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DECARBONISATION OPTIONS FOR THE DUTCH INDUSTRIAL GASES PRODUCTION

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Manufacturing Industry Decarbonisation Data Exchange Network

Decarbonisation options for the Dutch industrial gases production

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MIDDEN project coordination and responsibility

The MIDDEN project (Manufacturing Industry Decarbonisation Data Exchange Network) was initiated and is also coordinated and funded by PBL and TNO. 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 (TNO), Silvana.Gamboa@tno.nl.

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This report was reviewed by Air Products and Air Liquide. PBL and TNO remain responsible for the content. The decarbonisation options and parameters are explicitly not verified by the companies.

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FINDINGS

Summary

The industrial gases (hydrogen, oxygen, nitrogen, argon, carbon monoxide) sector produces widely adopted commodity chemicals that are used in many industrial sectors. In this report we discuss the production processes of hydrogen, nitrogen, oxygen and argon, and focus on decarbonisation options for hydrogen. The production of oxygen, nitrogen and argon is powered by electricity, and does therefore not generate direct carbon emissions.

Hydrogen and carbon monoxide

In the Netherlands, most of the hydrogen is produced by refineries and chemical companies for own use on-site. This 'captive' hydrogen production is described in the MIDDEN reports related to these specific industries. Only two EU ETS registered companies are primarily dedicated to the production of hydrogen: Air Liquide Industrie B.V. (Air Liquide) and Air Products Nederland B.V. (Air Products). The scope of the hydrogen production in this report is these 'merchant' gas producers. The hydrogen is sold mostly to refineries and chemical industry companies in The Netherlands.

The sites of Air Liquide and Air Products have a combined capacity of about 260 kilotonnes (kt) of produced hydrogen per year (excluding hydrogen present in gas mixtures such as syngas) and generate about 1.6 million tonnes (Mt) direct CO₂ emissions. Air Liquide has hydrogen production facilities located in the Botlek area and in Bergen op Zoom. Additionally, Air Liquide operates several energy production facilities in the Rotterdam Botlek area and delivers steam to various (chemical) industry companies. Air Products produces hydrogen in the Botlek area.

Hydrogen and carbon monoxide (CO) are produced mainly by steam methane reforming (SMR), delivering, depending which product is required, pure hydrogen, pure carbon monoxide or syngas which is composed mainly by CO and hydrogen. In this process, natural gas is used both as feedstock and fuel. Natural gas as a feedstock is catalytically reformed, with the addition of steam, into synthetic gas, or syngas. It is an energy-intensive process due to the fact that it is a highly endothermic reaction, and its energy demand is supplied by the combustion of natural gas (or refinery gas) as fuel. CO and hydrogen can be separated from the syngas and purified. Another hydrogen production process applied in the Netherlands and described in this report is autothermal reforming (ATR).

Decarbonisation options for the hydrogen production industry in this report are focused on four main types of technology. Firstly, hydrogen can be produced by electrolysis of water, which, when using renewable electricity, is referred to as green hydrogen. The production of green hydrogen by electrolysis depends mainly on the availability of renewable electricity, prices of electricity, and capital and operational costs for the required electrolyzers. Secondly, hydrogen can be produced using various types of biomass. Currently, the available capacity for sustainable biomass in the Netherlands is estimated between 27-75% of the hydrogen production demand for these applications. Thirdly, an alternative hydrogen production process is that of thermal methane decomposition, which produces also carbon black. Finally, the adoption of carbon capture technology and storage (CCS) in combination with current hydrogen production technologies results in the production of low-carbon hydrogen, which in the Netherlands is also referred to as blue hydrogen.

Oxygen, nitrogen and argon

Oxygen, nitrogen and argon are typically produced on a large-scale with the cryogenic distillation process. This technology is based on the liquefaction of atmospheric air in order to separate, through multi-column distillation, the different components that have a different boiling point. In such an air separation unit (ASU), the air compression step is estimated the most energy-intensive. The process is fully electric and the decarbonisation of the production of oxygen, nitrogen and argon is therefore relying on the decarbonisation of the electricity production.

Air Liquide, Air Products, Linde Gas and Gasunie own air separation units, which are located in industrial areas such as Rotterdam, Terneuzen and IJmuiden, as well as close to natural gas extraction locations in the northeast of The Netherlands.

FULL RESULTS

Introduction

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

Scope

This report will focus on the production of industrial gases in the Netherlands.

Main production locations include:

- For hydrogen (H₂), carbon monoxide (CO) and syngas:
 - Air Liquide Industrie B.V. in the Botlek area (Rotterdam, Zuid-Holland) and in Bergen op Zoom (Noord-Brabant).
 - Air Products Nederland B.V. in the Botlek area (Rotterdam, Zuid-Holland).
- For nitrogen (N₂), oxygen (O₂), and argon (Ar):
 - Air Liquide in Terneuzen (Zeeland).
 - Linde Gas Benelux B.V. at TATA Steel's site in Velsen-Noord.
 - Air Products in De Wijk.
 - Gasunie in Ommen and Zuidbroek.

Processes include:

- For hydrogen, CO and syngas production: Steam Methane Reforming (SMR) and Autothermal Reforming (ATR).
- For nitrogen, oxygen and argon production: Cryogenic Distillation Air Separation Unit (cryo ASU).

The main decarbonisation options (all related to hydrogen, CO and syngas production) are:

- Carbon Capture Utilisation and Storage (CCUS),
- Hydrogen from biomass,
- Biogas reforming,
- Water electrolysis,
- Thermal Decomposition of Methane.

Reading guide

Chapter 1 gives a general introduction to the industrial gases production industry in the Netherlands and describes the relevant actors involved in this sector. In chapter 2 we describe the current situation of industrial gases production processes in the Netherlands and in chapter 3 we describe the relevant products to these processes. Options for decarbonisation are systematically quantified and evaluated in chapter 4. The feasibility and requirements of those decarbonisation options are discussed in chapter 5.

1 Industrial gas production

1.1 Introduction to the industrial gases industry in the Netherlands

Industrial gases (hydrogen, oxygen, nitrogen, argon, carbon monoxide) are among the most widely adopted commodity chemicals since they are used in many industrial sectors. In 2008, the global industrial gases market reached a turnover of USD 52 billion (33 billion EUR) within production and consumption in the steel industry, chemical and pharmaceutical industries, electronic devices, solar cells, glass and food. The Dutch industrial gas market is highly dominated by a few major players that produce the largest share of the market volume: Air Liquide, Air Products, Linde AG and Gasunie.

Which companies produce hydrogen in The Netherlands?

The production of hydrogen in Dutch industry is divided over several industrial subsectors: the fertiliser industry, steam cracking, refineries, the biofuels industry and the production of industrial gases itself. Furthermore, hydrogen is also present in fuel gas from steam crackers and coke oven gas. For the purpose of this report, the focus is on the industrial gas producers (producing 'merchant hydrogen': Air Liquide and Air Products). Nevertheless, the decarbonisation options are related to production processes and are (at least partially) also applicable to hydrogen production processes beyond the industrial gas producers. Hydrogen production by the fertiliser industry, the steam crackers, the chlor-alkali industry, the refineries and the biofuels industry ('captive hydrogen' production) is briefly described in the corresponding MIDDEN reports, that can be found at middenweb.nl. On top of that, small volumes of hydrogen are produced at decentralised methane reformers or electrolyzers. Those volumes are estimated to be negligible in comparison to the aforementioned industrial gas producers.

Recent information about the volumes of all hydrogen production in The Netherlands can be found in DNVGL (2019) and Weeda & Segers (2020). Total production of hydrogen within The Netherlands is estimated at 1.5 Mt or about 178 PJ (LHV)¹ in 2019 (DNVGL, 2019; Weeda & Segers, 2020). This number includes hydrogen present in mixture gases. A more detailed breakdown of the hydrogen production in The Netherlands, by feedstock, application or industrial cluster, can be found in Weeda & Segers (2020).

1) Using an energy density of 120 GJ (lower heating value, LHV) per tonne hydrogen.

1.2 Production locations of industrial gases in the Netherlands

1.2.1 Hydrogen and carbon monoxide: Air Liquide and Air Products

The 'merchant' hydrogen producers are active in two main areas: Air Liquide and Air Products in the Botlek area (Rotterdam) and Air Liquide in Bergen op Zoom. The location of the production plants is shown in Figure 1. The hydrogen is mainly used to upgrade refinery products and as feedstock for chemicals production.

The capacities of Air Liquide and Air Products, reported for 2019, are shown in Table 1, with the respective CO₂ emissions retrieved from the NEa database published in 2020. It is important to note that the production capacities describe the potential production capacity of the plants, not necessarily the actual produced amounts.

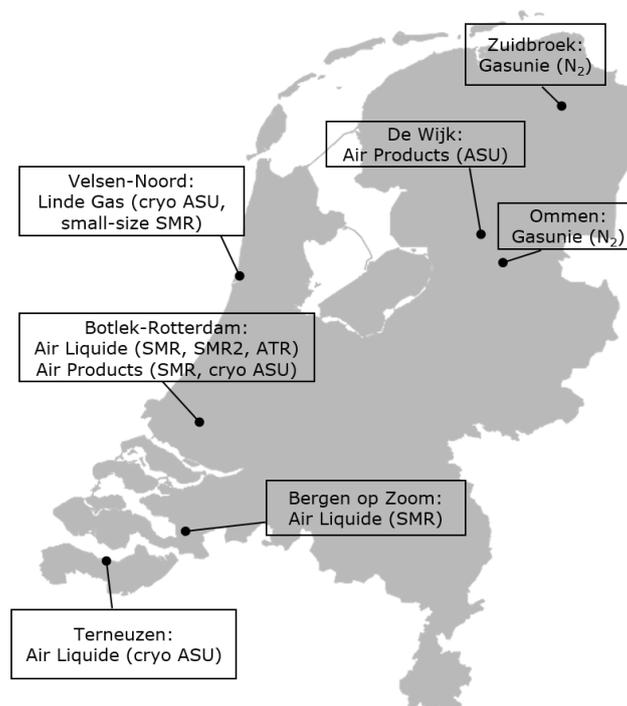


Figure 1 Production locations of the main industrial gas producers in the Netherlands. Abbreviations are explained in Tables 1 and 2.

Table 1 Overview of the EU ETS registered hydrogen production facilities owned by Air Liquide and Air Products in the Netherlands.

Company name (NEa)	Location	Main activity	Capacity [kt/yr]			Direct CO ₂ emission in 2019 (NEa, 2020) [kt/yr]
			H ₂	CO	Syngas	
Air Liquide Nederland B.V. (SMR2)	Botlek-Rotterdam	Steam methane reforming (SMR) with co-production of H ₂ and CO	114 ¹⁾	162 ¹⁾	138 ¹⁾	808
Air Liquide Industrie B.V., vest. Botlek-Rotterdam	Botlek-Rotterdam	Steam methane reforming (SMR) for CO production with H ₂ as by-product	9.5 ³⁾	27-48	-	107 ²⁾
Air Liquide Industrie B.V., vest. Botlek-Rotterdam	Botlek-Rotterdam	Syngas production with H ₂ by-product by autothermal reforming (ATR)	10.7 ⁴⁾	-	71 ³⁾	
Air Liquide Industrie B.V.	Bergen op Zoom	Steam methane reforming with co-production of H ₂ and CO	24.4 ³⁾	68-122	-	112
Air Products Nederland B.V., Locatie Botlek (Botlekweg)	Botlek-Rotterdam	Steam methane reforming for hydrogen production	106 ⁶⁾	-	-	767
Air Products Nederland B.V., Locatie Botlek (Merseyweg)	Botlek-Rotterdam	Steam methane reforming for hydrogen production	- ⁵⁾	-	-	87

- 1) Permit is for 119 kt H₂/yr (SMR, ATR and SMR2) (DCMR, 2009). SMR2 capacity was extended from 130,000 to 145,000 Nm³/hr (which is 114 kt H₂/yr using 0.0899 kg/Nm³ for H₂) (DCMR, 2016). Yearly allowed hydrogen production amounts to 98 kt H₂/yr, which corresponds to a maximum load factor of approximately 7500 hours or 85% given the hourly production value. This is without any CO delivery. Permit is further for 190 kt CO and 162 kt syngas, which translates to 162 kt CO and 138 kt syngas assuming maximum load.
- 2) The emission of these plants (SMR and ATR) is reported together under "Air Liquide Industrie B.V., vest. Botlek-Rotterdam" in emission database (NEa, 2020).
- 3) M. Weeda, personal communication (2019). Capacities may refer to permitted capacities and are not necessarily actual production levels.
- 4) According to Air Liquide H₂ production at full syngas production is 13,583 Nm³/hr. This is 10.7 kt/y at 0.0899 kg/Nm³ and 8760 hrs of operation.
- 5) The Merseyweg-plant is currently out of use pending final decisions on this plant (M. Weeda, personal communication (2020)).
- 6) Permit for Air Products Botlekweg states a capacity of 134,000 Nm³ hydrogen per hour (Staatscourant, 2009), or 106 kt/y at 8760 hours of operation.

The CO production of the Air Liquide facilities in Botlek and Bergen op Zoom is estimated based on EIGA (2013) that states a typical CO/H₂ mass ratio range of 2.8-5. SMR2 is a flexible plant that primarily produces hydrogen, but can also deliver CO. It can be noticed that CO₂ emission of the Air Products' hydrogen plant is higher than the one of Air Liquide even though it has a lower capacity. However, there may be a difference in the actual production of the sites and in the input gas composition (refinery gas and/or natural gas). Both SMR2 from Air Liquide and the SMR from Air Products use refinery gas from the ExxonMobil refinery.

Apart from the facilities included in the table above, Air Liquide owns co-generation plants (Combined Heat and Power, CHP) that cause CO₂ emissions registered in the EU ETS. These facilities include Pergem, Enecal and Eurogen and relate to steam and electricity production in the Botlek and Pernis area. Appendix A describes these facilities and their emissions. A map from Botlek and Pernis which includes these facilities is found in Figure 2.

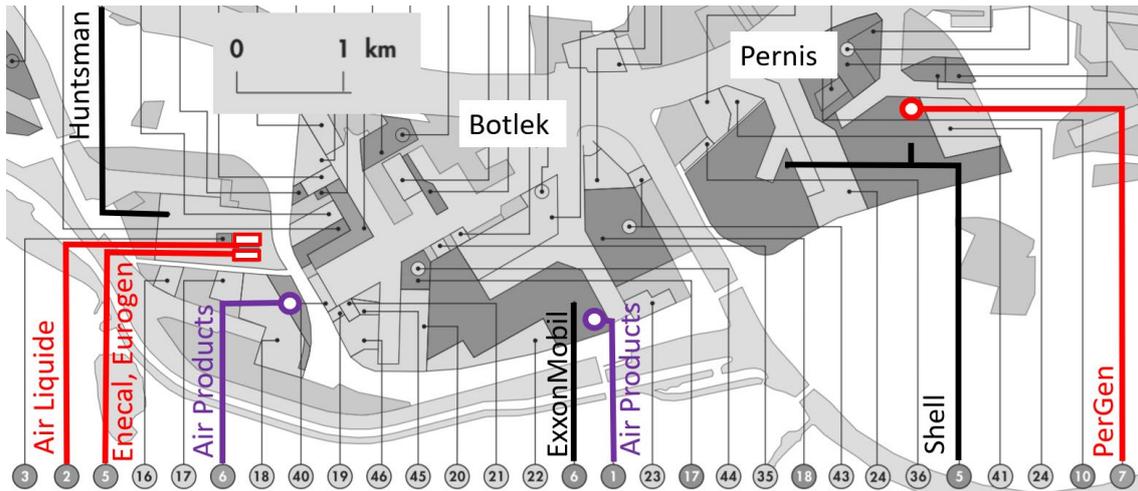


Figure 2 Location of the discussed entities in Botlek and Pernis. Adapted from the Facts & Figures of Port of Rotterdam (Port of Rotterdam, 2016)

1.2.2 Nitrogen, oxygen, argon: Air Liquide, Air Products, Linde, Gasunie

Production capacities for other industrial gases than hydrogen and carbon monoxide are summarised in Table 2. ASU plants do not produce direct CO₂ emissions since the total energy requirement is supplied by electricity. The plant in De Wijk supplies the nitrogen to local natural gas extraction facilities employed by the NAM (Air Products, 2020).

Table 2 Overview of the air separation unit (ASU) facilities of the main producers in the Netherlands, including the location and description of the main activity.

Company	Location	Main activity	Production capacity		
			O ₂ [Mt/y]	N ₂ [Mt/y]	Ar [kt/y]
Air Liquide Industrie B.V.	Terneuzen	Cryogenic Distillation ASU	0.44 ¹⁾	1.6 ²⁾	24 ²⁾
Air Products Nederland B.V.	Botlek-Rotterdam	Cryogenic Distillation ASU	1.2 ³⁾	4.2 ²⁾	-
Air Products Nederland B.V.	De Wijk (De Wolden)	Cryogenic Distillation ASU	0.08 ²⁾	0.29 ⁴⁾	-
Linde Gas	Velsen-Noord	Cryogenic Distillation ASU	0.63 ⁵⁾	2.7 ⁵⁾	32 ²⁾
Gasunie	Ommen	Nitrogen production	-	1.6 ⁶⁾	-
Gasunie	Zuidbroek	Nitrogen production	-	0.18 ⁶⁾	-

1) 1200 t oxygen per day (Air Liquide, personal communication, 2019).

2) Estimated by using a N₂/O₂ and Ar/O₂ mass ratio of 3.6 and 0.05 respectively (see Section 2.2).

3) Smith & Klosek (2001)

4) 800 t nitrogen per day (Air Products, personal communication, 2020).

5) Keys et al. (2019)

6) GTS, 2015; assuming 8760 hours.

1.3 Companies overview

1.3.1 Air Liquide

Air Liquide Industrie B.V. is part of Air Liquide, a multinational founded in 1902, present in 80 countries and having about 67,000 employees (Air Liquide, 2020).

In the Netherlands, Air Liquide started production and sale of industrial gases in 1931. Air Liquide Nederland B.V., Enecal B.V., Eurogen B.V., Maasvlakte Energie B.V., Air Liquide Technische Gassen B.V., and Pernis Energie B.V. are 100% participations of Air Liquide Industrie B.V. (Air Liquide Industrie, 2018).

Currently, in the Netherlands, the company has around 400 employees and more than 30,000 customers, supplying most of their industrial gases through 2,225 km of underground pipeline, a network from Bergen (Mons) (Belgium) to Rotterdam (Air Liquide, 2020a). Air Liquide Industrie B.V. has a production capacity of about 150 kt of pure hydrogen annually and a production capacity of carbon monoxide of about 300 kt per year. In the country, the company presents four facilities for the hydrogen production situated in Botlek-Rozenburg and Bergen op Zoom area as described in Figure 1. Moreover, the company has several "on-site" non-cryogenic air separation units, where a small amount of pure oxygen is required. In Terneuzen, a large-scale cryogenic air separation unit is running that produces a large amount of oxygen, nitrogen and argon as described in Table 2. In 2017, Air Liquide Industrie B.V. achieved an annual net turnover of EUR 195.8 million, with a total net profit after taxation of EUR 28.2 million (Air Liquide Industrie, 2018).

1.3.2 Air Products

Air Products Nederland B.V. was founded in 1967 in Utrecht and it started its business with the industrial gas production for petrochemical companies in the Rijnmond region. It is part of the US based corporation Air Products and Chemicals, Inc.

Air Products Nederland has a production capacity of about 100 kt of pure hydrogen annually. The company operates a steam methane reformer unit for the hydrogen production situated in the Botlek-Rozenburg area, as shown in Figure 1. This plant uses refinery gas of ExxonMobil as feedstock. A second steam methane reformer unit is currently not in use. Furthermore, Air Products Nederland B.V. has a cryogenic air separation unit in Botlek with a maximum capacity of about 3500 short tons per day or 1.16 (metric) Mt per year of pure gaseous oxygen (Smith & Klosek, 2001, p. 121). Currently, in the Netherlands, the company employs around 200 employees and has an annual net turnover of EUR 248.7 million with EUR 22.1 million of net profits (Air Products Nederland B.V., 2018).

1.3.3 Other actors

Linde Gas Benelux has its headquarters in Schiedam and has several air separation units in IJmuiden (on the site of TATA's steel plant), where liquid air is separated by cryogenic distillation (Linde Gas Benelux, 2018) to produce oxygen for steel manufacturing. Its ASU plant on TATA Steel's site produces almost 0.9 billion Nm³ (0.63 Mt) of pure oxygen annually and 3.3 billion Nm³ (2.7 Mt) of gaseous nitrogen (Keys, Van Hout, & Daniels, 2019). Linde Gas also produces a small volume of hydrogen at the TATA site by SMR, but it is negligible in comparison to the aforementioned hydrogen producers. Linde's industrial gases production in the Botlek area was terminated at the end of 2017. Currently, in the Botlek region, Linde Gas is active in the distribution of CO₂ through pipelines to greenhouses in the Westland, Lansingerland and Delfgauw (OCAP, 2019).

Another important nitrogen producer in the Netherlands is Gasunie, a Dutch natural gas infrastructure and transportation company that owns the Dutch gas transmission network

with a total length of over 12,000 kilometres. The company owns and operates four stations in which nitrogen can be added to imported high-calorific gas in order to decrease its calorific value and make it appropriate for domestic infrastructures. At two of these installations, Wieringermeer and Pernis, Gasunie adds nitrogen to the imported gas. Gasunie purchases nitrogen from other parties, at least Air Products, Linde Gas and Tata Steel (Gasunie, 2019, pp. 51, 56). At Ommen and Zuidbroek, it produces its own nitrogen from air. In 2018, Gasunie has a nitrogen capacity of 377,000 m³/h with two production plants located in Zuidbroek (16,000 m³/h) and Ommen (146,000 m³/h), and two conversion plant located in Wieringermeer (215,000 m³/h) and Pernis (45,000 m³/h) (GTS, 2015). Specifics of these production locations are not further discussed in this report.

2 Industrial gas production processes

2.1 H₂, CO and syngas production

In the Netherlands, hydrogen production by industrial gas producers is dominated by the Steam Methane Reforming (SMR) process, where natural gas and steam react to produce H₂ and, depending on the presence or absence of a water gas shift reactor, carbon monoxide (CO) (in case of SMR). For the production of raw syngas (H₂ and CO mixture), Autothermal Reforming (ATR) is the most widely used technology, since it presents the highest efficiency in terms of energy required and carbon dioxide emitted. An alternative method to produce syngas is the Partial Oxidation technology (POX), where hydrocarbons are partially oxidised instead of reformed, but to our knowledge this process is not applied on an industrial scale in the Netherlands and therefore not discussed in further detail.

As described on page 8, also a large amount of hydrogen is produced as 'captive' hydrogen in refineries and chemical companies, by catalytic reforming of naphtha and by gasification of heavy residues (Weeda & Segers, 2020). This production is not taken into account in this report, but discussed in MIDDEN reports related to the refineries and specific chemical companies.

2.1.1 Steam methane reforming (SMR)

In the steam reforming process, hydrocarbons are catalytically converted into hydrogen and carbon monoxide by reaction with steam. It is considered the most common mechanism to produce pure hydrogen. Typically, natural gas (NG) is adopted as a feedstock since it is one of the most cost-effective hydrocarbons (examples of other hydrocarbons are naphtha, LPG, refinery gases). For material limits, the reformer output temperature can reach up to 1200 °C.

Depending on the feedstock consumed, the amount of steam and the enthalpy change of the reaction varies. According to literature, this process has a conversion efficiency between 74–85% LHV (Nikolaidis & Poullikkas, 2017). IEA reports 76% (Base Case in Table 2 of IEAGHG, 2017). This number does not include re-use of waste heat, which is in practice an important feature in the design of an SMR. This technology has a potential capacity that can range between 1,350 and 18,000 kg/h of hydrogen (around 11.9–158 kt/y) (Air Liquide, 2018) and a production yield of 3.4 mol H₂/mol NG (Jakobsen & Åtland, 2016).

The overall SMR process is composed of five main steps which can be recognised in almost all of the large-scale hydrogen production facilities: natural gas pre-treatment, natural gas reforming, water gas shift, carbon capture and hydrogen separation. A flow chart of the process is shown in Figure 3.

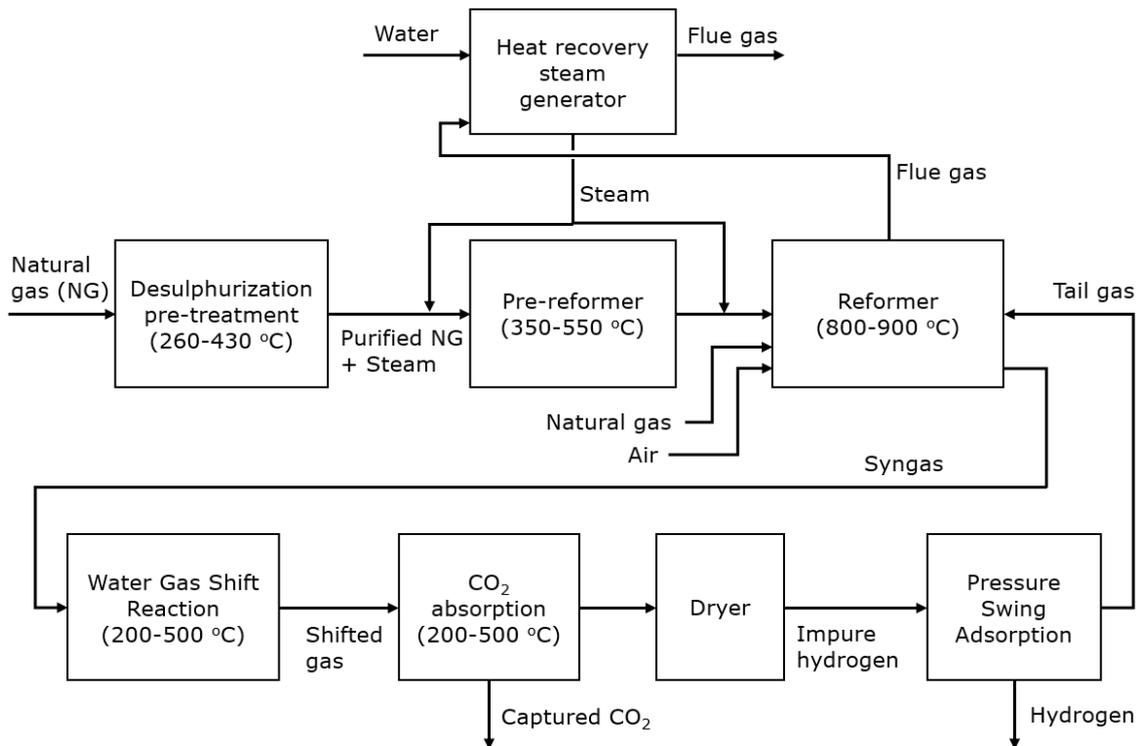


Figure 3 Schematic overview of the production process of H₂ using the Steam Methane Reforming process (partially based on information from Air Liquide, 2021).

Natural gas pre-treatment

Before entering into the reformer reactor, the feedstock needs to be purified to avoid corrosion or deposition issues during the reaction. Natural gas (NG) needs just desulphurisation as a pre-treatment process (Liu, Song, & Subramani, 2009), in order to decrease the amount of sulphur components. The inner tube catalysts are very sensitive to this component and even with a small variation of sulphur amount the overall efficiency of the reaction can decrease significantly (Dunleavy, 2006). In the pre-treatment step, the NG firstly passes through a flash drum, where all the liquids are removed. Then, a small amount of hydrogen is used to blow the organic sulphur out from the main stream and to release H₂S as a residual component. The H₂S molecule is adsorbed in a zinc oxide bed and zinc sulphide is formed as a result of the reaction, which finally, is removed as solid waste (Molburg & Doctor, 2003). The temperature of this process is between 260–430 °C and the pressure is around 50 bar.

Natural gas reforming

After the purification process, natural gas goes through the reforming step, which is divided into two main parts: pre-reforming and methane reforming.

In the pre-reforming reactor, the heaviest hydrocarbons are transformed into methane prior to the main reforming reactor. This occurs into a low-temperature adiabatic steam reforming unit within a nickel catalyst bed with operation temperature from 350–550 °C (Liu, Song, & Subramani, 2009). A gas heated reformer (GHR) is generally used as a pre-reformer since it has also the function of heat exchanger, cooling the methane reforming products (syngas) prior to the water gas shift reactors.

The steam reforming reaction is the next step and is highly endothermic, meaning energy is needed in order to convert the methane (CH₄) and steam (H₂O) into hydrogen (H₂) and

carbon monoxide (CO). Since natural gas is mainly composed of methane, we focus on methane reforming, which is described by the following equation:



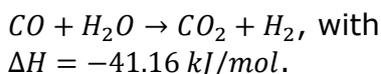
Several reactor tubes filled with nickel-based catalysts enable the reforming reaction while the methane and steam pass through them, with the heat necessary for the activation provided by a furnace in which methane fuel is burnt with air and tail gas recycled according to the following equation:



The optimal operating temperature is between 800–950 °C and the pressure around 20–25 bar (IEAGHG, 2017; Voldsund, Jordal, & Anantharaman, 2016). The steam-carbon (S/C) ratio should be around 3–4 since lower values can partially cause carbon deposition on the catalyst surface, and the conversion yield is positively affected by a high S/C ratio (Liu, Song, & Subramani, 2009). On the other hand, a low S/C ratio is preferred from energy efficiency and economic point of view. The upper-temperature limit is due to material limitations which cannot withstand higher temperature than 1200–1300 °C.

Water gas shift reaction (WGSR)

In combination with the steam reforming reaction, the water-gas shift reaction (WGSR) constitutes the conversion process of carbon monoxide and water vapour into carbon dioxide and hydrogen. The reaction is described below by the equation:



Here, additional hydrogen is extracted from the water in the steam accompanying the process. The reaction occurs at relatively low temperatures and usually takes place in two steps, a high-temperature shift (HTS) and a low-temperature shift (LTS). In the HTS, around 80% of CO is converted, with an inlet temperature between 350–550 °C. In the LTS, at temperatures from 190 to 250 °C, the CO mole fraction is reduced to 0.2–0.4 % (Liu, Song, & Subramani, 2009). The lower limit is determined by the water dew point of the gas.

Hydrogen separation

We consider hydrogen purification through Pressure Swing Adsorption (PSA), since more than 85% of the current hydrogen production units use PSA technology (Liu, Song, & Subramani, 2009). The reforming product, purified by the CO₂ and cooled down to 25 °C, pass through an adsorption column at high pressures letting through pure hydrogen while adsorbing the other impurities (CH₄, CO, CO₂, O₂ and a small amount of H₂). In order to restore the adsorption column, the pressure is lowered to atmospheric pressure leading to release the impurities from the adsorption material. Typical adsorbents are silica gel, alumina, activated carbon and zeolite (Voldsund et al., 2016). This technology operates at a pressure between 20–60 bar and ambient temperature. Hydrogen is then purified with a pressure drop of 1–2 bar. The purified gas, called “tail gas”, exits the PSA unit with a pressure between 1–2 bar. A PSA unit typically has a hydrogen recovery rate between 60–95 % with a purity of 99% (Voldsund et al., 2016).

Carbon capture

After the WGS reaction, the carbon dioxide component is separated from the shifted syngas prior to the hydrogen purification (IEAGHG, 2017). To the best knowledge of the authors, carbon capture after the WGS is applied by Air Liquide and Air Products. The captured CO₂ is

sold to e.g. horticulture greenhouses and soda manufacturing industry. Although the CO₂ is captured, the emissions are nevertheless included in the emission statistics under EU ETS; captured emissions are only excluded when the CO₂ is stored in a long-term storage facility (like in CCS) (NEa, 2014).

It is assumed that the CO₂ capture is done using the absorption method, which is the most commercially mature technology. This method is characterised by the use of a liquid solvent in order to remove the CO₂ from the main stream. The solvent can be chemical or physical. Chemical solvents require heat to react with CO₂ and absorb it since the reaction must occur quickly into a relatively small reactor. MDEA, MEA, TEA and potassium carbonate are solvents typically used for the chemical CO₂ capture. Physical solvents do not react with CO₂, but they dissolve it, requiring less energy than chemical solvents (Voldsund et al., 2016). According to several studies, the use of MDEA as solvents can lead to a separation of 95% of CO₂ from the main products with a purity of above 99% (Voldsund et al., 2016). A drying step is required to remove water from the syngas which originates from the CO₂ absorption step.

A summary of the material and energy flows based on two different cases (with and without CO₂ capture) and two sources can be found in Table 3.

Table 3 Summary of the material and energy flows for the SMR process, based on different cases and sources.

Reference	IEAGHG (2017); base case (no CO ₂ capture)	IEAGHG (2017); standard case with CO ₂ capture using MDEA (1A) ²⁾	Jakobsen & Åtland (2016) ³⁾
Raw materials	Unit ratio [t/t H₂]		
Natural gas feed	2.9	2.9	2.6
Water	6.6	6.8	7.2 ¹⁾
Air	PM	PM	15.8
By-products	Unit ratio [t/t H₂]		
CO₂ captured	0	5.2	6.4
CO₂ emitted	9.0	4.1	2.4
Energy	Specific consumption [GJ/t H₂]		
Natural gas as fuel	22.4	27.4	21.7
Electricity	0.48	2.1	2.6
Total primary energy required	23.6 ⁴⁾	32.7 ⁴⁾	28.2 ⁴⁾

¹⁾ Water consumption does not include cooling water used in the process and generated by the process.

²⁾ MDEA absorption is used as CO₂ separation unit and it is applied to the reformed gas (after reformer) with an efficiency of 90%.

³⁾ For optimized process at 950 °C reforming temperature.

⁴⁾ Conversion factors to primary energy are: 1 GJ steam = 1.11 GJ_p; 1 GJ natural gas = 1 GJ_p; 1 GJ electricity = 2.5 GJ_p (RVO, 2020).

The reforming process is the most energy-intensive part of the entire production process, which is not surprising, since the methane reforming is highly endothermic, and a high amount of energy is required that is provided by the combustion of fuel in the furnace.

In the hydrogen production process, CO₂ is produced in two ways:

1. Flue gas from fossil fuel combustion
2. After the WGS reaction.

The first amount of CO₂ is the part emitted by the plant and released into the atmosphere, while the second is in the described configuration removed and captured from the shifted gas through an absorption CO₂ unit with a capture efficiency of 90-95%.

2.1.2 Cogeneration of hydrogen and carbon monoxide

Hydrogen and carbon monoxide can be co-produced through the same SMR process aforementioned, together with steam and carbon dioxide as by-products. The two main differences in this process, compared with the standard SMR, are the dryers and ColdBox unit and the absence of the WGS reactor. A schematic of the process is shown in Figure 4.

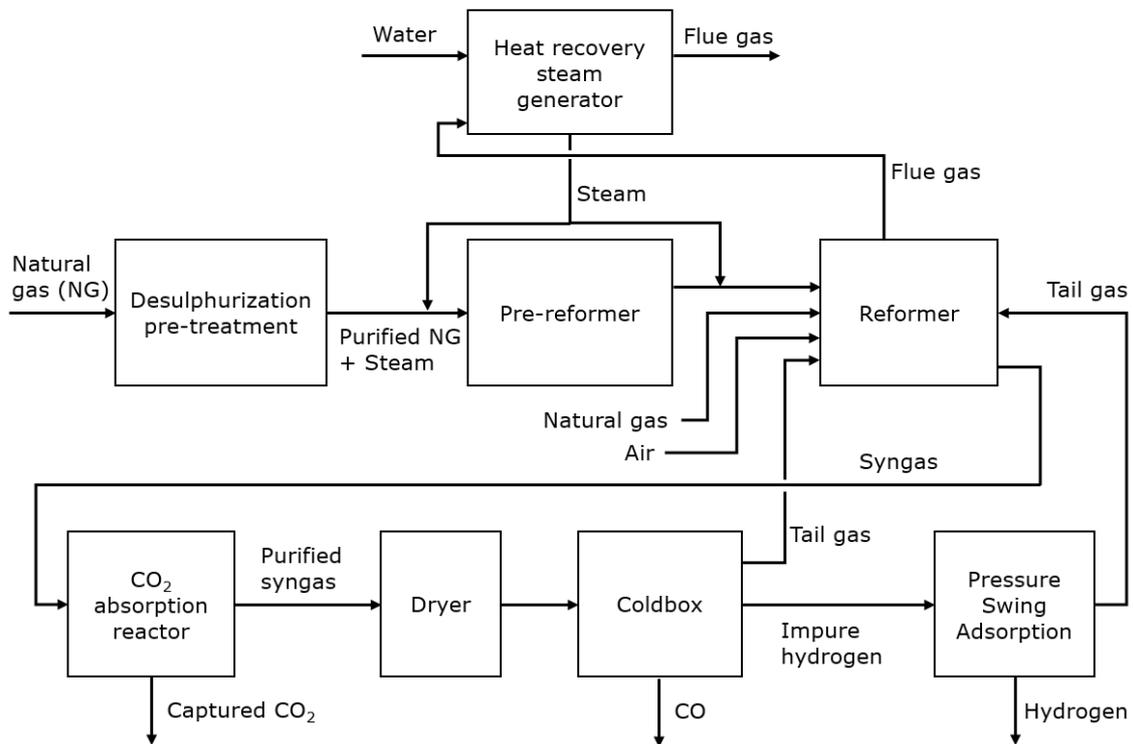


Figure 4 Schematic overview of the co-production process of hydrogen and carbon monoxide using cogeneration of hydrogen and carbon monoxide (partially based on information from Air Liquide, 2021).

The raw syngas leaving the reforming step is fed into the absorber column where CO₂ is washed out from the syngas by a counter-current flow of lean solvent. The treated raw H₂ contains 0.26% CO₂ after the removal step. The absorbed CO₂ is sent to the stripper column, where the rich solvent flowing down from the top of the column is stripped of its CO₂ by the vapour generated from the reboiler. In order to separate the carbon monoxide from the process gas, the ColdBox uses a cryogenic distillation process that can obtain high purity CO (>95%). The feed gas is pre-treated to remove impurities which will freeze at cryogenic temperatures encountered in the process. It is then partly condensed in heat exchangers and flashed in a syngas drum before being purified step by step through distillation columns.

According to the European Industrial Gases Association (EIGA), this so-called HyCO process enables a very flexible plant operation with a co-production yield that ranges from 0.20 to 0.36 kg H₂/kg CO (EIGA, 2013). The raw syngas from the reformer stream is sent directly to the

CO₂ removal unit to maintain a high CO/H₂ ratio. As of 2013, a typical HyCO plant can produce 3,000-3,600 Nm³ of hydrogen per tonne of feedstock (EIGA, 2013).

Typical mass and energy flow parameters are taken from the EIGA report (EIGA, 2013) and shown in Table 4.

Table 4 Raw materials, by-products, and energy for the co-production of H₂ and CO with HyCO process.

Reference	EIGA (2013)
Raw materials	Unit ratio [t/t H₂]
Natural gas feed	3.1 – 3.71
Water	2 – 8
Air	PM
By-products	Unit ratio [t/t H₂]
CO ₂ captured	0 ¹⁾
CO	2.8 - 5
Energy	Specific consumption [GJ/t H₂]
Natural gas as fuel	20 – 30
Electricity	0.72 – 1.44
Total primary energy required	21.8 – 33.6²⁾

¹⁾ No CO₂ absorption is assumed in this process. However, CO₂ may be captured in a similar way as with the SMR. The CO₂ component in the raw syngas (after SMR) may be removed and captured through absorption with an efficiency of up to 90%.

²⁾ Conversion factors to primary energy are: 1 GJ steam = 1.11 GJ_p; 1 GJ natural gas = 1 GJ_p; 1 GJ electricity = 2.5 GJ_p (RVO, 2020).

2.1.3 Autothermal Reforming Method (ATR)

The Autothermal Reforming technology (ATR), schematically shown in Figure 5, is a process for syngas production, by partially oxidizing natural gas with oxygen and steam and then reforming it catalytically (Air Liquide, 2018a). The shown production process allows for variable production of syngas composed of hydrogen and carbon monoxide, in various composition ratios.

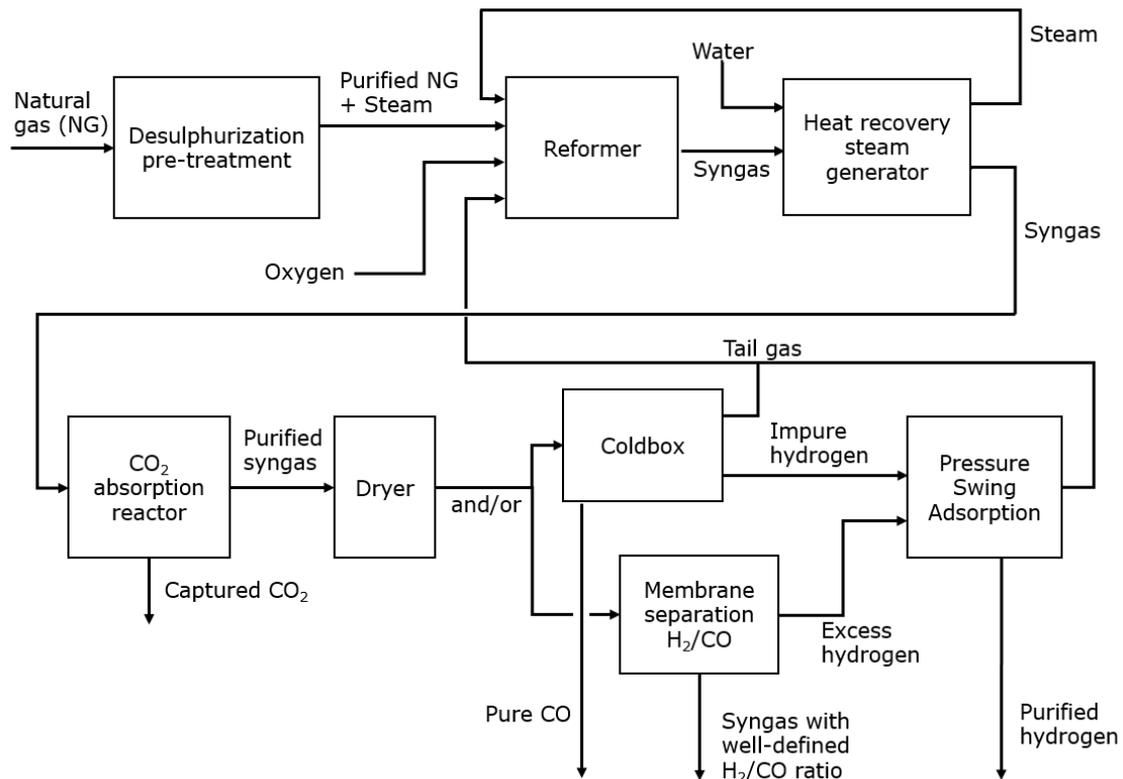
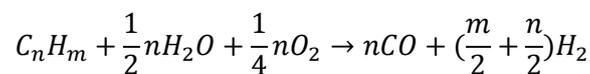


Figure 5 Schematic overview of the production process of syngas, carbon monoxide and hydrogen using the Autothermal Reforming process (based on information from Air Liquide, 2021).

After the desulphurisation step, the feed gas (natural gas) is pre-heated and optionally pre-reformed before entering the ATR reactor at 30 to 100 bar via the burner. In the first reaction area, the feed gas reacts with oxygen (partial oxidation) and steam to produce syngas. Successively, the raw syngas passes through a catalyst bed inside the same reactor for further methane reforming in order to achieve a high conversion yield. Finally, the syngas is cooled in a process gas boiler, generating high-pressure steam which can be exported or used for power generation. The syngas can be used as feedstock for various synthesis processes, including methanol and Fischer-Tropsch synthesis. Steam methane reforming and partial oxidation takes place simultaneously, as described by the equation:



Using methane as feedstock ($n=1$ and $m=4$), the thermal efficiency is evaluated around 60-75%, with optimum operation parameters in the reactor of 700 °C inlet temperature, ratio $S/C=1.5$ and $O_2/C=0.45$ (Ersöz, 2008). This process can achieve a syngas yield of 2.5 to 4.0 Nm^3/Nm^3 natural gas (NG fuel is included) and oxygen consumption of 0.15 to 0.25 kg/Nm^3 syngas (Air Liquide, 2018a).

After the reformer and heat recovery, the syngas is subject to CO_2 absorption and a drying step to remove water. The syngas can then be treated in a ColdBox process or by membrane separation. The ColdBox allows for high-purity CO, while in the membrane separation process a well-defined H_2/CO ratio can be achieved. Any excess hydrogen is purified by PSA afterwards.

The inputs for the syngas production process, as shown in Table 5, were based on data collected in the report of Jakobsen & Åtland (2016). These data exclude the membrane separation and Coldbox.

Table 5 Material and energy input for syngas production with ATR process (Jakobsen & Åtland, 2016). The used composition of syngas is 56% CO, 32% CO₂, 11% H₂, 0.6% CH₄ (mass percentages).

Materials	Unit ratio [t/t syngas]
Natural gas	0.27
Oxygen (pure)	0.28
Water	0.45 ¹⁾
Energy	Specific consumption [GJ/t syngas]
Electricity	0.1
Natural gas	10.5
Total primary energy input	10.8²⁾

- 1) Water consumption does not include cooling water used in the process.
- 2) Conversion factors to primary energy are: 1 GJ steam = 1.11 GJ_p; 1 GJ natural gas = 1 GJ_p; 1 GJ electricity = 2.5 GJ_p (RVO, 2020).

Since the syngas and CO are the only carbon-containing output streams, no CO₂ is assumed to be emitted from the ATR process.

2.2 O₂, N₂ and Argon production

Oxygen and nitrogen, with argon as a by-product, are produced by air-separation units (ASU). The technology can be divided into two main technologies: cryogenic distillation for large amounts of air, and the non-cryogenic technologies, for small scale production, which separate air at ambient temperatures through a process called pressure swing adsorption (PSA), or polymeric membranes. This report will focus on the cryogenic distillation.

2.2.1 Cryogenic Separation

The cryogenic air separation unit (ASU) is considered the most effective technology for the production of a high amount of pure oxygen, nitrogen and a small amount of argon. The process is based on the different boiling points of the air components, which are achieved by cooling down the atmospheric air to liquefy it. The liquefaction of a large part of air is necessary in order to start the separation of air components, reaching the operational temperature and pressure below the critical point which is around $T_{crit} = -140.7 \text{ °C}$ (132.5 K) and $P_{crit} = 37.7 \text{ bar}$ (3.77 MPa) (Linde, 2019). Figure 6 illustrates a standard cryogenic distillation plant that produces gaseous oxygen, gaseous and liquid nitrogen and argon (Air Liquide, 2017).

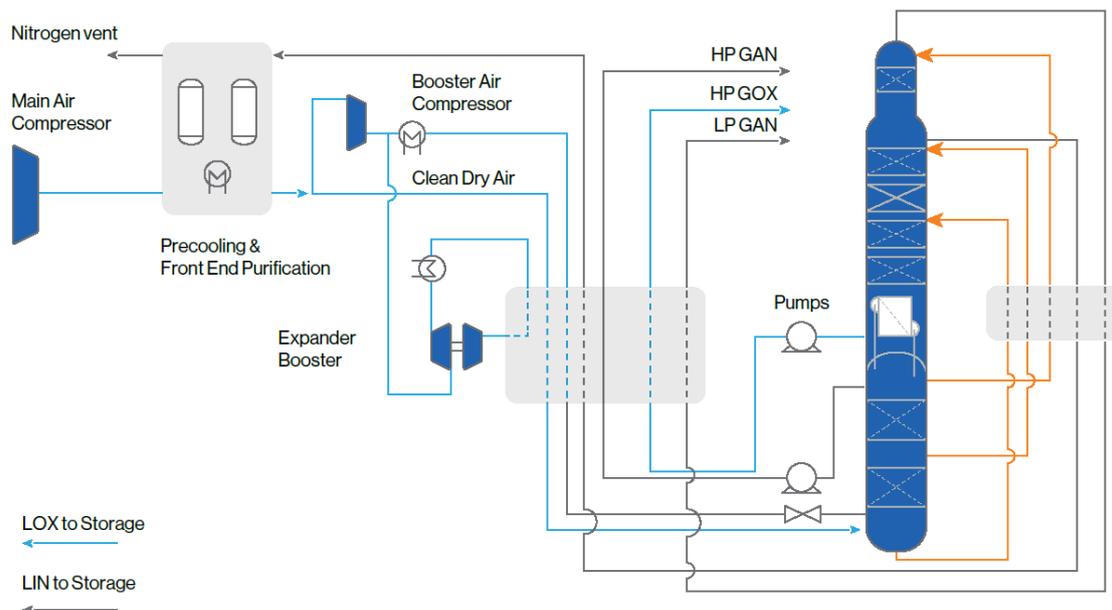


Figure 6 Overview of a standard cryogenic air separation plant by distillation. Retrieved from Air Liquide (2017). The only main outputs are high-pressure gaseous oxygen (HP GOX), high-pressure gaseous nitrogen (HP GAN), low-pressure gaseous nitrogen (LP GAN). LOX and LIN refer to liquid oxygen and liquid nitrogen, respectively.

Air compression and cooling

The process starts with the flow of atmospheric air through filters that remove dust and other particles harmful to the process. Then strong compression of the stream occurs through the adoption of alternate steps of compressors and heat exchangers. The heat obtained by the increase of pressure is transferred to a counter current water stream which is chilled by the cold gaseous mix recycled from distillation columns, to decrease the temperature to ambient temperatures or below. At the end of this stage, the air is compressed to around 670 kPa and reach a temperature of around 160 °C (Ebrahimi et al, 2015).

Air purification

The second step is characterized by the purification of air from carbon dioxide and water vapour since during cryogenic distillation they can form solid contaminants that can negatively affect the entire process. Water vapour is condensed and removed by a direct contact cooler and liquid separation of the stream, while carbon dioxide and other hydrocarbons are removed by a molecular sieve pre-purification unit.

Cold production and internal product compression

After the purification process, the air stream is further compressed by an air booster compressor in order to reach the pressure of around 1,210 kPa and a temperature of 110 °C. The air-cooling method here is represented by the expansion of the gas which decreases its pressure in order to reach the cryogenic temperature necessary for the further distillation. This process is accomplished by an expansion turbine that produces mechanical energy from the expansion for driving a process compressor or another energy-consuming machine. Moreover, pumped pure oxygen and nitrogen from distillation columns are warmed to ambient temperature or just below by the application of a multi-stream high-pressure heat exchanger.

Cryogenic distillation of air

The most important part of an air separation unit is the separation of air components into distillation columns. A double-column rectification system composed by a high-pressure (HP) columns installed below a low-pressure (LP) column which are connected by a condenser and evaporator. Partially condensed air flows at the bottom of the HP column and it rises up letting cold gaseous nitrogen, with a lower boiling point than oxygen (-196 °C), to reach the top column, while liquid air is collected in the perforated trays. At the LP column, the oxygen-enriched liquid is then separated into pure oxygen streams and nitrogen waste gas at the top column.

The connection between the two columns is characterized by the condenser/evaporator which liquefies gaseous nitrogen at top HP column against boiling pure oxygen at the bottom of LP column (with a purity higher than 99%) (Burdyny & Struchtrup, 2010). For large scale production of several thousand tonnes of oxygen needed by the oxy-fuel process, the current work requirement is 220 kWh/tonne O₂ based on the analysis of Seltzer et al. (Seltzer, Fan, & Hack, 2007) and 245 kWh/tonne O₂ according to Hong et al. (Hong, et al., 2009). The amount of energy required depends also on the production volume. For an oxygen production between 500 and 1000 tonnes, the work required by cryogenic distillation lies between 280 and 340 kWh/tonne O₂ (Hong, et al., 2009).

Argon production

The production of argon occurs within a “side arm” column, which receives a feed vapour from the low-pressure column with the maximum argon concentration (between 10 to 20%), and the lowest nitrogen concentration (Agrawal, Auvil, Choe, & Woodward, 1990). This column enables the collection of gaseous argon at the top of the column, condensing oxygen at the bottom that is successively recirculated into the distillation column. Although argon is less than 1% of the air composition, the typical argon recovery rate in a large ASU may exceed 95% (Agrawal et al., 1990).

The input and output flows and energy use, as described by several sources, are listed in Table 6.

Table 6 Input and output flows for production of industrial gases by cryogenic air separation, normalised to 1 t O₂ produced.

Raw materials	[t/t O ₂]	Source
Air	5.3	Ebrahimi et al., 2015
Cooling water	18.9	Ebrahimi et al., 2015
By-products	[t/t O ₂]	
Nitrogen	4.0	Ebrahimi et al., 2015
Argon	0.05	Ebrahimi et al., 2015
Specific energy consumption	[GJ/t O ₂]	
Electricity	0.6 – 1.8	Air Liquide, 2018
Total primary energy required for utilities	1.5 – 4.5 ¹⁾	

¹⁾ Conversion factors to primary energy are: 1 GJ steam = 1.11 GJ_p; 1 GJ natural gas = 1 GJ_p; 1 GJ electricity = 2.5 GJ_p (RVO, 2020).

Of the separation process, air compression is the most energy-demanding step since a strong increase in pressure (101.3 kPa – 650 kPa) is required for the distillation column.

3 Industrial gas products and applications

Industrial gases are widely requested due to their several applications in a wide range of industries. The most widely used industrial gas is nitrogen. Oxygen is the second most widely used industrial gas, with a global production in 2006 of 440 million tonnes (Gasworld, 2007). The global production of hydrogen was estimated in 2010 to be between 45 and 50 million tonnes, of which 7.8 million tonnes (17.3–15.6%) was produced in Europe (WEC, 2019). CO₂ is captured in the hydrogen production facilities. Therefore, we have added the application of CO₂ in this overview as well.

3.1 Hydrogen market

The total European hydrogen consumption in 2010 was estimated to be 7 Mt (CertifHy, 2015; Mulder, Perey, & Moraga, 2019). The production of hydrogen in The Netherlands was estimated to be about 0.8 Mt during the early 2010s (CE Delft, 2018). Recent estimates are larger, about 0.97 Mt¹ when including only pure hydrogen, and 1.5 Mt when including hydrogen present in gas mixtures (Weeda & Segers, 2020; DNVGL, 2019).

As described before on page 8, the produced hydrogen can be divided into 'captive' and 'merchant' production. Captive production is usually part of a larger process and used on-site, e.g. ammonia production and in refineries. Merchant hydrogen is produced by industrial gas producers and sold to third parties. 64% of the total European hydrogen is produced on-site by and for large consumers in the chemical industry, and another 27% is produced as a by-product in chemical production such as crackers (CertifHy, 2015).

In terms of consumption, the current hydrogen application is dominated by ammonia production and refinery feedstock, together more than two-thirds of the total hydrogen production in The Netherlands.

Other applications include the reduction of iron in metal processing. For this sector, the hydrogen consumption reached 0.7 million tonnes in Europe and a market share of around 10%, with an annual consumption per single plant of up to 720 tonnes/year (Mulder, Perey, & Moraga, 2019). Other non-energy-related applications of hydrogen are the production of synthetic materials (plastics, polyester, nylon) and hydrogenation of fats and vegetable oils in food industry, while energy-related applications are mainly represented by production of high-temperature heat for industrial processes (chemical, steel or oil refinery sector) and production of electricity in flexible power stations (combined cycle gas turbine or future fuel-cell plant). The hydrogen production facilities discussed in this report do presently (2020) not produce their hydrogen for these applications (M. Weeda, personal communication, 2020).

¹ Excluding hydrogen-rich residual gas from naphtha catalytic reforming in refineries.

A detailed breakdown by application is shown in Table 7 (Weeda & Segers, 2020).

Table 7 Dutch hydrogen production by application type. Source: Weeda & Segers (2020)

Application type	Estimated hydrogen production		
	bcm/y	kton/y	PJ/y (LHV)
Ammonia ^{a)}	5.3	480	58
Refinery ^{b)}	6.1	548	66
Other pure hydrogen use ^{c)}	1.6	148	18
Methanol ^{d)}	1.1	102	12
Fuel gas ^{e)}	2.3	214	24
Total	16.5	1,481	178

^{a)} SMR-natural gas

^{b)} SMR-natural gas and refinery gas; Shell Gasifier; Naphtha catalytic reforming

^{c)} SMR/ATR-natural gas; by-product chlor-alkali; water-electrolysis

^{d)} SMR-natural gas

^{e)} Various catalytic reforming; naphtha steam cracking; by-product chlor-alkali; Flexicoker fuel gas (but excluding small fractions of hydrogen that may be present in other residual refinery gas) and coke oven gas.

Producing hydrogen by steam methane reforming based on natural gas ('grey' hydrogen) is currently the cheapest option. According to the World Energy Council (2019), the production cost for hydrogen using mature technology is between EUR 1 and EUR 1.5 per kilogram of H₂ (WEC, 2019). CO₂ is currently captured partially (around 45% on the total emitted in the process) and the cost of the CCS technology varies depending on the supply-chain aspects. An average production cost for 'blue' or low-carbon hydrogen is estimated around 1.5 EUR/kg. However, production costs are expecting to increase for both production routes due to the increase of natural gas price. On the other hand, 'green' and 'import' hydrogen ('import' means generated using renewable energy generated outside the country and then imported) have an opposite trend since, with technology development and rise of renewable electricity production, by around 2030 these sustainable pathways is expected to reach the same cost range as 'blue' route (2–3 EUR/kg) (CE Delft, 2018). Figure 7 describes an overview of the trends of different type of hydrogen in terms of total supply-chain costs.

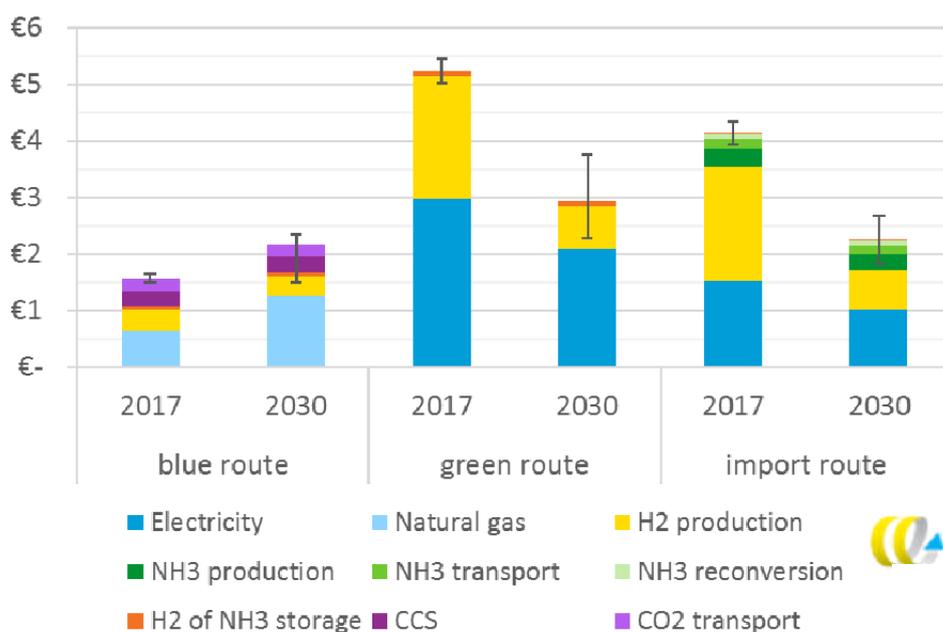


Figure 7 Overview projected trends of integral supply-chain costs of three different hydrogen pathways (CE Delft, 2018).

Currently, hydrogen from electrolysis is present as by-products of the chlor-alkali process for the production of chlorine and sodium hydroxide. Otherwise, no industrial-scale volumes of hydrogen production by water-electrolysis takes place in The Netherlands by 2021.

As mentioned above, the produced hydrogen is used as an industrial gas for non-energetic applications. Hydrogen is also used as fuel for transport applications. Beyond 2030, hydrogen may play a larger role in Dutch industry as a fuel for high- and low-temperature process heat and possibly for power generation. Furthermore, it is considered as a possible replacement of natural gas for heating purposes in the built environment and as transport fuel for heavy duty vehicles and buses. According to this scenario, depending on the production route taken into consideration by the government, experts predict an important growth of hydrogen market towards 2030 by 0.6 Mt/yr (72 PJ/yr) (CE Delft, 2018), although the scenarios differ as to how large the future role of hydrogen as fuel is (Detz, Lenzman, Sijm, & Weeda, 2019; Mulder, Perey, & Moraga, 2019).

3.2 Carbon monoxide market

Carbon monoxide is an industrial gas that has many applications in bulk chemicals manufacturing. Over 90% of carbon monoxide is used in the form of synthesis gas, so in coexistence with hydrogen, to produce methanol. The rest is consumed directly for the production of phosgene, acrylic acid, acetic acid, dimethylformamide, propionic acid, pivalic acid, and many other copolymers. According to "Global Carbon Monoxide Market Research Report 2017" (QYResearch, 2017), its global market value was estimated around 2,790 million USD and it is expected to grow at 3,219 million USD by 2022. In addition, the global production of carbon monoxide reached about 3,757 Gt in 2016, with a growth of 23% by 2022. The global production market of this industrial gas is dominated by Linde Gas, Air Liquide, Air Products and Praxair with a total share of 63% in 2016 (QYResearch, 2017).

3.3 Carbon dioxide market

The carbon dioxide is gradually gaining more importance in the Dutch market, and instead of being simply emitted into the atmosphere, it can represent a product to supply to other companies. The global CO₂ demand is estimated to be about 250 Mt in 2020 (IEA, Putting CO₂ to use, 2019), mainly for urea production and Enhanced Oil Recovery (EOR). Other than these, the largest end-user of 'merchant' carbon dioxide is the beverage industry, which uses this gas to carbonated soft drinks, beer and wine and to prevent bacterial growth.

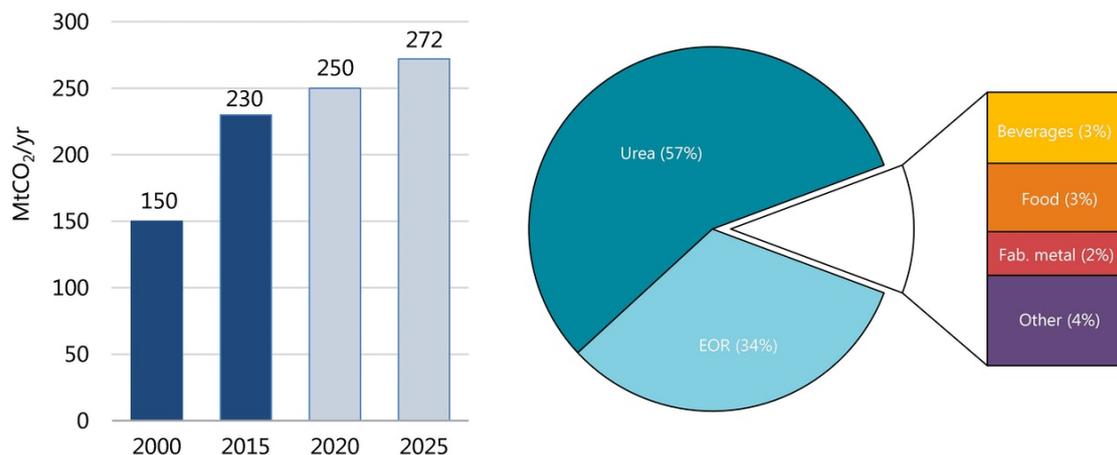


Figure 8 Growth in global CO₂ demand (left); breakdown of demand in 2015 (right). Copied from (IEA, Putting CO₂ to use, 2019)

The greenhouse horticulture sector also represents also an important end-user of CO₂. It is used in greenhouses as a fertiliser to enhance growth. In 2015, around 1.3 Mt of CO₂ was supplied to Dutch greenhouses, of which 60% is provided through exhaust gases of CHP plants while 40% is supplied via pipelines or by trucks from external sources (Mikunda, Neele, Wilschut, & Hanegraaf, 2015). According to Mikunda et al., 80% of the total CO₂ exported for greenhouses in the Netherlands is supplied by OCAP CO₂ B.V., a 100% subsidiary of Linde Gas. The current CO₂ sources of OCAP are the Shell Refinery and the Alco bioethanol plant (Khandelwal & van Dril, 2020).

A potential future application for CO₂ could be the use in methanol production. Currently, BioMCN already adds CO₂ into the methanol production process as it has an excess of hydrogen in the process. Depending on the energy balance of this process, it may be applied on a large scale in the future, as methanol can act as a building block for basically any organic chemical (M. Weeda, personal communication, 2020).

3.4 Oxygen market

The overall global oxygen consumption in 2006 was 440 million tonnes (Gasworld, 2007), and it has maintained a constant growth of 5-6% (Gasworld, 2007). In Western Europe, there was an important oxygen supply growth of 46% from 1995 to 2005 due to a rapid establishment of ASU facilities in the area, but it currently grows by less than 1% annually. Unfortunately, there is no specific data available about the total volume of oxygen consumed in the Netherlands, but if we observe the current production capacity of the three main gas

companies, we assume a market share of minimally 0.6% of the global production (approximately 2.5 Mt in 2017).

The steel industry represents the largest end-user industry sector, which consumes 48% of the global oxygen demand (580 kt/day). In this sector, the oxygen is used to enrich air for the increase of combustion temperature and energy efficiency, and to replace coke with other combustible materials (Gasworld, 2007). The annual oxygen consumption by the Dutch steel industry (Tata Steel IJmuiden) is estimated to be 0.9 billion Nm³ or 0.63 Mt (Keys, Van Hout, & Daniels, 2019, p. 12).

The second main consumer of oxygen is the chemicals industry, which includes refineries, petrochemicals, agrochemicals, pharmaceuticals, polymers, pigments and oleochemicals. This sector represents 19% of the global oxygen consumption with 40% of this is produced on-site (Gasworld, 2007). The oxygen is used in large quantity for coal gasification to generate synthesis gas or to enrich air feed for catalytic cracking in refineries.

3.5 Nitrogen market

Although we have not found information about the total nitrogen market in the Netherlands, global information can be used to give a broad view on this matter. In 2017, the global industrial nitrogen market was valued at EUR 13.5 billion with an increase expected for 2020 to EUR 18 billion (Research and Markets, 2019).

The industrial nitrogen has different applications that differ depending on its phase. Gaseous nitrogen is used mainly for the ammonia production and as shield gas thanks to its inert property. Liquid nitrogen has its main application for the cooling systems due to its low cost.

In the Netherlands, industrial nitrogen has an additional fundamental application by being added to high-calorific natural gas imported from Norway and Russia in order to decrease its calorific value and make the natural gas appropriate for domestic infrastructures. An increase in nitrogen demand is expected due to an increase of high-calorific gas import and a reduction of Groningen gas extraction. Gasunie in 2017 increased its high calorific natural gas demand by 11% through the nitrogen application. In 2018, the total amount of nitrogen available from the national pipeline network for this purpose reached 627,000 m³/h (reserve capacity included) (Gasunie, 2019).

3.6 Argon market

Argon is the most abundant, cheapest noble gas. The market of this industrial gas is expected to annually grow 5.5% from 2018 to 542 million USD in 2023. In 2016, about 700 kt of argon was produced worldwide (Market Research Future, 2019).

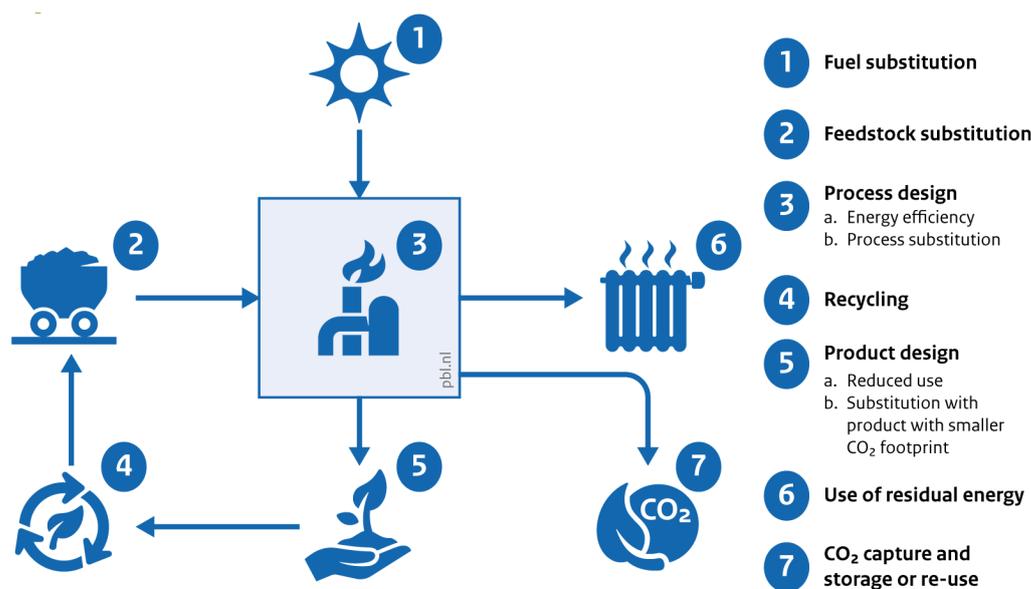
The main use of argon is related to the production, processing and fabrication of metals. Argon is a significant shielding gas used during arc welding processes. It is also used as the inert gas in electric light bulbs (when mixed with nitrogen), and for semiconductor manufacturing.

4 Options for decarbonisation

This chapter will describe potential options to achieve a reduction of energy use and/or CO₂ emissions for the production of hydrogen. The final section of this chapter, section 4.6, briefly discusses the use of green electricity for oxygen, nitrogen and argon production, which is the only decarbonisation option of these production processes.

Regarding hydrogen, in a number of plants not only hydrogen is a product of the processes, but also syngas or CO. Decarbonisation options should then in fact also include decarbonised syngas and CO production. This is taken into account for some of the options below, but not for all.

We have determined seven categories along which decarbonisation of a process can be tackled. These are shown in Figure 9.



Source: PBL

Figure 9 Categories of CO₂ reduction

For the hydrogen production process, we have identified the most important options along those categories, and list them in Table 8. It should be noted that this is not an exhaustive list of options, and additionally, options and their characteristics are likely to develop in the future.

Table 8 Overview of seven categories of decarbonisation options for the hydrogen production industry. The underlined options are addressed in more detail in this chapter.

Category	Description	Decarbonisation options	
1	Fuel substitution	Substitution of the current fuel/energy supply	<u>Biogas</u>
2	Feedstock substitution	Substitution of the current feedstock supply	<u>Hydrogen from biomass</u>
3	Process design	Substitution of the current production process based on a different fuel, feedstock or an entirely different process, to create the same product with energy/emissions reduction	<u>Electrolysis</u> <u>Thermal decomposition of methane</u>
4	Recycling	Recycle of some products or by-products to save energy/heat consumption from the entire process	
5	Product design	Reduction of the total product demand or substitution	Possible decline in oil refinery
6	Use of residual energy		Delivery of steam to surrounding plants (Air Products delivers to Exxon Mobil, Air Liquide to Huntsman, Wilmar and LyondellBasell)
7	CO ₂ capture and storage or re-use	Carbon capture and storage processes or capture and direct use of CO ₂ in another process	<u>CCS to flue gas</u> <u>CCS to raw syngas before PSA</u> <u>CCS to tail gas after PSA</u> <u>CCU</u>

4.1 Feedstock/fuel substitution: Hydrogen from biomass

The production of hydrogen through biomass is considered a valuable decarbonisation option since CO₂ released during biomass gasification process is then absorbed by growing plants through photosynthesis that represent future biomass feed (Ni, Leung, Leung, & Sumathy, 2006). Hydrogen production processes from biomass can be divided into two main categories: thermochemical processes such as pyrolysis or steam reforming of bio-oils, gasification, steam gasification, and supercritical water gasification; or biological processes such as biophotolysis of water using green or blue algae, photo-fermentation, dark-fermentation, and a hybrid reactor system (Ni et al., 2006). The former type of thermochemical processes can achieve higher overall efficiency (thermal energy to hydrogen) (>50%) and lower production cost with the disadvantage of formation of char and tar. Biological production requires less conversion energy with less CO₂ emissions with the drawback of a low hydrogen yield (<12 wt%) (Ni et al., 2006). The CO₂ emissions from hydrogen production through biomass are higher than the ones produced by a standard SMR plant because of the higher carbon content of biomass. However, the net carbon emissions using biomass as feedstock can be considered neutral if we considered the amount of CO₂ equivalent released by combustion equal to the amount of CO₂ recapture by the plants used to produce the feedstock. It should thus be decided whether this process is the best candidate for using the relatively scarce amount of biomass. Also, it should be investigated

whether the required amount of biomass can be obtained in The Netherlands or whether it can be imported in a cost-effective manner, or whether the required amount is simply too large.

4.1.1 Biogas reforming

One of the options to produce green H₂ is through the replacement of natural gas with biogas during the reforming process and fuel combustion in SMR furnace. This method, despite the non-avoided CO₂ emissions, is considered “green” due to its potential to achieve zero or even negative net carbon emissions (when combined with CCS). The source and production method of the biogas are determinant in the carbon footprint and its potential for sustainable application.

The most important difference between the steam methane reforming process and the biogas steam reforming is the presence of CO₂ in the feedstock, which can lead the system to high sensitivity to carbon formation in the operation regime, which could deposit in the material bed of the reactor. For this reason, an excess of steam supply is necessary and then it can be removed through condensation.

Availability of biogas is one of the challenges of this decarbonisation option. Biogas currently cannot be produced on the scale required for a hydrogen plant, since a typical existing biogas plant can produce around 0.25 Nm³/s, with respect to 25-30 Nm³/s used in a large scale SMR plant (Yao, Kraussler, Benedikt, & Hofbauer, 2017).

4.1.2 Biomass pyrolysis and steam reforming of bio-oils

Fast pyrolysis of biomass is an alternative option for hydrogen production where a thermal decomposition occurs that transforms biomass into bio-oil with a yield between 70-80% (water included) based on starting mass (Borole, et al., 2017). In absence of air or oxygen, biomass is rapidly decomposed at high temperature (between 400-500 °C) into liquid and gaseous products, without the formation of carbon oxides such as CO and CO₂. The bio-oil product is then finally obtained with a fast cooling step of pyrolysis vapours to below 400 °C (Czernik, Evans, & French, 2007). Hydrogen production from bio-oil feedstock is then carried out using a fluidized bed reactor as a steam methane reforming unit. Theoretically, the overall stoichiometry describes a maximum H₂ yield of 17.2% based on the whole bio-oil weight but this can be increased by around 10% with the application of a WGS reactor (Borole, et al., 2017). This process currently has two disadvantages, which are a low thermal efficiency (around 56%) compared to other standard hydrogen production processes (SMR, ATR), and formation of tar and char that can induce unwanted secondary reactions decreasing the overall efficiency.

4.1.3 Biomass gasification

This process consists of several steps that transform a carbon-rich solid fuel to syngas with the application of a gasification agent:

- Drying process to remove moisture (150°C);
- Pyrolysis to produce volatiles such as H₂, CO, CO₂, CH₄, tar, etc. (200-650 °C);
- The reaction of volatiles in product gas (700-1000 °C);
- The heterogeneous reaction of char (700-1000 °C).

Figure 10 shows a very common and commercialized biomass gasifier that is used for large-scale production. The composition of product gas depends mainly on the gasifier type, biomass fuel and gasification agent.

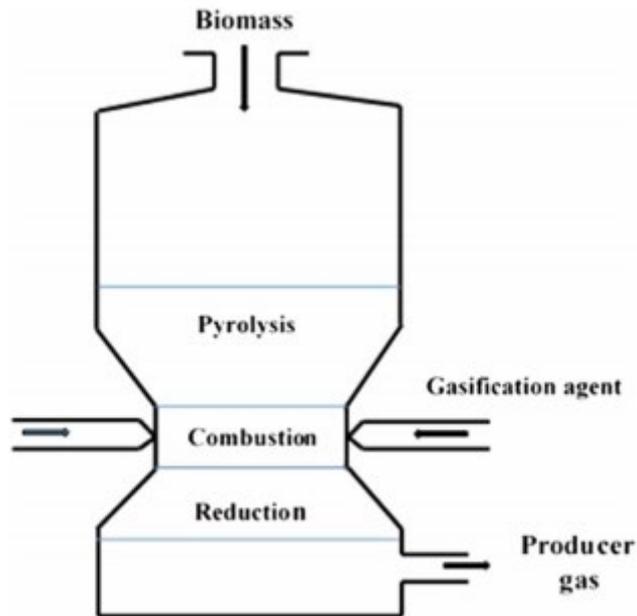
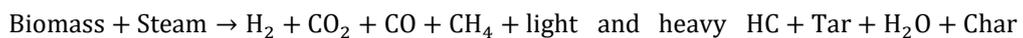


Figure 10 Overview of a downdraft biomass gasifier (Hannula, 2009).

Typical gasification agents for combustion reaction are O_2 , H_2O , CO_2 , and H_2 . In addition, the heat requirement for gasification reactions is provided by partial oxidation of biomass fuel through heat pipes or circulating bed material depending on the type of gasifier. An N_2 free product gas is necessary for hydrogen production so pure O_2 gasification agent is considered for the combustion reaction (Binder, Kraussler, Kuba, & and Luisser, 2018).

Steam gasification of biomass

Biomass steam gasification is considered an efficient type of the general biomass gasification process described above because less tar and char are produced during the process due to the application of steam as a gasification agent instead of air. The overall steam gasification reaction is described below:



The advantages of this process are a higher hydrogen yield reaching values between 50 to 80 g H_2 /kg of biomass (with temperature varying from 800 to 950 °C) and up to 55 vol.% of H_2 concentration in the output product (Binder, Kraussler, Kuba, & and Luisser, 2018). Finally, the hydrogen yield increases with the application of steam methane reforming and WGS reaction of the product gas mixture. Figure 11 describes an overview of a biomass steam gasification process.

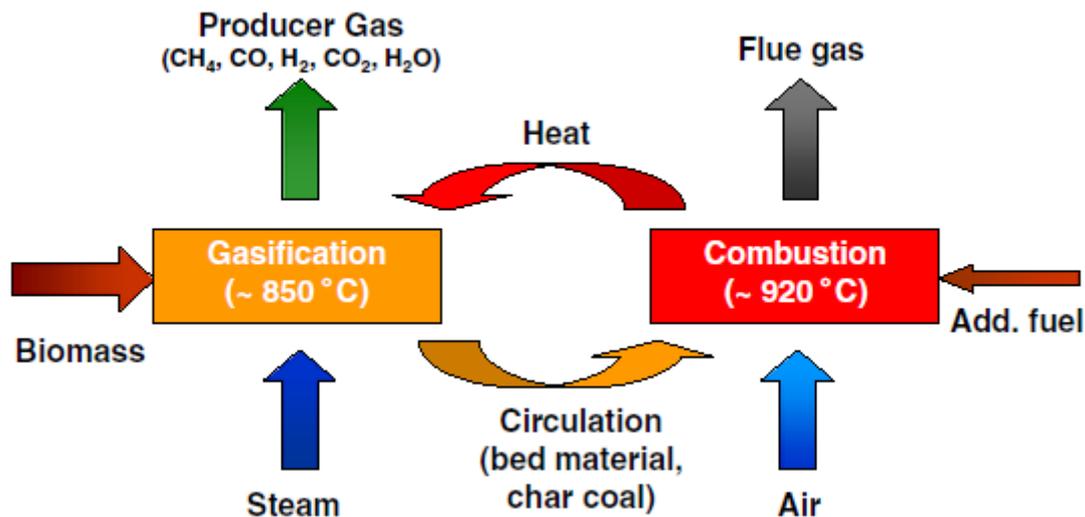


Figure 11 Overview of the steam gasification process (Hannula, 2009).

4.1.4 Cost of hydrogen production using steam gasification of biomass

The H₂ production costs of steam gasification depend on the feedstock price and quantity required. For the cost assessment, we considered H₂ production through biomass gasification in a dual fluidized bed steam gasification system and gas separation membrane as H₂ purification technology. According to Müller et al., steam gasification technology is capable to produce 1 tonne of hydrogen with a reasonable consumption of biomass, 14.2 tonnes, and process water, 0.3 tonnes (Müller, Stidl, Pröll, Rauch, & Hofbauer, 2011). In addition, almost 6 MW_e of electricity is required for the production process compared to a standard SMR plant that has an electricity surplus delivered to the grid. The high consumption depends also to the application of the gas permeation membrane that use electricity to compress H₂. The cost and energy requirement are summarised in Table 9.

CO₂ emissions through steam gasification are higher than those of a standard SMR plant because of the higher carbon content of biomass. However, the net carbon emissions using biomass as feedstock can be considered neutral if we considered the amount of CO₂ equivalent released by combustion equal to the amount of CO₂ recaptured by the plants used to produce the feedstock.

Table 9 Techno-economic parameters H₂ production through steam gasification

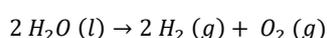
Hydrogen production through steam gasification			
	Value	Comment	Source
CO₂ emissions (t CO₂/t H₂)	21.5	Considering an emission factor of 109.6 kg CO ₂ /GJ as solid biomass and a feed/H ₂ ratio of 14.2. This direct emission is produced through the combustion of biomass and tail gas recycled in order to supply heat to the gasifier.	RVO, 2020a; Müller et al., 2011
Electricity demand [TJ/kt H₂]	11.2	This value includes the demand for air compression and product gas compression before membrane separator unit.	Müller et al., 2011
CAPEX [MEUR2017/kt H₂]	2.5	Based on investment cost of EUR 50 million for a 20 kt/yr H ₂ facility.	Müller et al., 2011
OPEX [EUR2017/t H₂]	0.05	Assumed 2% of CAPEX	

4.1.5 Supercritical water gasification

Supercritical water gasification represents an alternative to biomass gasification with the adoption of water at supercritical state (22.1 MPa and 374 °C) as oxidant agent in the gasifier. When water reacts with biomass, its oxygen molecules oxidize the carbon atoms of biomass releasing CO particles in the reactor, that are further converted into CO₂ and H₂ by water gas reactions. The main disadvantages of this type of production process are: hydrogen production cost is way higher than the one with SMR since it requires high moisture content biomass, and the technology is still under development (Parthasarathy & Narayanan, 2014). SCW Systems is developing this technology in The Netherlands (Topsector Energie, 2019; Gasunie New Energy, 2020).

4.2 Process design: Electrolysis

Water electrolysis (NOW, 2018; FCH, 2014; IEA, 2019) is a carbon-free process that splits water into pure hydrogen and pure oxygen with the use of electricity. The process is described by the equation below:

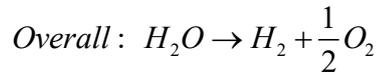
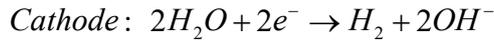
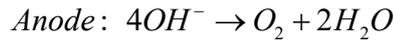


The most developed and commercialised electrolyser technologies are: alkaline water electrolysis (AEL) and proton exchange membrane electrolysis (PEM); solid oxide electrolysis cells (SOEC) units are an additional valuable option but still under development for their issues with corrosion, seals, thermal cycling, and chrome migration. The PEM technology has the lowest footprint and potential for operation at higher pressures, but the need for platinum group pressures is a disadvantage (M. Weeda, personal communication, 2020). Alkaline electrolysers are the most developed technology with the lowest costs and lower energy consumption (Nikolaidis & Poullikkas, 2017). Currently, a commercial electrolyser (both AEL and PEM are available at a scale of 1-5 MW) has an average overall efficiency of 61% (LHV) with an energy consumption of 55 kWh/kg (PEM has a slightly higher value of 60 kWh/kg), and in 2030 is predicted an increase to a minimum of 67% (LHV) of efficiency (Gigler & Weeda, 2018).

Availability of renewable energy is a precondition for producing green hydrogen. Currently, shifting H₂ production from 'grey' hydrogen (SMR based on natural gas) to 'green' hydrogen through electrolysis would actually imply an increase in CO₂ emissions per kilogram of hydrogen produced due to the average European electricity mix which is still dominated by fossil fuel. Hydrogen production by electrolysis can be already considered a valid alternative for local production where there is a surplus of green electricity, for example on offshore wind farms (WEC, 2019). Alternatively, electrolysis can be applied abroad at locations with an abundance of green electricity, such as in deserts, which is already being developed by Air Products amongst others (Power Technology, 2020). Ammonia can be produced on-site using the green hydrogen, which is easier to transport than the hydrogen itself.

4.2.1 Alkaline water electrolyser (AEL)

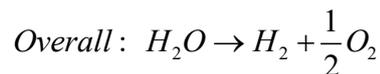
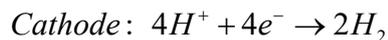
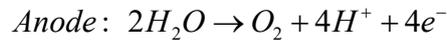
The main structure of an alkaline electrolyser is composed of electrodes, a microporous separator and a liquid alkaline electrolyte of around 30 wt.% KOH or NaOH. Water is introduced in the cathode, typically containing nickel with a catalytic coating, and is separated into hydrogen and OH⁻ ions. Hydroxide ions flow through the electrolyte and react in the anode (nickel or copper metals with metal oxides coating) where they are transformed into O₂ and water. Hydrogen atoms remain in the alkaline solution and pure H₂ is then formed in a gas-liquid separation unit connected to the electrolyser (Nikolaidis & Poullikkas, 2017). Overall processes are described by equations below:



$$\Delta H = -288 \text{ kJ / mol}$$

4.2.2 Proton exchange membrane electrolyser (PEM)

Proton exchange membrane electrolysers (PEM) are characterised by electrode catalysts made with platinum black, iridium, ruthenium, and rhodium materials, and by the presence of a Nafion membrane that operates both as electrodes separator and as the gas separator. Water flows into the anode where it is separated into oxygen and H^+ positive ions, where the latter react further in the cathode forming hydrogen molecules. This type of electrolyser does not need a gas separator to produce pure hydrogen and presents low ionic resistances and so high currents without affecting the high efficiency of 55-70% (LHV) (Nikolaidis & Poullikkas, 2017). Overall processes are described by equations below:



$$\Delta H = -288 \text{ kJ / mol}$$

4.2.3 Cost of H_2 production from electrolysis

The cost of "green" hydrogen production depends mainly on the electricity price, capital, operational and maintenance costs for the required electrolyser. IRENA discusses the case of an alkaline system (AEL) and a proton exchange membrane, both for 2017 and 2025 (IRENA, 2018). The cases (based on a 20 MW system) are summarised in Table 10, both cost and energy requirements.

Water consumption of 15 kg and electricity demand of 49-58 kWh are necessary for one kilogram of hydrogen produced (FCH, 2017). The main advantage of this technology is the elimination of direct CO_2 emissions with the only drawback of high electricity consumption, which currently still implies high indirect emissions depending on the electricity mix in the Netherlands.

The CAPEX evaluation considers the capital costs for the electrolyser plant, the cell stack reinvestment, transport cost, control system, engineering, building, and grid connection (FCH, 2017, p. 165). It is assumed that the electrolysers are designed for 20 years lifetime and over 98% availability rate (FCH, 2017, p. 48). OPEX without costs of electricity is assumed to be around 2% of CAPEX (IRENA, 2018).

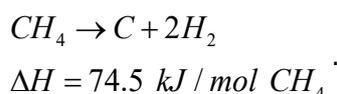
A recent study by Berenschot and Kalavasta finds slightly lower costs for PEM and AEL electrolysis in The Netherlands, of 2.2-2.4 MEUR₂₀₂₀/kt H_2 in 2025 (Berenschot & Kalavasta, 2020).

Table 10 Techno-economic parameters of H₂ plant through electrolysis, for a 20 MW plant. Calculated based on IRENA (2018)

Hydrogen production through electrolysis				
	AEL (2017)	AEL (2025)	PEM (2017)	PEM (2025)
Direct CO₂ emissions (kt CO₂/kt H₂)	0	0	0	0
Efficiency (kWh/kg H₂)	51	49	58	52
Efficiency (LHV) (%)	65	68	57	64
Electricity demand (TJ/kt H₂)	184	176	209	187
CAPEX (MEUR2017/kt H₂)	4.5	2.7	8.2	4.2
OPEX (MEUR2017/kt H₂)	0.09	0.05	0.16	0.08

4.3 Process design: Thermal decomposition of methane

Thermal decomposition of methane (TDM) is an endothermic process that separates methane into solid carbon and H₂ without CO₂ formation. The process equation is shown below:



The main advantage to using this process, compared to a standard SMR, is that it produces a marketable product as carbon black instead of CO₂. A thermal non-catalytic TDM reaction requires high-temperature heat or electricity demand (reaction temperature around 1300 K) (Keipi, 2017). The process requires about twice as much natural gas to produce the same amount of hydrogen compared to SMR (Weeda, personal communication, 2020). Even when the reaction heat is provided by natural gas, the CO₂ emissions are lower than for SMR processes. For small scale production of hydrogen (<200 GWh_{H2} or <5 kt H₂ per year) it could provide hydrogen at a cheaper value than SMR and with less CO₂ emissions, but this only holds provided an application for carbon black is found and marketed (Keipi, 2017). One could argue that this is merely an alternative production for carbon black with hydrogen as a by-product. Additionally, this method is still under development for application in a large-scale production plant. Higher reaction rates, as well as low reaction temperature, can be achieved with the application of a metal catalyst but with the drawback of carbon deposition that has to be oxidised (more energy demand) in order to regenerate the metal (Dunker, Kumar, & Mulawa, 2006). A carbon catalyst is the preferred option, despite its lower methane conversion rate, due to the lower cost compared to the metal type and the capacity to produce pure carbon black, which can be sold and make H₂ production cost more attractive. More information on present carbon black production and market can be found in the MIDDEN report by Abdallas Chikri and Wetzels (Abdallas Chikri & Wetzels, 2020).

In this report three different thermal decomposition processes are analysed:

1. TDM using natural gas-based regenerative heat exchanger reactor (NGRHER);
2. TDM using plasma torch (power-to-carbon, PTC);
3. TDM using electricity-based regenerative heat exchanger reactor (ERHER).

Natural gas-based regenerative heat exchanger reactor (NGRHER)

This process is the most mature and industrially adopted among all of the thermal decomposition methods. The CH₄-rich feedstock enters the regenerative heat exchanger reactor (RHER), where it is preheated by the counter-flow of the bed material and then reacted with the addition of heat supplied by the combustion of extra natural gas. The carbon black is then removed from the bed material and also partly filtered from the product gas. Hydrogen is purified through membrane technology, while the tail gas remaining is then recirculated to the RHER. Compared to the SMR process, TDM reaction has low hydrogen yield up to 0.2 kg H₂ per kilogram of feedstock introduced. However, this process enables to reduce CO₂ emissions to 2 kg/kg H₂, compared to 4.7–8.5 kg/kg H₂ in a SMR process (see Section 2.1.1). An overview of the H₂ production process through NGRHER method is described in Figure 12. In Table 11 the techno-economic parameters for this process are summarised.

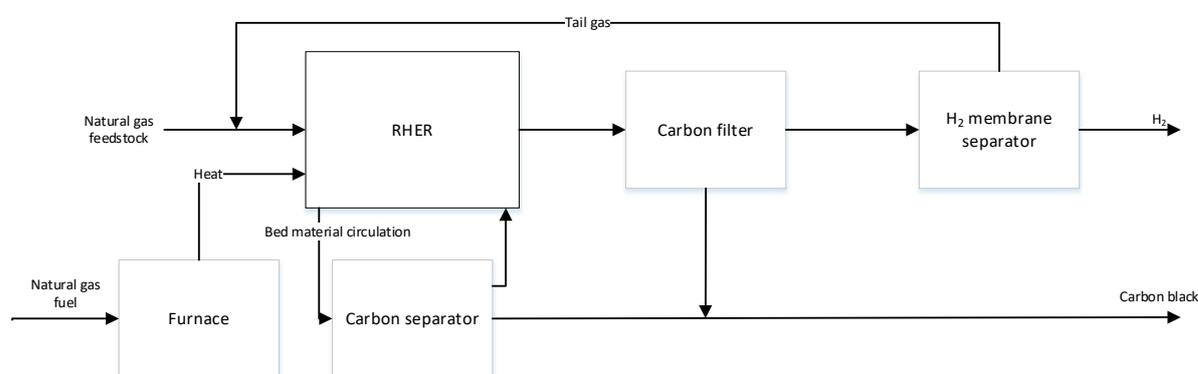


Figure 12 Flow chart of the TDM process by NGRHER for hydrogen and carbon black production (Keipi, 2017).

Table 11 Techno-economic parameters of H₂ plant through TDM with natural gas-based RHER.

Hydrogen production through thermal decomposition of methane			
	Value	Comment	Source
Direct CO₂ emissions [kt CO₂/kt H₂]	2	Direct emissions are generated through the combustion of natural gas into the furnace.	Keipi, 2017
Natural gas demand [TJ/kt H₂]	280	Of which 1/6 th as feedstock and the rest as fuel. This type of TDM plant uses heat supplied by partial oxidation for the energy requirement.	Keipi, 2017
Electricity demand [TJ/kt H₂]	-	This value does not consider the electricity consumption for air compression and tail gas pumping.	Keipi, 2017
CAPEX [MEUR2017/kt H₂]	4.2	This value includes the investment for the equipment of EUR 1.465 million for a 34.3 kt H ₂ /yr reactor, a 30% contingency, and is calculated for small-scale hydrogen capacity (around 1 kt/y of H ₂ , using a scale factor of 0.6).	Keipi, 2017
OPEX [MEUR2017/kt H₂]	0.003	Excluding feedstocks and fuels.	Keipi, 2017

4.4 Carbon capture and storage (CCS)

There are several CO₂ capture technologies that can be used to separate pure CO₂ from flue gas or syngas depending on the location. There are technologies already mature and adopted in several industrial plants in Europe and globally (Santos, 2015; Meerman, et al., 2012), and technologies that require more research and development to be feasible in terms of energy consumptions and costs. These technologies are compared in Table 12, and detailed descriptions are presented below.

Table 12 Comparison different CO₂ capture options.

Technology	Advantages	Disadvantages
Absorption	<ul style="list-style-type: none"> - High CO₂ separation rate (>90%); - Regeneration through heating and/or depressurization; - Already developed technology. 	<ul style="list-style-type: none"> - Absorption efficiency depends on CO₂ concentration; - High thermal energy demand for the regeneration process; - Risk of corrosion.
Adsorption	<ul style="list-style-type: none"> - The adsorbent can be recycled; - High CO₂ separation rate (>85%). 	<ul style="list-style-type: none"> - High-temperature adsorbent requirement; - High energy demand for the desorption process.
Chemical looping combustion	<ul style="list-style-type: none"> - No separation energy because CO₂ is the main combustion product, with N₂ unmixed. 	<ul style="list-style-type: none"> - No large-scale operation; - R&D stage of technology.
Membrane separation	<ul style="list-style-type: none"> - The technology used to separate different type of component of mixture gas; - High CO₂ separation rate (>80%). 	<ul style="list-style-type: none"> - Operational limits such as high CO₂ concentration.
Hydrate-based separation	<ul style="list-style-type: none"> - Small energy penalty. 	<ul style="list-style-type: none"> - R&D stage of technology
Cryogenic distillation	<ul style="list-style-type: none"> - Already developed technology; - High CO₂ separation rate (90-95%). 	<ul style="list-style-type: none"> - Very energy-intensive process for extremely low temperature and high pressure; - Only viable for high CO₂ concentration (>90% vol.)

4.4.1 Absorption

This technology uses a liquid absorbent, physical or chemical, that isolates CO₂ from the main mixture of gas. Most adopted solvents are monoethanolamine (MEA), diethanolamine (DEA) and potassium carbonate (Leung, Caramanna, & Maroto-Valer, 2014). Among the various options, MEA represents the most efficient one in terms of CO₂ absorption with an efficiency over 90%. However, the process is expensive in terms of thermal energy required to regenerate the solvent. The technology consists of absorption and desorption columns with heat exchangers and auxiliary equipment as shown in Figure 13.

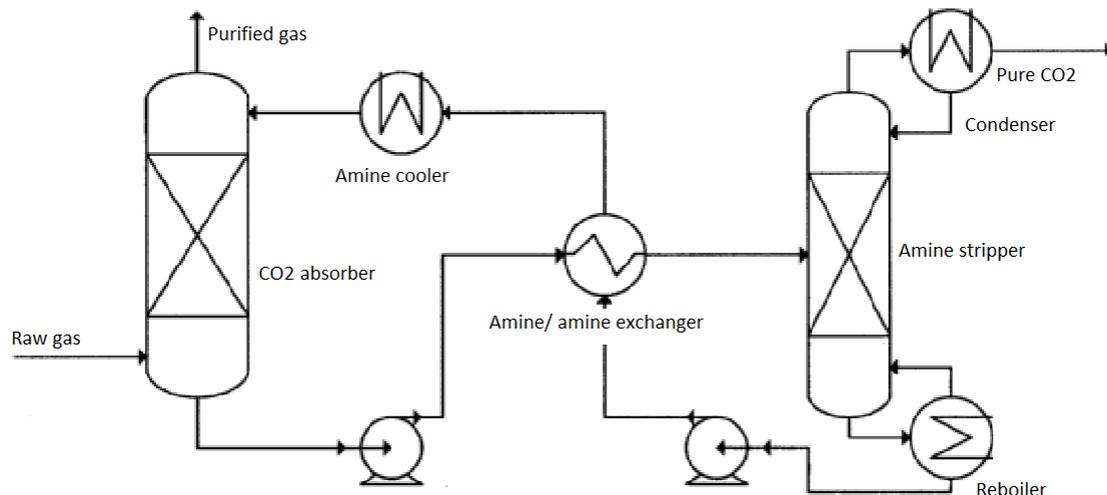


Figure 13 CO₂ removal process based on absorption in amine solution (Øi, 2012).

In the absorption column, CO₂-rich gas flows upwards and the sorption liquid flows downwards. The solvent (amine liquid containing CO₂) is pumped further through a heat exchanger to the desorption (stripper) column where the CO₂ absorbed is regenerated, and the solvent is recirculated back to the absorption column and cooled in a heat exchanger and a cooler (Øi, 2012).

There are two main drawbacks using this type of technology:

- High energy consumption;
- High amine degradation.

The former is due to high desorption energy demand for breaking the strong bonds created between CO₂ and the solvent, while the amine degradation can lead to high corrosion of the reactor.

4.4.2 Adsorption

CO₂ adsorption, instead of using a liquid solvent, use a solid sorbent that captures CO₂ molecules at its surface. Further, the sorbent can be regenerated by lowering the pressure to atmospheric (PSA) or vacuum one (VPSA), or by increasing the temperature (Temperature Swing Adsorption) through hot air or steam application, where the former option is already commercially available with an efficiency higher than 85% (Leung, Caramanna, & Maroto-Valer, 2014). Zeolite or activated carbons are the main CO₂-adsorbing materials used for their low costs and availability. Compared to the absorption process, this technology requires less thermal desorption energy since solid adsorbent has a lower heat capacity than an aqueous solvent (Global CCS Institute, 2019).

4.4.3 Chemical looping combustion

A metal oxide is adopted as oxidizer carrier instead of atmospheric air/pure oxygen directly during combustion in SMR furnace. During oxidation, the metal is reduced while the fuel is oxidized to CO₂, water and other gases. Further, the metal is oxidized in another process and recycled back to the combustion chamber, while water and by-products are easily removed by condensation. In this way, pure CO₂ is then obtained without any separation energy requirements (Leung, Caramanna, & Maroto-Valer, 2014). Different materials can be used for this separation process such as Fe₂O₃, NiO, CuO and Mn₂O₃.

4.4.4 Membrane separation

This technology, illustrated in Figure 14 exploits the different molecular volume of gases in order to allow only certain molecules such as CO₂ from natural gas or O₂ from N₂, to pass through the membrane. The structure of the membrane is made by a thin layer of composite polymer connected to a thicker, non-selective and cheap layer that supports mechanically the membrane. The development of a different type of membranes such as ceramic, metallic or polymeric, improved the separation efficiency of this process up to 88% (Leung, Caramanna, & Maroto-Valer, 2014). A disadvantage is a strong decrease in efficiency when gases with low CO₂ concentration pass through the membrane.

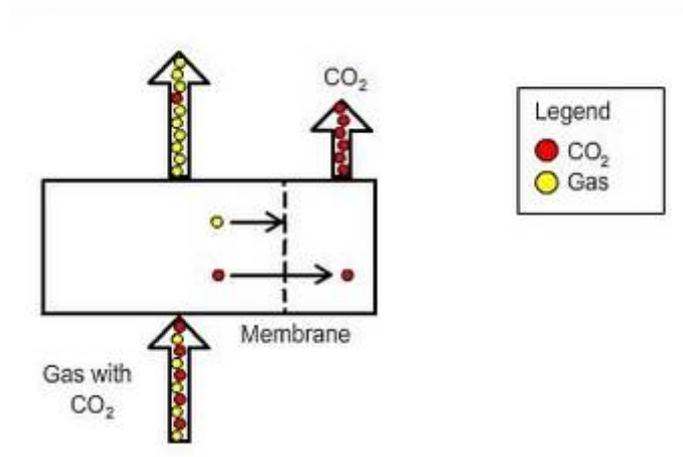


Figure 14 CO₂ removal process based on membrane separation (Bellona, 2019).

4.4.5 Hydrate-based separation

In this process, carbon dioxide presented in exhaust gas forms hydrates with water under high pressure. Different equilibrium phase of CO₂ compared to other gases is exploited to form hydrates easily. Small energy penalty (6-8%) and low energy demand (around 570 kWh/t CO₂) are the main advantages of hydrate separation technology. Increasing the hydrate formation rate and reducing the pressure of the process is possible to improve the CO₂ capture efficiency. According to the US Department of Energy (Babu, Kumar, & Linga, 2013), hydrate option is considered currently the most promising separation process in the long term and is under R&D. The whole process is described below in Figure 15.

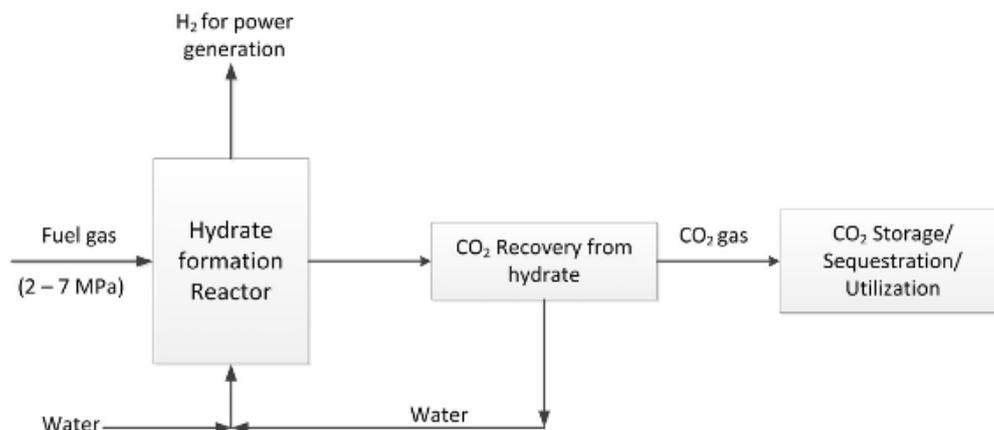


Figure 15 CO₂ capture based on hydrate separation (Babu, Linga, Kumar, & Englezos, 2015).

4.4.6 Cryogenic distillation

Cryogenic distillation is a separation process that exploits the different boiling points of the several components of a gaseous mixture, in order to separate them at very low temperature and high pressure. From flue gas, CO₂ is cooled at desublimation temperature (between -100 and -135 °C) and then solidified to be separated from other light gaseous components, and finally compressed to around 100-200 bar. The CO₂ recovery rate achievable is around 90-95% with the drawback of requiring high energy consumption due to the necessity to reach extreme operational temperature and pressure. Energy consumption is estimated to reach around 600-660 kWh/t CO₂ captured in liquid form (Göttlicher & Pruscek, 1997) and the process necessitates high-CO₂ concentration in the flue gas to be feasible (>90% vol.) (Leung, Caramanna, & Maroto-Valer, 2014).

4.4.7 Carbon capture applicability

In a standard SMR plant, CO₂ emissions come only from the flue gas but they are generated by two different processes:

- CO₂ generated by steam methane reforming and additional water-gas shift reaction;
- CO₂ generated by the combustion of natural gas fuel and recycled tail gas in the SMR furnace.

For this reason, CO₂ capture technology can be applied in three different locations of the plant:

- 1) After SMR and eventually WGS reactions to shifted syngas;
- 2) After PSA to tail gas;
- 3) After combustion to SMR flue gas.

For the first option, considering a chemical absorption unit, a CO₂ capture rate can be achieved of around 55% of the total emissions of a base SMR case without CCS that produces the same amount of hydrogen. Compared to the same base case, using chemical absorption technology in the second option an average of 52.2% CO₂ captured on total emission can be achieved, with an increase to 53.4% in case of low-temperature and membrane separation unit adoption. The highest amount of CO₂ captured is reached in the third option, where around 90% of CO₂ is separated and captured from the flue gas stream (IEAGHG, 2017). An overview of the three CCS options located in a hydrogen production process through steam methane reforming is described in Figure 16.

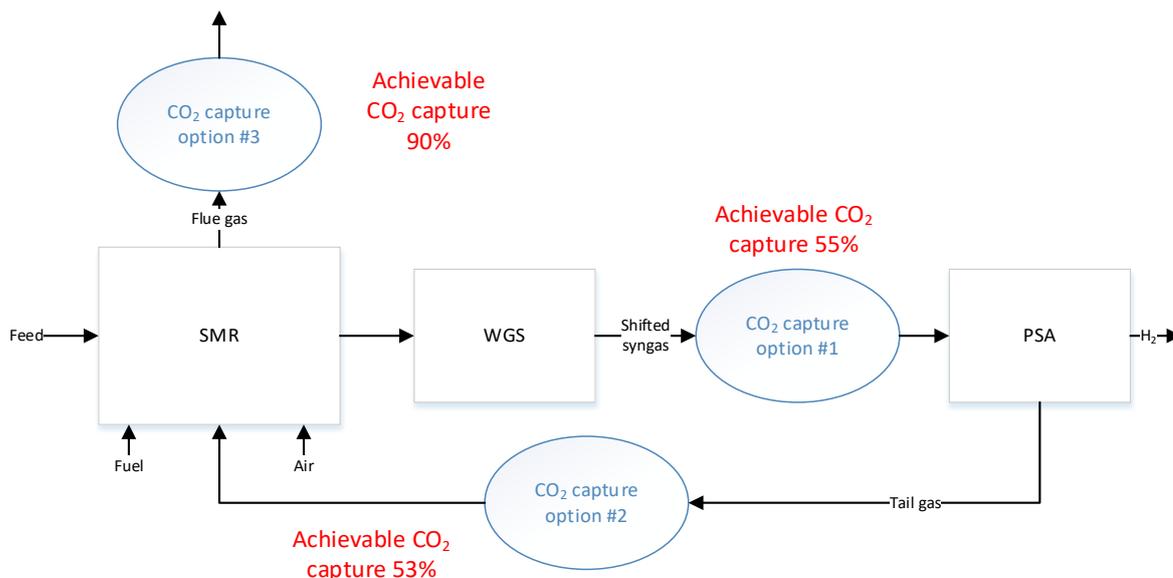


Figure 16 Overview of several CCS option in SMR hydrogen plant.

4.4.8 CO₂ transport and storage

In order to store the captured CO₂, offshore fields in the North Sea are most promising in The Netherlands. The area around the port of Rotterdam represents a CO₂-hub where greenhouse gas is produced and captured. A consortium of several CO₂ emitters, energy infrastructure organisations and government are presently (2021) developing a CO₂ pipeline and subsea injection facility in the Rotterdam port under the name Porthos. Air Liquide and Air Products are participating in this consortium as suppliers of CO₂ (Porthos, 2020). For sites that are not connected to the CO₂ pipelines, transport of CO₂ by ship can be a future possibility.

4.4.9 Cost of hydrogen production with CCS

The costs of carbon capture technology and its application are highly varying and they depend on the type of technology adopted for CO₂ capture, operational location of the technology into the plant, the transport system used and the availability of adequate storage unit capacity. In this analysis, chemical absorption through MDEA is taken as the reference separation technology used for all of the three options of CCS mentioned above, since it is the most efficient and mature technology for large-scale H₂ production (Leung, Caramanna, & Maroto-Valer, 2014).

According to IEA (IEAGHG, 2017), CO₂ absorption applied to syngas after WGS reaction can capture from 55.7% to 66.9% of the total CO₂ emitted depending on the recycle rate of H₂ to the furnace. The same technology applied to the PSA tail gas is estimated to reach CO₂ capture rate up to 54.1%, while for CCS to flue gas arrives at 89%. The drawback of this application is the energy requirement since the three CCS options demand more energy than the one consumed by a normal SMR (considering heat required for regeneration, electricity for CO₂ capture and CO₂ compression and drying). It is important to mention that CO₂ emission reduction depends also on the type of production process to which CCS technology is applied (IEAGHG, 2017).

In addition to the energy requirement, CCS technologies need capital costs that are estimated by IEAGHG in the range between 47-70 EUR/t CO₂ avoided, depending on the CCS option adopted. IEAGHG assumes 10 EUR/t is for transport and storage, which will likely be higher in The Netherlands (most recent SDE++ advice: 47 EUR/t (Lensink & Schoots, 2021)). Finally, an increase of operational and maintenance costs is observed with CCS

mainly due to higher feedstock/fuel demand, high energy requirements and transportation & storage costs.

Table 13 Techno-economic parameters of CCS method from shifted syngas in SMR based H₂ plant.

	Value	Comment	Source
CO₂ emissions [kt CO₂/kt H₂]	4.4	Chemical absorption with MDEA considered as capture technology. Location of the separator is after the WGS reactor with shifted syngas. CO ₂ emissions reduced by 54%.	IEAGHG, 2017
Electricity demand [TJ/kt H₂]	1.5	Includes CO ₂ capture, compression and drying.	IEAGHG, 2017
CAPEX [2017MEUR/kt H₂/yr]	0.57	This value includes capital investments for CO ₂ capture plant and CO ₂ compression plant. This value is calculated for large-scale hydrogen capacity (around 70 kt/y of H ₂).	IEAGHG, 2017
OPEX [2017MEUR/kt H₂/yr]	0.19	This value includes labour and maintenance costs.	IEAGHG, 2017

Table 14 Techno-economic parameters of CCS method from tail gas in SMR based H₂ plant.

	Value	Comment	Source
CO₂ emissions [kt CO₂/kt H₂]	4.6	Chemical absorption with MDEA considered as capture technology. Location of the separator is after the PSA reactor with tail gas. CO ₂ emissions reduced by 52%.	IEAGHG, 2017
Electricity demand [TJ/kt H₂]	2.7	Includes CO ₂ capture, compression and drying.	IEAGHG, 2017
CAPEX [2017MEUR/kt H₂/yr]	0.92	This value includes capital investments for CO ₂ capture plant and CO ₂ compression plant. This value is calculated for large-scale hydrogen capacity (around 70 kt/y of H ₂).	IEAGHG, 2017
OPEX [2017MEUR/kt H₂/yr]	0.23	This value includes labour and maintenance costs.	IEAGHG, 2017

Table 15 Techno-economic parameters of CCS method from flue gas in SMR based H₂ plant.

	Value	Comment	Source
CO₂ emissions [kt CO₂/kt H₂]	1.1	Chemical absorption with MDEA considered as capture technology. Location of the separator is after the SMR furnace with flue gas. CO ₂ emissions reduced by 89%.	IEAGHG, 2017
Electricity demand [TJ/kt H₂]	3.6	Includes CO ₂ capture, compression and drying.	IEAGHG, 2017
CAPEX [2017MEUR/kt H₂/yr]	1.8	This value includes capital investments for CO ₂ capture plant and CO ₂ compression plant. This value is calculated for large-scale hydrogen capacity (around 70 kt/y of H ₂).	IEAGHG, 2017
OPEX [2017MEUR/kt H₂/yr]	0.35	This value includes labour and maintenance costs.	IEAGHG, 2017

A study by a consortium of companies in the Rotterdam-Moerdijk industrial cluster (including Air Liquide) has presented a feasibility study into blue hydrogen ('H-vision') in 2019. This study investigates the technical possibility for low-carbon hydrogen production by means of ATR with CCS, as fuel for refineries and electricity production (H-Vision, 2019).

Table 16 shows a cost estimate for a large-scale ATR plant with CCS, based on natural gas feedstock. The numbers were provided by Air Liquide for the H-vision project (H-Vision, 2019, p. 51), and the units adapted to the ones above. The plant can produce about 2.4 GW_{th} (LHV) hydrogen (and some 305 t/h HP steam and 100 t/h MP steam) from a total feedstock (natural gas and refinery fuel gas) of 3.13 GW_{th} (LHV).

Table 16 Techno-economic parameters of a high-pressure ATR based H₂ plant with CO₂ capture. All numbers based on 8760 operating hours per year.

	Value	Comment	Source
CO₂ emissions [kt CO ₂ /kt H ₂]	0.1	Direct emissions at the H-vision plant. Overall capture rate is 88%.	H-vision, 2019
Electricity demand [TJ/kt H ₂]	4.5	Total imported electricity.	H-vision, 2019
CAPEX [2019MEUR/kt H ₂ /yr]	1.8	This value is the total plant costs of ATR with CO ₂ capture. This value is calculated for large-scale hydrogen capacity (around 500 kt/y of H ₂).	H-vision, 2019
OPEX [2019MEUR/kt H ₂ /yr]	0.04	2.5% of CAPEX	H-vision, 2019

4.5 Carbon capture and utilisation (CCU)

Carbon capture and utilisation use the same capture technologies presented in the previous chapter with the same consideration for applicability and transportation. An overview of European CCU technologies is shown below and it is retrieved from research conducted by the European Commission Joint Research Centre. This gives an overall picture of potential CO₂ uptake per type of utilisation. It is important to consider that CO₂ has also a consistent market value in the Netherlands as feedstock for crop nourishment (OCAP project). In addition, a Technology Readiness Level (TRL) assessment is described in order to define the technological and commercial potential of each technology ranging from "1", which means basic concept level, to "9", commercial-scale (Bocin-Dumitriu, Perez Fortes, Tzimas, & Sveen, 2013).

Table 17 Overview of the most promising European CCU utilisations with CO₂ potential uptake and the TRLs descriptions (Bocin-Dumitriu, Perez Fortes, Tzimas, & Sveen, 2013).

CO ₂ utilisation	Uptake potential (Mt/y)	TRLs
Methanol production	>300	4-6
(Carbonate) Mineralisation	>300	3-6
Polymerisation	5-30	8-9
Formic acid	>300	2-4
Urea	5-30	9
Enhanced coal bed methane recovery	30-300	6
Enhanced geothermal systems	5-30	4
Algae cultivation	>300	3-5
Concrete curing	30-300	4-6
Bauxite residue treatment	5-30	4-5
Fuels engineered micro-organism	>300	2-4
CO ₂ injection to the methanol synthesis	1-5	2-4

An alternative possibility of CCU would be the utilisation of CO, rather than CO₂, if the production process delivers its carbon as CO. It is state of the art to utilise CO for several applications, as described in Section 3.2.

4.6 Oxygen, Nitrogen and Argon: Green electricity consumption

Air industrial gas production (to produce O₂, N₂ and Ar) does not produce direct CO₂ emissions, but it generates indirect CO₂ emissions due to the heavy electricity consumption (around 220-340 kWh/t O₂). According to the Climate and Energy Outlook (KEV) 2020, the emission factor of the electricity (integral method) was around 0.43 kg CO₂/kWh, and is projected to be around 0.12 kg CO₂/kWh in 2030 (PBL; TNO; CBS; RIVM, 2020). In order to make this value equal to zero and to completely decarbonise the air industrial gas production, fully renewable electricity supply is required. According to the 'Klimaatwet' (Climate Act), adopted in 2019, The Netherlands strives to reaching 100% renewable electricity supply by 2050.

As of 2019, the production of green electricity amounts to 21.8 TWh or 78 PJ, which is about 18 percent of the total electricity consumption in The Netherlands (CBS, 2020).

5 Discussion

From the previous Chapter, it can be noticed that possible decarbonisation options for the industrial gases production industry involve the categories of fuel substitution, feedstock substitution, process design and carbon capture utilisation and storage (CCUS). The application and feasibility of the options is highly dependent on several factors that will be discussed in this Chapter.

First of all, the **thermal methane decomposition** alternative can be currently considered a suitable technology for small or medium-scale industrial hydrogen production (less than about 10 kt H₂) that can be adopted for on-site demand (Keipi, Tolvanen, & Konttinen, 2018). As benefits, the CO₂ emissions in hydrogen production by TDM are low (2 tCO₂ / tH₂) and the technology has the ability to utilise the current natural gas network for the feedstock supply with a good feedstock availability. The major issues for this option, that need to be addressed, are presently a limited market for the product carbon black and the production cost being relatively high compared to a conventional SMR plant. A sufficiently large carbon black market would increase the interest in the TDM process and tighter emission regulations would decrease the feasibility gap between TDM and SMR hydrogen production process. It is also relevant where the carbon will then end up and in which timeframe. This determines whether it can be considered to be a type of CCS or CCU.

Secondly, the realisation of the other discussed decarbonisation options related to both feedstock replacement and process design with the adoption of **biomass** is dependent on the choice of the type of biomass, its availability and the gasification agent adopted. Currently, the available capacity for sustainable biomass in the Netherlands is evaluated between 250 and 700 PJ per year (Gigler & Weeda, 2018; PBL, 2016; PBL & ECN, 2011). Without taking into account the process losses, the hydrogen production demand for these applications is considered around 930 PJ, with an electrical demand of 388 TWh. The discussed process chains are based on the adoption of already mature technologies (TRLs of 8 or above for gasifier, gas cleaning and upgrading) and therefore, the improvement of the overall process to be competitive with conventional plants could be achieved in the near future. From the analysis, it can be noticed that the pure steam is the best gasification agent for the hydrogen production but if a higher purity is requested, the use of a catalyst is necessary for a higher yield and purity. Despite the fact that production of hydrogen from biomass is already economically competitive, the technology needs further development and demonstrations (Czernik, Evans, & French, 2007).

Thirdly, the production of green hydrogen by **electrolysis** depends mainly on the prices of electricity, capital and operational costs for the required electrolyzers, without considering transportation costs since it is assumed an on-site hydrogen production. The CAPEX cost is expected to decrease by 70% in 2030 due to potential improvements in capacity and production efficiency (WEC, 2019). Furthermore, the production cost is predicted to drop to EUR 2-3 in 2030, which is almost the current price for hydrogen from SMR, thanks to a sufficient amount of renewable electricity produced at an affordable price. Shifting from natural gas-based to electrolytic hydrogen production with the current electricity grid conditions would actually lead to an increase in CO₂ emissions per unit of hydrogen produced due to the emission factor of the Dutch electricity mix, so at the moment it can only be considered a sustainable decarbonisation option if the electrolyser is directly coupled to a renewable electricity plant without grid connection, or if only grid electricity is used at periods of excessive supply of renewable electricity. But, in the coming decade, the supply of

renewable electricity will grow considerably, and this option may then be well advantageous to make effective use of the renewable electricity.

Finally, the adoption of **carbon capture** technology is currently considered. CO₂ is used for the production process of some types of fertilisers or for direct use in beverages or in greenhouses, but the CO₂ market potential is too limited to be considered a valuable by-product. In the future this may change when CO₂ would be used for other applications, such as in the methanol production process. But for now, the capture and storage of CO₂ in depleted offshore gas fields are necessary to make this decarbonisation option feasible. The trade-off is between CO₂ costs and CCS costs. In 2030, technological improvements and increase of scale will lead to a drop of around 36% of CCS costs and the ETS price level is expected to increase significantly (WEC, 2019). 'Blue hydrogen' (reforming with carbon capture and storage) is therefore considered the most promising decarbonisation option in the near future.

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Appendix A: CHPs owned by Air Liquide

One of the major sources of emissions of Air Liquide is a gas-fired CHP (combined heat and power) installation under the name PerGen VOF, which is located at the Shell refinery at Pernis. The CHP produces steam and electricity. A large part of this steam (about 450 t/h at 90 bar (R. Stikkelman, personal communication, 2020), i.e. 4.9 PJ/yr) is used by Shell. The electricity is sold to Eneco. For completeness, we include the emissions of this CHP in this report; nevertheless, it should be understood that these emissions should (largely) not be allocated to the production of industrial gases.

Furthermore, Air Liquide owns energy producers Enecal Energy VOF and Eurogen C.V. (ACM, 2014), which are separate NEa entities. Enecal and Eurogen are located at the site of chemicals manufacturer Huntsman in Botlek. Enecal delivers steam to Air Liquide and electricity to Eneco. Eurogen delivers steam to Air Liquide, Lyondell and Huntsman and electricity to Eneco (Port of Rotterdam, 2016).

Table 18 CO₂ emissions and energy consumption and production by Air Liquide in Rotterdam

Company and location	Installation (EEA, 2019)	Production capacity [PJ/yr]		Direct CO ₂ emission in 2018 (nea, 2020)[kt/yr]	Natural gas consumption in 2018 [PJ] (calculated from 2018 emission)
		Electricity	Steam		
PerGen VOF - Vondelingenplaat (Shell refinery)	CHP (STEG)	8.5 ¹⁾	8.7 ²⁾	1,267	22.4
Enecal Energy VOF - Botlek	CHP (STEG)	1.1 ³⁾	1.1 ³⁾	174	3.1
Eurogen C.V. - Botlek	CHP (STEG)	2.1 ³⁾	2.2 ³⁾	237	4.2

- 1) The installed power of 300 MWe (excluding about 8 MW for internal use), assuming utilisation ratio of 90% (2018), corresponds to 2.4 TWh/yr or 8.5 PJ/yr. Source: (PerGen, 2020)
- 2) Production capacity is 800 t/h (Port of Rotterdam, 2016, p. 32) at 90 bar (R. Stikkelman, personal communication, 2020). This corresponds to 8.7 PJ/yr, using 1.37 MJ per kg steam and a utilisation ratio of 90%.
- 3) Estimates for the PBL SAVE model (Van Hout, Wetzels, & Daniels, 2019); assuming 48 MWe and 88 MWe for Enecal and Eurogen, respectively (Port of Rotterdam, 2016, p. 32).

The decarbonisation options of these CHPs include replacement of the fuel (natural gas), by either biogas, biomass or hydrogen (H-Vision, 2019). Note that the CHPs produce both steam and electricity; the steam supply may be electrified (although this likely requires a reinforcement of the local grid), but this requires the electricity production to be taken over by other power plants.

Another option for the CHPs would be carbon capture and storage (CCS), applied to the flue gases of the CHPs. The latter is particularly convenient because the CHPs are located very close to the planned CO₂ pipelines related to the 'Porthos' CCS project in the Rotterdam.