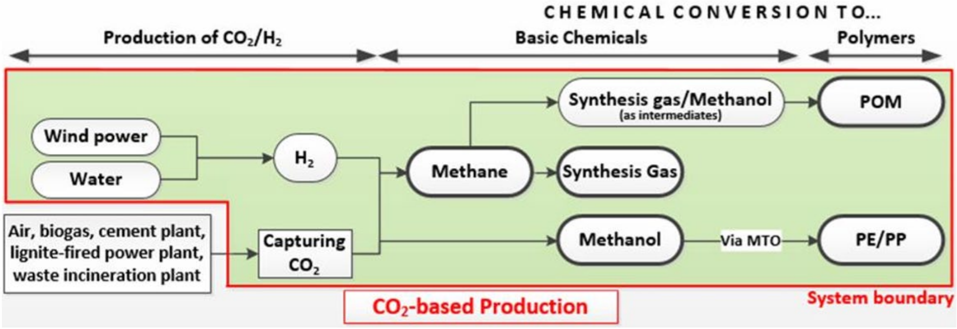


Figure 16 CO_2 based production of POM and other Polymers (European commission, 2019)

As stated by recent studies, according to some polymer manufacturing companies, this technology could be ready for a pilot plant in approximately five years, having investment costs from €1 million to €3 million. The main determining factor is the capital investment, but not the CO_2 or energy prices (European commission, 2019). The binding capacity[35] is similar to methanol but lower than for methane, PE, and PP. EU production from methanol could be replaced with methanol from CO_2.

In table 33, the results of an economic and CO_2 binding capacity evaluation for methanol and POM are presented (European commission, 2019).

Table 33 Economic analysis and CO_2 binding capacity for methanol and POM (European commission, 2019)

Product	Methanol	POM
Total EU Production and Imports (Mt/year)	8.04	0.21
Share of Imports	85	0
Product Price (EU 2019/t)	160	2,780
EU Economic Value (billion €2019)	1.29	0.58
CO_2 Binding Capacity (kg CO_2/kg product)	1.37	1.47
CO_2 Binding Volume (Mt CO_2/year)	11.04	0.31
Estimated Retention Time (years)	1	10
EU Economic Value (billion € 2019)	1.29	0.58

The main sources of CO_2 for CCU are direct capture from air, biogas, cement plants, lignite-fired power plants, waste incineration plants and fossil power plants. These sources and the energy required to produce hydrogen are determinants to measure the emission reduction impact and each CCU process's energy consumption. These routes can be classified as sustainable options if a significant share of renewable or waste energy is used. For all the aforementioned CO_2 sources, the global warming impact (GWI) per kg of POM decreases compared to the conventional route (European Commission, 2019). However, resource consumption does not decrease because of the power input required for electrolysis. Nevertheless, the increase in energy consumption is compensated by reducing GHG emissions (European Commission, 2019).

4.7 Dow specific options

4.7.1 Recycling

Processing copolymers is not an easy endeavor, and options such as mechanical recycling are still limited. That is due to the loss of transparency of the resin after second processing. However, in 2019, Dow participated in a project of 40% recycled Surlyn caps for the perfume market, using mechanical recycling. Additionally, there are some studies about solvent-based recycling of Surlyn resins, using xylene and n-butanol as solvents (Poulakis and Papaspyrides, 2000). Here, the polymer is precipitated in the form of microfibers using methanol, making it possible to recover the polymer and solvent. The process was applied duplicated without affecting the polymer's final properties, and when compared with the ones of virgin material, favorable results were obtained (Poulakis and Papaspyrides, 2000).

Furthermore, because recycling of multilayers packaging is complex, mostly post-consumption wastes, resins such as Fusabond are used to improve the compatibility of different resins and improve the properties of recycled resins. These polymers are valuable materials for recycling projects.

---

[35] kg of CO_2 per kg of generated product. It shows the stoichiometric amount of CO_2 that is theoretically bound in all products.

4.7.2 Bio-based acrylic acid

Acrylic acid is one of the main feedstocks to produce polyethylene copolymers. Conventionally, acrylic acid is produced by the oxidation of propene; however, there is a trend in demand for bio-based acrylic acid, which would directly influence the ethylene acrylic acid (EAA) industry (Transparencymarketresearch, 2018). Some companies, such as Cargill and P&G are joining efforts to develop different alternatives of production (Pramod et al., 2018).

After converting carbohydrates to propylene glycol, the dehydration of propylene glycol takes place to produce allyl alcohol using a zirconia (ZrO_2) catalyst, and then the oxidation of allyl alcohol at atmospheric pressures, using a molybdenum oxide catalyst. Propylene glycol, in the aqueous phase, is evaporated and then fed to a reactor for dehydration. After that, a distillation step separates lighter products, like propanal, from the top of the column, and heavy products, like unreacted propylene glycol, from the bottom of the column for recycling. The product stream is allyl alcohol, which is mixed with air to go into an oxidation step to produce acrylic acid and propionic acid. Subsequently, a non-distillation separation process takes place to obtain the final product. This process's economic feasibility still depends on future research to improve water consumption, selectivity, and the formation of some by-products. This technology has a TRL of 3-5.

In the next schematic diagram, there is an illustration of a potential industrial process to produce acrylic acid from propylene glycol.

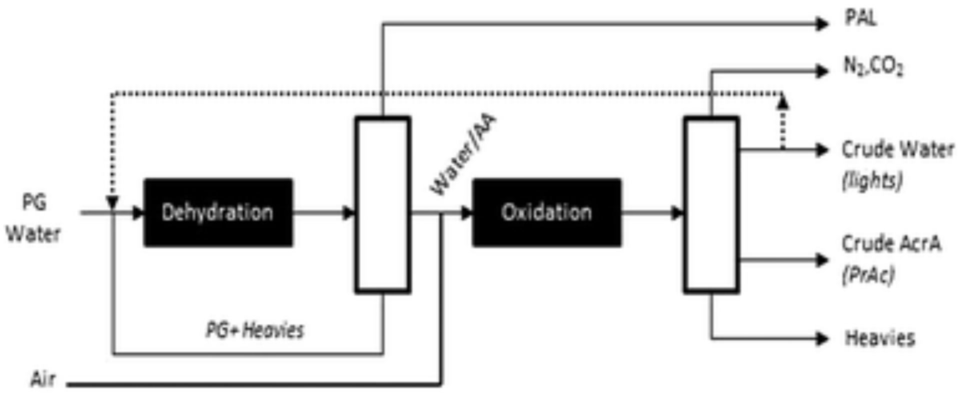


Figure 17 Production acrylic acid from biobased propylene glycol (Pramod et al., 2018)

Many other chemical routes can produce bio-based acrylic acid. One path is the dehydration of glycerol to acrolein (ACR) and the oxidation of ACR to acrylic acid. Conventionally, the oxidation is based on propene oxidation, through acrolein, and using molybdenum oxide catalysts. Another chemical path proposed in recent studies is hydro-deoxy-dehydration of glycerol to allyl alcohol, using formic acid as a sacrificial reagent, to be later oxidized to acrylic acid, using molybdenum oxide catalysts. This last route is not so straightforward due to the need for sacrificial formic acid and the oxygen requirements for the oxidation process. Other routes imply the conversion of carbohydrates to lactic acid, and further, the dehydration of the lactic acid into acrylic acid. Lactic acid is another alternative for converting propylene glycol to acrylic acid (Pramod et al., 2018).

4.8 Summary of decarbonisation alternatives per company

4.8.1 Chemours decarbonisation options

As explained in chapter 1, 41% of Chemours' energy consumption comes from steam, 29% from natural gas, and 30% from electricity. The main sources of CO_2 emissions of Chemours are the equipment that operates with natural gas, which are the thermal converter, two pyrolysis furnaces for the production of monomers, and a back-up boiler. In terms of F-gases, the main emissions come from HFC-23 (especially in downtimes of the thermal converter) and other fugitive emissions of F-gases (from HCFC-22 and monomers production processes, refrigerants blending operation, and the refrigeration machines). The thermal oxidation furnaces down-time results in high impact, which is estimated to be around 5-10% of the HCFC-22 production (Environmental investigation agency, 2013). In these down-times, HFC-23 is emitted to the atmosphere; hence it is required to capture and store these emissions to incinerate them later when the units are operating again. By implementing stop protocols and increasing the storing buffer capacity, some of these emissions can be reduced. Chemours is already working on these initiatives.

The thermal converter of Chemours was installed almost 20 years ago, so there can be an opportunity to increase its efficiency or replace it with a new converter with higher efficiencies. Although the combustion of natural gas in the thermal converter is free of rights in the EU ETS programme, this report includes these emissions as part of the reduction alternatives analysis.

The main decarbonisation options are presented in Table 34 and will be further discussed.

Table 34 Chemours main alternatives to reduce GHG emissions[36]

Alternative	Process	GHG emissions reduction	TRL	CAPEX	OPEX	Comments
Electricity	Thermal converter to destroy F-gases	100 % of CO_2 emission reduction from the combustion of NG in the thermal converter. 99,9% of abatement of the F-gases sent to thermal treatment	9	2.11 mln. €$_{2019}$/100 tonne HFC-23/year	2.53 €$_{2019}$/kg HFC-23	The use of plasma technology to reduce F-gases implies reducing CO_2 because it does not combust NG. It is based on electricity. Capital costs are estimated to destroy 100 tonne of HFC-23 per year. Operating costs are estimated per kg of HFC destroyed. (European Commission, 2015). F-gases are currently incinerated in a thermal converter at the Dordrecht site.
	Back up electrode boiler	100 % of CO_2 emission reduction from NG used in the backup boiler	9	77.4 – 126.6 €$_{2019}$/kW$_e$ (Planbureau voor de Leefomgeving (PBL), 2020; Element Energy; Jacob, 2018)	1.4 – 48 €$_{2019}$/kW$_e$/year (Planbureau voor de Leefomgeving (PBL), 2020; Element Energy; Jacob, 2018)	Electrode boilers have higher capacities (up to 70 MWe) than electric ones. (Berenschot, Matters, Delft, & Matters, 2017). Electric boilers are generally used as flexible capacity (Marsidi,2018). Green electricity prices influence their economic viability.
	Pyrolysis furnaces	100 % of CO_2 emission reduction from NG used in the furnaces	5	3.5-5.0 (mln. €/MWth) (VNPI/ DNV-GL, 2018)	0.07-0.1 (mln. €/MWth) (VNPI/ DNV-GL, 2018)	Electric furnace (reference capacity 10 MWe) (VNPI, 2018). Due to the high temperatures required for the pyrolysis processes (> 700 °C), the implementation of an electric furnace still involves research and innovation (Berenschot, Energy Matters, CE Delft, Industrial Energy Experts, 2017).
Hydrogen	Back up boiler	100 % of emission reduction from NG used in the backup boiler	New boiler: 9 Retrofitted boiler:7 Green hydrogen: 6-8 Blue hydrogen: 9	New boiler: 128 €$_{2019}$/kW$_e$ (Rutten, 2020) Retrofitted boiler: 15 – 21 €$_{2019}$/kW$_e$ (Durusut, et al., 2019)	New boiler: 27 €$_{2019}$/kW$_e$/year (Navigant, 2019) Retrofitted boiler: 3% €$_{2019}$/kW$_e$/year (Durusut, et al., 2019)	Hydrogen application in steam generation to replace natural gas in gas boiler (Khandelwal and van Dril, 2020)
	Furnaces	100 % of CO_2 emission reduction from NG used in the furnaces	Green hydrogen 6-8 Blue hydrogen 9	400-1,200 €$_{2019}$/kWth (VNPI, 2018)	4-12 €$_{2019}$/kWth (VNPI, 2018)	Hydrogen used as fuel for a 10 MWth furnace

---

[36] All the costs are expressed in Euro 2019.

Alternative	Process	GHG emissions reduction	TRL	CAPEX	OPEX	Comments
Biomass	Back up boiler	100 % of CO_2 emission reduction from NG used in the backup boiler	9	550 €2019 /kWth (Uslu, 2018)	4 €2019/kWth (Uslu, 2018)	Sustainable biomass boilers > 5 MWth
Heat pump	Back up boiler Distillation columns Thermal converter	100 % of CO_2 emission reduction from NG used in the backup boiler Energy efficiency during separation process by using heat integration (HIDiC) Heat recovery from thermal converter	9 (heat pumps around 90 °C) 4-5 (heat pumps above 160 °C)	800-2,000 €2019/kWth (up to 90 °C) 2,000-5,000 €2019/kWth (up to 140 °C) (Noothout et al. 2019)	0.06 €2019/kWth (Marsidi, 2018)	Costs are for heat pumps up to 90 °C Capex includes installation and grid connection costs
CCS	All current stacks. Thermal converter	Up to 90% of CO_2 emissions reduction	7	75.3 million €2019 (PBL, 2019)	Fixed: 1.5 million €2019/yr Variable: 23.3 €2019/tCO_2 (PBL, 2019)	CAPEX of CO_2 capture and connection (0.16 Mt CO_2/yr)
Process efficiency	F-gases emissions sent to the thermal converter and other fugitive emissions	-	9	-	-	• Reducing of HFC-23 production from the fluorination reaction. Emission monitoring mechanisms. • Stop protocols to decrease fugitive emissions. • Increasing of the storing buffer capacity of residual gases. (Chemours are already implementing these alternatives). By decreasing the residual gas production, the CO_2 emissions from burning them reduce.
Recycling	Mechanical recycling to produce new grades of product Chemical recycling to produce the monomers	NA	Mechanical recycling 9 Chemical recycling 7	NA	NA	These emissions are no direct emissions. However, by recycling some fluoropolymers to produce the monomers, energy consumption and its related CO_2 emissions can be reduced.

In addition to the options described in the table above, and as part of the general measures to reduce the emissions and energy consumption of the whole process, recycling should be considered in a long term perspective. The recycling of fluoropolymers can reduce not only energy consumption but also feedstock consumption, waste production, and CO_2 emissions. However, and due to the wide variety of fluoropolymers, several considerations apply to determine the best recycling alternatives. (Hintzer and Schwertfeger, 2014).

4.8.2 DuPont reduction alternatives

Approximately 57% of the DuPont emissions come from natural gas combustion in furnaces and boilers; 35% comes mainly from residual gases and by-products incineration in the furnace, 2% from the ECS unit, where some organic substances from formaldehyde production are oxidized to CO_2, and 6% from biogas combustion in the furnace. This biogas is produced in the anaerobic water treatment plant.

The decarbonisation options are presented in the next table for the main sources of emissions.

Table 35 DuPont main decarbonisation options for CO_2 emissions

Alternative	Process	CO_2 emissions (kt)	TRL	CAPEX	OPEX	Comments
Electricity	Furnaces	100 % of emission reduction from natural gas used in the furnace	5	3.5-5.0 (mln. €/MWth) (VNPI/ DNV-GL, 2018)	0.07-0.1 (mln. €/MWth) (VNPI/ DNV-GL, 2018)	Electric furnace (10 MWe) Due to the high temperatures required for the incineration of by-products and residual gases (> 700 °C), the alternative of an electric furnace still involves research and innovation to be implemented. (Berenschot, Energy Matters, CE Delft, Industrial Energy Experts (2017))
	Back up electrode boiler	100 % of CO_2 emission reduction from NG used in the backup boiler	9	77.4 – 126.6 $€_{2019}/kW_e$ (Planbureau voor de Leefomgeving (PBL), 2020; Element Energy; Jacob, 2018)	1.4 – 48 $€_{2019}/kW_e$/year (Planbureau voor de Leefomgeving (PBL), 2020; Element Energy; Jacob, 2018)	Electrode boilers have higher capacities (up to 70 MWe) than electric ones. (Berenschot, Matters, Delft, & Matters, 2017). Electric boilers are generally used as flexible capacity (Marsidi,2018). Green electricity prices influence their economic viability.
Hydrogen	Furnaces	100 % of CO_2 emission reduction from NG used in the furnaces	Green hydrogen 6-8 Blue hydrogen 9	0.4-1.2 (mln. € /MWth) (VNPI, 2018)	0.004-0.012 (mln. € /MWth) (VNPI, 2018)	Hydrogen used as fuel for a 10 MWth furnace

Alternative	Process	CO$_2$ emissions (kt)	TRL	CAPEX	OPEX	Comments
	Back up boiler	100 % of emission reduction from NG used in the backup boiler	New boiler: 9 Retrofitted boiler:7 Green hydrogen: 6-8 Blue hydrogen: 9	New boiler: 128 €$_{2019}$/kW$_e$ (Rutten, 2020) Retrofitted boiler: 15 – 21 €$_{2019}$/kW$_e$ (Durusut, et al., 2019)	New boiler: 27 €$_{2019}$/kW$_e$/year (Navigant, 2019) Retrofitted boiler: 3% €$_{2019}$/kW$_e$/year (Durusut, et al., 2019)	Hydrogen application in steam generation to replace natural gas in a gas boiler (Khandelwal and van Dril, 2020)
Biomass	Back up boiler	100 % of CO$_2$ emission reduction from NG used in the backup boiler	9	550 €$_{2019}$ /kWth (Uslu, 2018)	4 €$_{2019}$/KWth (Uslu, 2018)	Sustainable biomass boilers > 5 MWth
Heat pump	Back up boiler Distillation columns Thermal converter	100 % of CO$_2$ emission reduction from NG used in the backup boiler Energy efficiency during the separation process by using heat integration (HIDiC) Heat recovery from the thermal converter	9 (heat pumps around 90 °C) 4-5 (heat pumps above 160 °C)	800-2,000 €$_{2019}$/ KWth (up to 90 °C) 2,000-5,000 €$_{2019}$/KWth (up to 140 °C) (Noothout et al. 2019)	0.06 €$_{2019}$/ KWth (Marsidi,2018)	Costs are for heat pumps up to 90 °C Capex includes installation and grid connection costs

Alternative	Process	CO_2 emissions (kt)	TRL	CAPEX	OPEX	Comments
CCS	All current stacks	Up to 90% of CO_2 emissions reduction	7	75.3 million € (PBL, 2019)	Fixed: 1.5 million €/yr Variable: 23.3 €/tonne CO_2 (PBL, 2019)	CAPEX of CO_2 capture and connection (0.16 Mt CO_2/yr)
CCU	All current stacks. CO_2 based production of POM	Up to 90% of CO_2 emissions reduction from POM production 90% of CO_2 emissions reduction from methanol production	7	1-3 million € (Utilization of CO_2) (European Commission, 2019)		Investment for a pilot plant
Process efficiency	Residual gases sent to the incineration furnace	NA	9	NA	NA	Process parameters determine the selectivity of formaldehyde reaction, so the level of emissions of CO_2 depends on that. Through process efficiency in the formox process, some emissions can be reduced. By decreasing the residual gas production, the CO_2 emissions from burning them reduce.
Biobased feedstock	Methanol substitution using biomethanol	NA	7	NA	NA	These emissions are not direct. However, it is important to include the fossil fuel based feedstock alternatives
Recycling	Mechanical recycling Chemical recycling to produce high-value products (cyclic acetals)	NA	Mechanical recycling 9 Chemical recycling 3-4	NA	NA	These emissions are no direct emissions.

By replacing the furnace and the steam boiler natural gas consumption with electricity from renewable sources or green hydrogen, the CO_2 emission reduction would be around 53%. However, because of its TRL, furnace electrification would be possible only in the long-term. Moreover, even though electric furnaces are expected to have higher efficiencies, they generate less excess heat (De Pee et al., 2018). Less residual heat would have implications for DuPont processes, which, as mentioned, are highly integrated.

By fuel substitution, the remaining emissions would be approximately 15 kt/year, basically from the combustion of residual process gases in the furnace and the ECS unit.

As in the case of Chemours, from a long-term perspective, the steam supply should include alternatives beyond HVC.

4.8.3 Dow reduction alternatives

As explained in section 2.3, the Dow processes taking place in the Dordrecht site do not have high CO_2 emissions (i.e., not above 5 kt), and most of the energy consumption comes from electricity. Thus, the main potential for decarbonisation, from a long term perspective, comes from the steam supply, biobased feedstocks, and recycling of copolymers.

Dow processes in Dordrecht are already highly dependent on electricity; thus, a scope two decarbonisation by reducing its electricity-related carbon emissions could also be an option. Although electricity production is not under the scope of this report, as mentioned, reducing these emissions has a significant influence on Dordrecht processes decarbonisation.

Dow foremost opportunity is associated with the steam supply. Currently, the Dow steam supply comes from Chemours; thus, the main changes would rely on Chemours steam production.

5 Discussion

Through this research, a detailed assessment of the processes of the three companies located in the Dordrecht industrial cluster, Chemours, DuPont, and Dow, was developed. It was carried out to quantify the main GHG emissions and their main sources, energy consumption, and the processes' most energy-intensive steps. Subsequently, the main alternatives are suggested to reduce emissions and energy consumption.

The decarbonisation alternatives explored for Dordrecht chemical site are based on the processes assessment and also on the available options to reduce energy consumption and GHG emissions from previous studies. Implementing the alternatives described in this report can lead to a decrease from 90 to 100% in GHG emissions from the Dordrecht site by combining options that use carbon-free and sustainable energy sources, like carbon-free electricity, green hydrogen, and sustainable biomass[37]. By using biobased feedstock and CCS on the process emissions, the reduction could be more than 100% of GHG emissions.

Figure 19 shows a representation of the time horizon for the full-scale implementation for the different alternatives included in this report, based on its TRL. In the case of bio-based feedstock, even though this category includes various technologies and products, as an average, the industrial-scale implementation would be in the range of 2030 to 2040.

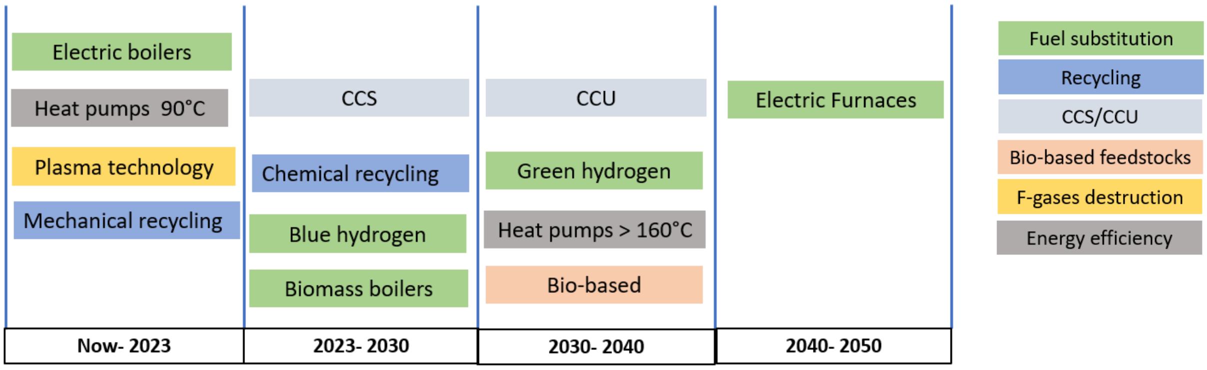


Figure 18 Industrial-scale implementation timeframe for the different decarbonisation alternatives (adapted from VNCI, 2018)

F-gases emission

Because of the nature of the processes taking place in the Dordrecht industrial cluster, some emissions are unavoidable such as the F-gases from Chemours operations. The quantity of HFC-23 produced depends directly on the process conditions, such as temperature, pressure, mix ratios, amount of catalyst, and then, on the process optimization. In the most optimized processes, the emissions of HFC-23 are between 1.5% and 3% of the HCFC-22 production. Chemours has already optimized the emissions of HFC-23, and its efficiency has been a referral point for clean development mechanism (CDM) projects in developing countries (McCulloch, 2004).

---

[37] It is still under debate if biomass would be a long-term sustainable alternative fuel for electricity/heat production in The Netherlands

Nevertheless, there are some additional improvements opportunities related to diffuse emissions of other F-gases, such as the blending of refrigerants and during the plant's planned shutdowns. Monitoring and mitigation strategies are determinants to control and reduce F-gases emissions.

Because of the F-gases' high global warming potential (12,400 tonne CO_2-eq per tonne of HFC-23), the emission of even small amounts of gases has a significant impact. Therefore, final destruction technologies are the more relevant alternative. These technologies can reduce emissions considerably by increasing the efficiency of the ones already in place, such as the thermal converter, or implementing new technologies, like the plasma technology. Although plasma has been implemented in some industrial facilities, its implementation may be limited by its costs.

CO_2 emissions

The CO_2 emissions at Dordrecht come from two main categories: Process emissions and natural gas combustion. Process emissions are from the oxidation of DuPont formaldehyde production off-gases and the incineration of liquid and residual gases from the POM production. These emissions can also be reduced by process optimization and technology innovation.

Besides process emissions, the Dordrecht site's decarbonisation relies mainly on fuel substitution. The processes taking place at this industrial site are highly energy-intensive, and their main CO_2 emissions source is the combustion of natural gas to operate furnaces and boilers. The cooperation agreement with HVC lowered on-site steam production-related emissions in the past years. Nonetheless, other steam production alternatives should be considered in a future circular economy.

Heat supply

Due to its high TRL, electric boilers and hybrid boilers with electricity and natural gas are suitable for reducing CO_2 emissions in the short term. Both technologies are intended for low and medium-temperature heat applications. It is expected that electric boilers have similar efficiency as conventional gas-based ones (De Pee et al., 2018). However, besides innovation, it is essential to consider two factors that will facilitate its implementation: broader participation of renewables in the electricity mix and lower electricity prices. According to electricity suppliers in The Netherlands, renewable electricity prices are higher than non-renewable. This price difference affects the costs and the attractiveness of this alternative. Thus, a good option could be a hybrid boiler, which combines an electrode boiler and gas boiler to switch according to electricity prices (Berenschot, 2017). Hybrid boilers are more flexible and can balance its capacity, supporting the intermittencies of renewables to the grid (De Pee et al., 2018).

Hydrogen boilers are also an option to substitute natural gas for low-and-medium-temperatures heat. The Dordrecht natural gas backup boilers could be retrofitted to use hydrogen as a fuel.

If renewables prices decrease, carbon-free electricity and hydrogen would have lower costs than CCS technology. Moreover, reducing capital equipment or innovations costs can increase carbon-free electricity and hydrogen's economic feasibility at higher electricity prices (De Pee et al., 2018).

Regarding electric furnaces, there are still some technical limitations to implementing this alternative in high-temperature furnaces, like the ones of pyrolysis and incineration used in the Dordrecht site. Therefore, this is a long-term alternative. Moreover, because of the high

DuPont process integration, any change in a specific part of the process would affect the other parts. The incineration furnace generates high amounts of steam to supply other processes. Downstream processes that are dependent on its residual steam would have to be adjusted. This fact also applies to hydrogen furnaces.

Heat pumps are also a recommended option for some of the processes taking place at Dordrecht. Given that electric heat pumps are several times more efficient than boilers (De Pee et al., 2018), this could be a suitable option for low-temperature heat applications. Likewise, heat pumps could be applied in the thermal converter of Chemours for heat recovery, and in the form of Heat Integration in Distillation Columns (HIDiC) for the distillation columns used in the separation processes of Chemours.

CCUS

CCUS is another of the Dordrecht site alternatives to capture CO_2 from all the current stacks, which can possibly reduce around 90% of the emissions. This technology could be the lowest-cost option at the current high prices of renewable electricity. Nonetheless, CCS implementation requires available carbon-storage locations. In The Netherlands, CO_2 storage underground (onshore) is not allowed; thus, as part of the PORTHOS project, storage would be offshore, under the North Sea.

Besides, social support is crucial. In 2010, in Barendrecht, a city close to Dordrecht, the first CCS project underground was cancelled due mainly to social pressures. The main barriers are still related to the clarity of the potential future liabilities for CO_2 underground storage (van Cappellen, 2018). Scalability is also a relevant aspect; therefore, higher amounts of CO_2, above 50 kts CO_2/year, from a single cluster, as in Dordrecht's case, increase its feasibility (van Cappellen et al.,2018). Additionally, the HVC plant, adjacent to the Dordrecht site, could apply CCS to capture CO_2 from its incineration processes.

Beyond CCS and aligned with a circular economy, CCU can increase the circularity of carbon (De Pee et al., 2018). Although some criticism has emerged to CCU processes energy consumption, the reduction of GHG emissions from carbon utilisation seems to offset the energy increase in the carbon-based POM production, which is relevant for DuPont production.

Feedstock options

Feedstock substitution is also an alternative, which should be included for processes that imply the use of fossil fuel-based raw materials. In the case of Dupont POM production, the use of biomethanol is an option. Nevertheless, there are still limitations in terms of economic feasibility. The production costs of biomethanol or renewable methanol (from CO_2 and hydrogen) are higher than conventional methanol production. In the case of Dow copolymers of ethylene, the use of biobased acrylic acid is an option already explored by Dow. Similarly, there are still barriers to scale up its production at the industrial level. It is necessary that the demand for biobased products increases.

In terms of recycling, although the initiatives of Chemours, DuPont, and Dow to this respect are usually managed by global R&D and not at Dordrecht, it is important to include this alternative. Recycling is aligned with the future circular economy and implies reducing energy and feedstock consumption.

References

Abdelaziz, O., Booten, C., Mann, M., & Nicholson, S. (2020, February). *Refrigerants: Market Trends and Supply Chain Assessment* (Tech.). Retrieved May 20, 2020, from CEMAC, Clean Energy Manufacturing Analysis Center website: https://www.nrel.gov/

Albul, A. (2014) Combined cycle gas turbine efficiency enhancement using heat pumps for thermal power plants. The International Gas Union Research Conference 2014 Proceedings, Copenhagen, Denmark. Retrieved from http://members.igu.org/old/IGU%20Events/igrc/igrc-2014/papers/to6-2_albul.pdf

Andersson, A., Holmberg, J., & Häggblad, R. (2016). Process Improvements in Methanol Oxidation to Formaldehyde: Application and Catalyst Development. *Topics in Catalysis, 59*(17-18), 1589-1599. doi:10.1007/s11244-016-0680-1

Ahner, J., Bode, S., Micheel, M., Dietzek, B., and Hager, B. (2008). *Self-Healing Functional Polymeric Materials*. In Self-Healing Materials. Hager, D., Zwaag, S. and Schubert, U. (Eds.) Springer Netherlands.

Ahuja, K. and Singh, S. (2018). Fluorochemicals Market Size By Product (Fluorocarbon [HCFC, HFC, HFO], Inorganics & Specialties, Fluoropolymer), By Application (Refrigerant, Aluminum Production, Blowing Agent, Components & Others), Industry Analysis Report, Regional Outlook, Application Potential, Competitive Market Share & Forecast, 2018 – 2024. Global Market Insights.

Ali, S., Ji, Y., Zhang, Q., Zhao, H., Chen, W., Wang, D., . . . Li, L. (2019). Preparation of Polyethylene and Ethylene/Methacrylic Acid Copolymer Blend Films with Tunable Surface Properties through Manipulating Processing Parameters during Film Blowing. *Polymers, 11*(10), 1565. doi:10.3390/polym11101565

Bahmanpour, A. M., Hoadley, A., & Tanksale, A. (2014). Critical review and exergy analysis of formaldehyde production processes. *Reviews in Chemical Engineering, 30*(6). doi:10.1515/revce-2014-0022

Basile, G., Santacesaria, E., Di Serio, M., Carra, S. (1989). *Kinetics Of Chloroform Fluorination By Hf Catalyzed By Anti- Mony Pentachloride*. Journal of Fluorine Chemistry, 44. pp 87-111

Berenschot, CE Delft, & ISPT. (2015). POWER TO PRODUCTS. Retrieved from https://www.topsectorenergie.nl/sites/default/files/uploads/Eindrapport_Power_to_Prod ucts_externe_link.pdf

Berenschot, Ouden, B. Den, Lintmeijer, N., Van, J., Ce, A., Maarten, D., … Grift, J. (2017). *Electrification in the Dutch process industry In-depth study of promising transition pathways and innovation opportunities for electrification in the Dutch process industry*. Retrieved from http://www.ispt.eu/media/Electrification-in-the-Dutch-process-industryfinal-report-DEF_LR.pdf

Berghout, N., Kuramochi, T., Broek, M., & Faaij, A. (2015). Techno-economic performance and spatial footprint of infrastructure configurations for large scale CO_2 capture in industrial zones. A case study for the Rotterdam Botlek area (part A). *International Journal of Greenhouse Gas Control, 39*, 256-284.

Beydoun, K., & Klankermayer, J. (2020). Efficient Plastic Waste Recycling to Value-Added Products by Integrated Biomass Processing. *ChemSusChem, 13*(3), 488-492. doi:10.1002/cssc.201902880

Block, T., Palacios, S., & van Dril, T. (2020). Decarbonisation Options For Large Volume Organic Chemical Production, Shell Nederland Chemie Pernis Site. PBL & TNO, in preparation.

Bozzano, G., & Manenti, F. (2016). Efficient methanol synthesis: Perspectives, technologies and optimization strategies. *Progress in Energy and Combustion Science, 56*, 71-105. doi:10.1016/j.pecs.2016.06.001

Boulamanti, A., & Moya, J. A. (2017). Production costs of the chemical industry in the EU and other countries: Ammonia, methanol and light olefins. *Renewable and Sustainable Energy Reviews, 68*, 1205-1212. doi:10.1016/j.rser.2016.02.021

Bruinsma, O., and Spoelstra, S. (2010). Heat pumps in distillation. Energy Research Centre of The Netherlands (ECN). The Netherlands

Bui, M., Adjiman, C. S., Bardow, A., Anthony, E. J., Boston, A., Brown, S., . . . Dowell, N. M. (2018). Carbon capture and storage (CCS): The way forward. Energy & Environmental Science, 11(5), 1062-1176. doi:10.1039/c7ee02342a

Burenraad DuPont and Chemours (2020) DuPont and Chemours neighborhood council. Retrieved in May 12, 2020, from https://www.burenraad.nl/

Burenraad DuPont and Chemours (2018). Report of the Buren Council DuPont and Chemours meeting, 12 March 2019. (*Verslag vergadering Burenraad DuPont en Chemours, 12 maart 2019*) Retrieved in May 12, 2020, from https://www.burenraad.nl/

CBS (2020). *Goederensoorten naar land; minerale brandstoffen en chemie.* Retrieved in April 23, 2020 from https://opendata.cbs.nl/statline/#/CBS/nl/dataset/81268ned/table

Chavda, E. (2020). *Europe methanol spot prices firm but remain at fou-year lows.* Retrieved from https://www.icis.com/explore/resources/news/2020/04/20/10498138/europe-methanol-spot-prices-firm-but-remain-at-four-year-lows

Chen, S., Živný, O., Mašláni, A., & Chau, S. (2019). Abatement of fluorinated compounds in thermal plasma flow. *Journal of Fluorine Chemistry, 217*, 41-49. doi:10.1016/j.jfluchem.2018.10.004

Chemours (2018). Chemours energy overview 2018.

Chinoy, P. B., & Sunavala, P. D. (1987). Thermodynamics and kinetics for the manufacture of tetrafluoroethylene by the pyrolysis of chlorodifluoromethane. *Industrial & Engineering Chemistry Research, 26*(7), 1340-1344. doi:10.1021/ie00067a013

Christmas, M., & Dimitratos, Y. (2008). *U.S. Patent No. US 2008/0194779 A1*. Washington, DC: U.S. Patent and Trademark Office.

Dams, R., & Hintzer, K. (2017). Industrial aspects of fluorinated oligomers and polymers. In B. Améduri and H. Sawada (Eds), Fluorinated polymers (Vol. 2). Cambridge: Royal Society of Chemistry. doi:10.1039/9781782629368-00001

Dechema E.V. (2017). *Low carbon energy and feedstock for the European chemical industry*. Frankfurt: DECHEMA e.V

Dian, G. C. (2004). Chain copolymerization. In *Principles Of Polymerization* (pp. 465-530). Hoboken, NJ: JOHN WILEY & Sons.

DNV, 2017. Biomassapotentieel in Nederland. Verkennende studie naar vrij beschikbaar biomassapotentieel voor energieopwekking in Nederland. Paula Schulze, Johan Holstein, Harm Vlap. CS.17.R.10032629.2

Dordrecht regional archives. (2020). *(Regionaal Archief Dordrecht)* Retrieved May 20, 2020 from https://www.regionaalarchiefdordrecht.nl/english/

Dordt Duurzaam (2016). *Samenwerking HVC en Chemours levert forse verduurzaming Dordrecht op* [Cooperation HVC and Chemours provides substantial sustainability Dordrecht]. Retrieved from https://www.dordtduurzaam.nl/actueel/oude-nieuwsberichten/february-2016/samenwerking-hvc-en-chemours-levert-forse-verduurzaming-dordrecht-op

Drobny, J. G. (2009). *Technology of fluoropolymers* (Second ed.). Boca Raton, FL: CRC Press.

DuPont (2018). DuPont milieuvergunning 2018.

Dow (2020a). Dow in the Benelux. Retrieved from https://nl.dow.com/nl-nl.html

Dow (2020b). *Product Catalog: Portfolio of products and solutions.* Retrieved July 30, 2020 from https://www.dow.com/en-us/product-catalog.html

DuPont (2017). DuPont Insight (DuPont Inzicht). Retrieved May 12, 2020 from www.dupontdordrecht.info

DuPont (2020a). History. More than 50 years of DuPont in Dordrecht. Retrieved May 09, 2020, from https://www.dupontdordrecht.info/dupont-dordrecht/

DuPont (2020b). Onze vestigingen in Nederlan (Our offices in The Netherlands). Retrieved from https://www.dupontnederland.nl/

DuPont (2020c). Telephonic interview. October 20 2020.

Durusut, E., Mattos, A., Simon, R., Moore, I., Kiely, C., Yousid, S., . . . Giles, A. (2019). *Conversion of Industrial Heating Equipment to Hydrogen.*

E4tech & Energy, Development of water electrolysis in the European Union, 2014.

Ebnesajjad, S. (2015). *Fluoroplastics* (Second ed., Vol. 1, PDL Handbook series). Waltham, MA: Elsevier. doi:10.1016/B978-1-4557-3199-2.00003-3

ECN (2017). Dutch program for the acceleration of sustainable heat management in industry.

Ecodesign (2014). Preparatory Study on Steam Boilers, PwC, Fraunhofer ISI and ICCS-NTUA.

Elektronisch Milieujaarverslag (2018). *Chemours Netherlands B.V.*

Elliott, A., Sowerby, B., & Crittenden, B. (1996). Quantitative environmental impact analysis for clean design. *Computers & Chemical Engineering, 20*. doi:10.1016/0098-1354(96)00236-0

Ellis, V. (2019). *Europe methanol enters age of mega plants and shocks*. Retrieved from https://www.icis.com/explore/resources/news/2019/01/11/10305041/europe-methanol-enters-age-of-mega-plants-and-shocks/

Element Energy; Jacob. (2018). *Industrial Fuel Switching Market Engagement Study.*

Environmental Investigation Agency (2013). The Two Billion tonne Climate Bomb: How to Defuse the HFC-23 Problem. Retrieved from https://issuu.com/eia1984/docs/eia_hfc-23_report_0613_final

Eurofluor, Comité Technique Européen du Fluor (2019). EUROFLUOR HF A snapshot of the fluorine industry. Fourth edition. Cefic. Retrieved June 02, 2020 from www.eurofluor.org

European Commission (2015) *F-Gas Regulation (Regulation (EU) No 517/2014): Technical Advice to Member States on implementing Article 7(2). Discussion Paper.* Retrieved from https://ec.europa.eu/clima/sites/clima/files/f-gas/docs/151023_hfc23_by-production_en.pdf

European Commission (2019). *Identification and analysis of promising carbon capture and utilisation technologies, including their regulatory aspects.* Brussels: Ramboll, the Institute for Advanced Sustainability Studies, CESR – Center for Environmental Systems Research at the University of Kassel, CE Delft, and IOM Law.

Evangelopoulou, S., De Vita, A., Zazias, G., & Capros, P. (2019). Energy System Modelling of Carbon-Neutral Hydrogen as an Enabler of Sectoral Integration within a Decarbonisation Pathway. Energies, 12(13), 2551. doi:10.3390/en12132551

Executive Committee Of The Multilateral Fund For The Implementation Of The Montreal Protocol (2018). *Cost-Effective Options For Controlling Hfc-23 By-Product Emissions (Decision 81/68(E))* Retrieved from http://multilateralfund.org/82/English/1/8268.pdf

Ferrero, F., and Shanton, M. (2017). *Guide for the Safe Handling of Tetrafluoroethylene.* PlasticsEurope. Retrieved April 29, 2020 from https://www.researchgate.net/publication/324780228_Guide_for_the_Safe_Handling_of_Tetrafluoroethylene

Gammelgaard, E. (2018). *Monolithic Pt & Pd catalyst Method for development of Pt & Pd monolithic catalyst in FORMOX™ ECS unit.* Johnsson Matthey. Retrieved from http://lup.lub.lu.se/luur/download?func=downloadFile&recordOId=8962987&fileOId=8962989

German Association for Semi-finished Plastics and Consumer Products. Fluoropolymers group (2017) Fluoropolymers: German industry association expects price hikes for PTFE / Capacity shortage in China. Retrieved May 27, 2020 from https://www.plasteurope.com/news/FLUOROPOLYMERS_t236919/

Graphical Research Report (2019). *Europe Polyoxymethylene (POM) Market Size By Type, By Application, By Industry, Analysis Report, Regional Outlook (Germany, France, Italy, Spain, Russia), Growth Potential, Price Trends, Competitive Market Share & Forecast, 2019 – 2024* Retrieved from https://www.graphicalresearch.com/industry-insights/1241/europe-polyoxymethylene-market

Grand View Research (2017). *Ethylene Copolymers Market Size, Share & Trends Analysis Report By Application (Hot Melt Adhesives, Asphalt Modification, Thermo Adhesive Films), By Type (Ethylene-Vinyl Acetate, Ethylene Ethyl Acrylate), By End-use, And Segment Forecasts, 2018 – 2025.* Retrieved from https://www.grandviewresearch.com/industry-analysis/ethylene-copolymers-market

Hart, D., Howes, J., Lehner, F., Dodds, P., Hughes, N., Fais, B., . . . Crowther, M. (2015). *Scenarios for deployment of hydrogen in contributing to meeting carbon budgets and the 2050 target.*

Heberlein, J., & Murphy, A. B. (2008). Thermal plasma waste treatment. *Journal of Physics D: Applied Physics, 41*(5), 053001. doi:10.1088/0022-3727/41/5/053001

Heim, L. E., Konnerth, H., & Prechtl, M. H. (2017). Future perspectives for formaldehyde: Pathways for reductive synthesis and energy storage. Green Chemistry, 19(10), 2347-2355. doi:10.1039/c6gc03093a

Hong, S., Jie, Y., Li, X., and Liu, N. (2019). China’s chemical industry: New strategies for a new era. McKinsey & Company.

Hintzer, K. and Schwertfeger, W. (2014). Fluoropolymers-Environmental aspects. In D.W Smith, S.T. Iacono and S.S. Iyer (Eds.) Handbook of Fluoropolymer Science and Technology (pp 495-516). Hoboken, NJ: Wiley.

IEAGHG. (2007). CO_2 Capture from Medium Scale Combustion Installations.

Isac, S. (2001). *Modification of polyethylene by reactive extrution.*(Doctoral dissertation, Cochin University of Science and Technology, Cochin, India).Retrieved from http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.469.1878&rep=rep1&type=pdf

ICIS. (2002). *Product profile*: Chloroform. Retrieved from https://www.icis.com/explore/resources/news/2002/06/12/174664/product-profile-chloroform/

Industryarc (2020). Ethylene Copolymers Market-Forecast (2020-2025). Retrieved from https://www.industryarc.com/Report/1278/ethylene-copolymers-market-analysis.html

IPCC (2005). Carbon Dioxide Capture and Storage - Summary for Policy makers. Montreal: IPCC.

Irving, W., and Brascombe, M. (2000). *HFC-23 Emissions From HCFC-22 Production.* Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. Retrieved from https://www.ipcc-nggip.iges.or.jp/public/gp/bgp/3_8_HFC-23_HCFC-22_Production.pdf

Ivanov, K. I., & Dimitrov, D. Y. (2009). Methanol Oxidation over Iron-Molybdate Catalysts: Optimization of the Process. Topics in Catalysis, 52(6-7), 813-822. doi:10.1007/s11244-009-9236-y

Leung, D. Y., Caramanna, G., & Maroto-Valer, M. (2014). An overview of current status of carbon dioxide capture and storage technologies. *Renewable and Sustainable Energy Reviews, 39*, 426-443

Lozano, S.(2008). *CDM monitoring report of Quimobásicos HFC Recovery and Decomposition Project.*Cydsa*.* Retrieved from *https://cdm.unfccc.int/Projects/DB/DNV-CUK1138260062.21/iProcess/TUEV-SUED1208518639.81/ReviewInitialComments/21XP4YF04QGLVZU1OMYA2PNGF8IXNE*

Lüftl, S., P.M., V., & Chandran, S. (2014). *Polyoxymethylene handbook: Structure, properties, applications and their nanocomposites*. Hoboken, NJ: John Wiley & Sons.

McCulloch, A. (2005). *Incineration of HFC-23 Waste Streams for Abatement of Emissions from HCFC-22 Production: A Review of Scientific, Technical and Economic Aspects*. Comberbach, England. Marbury Technical Consulting. Retrieved from https://cdm.unfccc.int/methodologies/Background_240305.pdf

Mader, F.W. (1984) European Patent. *0.129.863. B1.* Pennsilvanya Kennett Square. European Patent Office

Markets and Markets Analysis (2014). *Polyoxymethylene Market by Applications and Geography – Trends and Forecasts to 2018.* Retrieved from https://www.marketsandmarkets.com/Market-Reports/polyoxymethylene-market-126414942.html

Marks, S., and Wagner, J.R. (2010). *Introduction*. In Wagner, J. R. (Ed.) Multilayer flexible packaging (1st ed., pp. 3-11). MA: William Andrew.

Marsidi, M. (2018a). *Technology Factsheet Electric Industrial Boiler.* TNO

Marsidi, M. (2018b). *Technology Factsheet Industrial High Temperature Heat Pump.* TNO

Masamoto, J., Matsuzaki, K., & Morishita, H. (1994). Purification of Formaldehyde by Distillation. Journal Of Chemical Engineering Of Japan, 27(1), 12-16. doi:10.1252/jcej.27.12Niaounakis, M. (2020). *Polymers Used in Flexible Packaging*. In Recycling of flexible plastic packaging (pp. 57-86). Oxford: William Andrew, an imprint of Elsevier.

Moore, A. (2006) Flouroelastomers Handbook (William Andrew: Norwich, NY).

Mursics, J., Urbancl, D., & Goricanec, D. (2020). Process of Formaldehyde and Volatile Organic Compounds' Removal from Waste Gases. Applied Sciences, 10(14), 4702. doi:10.3390/app10144702

Navigant, (2019). Verkenning uitbreiding SDE+ met industriële opties

Niaounakis, M. (2020). *Recycling of flexible plastic packaging*. Oxford: William Andrew, an imprint of Elsevier.

Nouryon (2020). Chloroform. Retrieved April 21, 2020 from https://industrialchemicals.nouryon.com/chlorine-derivatives/chloromethanes/chloroform/

Noothout, P.; de Beer, J.; Quant, M.; Blok, K. (2019) Verkenning uitbreiding SDE+ met industriële opties

Odian, G. (2004). Chain Copolymerization. *Principles of Polymerization,* 464-543. doi:10.1002/047147875x.ch6

Olabisi, O., & Adewale, K. (2016). Polyacetals. In *Handbook of thermoplastics* (pp. 201-235). Boca Raton: CRC Press, Taylor & Francis Group.

Oliveira, C., & Schure, K. (2019). Decarbonisation Options for the Dutch Refinery Sector. Den Haag: PBL Netherlands Environmental Assessment Agency.

Pee, A. de, Pinner, D., Roelofsen, O., Somers, K., Speelman, E., & Witteveen, M. (2018, June 10). How industry can move toward a low-carbon future. Retrieved September 25, 2020, from https://www.mckinsey.com/business-functions/sustainability/our-insights/how-industry-can-move-toward-a-low-carbon-future

Plastemart News (2011)*"DuPont Packaging & Industrial Polymers to increase capacity at Dordrecht, Netherlands"* Plastemart news. May 16, 2011. Retrieved from http://www.plastemart.com/news-plastics-information/DuPont-Packaging-Industrial-Polymers-to-increase-capacity-at-Dordrecht-Netherlands/19880

PlasticsEurope.(2018).The Fluoropolymer Industry In Europe. A Socio-Economic Perspective. Association of plastics manufacturers. Fluoropolymers products group. Retrieved May 15, 2020 from https://www.plasticseurope.org/en/resources/publications/465-fluoropolymer-industry-europe

Planbureau voor de Leefomgeving (PBL). (2020). *Eindadvies Basisbedragen SDE++ 2020.*

Plasteurope (2015). *World's first fluoropolymer recycling facility starts operations.* Retrieved from https://www.plasteurope.com/news/DYNEON_t230856/

Port of Rotterdam (2020). *Rotterdam CCUS - Project Porthos:* CO_2 *transport and storage.*

PORTHOS. (2020). *Possible EU subsidy for international* CO_2 *storage cooperation*. Retrieved November 03, from https://www.porthosCO_2.nl/en/possible-eu-subsidy-for-international-CO_2-storage-cooperation/

Poulakis, J. G., & Papaspyrides, C. D. (2000). A model process for the recycling of a Surlyn Ionomer. *Advances in Polymer Technology, 19*(3), 203-209. doi:10.1002/1098-2329(200023)19:33.0.co;2-7

Pramod, C. V., Fauziah, R., Seshan, K., & Lange, J. (2018). Bio-based acrylic acid from sugar via propylene glycol and allyl alcohol. Catalysis Science & Technology, 8(1), 289-296. doi:10.1039/c7cy01416c

Po, M. (2017, August 03). *Industry Update – Introduction of the fluorochemical industry in China*. China Galaxy International. Retrieved from http://www.chinastock.com.hk/ewebeditor/uploadfile/20170803181054854.pdf

Ricardo-AEA (2015). Review of the Reference Values for High-Efficiency Cogeneration. Retrieved from https://ec.europa.eu/energy/sites/ener/files/documents/review_of_reference_values_final_report.pdf

Roelofsen, O., Somers, K., Speelman, E., & Witteveen, M. (2020) Plugging in: What electrification can do for industry. Mckinsey & Company. Retrieved from https://www.mckinsey.com/industries/electric-power-and-natural-gas/our-insights/plugging-in-what-electrification-can-do-for-industry#

Rudin, A., & Choi, P. (2013). Polymer Reaction Engineering. The Elements of Polymer Science & Engineering, 495-520. doi:10.1016/b978-0-12-382178-2.00012-2

Rutten, L. (2020). *Technology Factsheet H2 Industrial boiler.* TNO

Santacesaria, E., Serio, M. D., Basile, G., & Carra, S. (1989). Kinetics of chloroform fluorination by HF catalyzed by antimony pentachloride. *Journal of Fluorine Chemistry, 44*(1), 87-111. doi:10.1016/s0022-1139(00)84373-0

Smith, D., Lacono, S., Lyer, S. (2014). Handbook of Fluoropolymer Science and Technology.

Specialchem (2020). *Ethylene Copolymers in Hot-melt Applications: A Complete Guide.* Retrieved from https://adhesives.specialchem.com/selection-guide/ethylene-copolymers-for-adhesives-and-sealants

Stork, M., Beer, J., Lintmeijer, N., and Ouden., B. (2018). *Chemistry for Climate: Acting on the need for speed. Roadmap for the Dutch Chemical Industry towards 2050*. Utrecht: Ecofys Netherlands B.V. by order of VNCI.

Svensson, C.(2012). Formox one of the "Innovative energy use award" finalists. Formalin technology & catalysts. Perstorp. Retrieved from https://www.perstorp.com/en/news_center/news/2012/20121023_formox_one_of_the_innovative/

Sykutera, D., and Czyżewski, P.(2012) *Recycling Abilities Of Thermoplastic Ionomers, As Examplified By Surlyn.* Journal of Polish CIMAC. Retrieved from http://www.polishcimeeac.pl/Papers3/2012/040.pdf

Tanny, S. (2010). *Adhesives, Extrudable*. In Yam, K. L. (Ed.) The Wiley encyclopedia of packaging technology (3rd ed., pp. 22-24). S.l.: Wiley Online Library.

Teng, H. (2012). Overview of the Development of the Fluoropolymer Industry. Applied Sciences, 2(2), 496–512. doi: 10.3390/app20204

TNO (2019). H- Vision - Blue hydrogen as accelerator and pioneer for energy transition in the Industry. Rotterdam: Deltalinqs/TNO

Transparencymarketresearch (2020). Ethylene Acrylic Acid (EAA) Copolymers Market - Global Industry Analysis, Size, Share, Growth, Trends, and Forecast 2018 – 2026. Retrieved from https://www.transparencymarketresearch.com/ethylene-acrylic-acid-copolymers-market.html

Trends Market Research. (2020, May 05) *Fluoropolymer Market Growth Forecast Analysis by Manufacturers, Regions, Type and Application*. (press release). Retrieved April 10, 2020 from https://www.marketwatch.com/

Tretyakova, P. (2017). The effectiveness of heat pumps as part of CCGT-190/220 Tyumen CHP-1. *MATEC Web of Conferences, 106*, 06017. doi:10.1051/matecconf/201710606017

Uslu, A. (2018). *Biomass Steam Boiler For Industry > 5 Mwth.* Technology Factsheet. ECN-TNO.

Van Cappellen, L., Croezen, H., & Rooijers, H. (2018, July). Feasibility study into blue hydrogen. Retrieved September 28, 2020, from https://www.cedelft.eu/en/publications/2149/feasibility-study-into-bleu-hydrogen

VNP (2018). Decarbonising the steam supply of the Dutch paper and board industry.

VNPI, DNV-GL (2018). CO_2 Reductie Roadmap van de Nederlandse raffinaderijen

Wells, G. M. (2020). Formaldehyde. In Handbook Of Petrochemicals And Processes. S.L.: Routledge.Wilson, S., Carlson, A., & Szeman, I. (2017). Petrocultures: Oil, politics, culture. Montreal, Wuebec: McGill-Queen's University Press.

Willson, A. (2012). Latest News DuPont and Invista settlement. Retrieved from https://www.nonwovensnews.com/news/11441-koch

Zion Research Analysis. (2017, January 03). *Fluoropolymer Market by Types (PTFE, PVDF, FEP, and Fluoroelastomers), for Automotive & Transportation, Electrical & Electronics, Chemical Processing, and Industrial Equipment Applications – Global Industry Perspective, Comprehensive Analysis and Forecast 2016 – 2022*. Zion Market Research. (press release). Retrieved from https://www.zionmarketresearch.com/market-analysis/fluoropolymer-market

Appendix A Value chains

1. Fluoropolymers value chain

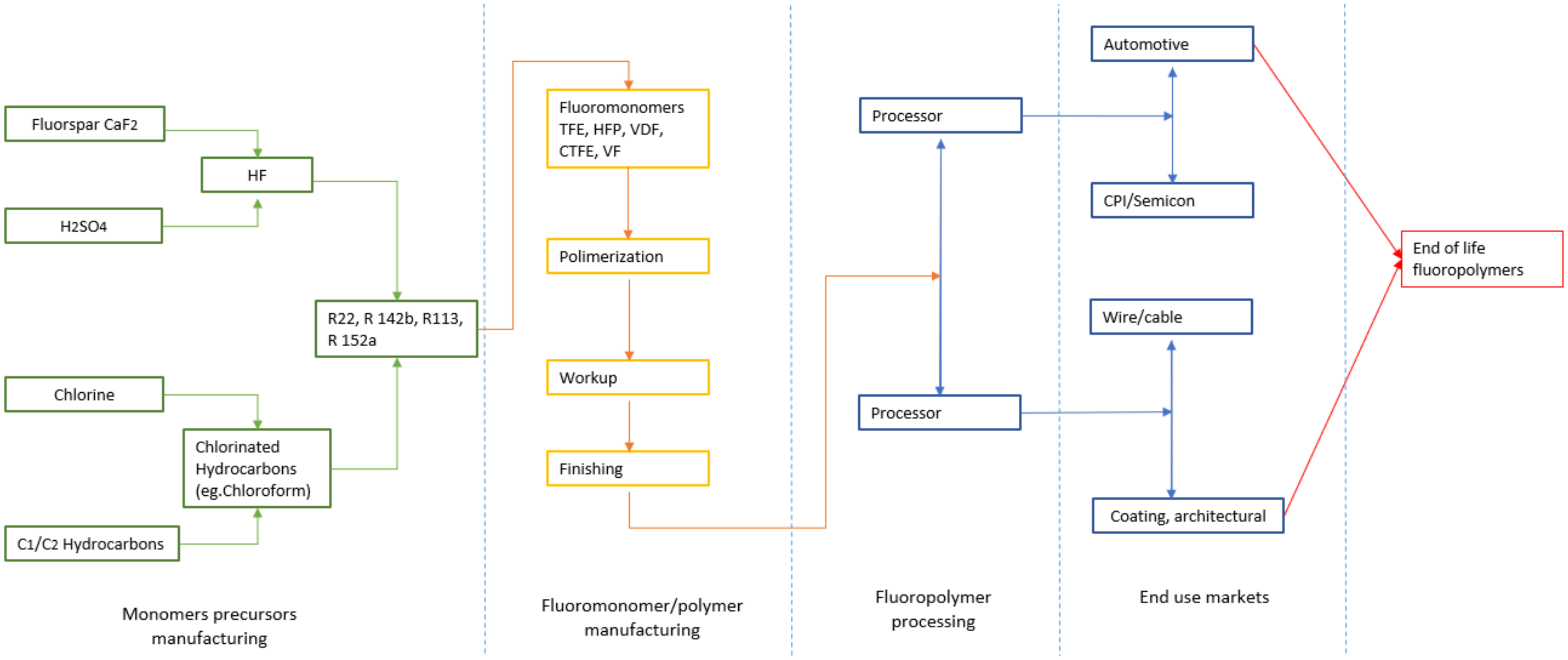


Figure 19 Fluoropolymers Value Chain

2. POM value chain

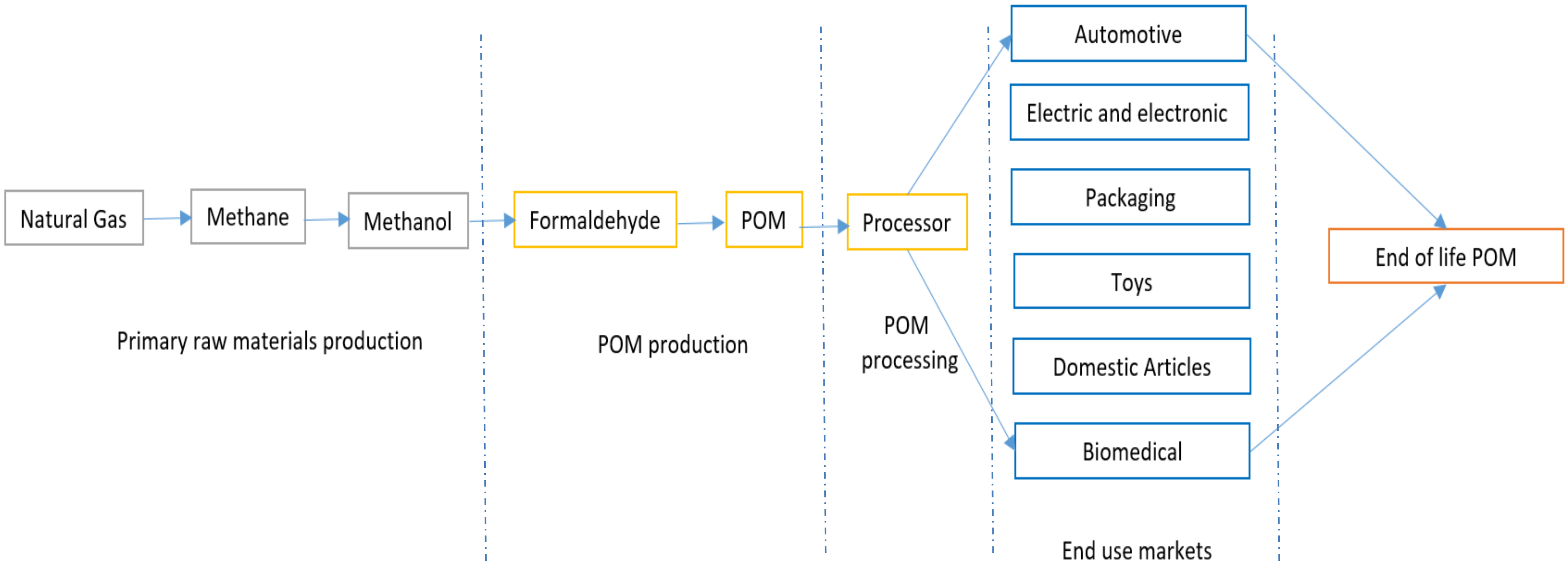


Figure 20 POM Value Chain