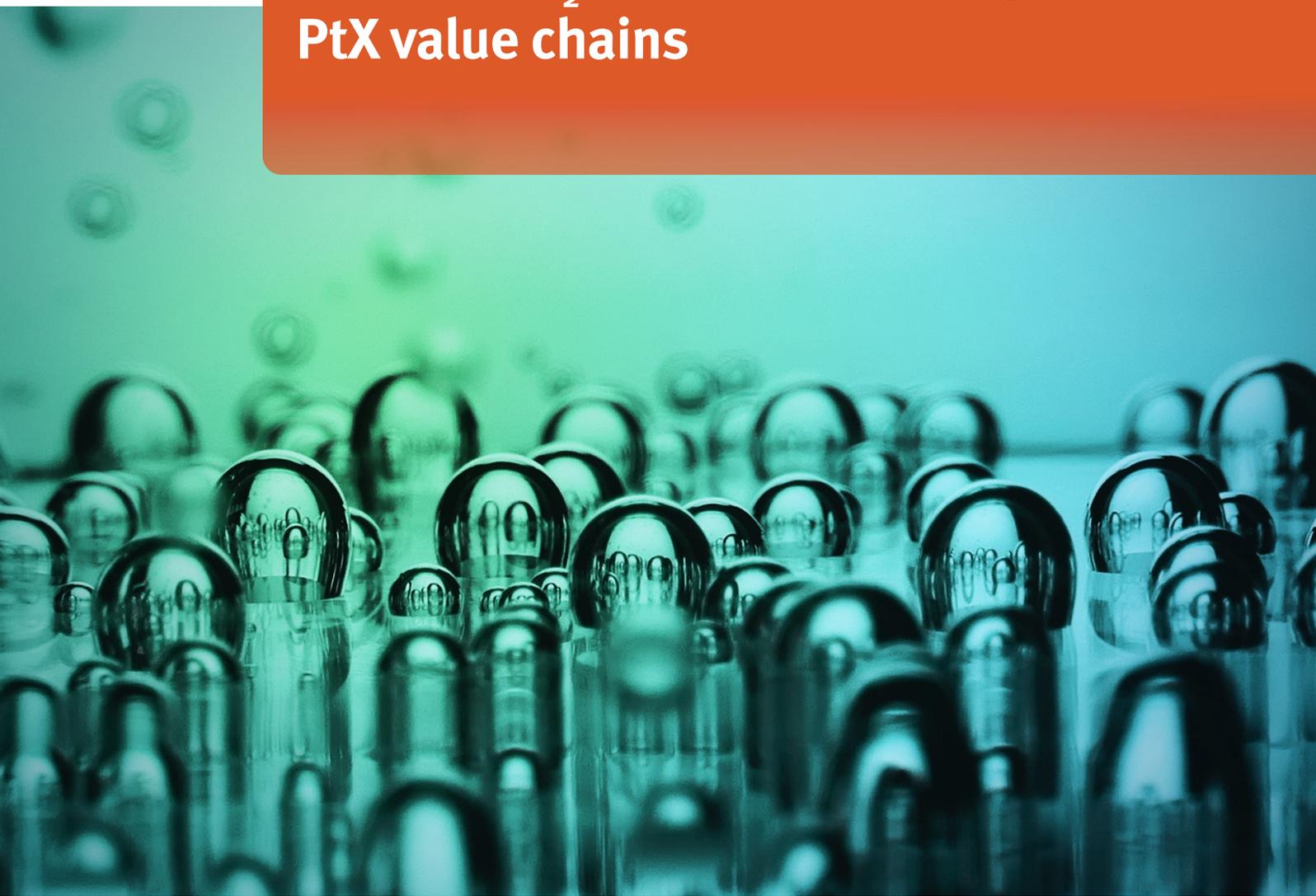


Report

Carbon for Power-to-X

Suitable CO₂ sources and integration in PtX value chains



IMPRINT**Authors**

Anusha Roshini Alagu
Chokri Boumrifak
Luisa Fernanda López González

Editor

DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V.

Responsible for content under the terms of press legislations

Chokri Boumrifak
DECHEMA e.V.
Theodor-Heuss-Allee 25
60486 Frankfurt am Main
Germany

Email: chokri.boumrifak@dechema.de

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Graphics and typesetting

Chokri Boumrifak

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DECHEMA
Gesellschaft für Chemische Technik
und Biotechnologie e.V.
Theodor-Heuss Allee 25
60486 Frankfurt am Main
Germany
Phone: +49 (0)69 7564-0
Fax: +49 (0)69 7564-117
E-Mail: info@dechema.de

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Abbreviations

Aluminium Oxide	Al ₂ O ₃
Basic Oxygen Furnace	BOF
Bioenergy with Carbon Capture and Storage/Utilization	BECCS/U
Blast Furnace	BF
Carbon Capture and Storage	CCS
Carbon Capture and Utilization	CCU
Calcium Carbonate	CaCO ₃
Carbon Dioxide	CO ₂
Carbon Monoxide	CO
Chemical Looping Combustion	CLC
Combined Cycle Power Plant	CCPP
Dimethyl Ether	DME
Direct Air Capture	DAC
Direct Reduced Iron	DRI
Electric Arc Furnace	EAF
Enhanced Oil Recovery	EOR
Electroactive Bacteria	EAB
Greenhouse Gas	GHG
Hydrogen	H ₂
Integrated Gasification Combined Cycle	IGCC
Ionic Liquid	IL
Metal Organic Frameworks	MOF
Microbial Electrolytic Carbon Capture	MECC
Microbial Electrosynthesis	MES
Monoethanolamine	MEA
Oxygen	O ₂
Power-to-Gas	PtG
Power-to-Liquid	PtL
Power-to-X	PtX
Pressure Swing Adsorption	PSA
Renewable Energy	RE
Silicon oxide	SiO ₂
Sodium Carbonate	Na ₂ CO ₃
Technology Readiness Level	TRL
Tonne	t
Vacuum Pressure Swing Adsorption	VPSA
Water	H ₂ O

Preface

This document was conducted within the framework of the International PtX Hub. This project supports the development of sustainable Power-to-X (PtX) and hydrogen markets as a building block for the energy transition in countries such as Morocco, South Africa, and Argentina. The identification of suitable carbon sources for PtX production is currently taking place in these three countries. This document gives a general insight about carbon sources, separation methods, capture technologies and infrastructure requirements. In future in-depth studies, the conditions and developments of each partner country can be assessed.

For tackling climate change, these countries are in the process of developing various technologies to defossilize their processes and export sustainable molecules. To achieve this, fossil fuels need to be replaced by renewable electricity or by more sustainable alternatives such as renewable synthetic or biogenic fuels.

Power-to-X provides a sustainable solution to produce these sustainable molecules by combining electrolysis with CO₂ capture technologies from different industries, biogenic sources, waste management or atmospheric air. Aiming carbon neutrality for the long-term and thus replacing fossil routes, sustainable CO₂ sources from biogenic origin or via direct air capture (DAC) will be needed in large scale to cover the future CO₂ demand for PtX routes.

In this document, carbon sources from different sectors worldwide have been discussed. This provides an idea of the current amount of CO₂ emitted. Furthermore, the report covers numerous aspects of carbon capture technologies and processes, including the infrastructure for transport and storage. This is abetted by a description and evaluation of state-of-the-art technologies taking into account their potentials and limitations. Detailed transport and storage possibilities are highly constrained by regional circumstances and can be inferred in the future studies.

The implementation of carbon sources in PtX applications involves a myriad of challenges related to scalability and sustainability. Uncertainty over the likely costs of tapping into carbon sources is also a major challenge. All these challenges must be resolved for a successful roll-out of PtX technologies.

Executive Summary

On the path for an industrial transformation to become more sustainable and less reliant on fossil resources, the attention for alternative and innovative technologies is growing. So called Power-to-X technologies (PtX) play a major role in sectors which are hard to electrify. Despite the high potential of PtX, its reliance on a carbon source for most of the products, is often overlooked. The utilization of carbon dioxide (CO₂) represents a suitable option since CO₂ can be obtained as a waste product in many industrial sectors, extracted from biogenic sources or captured from the atmospheric air.

Applying carbon capture in the context of PtX requires the consideration of numerous aspects which include the identification of a reliable CO₂ source, the extraction of the gas with various methods and technologies and the final use as a carbon feedstock (Figure 0.1). Factors such as quantity, quality, sustainability, feasibility, and scalability of the various capture routes are crucial to enable industrial implementation of PtX.

Sources

Depending on the source of CO₂, its purity and the method for capturing the gas can vary a lot. Moreover, in case the process route also involves the use of fossil resources, additional implications concerning the sustainability and potential lock-in effects must be considered. Therefore, CO₂ can be categorized according to its origin from the

energy and industry sectors, biogenic sources, waste and wastewater or directly from the atmospheric air. The categorization of the carbon source origin already separates sectors that rely on combustion processes such as the energy and industry sector. Whereas sources from waste, biogenic CO₂ and direct air capturing have the potential to be implemented in a closed carbon cycle. However, quality and availability of these sources need to match the PtX process routes and rely in some parts on the maturity of the separation and capture methods.

The **energy sector** emits 43% of global CO₂ emissions, mainly from the combustion of fossil fuels for heat and electricity generation. The environmental benefits of using CO₂ from this sector is limited, since the CO₂ will be released into the atmosphere at the end-of-life of the PtX product. Additionally, efforts are globally being made to avoid emissions from the energy sector, which means that the CO₂ availability from this sector will be drastically reduced in the near future.

The **industry sector** is highly energy intensive, but besides energy emissions, industrial processes also produce CO₂ as a byproduct in some chemical reactions. These process emissions account for 4% of global CO₂ emissions and are originated in the production of cement, iron and steel, chemicals and petrochemicals, pulp and paper and aluminium, among others.

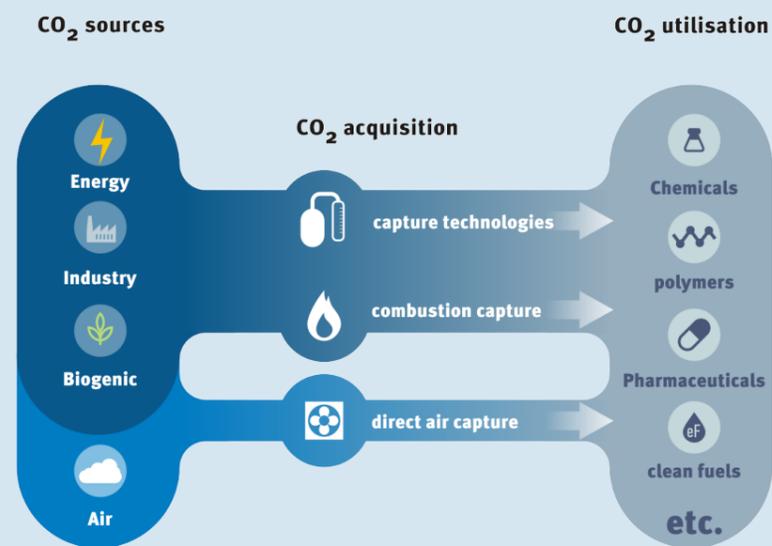


Figure 0.1 Carbon based PtX routes rely on three basic elements: identification of CO₂ source, CO₂ accumulation through a separation or capture method and the application of CO₂ to generate a value added product.

Biogenic CO₂ is produced either from the processing of biomass to further products such as bioethanol or biogas, or from the combustion of biomass and biomass derived products. The use of biogenic CO₂ for PtX production can promote a closed carbon cycle if the harvesting and use of the selected biomass is carried out considering sustainable criteria.

In the **waste and wastewater management** a considerable portion of organic material must be processed. Nowadays, solid waste incineration is the main source of CO₂ from this sector. Nevertheless, development of CO₂ capture through processing the organic material advances in this field. Materials from solid waste can be applied to for reuse in building materials and the CO₂ from the combustion can be captured to mitigate its emission. Wastewater can be treated via several microbial approaches which converts the organic material in value added chemicals and CO₂.

Atmospheric air contains CO₂ in extreme small proportions, and it is equally available as a source in all regions. Its separation is although energy intensive but could serve as a carbon source in regions with good availability of renewable resources. In parallel to biogenic sources, CO₂ from atmospheric air could create a closed carbon cycle, provided a 100% use of renewable energy for its capture.

Capture Technologies

Distinct separation methods are available to obtain CO₂ and depend on factors such as the quality of the stream composition, efficiency, and cost-effectiveness.

Amine gas treatment is among all CO₂ separation methods the most matured technology (TLR 9) and has already been widely commercialized. Several other separation techniques namely cryogenic separation, Pressure Swing Adsorption (PSA), Vacuum Pressure Swing Adsorption (VPSA), membrane separation, and chemical looping combustion are employed in carbon separation.

Capture Processes

There are three main approaches to capturing the CO₂ generated from combustion of fossil fuels, biomass, or mixtures of these fuels. Additionally, CO₂ can be captured directly from the atmosphere.

Direct Air Capture separates CO₂ from the air and has a high potential as a clean carbon technology in sustainable PtX. Nevertheless, this capture process is not yet mature for industrial scale applications and requires immense amounts of energy which should be supplied by renewable resources.

The **Post-combustion** approach separates CO₂ from the flue gases produced by the combustion of the primary fuel

in air. This technology is preferred for existing power plants, since it is already mature and can be easily incorporated into new and existing plants. Nevertheless, this technology is characterized by low carbon capture efficiency due to low CO₂ concentrations in the flue gas.

The **Pre-combustion** approach employs gasification of the primary fuel in a reactor with steam and air or oxygen to produce syngas. In this way, the CO₂ is removed from the process before the combustion takes place. Pre-combustion is implemented at power plants that employ integrated gasification combined cycle (IGCC) technology. This capture approach cannot be implemented to existing plants, but it is highly efficient, and the separation process is easier compared to the post-combustion approach.

The **Oxyfuel combustion** approach uses pure oxygen for the combustion of the primary fuel to produce a flue gas that consists mainly of water vapour and CO₂. The major advantages of oxyfuel combustion are reduced NO_x emissions, high CO₂ purity and lower gas volumes.

Utilization

Carbon sources can be utilized in many ways and through already existing production routes or new established processes to synthesize chemicals with added value. Most of the traditional production routes which are based on syngas (a mixture of hydrogen and carbon monoxide) can be carried out with sustainable hydrogen and carbon sources. Various commodity chemicals, polymers and synthetic fuels (efuels) can be produced through these processes. The primary production routes with CO₂ as feedstock include methanol synthesis (fuels, precursor for polymers, acids, etc.), Fischer-Tropsch (fuels, waxes, naphtha and methane) and carbonylation processes. Adaption of these production routes to a PtX concept require novel technologies to convert CO₂ to the respective precursor. One of the most advanced use case for PtX are Power-to-Liquid (PtL) processes for the production of efuels.

Infrastructure

With an increasing scale of PtX production and carbon supply, there will be a need for a dedicated and functional CO₂ infrastructure. This includes purification, compression, transport and storage to ensure a successful implementation into the PtX value chain. CO₂ can be transported in numerous ways such as trucks, ships, or pipelines. However at large scale and with increasing distances, deployment of pipelines is the most feasible way to manage CO₂ streams between supplier and off-taker.

1 Introduction

Mitigating anthropogenic carbon dioxide (CO₂) emissions is a necessary measure to reduce the impact of climate change. Therefore, CO₂ removal from the atmosphere and from emitting processes is a necessary contribution to greenhouse gas (GHG) reduction. CO₂ can either be stored permanently or used as a carbon feedstock. Most and foremost, Power-to-X (PtX) technologies offer a vast range of applications for CO₂ as a feedstock, especially in those sectors which are difficult to electrify, or which still need to produce hydrocarbons. PtX begins with the production of green hydrogen and branches out to numerous commodities which include hydrocarbons as following products (e-fuels, polymers, basic chemicals etc.). This enables fossil-based industries a transition to a sustainable operation. Main causes of the increasing CO₂ concentration in the atmosphere are commonly the extraction and burning of fossil hydrocarbons. This

process can be simplified as a reaction of fuel with oxygen, producing CO₂ and water (Figure 1.1).

Therefore, avoiding the burning of fossil resources, directly contributes to the reduction of CO₂ emissions. Nevertheless, certain industrial sectors, e.g., steel or cement industry, produce unavoidable emissions for process related reasons (not necessarily from fossil sources). In these cases, the processes are lacking alternative materials and production routes [1]. Furthermore, there are CO₂ sources which do not stem from fossil sources such as biogenic materials or waste treatment. All these examples are considered to be potential carbon sources for PtX applications. With innovative PtX processes CO₂ can be converted to hydrocarbons.

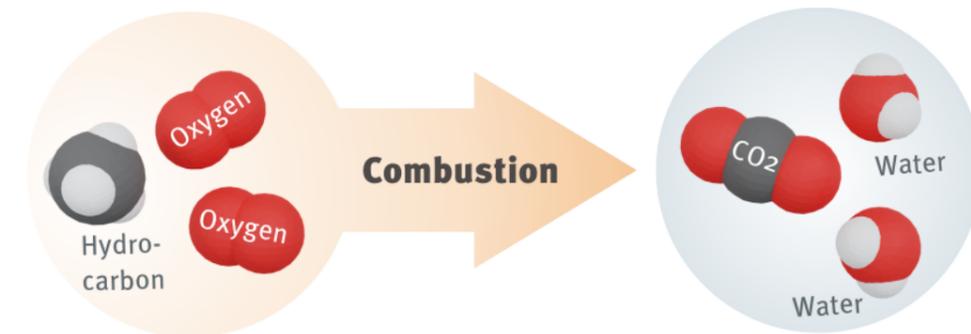


Figure 1.1 The main cause for the increase of climate harming CO₂ are combustion processes. Hydrocarbons react with oxygen and result in CO₂ and water.

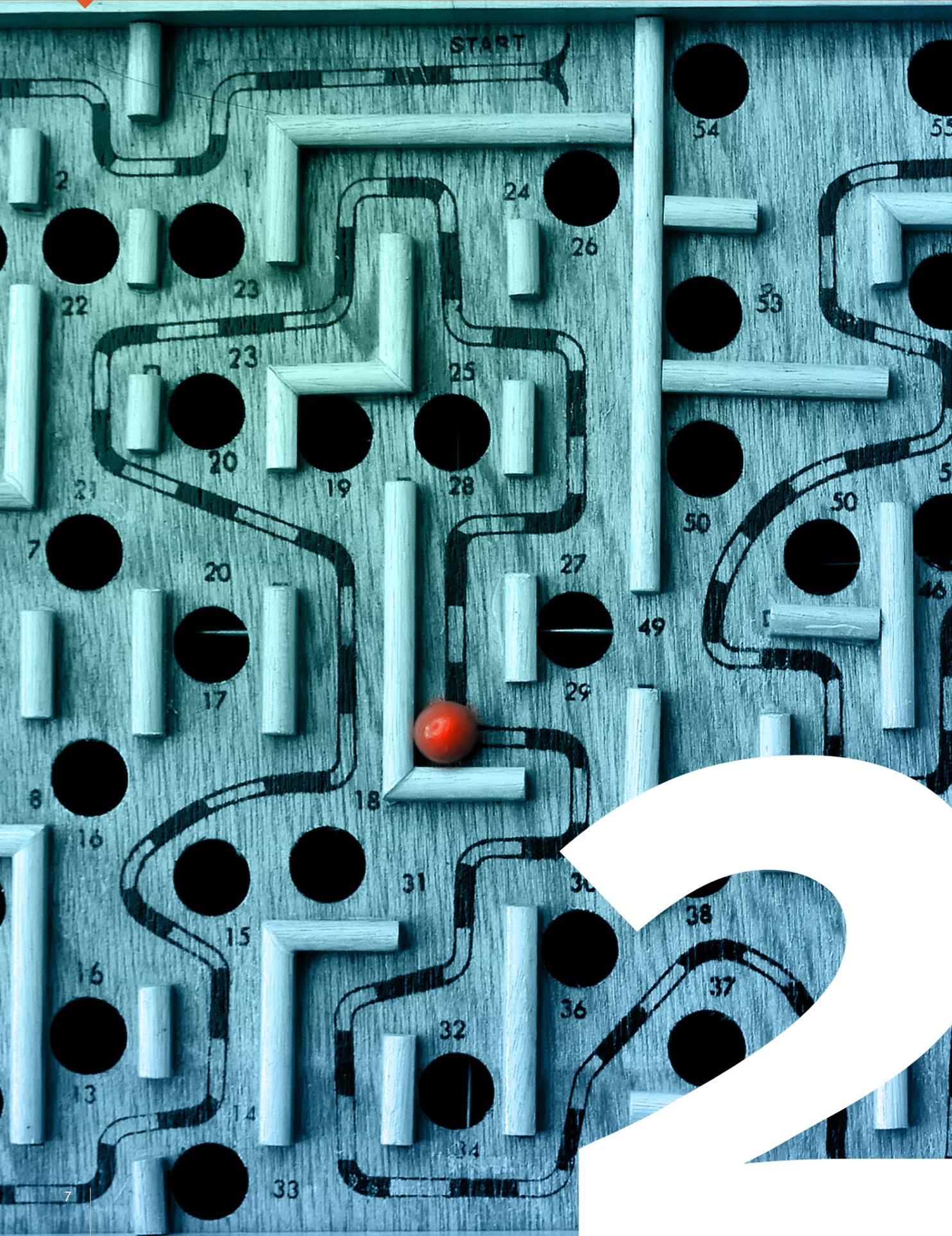
Today, CO₂ is already used in some fields such as the beverage industry to add gas to carbonated beverages, as cleaning agent in the textile industry, as feedstock in urea production and as cooling medium in various processes, among others. However, CO₂ as a relevant industrial carbon resource rarely comes to the fore and has been marginally considered in the past. Therefore, many questions concerning potential CO₂ sources, quantities and infrastructure for a large-scale deployment remain unanswered. Furthermore, the availability and maturity of carbon capture methods need to be addressed.

This report provides an overview about technical requirements and developments for CO₂ use in PtX applications with a focus on:

- CO₂ point sources
- CO₂ separation methods and capturing technologies
- CO₂ Infrastructure

Availability and maturity of technologies are displayed to have a comparison of various options for deployment.

2 Carbon Feedstock



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The concept of PtX is based on the conversion of renewable resources to energy carriers and materials as an alternative to conventional fossil production routes. The development of various PtX value chains could provide a remarkable array of products which can serve as a sustainable feedstock. Fostering profound implications of PtX commodities, these new production routes can be considered as crucial contributions for the transformation of the mobility sector and the chemical industry. Central to this concept is the synthesis of green hydrogen and more importantly its derivatives, including hydrocarbons and ammonia.

Chemicals

For a feasible implementation of PtX, it must compete with traditional chemical feedstocks such as syngas. Defined as a composite blend of hydrogen and carbon monoxide (CO), syngas has long been conventionally harnessed from fossil-based resources. The versatility of syngas, especially as a precursor for a myriad of hydrocarbons, underlines the importance for the chemical industry.

The primary hydrocarbon production pathways for PtX include methanol synthesis, Fischer-Tropsch process (fuels, waxes, naphtha and methane), carbonylation, oxo-alcohols and dimethyl ether (DME). As displayed in Figure 2.1, numerous hydrocarbons serve as base chemicals and can be produced via sustainable routes based on CO₂ as feedstock. Notably, naphtha produced from the Fischer-Tropsch process can be used as a base in the chemical industry. Consequently, sustainable CO₂ sources have gained prominence as vital feedstocks to unlock the deployment of PtX.

Henceforth, various PtX applications rely on CO₂ as a carbon source which can be either extracted from the atmosphere or from biogenic and industrial point sources. These innovative pathways will reduce the dependence of the chemical industries on fossil fuels and consequently contribute to the mitigation of industrial CO₂ emissions as well as via recycling and valorization of emitted CO₂. This undertaking necessarily requires a change in the conventional production of hydrocarbons to new PtX production routes [2].

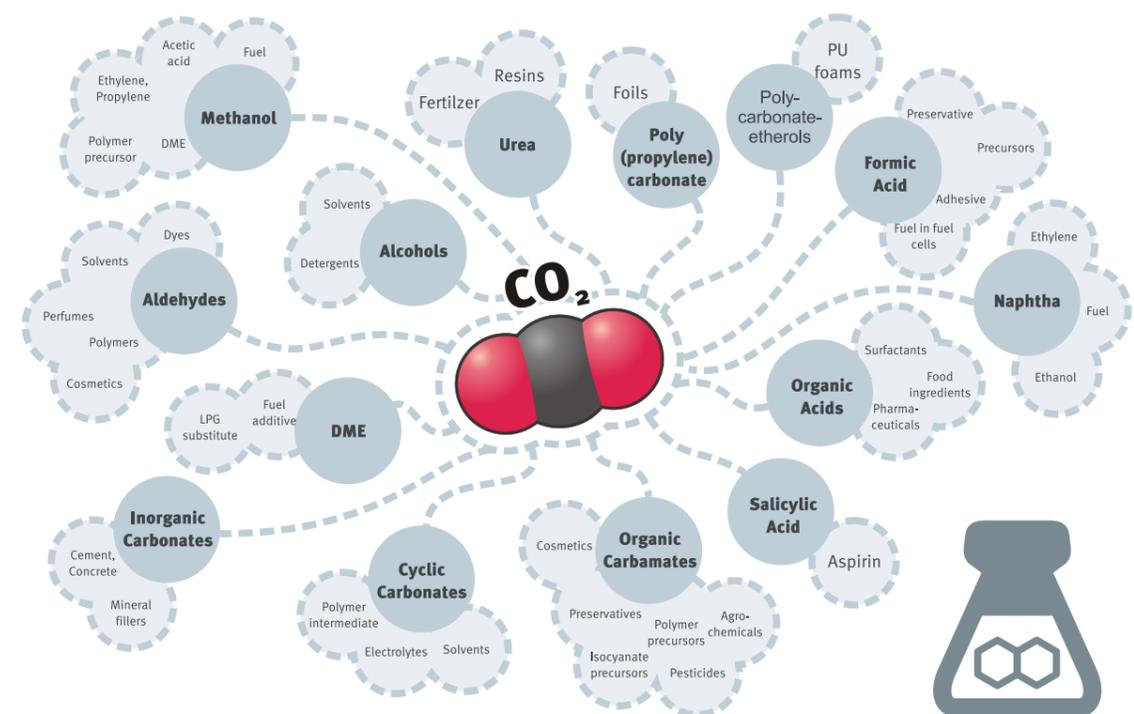


Figure 2.1 Routes and deployment of CO₂ as as feedstock for the production of chemical with added value.[2]

2 Carbon Feedstock

Currently, the largest CO₂ demand in absolute numbers derives from the urea production. However, numerous other processes apply CO₂ in a commercial scale with the production of cyclic carbonates and salicylic acids (0.1 Mio t/a) [2]. Furthermore, CO₂ serves as co-monomer for diverse polymers. Depending on the production route the CO₂ feedstock can vary between about 0.7 - 6 t_{CO₂}/t_{product} (see Figure 2.2).

Commonly used for the production of epoxides, foils and foams, poly(propylene)carbonate and polycarbonate etherols are polymers which can be based on CO₂. There are two industrial players (Novomer Inc., US; Covestro, Germany) who operate in this area (TRL 7-9). In a pilot scale, formic acid is produced with 1 kg/day though electrochemical CO₂ reduction (DNV, Norway) and another plant with an output of 100 kg/day by Mantra Energy Alternatives (Canada, TRL 7) were designed [3]. A crucial technology is the electroreduction of CO₂ which is still in development. However, commercial electrolyzers for CO₂ to CO reduction are provided by companies such as Topsoe [4]. Another small-scale process with high potential is the direct use of CO₂ for DME synthesis which requires 0.125 t_{CO₂} / t_{DME}.

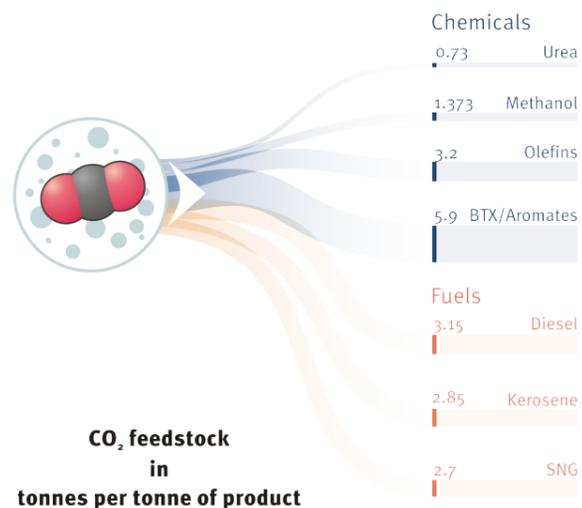


Figure 2.2 Comparison of CO₂ demand in low emission routes [2]

Synthetic Fuels

Since PtX technologies are not yet available in full industrial scale, there is still development needed to replace fossil-fuel-based processes. However, the maturity and potential of PtX grows rapidly and a multifold of production routes are being developed for an industrial scale.

Many other alternative paths to the PtX routes do exist such as efuels from microalgae [5] or high temperature thermochemical processes (e.g. Synhelion [6]) but these require much more research and development to reach a commercial scale [7]. Whereas efuel production via Fischer-Tropsch or methanol production are realized in a multitude of projects with increasing demonstration scale and high CO₂ demand.

A major advantage of efuel production lies in the seamless integration into existing infrastructure and moreover, technologies such as the Fischer-Tropsch process are well known and have been developed over a long time period. As a result, the Power-to-Liquid (PtL) branch of the broader PtX concept stands out as one of the most mature technologies compared to other PtX routes.

Various international projects work on the implementation of PtL technologies to reach a commercial scale. The construction of a PtL plant by the German company INERATEC has started in 2023 and will produce 2,500 t of fuel per year [8]. From 10,000 t of biogenic CO₂ up to 4.6 million liters e-Fuels will be produced in the industrial park Höchst. The carbon source for this project stems from a biogas plant. The German non-profit organization atmosfair uses 2.3% DAC and a biogas plant for CO₂ supply in an e-kerosene project [9]. Norsk e-Fuels also follows a combined approach with DAC and CO₂ from biogenic waste gas streams. In total Norsk e-Fuels wants to produce up to 250 million liters of efuels in 2030 with a focus on the aviation sector (80%) and residual naphtha as a feedstock for the chemical industry [10]. A green methanol plant in Tasmania by Abel energy will be supplied with biogenic carbon to produce about 200,000 to 300,000 t per year [11]. In France, 300,000 t of CO₂ per year will be captured by the steel manufacturer ArcelorMittal in corporation with ENGIE and Infinium for efuel production in a project called Reuze [12]. A Chinese plant will capture 150,000 t of CO₂ per year from other industrial processes to generate 100,000 t of methanol per year [13]. In the US, the company Infinium will use 18,000 t CO₂ per year to produce e-kerosene and e-diesel [14]. All these undertakings are first steps to reach industrial scale for efuel production. In long-term a sustainable and sufficient source of CO₂ as feedstock needs to be supplied for PtX products such as synthetic fuels.

2 Carbon Feedstock

Valorization of industrial point sources make it possible to cover the demand for PtX deployment. However, there is a danger of a bottleneck since all sectors aim to become carbon-neutral until 2050 and are eager to reduce CO₂ emissions. Over time, these carbon point sources will decrease. Therefore, alternative carbon sources from biogenic origin and especially deployment of DAC will become more important in the future (Figure 2.3) [2]. Although large-scale DAC is not yet established in the short-term, long-term scenarios show that the CO₂ demand will drastically rise. According to Ram et al. the

future CO₂ demand of fuel production should be mainly covered by contributions of DAC [15].

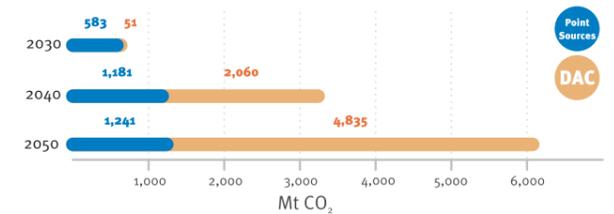


Figure 2.3 CO₂ demand for production of efuels [15]

Replacing Petrochemical Supply Chains

The chemical and petrochemical sector laid the foundation for numerous downstream value chains. With a global production worth about 6 trillion US dollars (2017) and still growing to this day, this sector underscores its economic relevance. However, the sector is heavily dependent on fossil resources and is in dire need of defossilization. Fossil resources are applied both as fuel and feedstock, making this sector a major contributor to global industrial CO₂ emissions [141-143].

The scale of production itself can become challenging in the transformation process. The production of plastics alone increased by 360 Mt/a in 2018. In 2020, ammonia production in the fertilizer industry reached 175 Mt/a, and another important base chemical, methanol, amounted to about 100 Mt/a in 2019 [141].

To replace these fossil value chains, new production routes are being deployed for a sustainable future in the

chemical and petrochemical sector with PtX technologies. As displayed in figure 2.4, fossil resources will be replaced by alternative raw materials that also contain carbon to produce hydrocarbons. Common options to establish alternative carbon sources include biomass, recycling processes, and CO₂ from various sources. Biomass has limited capacities, and despite long-term developments, circular economy approaches are not yet well deployed. CO₂, as a further pillar in establishing clean carbon sources, becomes indispensable.

However, this transition comes at a cost. Techno-economic analyses show that full defossilization in the petrochemical sector will increase costs for energy and feedstock by more than 35%. Low-carbon alternatives will come with a high cost and need additional regulatory measures to become competitive with fossil-based products [141].

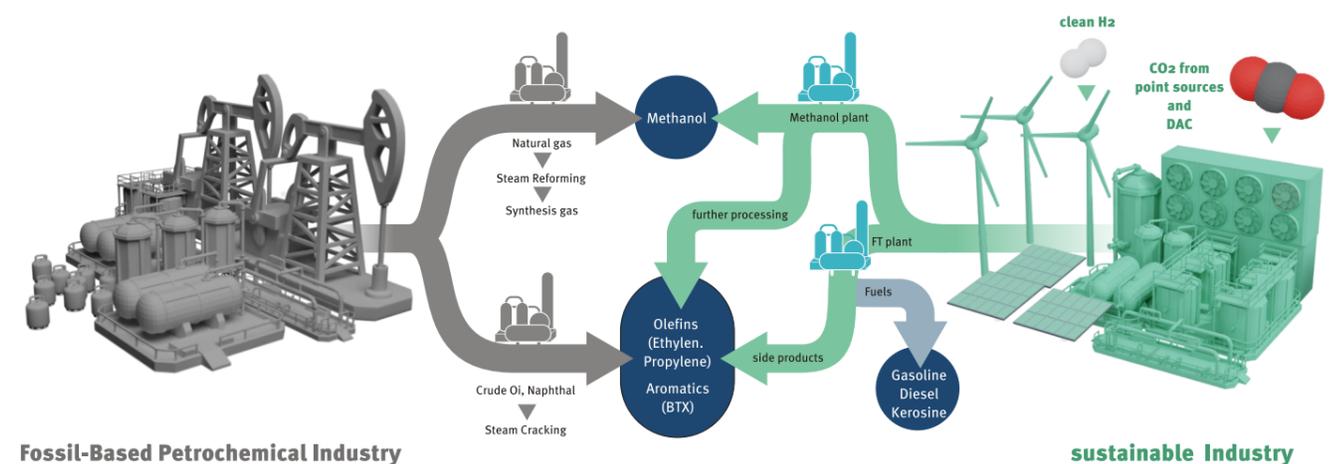


Figure 2.4 PtX technologies provide sustainable production routes for the petrochemical industry [142].

3 Carbon Sources



3 Carbon Sources

3 Carbon Sources

Industrial, biogenic sources and waste treatment offer CO₂ for PtX products. It can also be directly separated from the atmospheric air in a process known as Direct Air Capture (DAC).

It is important to notice that the CO₂ used for PtX production is not permanently captured because by the end-of-life of most PtX products, the bonded carbon will eventually be released into the atmosphere in form of CO₂. In the case of biogenic and atmospheric air sources, the CO₂ released at the end-of-life of the product equals the CO₂ previously captured by DAC or biomass. Consequently, these sources could provide a closed carbon cycle if the energy used for the capture process is renewable. On the other side, fossil sources will always generate positive emissions if used as a carbon feedstock. As a consequence, all carbon sources require a critical assessment in advance.

Additionally, numerous CO₂ point sources vary in concentration and energy consumption for the capturing process. For this reason, the choice of the source not only needs to match the required quality and quantity for the production routes, but also impacts the carbon footprint and thus the sustainability of the final product.

Point sources are stationary plants, which emit CO₂ to the atmosphere as a consequence of their production processes. These emissions can be the result of a combustion process (energy related emissions) or of a

process reaction in which CO₂ is a byproduct (process related emissions).

The energy and industrial sectors are considered as point sources and are described in chapters 3.1 to 3.3.

Figure 3.1 shows the shares of total CO₂ emissions in 2019, globally. It can be observed that the industry sector represents 4% of total CO₂ emissions while the energy sector (electricity and heat) represents 43% (which also accounts energy emissions for industry consumption) [16].

3.1. Energy sector

The energy sector includes all industries which extract, produce and deliver energy in the form of electricity and heat. Largely due to the combustion of fossil fuels as well as industrial and non-renewable municipal waste, the energy sector is responsible for 43% of total CO₂ emissions worldwide [16] (see Figure 3.1). In 2019, 84% of global primary energy consumption was supplied by fossil fuels (33% oil, 27% coal and 24% gas), while nuclear and renewable energies accounted for 4.3% and 11.4%, respectively [17] (see Figure 3.2).

In this sector, 72% of the CO₂ emissions are caused by the use of coal, which has the highest emission factor from all fossil fuels [18].

The CO₂ concentrations of the flue gas in coal- and gas-fired power plants varies between 10-15% and 4-5%, respectively [19].

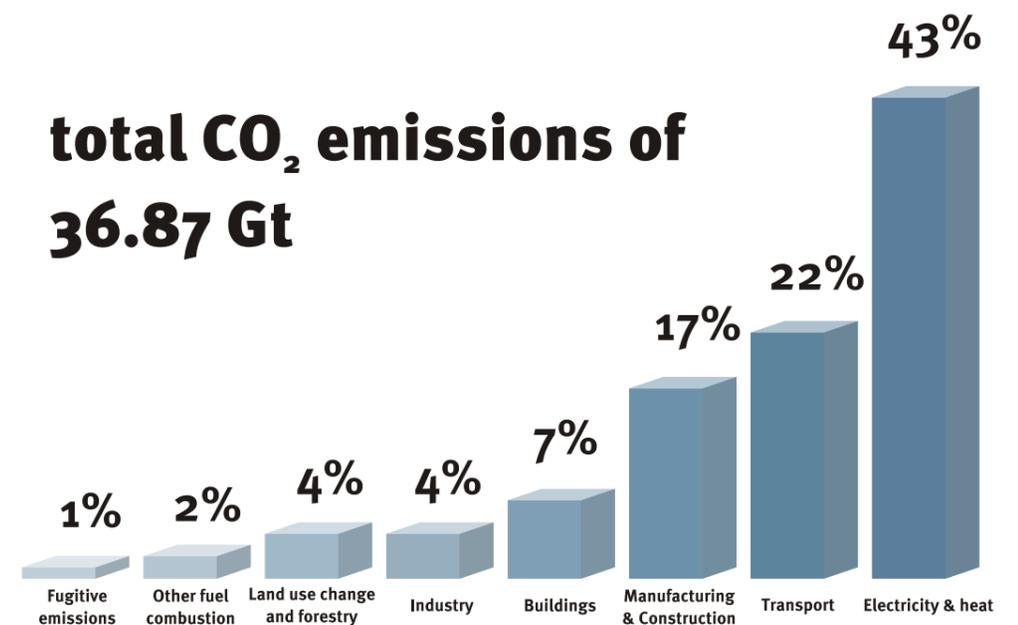


Figure 3.1 CO₂ emissions by sector in 2019. Own illustration based on [16]

3 Carbon Sources

However, the energy sector is not a suitable source of CO₂ for PtX in the long term for the following reasons:

- The energy sector has the possibility to replace its generation from fossil fuels with renewable energy production. Efforts are being made worldwide to decarbonize the sector and its greenhouse gas emissions, including CO₂.
- There is a risk of carbon lock-in effect in this sector by incentivizing the further use of fossil fuels if the emitted CO₂ develops a market. This is especially critical for high emitting resources like coal.
- The environmental benefit of using CO₂ from the energy sector is limited because at the end-of-life of the PtX product, the original fossil carbon will be released in form of CO₂.

3.2. Industry sector

The coupling of the industry sector to the PtX production offers the possibility of integrating the existing and high developed infrastructure of this sector to the PtX value chain.

The industry sector represents 4% of global CO₂ emissions [16] (See Figure 3.1). In 2018, CO₂ emissions from the industrial sector accounted 8.54 Gt_{CO₂} and their sectorial shares are shown in Figure 3.3. Major emitters of this greenhouse gas were the cement industry (27%) and the iron and steel industry (25%).

3.2.1. Chemical Industry

The chemical industry includes operation plants which process raw materials in different processes to manufacture a large variety of chemical products. CO₂ is generated along the different value chains in the chemical industry, either by the combustion of fossil fuels or as byproduct in different chemical reactions. These CO₂ emissions could be used as carbon source in PtX production.

Between the different chemical products, a distinction is made between basic and specialty chemicals. The former are produced at large scale in bulk quantities and can be used in various fields, while the latter are produced in small scale and are more specialized for certain applications.

In 2021, CO₂ emissions in the chemical industry accounted for 925 Mt_{CO₂}. About one quarter of these CO₂ emissions³ are process related emissions, while the rest are emitted by combustion processes to generate thermal energy. The chemical and petrochemical industry is responsible for about 14% of total industrial emissions (see Figure 3.3). Process related emissions are suitable for capture because of their high concentration of CO₂ and the consequently low energy requirement for the separation.

Only a limited number of basic chemicals are responsible for most of the emissions in this sector: ammonia (417 Mt_{CO₂}), methanol (250 Mt_{CO₂}) and high value chemicals⁴ (258 Mt_{CO₂})⁵[21].

Part of the CO₂ produced in ammonia plants is normally separated and utilized as feedstock for the production of urea. Yara International ASA currently operates a commercial CO₂ capture plant by means of water wash process from its ammonia production in Porsgrunn, Norway. This gas is then transported and commercialized by Praxair for commercial uses such as food and beverage, cleaning and chemicals [22].

3.2.2. Cement Production

Cement is the basic ingredient of concrete and hence, a very important building material. The cement industry has a large energy demand and is responsible for a large amount of CO₂ emissions. To produce cement, the main feedstocks (limestone, clay and marl) are broken down and mixed with additives, before being burned at approx. 1,450°C in a kiln to form clinker. In the final step, the clinker is ground down to a fine powder and mixed with more additives to obtain the final product [23]. Due to the high temperatures required, the process is highly energy intensive.

There are two direct sources of CO₂ in a cement plant:

- Energy related emissions: from the combustion of (fossil) fuels to heat limestone, clay and sand to 1,450 °C [24]. These emissions can be avoided using climate neutral fuels.
- Process related emissions: from the calcination of the feedstock, which produces lime and CO₂ as a byproduct. These emissions are unavoidable.

In total, the cement industry is responsible for about 8%

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of global emissions and 27% of industrial emissions, 50% of which are process related and unavoidable [25].

Partial oxyfuel combustion, amine scrubbing and calcium looping technologies (see chapter 4) for carbon capture in the cement industry have been demonstrated in small scale (TRL 6) but they still need to be up scaled. Hills et al. estimate that they will be commercially available between 2025 and 2030 [26]. Heidelberg Cement is currently planning the first industrial-scale carbon capture and storage (CCS) project in the world at a cement production plant in Brevik, Norway. This project will use post-combustion capture to separate, transport and permanently storage 400,000 t_{CO₂} per year [27]. This company is also collaborating in the projects Catch4Climate and LEILAC (25,000 t_{CO₂} per year [28]) to demonstrate the Oxyfuel and direct separation technologies at pilot plant scale [29].

3.2.3. Pulp and Paper Production

Large amounts of energy are required in the pulp and paper production mainly due to the drying processes involved. This results in a large production of CO₂ associated to that energy, which could serve as a carbon source for PtX production.

Paper and board are used in a variety of applications [30]:

- to store, collect and distribute information: newspapers, books, etc.
- for packaging: boxes, containers, etc.
- for hygienic uses: toilet tissue, hand towels, etc.
- for specialty papers: filters, backing paper, etc.

In 2021, 264 Mt of packaging paper and board, 96 Mt of graphic paper and 57 Mt of other papers were produced worldwide [31]. This industry is responsible for the consumption of 33-40% of all industrial wood trade globally [32].

During paper production, wood is first debarked, chipped and treated mechanically or chemically to separate its cellulose fibers (also known as pulp). The pulp is then refined, cleaned, and sent into the paper machine which removes water and presses the fibers into a sheet. The paper is then dried and prepared to be transported [30]. Drying is the most energy intensive step of the process and consequently, most of the CO₂ emissions are generated by combusting fuels in this step.

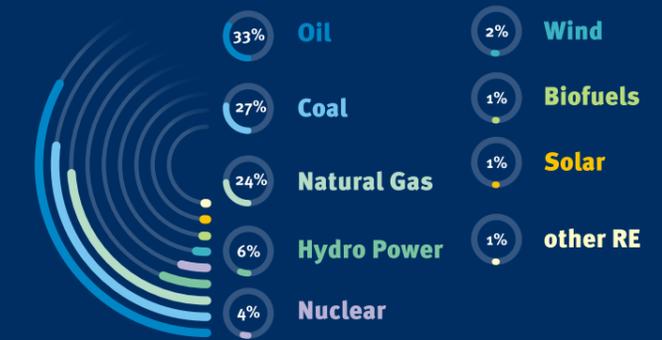


Figure 3.2 Global primary energy consumption by source in 2019. Source: own illustration based on Our World in Data [17], Licensed under CC-BY by the author Hanna Ritchie



Figure 3.3 Industry direct CO₂ emissions in 2018. Source: Own illustration based on IEA data [20]



Figure 3.4 Global waste composition Source: own illustration based on [59]

¹ Only process related emissions, as the energy related are located in the electricity and heat emissions in Figure 3.1.

² This number considers direct emissions of the industry sector and includes process as well as energy related emissions.

³ Process related emissions are products from a chemical reaction involved in the production of the main product and not from the combustion of fuels.

⁴ Ethylene, propylene, benzene, toluene and xylenes.

⁵ Total amount of emissions for the whole production processes

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Additionally, some process emissions are generated in the recovery cycle of the white liquor. These emissions stem from the wood raw material and are therefore considered biogenic [33].

In 2021, the pulp and paper industry emitted about 190 Mt_{CO₂}, which correspond to approx. 2% of the total industrial sector emissions [34] (see Figure 3.3).

A first commercial CCU project in the paper industry was demonstrated by SAIPEM and the partners Resolute Forest Products and Les Serres Toundra. For this, 30 t_{CO₂}/day were captured at Resolute's pulp mill in Saint-Félicien, Québec, and they will be reused at the nearby Les Serres Toundra Greenhouse complex in a further step. The capture unit was already built and successfully demonstrated but SAIPEM is currently adapting it [35].

3.2.4. Iron and Steel Manufacturing

Steel is an alloy of iron and carbon. It may also contain small amounts of other elements such as manganese and chromium. Due to its strength and low production costs, it is widely used in infrastructure, buildings, cars, machines, etc.

Steel manufacturing is an energy intensive industrial process and consequently a CO₂ emitter and potential carbon source for PtX.

The first step in the steel production process takes place in the Blast Furnace (BF) where the feedstock is melted (iron ore, coke and lime) and the iron ore is reduced to produce molten iron and CO₂. The molten iron is then mixed with scrap steel and treated with oxygen to remove coal and other impurities in the Basic Oxygen Furnace (BOF). In the BOF, CO₂ is also produced. Depending on the desired steel grade, some elements such as chromium are added at specific conditions to achieve the required composition. Afterwards, the molten steel is cooled down in special molds, cut into the desired length and formed into the desired shape and surface finish. In the last step, the final shape is achieved by different methods such as coating, thermal and surface treating, etc. [36] [37].

A second option to produce steel consists of the Direct Reduced Iron (DRI) in combination with the Electric Arc Furnace (EAF). In the EAF, scrap steel is melted by using high voltage electricity and mixed with iron from the DRI. The DRI/EAF process can be less emission intensive than the BF/BOF if the electricity mix used has a low emission factor and the reduction agent is less emission intensive than coal (e.g., natural gas or hydrogen) [38].

The iron and steel sector accounts for 25% of industrial CO₂ emissions (see Figure 3.3), which correspond to 2.6 Gt_{CO₂} per year [39].

CO₂ emissions in steel manufacturing are produced by three different kinds of processes [40]:

- From burning fossil fuels to achieve the high temperature needed to carry out chemical reactions and physical treatments.
- From the reduction of iron oxide with a reductant agent like CO.
- From the use of power and steam for the steelworks.

The typical CO₂ composition in steelworks process gases depend on the type of process and varies between 1 vol.% and 17 vol.% [40].

In the project Carbon2Chem in Germany, 75 l/d of raw methanol are planned to be produced from the metallurgical gases of the thyssenkrupp Steel Europe AG steel plant in Duisburg. The test phase will be run until May 2024, after which industrial production is expected to begin [41].

ADNOC completed the Al-Reyadah CCUS facility in 2016, with capacity to capture 800,000 t_{CO₂} per year from an Emirates Steel production facility in United Arab Emirates. They have plans to expand the capture capacity to approx. 5 Mt per year by 2030 [42]. As an additional example, ArcelorMittal Gent will commission a demonstration plant to capture around 300 kg_{CO₂} per day from the blast furnace and convert it into ethanol. Mitsubishi Heavy Industries Engineering will provide the capture technology and support the engineering studies [43].

3.2.5 Aluminium Manufacturing

The first step in aluminium manufacturing is the alumina (Al₂O₃) production, in which aluminium hydrate is extracted from bauxite with a solution of caustic soda at high temperatures. The aluminium hydrate is then recrystallized from the solution by decreasing the temperature, washed with water, dried and calcined to form alumina [44].

Alumina is then transformed into aluminium in an electrolysis process where the cathode and the anode are both made of carbon. In this process, the anode reacts with the oxygen from alumina which produces liquid aluminium and CO₂. Depending on the final application, the aluminium is processed into extrusion ingots, sheet ingots or foundry alloys [45].

Aluminium production is responsible for 3% of total

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industry's direct CO₂ emissions (see Figure 3.3). There are three different types of emissions in the manufacturing of aluminium [46]:

- About 62% are indirect emissions and arise from the use of electricity. These emissions could be avoided by the direct use of renewable electricity.
- About 15% are direct process emissions from the consumption of carbon anodes during aluminium smelting. The use of inert anodes is one alternative to avoid these emissions, although this technology is still under development and not commercially available.
- About 16% are direct energy emissions from the combustion of fossil fuels to generate the required high temperatures. The use of green hydrogen or other low-emission fuels could contribute to the abatement of these emissions.

3.2.6. Glass Manufacturing

Glass manufacturing generates large amounts of CO₂ emissions which could be used as feedstock in PtX production.

Sand is the main feedstock in glass production, which is composed of silicon oxide (SiO₂). To reduce the melting point of the silica, soda ash (Na₂CO₃) is added to the sand. Limestone or chalk, which are composed of calcium carbonate (CaCO₃) are also added to the glass with the objective of improving its hardness and chemical resistance [47]. Depending on the desired properties of the final product, many other intermediates and modifying materials are used.

In glass manufacturing, high temperatures of around 1,500°C are required to melt the feedstocks. To achieve such high temperatures a combustion process is carried out, where combustion products such as CO₂, sulphur dioxide and nitrogen oxides are produced and released into the atmosphere.

Combustion of fossil fuels in glass manufacturing accounts for 75%- 85% of total CO₂ emissions in this process [48]. The remaining emissions consist of by-products of the chemical reactions responsible of converting raw materials into the final product. Worldwide, the production of glass generates 95 Mt_{CO₂} emissions every year [49] which corresponds to approximately 1% of total industrial emissions⁶.

⁶ Own calculation based on data from Figure 3.1.

A project to demonstrate carbon capture in glass manufacturing is being planned by Glass Futures together with C-Capture at Pilkington UK Ltd. C-Capture aims to demonstrate its novel capture process in hard-to-decarbonize industries [50].

3.3. Biogenic Point Sources

Biogenic CO₂ is produced by the decomposition, digestion or combustion of biomass/biomass-derived products [51]. This chapter takes into account bioethanol and biogas production as biogenic point sources, although there are other biogenic sources available, e.g., the use of biofuels (including biogas and bioethanol) for electricity and heat generation.

Biogenic sources can be classified into three different types, depending on the feedstock:

- From edible feedstocks such as corn and sugar cane. This kind of source can be problematic since it arises a competition between energy and food crops.
- From lignocellulose biomass such as wood, paper and agricultural residues.
- From algae.

When using biomass as feedstock in industrial processes, sustainability criteria such as greenhouse gas emissions savings, sustainable forest management, protection of air, soil and water and biodiversity protection, among others, should be considered [52]. Additionally, the use of biomass for energy or industrial uses must avoid competition with food.

Biogenic CO₂ can be obtained either as a by-product in the processing of biomass (bioethanol and biogas production as explained below) or by the combustion of biomass for energy production, combined with carbon capture. Both paths are denominated Bioenergy with Carbon Capture and Storage/Utilization (BECCS/U).

Biomass combustion in the bioelectricity generation sector has potential as a flexible and grid balancing renewable resource complementing other renewable sources like wind and solar. Furthermore, heat generation with biomass as a fuel can find application in industrial processes which operate at high temperatures and currently rely on fossil fuels [53].

Bioethanol Production

Bioethanol is produced from the fermentation of different raw materials like corns and sugar cane. Other non-edible

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Table 3.1 Examples of CO₂ capture from biogas production [51]

Biogas plant	Location	Feedstock	CO ₂ production	CO ₂ use
Korskro biogas plant (Nature Energy)	Korskro, Denmark	manure	16,250 t _{CO₂} /a	food industry
Avedøre	Avedøre, Denmark	wastewater	800 t _{CO₂} /a	-
Metha Treil	Loire-Atlantique, France	livestock effluents, cover crops or corn silages, vegetable by-products	1,500 t _{CO₂} /a	greenhouses
Agricultural Cooperativa Speranza	Candiolo, Italy	agricultural by-products and animal wastes	4,000 t _{CO₂} /a	Industrial gases and mineral water industries
Greenville Energy Ltd	Northern Ireland	Crop residues, food waste, and livestock effluent	5 t _{CO₂} /day	dry ice
Carbon Harvest Project (Future Biogas) – under development, operational by 2025	East Anglia, UK	-	15,000 t _{CO₂} /a	Underground storage in the seabed of the North Sea
Revis Bioenergy – under development, operational by 2023	Cloppenburg, Germany	manure	103 t _{CO₂} /a	-
RENOVO – under development	Stord, Eldøyane, Norway	Salmon fish residues and livestock manure	11 t _{CO₂} /day	Dry ice
Dietikon – under development	Dietikon, Switzerland	wastewater	-	Methane production (power-to-gas)
STORE&GO Project	Solothum	wastewater	-	-

3 Carbon Sources

feedstocks are also being developed to produce bioethanol. For the production of bioethanol, the feedstocks are pretreated and hydrolyzed. In the hydrolysis, sugar monomers are produced from the cellulose contained in the biomass. These sugar monomers are subsequently converted into ethanol, acids and gases in a fermentation process using microorganisms as yeast, fungi or bacteria [54]. The fermentation product is finally distilled to obtain bioethanol at high purity.

In the fermentation process, around 0.075 t_{CO₂} (biogenic) are produced for each hectoliter of bioethanol [55]. This is equivalent to 0.95 t_{CO₂}/t_{bioethanol}⁷.

CO₂ capture from ethanol production industry is already state of the art in some places. In Kasas and Texas the ethanol industry supplies approx. 270,000 Mt_{CO₂} per year for Enhanced Oil Recovery (EOR) [56]. The bioethanol producing company POET in the USA started a partnership with Navigator CO₂ Ventures to capture CO₂ at different locations, where in total, 5 Mt of CO₂ are produced annually [57].

Additionally, the combustion of bioethanol as a fuel could be used as a carbon source if it takes place at a stationary place where it can be captured.

Biogas Production

Biogas is produced during anaerobic digestion of organic matter. Its main component is methane, which composition varies between 45 vol% and 75 vol% [58], depending on feedstock and process parameters. The remainder component in biogas is mostly CO₂ which is a byproduct in the digestion process and can be obtained highly concentrated after the biogas upgrading.

Suitable feedstocks for biogas production are crop residues, animal manure, organic fraction of municipal solid waste and wastewater sludge [58].

Biogenic CO₂ can be obtained both by the upgrading of biogas as described above, and by its use as fuel or feedstock in different processes, e.g., as fuel in a thermal power plant. The main difference between these two options is the concentration of the obtained CO₂, which is considerably low in the combustion flue gas (<10%) and high after the biogas upgrading.

Biogas upgrading is a mature technology and can be carried out by different methods such as PSA, water or amine scrubbing, membranes and hot potassium carbonate [51].

⁷ Assuming a bioethanol density of 785 kg/m³.

Table 3.1 gives an overview of CO₂ capture from biogas plants in different locations in Europe, some of which are under development.

3.4. Waste and Wastewater Management

Solid, liquid and gaseous waste is generated in different sectors including energy, industry and households. These residual components need to be specially treated to minimize environmental and social impacts.

Solid Waste

Global solid waste composition is shown in Figure 3.4, 44% of which correspond to food and green residues and can be used as a biogenic source of carbon (see section 3.3).

CO₂ emissions from solid waste management originate mainly due to the thermal recovery (incineration).

Depending on the waste composition, between 0.7 and 1.7 t of CO₂ are produced for each ton of municipal solid waste [60].

Numerous solid waste materials, including steel slag, concrete wastes, red mud, fly ash, and biomass wastes, have been investigated for their potential in carbon dioxide capture and utilization. These waste materials have shown promise in the production of useful building materials, catalysts, syngas, and functional materials. Among the methods explored, mineralization capture of CO₂ using alkaline solid wastes or carbonation from fly ash, steel slag, and carbide slag have been studied [61].

Particularly relevant to the PtX process are solid wastes like fly ash and biomass wastes, which are treated with amines to capture CO₂ at relatively low temperatures. In these concepts operation under low pressure conditions is aimed to facilitate the chemical and thereby eliminating the need for an additional desorption step [61].

In municipal solid waste plants, waste can be combusted for power or heat generation. The combusted organic waste leads to CO₂ emissions that can be captured and further processed. A calcium looping process can be applied to capture CO₂ from the plant exhaust gases. The supply of negative CO₂ emissions from a carbon capturing equipped plant combined with geological storage enables a cost-efficient solution to also provide clean heat or power [62].

Wastewater

A substantial amount of wastewater, approximately 1 petaliter per year (ca. 30% municipal and 60% industrial wastewater), is generated globally. Developed countries

3 Carbon Sources

manage to treat around 70% of these waste streams, whereas low-income countries only treat around 8% [63].

Wastewater treatment plants are major energy consumers in many urban areas and consequently significant contributors to greenhouse gas emissions. Besides ambitious approaches to increase energy efficiency of wastewater treatment plants, there are diverse routes to further mitigate CO₂ emissions through CO₂ capture [63].

The method of *microbial electrolytic carbon capture (MECC)* uses wastewater as the electrolyte for microbially assisted water electrolysis. Microorganisms, especially electroactive bacteria (EAB) oxidize biodegradable substances in wastewater to CO₂. However, the CO₂ is also sequestered as stable carbonates, which has low product value and must be chemically released for further use.

Similar to MECC the *microbial electrosynthesis (MES)* also applies EAB which oxidize organics in the wastewater. However, instead of the conversion to carbonates, autotrophic bacteria capture and convert CO₂ into value-added organic compounds (formic acid, propionic acid, ethanol and butanol [63]). At the moment, this design especially struggles with poor selectivity for high-value products.

There are various more CO₂ capture solutions for wastewater such as microalgae cultivation, biochar/biogas production and engineered wetland systems. For example, sewage-sludge produced in wastewater treatment can be anaerobically digested to produce biogas (see section 3.3). These approaches produce new biomass or organic compounds but are currently not suitable for classical PtX routes due to lack of scalability.

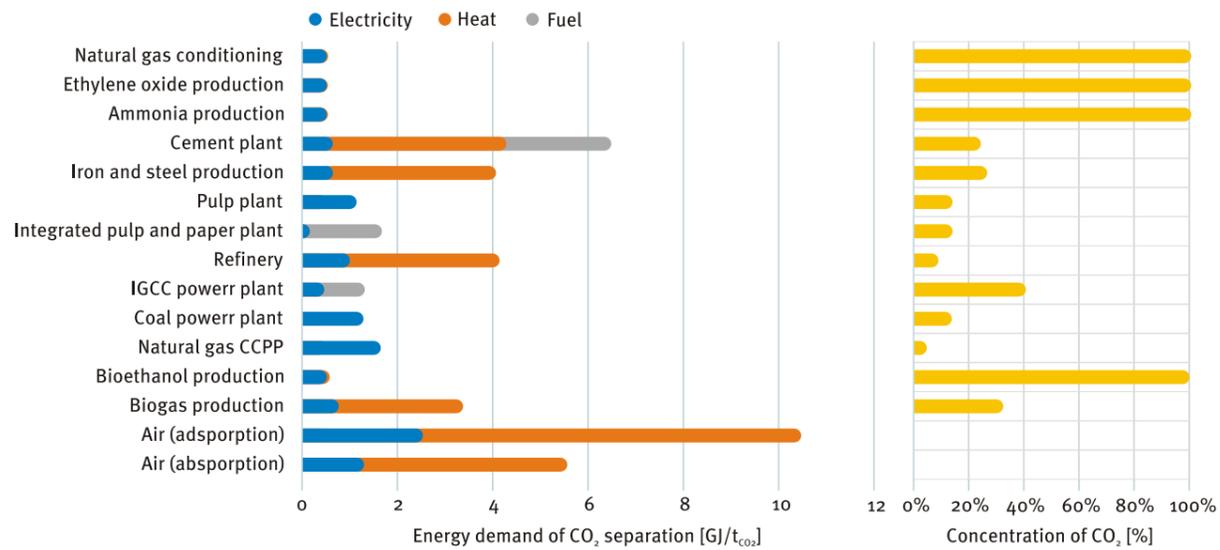


Figure 3.5 Energy demand and CO₂ concentration of different sources. CO₂ concentration in air is 0.04% and cannot be seen in the bars with the used scale. Source: own illustration based on Fröhlich et al. [65]

3.5. Atmospheric Air

CO₂ availability as a point source is limited to regions with energy and industrial production. Another important source of CO₂ is the atmospheric air, which concentration has increased by 47% since the industrial revolution, from 280 ppm to around 412 ppm in 2019 [64]. The reason for this increase is that the quantity of naturally occurred and anthropogenic CO₂ emitted is larger than the one extracted from the atmosphere by natural processes like the photosynthesis.

Atmospheric CO₂ can be captured by the Direct Air Capture (DAC, see chapter 4.2.1) technology. Using CO₂ from

atmospheric air to produce PtX products, would allow to produce them in isolated regions with good renewable energy resources without building a gas transport infrastructure for CO₂ or green hydrogen. Additionally, capturing CO₂ directly from the atmospheric air with renewable energy would ideally create a closed (CCU) or even negative (CCS) carbon cycle and would help to reduce climate impacts caused by greenhouse gas emissions.

Nevertheless, the main disadvantage of capturing CO₂ directly from the air is the enormous amount of energy required, due to the low CO₂-concentration.

3 Carbon Sources

3.6. Outlook of all CO₂ Sources

Fröhlich et al. [61] summarized information about energy demand and CO₂ concentration for the separation of different CO₂ sources (see Figure 3.5). The energy demand is divided into electricity, heat and fuel, depending on the type of energy required for the separation. **Electricity** is usually used for compressors and pumps. **Heat** (mostly in form of steam) is necessary for desorption processes. For some processes, like cement production, an extra **fuel** combustion is needed in case that the process heat is not enough to cover the energy required for the separation.

Bioethanol, ammonia and ethylene oxide production processes deliver a highly concentrated CO₂ gas stream, which only requires a small amount of energy for the conditioning. Combustion processes in powerplants often deliver a flue gas with low CO₂ concentration, which requires large amounts of energy for the separation. CO₂ present in atmospheric air is highly diluted and its separation requires the largest amount of energy. Nevertheless, this source is easily accessible regardless of the location.

Additionally, Figure 3.6 presents the levelized costs⁸ of CO₂ capture for different sectors in 2019 from the IEA [66].

Processes with high concentration of CO₂, like natural gas conditioning, ethylene oxide, ammonia and bioethanol production, present the lowest costs of CO₂ capture. On the other hand, CO₂ capture from atmospheric air represents the most expensive technology. However, it remains an important source of CO₂ which can contribute to stop the increase or even to reduce the concentration of this greenhouse gas in the atmosphere.

CO₂ point sources will reduce considerably until 2050, as a consequence of country commitments to achieve net zero emissions by reducing substantially the use of fossil fuels. According to these goals, remaining point source emissions will thus consist of unavoidable process emissions, biogenic emissions and a small portion of fossil emissions, which should be compensated by CCS. Consequently, DAC will gradually gain more importance and should complement point sources in supplying a reliable carbon source to the PtX market. For this to be achieved, energy consumption and separation costs of DAC should be minimized.

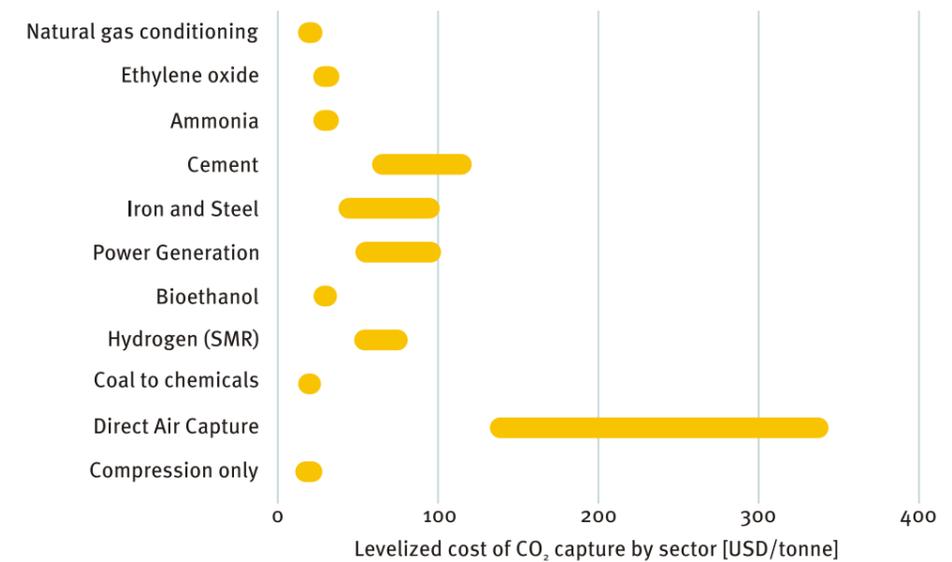


Figure 3.6 Levelized costs of CO₂ capture by sector, 2019. Source: own illustration based on IEA [66]

⁸ Including levelized capital, non-fuel-operations and maintenance and energy costs [66].



4 Capture Technologies and Processes

From the original CO₂ point source to the actual feed into other processes, a system is required which contains several steps for separation, treatment and utilization of CO₂ (Figure 4.1). At first, the separation of CO₂ from the point source like flue gases is performed through physical and chemical absorption, adsorption, membrane-based separation, and further technologies [68].

Depending on the CO₂ point source and the quality and quantity of CO₂ various methods for CO₂ capture can be applied. These technologies can differ widely in their maturity and costs for implementation and operation. As displayed in Figure 4.2, high costs for certain CO₂ capture processes such as DAC are mainly correlated with not full mature technologies. The Technology readiness level (TRL) refers to the maturity level of the technology ranging from 1 (basic concepts) to 9 (full industrial integration). The most mature and also cost-effective processes are already applied in refineries or the steel sector with liquid absorption and post-combustion processes.

4.1. Capture Technologies

The utilization of separation techniques in an industrial context varies based on numerous factors. Parameters such as the identification for suitable instruments, their effectiveness, and associated costs come into play. The dominant technology for reducing CO₂ emissions is post-combustion CO₂ capture using amines-based chemical absorption [70]. Common CO₂ removal methods range from simple direct wash treatments to sophisticated recycling systems. These methods were initially developed for cleaning natural gas treating and H₂ recovery from syngas. Today these processes have increasingly found application in capturing CO₂ from numerous sources such as flue gases. These gas streams often contain various contaminants (water, nitrogen, hydrogen sulphide, hydrocarbons etc.). Moreover, the presence of oxygen can pose challenges for specific CO₂ separation systems. The industry predominantly relies on established CO₂ removal technologies, that are mainly absorption, adsorption, membrane-based separation, and cryogenic processes [71]. The choice of the most suitable technology depends on factors such as flue gas composition, economic considerations, and the desired target products. Therefore, the selection of appropriate technologies for specific industrial emission sources depends on these factors to optimize the reduction of carbon emissions and maximize efficiency [72].

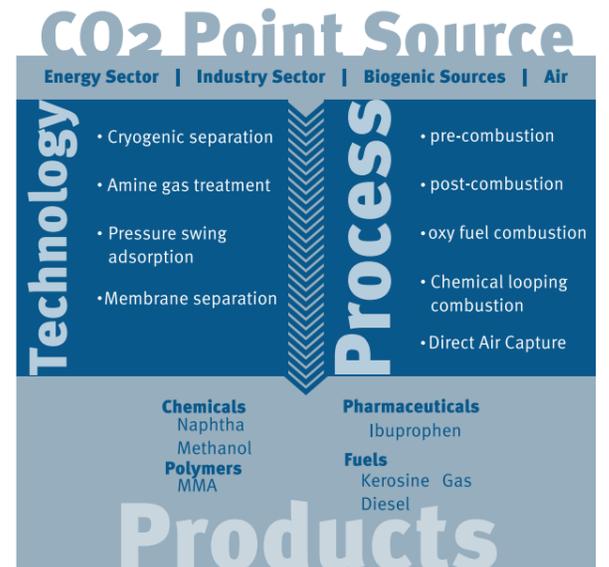


Figure 4.1 CO₂ capture and utilization for PtX production.

Various technologies have been developed to address the critical issue of CO₂ capture and reduce greenhouse gas emissions. Each of these technologies has its advantages and limitations, making them suitable for different applications and industries [72].

4.1.1. Chemical Absorption - Amine Gas Treatment

Absorption processes are widely applied in the chemical and petrochemical industries for the removal of CO₂ from process streams. This process removes CO₂ from product gases (e.g., hydrogen, syngas, natural gas, ammonia etc.), ensuring that the resultant gas meets process or product requirements effectively [71]. The absorption process is based on the chemical or physical interaction between a liquid solvent or solid matrix and the targeted solute, facilitating the selective absorption of CO₂ while sparing oxygen, nitrogen gas, and other flue gas constituents. The resulting CO₂-rich solution undergoes transfer to a regeneration column, where CO₂ is efficiently separated from the solvent, permitting its recycling for subsequent flue gas treatments [73]. Among CO₂ capture technologies, chemical absorption is the most matured (TRL 9) and consequently it has been widely commercialized. Additionally, it can be integrated into existing plants. Nevertheless, improvements are needed due to high energy consumption, low CO₂ loading capacity, high absorbent makeup rate and high equipment corrosion [74].

Established Separation Methods

Absorption technology relies on the principle of dissolving CO₂ into a liquid solvent or solid absorbent. This method is vastly applied in post-combustion capture systems, where flue gases are treated to remove CO₂ after combustion. The choice of solvent and process conditions plays a significant role in the efficiency of absorption-based capture [72].

Adsorption is based on the attraction of CO₂ to the surface of a solid adsorbent material. It is particularly relevant in pre-combustion and post-combustion capture systems. The efficiency of adsorption depends on the choice of adsorbent material, operating conditions, and regeneration methods [72].

Membrane separation technology employs selective membranes that allow CO₂ to pass through while blocking other gases. This approach is well-suited for applications with specific purity requirements, such as natural gas purification and biogas upgrading. Membrane separation efficiency relies on membrane material selection and operating conditions [72].

Cryogenic separation involves cooling the flue gas to extremely low temperatures to condense and separate CO₂ from other components. Cryogenic processes are energy-intensive but offer high purity and efficiency. They are often employed in large-scale applications and are crucial for the liquefaction of CO₂ for storage and transportation [72].

Chemical absorption involves a chemical reaction between the solvent and dissolved gas, with alkanolamines, notably monoethanolamine (MEA), serving as common reactive absorbents. Alkanolamines are suitable solvents for chemical absorption. Depending on the degree of substitution of the central nitrogen (single, double and triple substitution), they are classified in primary, secondary and tertiary amines, respectively. Alkanolamines have at least one hydroxyl group which reduces vapor pressure and increases solubility in water and an amine group, which promotes the reaction with acid gases like CO₂ [75]. Amines are widely used as solvents in gas treatment because they can react chemically with CO₂ to form salt and in that way, separate the CO₂ from the gas. The absorption takes place in a column at 40 – 60°C, where the flue gas flows counter-currently to the solvent and leaves the column with a low concentration of CO₂. This reaction is reversible, and the amine can be regenerated in a next step called desorption, which takes place in a second column (stripper) at high

temperatures of 120 – 140°C, releasing a CO₂ gas stream. The amine solution can be then used again in the absorption column in a cyclic process.

There are also physical absorption processes that rely on solvents with thermodynamic properties favouring CO₂ absorption over other gas components. Common physical solvents include methanol (Rectisol process) and glycol ethers (Selexol process). In many industrial applications, combinations of physical solvents and reactive absorbents are utilized in tandem to optimize CO₂ removal [71].

One significant benefit of chemical absorption lies in the recyclability of the solvent during the absorption process within the regenerator. This reduces material costs compared to solvent replacement after each absorption step. However, the choice of solvent depends on specific conditions. Liquid solvents like MEA are preferable when dealing with low-partial pressures of CO₂. In contrast, solid solvents such as lithium hydroxide and lithium zirconate

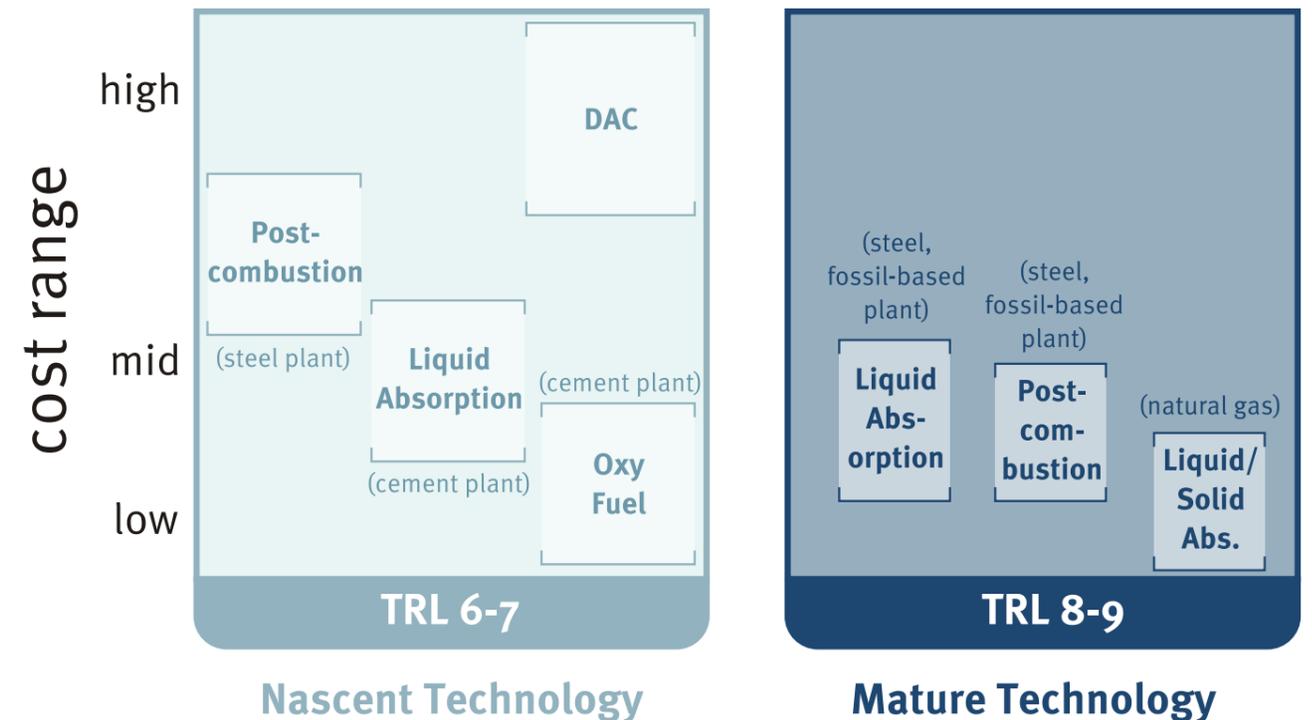


Figure 4.2 TRL and cost range for numerous established and developed CO₂ capture methods [69].

are more suitable for high-partial pressures of CO₂, owing to their superior CO₂ absorption capabilities and ease of regeneration [73]. The presence of sulfur compounds in flue gases during absorption adds to the drawbacks, resulting in the degradation of solvents. Approximately 3.5 pounds of solvent are lost for every ton of CO₂ separated, with the lost solvent precipitating as salts that do not dissociate in solution. Consequently, hybrid systems have been developed, combining absorption with other processes to reduce the costs associated with replacing degraded solvent. Trace gases like NO_x, sulfur-containing gases, oxygen, and others are either stored or subjected to reactions to neutralize their harmful effects [73].

MEA absorption is a prevalent post-combustion CO₂ capture technology. It consists of two main sections: absorption and stripping/desorption [72]. MEA absorption demonstrates the ability to achieve high-level CO₂ capture, often exceeding 90%. However, it faces several challenges, including solvent degradation, corrosion, and low solvent regeneration efficiency. Amines used in this process are susceptible to corrosion and degradation by trace constituents, such as sulfur-containing gases, and NO_x. Solvent degradation alone

contributes significantly to the overall CO₂ capture costs. Thermal and oxidative degradation are the primary mechanisms, influenced by temperature, CO₂ partial pressure, and the presence of impurity gases. Moreover, solvent regeneration demands a substantial amount of energy, resulting in increased electricity costs and reduced plant efficiency in power generation [72]. Nevertheless, the MEA process is vastly applied due to the effective and cost-efficient absorption of CO₂ [73].

MEA, with over six decades of use in the chemical industry, remains a prominent example, while ongoing research explores novel solvents operating on similar principles. The well-established nature of this method, coupled with a comprehensive understanding of the underlying mechanisms and thermodynamics, underscores the renewed research focus aimed at refining the absorption process, largely motivated by its regenerability, a truly compelling attribute [73].

Other absorption methods include Ionic Liquids (ILs), which are predominantly used as solvents for CO₂ capture in physical absorption due to their solvent properties such as extremely low volatility, tunable solvation capacity and high thermal stability [76].

4 Capture Technologies and Processes

The exploration of solid sorbents, such as calcium and lithium hydroxides, for CO₂ absorption represents a significant area of research interest. While solid sorbents are typically associated with higher temperatures (800°C for absorption and 1000°C for desorption), they offer the advantage of relatively rapid absorption rates, with 50% absorption achievable within a mere hour, and complete regeneration attainable in just 15 minutes. Nevertheless, certain challenges become evident in prolonged tests, where the absorption rate tends to diminish after the initial hour, potentially attributable to the accumulation of impermeable CaCO₃ on the surface of the packed beds. Given the stability of CaCO₃ as a mineral, such surface masking poses concerns and could entail additional costs for cleaning the sorbent surfaces [73].

4.1.2. Adsorption Methods

CO₂ adsorption involves a pre-treatment stage followed by the use of solid adsorbents like activated carbon, zeolites, or metal organic frameworks. Typically, multiple adsorption chambers are employed to ensure continuous operation. However, this method has limitations, including low CO₂ selectivity and capacity in available adsorbents, lower removal efficiencies compared to other technologies, and challenges related to regeneration and reusability of adsorbents [72].

Pressure Swing Adsorption (PSA)

This adsorption process relies on the attractive forces between CO₂ and the surface of the sorbent material. In the presence of flue gases containing various components (nitrogen, CO₂, water, NO_x, sulphur-containing gases, carbon monoxide, oxygen) adsorption can selectively capture CO₂ under specific temperature and pressure conditions. Typical sorbents are materials such as coal, activated carbon, molecular sieves, and zeolites. Two primary methods, pressure swing adsorption (PSA) and temperature swing adsorption (TSA), are employed to manipulate conditions for adsorption and desorption. PSA, known for its lower energy demand and superior regeneration rate, has emerged as a preferred choice. Furthermore, innovative techniques like electrical swing adsorption have shown promise, where CO₂ is efficiently released from a molecular sieve under the influence of an electric current. This adsorption approach provides a viable means to separate and capture CO₂ from flue gases and merits further exploration for its potential in carbon capture and sequestration processes [73].

PSA is a cyclic adsorption process for gas separation and purification. The adsorption process is primarily achieved on the binding of the gas molecules to an adsorbent [77].

The adsorbent bed is specially selected based on the gas that is to be adsorbed. The process takes place only when the gas to be separated is adsorbed, whereas all other gases in the mixture pass through the adsorbent bed.

Adsorbents such as carbonaceous adsorbents (e.g., activated carbon or carbon molecular sieves) and oxidic adsorbents (e.g., zeolite) are often used. Further, the purity of the adsorbed gas depends not only on the adsorbent used [78]. The temperature and pressure are also highly influential during the process. Since the process takes place based on pressure reduction, the control valves are mainly used and influence the quality of the product.

Other adsorbent materials are Metal Organic Frameworks (MOFs) which can be applied for PSA. MOFs are novel porous and crystalline materials with high adsorption capacity. They are therefore employed as physical and chemical sorbents mainly due to its large surface area, tunable pore shape and size, and chemical functionality based on the process [79]. Further research is being developed to synthesize carbon nanomaterials for CO₂ capture since they have relatively high capacities for CO₂. However, these materials are more time and labour intensive to produce as these materials are to be synthesised under supervised conditions in a lab for a specific adsorption process. In general, the research on carbon-based adsorbents for CO₂ capture is still in primitive stages [80].

PSA has many advantages in terms of carbon capture process. This includes the potential for reducing energy penalty, environmental impact, lower investment and operating costs and also lower cost of CO₂ capture [81]. PSA is an innovative and highly efficient way to recover and remove carbon dioxide from process gases such as synthesis gas streams and steelworks gases. In the case of syngas, PSA technology is used to recover CO₂ from upstream, high-pressure raw syngas streams or low-pressure off-gas streams generated by steam methane reforming or gasification processes [81].

Unlike other separation methods that require high temperature fluctuation or the handling of corrosive chemicals, physical adsorption requires vessels capable of withstanding only modest pressure changes. The regenerability of the sorbent in pressure swing adsorption (PSA), similar to chemical absorption, offers a sustainable and cost-effective approach as the sorbent can be reused numerous times for CO₂ separation. However, several limitations hinder adsorption from standing alone as a

4 Capture Technologies and Processes

CO₂ capture solution. Firstly, the system struggles with handling high concentrations of CO₂, typically found in flue gases of power plants, where concentrations can reach around 15%. Secondly, available sorbents lack the desired selectivity for efficient CO₂ separation, often allowing smaller gases like N₂ to penetrate the pores alongside CO₂, diminishing overall separation efficiency. Research endeavours are currently underway to develop highly selective sorbents tailored for CO₂ capture. Nevertheless, physical adsorption holds promise within hybrid systems, where it can be strategically positioned after another separation process to maximize its efficiency. Ongoing research focuses on enhancing the selectivity, capacity, operating conditions, and packing structures of sorbents, with the aim of transforming adsorption into a viable and effective method for CO₂ separation in the future [73].

Significantly, by-product CO₂ from hydrogen production through methane stream reforming is harnessed using PSA instead of traditional absorption methods [71]. Despite the increasing adoption of PSA systems for hydrogen recovery, it is worth noting that they yield a by-product CO₂ stream with a purity of only around 50 vol%, rendering it less attractive as a commercial CO₂ source. Efforts are underway to develop PSA systems capable of processing this tail gas into hydrogen and CO₂-rich streams [71].

Vacuum Pressure Swing Adsorption (VPSA)

Vacuum Pressure Swing Adsorption also known as VPSA is the process in which separation of gases from air takes place by means of vacuum decompression for desorption. In other words, the gas molecules bind with adsorbent material at different rates depending on the pressure. This allows operators to single out one specific gas from a gas mixture. This technique is usually used to produce oxygen up to 95 vol.% from air [82]. For this, the air is forced by a blower to pass under pressure through the adsorbent bed. The nitrogen, carbon dioxide and water in the air are adsorbed by the adsorbent, and the remaining components pass through the adsorbent for richer oxygen. Later, the pressure is being lowered, the nitrogen, carbon dioxide and water are desorbed, and the adsorbent can be regenerated in the similar method. The reciprocating process continues the basic principle of vacuum pressure swing adsorption oxygen generation.

VPSA can also be applied to separate CO₂ from flue gases. If the separation is carried out in a single stage, a deep vacuum level is needed to achieve a high CO₂ purity. For this reason, two stages VPSA is being studied, in which two different adsorbents can be utilized. Suitable

applications for VPSA are IGCC, petrochemical and steel and cement processes since the CO₂ partial pressure in the respective flue gases is high and the volumetric flows low [83].

The VPSA process is run continuously with selective adsorption of the more strongly adsorbed component and periodic desorption of the extract by pressure swing [84]. VPSA process depends on the adsorbent and an efficient VPSA cycle configuration to improve separation efficiency for a feed mixture [85]. The adsorbents are used based upon either equilibrium selectivity or kinetic selectivity. Activated carbon, silica gel, zeolite and MOFs are mostly equilibrium selective adsorbent. These adsorbents are dependent based on the difference in equilibrium adsorbed amount at process conditions over the course of the adsorption-desorption cycle.

Compared to PSA, VPSA provides with the vacuum an efficient way to desorb CO₂ from sieve material while delivering the highest purity of oxygen [86]. This process leaves sieve material as good as it was at the start of each sieve bed cycle. Further, VPSA is credited to its simplicity, reliability to separate and low operating costs [87].

4.1.3. Cryogenic Separation

CO₂ can be separated from a gas mixture by cooling it under its critical temperature, where it liquefies or solidifies. Cryogenic methods utilize the distinct condensation and desublimation properties of CO₂ gas to achieve exceptional levels of CO₂ recovery and purity, often surpassing 99.99%. Among the various separation technologies, cryogenic approaches stand out for their ability to deliver exceptional results in terms of CO₂ capture [72]. Therefore, cryogenic separation allows the direct production of highly pure liquid CO₂ suitable for efficient transportation via pipelines or tankers. However, this method demands significant energy for refrigeration and necessitates the removal of substances like water and heavy hydrocarbons [71]. Since cryogenic CO₂ recovery is mainly applied to CO₂ streams with high purity, this separation method is less viable for low concentration stream, which are common for most of industrial CO₂ emission sources. Therefore, cryogenic CO₂ separation finds its niche in high-pressure gas streams, such as those encountered in pre-combustion and oxyfuel combustion processes. Moreover, this method is applied in ethanol production through fermentation, that yields remarkably pure liquid CO₂ product [71].

For deployment of cryogenic distillation with CO₂ from flue gas streams, the preliminary removal of all other gas components and particulates is required. In this process,

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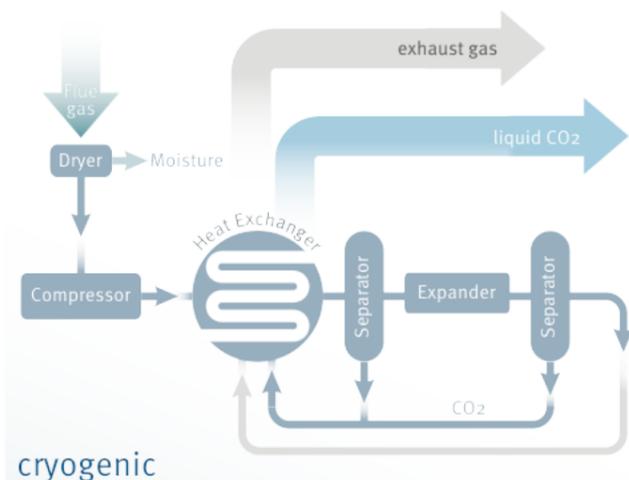


Figure 4.3 Process flow diagram of cryogenic separation

the temperature and pressure are manipulated to induce the liquefaction of CO₂, while nitrogen remains in the gaseous state [73]. This process is based on different boiling points of the gases in the mixture to be separated, being the boiling point of CO₂ -78.5°C, higher than the one of oxygen and nitrogen. This technology offers high CO₂ purity levels without the use of chemical solvents. However, it requires large amounts of energy and presents therefore high operational costs [88].

The conventional vapor-liquid separation uses high pressure to avoid solid formation and consequently damage in the equipment. A CO₂ concentration higher than 50% is recommended for this method, in order to limit the energy demand [88]. The process of cryogenic separation is described in Figure 4.3.

4.1.4. Membrane Separation

Membrane diffusion is a well-established technique in the fuel and chemical industries. These membranes exist in diverse variations, such as polymeric, ceramic, metallic, and gas absorption variants [73]. The strength of membrane processes lies in the absence of a separating agent and phase changes, thereby eliminating the associated processing costs. Furthermore, membrane systems occupy small footprints compared to alternative separation methods and require minimal maintenance. Their compact, lightweight design allows for versatile placement, whether horizontally or vertically, making them especially well-suited for retrofitting applications. Additionally, the modular nature of membrane units permits multi-stage operation and facilitates linear scale-up, thus managing costs effectively [71]. With few moving parts and straightforward construction, membrane separation systems are relatively simple to implement.

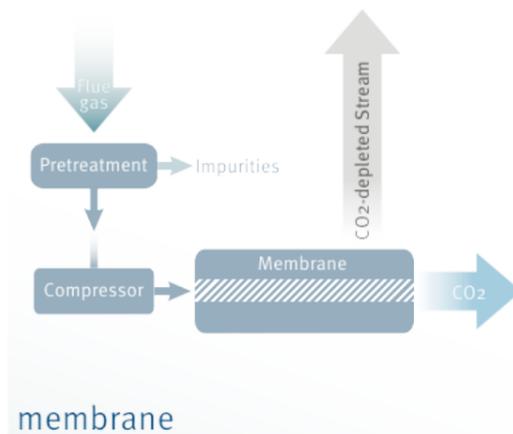


Figure 4.4 Process flow diagram of membrane separation

While some compression of the flue gas is needed before separation, this compression is notably less energy-demanding than that required for PSA. However, membrane technology faces inherent trade-offs between selectivity and permeability. Highly selective membranes tend to exhibit lower permeability, whereas permeable membranes may allow the passage of unwanted gases alongside CO₂, necessitating secondary separation processes [73].

Membranes require strict temperature control and are sensitive to corrosive gases (sulphur-containing gases, NO_x, etc.) necessitating pre-treatment. Maintaining membrane performance over long-term operation is challenging, limiting their practical industry use. Additionally, when the CO₂ concentration in the feed stream is diluted, multiple stages and/or recycling may be necessary [72].

In comparison to the conventional separation methods like absorption and adsorption, membrane separation is preferred in industry due to its low carbon emissions which leads to a smaller carbon footprint and because of its simple, easy design of operation. Further, membrane separation can be operated as a continuous separation system whereas absorption and adsorption operate as a batch system [89]. The process of membrane separation works on the mechanism that the membrane 'selectively' separates or permeates the desired components and leaves the other components out. In the case of CO₂ capture technologies, CO₂ must be separated from the exhaust gas streams using the membrane as the filter.

In this separation process, both membrane properties and process parameters play an important role in determining the overall performance of the process. Factors such as

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membrane selectivity and permeability and the pressure ratio between the feed and the permeate sides are important [90]. Figure 4.4 depicts the carbon separation via membranes.

4.1.5. New Developments with Microalgae and Enzymes

CO₂ bio-fixation via microalgae is gaining momentum due to its high photosynthetic rate, which makes it more efficient than terrestrial plants. This process utilizes solar energy and co-produces valuable ingredients from biomass, such as food, animal feeds, cosmetics, medical drugs, and biofuels. However, challenges include the need for inorganic nutrient sources, intensive energy requirements for microalgae cultivation, harvesting, and drying, and the low solubility of CO₂ in water [72].

Furthermore, there are new approaches for replacing amines with biocatalysts. An enzymatic carbon capture process was developed that works similarly to a post-combustion process. The biocatalyst called carbonic anhydrase is deployed in the absorber. The enzyme converts CO₂ from Flue gas to bicarbonate. The resulting bicarbonate fluid is then heated in a column at relatively low temperatures (75°C) to release the CO₂ [144].

4.2. Capture Process

CO₂ capture technologies consist of a tool set of techniques based on the previously mentioned separation methods specified to remove carbon dioxide. This chapter focuses on technologies which can be deployed for CO₂ utilization. Thus, carbon capture approaches which include storage measures, i.e. BECCS or mineralization methods are not described.

4.2.1. Direct Air Capture

Direct air capture technologies (DAC) separate CO₂ from the air and deliver it in high purity from the ad- or absorbing material [91]. This technology has therefore the potential to become an important contribution in global mitigation of CO₂ emissions [91]. Its ongoing development can lead to a mature technology which not only removes CO₂ from the air but can also be deployed as a clean carbon source for PtX applications. According to the IEA, eighteen DAC plants are operating globally and capture 0.01 Mt_{CO₂} per year [92]. However, to aim for a gigatonne scale by 2050 scenario, a tremendous annual growth rate of nearly 50% [91], [93] and a production scale of 60 Mt_{CO₂} per year by 2030 needs to be achieved [92].

Technical Background

Separating CO₂ from the air is energy intensive since CO₂ makes up only 0.04 % of the total composition of the atmosphere (421 ppm [94]). These are small quantities

compared to point sources from industrial processes or biogenic origin. Therefore, DAC still is a relatively costly capturing technology due to the high energy demand [92].

There is a myriad of possible optimized DAC processes which are currently in development [91]. However, even the more mature DAC processes are still at a technology readiness level of 6-7 [95] and need to overcome the pilot and demonstration phase to be rolled out for a broad industrial application. Two distinct processes exist to perform DAC: either with solid sorbents or liquid solvents (Figure 4.5) [91].

Solid sorbent DAC (sol-DAC) consists of porous materials that can separate CO₂ from a gas stream [91]. The sol-DAC typically operates at ambient to low pressure and medium temperatures of 80-120°C [91], [92]. DAC based on liquid solvent (liq-DAC) absorbs gaseous CO₂ into a basic solution. As a result, CO₂ is enriched in a liquid stream [91]. The liq-DAC requires high temperatures (300 – 900°C) to release the CO₂ from precipitated calcium carbonate [92].

Energy

The required energy of the solid sorbent and liquid solvent DAC are relatively similar from one another. In a rough estimate operating DACs (solid sorbent and liquid solvent) use 80% thermal energy and 20% electricity [69], [91], [96]. In sol-DAC the electricity is needed for the contactor fans [91], [97].

The sol-DAC has the advantage of being powered by various sustainable energy sources. The source can be adjusted to the requirements of the plant site (waste heat, geothermal, etc.). Since the sol-DAC runs at temperatures between 80-130°C, the thermal energy can also be supplied via commercial industrial heat pump [91], [98]. Through deployment of heat pumps the thermal energy demand can be reduced with electricity and costly resistive heating replaced [91].

In the case of liq-DAC, the access to energy sources is more restricted due to the higher operating temperature at around 900°C [91]. A relatively higher temperature is necessary to convert CaCO₃ to CaO and CO₂ [91], [99]. In large-scale liq-DAC, the heat is provided through natural gas and the emitted CO₂ is captured during combustion [92]. An electric option might be available in the future through the development of commercial electric calcination technologies [92].

The process by Carbon Engineering for capturing a tonne of CO₂ has an energetic requirement equivalent to either 8.81 GJ Natural Gas or 5.25 GJ natural gas coupled with

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366 kWh of electricity [91]. Global Thermostat focuses on using process heat to regenerate the sorbent after capture, with steam near 100 °C up to roughly 130 °C, with the preferred range being 105 °C–120 °C [100].

Commercial Scale DAC

At the moment many new DAC companies are evolving. Whereas established companies such as GE [101] push their development of own DAC technologies, new start-ups like CarbonCapture Inc. [102], [103] emerge to provide engineered carbon removal credits. Today, the major

global players and developers of DAC are Global Thermostat, Carbon Engineering and Climeworks [91], [97]. These companies displayed ambitious plans to overcome the transition from demonstration plants to a megaton scale.

In 2017, Climeworks launched its first commercial DAC plant, which removes 900 t of CO₂ per year from the atmosphere and operates in Hinwil, Switzerland. The DAC plant was installed at a waste recovery facility (KEZO) and is powered by its waste heat [104].

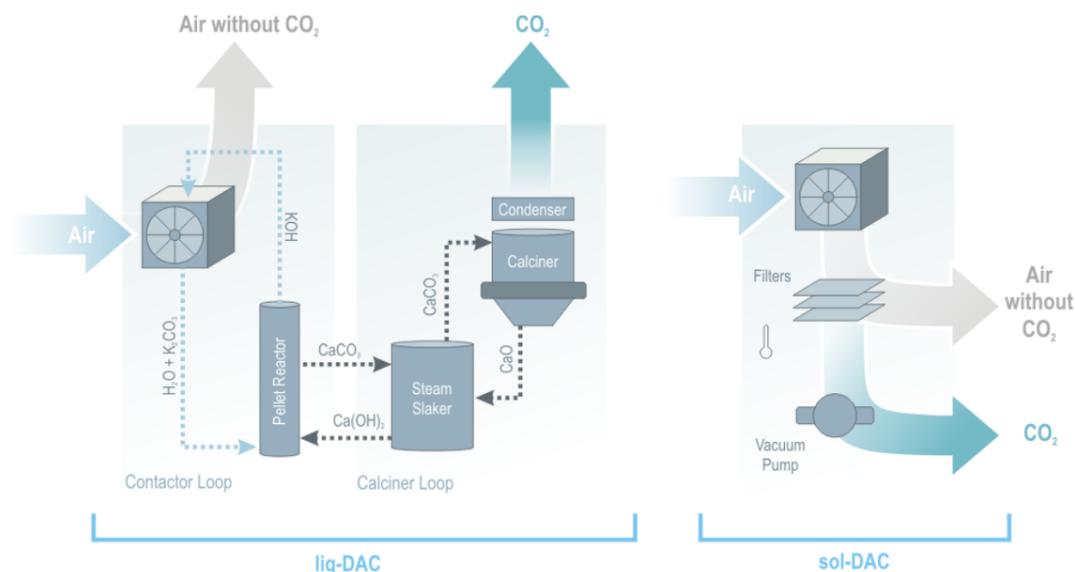


Figure 4.5 Examples for liquid sorbent (left) and solid solvent DAC (right)

The construction of the plant needed capital cost of \$3–4 million [105]. A new DAC plant named Orca captures 4,000 t per year (eight modules with 500 t_{CO₂}/y each) is located in Hellisheidi, Iceland and is powered by a geothermal powerplant [106], [107]. A second plant in Iceland was announced in 2022 which is designed to have a capture capacity of 36,000 t_{CO₂} per year [91], [108].

Global Thermostat is building two commercial DAC plants with a capturing capacity of 2,000 t_{CO₂} per year each [91], [93]. The DAC technology of Global Thermostat is based on process heat to regenerate the sorbent after CO₂ capture. Global Thermostat announced a cooperation with Black & Veatch for a construction of a large-scale project with the capacity of 100,000 tCO₂ per year [93], [109]. This project is placed in three geographically separate locations in the USA (Odessa, Texas; Bucks, Alabama; Goose Creek, Illinois).

The Canadian company Carbon Engineering is working on commercial DAC technologies based on a liquid solvent

[91]. In the Permian Basin, Texas USA, Carbon Engineering plans to construct their first commercial plant that captures 1 Mt_{CO₂} per year [91], [93], [110]. This plant should be operational in the mid-2020s. Moreover, Carbon Engineering announced a further plant in North-East Scotland, UK which is designed to capture 0.5 to 1 Mt_{CO₂} per year [93], [111]. Carbon Engineering estimates levelized costs of 94–232 USD per t of CO₂ [91], [99].

Scale

In scalability, the DAC approaches can vary greatly. The sol-DAC in small scale is easier to develop compared to liq-DAC and thus achieve higher modularity. One example is the Climeworks approach, in which the process is divided in segments with small units capturing 50 t_{CO₂} per year [112], [113]. The competitor Global Thermostat deployed in their first pilot plant containers as modules with a capacity of 1,000 – 4,000 t_{CO₂} per year [91], [114]. These modular concepts offer more flexibility in the scale of the plant. The liq-DAC system is much harder to develop in a small modular way. The approach of liq-DAC relies on

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a highly integrated system where the entangled processes are hard to segment. Therefore, the smallest possible scale is significantly larger compared to sol-DAC [91]. A small-scale approach is a pellet reactor and air with minimum capacities of 10 kt_{CO₂} per year [91], [99]. A benefit of liq-DAC is a significant economy of scale due to large components (calciner, slaker) [91], [99]. The economic optimum is estimated at about 1 Mt of CO₂ per year [99] and therefore beneficial for a large-scale operation [91], [99].

Potential and Emerging Perspective of DAC

In recent years, various companies discovered DAC as a technology to reduce their carbon footprint. Whereas big globally active companies invest in large-scale DAC, e.g. Microsoft and Climeworks (Orca plant), many new actors emerge who participate in the development of new DAC technologies. While the large-scale projects enable future industrial scale of DAC, new still niche and low TRL DAC technologies may improve in efficiency. Both paths have the potential to improve DAC to become less energy intensive and establish optimized sorbents for large-scale production. Various start-ups specialize in the development of sorbents, air contactors and low-energy regeneration [93]. Especially, advances in passive air contactors and more cost-efficient sorbents become increasingly pursued in the field of DAC technologies [93]. Today's research investigates materials and their structure for sol-DAC applications such as metal–organic frameworks (MOFs), zeolites, carbon molecular sieves and activated carbon [91]. Today, DAC still remains a cost and energy intensive technology. However, via extensive industrial implementation of DAC the cost can be lowered and the technology itself further improved [91]. Therefore, DAC has the potential to become successively more feasible and economical in the future [91]. DAC has developed tremendously as a new modern technology. However, for full maturity further research, development and investment are needed to make it more feasible for industrial scale.

4.2.2. Capturing Strategies for Fuel Combustion

Depending on whether the CO₂ separation takes place before or after a combustion process and on the purity of oxygen used, the CO₂ capture processes can be categorized in three main approaches: post-combustion, pre-combustion and oxyfuel combustion capture, each with its unique advantages and challenges [72].

Figure 4.6 offers an overview of these three processes. These strategies for CO₂ capture play a crucial role in advancing carbon capture and storage (CCS)

technologies and reducing the environmental impact of fossil fuel combustion. Researchers continue to explore improvements in efficiency and cost-effectiveness to accelerate the adoption of these methods in the fight against climate change [72]. The advantages and disadvantages of the three combustion processes are summarized in Table 4.1.

Pre-combustion

Pre-combustion is a CO₂ capture strategy that involves the reaction of fuel with oxygen and water before combustion. During this process, carbon in the fuel is converted to CO₂ and carbon monoxide, with simultaneous hydrogen production. In a further step the carbon monoxide is converted to CO₂ (water-gas shift reaction), resulting in a mixed gas with approximately 60–80% hydrogen and 20–40% CO₂. Pre-combustion capture is primarily used in integrated gasification combined cycle (IGCC) systems. One significant advantage is the production of H₂, an energy source with various applications, such as fuel cells, new energy vehicles, and the chemical and aerospace industries [72].

The high CO₂ concentration in syngas greatly increases adsorption efficiency and leads to the formation of a fuel that can be less harmful to the environment. In addition, researchers have studied this method extensively and developed it to be widely adopted and eventually commercialized. It is important to take note of the major disadvantages of pre-combustion capture, being decay issues due to the utilization of hydrogen-rich fuel i.e., fuel contamination, and heat transfer challenges [118].

Post-combustion

Post-combustion carbon capture is the process which involves the removal of CO₂ at low pressure from a gas mixture after combustion takes place completely. This technology is widely preferred for existing power plants, and it has been proven to recover CO₂ at a rate up to 800 t/d. In addition, post-combustion carbon capture significantly increases the energy penalty, transportation, and storage costs due to the low concentration of CO₂ in flue gas, which is in the range of 7% - 14% in coal-fired plants and less than 4% in gas-fired plants. The percentages are significantly lower than the pre-combustion carbon capture method [42]. Moreover, this technology involves 70% higher electricity production cost due to its inefficiencies. Although these factors are present, operators are still implementing this carbon technology in their power plant projects.

The main advantage of the post-combustion carbon

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capture technology is its maturity compared to existing carbon capture alternatives as there are standardized techniques to incorporate this technology into various industrial applications for maintenance when needed. Another major advantage is the ease and relatively low technological barriers to incorporate this technology into new and existing plants. On the other hand, a major disadvantage is the low carbon capture efficiency due to low CO₂ concentration in the flue gas. Other disadvantages include large parasitic loads (refers to the energy that is used to power the lights, motors, pumps, auxiliary facilities of the well field, control systems, cooling systems, ancillary equipment, and other electrical loads that are necessary for the operation) and high electrical energy generation costs [119].

Calcium Looping

Calcium looping is characterized by CO₂ capture at elevated temperatures employing two reactors, employs lime (CaO) as a sorbent to form calcium carbonate (CaCO₃) from CO₂ in the first reactor. Subsequently, CaCO₃ is

transported to the second reactor for regeneration, resulting in a pure CO₂ stream and lime, which is then recirculated to the first reactor. Presently, calcium looping remains in the pilot/pre-commercial stage, having undergone trials in coal-fired fluidized bed combustors and cement manufacturing processes [115]. This approach can also be combined with the oxyfuel combustion.

Oxyfuel Combustion

This process combusts fuel with pure oxygen, leading to a high CO₂ concentration (over 80%) in the flue gas. The volume of flue gas from oxyfuel combustion is approximately 75% less than from air-fired combustion [121].

Purifying CO₂ in oxy-fuel combustion is relatively straightforward compared to post-combustion methods, and NOx emissions are lower due to the lack of nitrogen. Optimization and heat integration are essential to minimize the energy penalty associated with air separation and compression units [72].

4 Capture Technologies and Processes

Table 4.1 Overview of combustion processes

Process	CO ₂ (vol%)	Advantages	Disadvantages
Pre-combustion	15% – 50%	<ul style="list-style-type: none"> Higher energy efficiency compared to post-combustion Less environmental impacts 	<ul style="list-style-type: none"> Decay issues Heat transfer challenges Only for new plants
Post-combustion	3% – 15%	<ul style="list-style-type: none"> High maturity Implementation in existing plants possible 	<ul style="list-style-type: none"> Low efficiency High energy production costs
Oxyfuel combustion	~70%	<ul style="list-style-type: none"> Reduced NOx emissions High CO₂ purity Lower gas volumes due to increased density 	<ul style="list-style-type: none"> High energy requirement High temperatures produced by combustion in pure oxygen environment

Due to the composition of the resulting flue gas (primarily CO₂ and water vapor) straightforward dehydration yields a high-purity CO₂ stream [120]. While oxy-fuel separation is in the large prototype/pre-demonstration phase, it has already been employed in coal-based power generation and cement production. Membrane separation, based on polymeric or inorganic membranes with high CO₂ selectivity, allows CO₂ to permeate while retaining other gases in the stream. Its readiness varies by application, with natural gas processing in the demonstration stage, and the sole large-scale membrane separation facility is operated by Petrobras in Brazil. Membrane technology for CO₂ removal from syngas and biogas is commercially available, while development continues for flue gas treatment [115].

Oxyfuel combustion is a highly interesting option for CO₂ capture due to the possibility to use the advanced steam technology, i.e. with higher purity, reduced equipment size or cost and to design a zero-emission power plant [122]. The major advantages of oxyfuel combustion are reduced NOx emissions, high CO₂ purity, and lower gas volumes due to increased density [123]. Currently, the oxyfuel combustion process is implemented to reduce CO₂ emissions by about 90% [124]. As an outlook, several improvements are being researched in materials and process designs so that very high capture rates can be achieved, specifically for the air separation unit [125].

Metal-based adsorbents for oxyfuel combustion are used as chemical adsorbents and studies have shown that higher CO₂ capture performance has been achieved [126]. Biomimetic solvents, e.g. haemoglobine derivatives are being studied to advance absorption based oxyfuel combustion. Carbon molecular sieve (CMS) adsorbents

are being optimized to enhance carbon capture via adsorption based oxyfuel combustion [127]. Other oxyfuel combustion approaches are chemical looping and conventional oxyfuel with recirculation.

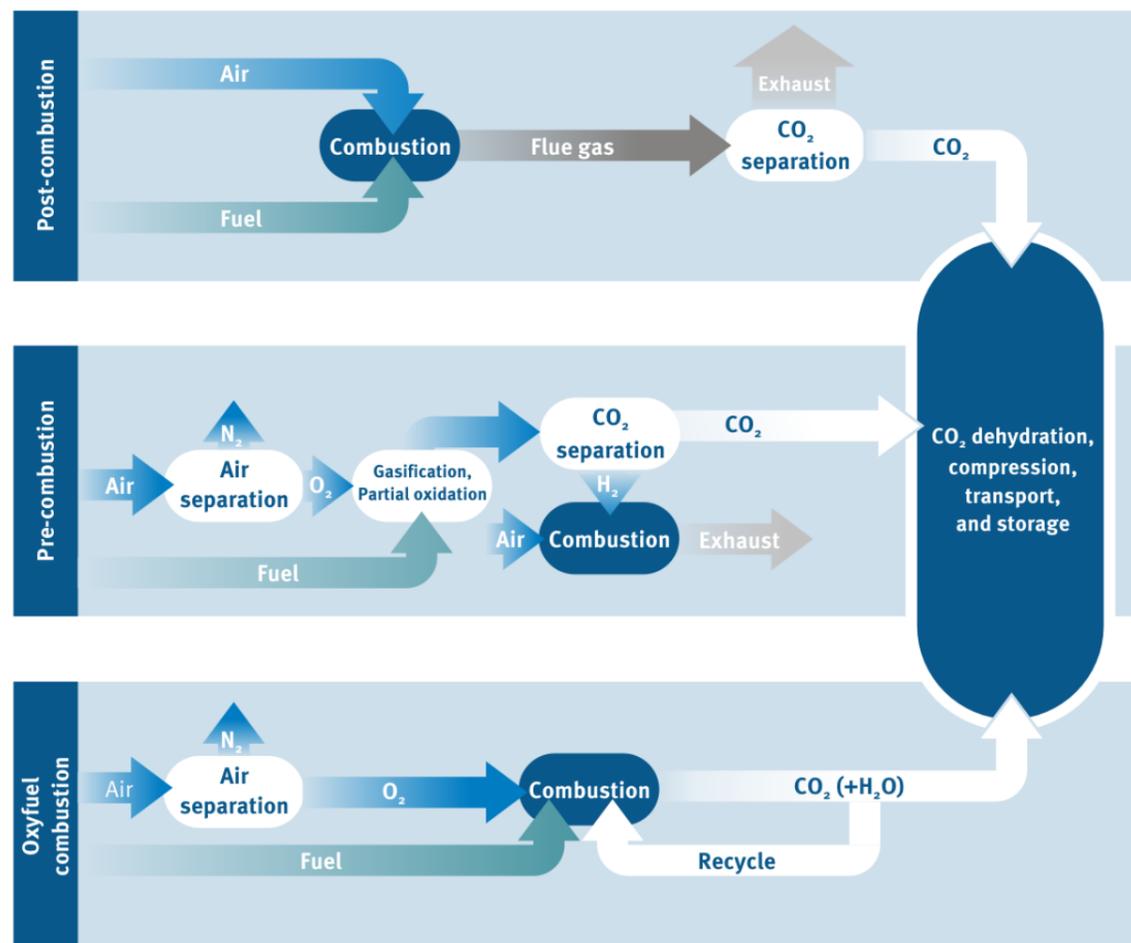
Chemical Looping Combustion

Chemical Looping Combustion (CLC) is a promising technology for fossil fuel combustion that uses the concept of preventing CO₂ dilution with flue gases by avoiding the direct contact between flue and combustion air [128]. In this process, the oxygen required for fuel combustion is supplied as metal oxide in solid phase. Good oxygen carriers are required for this process. Transition metal oxides such as nickel, copper, cobalt, iron and manganese oxides are good oxygen carriers.

In the CLC process, two interconnected fluidized beds are used as air reactor and fuel reactor, respectively. As the feed, gaseous fuel is fed into the fuel reactor, where it is oxidized by lattice oxygen of metal oxide, which is then circulating between the reactors. Complete combustion in fuel reactor produces condensable water vapor and CO₂ [129]. Therefore, the CO₂ formed can be readily recovered by condensing water vapor, eliminating the need of an additional energy intensive CO₂ separation process [129].

The primary benefit is the natural separation of CO₂ and H₂O from the flue gases. The reduced oxygen carrier is re-oxidized in the air reactor in the absence of a fuel at relatively lower temperatures, and this reduces NOx formation because the fuel burns in the fuel reactor in an airless environment [130].

Chemical looping has undergone testing through approximately 35 pilot projects, encompassing coal, gas, oil, and biomass combustion [115].

Figure 4.6 Overview of CO₂ Capture approaches. Source: own illustration based on [108]



Adsorption
Tower 1-B

5 Transport & Storage

The successful implementation of carbon capturing technologies requires a functional CO₂ infrastructure. The CO₂ point sources are not necessarily closely located at the off-taker facilities. Connecting sources and sinks is therefore a crucial objective for PtX plants. Transport and storage capacities need to be established for a steady CO₂ supply. A CO₂ infrastructure needs to implement the treatment of the CO₂ (purification), compression, transport, storage capacities and in some cases compressor booster stations (for intermediate recompression) [69], [131].

For CO₂ storage, there are two options: underground storage and surface storage in gas holders. Gas holders can be used to store 180 kg to 60 t of CO₂. [132]. Underground storages reach capacities in Mt to Gt scale depending on the geological conditions [133]. Typical areas are depleted oil and gas fields, aquifers, and deep-seated coal bearing layers [133]–[135]. Materials and equipment for CO₂ handling, connection to pipeline and injection can be compared to established components of gas production [136].

The transport of CO₂ has been practiced for several decades and can be performed similarly to the transport of natural gas. Gaseous or liquid CO₂ transport at industrial scale is possible via employment of tanks, ships, or pipelines [69], [131]. In small scale and over short distances, the use of trucks can be preferred depending on the local conditions (availability of roads, rails etc.). It is estimated that the use of trucks can be feasible if the quantities are below 5,000 kt_{CO₂} per year [69]. However, large scale industrial CO₂ pipelines are broadly deployed and, in many cases, economically more feasible compared to the alternatives [69], [131]. CO₂ transport via ships becomes a viable option when crossing the sea over long distances is unavoidable [131]. Nevertheless, pipelines are still needed to connect to the port terminals [131].

CO₂ Pipelines

Main application for large volume transport of CO₂ was especially for Enhanced Oil Recovery (EOR) which is established for more than 40 years [69], [131]. Thousands of km of CO₂ pipelines through North America, Europe, Middle East, Africa, and Australia have been used for EOR operations. Besides EOR, CO₂ pipelines are also in use for CO₂ utilization (CCU) or Carbon Capture and Storage (CCS)

[137]. A new European CCS project plans with a 900 km pipeline that will transport CO₂ from Germany to Norway [138].

Design and construction of pipelines for dry CO₂ (low water content) is very similar to natural gas pipelines. With low water content (~500 ppm) CO₂, the pipeline material of carbon steel remains unproblematic. Far more critical is the operational pressure which needs to be at least at 85 bar for CO₂ transport, but most natural gas pipelines operate below this threshold [131].

Critical aspects for pipeline transport are the chemical and physical properties of the CO₂ [131]. The composition and therefore also the properties of CO₂ impact the form in which CO₂ is transported (gaseous, liquid or mostly in supercritical phase). These parameters are necessary to adjust and maintain the pressures for respective phases. Typically, CO₂ is transported as a fluid with a high density. This is possible in a supercritical phase. To ensure supercritical conditions, CO₂ needs to be compressed to pressures of at least 73.8 bar and a minimum temperature of 31.1 °C. Common pipeline operation parameters are 85-150 bar and 12-44 °C (for supercritical but also multiple phases). Offshore pipelines can be beneficial due to high pressures up to 300 bar [131].

Impurities affect the physical properties and therefore the phase density. For this reason, there needs to be an adjusted pipeline design to the CO₂ source or special treatment of the CO₂ to increase its purity. Common impurities derive from combustion of fossil fuels or the industrial sector such as cement or steel plants. In these cases, CO₂ can have traces of CO, N₂, O₂, H₂S or water. It is also possible to adjust only the pressure during operation to ensure supercritical pressure and the flow behavior of the fluid phase [131]. Typically, the purity of CO₂ in pipelines exceeds 95% and about 1/3 of the pipelines deliver a purity greater than 99% [137] to ensure a dense and stable phase. Additionally, impurities can be corrosive to the pipeline material and lead to higher maintenance costs. A major and well-known problem is the presence of water which forms corrosive carbonic acid with CO₂ [131].

5 Transport & Storage

Operations with high pressures require not only compressors but also intermediate boosting stations to prevent pressure drops depending on the transport distance [131]. Phase change is avoided in operation through cautious control of the phase boundaries. The US which has the most experience in CO₂ transport, does not record any civilian incidents for over 40 years of operation [137].

The type of CO₂ source, storage capacities, sinks and the environment determine the pipeline design. These will affect requirements such as length, diameter, and compressor stations.

Infrastructure Cost

A multifold of parameters such as safety conditions, land stability, environmental constraints can lead to various outcomes for a deployment of an CO₂ infrastructure [131]. Estimating the overall costs for a CO₂ infrastructure is quite challenging due to the highly fluctuating variables involved. Depending on region and resources, individual cases need to be assessed. However, key parameters can be defined which affect the cost. There are basically two categories: storage and transportation costs. For storage quantity defines the storage method and thus also the cost of implementation and operation. In the case of transportation, large quantities are most cost-effective when pipelines are used. However, pipelines come with high implementation costs. Table 5.1 shows some costs for transport and storage of CO₂.

Table 5.1 Estimates for the main CO₂ transport costs (numbers can vary depending on the country's conditions and regulations and, therefore serve as a rough guideline) [140]

Transport and storage	Cost
CO ₂ transport and storage	10 € ₂₀₁₇ / t _{CO₂}
Offshore transport and storage	14.2 – 32.7 € ₂₀₁₇ / t _{CO₂}
Truck transportation of the CO ₂	0.22 € ₂₀₁₇ / t _{CO₂} per km

Key cost factors

Main cost factors for storage [139]:

- Site identification
- Operational costs
- Quantity of CO₂
- Geology of plant site
- Component procurement
- Labor

Main cost factors for transport [139]:

- Distance
- Quantity of CO₂
- Type of transportation
- Geology depending on type of transportation
- Operational costs
- Component procurement
- Labor

6 Conclusions

6 Conclusions

Identifying suitable carbon sources and supplying them for numerous PtX technologies is a crucial contribution to push forward an industrial transformation towards climate neutrality. Thus, CO₂ as a feedstock increases in importance for the chemical industry, energy, and heavy-duty mobility sector to replace fossil resources. Diverse point sources for CO₂ are available today and the handling of this gas in an industrial scale does not need major development of technologies. However, not all carbon sources can be deployed equally since various factors make some CO₂ sources more favorable. Therefore, the selection of a CO₂ source for a PtX production should consider different aspects such as availability, energy consumption and sustainability. For a better decision-making process regulations and certification for determining clean and sustainable carbon source would be a helpful measure. Especially a future carbon management strategy could clear the path for a sustainable CO₂ market and the required infrastructure.

Carbon capture from fossil fuels combustion in the energy and industry sectors would provide high quantities of CO₂. However, this process is controversial due to the peril of potential lock-in effects. Promoting further use of fossil resources could contradict emission neutrality goals. In the same way, it is expected that in the next decades, these emissions will be reduced to near zero and won't be available in the same way as at the present time. Moreover, the concentration of CO₂ in combustion flue gases is low and its separation requires high amounts of energy. Unavoidable CO₂ emissions from the industry are considered a further option to obtain CO₂ for PtX, because their emissions cannot be avoided with current technologies or there are no alternative materials for the final product. One example for this, are process emissions from the cement industry, which partially result from a chemical reaction and not combustion.

Biogenic sources represent a most accepted source of carbon because during the growing process of biomass, CO₂ is captured from the air, creating a closed carbon cycle. Nevertheless, it should be considered that biomass availability for energetic and industrial uses is limited and so is biogenic CO₂. The use of CO₂ from biomass should apply to sustainability criteria, such as greenhouse gas emissions savings, sustainable forest management, protection of air, soil and water and biodiversity protection.

CO₂ from atmospheric air is available in every region of the world. Nevertheless, its low concentration results in high energy demand for the capture process with state-of-the-art DAC plants. DAC is considered as a clean technology in a sense that it can be operated with renewable electricity. Several companies offer commercial DAC modules in various scales. However, the technology still lacks in maturity for a complete industrial implementation. A major drawback is the very high energy consumption which increases the operation costs dramatically. Further development of this technology is needed to reduce its costs. The future CO₂ demand for e-fuel production might be a driving force for DAC roll-out due to the lack of sustainable and largely scalable alternatives.

Alternatively, there are numerous separation methods which are applicable for most processes that produce CO₂. A myriad of already mature separation methods for various capture technologies are applied today in the industry. Absorption and adsorption are principles which aid in the carbon capture via pre-, post- or oxyfuel combustion. Amine gas treatment and PSA are some absorption- and adsorption-based technologies which are commercially available. Other pathways to capture carbon include membrane and cryogenic separation. The membrane process has several advantages compared to conventional processes due to its simplicity and ease of separation, but its capacity and commercial stability are still under research. The cryogenic process produces liquid CO₂ and requires no separation media. Cryogenic separation could reduce carbon emissions produced from fossil-fuelled power plants by approximately 95–99%, at a lower cost and energy. Each technology has its own advantages and limitations. However, the reliability, stability and removal efficiency of these technologies are the main challenges. Hence, this requires a great need for understanding the existing technologies to improve their performance, and reduce the cost and energy required for CO₂ separation. Currently, research is being carried out to improve the efficiency of the carbon capture technologies.

Pre-combustion carbon capture stands out as a highly efficient method for extracting carbon from fossil fuels, surpassing the conventional post-combustion approach. The process benefits from the high concentration of CO₂ in syngas, leading to enhanced adsorption efficiency and resulting in a cleaner fuel with reduced environmental impact. Extensive research efforts have been devoted to

6 Conclusions

the development and widespread adoption of this technology, aiming for eventual commercialization. However, decay issues arising from the utilization of hydrogen-rich fuel can lead to fuel contamination, and there are heat transfer challenges in the process.

Post-combustion carbon capture technology offers several key advantages over existing carbon capture alternatives. Its main strength lies in its maturity, with established techniques readily available for integration into diverse industrial applications and easy maintenance when required. Additionally, this technology exhibits relatively low technological barriers, making it accessible for both new and existing plants. However, post-combustion is relatively low in its carbon capture efficiency and operates with high electrical energy generation costs.

Oxyfuel combustion effectively reduces CO₂ emissions by approximately 90%. However, this process demands a substantial amount of energy and generates extremely high temperatures due to combustion in a pure oxygen environment. This necessitates a significant recycle of flue gas to maintain the required temperatures for the combustion process. To enhance the capture rates, ongoing research focuses on material advancements and process designs, particularly targeting improvements in the air separation unit.

Implementation of complete PtX value chains not only relies on viable carbon sources but also on a suitable network for CO₂ transportation. Establishing connections between sources and sinks becomes a critical objective for PtX plants, requiring the integration of transport and storage capacities to ensure a steady CO₂ supply. Technically, the handling of CO₂ can be compared to the transport of natural gas and does not necessitate major developments. As soon as large-scale CO₂ quantities are reached, pipeline transportation becomes most feasible compared to ships and trucks. However, cost calculations are highly depended on distance, regulation and geological conditions.

Overall, there are many options to operate PtX plants with numerous CO₂ point sources. Current pilot and demonstration projects partially consider also a mix of different carbon sources, e.g. combination of biogenic CO₂ and DAC. Controversial CO₂ from fossil sources can only serve for transitioning to cleaner sources since these emissions will be also reduced to reach the climate goals. While biogenic sources will be limited in their capacity for large scale supply of CO₂, DAC is a costly source due to the high energy demand. Therefore, finding suitable carbon

sources will also heavily depend on specific regional resources. Regions with high potential for renewable energies are more likely to deploy DAC and regions with sustainable biomass or waste processing are more likely to apply these sources. However, future CO₂ demands for PtX products such as efuels will drastically rise. In the short and medium-term the demand for CO₂ will be hardly covered by DAC and biogenic sources solely. For this reason, carbon captured with combustion methods in the industry is needed to provide sufficient quantities of CO₂ in early stages and in regions with limited capacities for RE and biogenic sources. These carbon sources are also connected to lower investment costs due to the widespread availability of mature separation methods. For the long-term, as large-scale CO₂ streams need to be transported also over large distances, a network for CO₂ pipelines will be needed since it is the most cost-effective measure. For this, already existing networks for natural gas can be used or even replaced to reduce investment cost. Consequently, an emerging PtX industry requires a rapid expansion of RE to push forward deployment of sustainable CO₂. Similarly, to green hydrogen, this undertaking might also necessitate national and international strategies for a carbon management plan as a foundation for guaranteeing steady and sustainable CO₂ supply in the future.

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