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# Industrial CO2 supply pathways for CCU-based electrofuel production in Finland

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# **Industrial CO2 supply pathways for CCU-based electrofuel production in Finland**

E-Fuel WP2 Task 2.1 Deliverable

Linjala, Onni & Kajolinna, Tuula VTT Technical Research Centre of Finland 6.3.2023

# ABSTRACT

This work evaluates potential industrial CO<sub>2</sub> supply pathways for CCU-based electrofuel production in Finland. We examine the common stages and costs of CCUS, mature and emerging carbon capture technologies, and carbon capture potential of Finnish industries. CCUS costs range around 42–161 €/tCO<sub>2</sub>, deriving from several case-specific stages that vary depending on source stream properties, capture technology, location, logistics, and enduse of CO<sub>2</sub>. Various technologies are in development for carbon capture. Post-combustion capture is appealing for industrial applications due to retrofittable nature and wide applicability of the technologies. In post-combustion capture, amine absorbents are a low-risk technology choice with commercial maturity and high capture performance, although suffering from toxic degradation products and high regeneration energy requirement. Carbonate salt absorbents (e.g., hot potassium carbonate and enzyme-enhanced K<sub>2</sub>CO<sub>3</sub>) have emerged as viable, eco-friendly options to consider at commercial level alongside amines. Also, technologies like membranes and solid sorbent processes are on the brink of commercialization. In Finland, pulp mills are the most appealing targets for carbon capture with high quantity of biogenic  $CO_2$  available and suitable preconditions for CCUS implementation. Processes with a high CO<sub>2</sub> concentration exhaust stream (e.g., ethanol fermentation and HVO) are a low hanging fruit regarding capture cost but with low quantitative capture potential. To evaluate techno-economic feasibility of carbon capture in a certain application in more detail, a specified case study with process modelling is required.

**Keywords:** carbon dioxide, CO<sub>2</sub> capture, carbon capture and utilization, CCU, post-combustion capture, point source capture, industrial emissions, forest industry, petroleum refining, biorefining, power-to-X, electrofuels, drop-in fuels, Fischer-Tropsch, SOEC, RWGS, CPOX

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# ABSTRACT

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# SYMBOLS AND ABBREVIATIONS

AMP	amino-2-methyl-1-propanol
BPMED	bipolar membrane electrodialysis
CAP	chilled ammonia process
CaL	calcium looping
CPOX	catalytic partial oxidation
CCUS	carbon capture, utilization, and storage
DAC	direct air capture
FGD	flue gas desulfurization
FT	Fischer-Tropsch synthesis
GHG	greenhouse gas
HTCE	high-temperature co-electrolysis
HTE	high-temperature electrolysis
HVO	hydrotreated vegetable oil
KPI	key performance indicator
MCFC	molten carbonate fuel cell
MEA	monoethanolamine
P2X	power-to-X
PCET	proton coupled electron transfer
PSA	pressure-swing adsorption
PZ	piperazine
RWGS	reverse water-gas shift
SCR	selective catalytic reducer
SMR	steam methane reforming
SOEC	solid-oxide electrolyser cell
t	tonne
toe	tonnes oil equivalent
tpa	tonnes per annum
tpd	tonnes per day
TRL	technology readiness level
TSA	temperature-swing adsorption
VSA	vacuum-swing adsorption

## **1 INTRODUCTION**

Pursuit towards carbon-neutral society necessitates major reforms in transportation, a sector highly dependent on fossil fuels. Transportation generates around 8 Gt of greenhouse gas (GHG) emissions annually, accounting for a 16 % share of the global GHG emissions (Ritchie & Roser, 2020). Emissions of transportation divide roughly in half between light-duty transportation (i.e., passenger vehicles) and heavy-duty transportation (i.e., shipping, aviation, and haulage) (IEA, 2021). Direct electrification with renewable energy is a potential solution to decarbonize light-duty transportation but inadequate for heavy-duty transportation due to inefficiency of current battery technologies. Heavy-duty transportation depends on fuels with high energy densities and specific energies to ensure efficient logistics for the long transport distances and heavy working loads. Therefore, replacing conventional fossil fuels with carbon-neutral fuels like hydrogen, ammonia, biofuels, or synthetic hydrocarbons provides a more potential decarbonization pathway for the hard-to-abate sectors of transportation (Gray et al., 2021).

### **1.1** Electrofuels as a green alternative for fossil fuels in transportation

The ongoing transition towards energy system electrification and hydrogen economy has emerged electrofuels (e-fuels) as a potential complementary solution to decarbonize transportation. E-fuels offer a way for indirect electrification of transportation by converting electricity into fuel forms via power-to-X (P2X) technologies. Initially, green hydrogen is produced by decomposing water with renewable electricity via water electrolysis. Hydrogen can be used directly as a fuel or synthesized with CO<sub>2</sub> or N<sub>2</sub> to produce fuels like ammonia, methanol, or hydrocarbon chains. It is unlikely for hydrogen to become a relevant transport fuel soon as hydrogen infrastructure is at an early development stage in most areas and as it would require renewing the transport fleet to hydrogen-powered using fuel cells or hydrogen combustion engines for which the market is still limited. Therefore, carbon-neutral fuels directly applicable to the existing infrastructure, referred to as drop-in fuels, currently offer a more attracting option to decarbonize heavy-duty transportation. As direct alternatives to conventional fuels drop-in fuels have potential for rapid commercial deployment if proven techno-economically feasible. Technologies used in production of drop-in e-fuels are proven technically feasible but commercial breakthrough is yet to happen due to weak cost-competitiveness against conventional fuels. A major challenge of e-fuels is the weak electricity-touseful-energy efficiency that typically ranges around 10–35 % (Ueckerdt et al., 2021), leading to high electricity demand and production cost.

Fischer-Tropsch synthesis (FT) is a relevant technology for drop-in e-fuel production. It can be used to produce synthetic alternatives to conventional fuels like gasoline, diesel, and jet fuel. A mixture of hydrogen and carbon monoxide known as synthesis gas (or syngas) is converted into liquid hydrocarbons using a catalyst and elevated temperature and pressure. Syngas is conventionally produced via coal or biomass gasification or steam methane reforming of natural gas, but in P2X routes, alternative technologies powered with renewable energy are used, e.g., co-electrolysis of water and CO<sub>2</sub> or reverse water-gas shift reaction (RWGS). According to IEAGHG (2021), lifecycle emissions of drop-in FT fuels produced with renewable electricity are 68–87 % lower than their fossil-based counterparts. However, production of FT fuels is currently significantly more expensive compared to conventional fuels, mainly due to the high price of green hydrogen. Zang et al. (2021) calculated that with a hydrogen price of \$5.0/kg (from water electrolysis) and a CO<sub>2</sub> price of \$17.3/ton (from ethanol fermentation), the minimum fuel selling price of FT fuel is 10.8–12.3 USD/gal ( $\approx 2.4-2.8 \ ell)$ . With a hydrogen price of \$2/kg the price of FT fuel decreases significantly to 5.8–6.3 USD/gal ( $\approx 1.3-1.4 \ ell)$ .

Globally, there are some projects underway aiming for commercial deployment of drop-in electrofuels. The Norsk e-Fuel project aims for production of 12.5 million liters of aviation electrofuels by the end of 2024 and 25 million liters by 2026 at Mosjøen, Norway, based on which a plant with 100-million-liter capacity is built by 2029 (Norsk e-Fuel, 2022). At Herøya, Norway, Nordic Electrofuel AS is constructing an electrofuel plant with a 10-million-liter capacity of jet fuel, aiming to start production in 2024. In project Reuze, ENGIE and Infinum have partnered up to develop production of synthetic fuels at ArcelorMittal's Dunkirk factory in France, aiming for production capacity of 100 tonnes of electrofuels and naphta by 2026 (Reuze, 2022).

### **1.2** Carbon capture as a CO<sub>2</sub> supply for P2X

Carbon capture refers to capturing  $CO_2$  from emission point sources or directly from the atmosphere. It is an essential technology for P2X value chains where carbonaceous products

such as synthetic hydrocarbons are manufactured. Majority of research on carbon capture has focused on carbon capture and storage (CCS) where the captured  $CO_2$  is stored into geological formations preventing it from returning to the atmosphere to avoid greenhouse effect. Concepts where  $CO_2$  is utilized as feedstock for processes or value-added products is referred to as carbon capture and utilization (CCU). In addition to generating value, CCU can provide positive climate impact if used to replace unsustainable production based on fossil sources. Although this work focuses on electrofuel production, which is a CCU value chain, also CCS activities are examined as same methods and technologies are used in both concepts to capture, condition, and transport the  $CO_2$ .

Regarding economics, capturing  $CO_2$  from emission point sources like flue gas or other industrial exhaust streams is often preferred over direct air capture (DAC) where the  $CO_2$  is captured from ambient air. Generally, significantly lower capture costs can be achieved with point source capture compared to DAC as  $CO_2$  concentration of emission point sources that often ranges around 3–25 vol-% is significantly higher than in ambient air (0.041 vol-%). Post-combustion capture, i.e., capturing  $CO_2$  from flue gas and process exhaust streams using end-of-pipe technologies, is often the primary method of point source capture due to retrofittable nature and high maturity compared to alternative methods of carbon capture.

Numerous technologies have been developed to capture CO<sub>2</sub> from various types of gas streams, utilizing chemical and physical phenomena like absorption, adsorption, membranes, electrochemical reactions, and cryogenics. In post-combustion capture, absorption via amine-based liquid solvents currently represents the state-of-the-art technology. Amines yield high CO<sub>2</sub> capture performance and have high maturity having been used in industrial gas purification applications for decades. There are several vendors on the market offering commercial amine-based technologies. However, there is interest for alternative technologies as amines face challenges such as energy-intensive regeneration, volatility, toxicity and corrosivity, although these challenges have been reduced with advanced solvents and novel process configurations (Rochelle, 2016). Several novel technologies are currently emerging such as alternative liquid absorbents, solid sorbents, membranes, fuel cell-based capture, and various hybrid systems. Many of the emerging technologies are on the brink of commercial-ization, having reached the level of industrial demonstration. Therefore, it has become

reasonable to consider alternative technology options alongside amines when evaluating technology options for a new carbon capture project. As characteristics of different capture technologies and emission point sources vary, identifying suitable technology options for a carbon capture project is a case-by-case matter determined by the operating environment, characteristics of the feed gas stream, and the desired capture performance.

### **1.3 E-Fuel project overview**

In project E-Fuel, VTT Technical Research Centre of Finland has teamed up with industrial and academic partners to plow the way for commercial production of electrofuels. The public, three-year research project is jointly funded by Business Finland, VTT, and the company partners. In E-Fuel, we examine a novel P2X/CCU value chain for production of paraffinic drop-in e-fuels from green hydrogen and sequestered CO<sub>2</sub>. High-temperature co-electrolysis (HTCE) of water and CO<sub>2</sub> using solid oxide electrolyser cells (SOEC) is examined for production of synthesis gas that is then converted to liquid hydrocarbons via Fischer-Tropsch synthesis. Additionally, an alternative route using high temperature electrolysis (HTE) followed by combined reverse water-gas shift reaction (RWGS) and catalytic partial oxidation (CPOX) is studied for synthesis gas production. Figure 1 illustrates the two routes for e-fuel production that are studied in project E-Fuel.



**Figure 1**. Two routes for electrofuel production are studied in project E-Fuel: Fischer-Tropsch synthesis preceded by (1) high-temperature co-electrolysis of water and CO<sub>2</sub>, and (2) high-temperature electrolysis followed by combined reverse water-gas shift reaction and catalytic partial oxidation.

In project E-Fuel, we are developing key technologies of the concept and evaluating technoeconomic feasibility and environmental impact of the value chain based on data collected in the project. Furthermore, we aim to validate the concept at VTT's Bioruukki piloting centre in a long-term (>1000 h) bench-scale test campaign by integrating carbon capture and green hydrogen production to a mobile synthesis unit for continuous production of paraffinic dropin fuels. Additionally, we develop readiness to scale-up the concept to industrial level upon project completion.

## **1.4 Desired CO<sub>2</sub> properties in E-Fuel**

 $CO_2$  collected via carbon capture may contain impurities that can negatively affect logistics or utilization processes. Therefore, identifying the desired  $CO_2$  properties facilitates selection of suitable  $CO_2$  supply pathways. Table 1 presents the desired properties of  $CO_2$  utilized via the E-Fuel concept.

	HTCE SOEC	RWGS/CPOX	FT, cobalt catalyst
Pressure	1 atm	Determined by FT	20–30 bar
H <sub>2</sub> O		Tolerates well	<0.4 vol-%
SO <sub>X</sub> , H <sub>2</sub> S, COS	<0.01 ppm	Determined by FT	<0.01 ppm
NO <sub>X</sub> , NH <sub>3</sub> , HCN	NH <sub>3</sub> <100 ppm	Determined by FT	<0.02 ppm
Siloxanes	<1 ppb	Determined by FT	
Halides and alkalis		Determined by FT	<0.01 ppm
O <sub>2</sub>	<0.1 vol-%	<0.1 vol-%	<0.1 vol-%

Table 1. Desired quality and properties of CO<sub>2</sub> in E-Fuel concept.

#### 1.4.1 SOEC

Effect of impurities on SOEC's used in high temperature co-electrolysis influence stack operations negatively, but due to low maturity long-term experience at industrial scale is lacking. According to various sources, especially sulphur compounds and siloxanes (organic silicon compounds) cause masking and degradation of the catalysts, but there are no exact limit values available due to variations of manufacturers and in stack chemistry. Also, the odorant in natural gas must be removed. Ammonia has a corrosive influence on interconnect plates inside the stacks, thus high concentrations of ammonia must be avoided. Presence of oxygen causes fuel electrode (cathode) nickel catalyst oxidation and reduces stack efficiency.

#### 1.4.2 RWGS/CPOX

Pressure used in RWGS/CPOX step is determined by operating pressure of the following FT reaction. For CPOX low sulfur content (<50 ppm) in feed gas is required to avoid catalyst poisoning (Vozniuk et al., 2019) that deactivates the catalyst, thus weakening conversion efficiency and H<sub>2</sub> selectivity (Bitsch-Larsen et al., 2008). Based on experience with VTT's RWGS equipment moisture is well tolerated but presence of oxygen increases temperature and thus oxygen concentration is typically adjusted to be around 0.1 vol-%. Other impurities influence catalyst degradation, affecting replacement schedule of the catalyst and therefore cost. Often gas quality requirements of RWGS are similar with the following FT synthesis.

#### 1.4.3 Fischer-Tropsch synthesis

Fischer-Tropcsh synthesis (FT) refers to a catalytic chemical reaction used to produce liquid hydrocarbons from syngas. We examine cobalt-based catalysts, which are commercially mature and have high syngas conversion efficiency and paraffin selectivity, and low water gas shift (WGS) activity. In the E-Fuel concept, FT is operated at a pressure level of 20–30 bar, which results in a desirable hydrocarbon yield regarding paraffinic drop-in fuels.

Effects of impurities on performance and lifetime of FT catalysts have been reported in several studies. The primary impurities related to catalyst poisoning are sulphur- and nitrogenbased compounds. Also, other species like alkali metals, carbon or metal carbonyls may be responsible for catalyst poisoning (Tsakoumis et al., 2010). Catalyst choice and operating conditions are important factors affecting the magnitude of impurity-related poisoning. Catalyst poisoning via sulphurous compounds is perhaps best known and it is reported that H<sub>2</sub>S adsorbs more rapidly to the surfaces and forms metal sulfides than COS and organic sulphurs. Sulphur level below 0.02 mg/m<sup>3</sup> is recommended for Co- and Fe-based catalysts to avoid poisoning (Dry, 2002). Nitrogen compounds (e.g., NOx, NH<sub>3</sub>, HCN) have also been reported to have a poisoning effect on cobalt catalysts, although appearing to be of reversible nature.

### **1.5** Objectives of this work

This work aims to identify potential  $CO_2$  supply options in Finland for the E-Fuel concept, which is a novel P2X/CCU value chain for production of paraffinic drop-in fuels from green hydrogen and sequestered  $CO_2$ . A review on common stages of CCUS is conducted to obtain a holistic understanding on technical requirements and economics of CCUS. Status, performance, and future projections of mature and emerging carbon capture technologies are reviewed to map potential technology options for carbon capture. We examine capturing  $CO_2$  from emission streams of forest industry, petroleum refineries and biorefineries, which have been recognized as potential industrial  $CO_2$  sources for CCUS in Finland. Processes of these industries are examined to identify emission point sources with high techno-economic potential for carbon capture implementation. Based on the technology and emission source reviews, we evaluate potential  $CO_2$  supply pathways for the E-Fuel concept.

## 2 TECHNICAL REQUIREMENTS AND COSTS OF CCUS STAGES

Carbon capture, utilization, and storage (CCUS) consists of several stages, which can be generally divided into source characterization, capture or separation, purification, compression or liquefaction, transportation, and utilization or storage (Pieri et al., 2018). Additionally, interim storage is essential if transportation or end-use of  $CO_2$  is done in batches as, for instance, in ship transportation. Figure 2 illustrates the common stages of CCUS and the order of these stages in the value chain.



Figure 2. The common stages of CCUS.

Stages required in CCUS are case-specific and may vary. For instance, transportation may not be required if the  $CO_2$  is utilized or stored in-situ, whereas purification required for the feed gas and/or the captured  $CO_2$  depends on characteristics of the emission point source and the carbon capture technology in use. The common CCUS stages are reviewed in more detail below with an objective to identify technical requirements and costs of each stage.

# 2.1 Source characterization

Source characterization refers to assessing properties of the emission source and operating environment to identify suitable pathways for carbon capture implementation and to evaluate economics of carbon capture for the case in question. Relevant factors regarding source stream properties, desired capture performance, and the operating environment are presented in more detail in Table 2.

Factor	Relevance	
Source stream properties		
Mass flow / scale	Affects the capture technology choice due to differences in scalability. For in- stance, liquid absorbent processes generally scale well to large-scale, whereas modular technologies like membranes may grow too capital-intensive.	
CO <sub>2</sub> concentration	The most relevant factor affecting capture technology choice and capture cost. At low CO <sub>2</sub> concentrations more selective and energy-intensive technologies are required, yielding higher capture cost compared to high CO <sub>2</sub> concentration sources.	
Present impurities	Impurities may negatively affect the capture process, e.g., via degradation of the capture substance. Purification may be needed depending on the present impurities and the capture technology in use.	
Temperature and pressure	Affects the required feed gas conditioning and the capture technology choice. Feed gas cooling may be required to avoid thermal degradation or weakening of reaction kinetics. On the other hand, some technologies benefit from high temperature and pressure, e.g., Hot Potassium Carbonate (see Chapter 3.1.2).	
Natural origin of CO <sub>2</sub>	Affects the climate impact of CCUS. Fossil-CCUS is carbon neutral at best, whereas bio-CCUS ranges from carbon neutral to carbon negative, depending on end-use application of the CO <sub>2</sub> .	
Desired capture performance		
Product CO <sub>2</sub> purity	Affects the capture technology choice and the required conditioning after capture. The desired purity is determined by logistics and the end-use application.	
Capture rate	Affects the capture technology choice and optimization of the capture process. For instance, in fossil-CCUS a high capture rate is desired as all excess $CO_2$ that is not captured increases the net amount of carbon in the atmosphere, whereas in bio-CCUS capture rate may not be as relevant as the $CO_2$ is considered carbon neutral, and focus can be placed on optimizing the capture process for the lowest capture cost possible rather than for high capture rate.	
Operating environment		
Utilizable energy supply	Affects feasibility of carbon capture implementation, the capture technology choice, and external energy needs. Many capture technologies require low-pressure steam in addition to electricity, whereas some can be operated using low-grade heat or solely electricity. Cooling demands should be also considered.	
Site restrictions	Affects the capture technology choice as the site may set restrictions for the cap- ture system, e.g., regarding equipment footprint.	
Location and readiness for CO <sub>2</sub> lo- gistics	Affects feasibility of the value chain and economics of CO <sub>2</sub> logistics. Logistics is often more favorable near harbors and industrial hubs, where ships and pipelines can be utilized for cost-efficient transport.	
Utility demands	Affects feasibility of carbon capture implementation and the capture technology choice. Utilities like feed gas or product CO <sub>2</sub> conditioning, emission control systems, or feedwater supply may be required depending on the emission source and the capture technology in use.	
Stability and flexibility of operation	Affects the capture technology choice, CO <sub>2</sub> yield, and capture performance as the number and duration of shutdowns and start-ups affect capture operation.	

Table 2. Relevant factors based on which suitable pathways for CO<sub>2</sub> capture implementation can be identified.

 $CO_2$  concentration of the feed gas is a relevant factor affecting economics of the capture process. Capture from high  $CO_2$  concentration sources is simpler and less expensive compared to low  $CO_2$  concentration sources, where energy-intensive capture technologies with high  $CO_2$  selectivity are required to reach high capture performance. Several categories for source classification by  $CO_2$  concentration have been suggested in literature (Pieri et al., 2018), generally including three to four categories for different  $CO_2$  purity levels, e.g., low <20 %, moderate 20–90%, and high >90 %. Although high  $CO_2$  concentration sources are the most appealing options regarding economics, majority of emission point sources, many of which are based on combustion processes, fall under the category of low  $CO_2$  concentration sources. Also, most of the work related to carbon capture focuses on low  $CO_2$  concentration sources.

Natural origin of the captured CO<sub>2</sub> affects how climate impact of CCUS is evaluated on a policy level. CO<sub>2</sub> of biogenic origin is part of the natural carbon cycle and therefore considered carbon neutral, whereas CO<sub>2</sub> originating from fossil sources adversely increases the net amount of carbon in the atmosphere. In CCU, the CO<sub>2</sub> is often released at the end of the product's lifecycle. Therefore, direct impact of CCU is carbon-neutral at best when utilizing biogenic CO<sub>2</sub>, whereas fossil-CCU yields net-positive carbon emissions. However, regardless of natural origin of CO<sub>2</sub>, CCU can provide indirect emission reductions by replacing unsustainable fossil-based production, e.g., by replacing conventional fossil fuels with sustainable alternative fuels produced via CCU. In CCS, the CO<sub>2</sub> is stored permanently into geological formations, preventing it from returning into the atmosphere to avoid greenhouse effect. Therefore, bio-CCS results in negative emissions as CO<sub>2</sub> is permanently removed from the natural carbon cycle. Fossil-CCS can reach carbon-neutrality at best, although it often results in net-positive emissions as all CO<sub>2</sub> emissions are not generally captured and as additional emissions may be generated in the value chain, e.g., during transportation.

Implementation of carbon capture into various industrial processes has been extensively studied in literature, based on which preliminary screening of carbon capture potential can be done to identify potential emission sources for implementation and to evaluate economics of various carbon capture pathways. In a carbon capture project, a detailed source characterization is conducted as part of the front-end engineering design (FEED) studies together with process modelling and possibly pilot/demonstration campaigns to evaluate feasibility and techno-economic performance of the concept prior to the final investment decision.

#### 2.2 Capture

Capture is the most widely studied stage of CCUS and generally the stage with highest impact on economics of the value chain. Capture refers to separating CO<sub>2</sub> from other components of the feed gas to produce a concentrated CO<sub>2</sub> stream. CO<sub>2</sub> can be captured from emission point sources or directly from the atmosphere via direct air capture (DAC). Although DAC is expected to have a significant role in climate change mitigation, point source capture is currently preferred in CCUS due to higher technological maturity and more favorable economics. In E-Fuel, we also focus on point source capture as there are several industries with potential for point source capture implementation in Finland. Figure 3 illustrates the main pathways of point source capture that are post-combustion capture, pre-combustion capture, oxy-combustion, and inherent capture.



**Figure 3.** The main pathways of point source carbon capture. Dashed line illustrates stages that are necessarily not required.

Post-combustion capture is the most common method of point source carbon capture. It refers to capturing  $CO_2$  from combustion flue gas or other similar exhaust streams typically with low  $CO_2$  concentration (<20 %) and near-atmospheric pressure. Generally, post-combustion capture technologies are end-of-pipe technologies that can be retrofitted into existing processes without major modifications on the original process.

Pre-combustion capture refers to separating  $CO_2$  prior to combustion or other utilization, e.g., by capturing  $CO_2$  from syngas produced via natural gas reforming or gasification of carbonaceous matter. Pre-combustion capture is a less studied subject than post-combustion capture as suitable applications for it are more limited.

In oxy-combustion, oxygen-enriched combustion conditions and flue gas recirculation are used to obtain flue gas with high  $CO_2$  concentration, which depending on the level of oxygen enrichment can make the capture process significantly easier or enable direct capture of  $CO_2$ . However, low maturity, weak retrofittability, and high capture costs have made oxy-combustion technologies marginal in the portfolio of carbon capture technologies.

Inherent capture refers to applications, where initial  $CO_2$  concentration of the feed gas is so high that only some gas conditioning, if any, is required to obtain  $CO_2$  applicable for utilization or storage. There are two pathways for inherent capture: (1) processes that naturally produce exhaust streams with high  $CO_2$  purity, e.g., ethanol fermentation, and (2) processes purposefully designed to produce pure  $CO_2$  for direct capture, e.g., chemical looping and oxyfuel combustion. The natural pathways of inherent capture often yield the lowest capture cost of all carbon capture pathways. However, the quantitative  $CO_2$  capture potential of such sources is low, as only few emission point sources are of such nature.

Several technologies have been developed for the different pathways of carbon capture. The technologies are based on various physical and chemical phenomena such as absorption, adsorption, membranes, electrochemical reactions, and cryogenics. Mature and emerging technology options for carbon capture are reviewed extensively in Chapter 3.

Capture is generally the most relevant stage regarding economics of CCUS. In CCS, capture costs account on average for 50–70 % of the costs deriving from capture, transport, and storage (Mazzetti et al., 2014). IEA (2019) estimates capture costs of 15–35 USD/tCO<sub>2</sub> (incl. compression) for high CO<sub>2</sub> purity streams (e.g., natural gas processing and ethanol fermentation) and 40–120 USD/tCO<sub>2</sub> (incl. compression) for dilute streams like combustion flue gases. However, capture costs are case-specific and depend on properties of the emission source, operating environment, and the capture technology in use. Especially CO<sub>2</sub> concentration of the feed gas and scale are relevant factors affecting capture cost as Figure 4 illustrates. Capture technologies suitable for fully electric operation can offer simple energy

integration, although not necessarily being the most energy- or cost-efficient option as electricity is generally more expensive than heat/steam. Technologies able to utilize low-temperature heat yield potential by allowing to cover the energy demand with waste heat.



**Figure 4.** Impact of  $CO_2$  partial pressure and scale on capture cost for a capture process using a 30 % MEA solvent. (Siemenski, 2021).

From Figure 4 by the Global CCS Institute (Siemenski, 2021) it can be observed that capture costs decrease as CO<sub>2</sub> partial pressure increases. With partial pressure of 1 kPa (~1 % CO<sub>2</sub>) the capture costs range around 170–300 USD/tCO<sub>2</sub>, falling significantly to around 70 USD/tCO<sub>2</sub> at 5 kPa. The capture cost decrease is not as radical at CO<sub>2</sub> partial pressures over 5 kPa, with the capture cost falling to 50 USD/tCO<sub>2</sub> at >20 kPa. Another observation is that for low CO<sub>2</sub> concentration sources increasing the capacity decreases the costs significantly, but with higher CO<sub>2</sub> concentrations the effect of the capacity is not as significant.

#### 2.3 Purification

After capture some impurities may occur in the product CO<sub>2</sub>. In purification, the CO<sub>2</sub> is conditioned to a desired purity regarding technical safety and health hazards. The desired

purity is determined by latter stages of the value chain, e.g., the transport method and the end-use application. Purification is not required if desired purity is achieved directly after capture. Nature and quantity of the impurities present in the product  $CO_2$  depends on properties of the emission source and the capture technology in use as Table 3 shows.

Source	Coal-fired power plant	Coal-fired power plant	Coal-fired power plant	Coal-fired power plant	Natural gas processing	Syngas pro- cessing
Technology	Amine-based absorption	Ammonia- based absorp- tion	Selexol-based absorption	Oxyfuel com- bustion	Amine-based absorption	Rectisol- based absorp- tion
CO <sub>2</sub>	99.8 %	99.8 %	98.2 %	95.3 %	95.0 %	96.7 %
N2	2000	2000	6000	2.5 %	5000	30
O <sub>2</sub>	200	200	1	1.6 %		5
Ar	100	100	500	6000		
NO <sub>x</sub>	50	50		100		
SO <sub>x</sub>	10	10		100		
CO	10	10	400	50		1000
H <sub>2</sub> S			100		200	9000
H <sub>2</sub>			1.0 %			500
CH <sub>4</sub>			1000		4.0 %	7000
$C_2+$					5000	1.5 %
NH <sub>3</sub>	1	100				
Amine	1					

**Table 3.** Typical composition of product  $CO_2$  streams obtained from various carbon capture pathways. Units in ppm if not labeled otherwise. (Modified from SINTEF, 2019).

The captured CO<sub>2</sub> generally contains moisture and some non-condensable and inert gases (e.g., N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, Ar). Also, pollutants originating from the emission source (e.g., SO<sub>x</sub>, H<sub>2</sub>S, NO<sub>x</sub>) or the capture process (e.g., absorbent traces) may be present. Generally, the purification stage consists of moisture removal (dehydration) and removal of sulfurous compounds (desulfurization) if such compounds are present. Removal on non-condensable and inert gases may also be desirable as these compounds affect CO<sub>2</sub> properties, altering the design conditions of equipment like compressors and increasing compression and transport costs.

Presence of moisture causes a risk of corrosive carbonic acid formation, hydrate formation and ice formation in low temperatures, making dehydration essential to avoid damage to fluid machinery, pipelines, and storage containers. Moisture level of 500 ppm is commonly recommended for pipeline transportation of  $CO_2$  (de Visser et al., 2008), whereas 10–50 ppm is recommended for ship transportation (al Baroudi et al., 2021). In Northern Lights, which is a trailblazer project aiming to develop full-scale CCS infrastructure in the Nordics, a maximum moisture content of 30 ppm is used as design basis to avoid presence of free water and hydrate formation in pipelines and subsea systems (Equinor, 2019). Several methods can be used for  $CO_2$  dehydration. Compression and interstage cooling with vapor-liquid separators is a common and simple method to remove bulk moisture to around 400–500 ppm, while also removing components with high solubility to water and components with higher boiling point than  $CO_2$  (Aspelund & Jordal, 2007). More effective dehydration can be achieved using liquid desiccants like triethylene glycol (TEG) or solid desiccants like molecular sieves, silica gel, or activated alumina (IEAGHG, 2014). Liquid desiccants can reach moisture levels of 30–150 ppm, whereas solid desiccants can reach levels of 0.1–10 ppm. Dehydration systems can be used in series to offload the latter, more complex and expensive systems.

Presence of sulphur oxides (SO<sub>x</sub>), hydrogen sulfide (H<sub>2</sub>S), and nitrous oxides (NO<sub>x</sub>) cause technical challenges and health hazards as these compounds are toxic and form corrosive acids in the presence of moisture. Regarding health and safety, a limit of 100 ppm is recommended for SO<sub>2</sub>, 100–200 ppm for H<sub>2</sub>S, and 100 ppm for NO<sub>x</sub> (de Visser et al., 2008; Shirley & Myles, 2019). Often majority of these impurities are removed prior to CO<sub>2</sub> capture in emission control systems of the facility. Therefore, the level of these impurities in the product CO<sub>2</sub> are often within recommended limits, as also seen in Table 3. However, especially in CCU pathways, stricter limits may be desired, e.g., due to risk of catalyst poisoning in synthesis processes. If selective removal of sulphurous compounds from CO<sub>2</sub> is required, it can be done using solvents like Rectisol and Selexol or adsorbent guard beds (IEAGHG, 2014). H<sub>2</sub>S can also be removed via selective catalytic oxidation using metal oxides (Bilsbak, 2009).

Non-condensable and inert gases (e.g., N<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, Ar) do not cause safety or health hazards at moderate levels but removal may be desirable as these compounds affect critical point and density of the CO<sub>2</sub>. These compounds alter design conditions of equipment like compressors and result in higher compression and transportation costs. Therefore, especially at large CO<sub>2</sub> volumes removal may be economically beneficial even if quality recommendations are otherwise met. Also in sensitive applications, such as the food and beverage industry or the pharmaceutical industry, removal is often required to avoid deteriorative reactions and contamination. In pipeline transportation of  $CO_2$ , a limit of <4 vol-% is recommended for all non-condensable gases (de Visser et al., 2008). Removal of non-condensable and inert gases can be done using distillation or flash evaporation (Bilsbak, 2009).

Cost of purification depends on the level of purification required, which is determined by purity of the  $CO_2$  stream after capture and the desired purity regarding logistics and end-use.  $CO_2$  conditioning costs (purification and compression) are often included to capture costs. The Global CCS Institute (Siemenski, 2021) assumes a cost range of 0–10 USD/tCO<sub>2</sub> for conditioning of CO<sub>2</sub> captured from high concentration sources, e.g., ethanol fermentation or natural gas processing.

#### 2.4 Compression and liquefaction

 $CO_2$  is often compressed or liquefied to obtain more efficient logistics. Processing the  $CO_2$  into a denser phase makes handling easier and decrease the costs of interim storage and transport. Figure 5 presents the dependency of  $CO_2$  phase on pressure and temperature. Compression and liquefaction are energy intensive processes and form a significant cost component in CCUS value chains.



Figure 5. Phase diagram of CO<sub>2</sub>. (EQUINOR, 2019)

There are three common conditions to store and transport  $CO_2$  that are (1) compressed gas, (2) compressed-to-liquid, and (3) cryogenic liquid. These conditions can be achieved with several techniques depending on factors like present impurities, flow rates, available energy utilities, and the required  $CO_2$  quality. Figure 6 presents the common pathways of  $CO_2$  conditioning.



Figure 6. The common pathways of CO<sub>2</sub> conditioning.

In gas compression the  $CO_2$  is kept in a gaseous phase and compressed into a denser state by increasing pressure. Other non-condensable gases (e.g., N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>) remain in the gas, but some water-soluble impurities may be removed alongside moisture removal. Liquefaction via compression refers to liquefying the CO<sub>2</sub> without refrigeration systems by compressing the CO<sub>2</sub> to around 70–80 bar while remaining below the critical point. Compression of CO<sub>2</sub> to liquid is typically used in small or medium scale storages where the CO<sub>2</sub> is stored at an ambient temperature. By compressing and heating the CO<sub>2</sub> above its critical point it can be processed into a supercritical fluid (also known as dense fluid). In cryogenic liquefaction the CO<sub>2</sub> is liquified using refrigeration systems and some compression. Prior to refrigeration thorough pre-removal of the impurities and moisture is required.

Multi-stage centrifugal compressors with inter-stage cooling are commonly used for  $CO_2$  compression at large volumes. Energy consumption of  $CO_2$  compression is generally around 90–120 kWh/tCO<sub>2</sub> (Aspelund & Jordal, 2007). The Global CCS Institute (Siemenski, 2021) assume that compression of  $CO_2$  to 150 bar and dehydration to 200 ppm yields costs ranging from 13 to 23 USD/tCO<sub>2</sub> for respective capacities of 5 to 0.4 MtpaCO<sub>2</sub>. Often, compression costs are included to capture costs.

Cryogenic liquefaction consists of compression, refrigeration, and purification if needed. The CO<sub>2</sub> is compressed to transport or storage pressure, commonly to 7–20 bar, and liquified at -30°C to -50°C using an external or integrated refrigeration cycle. Cryogenic technology (see Chapter 3.5) is costly and energy intensive as generation of very low temperatures and effective insulations are required. Therefore, it is mainly used for large-scale overseas transportation at long distances. Before liquefaction, moisture content is reduced below 50 ppm to avoid freeze-out in heat exchangers, and impurities (e.g., N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, Ar, CH<sub>4</sub>) are removed to avoid dry ice formation and higher liquefaction costs (Aspelund, 2010). Energy consumption of liquefaction processes are around 98–106 kWh/tCO<sub>2</sub> (Lee et al., 2012). According to Deng et al. (2019) liquefaction at 1 MtpaCO<sub>2</sub> capacity yields costs of 13–20 €/tCO<sub>2</sub>, depending on delivery pressure and CO<sub>2</sub> stream composition as illustrated in Figure 7.



**Figure 7.** Liquefaction cost ( $\ell$ /tCO<sub>2</sub>) of CO<sub>2</sub> captured from various pathways as a function of delivery pressure. (Deng et al., 2019)

From Figure 7 it can be observed that liquefaction cost ( $\notin/tCO_2$ ) is affected by CO<sub>2</sub> purity and delivery pressure after liquefaction. High purity CO<sub>2</sub> and high delivery pressure results in lower liquefaction cost. At delivery pressure of 10–30 bar the effect of CO<sub>2</sub> purity on liquefaction cost is significantly higher than at 40–70 bar. With pure CO<sub>2</sub>, the effect of delivery pressure on liquefaction cost decreases.

Chen and Morosuk (2021) evaluated four promising CO<sub>2</sub> liquefaction processes that can be used for port-to-port and port-offshore CO<sub>2</sub> ship transportation. The examined processes were three-stage vapor-compression as closed systems with propane-R290, ammonia-R717, and R134a as the working fluid, and the precooled Linde–Hampson process with R717 as an open system. Liquefaction pressure was set to 15 bar (at -30°C), which corresponds to the design of the existing CO<sub>2</sub> carriers. Liquefaction at a rate of 395 tCO<sub>2</sub>/h (equivalent to 9.5 ktCO<sub>2</sub>/d) available at 2 bar. The results showed that three-stage vapor-compression process R290 had the lowest energy consumption with CO<sub>2</sub> liquefaction cost 21.3 USD/tCO<sub>2</sub> and the cost of precooled Linde-Hampson process was 21.13 USD/tCO<sub>2</sub>. The highest cost was using vapor-compression with ammonia-R717, 23.2 USD/tCO<sub>2</sub>, mainly due to high capital costs.

SINTEF (Deng et al., 2019) studied high-capacity CO<sub>2</sub> liquefication with ammonia refrigeration cycle to estimate the feasible CO<sub>2</sub> conditions in ship transport. Liquefaction was studied for a pure CO<sub>2</sub> stream and three CO<sub>2</sub> streams with impurities at a rate of 37.31 kg/s (equivalent to 1 MtCO<sub>2</sub>/a) available at 1 bar and 40 °C. To identify the impact of CO<sub>2</sub> delivery pressure, technical-economic performance of the liquefaction processes was assessed for different delivery pressures post-CO<sub>2</sub> liquefaction (7, 10, 15, 20, 25, 30, 40, 50, 60, 70 bar). Three cases with different types and levels of impurities were also studied: (1) Amine-based post-combustion CO<sub>2</sub> capture from a cement plant (H<sub>2</sub>O 3 %, N<sub>2</sub> 0.11 %, O<sub>2</sub> 0.03 and Ar 0.0003), (2) Membrane-based post-combustion CO<sub>2</sub> capture from a refinery (H<sub>2</sub>O 1 %, N2 2 %), and (3) Rectisol-based pre-combustion CO<sub>2</sub> capture from a coal power plant (N<sub>2</sub> 0.44 %, Ar 0.09, MeOH 0.57 %, H<sub>2</sub> 0.45 %, CO 0.03 %, and H<sub>2</sub>S 0.0005 %). The results showed the liquefication cost of pure CO<sub>2</sub> is between 13.4 and 15.2 €/tCO<sub>2</sub>, depending on the pressure, while a minimum lies around 40–50 bar and maximum on 7 bar. The pure  $CO_2$  case evaluation demonstrated that at 15 bar a liquefaction cost is almost 7% lower than at 7 bar. The results also showed that the membrane-based case costs were the most affected (+3-34)%), followed by the Rectisol-based case (+0-14 %), and finally the amine-based case (+2-14 %)11 %). In was mentioned that differences between cases underline the fact that both the type and level of impurities have a significant impact on the liquefication costs. Results showed that water impurity had less impact on the liquefaction process cost as it is condensed during the compression train and dried before the refrigeration cycle. Impurities of N<sub>2</sub> and Ar were more difficult to separate and those increased the energy consumption in refrigeration cycle.

#### **2.5** Interim storage

Captured CO<sub>2</sub> may require interim storage before transportation, utilization, or geological storage. Common methods for interim storage of CO<sub>2</sub> are (1) compressed gas, (2) liquefaction via compression at >0 °C above the critical pressure of 73.8 bar, and (3) cryogenic liquefaction below 0 °C with low pressure. The suitable method of interim storage is chosen based on required storage capacity, transport method, and delivery pressure required in further stages. Generally, the most common method of interim storage is liquefaction via compression. If CO<sub>2</sub> is transported in large transportation capacities e.g., in ships, cryogenic liquefaction may be used already in the interim storing. With cryogenic liquid small amounts

of boil-off gases occur, which are typically cooled and liquefied back to liquid. In some cases, the cryogenic cooling uses CO<sub>2</sub> also as a refrigerant.

#### 2.6 Transportation

Transportation is often needed to deliver the  $CO_2$  to a suitable location of storage or utilization. Pipelines and ships are the primary options for large-scale transportation of  $CO_2$ , whereas road and railway transport are viable options for distribution at lower volumes. If carbon capture capacity will increase significantly, it is likely that the  $CO_2$  transportation infrastructure will come to consist of hubs located in key areas where  $CO_2$  captured from various sites is collected before being transported to storage or utilization sites.

#### 2.6.1 Pipeline transportation

 $CO_2$  is transported in pipelines as a supercritical fluid at pressure around 80–150 bar. Pipeline transportation of  $CO_2$  is a mature technology with majority of the operational pipeline networks located in the US. The Global CCS Institute (Siemenski, 2021) estimates transport costs of 3–25 USD/tCO<sub>2</sub> for onshore pipelines, with the lowest cost estimated for 20 Mtpa capacity and 180 km distance and the highest cost estimated for 1 Mtpa and 300 km. Regarding economics, pipeline transportation benefits from large scale operation, i.e., large mass flows transported, as Figure 8 illustrates.



**Figure 8.** Cost of onshore pipeline transportation (USD/tCO<sub>2</sub>) per a 100-mile distance as a function of  $CO_2$  mass flow rate (Mtpa). (E. Smith et al., 2021)

From Figure 8 it can be observed that pipeline transport cost decreases as  $CO_2$  flow rate increases. This is because pipelines are highly capital-intensive with CAPEX generally consisting of over 90 % of the pipeline costs (Global CCS Institute, 2011). Highest relative cost differences occur at low flow rates; between capacities of 1 Mtpa to 5 Mtpa the mean cost drops from  $7/tCO_2$  to around  $2.5/tCO_2$ .

#### 2.6.2 Ship transportation

In ship transportation CO<sub>2</sub> is transported at a liquid phase at pressure around 7–20 bar and temperature ranging from -50°C to -20°C. The working group of ZEP and CCSA (2022) report two primary conditions that are economically relevant to liquid CO<sub>2</sub> transport; a) "medium" pressure operated at conditions of 15–18 bar and -30°C and, b) "low" pressure operated at 5.5–7 bar and -50°C. So far CO<sub>2</sub> shipping has been done at small-scale with capacities up to 1000 m<sup>3</sup>, but infrastructure for large-scale ship transportation is currently being developed, e.g., in the Northern Lights project. Ship transportation of CO<sub>2</sub> has similarities to liquified petroleum gas shipping, which is well-established and mature technology. The International Organisation for Standardization has convened a working group ISO/TC265/WG7 on the transport of CO<sub>2</sub> by ship in order to better understand the technical requirements for a future CO<sub>2</sub> shipping standard.

Costs of ship transport depends on transport capacity and distance, ranging commonly around  $10-17 \notin/tCO_2$  (Olsson et al., 2020). As shipping is not as capital-intensive compared to pipeline transportation, transport distance has lower effect on ship transport cost as Figure 9 also shows.



**Figure 9.** Cost of ship and pipeline transport ( $\notin$ /tCO<sub>2</sub>) at various capacities (5/10/20 Mt) as a function of transport distance (km). The vertical dashed line represents the distance from which onwards ship transport cost is lower than pipeline transport cost. (Olsson et al., 2020)

From Figure 9 it can be observed that regarding cost, pipeline transportation is more feasible at lower distances and higher capacities, whereas ship transportation prospers at long transport distances with capacity having less effect on transport cost.

#### 2.6.3 Road and railway transportation

Transporting  $CO_2$  via road or railway can be used for  $CO_2$  distribution at low transport volumes and short distances with the  $CO_2$  being liquified and transported in tankers. Due to weak scalability, it is unlikely for road and railway transportation to have a major role in  $CO_2$  infrastructures at large-scale, but it may be essential before CCUS logistics has matured, e.g., in demonstration projects. The low transport capacities of road and railway tankers yield significantly higher transport cost compared to pipelines and shipping. According to the National Petroleum Council (2019) truck and rail transport yields three to ten times higher costs than pipeline transportation due to lacking economies of scale.

## 2.7 Utilization and storage

The final stage and the primary objective of CCUS is either utilization or storage of  $CO_2$ . Utilization refers to using the  $CO_2$  as feedstock to create benefit or value, whereas storage refers to permanently storing the  $CO_2$  into geological formations to avoid its adverse greenhouse effect in the atmosphere. The end-use application of the  $CO_2$  determines the desired properties regarding quantity and quality of the  $CO_2$ .

In utilization, the captured  $CO_2$  is used to create value directly or indirectly. Direct utilization refers to using the  $CO_2$  as it is as a component of a process, e.g., in beverage carbonation or greenhouse enrichment. Indirect utilization refers to using the  $CO_2$  as feedstock in processing or refining to create value-added products like fuels, chemicals, or materials. CCU-based products could be used to replace conventional products based on fossil sources. Figure 10 illustrates the various pathways of CCU.



Figure 10. Pathways for CO<sub>2</sub> utilization. (NETL cited in Smart Specialisation Platform, 2022)

 $CO_2$  utilization has economic appeal as value of the final product may enable benefitting from carbon capture even without incentives, which has been a major obstacle for introduction of carbon capture to commercial level. In most CCU pathways, the  $CO_2$  is released at the end of the product's lifecycle and thus CCU value chains do not directly provide emission reducing effects. However, CCU can indirectly provide positive climate impact if used to replace production based on fossil sources as many CCU products yield lower life cycle emissions than their fossil-based counterparts (IEAGHG, 2021).

CO<sub>2</sub> storage refers to permanently storing the captured CO<sub>2</sub> into geological formations, preventing it from being released into the atmosphere. Depending on natural origin of the CO<sub>2</sub> (i.e., biogenic or fossil), storage can be used to reduce the harmful fossil-based emissions or to produce negative emissions by removing biogenic carbon from its natural cycle. CO<sub>2</sub> can be stored into porous geological formations such as depleted oil and gas fields, saline aquifers, unmineable coal seams, and basalt formations. The CO<sub>2</sub> is injected underground through a well as a supercritical fluid, filling the pores of the reservoir and ultimately becoming trapped and sealed by a cap rock. To ensure storage permanence and safety, the reservoirs are monitored over the project lifecycles and at least 20 years after injection operations have been seized. The National Petroleum Council (2019) reports the costs of injection and geological storage to be around 1–18 USD/tCO<sub>2</sub> with the lowest cost estimated for onshore storage reservoirs and the highest for offshore reservoirs. For CO<sub>2</sub> monitoring and verification, Global CCS Institute (Siemenski, 2021) estimate a cost of 2–4 USD/tCO<sub>2</sub>.

# 2.8 Summary and cost breakdown of CCUS stages

Objectives, methods, and indicative costs of CCUS stages are summarized in Table 4. The data is collected from multiple sources that are presented in chapters above. All costs originally reported in USD are converted to EUR using a conversion rate of 1.1 USD/EUR.

Stage	Objective	Method	Indicative cost, €/tCO <sub>2</sub> *
Source	Characterization of the emission	Evaluating properties of the emis-	
characterization	source and operating conditions to	sion stream, operating environ-	
	evaluate feasibility and techno-	ment, and desired capture perfor-	
	economic performance of carbon	mance	
	capture		
Capture	Separating CO <sub>2</sub> from other gas	Various technology choices e.g.,	Dilute streams: 36–110 €/tCO <sub>2</sub>
	components to be collected as a	absorption, adsorption, mem-	(incl. compression)
	concentrated stream	branes, cryogenic separation, elec-	
		trochemical separation	Inherent: 14–32 €/tCO <sub>2</sub>
			(incl. compression)
Purification	Improving quality of CO2 to de-	Dehydration via compression and	0–9 €/tCO <sub>2</sub>
	sired level determined by latter	inter-cooling with vapor-liqud	
	stages of the value chain	separators or by using liquid and	
		solid desiccants	
		Desulphurization via solvents	
		(e.g., Rectisol, Selexol) or adsor-	
		bents (e.g., activated carbon)	
		Pamoval of non-condensables and	
		inerta (a a N H O Ar) via dia	
		tillation on flashing	
<u></u>	T C C C C C C C C C C C C C C C C C C C		12.21.0//00 (150.1)
Compression	Increasing pressure of the gas to	Centrifugal compressors with in-	$12-21 \notin (100 \text{ bar})$
	achieve more dense and logisti-	ter-stage cooling	
<b>X 1 1</b>	cally efficient form		12.20.01/00./110/
Liquefaction	Converting gaseous $CO_2$ into a	Compression and retrigeration	13–20 €/tCO <sub>2</sub> (1 MtpaCO <sub>2</sub> )
	liquid phase	with an external or integrated re-	
		frigerant cycle	
<b>.</b>		(7-20  bar, -50  to  -20  °C)	
Interim storage	Storage of $CO_2$ for a finite period	Compressed gas, liquefied com-	
	prior to transportation, utilization,	pressed gas at >0 °C, or cryogenic	
	or storage	liquefied at <0 °C	a aa ay aa
Transportation	Transporting $CO_2$ to a location of	Pipeline	3–23 €/tCO <sub>2</sub>
	interim storage, utilization, or geo-		
	logical storage	Shipping	10–17 €/tCO <sub>2</sub>
		Road- and railway (small-scale)	3–10x vs. pipeline transport
Utilization	Utilizing CO <sub>2</sub> in processes or as	Direct (e.g., greenhouse fertiliza-	Case-specific production cost and
	feedstock for products to generate	tion, food and beverage carbona-	income
	value	tion) or indirect (e.g., fuels, chem-	
		ical and materials)	
Storage	Storing CO <sub>2</sub> into geological for-	Injection into depleted oil and gas	Injection and geological storage.
Storage	mations, preventing it from return-	fields saline aquifers salt caverns	1–16 €/tCO2
	ing to the atmosphere	including monitoring	Monitoring and verification:
	ing to the atmosphere	mendung monitoring	$2-4 \notin t \cap \Omega_2$

Table 4. Summary of the common stages of CCUS (carbon capture, utilization, and storage).

\*All costs originally reported in USD are converted to EUR with an assumed currency conversion rate of 1 EUR = 1.1 USD.



Indicative costs of common CCUS stages are presented in Figure 11. It is noteworthy that all stages are not always necessary, whereas some stages are mutually exclusive.

**Figure 11.** Indicative cost of CCUS stages based on estimates collected from literature. The colored bar illustrates the average cost, whereas the error bar presents the range of minimum and maximum cost.

As Figure 11 shows, costs of CCUS derives from several stages. Capture is often the most impactful stage on cost unless possibilities for capture from high CO<sub>2</sub> purity sources are available. Required purification depends on purity of the product CO<sub>2</sub> after capture and desired quality determined by latter stages but generally purification cost is only a fraction compared to capture cost. CO<sub>2</sub> conditioning via compression or liquefaction is energy-intensive, also deriving a major cost component. Cost of transport, which at large scale is primarily done by pipelines or ships, depends on transport capacity and distance. Road and railway transport is expensive and lacks economies of scale, making it unappealing at large scale. Cost and income deriving from CO<sub>2</sub> utilization is dependent on the application and is

difficult to estimate at a general level. Cost of geological storage of  $CO_2$  depends on factors like volume and quality of the stored  $CO_2$  and properties of the storage site, e.g., onshore vs. offshore, existing infrastructure, and knowledge on site characteristics.

Indicative costs collected from literature can be used to roughly estimate the total cost of various types of value chains. Based on estimates collected from literature, a CCS value chain consisting of post-combustion capture, purification, liquefaction, ship transport and geological storage would yield a total cost of  $50-154 \notin/tCO_2$ , averaging around  $102 \notin/tCO_2$ . If supercritical compression and pipeline transport is used instead of liquefaction and shipping, the value chain yields a total cost of  $42-161 \notin/tCO_2$ , averaging around  $101 \notin/tCO_2$ . Table 5 shows how the costs are distributed between different stages.

Value chain	CCS, ship transport	CCS, pipeline transport
Total cost	50–154 €/tCO <sub>2</sub>	42–161 €/tCO <sub>2</sub>
Capture (post-combustion, excl. compression)	49–57 %	55–59 %
Purification	0-6 %	0-6 %
Liquefaction	13–26 %	-
Compression (supercritical)	-	13–28 %
Transport	11-20 %	7–14 %
Storage	5-13%	7–12 %

 Table 5. Distribution of CCS cost between different stages based on estimates collected from literature.

Based on estimates collected from literature, on average, cost of CCS and cost distribution of the stages are similar whether supercritical compression and pipeline transport or liquefaction and shipping is used.

#### **3 REVIEW ON CARBON CAPTURE TECHNOLOGIES**

There are several types of technologies available and in development for carbon capture as Figure 12 shows. In this chapter, we review the most mature and promising technologies, focusing on status, techno-economic performance, and future perspectives. We focus primarily on post-combustion capture that generally offers a straightforward and retrofittable option for point source capture at industrial applications, with emphasis on technologies that have reached pilot-scale or higher (TRL  $\geq$  6) and have ongoing development. The objective is to map potential technology options for point source capture.



Figure 12. Common methods and techniques for carbon capture (Madejski et al., 2022).

In carbon capture various chemical and physical phenomena can be utilized, e.g., absorption, adsorption, membranes, electrochemical reactions, and cryogenics. Technologies based on these phenomena can often be divided into more precise subcategories, which in turn may contain several types of technology configurations. We review the following technologies in more detail: absorption via liquid solvents, adsorption using solid sorbents, membrane separation, electrochemical separation, cryogenic separation, and inherent capture.
# 3.1 Liquid solvents

Solvent-based capture is the most common technology for carbon capture. Liquid solvents are  $CO_2$ -absorbing chemical mixtures that are used in a cyclic capture process consisting of two primary stages that are absorption and desorption. In absorption, the  $CO_2$ -rich target gas stream is mixed into the solvent typically using packed bed columns (Wilcox, 2012). The solvent then absorbs the  $CO_2$  via physical and/or chemical absorption. In desorption, the  $CO_2$  is released from the solvent, which is regenerated commonly via heating or flash evaporation. After regeneration, the  $CO_2$ -lean solvent is cycled back to absorption.

Several types of solvents have been developed for carbon capture, e.g., amines, carbonate salts, physical solvents, phase-changing solvents, water-lean solvents, and ionic liquids. Generally, capture solvents are aqueous meaning that a CO<sub>2</sub>-binding absorbent is dissolved to water. A significant challenge of solvent-based capture is the high energy demand deriving from solvent regeneration, which often requires heating large volumes of liquid. Energy consumption is the most significant cost factor, accounting for 60–75 % of the capture cost (Roussanaly et al., 2018). Aiming to reduce regeneration energy demand, alternative solvents such as water-lean and phase-separating solvents have been developed. Water-lean solvents use non-aqueous liquid mediums with lower specific heat capacities than water, whereas phase-separating solvents form CO<sub>2</sub>-rich and CO<sub>2</sub>-lean solvent phases that can be separated. However, maturity of these alternative solvents is still low compared to aqueous solvents are reviewed in more detail below.

#### 3.1.1 Amines

Amines are the most mature absorbents in solvent-based capture, having been used in industrial gas purification applications for decades. Amines are derivatives of ammonia (NH<sub>3</sub>) with one or more of the hydrogen atoms substituted by an organic group. Depending on the number of substitutions, amines can be categorized into primary ( $R_1NH_2$ ), secondary ( $R_1R_2NH$ ), and tertiary amines ( $R_1R_2R_3N$ ). Primary amines like monoethanolamine (MEA) have one carbon bonded to the nitrogen, secondary amines like diethanolamine (DEA) have two, and tertiary amines like methyldiethanolamine (MDEA) have three. Cyclic amines (e.g., piperazine PZ) refer to secondary and tertiary amines connected to a form of a ring. Sterically hindered amines (e.g., 2-amino-2-methyl-1-propanol AMP) refer to primary amines with the amino group attached to a tertiary carbon atom and secondary amines with the amino group attached to secondary or tertiary carbon atom (Sartorl & Savage, 1983). Primary and secondary amines react with CO<sub>2</sub> forming carbamates, while tertiary and sterically hindered amines form bicarbonates. Carbamate formation is rapid with high heat of absorption, whereas bicarbonate formation results in higher CO<sub>2</sub> loading and lower heat of absorption but with slower kinetics (P.-C. Chen et al., 2021; Rochelle, 2016). Sterically hindered amines benefit from moderately fast absorption kinetics while maintaining high CO<sub>2</sub> loading and low heat of absorption (DOE & NETL, 2015).

Generally, amines possess many favorable qualities for carbon capture such as high  $CO_2$  absorption capacity, rapid transfer kinetics, good reversibility, and high product  $CO_2$  purities. Amines can reach high capture efficiencies even with gases of low  $CO_2$  partial pressure, making them favorable for post-combustion capture. Despite high maturity and favorable qualities, amines face drawbacks such as energy-intensive regeneration, volatility, toxicity, and corrosivity. Many of these challenges have been improved with advanced solvents and process configurations but remain relevant in development of amine-based capture.

Variety of amines and amine-blends have been developed for carbon capture and there are several commercially available amine-based technologies, e.g., by Mitsubishi Heavy Industries, Shell, Fluor, BASF, and Aker Carbon Capture. An aqueous blend of 30 wt. % monoethanolamine (MEA) has been long considered as the benchmark technology of carbon capture due to high maturity and performance. An advanced amine blend of piperazine (PZ) and amino-2-methyl-1-propanol (AMP) – referred to as CESAR1 – has been suggested as the new benchmark technology due to having outperformed MEA in recent studies (IEAGHG, 2019). PZ is a cyclic diamine with rapid transfer kinetics, whereas AMP is a sterically hindered amine with high CO<sub>2</sub> loading and low heat of absorption. Commercial solvents like Shell's Cansolv, MHI's KS-1 and KS-21, and Fluor's Econamine FG+ are also promising. However, these solvents are difficult to evaluate in similar manner as MEA and CESAR1 as composition of these proprietary solvents is not reported in detail.

Amine-based solvents are typically regenerated at 100–150 °C using low-pressure steam. Conventional solvents based on primary and secondary amines suffer from energy-intensive thermal regeneration due to high absorption heat of carbamate formation. However, significant reductions in regeneration energy demands have been achieved with advanced solvents like sterically hindered amines or conventional amines promoted with additives. For the conventional aqueous 30 wt.-% MEA blend reboiler heat duties around 3.6–4.0 GJ/tCO<sub>2</sub> have been reported (Bui et al., 2018), whereas advanced solvents like Shell's Cansolv and MHI's KS-1 and KS-21 have reached reboiler duties around 2.3–2.6 GJ/tCO<sub>2</sub> (IEAGHG, 2019; Singh & Stéphenne, 2014).

Amines are prone to degradation, which leads to solvent losses and toxic degradation products such as ammonia, nitramines, and nitrosamines (Buvik et al., 2021). Degradation has been identified to be caused by heat and presence of  $CO_2$ ,  $O_2$ ,  $SO_x$  and  $NO_x$  (Vega et al., 2014). Thermal degradation occurs mainly in the stripper due to combination of high temperature (>100 °C) and high partial pressure of  $CO_2$ . Purification of  $SO_x$  and  $NO_x$  is required prior to capture to avoid degradation caused by these impurities. To mitigate the toxic solvent-based and degradation-based emissions, emission control systems such as water or acid washing may be required (Monteiro et al., 2020). Flue gas cooling to around 40 °C prior to capture is common as higher  $CO_2$  loadings are achieved in lower absorber temperatures (Kvamsdal et al., 2011).

Performance of 30 wt. % MEA and CESAR1 (~26.74 wt. % AMP, ~12.92 wt. % PZ) were evaluated in the ALIGN CCUS project (Moser et al., 2020, 2021). Two long-term postcombustion capture pilot campaigns with a ~13,000 h runtime and 7.2 tpd capture capacity were conducted using both solvents at a lignite-fired power plant in Niederraussem, Germany. A minimum specific heat demand of 2.97 GJ/tCO<sub>2</sub> was reported for CESAR1 and 3.45 GJ/tCO<sub>2</sub> for MEA. Degradation of CESAR1 showed a slowly progressing linear nature, whereas degradation of MEA shifted from linear to exponential after 220 days of operation. Solvent consumption of 0.45 kg/tCO<sub>2</sub> was identified before the exponential degradation phase occurred. Using an emission mitigation system referred to as the dry bed configuration, following emissions were reported in the CO<sub>2</sub>-lean flue gas with a CESAR1 solvent: 15–20 mg/Nm<sup>3</sup> AMP, 3–7 mg/Nm<sup>3</sup> PZ, and <3 mg/Nm<sup>3</sup> NH<sub>3</sub>. With MEA, emissions of <3 mg/m<sup>3</sup> MEA and 20–40 mg/m<sup>3</sup> NH<sub>3</sub> were reported. Economic performance of the two solvents were evaluated via process modelling based on the pilot test results (Garcia et al., 2021). With a 90 % capture rate in the lignite-fired reference plant, capture cost of 31.5  $\in$ /tCO<sub>2</sub> was calculated for MEA and 32.2  $\notin$ /tCO<sub>2</sub> for CESAR1. Garcia et al. (2021) suggest that CESAR1 should not be promoted to benchmark technology as there seems to be no clear performance advantage over MEA. They state that both are viable solvents and that the solvent choice is a case-by-case matter. Solvent cost of CESAR1 is significantly higher compared to MEA (8100  $\notin$ /t vs. 2100  $\notin$ /t), but due to lower specific energy demand CESAR1 may be a favorable option when the heat costs are high or if heat availability is limited.

#### 3.1.2 Carbonate salts

Carbonate salts such as potassium and sodium carbonate ( $K_2CO_3$ ,  $Na_2CO_3$ ) are promising, eco-friendly absorbents for carbon capture. Alkaline solutions based on carbonate salts have been widely used in industrial gas purification applications to remove acidic gases like  $CO_2$ and  $H_2S$ . Carbonates react with  $CO_2$  via chemical absorption by forming bicarbonate salts. Advantages of carbonates over amines are low toxicity and corrosivity, common and inexpensive absorbent materials, high degradation resistance and low regeneration energy demands (K. H. Smith et al., 2016).

Potassium carbonate is the most widely studied carbonate salt in carbon capture. It can withstand high temperatures, enabling absorption at elevated temperatures. This is beneficial regarding energy efficiency as the process does not require radical temperature changes between absorption and desorption. Also, flue gas cooling demand is lower or not necessarily required at all. Bicarbonates can be regenerated under a vacuum at around 60–80 °C, allowing the regeneration heat demand to be supplied using low-grade heat (e.g., waste heat) instead of steam. SO<sub>x</sub> and NO<sub>x</sub> treatment is not critical prior to capture as carbonates react with these impurities by forming heat stable salts that could be recovered via a purge stream, although the presence of these impurities increases absorbent consumption. Carbonates do not react with oxygen nor does oxidative degradation occur. A major disadvantage of carbonate salts is weak transfer kinetics, which is why higher solvent flow rates and larger equipment may be required to reach equivalent capture performance as with amines. However, absorption kinetics can be improved with promoters and catalysts. Another challenge is presented by precipitation of bicarbonates, which have lower solubility to water than carbonates. With too high absorbent concentrations unwanted precipitation may occur, causing a risk of clogging. Technologies that utilize precipitation or crystallization to separate the CO<sub>2</sub>-rich and CO<sub>2</sub>-lean phases of the solvent have also been developed. This however requires more complex equipment to handle the solid masses. Capture technologies using carbonate salts as CO<sub>2</sub> absorbents have been developed, e.g., by CO<sub>2</sub> Capsol, Saipem, KC8 Capture Technologies, Kleener Power Solutions, VTT, Baker Hughes, and Honeywell.

Capsol EoP (end-of-pipe) by CO<sub>2</sub> Capsol is a based on the hot potassium carbonate (HPC) process, which is a derivative technology of the Benfield process used to remove acidic gas components from industrial gases. The technology is currently at TRL 8 in post-combustion capture and TRL 9 in syngas applications i.e., pre-combustion capture. Figure 13 presents a schematic flow diagram of the process. The feed gas is pressurized to 8–20 bar with absorption taking place at an elevated temperature of 110–120 °C using an aqueous potassium carbonate solvent (Hamrin, 2016). Elevated pressure and temperature improve bicarbonate solubility, allowing to use high absorbent concentrations, thus improving capture efficiency. After absorption, the solvent is led to a desorber via an expander or control valve at 1–3 bar and regenerated using a reboiler that can be heated with steam, electricity, or both. CO<sub>2</sub> Capsol has improved energy efficiency of the HPC process by using steam recycling in the desorber.



Figure 13. A schematic flow diagram of the Capsol EoP process. (HZ Inova, 2022)

Energy consumption of the Capsol EoP process is estimated around 0.7–1.5 GJ/tCO<sub>2</sub>, depending on flue gas properties. Capture cost is estimated to be 30–37 USD/tCO<sub>2</sub> with a capture rate of 90–95 % (CO2 Capsol, 2022). The hot potassium carbonate technology has been successfully piloted in post-combustion capture at Stockholm Exergi's Värtaverket CHP plant (Beccs Stockholm, n.d.; Bryngelsson & Westermark, 2009). European Union granted funding to a project aiming to scale-up the process to full scale at the 375 MW Värtaverket bio-CHP plant.

CO<sub>2</sub> Solutions by Saipem is a technology where the weak absorption kinetics of potassium carbonate has been enhanced with a natural enzyme catalyst. The aqueous potassium carbonate solvent is catalyzed with a proprietary carbonic anhydrase enzyme named 1T1. The solvent can be regenerated at ~85 °C, allowing to use low-grade heat like waste heat in regeneration (Surprenant, 2019). Thermal energy demand is estimated at 2.4 GJ/tCO<sub>2</sub>. Capture cost is estimated to be 28 \$/tCO<sub>2</sub>, although with an assumption that the waste heat used in regeneration does not yield any costs (Fradette et al., 2017). The technology has been successfully piloted at several industrial sites. Currently, a commercial project capturing 30 tpd from Resolute's kraft pulp mill in Quebec is in operation. The technology is also demonstrated at TRL 7 with 2 tpd capture capacity at Store Enso's pulp mill in Sweden and a cement kiln in Poland as part of the EU-funded ACCSESS project (CORDIS, 2021).

UNO MK 3 by KC8 Capture Technologies is an absorption technology based on a catalytically enhanced potassium carbonate solvent (KC8, 2022). Unlike in conventional solventbased capture processes, the potassium bicarbonate formed in CO<sub>2</sub> absorption is allowed to precipitate, enabling to separate the CO<sub>2</sub>-rich phase from the solvent. This allows using higher solvent concentrations, greater CO<sub>2</sub> loadings and lower circulation rates, reducing energy requirement of the process. Regeneration energy requirement of the process is estimated at 2–2.5 GJ/tCO<sub>2</sub>. According to the company, the retrofittable UNO MK 3 process can achieve capture rates of >95 % in industrial pre- and post-combustion applications. The process has been piloted at the brown coal fired Hazelwood Power Station in Australia (K. H. Smith et al., 2017). KC8 has partnered with Cement Australia in project PACER, which includes installing a demonstration plant to a cement facility in Gladstone during 2023 (AFR, 2022).

Chilled Ammonia Process (CAP) is an ammonia-based capture process developed by Alstom that is currently owned and marketed by Baker Hughes. CAP has been previously studied as a precipitating process, but current development focuses on non-precipitating operation. The aqueous ammonium solvent consists of ammonium carbamate, ammonium bicarbonate, ammonium carbonate and some free ammonia. Steam is typically used as an energy supply for the high-pressure regeneration, but also other high-temperature heat sources or electrical heating can be used. The process produces high purity CO<sub>2</sub> (>99.5 %) at an elevated pressure of 14-25 bar, thus reducing downstream compression demands. Advantages of CAP are low oxidative, thermal, and impurity-related degradation and the use of low-cost, non-proprietary absorbent that is a global commodity. Challenges include controlling the hazardous ammonia-based emissions that are reduced by chilling the solvent. CAP has been validated with a design capacity of up to 100 ktpaCO<sub>2</sub>, reaching currently a TRL of 7. Demonstration at TCM with refinery cracker off-gas  $(13-15 \% \text{ CO}_2)$  resulted on a specific thermal energy consumption of 2.6 GJ/tCO<sub>2</sub> and ammonia emissions of <10 ppm (Augustsson et al., 2017). A specific heat energy consumption of 2.2 GJ/tCO<sub>2</sub> was determined when cooling water at adequate temperatures is available.

VTT has developed an enhanced soda scrubbing process combining a novel absorber configuration and low-temperature regeneration. An eco-friendly solution of aqueous sodium carbonate is used to capture CO<sub>2</sub> via chemical absorption. Instead of using a conventional absorber column, an ejector-like micro-bubble generator has been developed to create a large contact are for the solvent and feed gas. The micro-bubble generator can also reduce equipment size and capital cost. Absorption takes place at 1.2–1.7 bar and 30–40 °C. The solvent is regenerated under a 0.2–0.5 bar vacuum at a temperature of 60–80 °C, allowing to use low-grade heat as a regeneration heat supply. The process has been successfully tested at bench/small pilot scale (TRL 5) in post-combustion capture at realistic conditions (Linjala, 2021). Kleener Power Solutions has developed a proprietary alkaline capture solvent called the Kleener-liquid, which is manufactured from power plant ashes. The solvent has been operated using VTT's enhanced scrubbing process that has been licensed to Kleener Power Solutions. The solvent has high thermal stability, allowing to operate absorption at an elevated temperature around 50–65 °C. Regeneration is done at 0.2–0.5 bar and 60–80 °C. Regeneration heat can be supplied using low-grade heat like waste heat. As absorption and desorption can be operated at similar temperature levels, an energy efficient capture cycle with minimal heating and cooling demands can be achieved. The company has estimated energy consumption of the process at 2.6 GJ/tCO<sub>2</sub> and capture cost at 29  $\notin$ /tCO<sub>2</sub> (Kleener, 2021). Kleenerliquid scrubbing has been successfully tested in post-combustion capture at bench scale (Linjala, 2021). A 2 ktpd pilot system is currently under construction.

#### **3.1.3** Phase-separating solvents

Phase-separating (aka phase-changing or precipitating solvents) go through a phase change upon CO<sub>2</sub> absorption or change in process conditions. Depending on the solvent, the CO<sub>2</sub>-rich phase may precipitate to a solid or form a separate liquid phase, which can be separated from the CO<sub>2</sub>-lean solvent, thus reducing regenerated solvent volume and regeneration energy demand compared to conventional solvent processes. Challenges of phase-separating processes include adequate gas and solvent contact and process design regarding solid or slurry handling. Carbonate salts (e.g., K<sub>2</sub>CO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>), amino acids, tertiary amines, and ammonia can be used as CO<sub>2</sub> absorbents in phase-changing solvents.

DMX is phase-separating capture process developed by IFPEN and marketed by Axens. The process uses an aqueous solution of two organic compounds that separate under certain conditions of temperature and CO<sub>2</sub> partial pressure. After absorption the phases are separated, and the CO<sub>2</sub>-rich phase is led to regeneration. The DMX solvent has high stability, and it can be regenerated at higher temperature than amines such as MEA. Desorption can be done at an elevated pressure, producing CO<sub>2</sub> up to 7 bar, which can reduce downstream compression cost. The solvent is mentioned to be less corrosive than MEA, allowing to use carbon steel as the principal material, which reduces capital cost. A capture rate of >95 %, product CO<sub>2</sub> purity of >99 %, and steam energy consumption of 2.3–2.9 GJ/tCO<sub>2</sub> depending on application and capture rate have been reported for the DMX process (Kearns, 2022). Capture

cost is estimated at 30–40 €/tCO<sub>2</sub> (ArcelorMittal, n.d.). The process is demonstrated at TRL 7 at ArcelorMittal's steel plant in Dunkirk as part of the EU-funded 3D project (3D, 2023).

#### **3.1.1** Physical solvents

Physical solvents can be used capture  $CO_2$  via physical absorption, where the  $CO_2$  dissolves into the solvent without chemical reactions. To achieve high capture capacity, physical absorption requires high partial pressure of  $CO_2$ . Therefore, physical solvents are mainly suitable for pre-combustion capture applications (e.g., natural gas and syngas processing) where higher  $CO_2$  concentrations occur compared to post-combustion. Solubility of  $CO_2$  into the solvent is mostly affected by partial pressure of  $CO_2$  and temperature. As Henry's law states, higher partial pressure of the solute results in greater amount of dissolved gas. Also, solubility of  $CO_2$  increases as temperature decreases. In absorption, temperature is typically kept at room temperature or less and pressure is raised to improve  $CO_2$  solubility. Desorption is typically done with pressure reduction and/or temperature increase. There are several commercially available physical solvents for  $CO_2$  removal/capture that are used in refineries, natural gas upgrading, syngas processing and fertilizer production. Common physical solvents include Selexol (a mixture of dimethyl ethers of polyethylene glycols), Rectisol (methanol), Fluor (propylene carbonate) and Purisol (N-methyl-2-pyrrolidone).

CarbonReUse Finland has developed an enhanced water scrubbing process that uses plain water as a physical solvent in post-combustion capture. Water scrubbing is a mature technology for CO<sub>2</sub> removal from biogas, but a novel concept in carbon capture. In Carbon-ReUse's process the solvent water is cooled down to 5 °C and the feed gas is pressurized to 4–5 bar to improve the weak absorption capacity of plain water. Before absorption, water-soluble impurities like SO<sub>2</sub> and HCl are removed in a pre-scrubbing water-wash section. Regeneration is done via flash evaporation at 0.3–0.8 bar. Energy consumption of the fully electric process has been estimated at 0.34–0.40 MWh/tCO<sub>2</sub>. Advantages of water scrubbing are simplicity of retrofit with plug-in energy integration and a low-cost, eco-friendly, and non-volatile solvent. The biggest disadvantage is the low CO<sub>2</sub> solubility of water leading to large volume flows. The process is currently at pilot level (TRL 6), and it has been successfully tested at several industrial sites in Finland. In small pilot tests with biomass combustion

flue gases at 2 kgCO<sub>2</sub>/h capacity a product CO<sub>2</sub> purity of 97 vol-% with <20 ppm of N<sub>2</sub>O was reported (Linjala, 2021).

### **3.2** Solid sorbents

Solid sorbents are promising alternatives to liquid solvents with potential to reduce energy requirements and capture costs as sorbent regeneration does not require heating large liquid volumes. In adsorption, the  $CO_2$  binds onto the sorbent's surface via physical or chemical adsorption. In physical adsorption weak van-der Waals forces occur, whereas stronger chemical bonds take place in chemical adsorption. Challenges of sorbent-based capture include heat and flow management and durability of sorbent materials.

Adsorption technology has been used in industrial gas purification, for instance, to remove CO<sub>2</sub> and H<sub>2</sub>S from natural gas and synthesis gas. In carbon capture, there is significantly less activity compared to solvent-based capture, but some adsorption-based technologies have emerged to near commercial level. Solid sorbents have been studied in post- and pre-combustion, as well as direct air capture. Several sorbent materials have been studied for carbon capture, e.g., activated carbons, amine supported materials, zeolites, carbonates, and metallic organic frameworks. Characteristics of the sorbents differ regarding CO<sub>2</sub> selectivity, life-time, impurity-tolerance, thermal stability, and cost. Suitable sorbent choice depends on operating conditions and desired capture performance.

Solid sorbents are used in a cyclic adsorption/desorption process. The feed gas is led into the sorbent bed, for which several configurations have been studied, e.g., fixed, rotating, or fluidized. Typically, the feed gas must be pre-treated to remove excess moisture. After the sorbent is saturated, it is generally regenerated with temperature swings in chemical adsorption and pressure or vacuum swings in physical adsorption. Chemical adsorbents suffer from slow reaction kinetics, but high selectivity makes them suitable for low CO<sub>2</sub> concentration streams. The strong chemical bonds also make regeneration more energy intensive. Physical adsorbents have faster kinetics but weak selectivity and CO<sub>2</sub> loading, making them more suitable for high CO<sub>2</sub> concentration streams. Sorbent-based capture processes are generally categorized based on the regeneration method into temperature-swing adsorption (TSA), pressure-swing adsorption (PSA) or vacuum-swing adsorption (VSA) that are illustrated in Figure 14. Temperature and pressure swings may also be combined for more rapid regeneration. Also, electrical-swing adsorption (ESA) has been studied but it is considered unsuitable for treating large gas volumes (IEAGHG, 2019).



**Figure 14.** Schematic diagrams of temperature swing adsorption (TSA), pressure swing adsorption (PSA), and vacuum swing adsorption (VSA) processes. (Sumida et al., 2012)

PSA is a common gas purification technology used, for instance, in hydrogen production units of refineries and ammonia plants and in biogas upgrading. In carbon capture, PSA has potential for pre-combustion capture applications, where high CO<sub>2</sub> concentrations and pressures occur. It can be also used as a pre-concentration process. TSA is also a mature technology in gas purification and drying applications. In carbon capture, it is promising for postcombustion capture applications due to high selectivity, although it is critical to reach short process cycle times to make it cost-effective. Solid sorbent technologies for CO<sub>2</sub> capture or separation have been developed, e.g., by Svante, Shell, Kawasaki, Honeywell, and Linde.

Svante has developed an intensified rapid temperature-swing adsorption process called Veloxotherm that is based on structured adsorbent beds arranged on a rotating structure. The bed is divided into adsorption, desorption and conditioning segments that are operated simultaneously due to the rotating structure, which has allowed to reduce cycle time and capital cost compared to conventional TSA processes. Different sorbent materials can be used depending on properties of the feed gas. Veloxotherm has been successfully demonstrated at 10 ktpa capacity at a heavy oil site in Saskatchewan, Canada, capturing CO<sub>2</sub> from flue gases of a once-through steam generator (Cenovus, 2021a). At Chevron's Kern River oil field in San Joaquin Valley, California, a demonstration project is ongoing where the process will be tested both in coal and natural gas firing at 25 tpd capacity.

# 3.3 Membranes

Membranes are thin selective barriers that some compounds permeate easier than others. Selectivity of the membrane defines the ratio of permeability of gas components (e.g.,  $CO_2$  or  $N_2$ ). As partial pressure difference over the membrane is the driving force of separation, feed gas pressurization or permeate side vacuum may be needed to enhance permeability. In carbon capture, membranes can be used as a sole capture system or in hybrid systems as a pre-concentration process before a primary capture step. Membranes may be a poor option for post-combustion capture as low  $CO_2$  concentration creates a low driving force for separation, thus requiring large membrane areas or significant pressurization/vacuum for efficient capture. Membranes have shown cost benefit in partial capture, where lower capture rates than the common 90 % are used (Batoon et al., 2019). Advantages of membrane-based capture include compact and modular nature, simplicity of installation, eco-friendliness, low energy requirement, and flexibility of operation and maintenance. Challenges include tradeoff between permeability and selectivity and material challenges regarding stability and lifetime of membranes, especially when exposed to impurities (He, 2018).

Various membrane materials are potential for carbon capture applications including polymer membranes, microporous organic polymers, fixed-site carrier membranes, mixed matrix membranes, carbon molecular sieve membranes, and inorganic membranes such as ceramic, metallic, and zeolite membranes (He, 2018). The choice of suitable membrane material is done based on feed gas properties, operating conditions, and desired capture performance.

According to Chen et al. (2022) especially polymers, copolymers and polymer blends have shown promise for post-combustion capture processes, benefitting from low costs, good processability, and variety of material options. Polymer materials studied for post-combustion capture include polyacetylene, polyaniline, polyetherimides, polycarbonates, poly(phenyleneoxide), poly(ethyleneoxide) and polysulfone. Permeability and selectivity of polymer membranes can be affected by manipulating polymer preparation and chemical composition, although possible swelling and plasticization caused by CO<sub>2</sub> adsorption should be taken into account. For instance, a thermal rearrangement process has been used to significantly improve permeance of polymer membranes like polyamides and polyimides.

Relevant developers and suppliers of membrane-based CO<sub>2</sub> capture and separation include MTR, Air Liquide, Honeywell, Linde, and Schlumberger. MTR is one of the leading developers with their polymer membrane Polaris and PolarCap process (Figure 15) that is applicable for carbon capture in processes of energy, cement, steel, and refining sectors.



Figure 15. Schematic flow diagram of MTR's Polarcap process. (MTR, 2023)

Power requirement for a two-stage Gen-2 Polaris system with CO<sub>2</sub> selective flue gas recycling used in post-combustion capture is estimated to be 277 kWh/tCO<sub>2</sub> with a capture rate of 80 % (Baker et al., 2018). IEAGHG (2019) estimated a 47  $\notin$ /tCO<sub>2</sub> capture cost for the process in coal-firing with a 90 % capture rate. In partial capture applications with capture rates around 40–70 %, a capture cost around 35 \$/tCO<sub>2</sub> could be achieved (Baker et al., 2018). Gen-1 Polaris membranes have been piloted at National Carbon Capture Center and

B&W Research Center in US in coal and natural gas firing at 20 tpd capacity. Gen-2 Polaris membranes have been piloted at Technology Center Mongstad in Norway with fluid catalytic cracker flue gas at 10 tpd capacity. Aiming towards commercialization, a 10 MWe large pilot campaign in coal-firing will be conducted at Wyoming Integrated Test Center.

# 3.4 Calcium looping

Calcium looping (CaL) is based on an adsorption/desorption process, where the CO<sub>2</sub>-rich feed gas is led in contact with a fluidized bed of calcium oxide (CaO) sorbent that binds  $CO_2$ by forming calcium carbonate (CaCO<sub>3</sub>) at a temperature around 650 °C. The carbonate is regenerated at a separate fluidized bed reactor at around 850-950 °C. Flue gas impurities like SO<sub>2</sub> will also react to form calcium sulphate, and therefore fresh make-up limestone is needed. Advantages of CaL include non-toxic, low-cost, and widely available sorbent, maturity of fluidized bed reactor configurations, and potential for additional steam generation via energy recovery from the high temperature process. Disadvantages include sorbent degradation over several process cycles and high temperature requirement of regeneration, which is typically achieved using oxyfuel combustion. Calcium looping is a retrofittable technology for post-combustion capture, with potential especially in applications where additional steam generation capacity is needed. It also yields potential for cement plants and lime cycles of pulp mills (Romano et al., 2013; Santos et al., 2021). Calcium looping is developed in the EU-funded projects CLEANKER and CaLby2030. In project CLEANKER calcium looping is demonstrated at TRL 7, whereas in CaLby2030 it is piloted at TRL 6 at several industrial sites and framework for commercialization is developed. Sumitomo SHI FW is one of the companies offering calcium looping on their portfolio of carbon capture solutions. IEAGHG (2019b) calculated a 40 €/tCO<sub>2</sub> capture cost for calcium looping in coalfiring, yielding a lower capture cost than the 44 €/tCO<sub>2</sub> calculated for MEA.

# 3.5 Cryogenic separation

Cryogenic separation technologies are based on differences in dew points and freezing points of  $CO_2$  and other compounds to achieve  $CO_2$  phase change for separation via cooling. Cryogenic separation can be categorized into distillation, condensation and sublimation technologies.

According to a technology review by Font-Palma (Font-Palma et al., 2021), conventional cryogenic gas-liquid separation method with low temperature is recommended for streams with a  $CO_2$  concentration higher than 50 % to limit refrigeration and energy consumption. Required gas purity and recovery are done by the fine-tuning of the operating temperatures and pressures and including the additional flash separation stages to remove the lower boiling point gases like oxygen, nitrogen and argon. If inlet gas contains oxygen, the removal of trace oxygen from  $CO_2$  needs a separate distillation column to reach oxygen levels below 100 ppm. Another listed shortcoming is that the cryogenic method requires expensive methods to reduce water content to trace levels to avoid plugging caused by ice or the formation of solid  $CO_2$  on the heat exchanger surface.

Liquefaction process for high content  $CO_2$  flows to below 8 bar ship-transport condition has been developed and tested in the Research Institute of SINTEF (Trædal et al., 2021). The focus was set due to the knowledge that transport at 8 bar(a) enable significant cost reductions compared to transport at higher pressures for most transport distances and volumes. Liquefaction close to the triple point pressure of CO<sub>2</sub> have concerns related to dry ice formation and potential clogging in parts of the chain that could lead to operational issues during operation. Process works at low pressure of 5.4-6.5 bar and at temperature of -56 to -50°C, the scale of experiments is in the range of 150–200 kg per hour. In the process the CO<sub>2</sub> gas is compressed to 120 bar, cooled with water to around 20 °C, then CO<sub>2</sub> gas stream is aftercooled against the liquid CO<sub>2</sub> product stream. For further cooling of the stream down to the desired liquid separation temperature, three are three different possibilities. For pure  $CO_2$  the freezing point is predictable, but fractions of  $N_2$  are expected to lower the freezing point temperature. In the performed experiments, it is assumed that the CO2 stream is dehydrated before the liquefaction process. They performed the experimental campaign to derisk and gain operational experience using six experiments using pure CO<sub>2</sub> or CO<sub>2</sub>/N<sub>2</sub> mixtures: two experiments with high purity CO<sub>2</sub> (4.2 quality), and four using mixtures of 94.2 %, 86.5 % and 76.7 % CO<sub>2</sub> which represents simplified and synthesized CO<sub>2</sub> mixtures relevant for post-combustion capture. These experiments demonstrate that pure CO<sub>2</sub> can be safely liquefied at 5.8 bar(a) and a  $CO_2/N_2$  mixture can be liquefied at 6.5 bar(a) without issues related to dry ice formation. The power requirement of 71 kW was reported. Costs were not presented.

According to techno-economic analysis of Sustainable Energy Solutions a Chart Company and Brigham Young University (Hoeger et al., 2021), the Cryogenic Carbon Capture<sup>TM</sup> (CCC) process separates CO<sub>2</sub> from flue gases or light streams by cooling the gases to the frost or desublimation point of CO<sub>2</sub> (-100 to -135 °C), separates and pressurizes the solids, and warms all streams to produce a pure (>99 %) pressurized liquid CO<sub>2</sub> stream at ambient temperature and about 150 bar. Tested capacity has been nominally 1 tCO<sub>2</sub>/day with capture rate of 95–99 % and initial raw gas CO<sub>2</sub> contents in range from 4 to 28 %. The capture costs of 27 USD/t<sub>CO2</sub> was reported, with capture rate of 90 % and having power demand of 0.894 GJe/t<sub>CO2</sub>. From the power consumption the refrigerant compression share is about 94 %. Company is upscaling the systems which are capable from 20 to 100 tons per day liquid CO<sub>2</sub> production.

In the same report it was estimated the case with an assumption that CCC can also capture pollutants and can replace other pollutant equipment such as flue gas desulfurization (FGD), selective catalytic reducer (SCR) units for NO<sub>x</sub> reduction, activated carbon beds, and even baghouses or electrostatic precipitators for particulates. Carbon monoxide (CO) and any other compounds lighter than CO<sub>2</sub> cannot be captured by the CCC process. The case estimation was identical to the CCC case but removes the capital cost, operating cost, and electric load of the ancillary pollutant systems of FGD, SCR and baghouse since those can be replaced by CCC. The capture costs of 12.4 USD/tCO<sub>2</sub> was reported with power demand of 0.854 GJe/tCO<sub>2</sub>.

Air Liquide has a portfolio of cryogenic technologies (Cryocap) for different industrial sectors (Kearns, 2022). In most case technology uses pre-purification and pre-concentration before cryogenic purification. The pre-concentrated  $CO_2$  stream is compressed, dried and sent to a cryogenic unit, where the  $CO_2$  is separated from the other components by a combination of partial condensation and distillation.

 Cryocap H2 for hydrogen production for Steam Methane Reformer, AutoThermal Reforming, or Partial Oxidation with the capacity: 300–5000 tpd, recovery rate >98
 % from syngas and Opex+Capex: 30–50 €/tCO<sub>2</sub>

- Cryocap FG for flue gases is optimal for >15% CO<sub>2</sub> dry basis, flue gas is first compressed, dried and sent to a PSA (Pressure Swing Adsorption). The PSA pre-concentrates the CO<sub>2</sub> in the offgas. Capacity 300–10000 tpd, capture rate up to 95 %, 40 to 80 €/tCO<sub>2</sub>
- Cryocap Oxy for oxycombustion (flue gas >40 % CO<sub>2</sub>), includes flue gas drying, dust filtration, and cryogenic purification. Capacity 1000–15000 tpd, capture rate up to 90–98 %, 30 to 50 €/tCO<sub>2</sub>
- Cryocap Steel for steel production (content 20–50% CO<sub>2</sub>). The gas is first compressed, dried and sent to a PSA (Pressure Swing Adsorption). Capacity 300–5000 tpd, capture rate up to 80–95 %, 25 to 60 €/tCO<sub>2</sub>
- Cryocap NG for biogas, natural gas where >35 % CO<sub>2</sub>. Gas is first dried and sent to a cold process, where CO<sub>2</sub> is pre-separated with membrane and later from the other components through a combination of partial condensation and distillation. The CO<sub>2</sub>-enriched permeate stream of the membrane is sent back to the cold process. The CO<sub>2</sub> and heavy hydrocarbons condense in the cold process and are collected at high pressure. Process is tolerant to some content of H<sub>2</sub>S and it also allows for bulk removal of H<sub>2</sub>S from natural gas like streams. Capacity Up to 1,000,000 Nm<sup>3</sup>/h.
- Cryocap XLL is designed to liquefy large volumes of CO<sub>2</sub>. The solution allows aggregation of CO<sub>2</sub> from various emitters utilizing possibly different types of carbon capture technologies. On top of liquefying CO<sub>2</sub>, Cryocap<sup>TM</sup> XLL also allows the removal of moisture and other compounds (such as O<sub>2</sub>) to meet CO<sub>2</sub> sink specifications. Capacity 800-10000+ tpd, liquefies CO<sub>2</sub> at ambient temperature, 5–25 €/t CO<sub>2</sub> liquefied, Opex 30–130 kWh/tCO<sub>2</sub>.

CAPTICO2 has developed a cryogenic capture technology in collaboration with SINTEF (Kearns, 2022). According to the company, the cryogenic distillation process can separate 99 % of CO<sub>2</sub> from a flue gas source at a cost of 15–20  $\notin$ /tCO<sub>2</sub>. CAPTICO2's cryogenic capture is non-toxic, uses nitrogen and oxygen present in the flue gas as cooling medium to distil CO<sub>2</sub> from the flue gas. The process has been developed to be used as a part of mineralization of calcium carbonate. As a CCUS solution, it was estimated that the total cost of CO<sub>2</sub> capture and mineralization, including source supply and logistics for the end-product is

between 30–40 €/tCO<sub>2</sub>. Pilot test rig with a capacity of 1,300 tCO<sub>2</sub>/a capture and mineralization per year will be installed at Enea in Poland, thus elevating the technology to TRL 7.

# **3.6 Electrochemical separation**

Electrochemical CO<sub>2</sub> separation technologies utilize electrochemical potential difference (e.g., fuels cells, electrodialysis) or electrochemical cycles (e.g., pH swings, redox reactions) to capture or release CO<sub>2</sub>. Electrochemical methods are claimed to have higher energy efficiency and better flexibility compared to conventional CO<sub>2</sub> capture approaches due to the rapid and easily controllable nature of electric potential. Depending on the technology, the captured CO<sub>2</sub> stream may contain high amount of moisture and other gases thus the product CO<sub>2</sub> stream may need further purification. Electrochemical CO<sub>2</sub> capture is typically classified into four categories shown in Figure 16: (1) methods with pH-swing to capture and recover the CO<sub>2</sub>, (2) methods which use the binding affinity of CO<sub>2</sub> molecules to redoxactive species, (3) molten carbonate cells and (4) hybrid electrochemical processes that combine CO<sub>2</sub> capture and e.g., direct conversion.



Figure 16. The primary methods of electrochemical CO<sub>2</sub> capture (Sharifian et al., 2021).

pH-swing is a widely studied method of electrochemical separation. It is operationally straightforward method with relatively cheap and non-toxic chemicals. In theory, a mild pH-swing over ca. 2–3 pH units would allow to capture 98% of the CO<sub>2</sub>. It has been mentioned that in practice slow kinetics occur in such a mild swing, therefore either a wider pH range (ca. 5–6 pH units) or catalytic enzymes (e.g., carbonic anhydrase) could be applied to enhance kinetics. Electrochemical pH-swing can be done via electrolysis, bipolar membrane

electrodialysis (BPMED), redox active molecules that undergo proton coupled electron transfer or capacitive deionization. (Sharifian et al., 2021)

pH-swing electrolysis is the earliest method used for alkaline absorbent regeneration. Electrolysis enables pH-swing between two electrodes and can be enhanced using membranes for alkali absorbent regeneration or simultaneous H<sub>2</sub> production. Alkaline compounds form carbonates or bicarbonate with dissolved CO<sub>2</sub> at cathodic side and the absorbent is recovered at anode side. At the anode the CO<sub>2</sub> can be either released as a gas (e.g., in reaction 2 H<sub>2</sub>O +  $K_2CO_3(aq) \rightarrow 2 \text{ KOH}(aq) + CO_2(g) + H_2(g) + 0.5 O_2(g)$ ), or the bicarbonate products can be conducted to other process or to storage when fresh alkali must be added (e.g. 2 H<sub>2</sub>O + CaCO<sub>3</sub>(s) + CO<sub>2</sub>(g)  $\rightarrow$  Ca(HCO<sub>3</sub>)<sub>2</sub>(aq) + H<sub>2</sub>(g) + 0.5 O<sub>2</sub>(g)). In the latter case, theoretically if one mole of CO<sub>2</sub>(g) is captured per one mole of CaCO<sub>3</sub>, it is possible that 22 tonnes of CO<sub>2</sub> is captured per tonne of H<sub>2</sub> produced. Simultaneous hydrogen production can partially decrease costs of the process. It has been mentioned that upscaling of direct alkali electrolysis might be unfeasible due to low current density. Also, salt electrolysis using NaCl or KCl could be used for CO<sub>2</sub> capture. In direct salt electrolysis the chlorine gas would be released from the anode, thus ion change membranes can be used to avoid Cl<sub>2</sub> gas release. (Sharifian et al., 2021)

Bipolar membrane electrodialysis (BPMED) has a membrane with two exchange layers laminated together, an anion layer and a cation layer. When the electric field is applied, the BPM dissociates water into  $OH^-$  and  $H^+$ , producing a controllable pH change over the membrane. One benefit of the BPM is that it can dissociate the water with 2.5 times less energy compared to electrolysis and no gases are released. The cell configuration often consists also cation exchange membrane and anion exchange membranes, reactions follow their equilibria curves and, there are two different liquids used, e.g., at cathodic side acids  $KH_2PO_4 + H_3PO_4$ and at anionic side bases  $KHCO_3$ ,  $K_2CO_3$  and KOH. Energy consumptions between 100 and 500 kJ/mol<sub>CO2</sub> have been reported. (Sharifian et al., 2021)

Capacitive deionization is the membrane capacitive deionization method which utilizes local pH near the electrodes to capture and release  $CO_2$  by changing the current direction. Method uses deionized water, ion exchange membranes and inexpensive activated carbon electrodes.

Other type of porous electrodes and different kind of cell configurations can be also used. In the charging phase the  $HCO_3^-$  and  $H^+$  ions are adsorbed into the porous electrodes inside of the cell which causes a local low pH at the cathode and increases pH in the bulk bulk/deionized water. Increased pH at the electrolyte enables that more  $CO_2(g)$  can be absorbed in the deionized water, until no pH changes in electrolyte occur. In the discharging phase the current direction is turned and  $CO_2(g)$  is formed from the electrolyte. Method has been studied also in combination with NH<sub>3</sub>-based CO<sub>2</sub> capture process. (Sharifian et al., 2021)

PCET agents refers to proton-coupled electron transfer of organic molecules (so called redox-active carriers) which can generate H+ and OH- ions. Maturity level of the process is low with proof-of-concept studies reported. According to Renfrew et al. (2020) to enable effective CO<sub>2</sub> capture with PCET of an organic molecule, the catholyte must reach and be stable at a high pH which is controlled in part by concentration (solubility), mass transfer coefficient, and buffering capacity of the electrolyte. Also, ion selective membranes are needed to maintain the pH gradient, keeping the catholyte at high pH and the anolyte at low pH. Redox carriers can be organic or metal oxide-based compounds, mentioning, e.g., quinones (at least benzoquinone and 2,6-dimethylbenzoquinone), tiron (1,2-dihydroxybenzene-3,5-disulfonic acid) and MnO<sub>2</sub>.

Redox-active carriers can be divided into two categories as direct and indirect carriers. Even though some carrier compounds are the same as in PCET process, here are no pH changes during the process due to different cell structures using e.g., gas diffusion electrodes. In both cases the CO<sub>2</sub> is captured cathodically and released anodically. The direct carrier sorbent itself is redox-active and its nucleophilicity is directly modified electrochemically, activating and deactivating its affinity toward the sorbate (CO<sub>2</sub>). Direct redox-active methods are called electrochemically mediated complexation separations or electrochemically modulated complexation. The indirect carrier sorbent itself is not redox-active but it interacts with a redox-active competitor which has affinity for the sorbent when activated. Thus, the CO<sub>2</sub> binds to the sorbent and it is released when the competitor is activated with electricity. Indirect redox-active method might also be called as electrochemically mediated complexation separation. Interesting redox carrier compounds such as bipyridines, quinone species, disulfides and copper or amine systems are widely studied, especially quinone compounds have

high interest. Drawback of these techniques are that the presence of protons can neutralize the reduced carrier which lowers the efficiency as well as the capacity of  $CO_2$  capture. Also mentioned challenges for direct carrier approaches are slow kinetics, low solubilities, side reactions due to reactive intermediates, sensitivity to oxygen and the expense of ionic liquid electrolytes. At the moment quinone compounds incorporated into a carbon mesh and transition metal complexes are mentioned to be potential compounds. Also, the choices of catalysts on the surface of the electrodes to facilitate the electron transfer together with the type and concentration of the electrolyte are important in determining the process efficiency in terms of capture, kinetics, transport and release of  $CO_2$ . Redox-active systems have yet to achieve industrial utility, but they have the potential of producing a pure  $CO_2$  stream even from dilute gas mixtures. (Renfrew et al., 2020b)

High-temperature molten carbonate fuel cells (MCFC) have molten carbonate salt electrolyte sandwiched between ceramic membranes and in contact with the electrodes. The gas containing CO<sub>2</sub> and O<sub>2</sub> is fed to the cathode side of an electrochemical cell, where electricity is used to drive CO<sub>2</sub> and O<sub>2</sub> (in form of CO<sub>3</sub><sup>2-</sup>) across a molten carbonate salts electrolyte. In anode the carbonate ion will be reduced back to CO<sub>2</sub> and H<sub>2</sub>O, if H<sub>2</sub> is used as a fuel in anode. There are possibilities to use different kind of selective membranes which enables, e.g., molten carbonate fuel cell where CO<sub>2</sub> is captured while H<sub>2</sub> is also produced. Closedloop operation of MCFC consumes CO<sub>2</sub> and O<sub>2</sub> at cathode side which makes it to be good option for post-combustion caption from flue gases. MCFC can use any hydrogen-carbon mixtures as a fuel. Challenges due to high temperatures (>450°C), low tolerance for impurities, corrosion, development stage of CO<sub>2</sub> selective membranes have been reported. Impurities reported include particulates, sulphur compounds, halides, nitrogen compounds, trace metals, silicon compounds and long-chain hydrocarbons. (Sharifian et al., 2021; Slater & Chronopoulos, 2019). FuelCell Energy is one of the developers of electrochemical carbon capture with their MCFC system that is presented in Figure 17.



Figure 17. A schematic illustration of FuelCell Energy's MCFC-based carbon capture system (Leo, 2022).

FuelCell Energy received funding from the Clean Resource Innovation Network to pilot their MCFC technology in post-combustion capture at the Scotford oil sand upgrader in Alberta, Canada, capturing  $CO_2$  from process heater flue gases (CRIN, 2022; FuelCell Energy, 2022). The pilot system can capture 22 tonnes of  $CO_2$  while generating an additional electricity production capacity of 600 kW.

# 3.7 Inherent capture and purification

Inherent capture refers to processes where CO<sub>2</sub> capture can be inherently incorporated into design of the process. In practice this means that the process produces an exhaust stream with CO<sub>2</sub> concentration so high that a specific technology for carbon capture is not required to obtain CO<sub>2</sub> applicable for CCUS. We divide inherent capture into natural and technological pathways. Natural inherent capture refers to processes naturally producing exhaust streams of high purity CO<sub>2</sub> such as ethanol fermentation (Chapter 4.2.3) and production of hydrotreated vegetable oils via decarboxylation routes (Chapter 4.2.4). Technological inherent capture refers to technologies purposefully designed to produce a by-stream of pure CO<sub>2</sub> for inherent capture for instance as part of energy production, manufacturing, or refining. Technological pathways of inherent capture include, e.g., electrically heated calcination (Katajisto, 2020), chemical looping combustion, and NET Power's Allam-Fetvedt cycle based on oxy-combustion. Some treatment such as dehydration, desulphurization or other purification may be required, especially in the natural pathways of inherent capture. The common  $CO_2$  purification methods are reviewed in Chapter 2.3.

The natural pathways of inherent capture typically yield the lowest capture cost of all carbon capture pathways as little work is required to obtain a pure stream of CO<sub>2</sub>. Furthermore, the purification technologies used in these pathways are at mature level. IEA (2019) estimates a capture cost of 15-35 USD/tCO<sub>2</sub> (incl. compression) for high CO<sub>2</sub> purity streams (e.g., natural gas processing and ethanol fermentation), whereas the Global CCS Institute (Siemenski, 2021) assumes a cost range of 0-10 USD/tCO<sub>2</sub> for conditioning of CO<sub>2</sub> captured from high concentration sources. Although these sources are a low hanging fruit regarding capture cost, the quantitative capture potential is low as only a few emission point sources are of such nature.

In technological pathways of inherent capture, the capture cost is typically higher than in natural pathways as the high CO<sub>2</sub> purity exhaust stream is purposefully created via novel process designs rather than occurring as a natural by-product of the process. Furthermore, these processes are often not retrofittable and lack commercial maturity, with the most advanced technologies like the Allam-Fetvedt Cycle being at TRL 6–7. However, these technologies yield promise for the future. IEAGHG (2019b) calculated a  $34 \notin /tCO_2$  capture cost for the Allam cycle in gas-firing, yielding a significantly lower cost than the  $64 \notin /tCO_2$  calculated for MEA.

# 3.8 Summary of the reviewed carbon capture technologies

Multiple technologies have been developed for CO<sub>2</sub> capture, with different qualities regarding operating principle, technical properties, and performance. Maturity of the technologies vary, with some being commercially available, and some under demonstration, piloting, or conceptual research. Evaluating different technologies in a comparable way is difficult as there is little public information available on proprietary technologies, and as performance is always case-dependent. For instance, capture costs reported on literature may not be comparable as often the costs have been calculated using different limitations, assumptions, and estimates. Energy consumption is a relevant factor to compare as it is often the most significant factor affecting operating costs. However, there are also uncertainties on energy consumptions reported on literature as it may be measured, calculated, or estimated based on reaction kinetics. Also, depending on the capture technology and energy integration opportunities at the capture site, the energy supply and thus the energy costs may vary significantly, depending on if electricity, waste heat, low-pressure steam, or high-pressure steam is used.

Many carbon capture technologies are still a relatively novel in terms of relevant experience in industrial applications, therefore posing risks of technical failure and economic losses for potential technology implementors. The magnitude of technology implementation risk mostly relates to the level of technological maturity. Capture technologies based on scrubbing with amine solvents currently offer a low-risk option with proven high capture performance and high maturity with plenty of commercial experience. Also, inherent capture/CO<sub>2</sub> purification applications have low risk since a specific capture technology is not required. Some alternative technologies with more eco-friendly nature and potential to outperform amines have reached TRL 8-9 and have become reasonable options to consider alongside amines, e.g., carbonate salt processes by CO<sub>2</sub> Capsol and Saipem. Additionally, several emerging technologies with promising performance are at TRL 6-7 and facing large-scale demonstration soon, but before being proven at industrial scale the risk of implementation remains high. Technologies for post-combustion capture at this level include solid sorbents, membranes, cryogenic separation, and fuel cell-based capture. As intensive development is ongoing to commercialize the technologies, maturity levels, performance data and risk estimations may change rapidly as new development projects proceed.

This report does not include regulatory perspective, but environmental regulations should be carefully examined especially when considering capture processes that may produce toxic pollutants. In the European Union there are several regulations and guidance documents related to carbon capture.

With focus on post-combustion capture, technologies reviewed in this work were liquid solvents (amines, carbonate salts, phase-separating, physical), solid sorbents, membranes, electrochemical separation, solid looping, cryogenic separation, and inherent capture/purification technologies. Table 6 summarizes maturity, indicative capture cost, advantages and disadvantages and developers of the carbon capture technologies reviewed in this work.

Technology	TRL	€/tCO <sub>2</sub>	Advantages	Disadvantages	Developers/suppliers
Amines	6–9	25-40	High maturity, several commercial technology suppliers, high capture performance even with low CO <sub>2</sub> concentration streams	Thermal and oxidative degradation resulting in toxic emissions, en- ergy-intensive regeneration, corro- sivity, foaming possibility	Mitsubishi Heavy In- dustries, Shell, Fluor, BASF, Aker Carbon Capture, Honeywell
Carbonate salts	5–9	25–40	Non-toxic, low-cost, and widely available absorbent materials, ap- plicability to low-temperature re- generation, low corrosivity	Slow absorption kinetics, risk of solid formation, foaming	CO2 Capsol, Saipem, KC8, Kleener, VTT, Baker Hughes, Honey- well
Phase-separating solvents	6–7	30–40	Low regeneration energy require- ment, low corrosivity, stability	Adequate gas and solvent contact, solid or slurry handling	Axens/IFPEN
Physical solvents	8–9	30–55	Widely used in industrial gas puri- fication applications	Not suitable for low CO <sub>2</sub> concen- tration streams	Honeywell, Carbon- ReUse
Solid adsorbents	6–9	30–50	Mature technology in industrial gas purification, low regeneration energy, several sorbent choices	Slow transfer kinetics (chemisorp- tion), weak selectivity (physisorp- tion), sensitivity to impurities	Svante, Shell, Kawa- saki, Honeywell, Linde
Membranes	6–9	35–55	Compact and modular nature, sim- plicity of installation, eco-friendli- ness, low energy requirement, flexibility of operation and mainte- nance, several material choices	Tradeoff between permeance and selectivity, material challenges es- pecially in the presence of impuri- ties (e.g., lifetime and stability)	MTR, Air Liquide, Honeywell, Linde, Schlumberger
Calcium looping	6–7	40	Non-toxic, low-cost, and widely available sorbent, steam generation potential, maturity of fluidized bed technology	High temperature requirement of regeneration (~900 °C), sorbent degradation over several process cycles	Sumitomo SHI FW
Cryogenic separa- tion	6–9	30–70	High capture efficiency	Moisture removal required, high energy requirement of refrigeration	Air Liquide, CAP- TICO2, Honeywell
Electrochemical separation	4-6	35-	High efficiency and flexibility vs. thermochemical processes as elec- tric potential is easy and quick to control, power output potential	Demand for additional fuel, further CO <sub>2</sub> separation may be needed	FuelCell Energy
Natural inherent capture	9	0–25	Low capture cost as only some pu- rification if any required	Often low quantitative capture po- tential	
Technological in- herent capture	6–7	30–70	Simplicity of capture	Weak retrofittability, implemented as new installations	NET Power, VTT

Table 6. A summary of mature and emerging CO<sub>2</sub> capture technologies reviewed in this work.

# 4 CARBON CAPTURE POTENTIAL OF FOREST INDUSTRY, PE-TROLEUM REFINERIES AND BIOREFINERIES IN FINLAND

In project E-Fuel, we examine capturing CO<sub>2</sub> from emission streams of forest industry, petroleum refineries, and biorefineries to supply CO<sub>2</sub> as feedstock for CCU-based electrofuel production. As various emission point sources with unique characteristics occur in these industries, it is essential to identify streams with high potential for carbon capture implementation. In this chapter, carbon capture potential of relevant industries in Finland are evaluated by examining properties of the emission point sources and techno-economic feasibility and maturity of carbon capture implementation in these industries. The results are presented in Chapter 4.3. A scoring matrix based on key performance indicators (KPI) is used to score and rank carbon capture potential of the reviewed industries. Details of the KPI scoring matrix are presented in Table 7.

Key performance indica- tor	Scor	·e	Relevance	Method of evaluation	
Annual $CO_2$ emissions of the industry in Finland	0	<1 Mtpa			
	1	1–5 Mtpa	Quantitative carbon capture	Reported emissions of the industries	
the industry in Finance	2	>5 Mtpa	potential of the industry		
On-site CO <sub>2</sub> emissions of an average facility/complex	0	<100 ktpa	Ouantitative carbon capture	Finnish reference plants	
	1	100–500 ktpa	potential per facility and		
	2	>500 ktpa	economy of scale		
	0	To diminish		Planned and decided investments and de- commissioning	
Industry trend by 2030	1	To remain largely unchanged	Future CCUS potential		
	2	To grow			
Average CO <sub>2</sub> concentration	0	Low: <20 %	E GO di	Typical characteristics of the emission point sources	
of the emission point	1	Moderate: 20–90 %	capture cost		
sources	2	High: >90 %	L .		
Degree of earbon conture	0	Development (TRL 1-4)	Technological maturity,	Review on global pro- jects and technology suppliers	
implementation	1	Pilot (TRL 5–7)	readiness for implementa-		
ī	2	Industrial deployment (TRL 8-9)	uon		
	0	Implemented as new installations		Process reviews, litera- ture	
Ease of system integration	ration 1	Significant process modifications	Ease of integration and cap-		
, ,	2	Straightforward retrofit with minor	ital cost		
	2	effects on the original process			
	0	<25 % of biogenic origin	Climate impact (depends	Demonte I contrations of	
Natural origin of CO <sub>2</sub>	1⁄2	25–75 % of biogenic origin	tion of $CO_2$ and sustainabil-	the industries	
	1	>75 % of biogenic origin	ity of biomass use)		

**Table 7.** A scoring matrix based on key performance indicators developed to evaluate carbon capture potential

 of industrial emission point sources. Higher score indicates higher potential for carbon capture implementation.

The KPI matrix presented in Table 7 aims to include the most relevant factors regarding the potential of carbon capture implementation. Each factor is scored using a following scale: 0 = 1 ow potential, 1 = intermediate potential, and 2 = high potential. We consider natural origin of CO<sub>2</sub> to be less relevant than the other factors since climate impact of CCUS depends also on the end-use application of the captured CO<sub>2</sub> and sustainability of possible biomass use in addition to origin of the CO<sub>2</sub>. Therefore, we apply an alternative scoring of  $0/\frac{1}{2}/1$  for natural origin of CO<sub>2</sub>.

# 4.1 Industrial CO<sub>2</sub> emissions in Finland

According to the European Pollutant Release and Transfer Register (EEA, 2021), a total of 41.4 Mt of CO<sub>2</sub> emissions originated from industrial activity in Finland in 2020. The register includes facilities with annual emissions of  $\geq$ 100 ktCO<sub>2</sub>. Figure 18 illustrates sectoral distribution and natural origin (biogenic or fossil) of the reported emissions.



**Figure 18.** Sectoral distribution and natural origin (biogenic/fossil) of industrial CO<sub>2</sub> emissions in Finland in 2020. The data includes facilities with emissions of  $\geq 100$  ktCO<sub>2</sub>/a. (Based on data from EEA, 2021).

Of the annual 41.4 Mt of industrial CO<sub>2</sub> emissions in Finland, 59 % (24 Mt) are of biogenic origin and 41% (17 Mt) of fossil origin. Forest industry is the largest industrial emitter, accounting for 50 % (20.6 Mt) of emissions reported in E-PRTR, of which 92 % originates

from biogenic sources. Heat and power production in thermal power plants, waste-to-energy facilities and other combustion installations is the second largest industrial emitter accounting for 32 % (13.4 Mt) of the total emissions, of which 40 % are biogenic. Emissions from petroleum refining (2.9 Mt), production of iron and steel (2.6 Mt), cement (1.0 Mt) and chemicals (0.7 Mt) are predominantly fossil-based.

# **4.2** Carbon capture potential of forest industry, petroleum refineries and biorefineries in Finland

In this work, we examine carbon capture potential of forest industry, petroleum refineries and biorefineries, which are relevant  $CO_2$  sources in Finland. Although being a significant source of emissions in Finland, thermal power plants are excluded from this study having been the focus of VTT's project BECCU in years 2019-2022. However, carbon capture of thermal power plants is in many ways similar to processes reviewed in this study such as combustion processes in pulp mills.

#### 4.2.1 Pulp and paper mills

Forest industry is a significant emitter of  $CO_2$  in Finland, accounting for 50 % (20.6 Mt) of emissions reported in E-PRTR, although 92 % of the  $CO_2$  originates from biogenic sources. In 2022, there were 19 pulp and mass production plants and 14 paper mills in Finland (Metsäteollisuus ry, 2022). Focus of this study is in typical kraft pulp mill processes.

Majority of CO<sub>2</sub> emissions in pulp and paper mills originate from combustion processes in recovery boiler, power boiler, and lime kiln. Recovery boiler is used to regenerate pulping chemicals and to supply heat and power for the mill. It is fueled with black liquor, i.e., the spent pulping chemicals that have been concentrated by evaporating majority of the water content. Power boiler supplies additional energy for the mill, and it is commonly fueled with biomass residues such as bark, chippings, and bio-sludge. Lime kiln is used for calcination, where lime mud (Ca(OH)<sub>2</sub>) is converted into quicklime (CaO) at high temperatures, releasing CO<sub>2</sub> both via calcination reaction and combustion that is commonly fueled with fuel oil or natural gas. CO<sub>2</sub> emissions of recovery and power boilers are predominantly biogenic, whereas CO<sub>2</sub> emissions from the lime kiln are roughly 60 % biogenic (originating from calcination) and 40 % fossil-based (originating from fossil fuel combustion) (Onarheim et al.,

2017a). Table 8 presents typical flue gas properties of the recovery boiler, the power boiler, and the lime kiln in a modern kraft pulp mill.

	Unit	Recovery boiler	Power boiler	Lime kiln
Temperature	°C	184	189	250
Mass flow	MTPY	8 151 000	1 508 000	684 000
Share of mass flow		79 %	15 %	7 %
$CO_2$	mol-%	13	12.1	20.4
$N_2$	mol-%	67.6	53.4	47.4
$O_2$	mol-%	2.3	1.7	1.2
H <sub>2</sub> O	mol-%	17	32.7	30.9
SO <sub>x</sub>	ppm	60	40	50
NO <sub>x</sub>	ppm	125	150	175
TRS	ppm	15	15	15
PM	ppm	30	15	30

**Table 8**. Flue gas properties of recovery boiler, power boiler, and lime kiln in a modern kraft pulp mill with a pulp production capacity of 800 000 adt/y. (Adapted from Onarheim et al., 2017a).

As flue gas streams of the processes are separate and distributed at the site, it is unlikely that all  $CO_2$  emissions are covered with carbon capture unless a common stack is used to combine the flue gas streams. Recovery boiler is by far the largest point source of  $CO_2$  and therefore the most favorable option for carbon capture implementation, possessing economy of scale -benefit. With a capture rate of 90 % around 60–80 % of the mill's total  $CO_2$  emissions could be captured from the recovery boiler (Kuparinen 2019). Properties of the flue gas streams are similar, although lime kiln flue gas has a slightly higher  $CO_2$  concentration due to the  $CO_2$  released in calcination, which could possibly result in lower capture cost.

Carbon capture could be implemented into pulp and paper mills using various technologies. To ensure straightforward integration we consider retrofittability as an essential factor for suitable technology choices. Post-combustion capture technologies are commonly end-of-pipe solutions and could be retrofitted into the processes without major modifications, offer-ing presumably the simplest option for carbon capture. Technology options for post-combustion capture are reviewed in more detail in Chapter 3. Onarheim et al. (2017b) calculated a 52–66  $\notin$ /tCO<sub>2</sub> cost of CO<sub>2</sub> avoided for a modern kraft pulp mill and 71–89  $\notin$ /tCO<sub>2</sub> for an integrated pulp and board mill, when capturing 60–90 % of the emissions with amine-based post-combustion capture technology. Oxy-combustion technologies lack applicability for straightforward integration, requiring major modifications or new installations (e.g., an air

separation unit). Pre-combustion capture could be a potential technology for mills where gasification or pyrolysis are used to produce hydrogen, synthesis gas, or bioliquids, e.g., for biorefinery feedstock or as fuel. For the lime cycle, calcium looping is a potential, retrofittable option for carbon capture. Santos et al. (2021) estimated via modelling a 39  $\notin$ /tCO<sub>2</sub> cost of CO<sub>2</sub> avoided when implementing calcium looping to the lime of cycle of a kraft pulp mill. VTT has also studied calcination using an electrically heated rotary kiln (Katajisto, 2020), which would eliminate emissions deriving from combustion, enabling inherent capture of nearly pure CO<sub>2</sub> stream released in calcination, requiring only some gas conditioning, if any, to obtain CO<sub>2</sub> applicable for CCUS. VTT has estimated by modelling a production cost of 70  $\notin$ /tCO<sub>2</sub> for production 320 t of lime/day using an electrically heated rotary kiln concept, with the biggest cost impact deriving from electricity price (Tsupari et al., 2022).

A carbon capture system significantly affects mass and energy balances of the mill, although depending on the mills properties and the capture technology in use. According to Onarheim et al. (2017a) increases can be expected on steam and electricity consumption, and utility streams like process and cooling water, boiler feed water and condensates, and waste streams. Energy integration may present a challenge as most carbon capture technologies require steam for solvent or sorbent regeneration, which may not be available as steam supply is often effectively utilized in the mill's processes. Especially implementing carbon capture to the recovery boiler would significantly increase steam demand and reduce net electricity export. Onarheim et al. (2017a) estimate that in a stand-alone kraft pulp mill steam supply can cover the demand of an amine-based capture system, whereas in a pulp and board integrate an auxiliary boiler is required if carbon capture is implemented to the recovery boiler. Also, partial capture could be an option if the steam supply is inadequate to cover full-scale capture.

There has been some carbon capture activity in the forest industry globally. Saipem is operating a 30 tpd capture unit (TRL 8) at Resolute's kraft pulp mill in Quebec, Canada, capturing  $CO_2$  from lime kiln flue gases using an enzyme enhanced potassium carbonate solvent and utilizing the mill's waste heat in solvent regeneration (CO2 Solutions, 2021; Surprenant, 2019). The captured  $CO_2$  is utilized in a nearby greenhouse. Saipem's solvent is also demonstrated at TRL 7 together with Prospin's rotating packed bed technology at Stora Enso's pulp mill in Sweden as part of the ACCSESS project (ACCSESS, 2022).

#### 4.2.2 Petroleum refineries and steam methane reforming

In petroleum refineries crude oil is refined into usable products like gasoline, diesel, jet fuel and other petroleum-based products. Steam methane reforming (SMR) is widely used hydrogen production technology in industry and therefore also an essential technology for petroleum refineries where hydrogen is an important feedstock. Petroleum refining in Finland is solely focused at Neste's Porvoo refinery. In Finland around 80 % of SMR production locates in the Porvoo refinery area.

Petroleum refineries have generally several CO<sub>2</sub> emission point sources, e.g., process heaters, steam and electricity generation utilities, fluid catalytic crackers and hydrogen production units. CO<sub>2</sub> emissions of petroleum refineries, that are predominantly fossil-based, distribute as follows: 30-60 % from process heaters, 20-50 % from utilities, 20-50 % from fluid catalytic cracking and 5–20 % from hydrogen production (Bains et al., 2017). Process heaters (or furnaces) are used to generate heat needed, e.g., in pre-heating, distillation, hydrotreating, cracking, reforming, and coking. Steam and electricity are produced in utilities plant using gas turbines and heat exchangers. Heaters and utilities are generally fueled using natural gas or refinery fuel gas (RFG) that contains light hydrocarbons and hydrogen. In fluid catalytic cracking large hydrocarbons are fractioned into smaller, more valuable products via catalysts in an elevated temperature and pressure. Coke formed in the cracking process is combusted, releasing CO and CO<sub>2</sub> after which the CO is converted to CO<sub>2</sub> in a CO boiler. Hydrogen, which is an important feedstock for refineries, is generally produced via steam methane reforming, where methane and high-temperature steam react under catalysts, forming hydrogen, carbon monoxide and some carbon dioxide. Water-gas shift (WGS) reaction is used to increase hydrogen output by converting carbon monoxide and water steam into hydrogen and carbon dioxide. WGS is followed by hydrogen purification commonly using pressure-swing adsorption (PSA) or in some cases with other techniques like amine scrubbing. Table 9 presents typical characteristics of exhaust streams in petroleum refineries.

Point source	CO <sub>2</sub> concentration	Temperature	Pressure	Composition
Process heaters	8–10 %	160–190 °C	atm	Depends on fuel
Utilities (steam, electricity)	3–5 %	160–190 °C	atm	Depends on fuel
Fluid catalytic cracker (FCC)	10–20 %	160–190 °C	atm	O <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> O, N <sub>2</sub> , Ar, CO, NO <sub>x</sub> , SO <sub>x</sub>
Hydrogen produc- tion (SMR)	30–45 % (PSA) 98–100 % (scrubbing)	20–40 °C 100–120 °C	20–30 bar (PSA)	CO <sub>2</sub> , H <sub>2</sub> , CO, CH <sub>4</sub>

Table 9. Properties of emission point sources in petroleum refineries (Bains et al., 2017; Kearns et al., 2021).

Exhaust streams of process heaters, utilities, and fluid catalytic crackers are combustion flue gases with near-atmospheric pressure and low  $CO_2$  concentration. Composition and present impurities depend on the used fuel, but generally natural gas or refinery fuel gas are used. Natural gas combustion results in a rather pure flue gas stream, whereas in RFG combustion sulphureous impurities may occur. SMR exhaust stream has higher  $CO_2$  concentration and outlet pressure, offering greater potential for carbon capture.

Feasibility of carbon capture implementation to petroleum refineries has been evaluated e.g., by van Straelen et al. (2010), Johansson et al. (2012) and Bains et al. (2017). As there are multiple  $CO_2$  point sources in refineries, full-scale carbon capture implementation is challenging without a common stack. Therefore, the largest emission sources or units with highest carbon capture potential are likely to be prioritized. SMR units have high potential regarding economics as high  $CO_2$  concentration occurs in the exhaust stream. However, SMR capacity may reduce as green hydrogen capacity is expected to grow in the future. Flue gas streams of process heaters, utilities, and fluid catalytic crackers could be harnessed using post-combustion capture technologies. Refinery plants typically have multiple energy utilities available which is beneficial regarding system integration, but refineries have often limited amount of space, which may set size limitations for an additional carbon capture system. Regarding climate impact the carbon sources in refineries are typically fossil-based but transition toward non-fossils is ongoing in many refineries. Refineries are often located near coasts, which is favorable regarding logistics.

Carbon capture has been successfully implemented to petroleum refineries in several projects. In many of these projects, the high CO<sub>2</sub>-concetration exhaust streams of steam methane reformer units have been targeted. At Neste's Kilpilahti refinery in Porvoo, Finland, Linde is capturing around 400 ktpa of food-grade CO<sub>2</sub> for the market from a steam methane reforming unit using pressure-swing adsorption and an additional distillation (Teir et al., 2009). At Tomakomai, Japan, as part of the Tomakomai CCS project a total of 300 ktCO<sub>2</sub> (100 ktpa) was captured during 2016–2019 from an oil refinery's hydrogen production unit's PSA exhaust gases using BASF's OASE amine scrubbing process and stored into offshore reservoirs below the seabed (Sawada et al., 2021). The two-stage absorption process averaged a reboiler duty of 0.9 GJ/tCO<sub>2</sub> and gross capture energy of 1.2 GJ/tCO<sub>2</sub>. At Cenovus Energy's (formerly Husky Energy's) Pikes Peak South heavy oil site in Saskatchewan, Canada, a 10 ktpa pilot plant has been operated from 2019 onwards capturing CO<sub>2</sub> for enhanced oil recovery from the flue gases of a natural gas fired steam generator using Svante's rotating structured adsorbent bed technology (Cenovus, 2021b). At Sinopec's Qilu refinery in Shandong, China, a CCS project with capacity of 1 Mtpa started in 2022, capturing CO<sub>2</sub> for enhanced oil recovery from the coal gasification hydrogen production unit (McCoy, 2022).

#### 4.2.3 Ethanol fermentation

Ethanol fermentation is a biological conversion process used to produce ethanol from plantbased feedstock. In Finland bioethanol production capacity is currently less than 20 million litres in year, and mainly forest residues and biogenic wastes are used as feedstock in bioethanol production. Main developer and producer St1 has in Finland three plants using biogenic wastes and one plant using forest residues, total production capacity is annually between 11 and 19 million litres (St1 Oy, 2022). Bioethanol production capacity in Finland is expected to grow in the near future. Bioenergo (2022) has planned a bioconversion plant with bioethanol production capacity of 47 kt to Pori, whereas NordFuel (2022) has planned a biorefinery producing 65 kt of wood-based bioethanol to Haapavesi. However, final investment decisions on these projects have not been made.

Carbon capture from ethanol fermentation is a low-hanging fruit of biogenic CO<sub>2</sub>. Exhaust stream from ethanol fermentation is nearly pure CO<sub>2</sub> (~99 %) with low amount of impurities such as moisture, methanol, ethanol, H<sub>2</sub>S and dimethylsulphide (Sanchez et al., 2018; Xu et al., 2010). Generally, only dehydration is required before compression and transportation of CO<sub>2</sub> to avoid corrosion of pipelines (Xu et al., 2010). Purification may be required if CO<sub>2</sub>

quality requirement is high. For instance, in the food and beverage industry deodorization of  $CO_2$  is required before utilization. Carbon capture from ethanol fermentation is commercially proven and widely used in the US to provide  $CO_2$ . Dahowski & Dooley (2008) estimate that the cost for capturing  $CO_2$  from ethanol fermentation falls around 6–12 USD/tCO<sub>2</sub>, consisting of dehydration and compression. According to a more recent study by Sanchez et al. (2018), the cost estimates for  $CO_2$  capture and compression from ethanol fermentation are typically around 30 USD/tCO<sub>2</sub>.

Globally, as of 2021 there were several ethanol plants capturing  $CO_2$  with a combined capture capacity of 2.21 Mt  $CO_2$  per year, split roughly equally between  $CO_2$  storage and use, with 1.65 Mt  $CO_2$  per year from projects destined for enhanced oil recovery or storage (IEA, 2022).

#### 4.2.4 Hydrotreated vegetable oils

Hydrotreated vegetable oils (HVO) – also known as renewable diesel – are second generation biofuels that offer green alternatives to conventional petroleum diesel. In Finland, HVO's are produced by Neste and UPM. Neste's NEXBTL renewable diesel is produced from vegetable oils and waste fats, whereas UPM produces its BioVerno renewable diesel from tall oil – a by-product from kraft pulping. HVO production capacity in Finland is 520 ktoe, consisting of two Neste NEXBTL units at Porvoo with a total capacity of 420 ktoe and UPM's BioVerno unit at Lappeenranta with a 100 ktoe capacity (Sipilä et al., 2018). Calculated with a GHG emission factor of 4.48 gCO<sub>2</sub>eq/MJ for the hydrotreating stage in HVO production (Garraín et al., 2010), HVO production in Finland results in around 97.5 ktpa of biogenic CO<sub>2</sub> emissions (= $0.188 t_{CO2}/toe_{HVO}$ ). Global HVO production capacity in year 2021 was 16 000 million liters. HVO projects can provide new life for petroleum refineries, since 6 of the 18 projects and expansions are defined to be refinery conversions (International Energy Agency, 2021).

HVO's are produced via hydroprocessing, where biogenic oils and fats react with hydrogen under high pressure and catalysts to obtain paraffinic hydrocarbons equivalent to petroleum diesel. Hydrogen consumption and product yield of the process depend on reaction pathways that are controlled with catalyst choice and process conditions. There are three major reaction pathways for hydrotreatment: deoxygenation, decarbonylation, and decarboxylation, as Figure 19 shows. Deoxygenation has the highest hydrogen consumption but also resulting in the largest diesel yield with H<sub>2</sub>O as by-product. Decarbonylation has lower hydrogen consumption with lower diesel yield, releasing CO and H<sub>2</sub>O as by-product. Decarboxylation does not consume any hydrogen, while resulting in diesel yield equivalent to decarbonylation with CO<sub>2</sub> as by-product.



**Figure 19.** The three main hydrotreatment pathways to produce hydrotreated vegetable oils. (Kiefel & Lüthje, 2018)

Decarboxylation produces an exhaust stream with high CO<sub>2</sub> concentration (>90 %) that could be applicable for inherent CO<sub>2</sub> capture, requiring only some conditioning to produce high purity CO<sub>2</sub>. Some sulphur may be present in the exhaust stream as with some catalysts  $H_2S$  is added to the feed stream to avoid catalyst deactivation (Kiefel & Lüthje, 2018). Excess water can be reduced to low concentrations using compression and inter-stage cooling or more effective methods like liquid or solid desiccants. If CO is present, a water-gas shift reaction could be used to convert CO to CO<sub>2</sub>, producing a stream of  $H_2$  and CO<sub>2</sub> that could be separated, for instance, using pressure-swing adsorption. Although carbon capture in HVO production seems a promising, low-cost source of biogenic CO<sub>2</sub>, any activity related to carbon capture in HVO production has yet not been reported.
## 4.3 Industrial CO<sub>2</sub> sources with high carbon capture potential in Finland

In E-Fuel we examine forest industry, petroleum refineries and biorefining processes as potential  $CO_2$  supplies for CCU in Finland. Carbon capture potential of these industries in Finland were evaluated using a scoring matrix based on key performance indicators (Table 7). Results of the evaluation are presented in Table 10. **Table 10.** Carbon capture potential of various industrial CO<sub>2</sub> sources in Finland assessed using a scoring matrix on key performance indicators (KPI).

KPI	Pulp and paper mills		Pe	Petroleum refineries (excl. SMR)		Steam methane reforming		Ethanol fermentation		Hydrotreated vegetable oils	
Annual CO <sub>2</sub> emissions of the industry in Finland	2	20.6 Mtpa (2020)	1	2.9 Mtpa (2020)	1	Estimated based on facilities in Finland	0	18 ktpa (2017)	0	97.5 ktpa (est.)	
Onsite CO <sub>2</sub> emissions of an average Finnish facility/complex	2	1 Mtpa (average of facilities reported in E-PRTR)	2	2.7 Mtpa (Neste Kilpilahti)	1		0		0		
Industry trend in Finland by 2030	2	Capacity to grow, e.g., Metsä Fibre Kemi bioproduct mill	1	Capacity expected to remain similar	1	Capacity expected to remain similar	2	Capacity expected to grow, e.g., Bioenergo Pori and NordFuel Haapavesi	1	Capacity expected to remain similar	
Average CO <sub>2</sub> concentration of the emission point source(s)	0	12–13 % (recovery and power boiler) 20 % (lime kiln)	0	8–10 % (heaters) 3–5 % (utilities) 10–20 % (FCC)	1	30–45 % (PSA ex- haust stream)	2	>90 %	2	>90 % (decarboxyla- tion)	
Degree of carbon capture implementation	2	Industrial deploy- ment: e.g., Saipem at Resolute's kraft pulp mill in Quebec, Can- ada (TRL 8)	2	Commercial: e.g., Si- nopec at Qilu refin- ery, China	2	Commercial: e.g., Air Products Port Arthur and Linde Kilpilahti	2	Commercial: widely used in the US to provide CO <sub>2</sub> for en- hanced oil recovery	0	No reported activity	
System integration challenges (e.g., equipment size limitations, energy integration, utility and waste streams)	1	Requires post-com- bustion capture retro- fit. Steam supply may be inadequate, and an auxiliary boiler may be required if the re- covery boiler is tar- geted.	1	Several point sources of CO <sub>2</sub> , often limited space available, unique site configura- tions for which it is difficult to create a standard solution for CO <sub>2</sub> capture.	1	Requires PSA-based capture or solvent- based CO <sub>2</sub> scrubbing	2	Straightforward inte- gration, requiring only dehydration and purification of the ex- haust stream.	2	Straightforward inte- gration expected if the exhaust stream is not mixed with other streams, requiring only dehydration and purification.	
Natural origin of the CO <sub>2</sub>	1	>90 % biogenic	0	Fossil	0	Fossil	1	Biogenic	1	Biogenic	
Total score (max. 13)	10	High potential	7	Moderate potential	7	Moderate potential	9	High potential	6	Moderate potential	

Based on the chosen key performance indicators, pulp and paper mills and ethanol fermentation offer the highest carbon capture potential of the reviewed industries.

Pulp and paper mills yield high potential for bio-CCUS; the mills emit high quantities of biogenic  $CO_2$ , the industry is stable and has growth potential, and there is ongoing carbon capture activity in forest industry with successful demonstration projects. Also, the mills often have good preconditions regarding energy availability and logistics. Disadvantages include low  $CO_2$  concentration of the emission point sources and moderate difficulty of system integration, which makes carbon capture more costly than, for instance, in processes with high  $CO_2$  concentration exhaust streams and straightforward integration.

Ethanol fermentation is a low hanging fruit of bio- $CO_2$  regarding cost, but with low quantitative potential. Fermentation produces an exhaust stream with high concentration of biogenic  $CO_2$ , enabling low capture cost with little work required. Carbon capture from fermentation is also mature with decades of experience in the US. However, ethanol fermentation capacity in Finland is low, although new investments are expected to take place soon.

Petroleum refineries have high quantitative capture potential per facility and good preconditions for energy availability and logistics. However, carbon capture implementation is not appealing due to the fossil origin of the carbon, low CO<sub>2</sub> concentration exhaust streams that are distributed over several point sources at the site, and unique and hard-to-standardize site configurations.

Steam methane reformers have moderate quantitative capture potential per unit, exhaust streams with moderately high  $CO_2$  concentration, and commercial maturity in carbon capture. However, fossil origin of the  $CO_2$  and outlook of natural gas reforming amidst the growing green hydrogen capacity reduce the appeal.

Hydrotreated vegetable oil production based on decarboxylation emits a high  $CO_2$  concentration exhaust stream with potential to capture bio- $CO_2$  at low-cost and little effort. Low quantitative capture potential and lack of maturity in carbon capture reduce its relevance at national level, although still being promising regarding future sources of bio- $CO_2$ .

## 5 CONCLUSIONS

CCUS consists of several stages that can be generally divided into source characterization, capture or separation, purification, compression or liquefaction, interim storage, transportation, and utilization or geological storage. Stages required in CCUS are case-specific and may alter between different value chains depending on properties of the source stream, capture technology in use, location, logistical readiness and end-use of the CO<sub>2</sub>. A CCS value chain consisting of post-combustion capture, conditioning, transport, and storage yields a total cost ranging around  $42-161 \notin tCO_2$ , with the cost primarily depending on CO<sub>2</sub> concentration of the emission source, scale of operation, and required stages of logistics. Capture is typically the most impactful stage on cost, with post-combustion capture from dilute streams accounting for 50–60 % of total costs in CCS. Natural inherent capture/purification from high CO<sub>2</sub> concentration sources offers potential for significantly lower capture costs, but only few emissions point sources are of such nature.

There are several industrial emission point sources applicable for carbon capture and several technology options for capturing CO<sub>2</sub>. Therefore, finding the most cost-effective pathways for carbon capture in each application should be examined case-by-case. Selection of a suitable capture technology for a certain application is determined by operating conditions and desired capture performance regarding CO<sub>2</sub> purity and capture efficiency. Feasibility of implementation and techno-economic performance of carbon capture depends on factors like emission stream characteristics, available energy streams on site (steam, low-grade heat, electricity, cooling), equipment size restrictions, required emission and waste management, and other auxiliary demands. Also, additional treatment (e.g., cooling, purification, compression) may be required before and/or after capture depending on the emission source and the capture technology in use.

Several technology options are available and in development for carbon capture. Post-combustion capture is the most promising method of carbon capture for industrial applications due to retrofittable nature and wide applicability of the technologies. In post-combustion capture, scrubbing technologies using amine absorbents are proven, high-performing option with commercial maturity and several technology suppliers available, yielding a low risk of implementation. However, amines suffer from thermal, oxidative, and impurity-related degradation that leads to toxic degradation products, corrosivity and high regeneration energy requirement. Some alternative technologies with more eco-friendly nature and improved performance vs. amines have emerged to TRL 8–9 and have become reasonable options to consider for carbon capture implementors at commercial level. Carbonate salt absorbents (e.g., hot potassium carbonate and enzyme-enhanced K<sub>2</sub>CO<sub>3</sub>) are currently one of the most promising technologies to replace amines in similar applications of post-combustion capture. Several other technologies like solid sorbent processes, membranes, cryogenic separation, and fuel cell systems are on the brink of commercialization at TRL 6–7, but the risk of implementation is currently too high for an industrial party seeking a proven, commercial technology for carbon capture. As carbon capture requires energy integration and other utility demands, feasibility and techno-economic performance of carbon capture is highly case-specific.

Carbon capture potential of forest industry, petroleum refineries and biorefineries in Finland were evaluated by developing a scoring system based on key performance indicators. Based on the scoring results, pulp mills and ethanol fermentation plants yield the most potential for carbon capture implementation. Pulp mills have high potential for bio-CCUS as there is high quantities of biogenic CO<sub>2</sub> available, the industry is stable and has growth potential, and there are successful demonstration projects and ongoing research and development activity related to carbon capture. Due to low CO<sub>2</sub> concentration of the exhaust streams in pulp mills, moderate effort with a specific capture equipment is required for system integration and long-term commitment for the storage or utilization project is needed. High CO<sub>2</sub> concentration sources, e.g., exhaust streams from ethanol fermentation and HVO production, offer the lowest hanging fruits regarding capture cost, but quantitative capture potential of such sources is in Finland low. These sources could be used to provide low-cost CO<sub>2</sub> for in-situ CCU at small-scale with relatively low integration effort and little economic commitment. Petroleum refineries have low appeal for carbon capture as the fossil-based CO<sub>2</sub> emissions are distributed over several point sources, and as the site configurations are often unique and difficult to standardize for carbon capture. Capturing CO<sub>2</sub> from steam methane reformers yields lower capture cost vs. combustion processes but the fossil origin of carbon and outlook of steam methane reforming amidst the growing green hydrogen capacity reduces the appeal of carbon capture implementation compared to other options.

To evaluate feasibility and economics of a certain technology in a certain application, a detailed case-study with process modelling together with a well-known benchmark technology is required. As logistics yields significant costs, location and readiness for  $CO_2$  logistics should be carefully considered when screening potential emission point sources for carbon capture implementation. Joint development between industrial stakeholders is important for speeding up the introduction of CCUS in Finland. Pilot and demonstration campaigns at industrial sites are needed to develop shared knowledge and competence on carbon capture in the field of industry.

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