

LUT University

LUT School of Energy Systems

Energy Technology

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**Review on Post-Combustion Carbon Capture Technologies
and Capture of Biogenic CO₂ Using Pilot-Scale Equipment**

Master's Thesis

Examiners: Professor, D.Sc. (Tech.) Esa Vakkilainen

D.Sc. (Tech.) Katja Kuparinen

Supervisors: M.Sc. (Tech.) Janne Kärki

M.Sc. (Tech.) Timo Leino

ABSTRACT

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103 pages, 11 figures, 23 tables and one appendix

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Keywords: BECCU, CCU, bioenergy with carbon capture and utilization, biogenic carbon capture, post-combustion carbon capture, CO₂ utilization, pilot experiment

Bioenergy with carbon capture has emerged as a promising technological pathway in the pursuit of carbon-neutral energy production and industry. However, profitability of carbon capture remains as a large barrier in wide-scale deployment and as incentives are lacking benefit has to be sought, for instance, via CO₂ utilization.

In this thesis biogenic CO₂ emission sources as well as status and performance of state-of-the-art and emerging post-combustion capture technologies were reviewed. Additionally, absorption-based post-combustion capture technologies developed by CarbonReUse, Kleener Power Solutions and VTT were experimented at pilot-scale by using synthetic gas mixtures, biogenic flue gases and raw biogas.

Multiple industrial sources of biogenic CO₂ emissions into which carbon capture could possibly be applied were recognized. Numerous different carbon capture technologies based on various capture methods are currently in development with multiple large-scale demonstration projects ongoing and planned for the near future. Capture cost in post-combustion carbon capture is currently at around 34–80 €/tCO₂.

In the pilot tests, all tested technologies were proven functional in carbon capture at realistic conditions, while achieving promising results regarding capture performance. However, further work is required to evaluate the economic performance and commercial potential of the tested technologies.

TIIVISTELMÄ

LUT University

School of Energy Systems

Energiatekniikan koulutusohjelma

Onni Linjala

Katsaus polton jälkeiseen hiilidioksidin talteenottoon kehitettyihin teknologioihin sekä bioperäisen hiilidioksidin talteenotto pilot-mittakaavan koelaitteistolla

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Avainsanat: BECCU, CCU, bioenergia, bioperäisen hiilidioksidin talteenotto, polton jälkeinen hiilidioksidin talteenotto, hiilidioksidin hyötykäyttö, pilottikoe

Bioperäisen hiilidioksidin talteenotto on noussut lupaavaksi teknologiseksi ratkaisuksi hiilineutraalin energiantuotannon ja teollisuuden tavoittelussa. Talteenoton kannattavuus on kuitenkin suuri haaste sen laajamittaisessa käyttöönotossa ja koska kannustimia ei ole, on hyötyä haettava esimerkiksi hiilidioksidin hyötykäytön kautta.

Tässä työssä tarkasteltiin bioperäisten hiilidioksidipäästöjen lähteitä sekä polton jälkeisen talteenottoon kehitettyjen teknologioiden tilaa ja suorituskykyä. Lisäksi CarbonReUsen, Kleener Power Solutionsin ja VTT:n kehittämiä absorptioon perustuvia talteenottoteknologioita testattiin pilottimittakaavassa polton jälkeisessä talteenotossa käyttäen synteettisiä kaasuseoksia, bioperäisiä savukaasuja sekä raakaa biokaasua.

Työssä tunnistettiin useita bioperäisiä hiilidioksidipäästöjen lähteitä, joihin voitaisiin mahdollisesti soveltaa hiilidioksidin talteenottoa. Kehitteillä on lukuisia erilaisiin ilmiöihin perustuvia talteenottoteknologioita ja useita suuren mittakaavan demonstraatiohankkeita on meneillään ja suunniteltuna lähitulevaisuuteen. Hiilidioksidin talteenottokustannus polton jälkeisessä talteenotossa on tällä hetkellä noin 34–80 €/tCO₂.

Pilottikokeissa testatut teknologiat todistettiin toimivaksi todenmukaisissa olosuhteissa, saavuttaen myös lupaavia tuloksia suorituskyvyn osalta. Lisätutkimusta kuitenkin tarvitaan, jotta teknologioiden taloudellinen suorituskyky ja kaupallinen potentiaali voidaan tarkemmin selvittää.

PREFACE AND ACKNOWLEDGEMENTS

This thesis is conducted for the VTT Technical Research Centre of Finland as a part of the BECCU project. Led by VTT and financed primarily by Business Finland, BECCU is a co-operative project between a consortium formed by several Finnish companies and stakeholders from multiple industries together with international research partners. Objective of BECCU is to evaluate feasibility of a value chain utilizing captured industrial biogenic CO₂ emissions and clean hydrogen in CO₂-derived polyol production.

I wish to express my gratitude towards my supervisors and advisors Janne Kärki, Timo Leino, Kristian Melin and Tuula Kajolinna for their valuable assistance and encouragement. I am grateful for the trust and responsibility that I was given. I wish to thank Professor Esa Vakkilainen for his guidance on this thesis and for all the knowledge and expertise he has passed on during my studies. I also wish to thank the personnel of Kleener Power Solutions and CarbonReUse Finland for their co-operation in this project.

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Onni Linjala

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SYMBOLS AND ABBREVIATIONS

Abbreviations

AMP	2-amino-2-methyl-1-propanol
ASU	Air Separation Unit
BAT	Best Available Technology
BECCU	Bioenergy with Carbon Capture and Utilization
BECCS	Bioenergy with Carbon Capture and Storage
BtL	Biomass-to-Liquid
CFB	Circulating Fluidized Bed
CHP	Combined Heat and Power
DeCO	Decarbonylation
DeCO ₂	Decarboxylation
ESA	Electrical-Swing Adsorption
ESP	Electrostatic Precipitator
GHG	Greenhouse Gas
HDO	Deoxygenation
HEFA	Hydroprocessed Esters and Fatty Acids
HVO	Hydrotreated Vegetable Oil
LCOE	Levelized Cost of Electricity
L/G	Liquid-to-Gas -ratio
MCFC	Molten Carbonate Fuel Cell
MEA	Monoethanolamine
MSR	Microwave-Swing Regeneration
NGCC	Natural Gas Combined Cycle
NET	Negative Emissions Technology
PAH	Polycyclic Aromatic Hydrocarbons

PM	Particulate Matter
PZ	Piperazine
PSA	Pressure-Swing Adsorption
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
SOFC	Solid Oxide Fuel Cell
TRL	Technology Readiness Level
TSA	Temperature-Swing Adsorption
VOC	Volatile Organic Compounds
VSA	Vacuum-Swing Adsorption

Symbols

\dot{v}	volumetric flow rate	[m ³ /s, l/min]
x	volumetric concentration	[vol-%]

Indices

<i>in</i>	inlet
<i>out</i>	outlet

1 INTRODUCTION

The ever-rising greenhouse gas emissions with global warming effect have created an alarming need for a shift towards more sustainable actions and policies in all sectors of society. Majority of these harmful emissions derive from energy utilization, such as power and heat production, energy use in transportation and other energy-intensive industrial processes. Stricter emissions standards are required for these sectors to neutralize the adverse effects on climate. Inability to reach significant emission reductions will accelerate pace of global warming as energy demand continues to increase.

In their Special Report on Global Warming of 1.5 °C (2018) IPCC estimate carbon budget – i.e., the tolerable amount of emissions – for a 66 % chance to avoid global warming of 1.5 °C to be 420 GtCO₂ from 2018 onwards. According to UNEP (2019), the global greenhouse gas emission rate with land-use change emissions included was 55.3 GtCO₂ in 2018. Thus, the IPCC's carbon budget is equivalent to roughly 8 years of global emissions from 2018 onwards. Based on these estimates there is very little time and practically a non-existing chance to change the course of global warming from exceeding the limit of 1.5 °C, worsen by the fact that global GHG emissions are in a rising trend. IPCC states the limit of 1.5 °C will very likely be exceeded. With current policies – including implementation of Paris Agreement contributions – global warming is estimated to reach around 2.8–3.2 °C by the end of the century (CAT 2019; UNEP 2019).

Clean and cost-competitive energy sources (e.g., solar and wind) are already available to replace the emissive energy sources. However, rapid transformation of global energy system and energy-intensive industries to solely base on these clean energy alternatives is challenging. Too rapid system transition could endanger the security of supply due to high variability of renewable energy, especially since efficient and large-scale energy storages are still lacking (Heuberger & MacDowell 2018). Other slowing factors on system transition include lack of determined and global-scale policymaking, slow construction pace of electrification infrastructure and subsidies for fossil-fuels. Nevertheless, striving for a fully renewable and sustainable energy system should remain

as a top priority and it should be pursued urgently to neutralize the undeniably harmful effects caused by non-renewable energy. According to a study by LUT and EWG (Ram et al. 2019) a more cost-effective global energy system based solely on renewables with net-zero greenhouse gas emissions could be reached before 2050.

1.1 The role of carbon capture in future energy systems

Carbon capture can offer a complementary solution to climate change mitigation by capturing carbon dioxide (CO₂) emissions from large emission point sources, preventing to release the CO₂ into the atmosphere. Initially, carbon capture has been developed to reduce emissions in fossil-based energy conversion processes. However, it has not reached commercial popularity due to high costs and weak competitiveness against renewable alternatives (Sgouridis et al. 2019).

When combined with applications that generate biogenic emissions (i.e., emissions that originate from renewable biomass), the climate benefit of carbon capture is higher. Fossil-based carbon capture merely reduces the amount of released fossil-based emissions, which still increases the amount of GHG's in the atmosphere since all of the emissions cannot be typically captured. Biogenic carbon capture targets the carbon, which is in natural circulation between the atmosphere and growing biomass. Depending on how the captured biogenic CO₂ is dealt with, carbon neutrality or even negative emissions can be achieved. Negative emissions can be achieved by storing the captured biogenic CO₂ in a way that prevents it from returning into the atmosphere – a concept known as BECCS (bioenergy with carbon capture and storage). In theory, even if the carbon budget for the 1.5 °C target was momentarily exceeded, it could be reached afterwards with negative emissions achieved via biogenic carbon capture. However, too much reliance on negative emissions should be avoided since many of these technologies are still unproven at industrial-scale (EASAC 2018). The captured CO₂ can also be utilized directly or indirectly as feedstock for value-added products, like chemicals, fuels, or materials via a concept known as BECCU (bioenergy with carbon capture and utilization). BECCU can offer significant climate benefit by replacing conventional unsustainable production that

is based on fossil sources with production that utilizes biogenic CO₂ as feedstock. Further research and industrial-scale demonstration are still required to unravel the true potential of carbon capture technologies.

Role of carbon capture is emphasized in several climate scenarios. For instance, it plays a crucial role in three of the four pathways presented in IPCC's SR 15 (2018). An interquartile range of 550–1017 GtCO₂ is estimated for cumulative captured carbon until 2100, of which bioenergy applications account for 364–662 GtCO₂. Also, IEA's Sustainable Development Scenario, targeting to limit temperature increase to well below 2 °C, includes rapid commercial deployment of carbon capture and storage or utilization in energy and industrial sectors. The scenario is targeting to annually capture 310 MtCO₂ in 2030 and 1320 MtCO₂ in 2040 in the power sector (IEA 2019b) and 450 MtCO₂ in 2030 and 1030 MtCO₂ in 2040 in the industrial sector (IEA 2019a). Trend to reach these targets is currently way off track: in 2019 capture capacity was only 2.4 MtCO₂ in the power sector and 32 MtCO₂ in the industrial sector (IEA 2019a; IEA 2019b).

1.2 Concept of BECCU

Bioenergy with carbon capture and utilization (BECCU) is a concept that combines bioenergy production, carbon capture, and utilization of the captured CO₂. It offers a way for carbon-neutral energy production, while producing feedstock for various CO₂ utilization applications. The objective is to capture biogenic CO₂ from side-streams of processes using biomass either directly or indirectly for energy production. The captured CO₂ can be used as feedstock to produce value-added products like chemicals, fuels, and materials, thus offering more sustainable alternatives for conventional fossil-based products. If proven viable after further research and industrial-scale demonstration, value chains based on the concept of BECCU offer a potential solution to reach emission reductions alongside energy production by replacing fossil-based products with sustainable biogenic alternatives. Potential of BECCU is increasing due to the significant and constantly growing role of bioenergy in the global energy supply as a source of renewable energy. The potential is especially high in countries with strong bioeconomies,

such as in Finland, which has a lot of bioenergy production and a strong forest industry sector.

Combustion of solid biomass is globally a traditional way to produce energy, but also liquid biofuels, biogas and the use of biogenic wastes are conquering a constantly growing share of the modern energy market. In 2018, share of bioenergy in global final energy consumption was 12 % (45.2 EJ), making it currently the largest renewable source of energy in global energy supply (REN21 2020). CO₂ emission factor for biomass is generally around 100 tCO₂/TJ (Alakangas et al. 2016). Thus, with a rough estimate the global bioenergy consumption of 45.2 EJ results to around 4.5 Gt of biogenic CO₂ emissions annually. These emissions can be considered as target emissions of BECCU and BECCS.

1.3 Objectives of the thesis

This thesis is conducted as part of VTT's BECCU project. Aim of the project is to evaluate feasibility and performance of a value chain utilizing industrial biogenic CO₂ emissions and clean hydrogen in CO₂-derived polyol production. In this thesis the value chain is examined in terms of biogenic CO₂ emissions sources and carbon capture technologies via a literature review and pilot-scale carbon capture experiments. The main objectives of the thesis are to:

- 1) Identify typical operating conditions in various sources of biogenic CO₂ emissions and evaluate the applicability of these sources to carbon capture.
- 2) Review the status and techno-economic performance of state-of-the-art and emerging carbon capture technologies, focusing on post-combustion capture.
- 3) Present results from the pilot-scale carbon capture experiments that were conducted as part of VTT's BECCU-project during autumn of 2020 by using three different absorption-based carbon capture technologies and multiple CO₂ sources.

- 4) Evaluate performance, applicability and scalability of technologies tested in the pilot experiments and compare the results to the technologies examined in the literature review.

1.4 Structure of the thesis

The thesis is divided into a literature review (Chapters 1–4) and an experimental part that focuses on pilot-scale carbon capture tests (Chapters 5–7). The first chapter introduces the subject, presents the research methods and summarizes the main objectives of the thesis. The second chapter reviews the typical operating conditions in sources of biogenic CO₂ emissions. The third chapter provides an overview on the various stages of a value chain based on the concept of BECCU. In the fourth chapter, status and performance of various state-of-the-art and emerging carbon capture technologies are reviewed, with a focus on post-combustion capture. In the fifth chapter objectives and arrangements of the pilot-scale carbon capture tests are presented, whereas the sixth chapter presents the test results. Performance, applicability and scalability of the tested technologies are evaluated in the seventh chapter. Summary of the work is presented in the eighth chapter.

2 BIOGENIC CO₂ SOURCES IN ENERGY PRODUCTION AND ENERGY-INTENSIVE INDUSTRIES

In this thesis carbon capture is examined from perspective BECCU, thus focusing on carbon capture from large point sources of biogenic CO₂ emission with a further objective to utilize the captured CO₂. The target industries are the bioenergy sector and energy-intensive industries that utilize biomass. Fossil-based processes are not addressed since renewable and cost-competitive alternatives are often available for these processes. However, data from fossil fuel -based carbon capture projects is used to evaluate techno-economic performance of various capture technologies due to the roughly similar operating conditions.

This chapter focuses on reviewing various processes of the chosen target industries to recognise typical conditions in possible carbon capture applications. Objective is to identify typical gas compositions, occurring impurities, and how operating conditions and choice of fuel or feedstock affect these factors. By understanding the conditions, suitable carbon capture technologies that could be implemented into the processes can be more easily identified.

2.1 Biomass combustion

Combustion of biomass is the most traditional way to produce energy. It is used in heat generation, power production and in combined heat and power (CHP) systems. At industrial-scale, biomass is typically combusted in a boiler, where heat released in combustion is transferred to water circulating in walls of the boiler to generate either steam or high temperature water to produce power, heat, or both. Several boilers types with varying water-steam circulation systems, furnace structures and combustion methods are used.

Primarily solid biomass is used as fuel, but alternative sources are also gaining popularity. Globally, solid biomass accounted for an 86 % share of total primary energy supply of biomass in 2017, whereas the share of various biogenic wastes was roughly 5 %.

Additionally, agricultural residues have great potential: theoretical energy potential of agricultural residues that currently are not utilized is estimated to be 18–82 EJ, which would account for a 3–14 % share of the current global total energy supply. (WBA 2019.)

2.1.1 Biomass composition

Chemical composition of biomass is the most important factor affecting flue gas composition. Many types of feedstock can be used as fuel in combustion processes such as wood-based biomass, herbaceous and agricultural biomass, as well as biogenic wastes. Different biomass types have varying chemical compositions, thus resulting in varying flue gas compositions in combustion. Mean compositions for biomass types that are typically used in bioenergy applications are presented in Table 2.1 by using proximate and ultimate analysis.

Table 2.1. Mean composition values (%) for biomass types typically used in bioenergy applications. Ultimate analysis values are measured for dried and ash-free biomass, except for Cl which is measured for dried biomass. (Vassilev et al. 2010.)

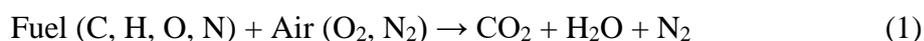
Method	Component	Wood and woody biomass	Herbaceous and agricultural biomass	Contaminated biomass (e.g., wastes, sludges)
Proximate analysis	Volatile matter	62.9	66.0	63.7
	Fixed carbon	15.1	16.9	8.0
	Moisture	19.3	12.0	11.6
	Ash	2.7	5.1	16.7
Ultimate analysis	C	52.1	49.9	53.6
	O	41.2	42.6	37.0
	H	6.2	6.2	7.3
	N	0.4	1.2	1.7
	S	0.08	0.15	0.46
	Cl _(db)	0.02	0.20	0.31

All biomass types generally contain a lot of volatile matter. Other components, like moisture and ash content, may significantly vary depending on the biomass type. Wood-based biomass can be considered as the purest type of biomass since it has the lowest

content of impurities like sulphur, chlorine and ash components. In herbaceous biomass, like grasses and straws, these contents are slightly higher, whereas biogenic wastes and sludges have significantly higher contents of these impurities. CO₂ concentration of the flue gas is related to the carbon content of the fuel. All biomass types have roughly similar carbon contents at around 50 %, but the amount of fixed carbon, i.e., non-volatile carbon varies.

2.1.2 Flue gas properties

In combustion, the fuel reacts with combustion air in high temperature and releases energy in formation of combustion compounds (i.e., flue gas). When the fuel composition is known, the expected flue gas composition can be solved via stoichiometry. A simplified stoichiometric equation for a combustion process is presented in Equation 1.



In actual combustion processes both fuel and combustion air contain more elements than is presented above and more combustion compounds are formed. Fuels contain elements like sulphur, chlorine, and metals, some of which take part in the combustion process creating compounds like sulphates, chlorides, and metal oxides (Jones et al. 2014). Some of these compounds are harmful and can cause damage to the equipment and environment. Also, due to lack of optimal conditions, the combustion processes are partly incomplete meaning that all the carbon does not burn into carbon dioxide. Concentration of CO₂ in flue gases is relative to the carbon content of the fuel. Typically, it ranges somewhere around 8–15 % in biomass combustion.

Exit temperature of flue gas in a thermal power plant is typically around 150–180 °C, but if a wet flue gas scrubber is used, significantly lower exit temperatures at around 50–70 °C occur (Zagala & Abdelaal 2017). Flue gas exit pressure is slightly above

atmospheric pressure. To avoid water corrosion and condensate formation in the stack, exit temperature is limited by the water dew point of the flue gas (Kaltschmitt 2019), which is typically 40–60 °C (Huhtinen et al. 1994). When using sulphur-rich fuels, another limiting factor for exit temperature is the acid dew point. Vapour containing SO₃ condensates in a much higher temperature than water dew point and forms highly corrosive sulfuric acid (H₂SO₄). Sulphuric acid dew point typically ranges around 110–160 °C (Hupa et al. 2017). In biomass combustion, sulphuric acid formation must be noted with fuels of high sulphur content, like wastes and possibly agricultural residues. Chemically untreated wood fuels rarely face this problem due to naturally low sulphur contents. (Kaltschmitt 2019.)

2.1.3 Impurities in biomass combustion

Common impurities and pollutants that occur in biomass combustion flue gas are sulphur and chlorine compounds, nitrous oxides and other nitrogen compounds, carbon monoxide, unburnt matter, volatile organic compounds, and smoke containing particulate matter and ash (Jones et al. 2014). Chlorine and sulphur can be found in biomass as organic compounds and as inorganic salts. In combustion process, chlorine is released as KCl, which causes formation of deposits on the boiler surfaces, and as HCl, which has a corrosive effect due to its strong acidity. Sulphur releases mainly as SO₂, which is an acidic air pollutant. Small amount of SO₂ is oxidized into SO₃, which further reacts with water to form highly acidic H₂SO₄. Nitrogen oxides (NO_x) release in combustion mostly as NO of which some converts to NO₂ when reacting with oxygen. NO_x emissions cause acid rain, harmful tropospheric ozone and have toxic health effects. Also, some nitrous oxide (N₂O) is formed, which is a direct greenhouse gas. Carbon monoxide (CO) is a toxic gas formed in incomplete combustion due to lack of oxygen. In addition to its toxicity, a significant amount of energy is not released if the carbon does not fully burn to carbon dioxide. Unburnt matter like methane and other volatile organic compounds (VOC's), as well as polycyclic aromatic hydrocarbons (PAH's), occur in incomplete combustion and cause direct and indirect greenhouse effects and health problems. Some

inorganic elements release as particulate matter, which can have harmful health effects, such as respiratory problems and carcinogenic effects. (Jones et al. 2014; Kaltschmitt 2019). Table 2.2 presents typical emission levels from combustion of woody biomass with different boiler types.

Table 2.2. Typical emissions levels (mg/Nm³) from combustion of woody biomass. (Vakkilainen 2016.)

Boiler type	Grate	BFB	CFB	Recovery boiler
CO ₂	150 000–~200 000	150 000–~200 000	150 000–~200 000	210 000–~240 000
CO	100–600	100–250	50–100	50–200
H ₂ S	3–20	1–20	1–5	0–4
SO ₂	250–400	30–150	5–50	0–5
NO _x	100–400	250–450	150–250	150–250
N ₂ O	0–1	4–8	5–10	0–1
HF	1–5	1–5	1–5	0
HCl	5–30	5–30	5–30	0–2
Dust, ESP	10–20	10–20	10–20	10–50
Dust, FF	1–5	1–5	1–5	n.a.
Dioxins and furans	<0.0001	<0.0001	<0.0001	<0.00001

Boiler type, which is mainly determined by scale and fuel type, affects, for instance, on how complete the combustion process is. Large-scale boilers that are typically equipped with fluidized beds have better mixing properties due to the more dynamic nature of the bed, thus resulting in more complete combustion. The CO₂ level in combustion of woody biomass is often quite similar regardless of the boiler type, at around 8–14 %.

2.1.4 Effect of combustion conditions on impurity formation

Combustion temperature above 1300 °C significantly increases thermic NO_x formation, whereas too low temperature (<800 °C) leads to incomplete combustion, i.e., unburnt matter and toxic CO emissions. More complete combustion can be achieved by using a secondary air flow to improve mixing, sufficient residence time of gas compounds and excess air. Excess combustion air means using more air than the combustion process would require in theory. Increasing the amount of combustion air increases the amount of oxygen, which is needed for the carbon to fully combust to CO₂. On the other hand,

too much excess air can result in increasing amount of NO_x emissions since the amount of nitrogen increases as well. This occurs especially in high burning temperatures. NO_x emissions are typically reduced with staged combustion (i.e., air or fuel staging), which means creating separate combustion stages in the furnace by supplying air/fuel at multiple locations. Staged combustion increases the residence time of compounds in the combustion area leading to more complete combustion, while also allowing better control of the combustion process. Boiler type has a large effect on the combustion conditions. For instance, fluidized bed boilers generally offer significantly better control over the combustion conditions than grate-firing boilers. Also, different burner configurations for different conditions and fuels can be used to reach suitable combustion conditions. (Kaltschmitt 2019.)

2.1.5 Flue gas purification and emission control

National and regional policies have set emission limits that energy production facilities must fulfil. These limits aim to ensure that operation of the facilities follow the BAT-principle (Best Available Technology) to minimize harmful effects of pollutants on environment and society. Meeting these emission limits often requires using flue gas purification technologies or specific combustion configurations. Flue gas purification is typically done by using flue gas scrubbers, impurity-binding additives, electrostatic precipitators, and filters. Some purification methods can be combined with heat recovery to improve the energy efficiency of the facility.

Common methods to remove NO_2 from the flue gas stream are SCR (Selective Catalytic Reduction) or SNCR (Selective Non-Catalytic Reduction). In SCR a reactant (e.g. ammonia/urea) is fed to the flue gas stream, which is then led to a catalytic reactor where NO and NO_2 compounds reduce to H_2O and N_2 (Huhtinen et al. 1994). SCR is an effective method, reducing 80–95 % of the NO_x emissions. In SNCR a catalytic reactor is not used, but a reactant (typically ammonia) is fed to the combustion chamber, causing reduction reactions of the NO_x 's due to high temperature (850–1000 °C). SNCR is not as effective,

achieving a 30–60 % reduction in NO_x emissions. Also, it is a costly method and sensitive to changes in combustion conditions and fuel properties. (Zagala & Abdelaal 2017.)

Sulphur emissions are often removed with methods based on absorption, adsorption, or catalysis, typically by using flue gas scrubbing. These methods can be categorized into wet, semi-dry and dry processes as well as regenerative or non-regenerative processes. Most common and effective method is a non-regenerative wet absorption process, which is applicable for all fuel types. The flue gas is led to an absorber column, where wet absorbent is sprayed against the flue gas stream, often resulting in a desulphurization rate of >90 %. Wet scrubbers are commonly operated by using water, possibly with additive absorbent materials like calcium compounds (e.g., lime or limestone), which react with SO₂ to form slurry of calcium sulphite. The slurry is oxidized into calcium sulphate, concentrated, and dried to produce gypsum, which is utilizable for example in construction. In semi-dry processes, an absorbent slurry is sprayed to the flue gas stream as droplets to form dry calcium sulphate, which is collected from the bottom of the reactor or in a specific separator. Semi-dry processes have a good desulphurization rate (~85%) and compared to wet processes they are more cost-effective in small and low-usage boilers. Dry processes include methods like adsorption through sorbent injection into combustion chamber or flue gas duct, mixing sorbents into bed material, and dry reactor processes. Dry processes are generally simpler and cheaper, but not as effective, reaching a desulphurization rate of 30–50 %. (Zagala & Abdelaal 2017; Huhtinen et al. 1994.)

Particulate matter (PM) such as inorganic solid particles, soot, and liquid droplets travel in the flue gas as fly-ash and smoke. Several techniques can be used to remove PM emissions, most common ones being cyclones, electrostatic precipitators (ESP), fabric filters and scrubbing. In a cyclone a centrifugal force, generated with a spiral stream, drives the particles to the outer walls from where they move to the collector. Cyclones are not effective enough to be a sole PM purification method, but they are used with other purification methods to control dust emissions. ESP's utilize an electrostatic field to capture electronically charged particles, generally located before or after an air preheater. With fabric filters (e.g., polyester, fibre glass), particles are filtrated from the flue gas

stream, typically operating at a temperature level of 120–220 °C. Both ESP's and fabric filters are very effective and widely used techniques to remove PM emissions. Scrubbing is less effective and less popular, but it can be combined for example with desulphurization scrubbers. (Lecomte et al. 2017.)

2.2 Biogas

Biogas is a flammable and clean-burning gas mixture that is formed in anaerobic digestion of organic matter. By removing impurities, biogas can be upgraded into higher calorific value biomethane, which can be used as a sustainable alternative for fossil-based natural gas. CO₂ is formed in the digestion process as well as in combustion of biogas or biomethane. Therefore, carbon capture could be applied to raw biogas purification as well as biogas-fired combustion processes.

2.2.1 Composition of raw biogas

Chemical composition of biogas depends on the used feedstock and digestion conditions. Energy crops, residues and biogenic wastes are typically used as a feedstock for biogas production. Table 2.3 presents typical biogas compositions for feedstock sources that are commonly used in biogas production.

Table 2.3. Typical biogas compositions for various feedstock sources. (Carillo, cited in Huertas et al. 2011.)

Component (%)	Agricultural waste	Landfills	Industrial waste
CH ₄	50–80	50–80	50–70
CO ₂	30–50	20–50	30–50
N ₂	0–1	0–3	0–1
H ₂	0–2	0–5	0–2
O ₂	0–1	0–1	0–1
H ₂ S	0.7	0.1	0.8
CO	0–1	0–1	0–1
NH ₃	Traces	Traces	Traces
Siloxanes	Traces	Traces	Traces
H ₂ O	Saturation	Saturation	Saturation

Raw biogas consists mainly of methane and CO₂. Compared to flue gases, concentration of CO₂ in raw biogas is significantly higher, at around 20–50 %.

2.2.2 Impurities in raw biogas

Raw biogas can contain compounds that are toxic or have harmful impacts to equipment or environment and depending on the application, removal of these impurities may be required. Some impurities can be removed during biogas upgrading, but it may be necessary to purify the biogas in advance to avoid any impurity-caused damage to the upgrade equipment. Impurities that are commonly present in raw biogas are summarized in Table 2.4.

Table 2.4. Impurities that commonly occur in raw biogas. (Ryckebosch et al. 2011).

Impurities	Impacts
Moisture, H ₂ O	Corrosion due to acid formation with other compounds, condensation, freezing and accumulation of water in pipes
Hydrogen sulphide, H ₂ S	Corrosive and toxic, SO _x formation in combustion
Carbon dioxide, CO ₂	Calorific value reduction
Ammonia, NH ₃	Corrosive when dissolved in water, NO _x formation
Oxygen, O ₂	Corrosion, explosion risk
Halogens, Cl ⁻¹ , F ⁻¹	Corrosion in combustion engines
Dust	Deposition and clogging
Halogenated hydrocarbons	Corrosion due to combustion
Siloxanes	SiO ₂ and microcrystalline quartz formation in combustion, deposition and erosion

CO₂ is an inert gas, binding energy and lowering the efficiency of the combustion reaction. Thus, CO₂ lowers the calorific value of the biogas and increases transportation costs, which is why it is often removed alongside other impurities.

2.2.3 Biogas upgrading

By removing the impurities, raw biogas can be upgraded to higher calorific value biomethane, which is similar in composition to natural gas and suitable for natural gas grids if quality requirements are fulfilled. Depending on the application, also more inexpensive light upgrading methods can be used if high purity is not required. Due to harmful effects on the upgrading equipment, impurities are often removed before CO₂ separation with pre-treatment methods. Especially removal of H₂S is common and it's typically done with an absorption process, such as water or solvent scrubbing. (Tabatabaei & Ghanavati 2018.) The CO₂ removal can be done by using several different technologies. Conventional upgrading technologies often use water/solvent/chemical scrubbing, pressure swing adsorption (PSA) and membranes, but alternative technologies such as cryogenic separation and chemical hydrogenation are also emerging (Angelidaki

et al. 2018). Generally, the removed CO₂ is led into the atmosphere as incentives for carbon capture are lacking.

2.3 Liquid biofuel production

Liquid biofuels are currently the fastest growing form of bioenergy, having increased their production nearly sevenfold from beginning of the century. In 2017, liquid biofuels accounted for a 7 % share of total primary energy supply of biomass. (WBA 2019.) Biofuel production processes that possibly could be applicable for carbon capture are reviewed below.

2.3.1 Bioethanol

Bioethanol is the most common liquid biofuel, accounting for a 62 % share of global biofuel production (WBA 2019). It can be used as an alternative for conventional fuels, like gasoline. Bioethanol has been typically produced from biomass containing sucrose or starch, such as sugarcane and corn. However, conventional bioethanol production is often critiqued since it requires large land areas and endangers food security by competing of the same areas with food production. With more advanced technologies cellulosic biomass and biogenic wastes can be used as feedstock for bioethanol production. St1 is one of the leading developers of these advanced bioethanol production processes with their Etanolix, Cellunolix and Bionolix processes (St1 2020). These advanced processes are more sustainable since forestry residues as well as municipal and industrial wastes can be used to produce bioethanol.

Bioethanol is typically produced in a fermentation process, where sugars of the biomass are converted to ethanol. The process also consists of different pre-treatment methods to obtain fermentable sugars and after-treatment methods to ensure high ethanol quality. Exhaust stream from fermentation is nearly pure CO₂ (Fry et al. 2017) and if carbon capture is desired, specific carbon capture technology is not required. Amount of impurities in exhaust stream is also generally low and depending on the application only

minor purification, if none, is required. Typical impurities are organic compounds, such as ethanol and methanol, and sulphur compounds, such as H₂S and dimethyl sulphide. (Xu et al. 2010.) Since specific carbon capture technology is not required, CO₂ capture cost in bioethanol production processes is significantly lower than in combustion processes. Cost of CO₂ capture and compression alongside bioethanol production is estimated to be around 30 \$/tCO₂ (Sanchez et al. 2018). It is already at a mature level, having been used for decades in the U.S. to provide CO₂ for enhanced oil recovery.

2.3.2 Biomass-to-Liquid (BtL)

Biomass-to-Liquid refers to multi-phase processes producing synthetic liquid biofuels from biomass. Generally, the process involves gasification of solid biomass to produce syngas – a gas mixture consisting mainly of H₂, CO and CO₂. The syngas is purified and converted into liquid hydrocarbons or alcohols through various conversion processes, like the Fischer-Tropsch synthesis. (Kaltschmitt 2019.) Composition of the syngas depends on feedstock and gasification technology, as seen from Table 2.5.

Table 2.5. Typical compositions for wet syngas and dry syngas produced with different gasification technologies. (Mansfield & Wooldridge 2015; Rauch et al. 2014.)

Compound		Wet syngas	Dry syngas	Dry syngas	Dry syngas
		typical industrial applications	biomass oxygen gasification, entrained flow	biomass oxygen gasification, fluidized bed	biomass steam gasification, indirect
H ₂	vol-%	25–30	15–20	20–30	30–45
CO	vol-%	30–60	40–60	20–30	20–25
CO ₂	vol-%	5–15	10–15	25–40	20–25
H ₂ O	vol-%	2–30	-	-	-
CH ₄	vol-%	0–5	0–1	5–10	6–12
N ₂	vol-%	0–4	0–1	0–1	0–1
Ar, N ₂ , H ₂ S, COS, NH ₃ , Ash	vol-%	0–1	n.m.	n.m.	n.m.
Trace Impurities (e.g., Fe, Cl, Si, metals)	ppm	<100	n.m.	n.m.	n.m.
Tar	g/Nm ³	n.m.	<0.1	1–20	1–10

Typically, a water-gas shift reaction (Eq. 2) is used to improve the H₂/CO ratio of the syngas, which also increases CO₂ concentration.



The shift reaction increases CO₂ concentration of the syngas to 15–50 % (U.S. DOE n.d.). Carbon capture could be applied to the process after the shift reaction, by using various technologies applicable for pre-combustion capture, such as absorbents (See Section 4.1) and membranes (See Section 4.8).

2.3.3 Hydrotreated Vegetable Oils (HVO)

Hydrotreated vegetable oils, also known as hydroprocessed esters and fatty acids (HEFA) and renewable diesel (not to be mistaken with conventional biodiesel), are second-generation biofuels with great potential in the liquid biofuel market. HVO's are paraffinic hydrocarbons chemically equivalent to fossil diesel fuel and therefore suitable to replace fossil diesel fuel without any blending. Market for commercial HVO production is growing rapidly. The current market leader is Neste with their NEXBTL technology. Currently, Neste has capacity to produce 3 million tonnes of renewable diesel annually (Neste 2020).

HVO's are produced from oils and fats in hydroprocessing. Various plant- and animal-based oils, as well as oil-wastes, can be used as feedstock for HVO production. In the process, hydrogen is used to convert unsaturated compounds of oils or fatty acids to paraffinic hydrocarbons via a hydrotreatment process (Figure 2.1). Bio-based propane is also formed as a by-product. After the hydrotreatment, fuel quality is improved via hydrocracking/isomerisation to correspond properties of conventional fuels. (ETIP 2020.)

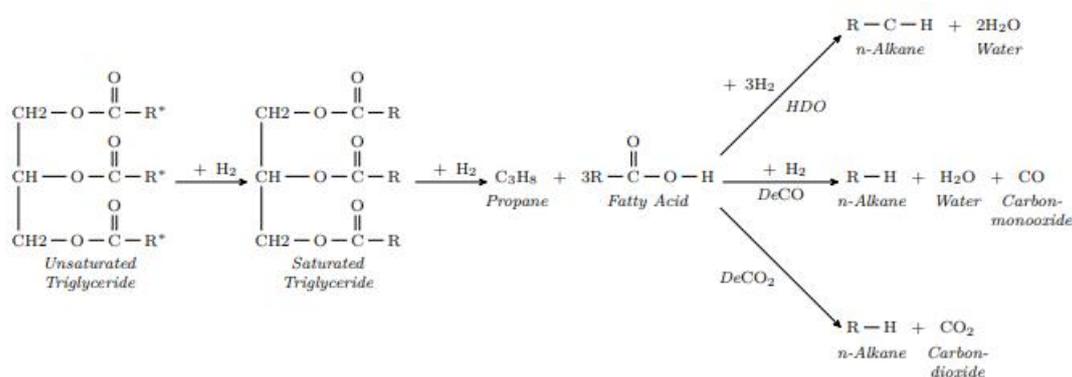


Figure 2.1. Hydrotreatment – the first stage of hydroprocessing. CO₂ is formed in the decarboxylation route. (Kiefel & Lüthje 2018.)

Paraffinic hydrocarbons are formed via three possible reaction routes: deoxygenation (HDO), decarbonylation (DeCO) or decarboxylation (DeCO₂). With process condition

adjustments and catalyst choice, the reaction can be shifted to favour one over the other. Choice of reaction significantly affects hydrogen consumption and output composition, as seen in Table 2.6. Note that the third plausible reaction, decarbonylation (DeCO), is not presented in the table.

Table 2.6. Theoretical hydrogen consumption and output compositions for decarboxylation (DeCO₂) and deoxygenation (HDO) of brown grease. (Marker 2005).

Method	H ₂	H ₂ S+NH ₃	C ₁ -C ₄	Naphtha	CO ₂	H ₂ O	nC17	nC18
DeCO ₂	0.8	0.04	0.6	2.5	15.5	0	82.2	0
HDO	2.9	0.04	0.7	2.4	0	12.7	0	87.2

Deoxygenation results in H₂O formation and high hydrocarbon yield as carbon does not bound to the by-product compounds. In decarboxylation CO₂ is released in relatively pure state as a by-product. However, the hydrocarbon yield is lower compared to deoxygenation as some of the carbon bounds to CO₂. In decarbonylation H₂O and CO are released as by-product. Presumably, highest potential for carbon capture in HVO production lies in hydrotreatment processes favouring the decarboxylation route. Additionally, decarboxylation has lower hydrogen consumption and better catalyst performance preservation properties than deoxygenation and decarbonylation (Marker 2005; Kiefel & L uthje 2018). There may occur some catalyst-derived impurities such as diglycerides, monoglycerides, olefins, esters, and alcohols (Kiefel & L uthje 2018). Since decarboxylation results in relatively pure stream of CO₂, specific carbon capture technologies would presumably not be required and the CO₂ could be captured only after minor purification and drying. However, research on carbon capture in HVO production processes has not been conducted.

2.4 Chemical pulping

Modern pulp and paper industry is predominantly based on chemical pulping (e.g., kraft pulping). Chemical pulping is energy-intensive and a significant source of biogenic CO₂

emissions. Around 75–100 % of pulp mills' CO₂ emissions are biogenic (Onarheim et al. 2017). Via carbon capture pulp mills could become a major source of biogenic CO₂.

Majority of the CO₂ emissions from kraft pulp mills originate from combustion processes at biomass/multi-fuel boiler, recovery boiler and lime kiln. Biomass and recovery boilers produce steam and electricity for the pulping process. Often excess electricity and heat is produced, which can be utilized internally or sold to the energy market. Biomass boilers typically use biomass residues from wood handling as fuel, whereas in recovery boilers the organic pulping process residues (black liquor) are combusted. Fossil-based CO₂ emissions typically derive from the lime kiln that is used to produce lime from lime-mud in high temperature calcination reaction, also releasing CO₂. Lime kilns often use fossil fuels, like oil or natural gas, due to stable combustion conditions and high adiabatic flame temperature that are needed for optimal lime kiln operation. Fossil-based CO₂ emissions from lime kilns could be neutralized by using alternative fuels, such as biogas, pulverized wood or hydrogen. (Kuparinen 2019.) The combustion processes are separate and if all CO₂ emissions would be targeted, each flue gas stream would require carbon capture equipment. Kuparinen (2019) discusses that applying carbon capture into all the streams is likely not feasible and that only the most significant streams should be focused upon. Recovery boiler is the largest source of emissions. Via reference case calculations, Kuparinen estimates that with a capture rate of 90 %, around 60–80 % of typical kraft pulp mill's total CO₂ emissions could be recovered when carbon capture is applied only to the recovery boiler. Operating conditions and flue gas composition in recovery boilers are similar as in other biomass combustion processes, although the CO₂ concentration in the flue gas is often slightly higher (See Table 2.2).

Onarheim et al. (2017) estimate that cost of CO₂ avoided in typical modern Finnish kraft pulp mills and integrated pulp and board mills are 52–66 €/tCO₂ and 71–89 €/tCO₂, respectively, when capturing 60–90 % of the emissions with amine-based post-combustion capture technology. They conclude that negative emission credits or other supporting policies are required to implement carbon capture to the pulp and paper industry.

3 CO₂ CAPTURE, TREATMENT, TRANSPORTATION AND UTILIZATION

This chapter provides an overview on the various stages of BECCU, including carbon capture, after-capture treatment, transportation, as well as utilization. Utilization is reviewed from the point of view of polyol production, as it is the focus of VTT's BECCU project.

3.1 Carbon capture

Carbon capture refers to a process that separates and captures carbon dioxide from CO₂ emission point sources instead of releasing the CO₂ to the atmosphere. Additionally, the objective is to capture a relatively pure stream of CO₂. Research and development regarding carbon capture has mostly been focusing on energy production but opportunities have been identified also in other energy-intensive and high-emissive industries, such as in forest, steel and cement industries and in refineries.

Carbon capture technologies are often categorized into post-combustion technologies, pre-combustion technologies and oxyfuel combustion technologies. There are also applications with high CO₂ concentrations that do not need specific carbon capture technology, requiring only purification. The capture technologies can be further categorized based on the method of capture such as absorption, adsorption, membranes or electrochemical potential. Various capture methods and promising technologies based on these methods are reviewed in Chapter 4.

Implementing carbon capture on a power plant or other industrial facility has drawbacks. It increases both capital and operational cost, often weakens the energy efficiency of the plant or increases need for external energy and requires installation and maintenance of possibly large-sized capture equipment. Depending on the capture method it can also increase waste streams and cause additional pollutant formation.

3.1.1 Post-combustion capture

In post-combustion capture CO₂ is captured from flue gases typically formed in combustion processes (Figure 3.1). As an end-of-pipe technology, it is currently the most favoured method of carbon capture due to suitability for retrofitting and applicability to many different processes.

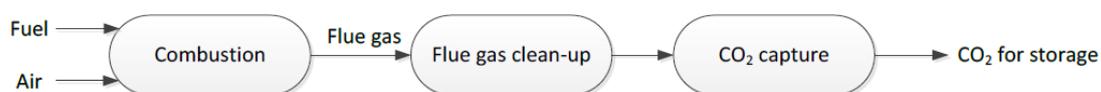


Figure 3.1. A simplified post-combustion capture process. (IEAGHG 2019a.)

The combustion process remains the same as without carbon capture, so there is no need for large process modifications other than installing the capture equipment to the end of the flue gas line. After combustion, the flue gas is purified, if necessary, and led to the capture equipment, which separates CO₂ from the flue gas stream. CO₂ concentration of flue gases is often low at around 3–15 %, which can make the capture process challenging.

3.1.2 Pre-combustion capture

In pre-combustion capture the CO₂ is removed from the feedstock before combustion or utilization (Figure 3.2). If a solid fuel is used, a synthesis gas consisting mainly of H₂, CO and CO₂ is produced in a gasification process. Then, a water-gas shift reaction is typically

used to increase the H_2/CO ratio, creating a gas mixture rich in H_2 and CO_2 from which the CO_2 could be captured.

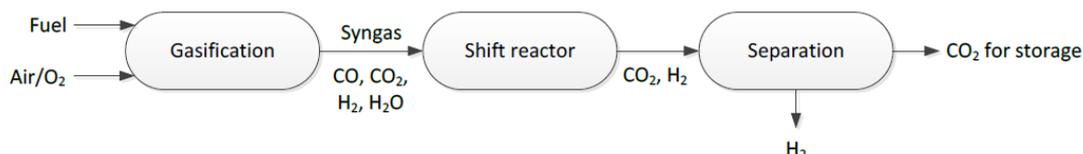
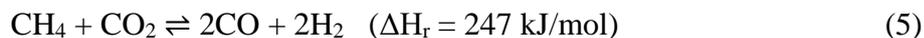
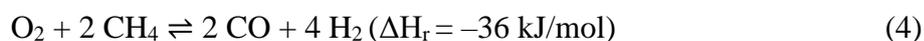
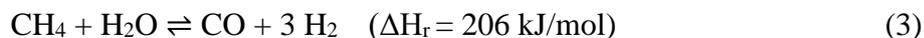


Figure 3.2. A simplified pre-combustion capture process. (IEAGHG 2019a.)

If a gaseous fuel is used, the syngas can be produced via steam methane reforming (Eq. 3), catalytic partial oxidation (Eq. 4) or dry reforming (Eq. 5).



Compared to post-combustion applications CO_2 concentration in pre-combustion is generally higher, at around 15–50 %. Syngas properties are more specifically reviewed in Subsection 2.3.2.

3.1.3 Oxyfuel combustion

Oxyfuel technologies utilize combustion in oxygen-rich conditions instead of regular air (Figure 3.3), which increases CO_2 concentration of the flue gas. This requires separation of nitrogen from the combustion air with an air separation unit or using an external source of high purity oxygen.

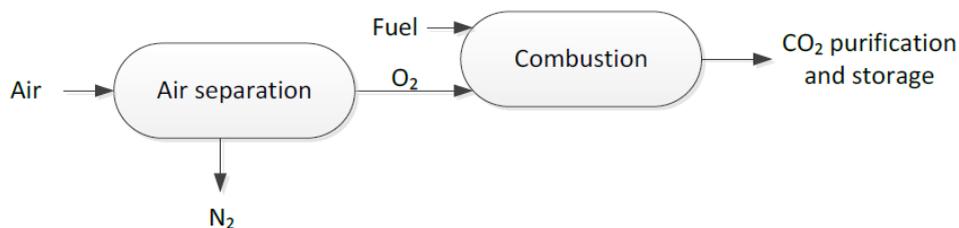


Figure 3.3. A simplified process chart of oxyfuel combustion with carbon capture. (IEAGHG 2019a.)

Flue gases in oxyfuel combustion mainly consist of CO_2 , H_2O , and some impurities. Flue gas is typically recycled back to the combustor to work as a heat carrier and to reduce the flame temperature, which would otherwise become too high if combustion air was only pure oxygen. CO_2 concentration of the flue gas depends on the amount of oxygen in combustion and fuel composition. With pure oxygen combustion the CO_2 concentration can be up to 90 %. Therefore, pure oxyfuel processes do not necessarily require specific carbon capture equipment since purification and drying can be enough to produce high purity CO_2 . Oxygen enriching can also be used to increase the CO_2 concentration to facilitate carbon capture. Significant disadvantage of oxyfuel processes is the difficulty of air separation and the amount of energy it requires. In addition, to avoid any leaks sealing of the combustion process becomes very important, which causes additional maintenance challenges. (Nemitallah et al. 2019.)

3.2 Pre-treatment and transportation of CO_2

The captured CO_2 typically contains some impurities and to guarantee safe and efficient handling and transportation some pre-treatment is often required. Effect of impurities as well as common pre-treatment and transportation methods are reviewed below.

3.2.1 Effect of impurities on handling and transportation

Chapoy et al. (2013) studied the effect of impurities on properties of captured CO_2 through experiments and theoretical models, by comparing nearly pure CO_2 (99.995 vol-

%) and a CO₂-rich mixture including Ar, O₂, N₂ and H₂O. The impurities caused an increase in the mixture's liquid phase region, thus requiring higher liquefaction pressure. Other effects were decrease of water dissolution to the stream and decrease of density, which increases compression and transportation costs.

According to Race et al. (cited in Rabindran et al. 2011) impurities (SO_x, NO_x, H₂, Ar) in pipeline transportation of CO₂ change the design conditions of equipment such as compressors and pumps, cause toxicity and corrosivity, reduce the transport capacity, cause the need for higher inlet pressure and/or more recompression stations, increase the risk of fractures due to higher pressure and cause embrittlement.

3.2.2 Pre-treatment

Stages of CO₂ pre-treatment depend on the desired CO₂ properties that is often determined by the transportation method and the end-use application. Generally, pre-treatment includes purification, dehydration and compression. CO₂ is compressed into a dense and easily transportable state to maximize transport efficiency and to lower transport costs. Impurities are removed due to their negative effects in handling and transportation and to match the quality requirements of end-use applications. Water-soluble impurities, like SO₂, can be removed with water-wash process during the first stages of compression. Moisture is removed due to its corrosive nature in pipelines and risk of ice formation in low liquefaction temperatures. Moisture removal can be done via cooling during the compression stages. Possible volatile impurities and non-condensable gases are removed via distillation or flashing at a pressure of ~60 bar. (Teir et al. 2011.)

3.2.3 Transportation

If the captured CO₂ is not utilized in-situ it must be transported to the place of utilization. At industrial-scale, suitable methods of transportation are pipelines and ships due to large transport capacities. Road and railway transportation, which are more suitable for demonstration-scale, have large costs per transported unit due to small capacities. Pipeline transportation of CO₂ is already successfully implemented commercially: in the

US millions of tonnes of CO₂ is transported via pipelines for enhanced oil recovery (IEAGHG 2013). Ship transportation of CO₂ is comparable to transportation of liquefied petroleum gases due to similar properties and thus it is also considered as a mature method of CO₂ transportation (Brownsort 2015). In pipeline transportation the CO₂ is compressed above its critical pressure to over 80 bar to avoid gas formation and two-phase flows. In ship transportation the CO₂ is liquefied near its triple point to reach high density. Typical conditions in pipeline transportation are 110 bar and 35 °C and in ship transportation 7 bar and -50 °C (Wilcox 2012). To avoid technical difficulties and health concerns, the CO₂ must meet necessary quality recommendations, such as the DYNAMIS quality recommendations for pipeline transportation presented in Table 3.1.

Table 3.1. DYNAMIS CO₂ quality recommendations for pipeline transportation. (de Visser & Hendricks 2007.)

Component	Limit	Cause of limitation
H ₂ O	500 ppm	Technical
H ₂ S	200 ppm	Health and safety
CO	2000 ppm	Health and safety
O ₂	Aquifer < 4 vol%, EOR 100 – 1000 ppm	Technical
CH ₄	Aquifer < 4 vol%, EOR < 2 vol%	ENCAP project
N ₂	< 4 vol % (all non-condensable gases)	ENCAP project
Ar	< 4 vol % (all non-condensable gases)	ENCAP project
H ₂	< 4 vol % (all non-condensable gases)	High energy content
SO _x	100 ppm	Health and safety
NO _x	100 ppm	Health and safety
CO ₂	> 95.5 %	Balanced with other compounds

Cost of transportation depends on distance and method of transportation. Cost estimates for CO₂ transportation at demonstration-scale and large-scale are presented in Table 3.2.

Table 3.2. Transportation cost estimates (€/tCO₂) for demonstration-scale (2.5 MtCO₂/a) and large-scale networks (20 MtCO₂/a) in natural gas or coal-based CCS projects. (GCCSI 2011.)

Spine distance	180 km	500 km	800 km	1500 km
Demonstration-scale				
Onshore pipe	5.4	n.a.	n.a.	n.a.
Offshore pipe	9.3	20.4	28.7	51.7
Ship	8.2	9.5	10.6	14.5
Liquefaction (for ship transport)	5.3	5.3	5.3	5.3
Large-scale				
Onshore pipe	1.5	3.7	5.4	n.a.
Offshore pipe	3.4	6.0	8.2	16.3
Ship (incl. liquefaction)	11.1	12.2	13.2	16.1

At demonstration-scale ships are the most cost-efficient method in long distances, whereas in short distances (e.g., domestic networks) pipe transportation reaches the lowest cost. At larger scale pipe networks are the most cost-efficient method of transportation all the way up to 1500 km distances, at which point ship transportation becomes slightly more inexpensive method compared to offshore pipe networks.

3.3 CO₂ utilization

Wide deployment of carbon capture at industrial-scale would provide a large source of CO₂. If it is not stored underground, the captured CO₂ can be utilized either directly or indirectly as a feedstock for various value-added products. As the current operating environment lacks incentives for CO₂ storage, utilization presents an option to profit from carbon capture.

Global CO₂ demand is currently relatively small at around 250 Mt in 2020. Majority of current CO₂ consumption is direct, i.e., used in non-conversion processes. Largest commercial consumers of CO₂ are fertiliser industry in urea manufacturing, oil industry in enhanced oil recovery, and food and beverage industry. Current CO₂ demand is imbalanced and depends highly on the season, which also affects the price of CO₂. Typically, the demand is at highest before spring due to increasing fertilizer production ahead of planting season. Price of CO₂ differs a lot depending on purity, region and

industry. Prices of 3–15 USD per CO₂ tonne are typical in long-term contracts with ammonia producers, whereas in niche-markets the price of highly pure CO₂ can exceed even 400 USD/tCO₂. (IEA 2019c.)

Demand of CO₂ is expected to grow as CO₂ utilization increases. Especially indirect utilization of CO₂ to produce fuels, chemicals and materials via various conversion processes has generated a lot of interest. CO₂-derived products can provide climate benefit if that production is used to replace conventional unsustainable production methods based on fossil sources. IEA (2019c) estimates an annual demand of 272 Mt for 2025. Estimates for global annual demand in 2030 range from <1 Gt to 7 Gt. Estimating future demand is challenging due to dependence on policies and because the technologies aiming for CO₂-derived products are still at an early stage. (Winberg & Mäki 2020.)

3.3.1 CO₂-derived polyols

In VTT's BECCU project, CO₂ utilization is studied in polyol production. According to a recent publication by VTT (Lehtonen et al. 2019), CO₂-derived polyols are high-value products that possess high commercialization potential in the CO₂ utilization market. Polyols can be used as building blocks to produce polymers such as polycarbonates, polyesters or polyurethanes. Figure 3.4 presents CO₂ utilization route in polyurethane production.

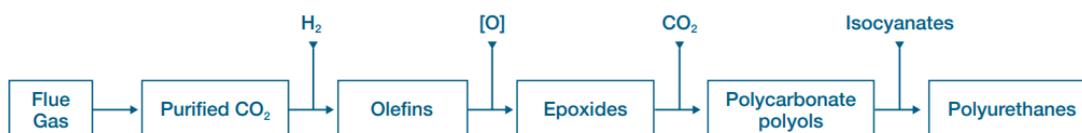


Figure 3.4. CO₂ utilization in polyurethane production. (Lehtonen et al. 2019.)

Polymers are one of the most desirable CO₂-derived products due to high versatility and applicability. Polymers are long-chain macromolecules with various unique properties depending on the bonding of the molecule. They are building blocks for variety of materials like plastics, rubbers, synthetic fibres, resins, and foams. Polymers are

conventionally produced in petrochemical processes via fossil-based carbon. Alternatively, CO₂ can be used to produce polymers via multiple routes such as chemocatalytic reactions, electrochemistry or by producing indirect products like methanol or syngas to be used as source of polymers via various conversion reactions (Nova Institute in Bioenergy International 2019a). Some CO₂-derived polymer production can even compete with conventional production due to low energy requirement. For example, carbonates have a lower energy state than CO₂, meaning that CO₂-to-polycarbonate conversion process require only little energy. Some CO₂-derived polymer production is currently on operation, but the potential market is still relatively small. Highest potential for CO₂-derived polymer production lies in polymer plants that can be modified to use CO₂ as feedstock and in areas where cost of fossil sources used in polymer production is high. (IEA 2019c.)

4 STATE-OF-THE-ART AND EMERGING POST-COMBUSTION CARBON CAPTURE TECHNOLOGIES

In this chapter various methods of carbon capture and some of the most promising technologies are reviewed. The reviews include rough operational description, current state of the technology and techno-economic performance properties like energy consumption, capture rate and capture cost. Maturity of the technologies is evaluated by using Technology Readiness Level (TRL). The TRL scale is presented in Table 4.1.

Table 4.1. Technology Readiness Level scale. (IEAGHG 2019a.)

State of technology	TRL	Description
Demonstration	9	Normal commercial service
	8	Commercial demonstration, full-scale deployment in final form
	7	Sub-scale demonstration, fully functional prototype
Development	6	Fully integrated pilot tested in relevant environment
	5	Sub-system validation in relevant environment
	4	System validation in laboratory experiment
Research	3	Proof-of-concept tests, component level
	2	Formulation of the application
	1	Basic principles observed, initial concept

In addition to the technologies addressed in the literature review of this study, there are numerous of other technologies currently under research and development. The reviewed technologies are chosen due to being among the most mature representatives of various carbon capture methods with ongoing development and upcoming demonstration projects. Also, most of these technologies have at least some demonstration experience in realistic conditions, meaning that their techno-economic performance and potential can be assessed with some realistic basis.

4.1 Liquid absorbents

Carbon capture via liquid absorbents is currently the most mature capture method available. These technologies are based on absorption/desorption process where CO₂

from the target gas stream is caught into an absorbent solution via physical or chemical absorption. The captured CO_2 is released in a separate process phase to produce as pure stream of CO_2 as possible. Flow chart of a typical capture process using liquid absorbent is presented in Figure 4.1.

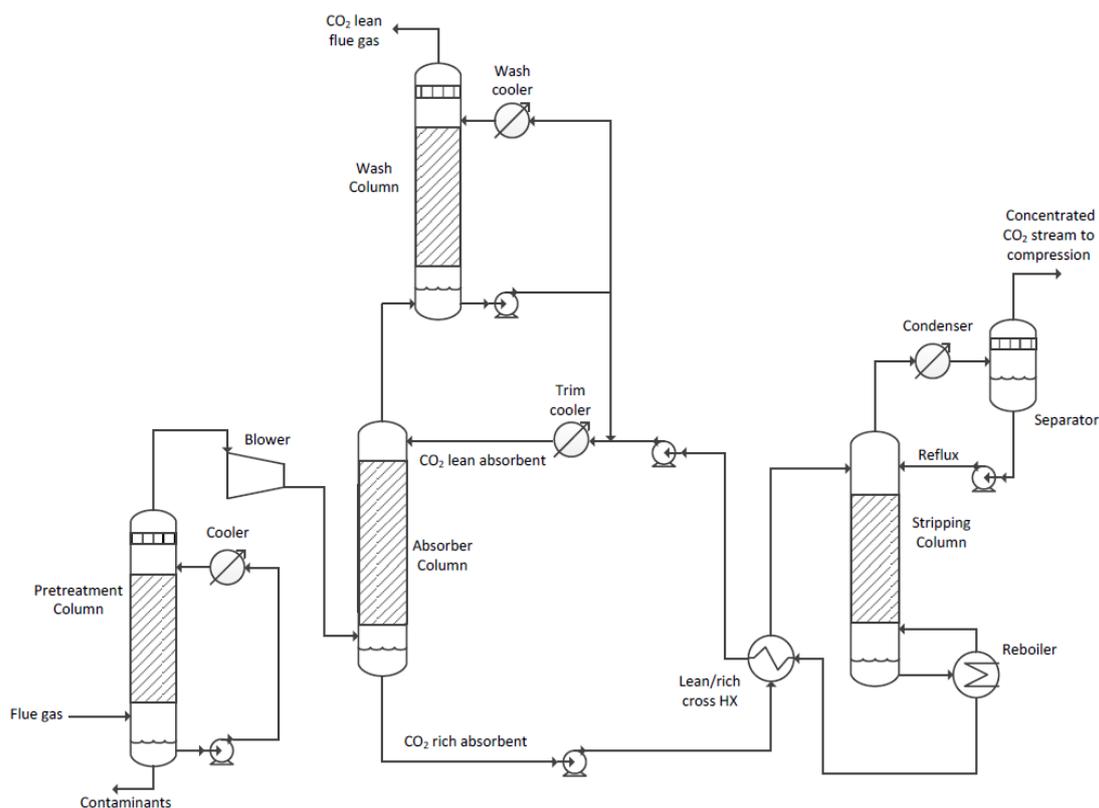


Figure 4.1. Flow chart of a typical post-combustion capture process using liquid absorbent. (IEAGHG 2019a).

Absorption is a mass-transfer process where particles of gaseous or liquid solute transfer and bind to the absorbent. An opposite process, where the solute is released from the absorbent is called desorption or stripping. In carbon capture, the liquid capture solution absorbs the gaseous CO_2 , which initially converts into liquid phase via dissolution (physical absorption) and possibly reacts with the absorbent, binding into the solution via

chemical bonds (chemical absorption). Capture technologies based on absorption require a separate regeneration process phase to strip the CO₂ from the solution. The solution is typically regenerated in high temperature or low pressure to release the absorbed the CO₂, which can then be captured as a relatively pure stream. Regeneration also allows the absorbent solution to be recycled in the process, although some of it might degrade, meaning that some additive absorbent must be added to the process. (Wilcox 2012.) Regeneration is generally very energy-intensive since it requires heating of large solution volumes, which is significant disadvantage of absorption-based capture since it vastly decreases the energy efficiency of the facility, increases capture costs, and often also requires large-sized equipment for the large solution flows.

Various absorbents with diverse properties have been researched for carbon capture purposes, mainly for post-combustion capture applications. However, many of the absorbents are also applicable for pre-combustion capture. The most mature and promising liquid absorbents are reviewed below.

4.2 Amine-based liquid absorbents

The most mature liquid absorbents are currently based on amines, which are nitrogen-containing organic compounds considered as derivatives of ammonia. Amines have suitable properties for catch-and-release type of capture, such as good reversibility and fast transfer kinetics. However, amine absorbents face challenges such as high energy-intensity, corrosivity, volatility and sensitivity to impurities. Amine-based absorbents generally release some amine emissions, which result in formation of toxic and harmful compounds, such as nitrosamines and nitramines (Karl et al. 2011). To lower the amount of these harmful emissions emission limits are being introduced for carbon capture facilities, as has been done, for instance, in Norway (CLIMIT 2020). Various amines and amine blends have been researched for carbon capture purposes, of which the most mature and potential ones are reviewed below.

4.2.1 MEA

The most mature and well-known liquid absorbent is a primary amine called monoethanolamine (MEA), which has been proven feasible in commercial-scale carbon capture, achieving a TRL of 9. For a long time, MEA was considered as the state-of-the-art technology for carbon capture, but in recent studies it has been displaced it with emerging technologies that reach better techno-economic performance, such as the PZ+AMP solution (IEAGHG 2019a). Due to the long-term state-of-the-art status, MEA has often been used as benchmark technology to evaluate the performance of emerging technologies. This may however change in future research, since MEA is no longer considered as state-of-the-art technology.

Advantages of MEA include fast reactivity, high loading capacity and suitability to applications with low CO₂ concentration. Challenges include high energy-intensity, high corrosivity, solvent degradation and degradation-derived amine emissions. (Bui et al. 2018.) In addition, the production of MEA from ammonia is energy-intensive and causes direct and indirect CO₂ emissions (Luis 2015). Due to the significant disadvantages of MEA, a lot of research has been conducted aiming to find alternative technologies with better techno-economic performance.

A typical benchmark MEA solution contains 30 wt. % MEA and 70 wt. % water. Inhibitors can be used to decrease harmful properties like corrosivity and volatility. MEA reacts with CO₂ via chemical absorption to form relatively stable carbamates. Absorption occurs at atmospheric pressure and a temperature of 40–60 °C (Ziaii et al. 2009). Regeneration is typically done with hot steam at a temperature of 120–140 °C and a pressure of 1–2 bar, which is highly energy-intensive (McGurk et al. 2017). Reboiler duty for a conventional 30 wt. % MEA process with a 90 % capture rate is typically around 3.6–4.0 GJ/tCO₂ (Bui et al. 2018), whereas more advanced formulations, such as Fluor's EFG+ process, can reach lower reboiler duties at around 3.3–3.7 GJ/tCO₂ (Svendsen 2014). Due to the high-energy intensity of conventional steam-regeneration alternative methods, such as microwave-swing regeneration (MSR), have been proposed. MSR could

improve rate of regeneration, decrease energy-intensity (regeneration at 70–90 °C) and reduce corrosion, solvent degradation, and equipment size. (McGurk et al. 2017.)

MEA degrades via carbamate polymerization and oxidative and thermal degradation, meaning that some additive solvent is generally needed. According to Chapel et al. (1999) amine consumption in conventional post-combustion capture process is around 1.6 kg/tCO₂. Thorough flue gas cleaning is required due to sensitivity of MEA to impurities. NO_x causes MEA to degrade into a secondary amine, diethanolamine (DEA), which further reacts to form harmful nitrosamines and nitramines (Fostås et al. 2011). At some levels SO₂ can even inhibit oxidative degradation of MEA, but thermal degradation is significantly increased since sulphites promote the formation of ammonia through degradation (Zhou et al. 2013). Presence of oxygen also increases oxidative degradation of MEA (Chi & Rochelle 2002).

Based on data collected from related literature, IEAGHG (2019a) estimates that capture costs for MEA-based capture processes are around 44 €/tCO₂ in coal-firing and 64 €/tCO₂ in gas-firing.

4.2.2 EFG+ by Fluor

One of the developers of MEA-based carbon capture is Fluor with their post-combustion applicable Econamine FG Plus (EFG+) technology. The precursory Econamine FG process was based on a 30 wt. % MEA solution together with some corrosion resistant inhibitors (Chapel et al. 1999). The more advanced EFG+ process uses an advanced solvent formulation, with MEA still being the base absorbent. EFG+ can use higher amine concentrations together with corrosion and degradation resistant inhibitors, resulting in faster reaction rate and higher loading capacity. (Reddy et al. 2003.) Typical reboiler duty for the EFG+ process is 3.3–3.7 GJ/tCO₂, while reaching high CO₂ purity (>99.8 %) (GCCSI in Svendsen 2014). The process is suitable for multiple applications such as power plants, refineries, and chemical applications. It has been demonstrated at several

commercial applications for nearly 20 years, with 27 licensed plants currently in commercial operation. (Fluor 2020.)

4.2.3 PZ + AMP

One of the most potential challengers for MEA is an aqueous amine blend consisting of piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP). PZ is an advanced amine that has high loading capacity and fast absorption rate, whereas AMP is a sterically hindered amine, which when reacting with CO₂ forms unstable carbamates that require only low regeneration energy (Bougie & Iliuta 2012). IEAGHG (2019a) chose PZ+AMP as their state-of-the-art technology of carbon capture as it reached the highest techno-economic performance off all the capture technologies assessed in their study regarding emerging carbon capture technologies. Their benchmark solution consists of a 40 wt. % PZ+AMP blend with 1:2 molar ratio. The technology currently reaches a TRL of 6, having been demonstrated at pilot-scale, while still lacking large-scale industrial demonstration. Compared to MEA, PZ+AMP has lower energy requirement, cost, and degradation rate. By adjusting the PZ/AMP ratio, the process can be shifted to favour faster mass transfer (larger ratio) or lower reboiler duty (smaller ratio) (Khan et al. 2015). PZ+AMP also faces the challenge of solvent degradation resulting in harmful amine emissions.

In an experimental study based on a PZ/AMP capture process with synthetic flue gases, Spietz et al. (2020) evaluated the amine emission levels in the treated flue gas and in the produced CO₂. The major contaminants in the treated flue gas were ammonia (6–8 ppm) and AMP (9–13 ppm), whereas the product CO₂ contained AMP (7 ppm), ammonia (3–5 ppm) and formic acid (2 ppm). The amine emissions significantly increased with higher temperature lean solvent and during the absence of make-up water in the absorber.

In a pilot-scale study Rabensteiner et al. (2016) calculated a reboiler duty of 3.15 GJ/tCO₂ for a 17/28 wt. % PZ/AMP solution used in post-combustion capture in coal-firing. Based on simulations IEAGHG (2019a) calculated a reboiler duty of 2.46 GJ/tCO₂ for a PZ+AMP-based post-combustion capture in an ultra-supercritical pulverized coal plant.

Based on data collected from related literature, IEAGHG (2019a) estimates that capture costs for PZ+AMP-based capture are 34 €/tCO₂ in coal-firing and 56 €/tCO₂ in gas-firing. IEAGHG updated PZ+AMP as their state-of-the-art representative of carbon capture technology due to reaching better techno-economic performance than their previous state-of-the-art technology, MEA. There are currently no commercial developers for a PZ+AMP -based carbon capture technology.

4.2.4 **KS-1 & KS-21 by MHI**

KS-1 and KS-21 are advanced amine capture solvents based on sterically hindered amines. The solvents are developed by Mitsubishi Heavy Industries (MHI) together with The Kansai Electric Power Company (KEPCO) for their KM CDR -capture process suitable for various flue gas applications. KS-1 is an earlier version of the two and it has been proven commercially viable (TRL 9). KS-21 is an advanced version developed to achieve better techno-economic performance than its earlier counterpart and it has been demonstrated at small industrial scale (TRL 7).

Compared to MEA, KS-1 has lower regeneration energy, higher loading capacity and lower degradation rate and corrosivity. Loading capacity is up to 40 % higher, meaning that the solvent circulation rate is lower, which also reduces equipment size and capital costs. (Iijima 2005.) Reboiler duty is estimated to be 2.6 GJ/tCO₂. The solvent suffers from amine losses mainly caused by thermal degradation, but at around 0.35 kg/tCO₂ the amine consumption is still significantly lower than with MEA. (Yagi et al. in IEAGHG 2019a.) KS-1 has been demonstrated and proven commercially viable together with MHI's KM CDR -capture process. The process is used, for instance, in the Petra Nova project at coal-fired W.A. Parish power plant located in Texas, where of 4776 tonnes of CO₂ per day is captured with a capture rate of 90 %. (MHI n.d.)

KS-21 is an advanced version of the KS-1 aiming to reduce the amine losses to increase the overall techno-economic performance of the KM-CDR capture process. Both solvents were demonstrated in preliminary piloting at KEPCO's gas-fired Nanko Pilot Plant

capturing 2 tonnes of CO₂ a day with a 90 % capture rate. KS-21 performed better than KS-1 in volatility, thermal degradation rate, oxidation rate, heat of absorption and cost. It reached 50 % lower amine emissions levels, while still reaching equal capture performance as KS-1. However, a higher solvent rate was required to achieve an equal capture rate, though the reboiler duty remained similar to its predecessor. (Tanaka et al. 2018.)

Small industrial scale (25 MW) demonstration with the KM-CDR process and both solvents was conducted at the coal-fired Plant Barry Power Station in Alabama, U.S. Fluor's MEA-based Econamine FG+ process was used for benchmarking. With a capture rate of 90 %, 500 tonnes of CO₂ per day was captured. Following capture costs were achieved: \$66.4/tCO₂ for EFG+; \$58.8/tCO₂ for KS-1; \$56.0/tCO₂ for KS-21; and \$54.8/tCO₂ for KS-21 with auxiliary turbine. (Carroll 2017.)

Starting from autumn of 2020 both solvents will be demonstrated in a biomass-firing at Drax Power Station in UK, aiming to capture around 300 tCO₂/d (MHI 2020). Successful demonstration at Drax will advance the TRL of KS-21 to 7–8.

4.2.5 CANSOLV by Shell

Shell's CANSOLV process represents another amine-based post-combustion capture process that has reached commercial status (TRL 9). In addition to CO₂ recovery, the process can recover SO₂ emissions as a useful by-product (e.g., as sulphuric acid or liquid SO₂). Shell has researched multiple solvents for the CANSOLV process, such as the DC-103, which is a 50 wt. % aqueous amine blend formulation. In commercial-scale operation (120 tCO₂/d) the DC-103 has reached an average capture rate of 90 %, while producing high purity CO₂ (>99.75 %). A steam demand worth of 2.3 GJ/tCO₂ was required for solvent regeneration. (Singh & Stéphenne 2014.) The process is in operation at the coal-fired Boundary Dam power station located in Saskatchewan, Canada, with an annual capture capacity of 1 Mt of CO₂. The captured CO₂ is mainly utilized in enhanced oil recovery. (Shell 2020.)

4.3 Multi-phase absorbents

Multi-phase absorbents (or phase-separating absorbents) go through a phase change upon certain amount of loading in absorption. When entering the absorber, the CO₂-lean solvent is at liquid phase but during absorption the solvent can form a separate immiscible liquid phase or precipitate into a solid phase. Due to phase difference between the CO₂-lean solvent and the CO₂-rich solvent, they can be easily separated, which reduces the high regeneration volumes that are characteristic to liquid absorbents. Multi-phase absorbents can be categorized into liquid-solid and liquid-liquid phase separating absorbents. (Bui et al. 2018.) Solid formation complicates the process and requires a specific solid handling system, such as hydrocyclone separator. However, multi-phase absorbents can also be operated in non-solid mode, where unwanted solid formation is avoided by adjusting the process conditions and/or sorbent concentration. Non-solid mode is often desired due to simplicity. Development of multi-phase absorbents has mainly focused on post-combustion applications.

4.3.1 Aqueous ammonia (NH₃)

Ammonia-based solvents are one of the most mature multi-phase absorbents. Ammonia reacts with CO₂ to form ammonium and bicarbonate ions, which further react to form compounds such as ammonium carbamates, carbonates, and bicarbonates. Depending on the process conditions, the solvent may precipitate and form a slurry during absorption. Precipitation can be avoided with low ammonia concentration or high temperature conditions, which in turn reduces absorption capacity. Aqueous ammonia capture has several advantages: common and low-cost solvent chemical, non-corrosive process, good absorption capacity and a low reboiler duty of 2–3 GJ/tCO₂. Ammonia can also capture NO_x and SO_x emissions by forming ammonium sulphate and ammonium nitrate, which can be recovered and utilized, e.g., in fertilizing. Challenges of ammonia-based capture include a risk of unwanted precipitation and high volatility, which causes solvent losses and harmful ammonia emissions via ammonia slip. (Yang et al. 2014.) Higher ammonia concentrations result in better capture rate but also in higher ammonia slip and

precipitation. Ammonia slip can be reduced with a low absorption temperature, which in turn increases precipitation. (Versteeg & Rubin 2011.)

CSIRO conducted a pilot-scale demonstration for post-combustion capture using aqueous ammonia solvent at the Munmorah black coal fired power station located in Australia. Even with low ammonia concentrations (up to 6 wt. %) a capture rate of 85 % with high CO₂ purity (99–100 %) was achieved, while also removing over 95 % of the SO₂ emissions. (Yu et al. 2012.)

According to a model-based techno-economic assessment by Li et al. (2016), an advanced aqueous ammonia post-combustion capture process can reach capture cost of \$53/tCO₂ in coal-firing (vs. MEA \$75/tCO₂). Reboiler duty of the process was calculated at 2.46 GJ/tCO₂ and ammonia emissions after the wash column at 15 ppm_v.

4.3.2 Chilled Ammonia Process by GE

GE (formerly Alstom) has aimed to advance aqueous ammonia capture with their Chilled Ammonia Process (CAP). By cooling the aqueous ammonia solvent to a temperature of 0–10 °C solubility of ammonia to water can be improved, which improves CO₂ absorption capacity since the solvent can contain more ammonia. Cooling also reduces ammonia vaporization thus lowering the harmful ammonia slip. Due to the low temperature the solvent precipitates in lower loading compared to non-chilled process. GE has researched both solid-mode and non-solid mode CAP processes. GE has successfully demonstrated the process in several pilot-scale applications (TRL 6), such as with synthetic gases and flue gases from coal-, gas- and oil-firing. (Augustsson et al. 2017.)

One of the demonstration projects was conducted at AEP's Mountaineer coal-fired power plant for a flue gas feed flow of ~84 t/h. The process reached a capture rate of 65–85 % and resulted in a feed of very high purity CO₂ (>99.9 %). CAP caused a 9.5 %-point loss on power generation efficiency and a 59 \$/MWh increase in the LCOE, nearly doubling

the LCOE compared to non-CCS operation. Reboiler duty of 2.8 GJ/tCO₂ was measured for the process. However, the process was initially designed for solid-mode operation but was operated in non-solid mode, which significantly impacted the measured energy consumption. A corrected reboiler duty, taking into account the effect of non-solid operation in solid mode design, was calculated at 2.2 GJ/tCO₂. Ammonia emissions remained under 10 ppm_v. (Augustsson et al. 2017.) There are currently no plans for future demonstration.

4.3.3 UNO MK 3 by CO2CRC

CO2CRC has developed a precipitating UNO MK 3 process based on an aqueous potassium carbonate (K₂CO₃) absorbent, aiming to reach a 90 % capture rate in pre- and post-combustion applications. Aqueous potassium carbonate has several advantages as a CO₂ capture absorbent: low regeneration energy (2.0–2.5 GJ/tCO₂); low volatility and corrosivity; non-toxic sorbent; good oxidative degradation resistance; applicability to high absorption temperatures; and ability to capture also SO_x and NO_x emissions (Mumford et al. 2015; Smith et al. 2014). SO_x and NO_x emissions react with K₂CO₃ to form potassium sulphate (K₂SO₄) and potassium nitrate (KNO₃), which can be recovered and utilized as fertilizers (UNO 2014). Biggest disadvantage of the process is the slow reaction rate, which can be improved by using catalysts or promoters, such as boric acid, amines or amino acids (Hu et al. 2016). With unpromoted solvent the capture rate remains low at around 20–25 % (Mumford et al. 2012).

CO2CRC has successfully demonstrated the process in laboratory-conditions and at pilot-scale, thus achieving a TRL of 6. Pilot-scale demonstration was conducted at the coal-fired Hazelwood Power Station located in Australia, capturing 1 tCO₂/d from the plant's flue gases. With an unpromoted solvent containing 20–40 wt.-% of K₂CO₃, a CO₂ removal efficiency of only 5–15 % was achieved. (Smith et al. 2014.) In more recent pilot-scale experiments Smith et al. (2017) reached capture rates of 10–50 % by using a promoted K₂CO₃ solvent. With high solvent concentration (45 wt. %) the process faced

some difficulties such as absorber flooding and blockages due to solvent foaming and precipitation.

UNO Technology Ltd. has scaled-up the process, aiming for full commercial scale operation. The company estimates the capture cost for the UNO MK 3 process to be around \$60 AUD (\approx \$45 USD) per CO₂ tonne. (UNO 2014.) Uno Technology is among the partners of 8 Rivers, which received funding from U.S. DOE to develop emerging carbon capture technologies. The companies have preliminary plans to retrofit and demonstrate the UNO MK 3 process in natural gas power generators. (UNO 2020.)

4.3.4 Hot-CAP by the University of Illinois

Hot carbonate processes use a solution of concentrated carbonate salt (e.g., K₂CO₃) at an elevated temperature to chemically absorb CO₂, and possibly SO₂. Hot carbonate processes have been used in several industries to remove CO₂ from various industrial gases (Chapel et al. 1999), but in carbon capture it is still a relatively novel technology.

Lu et al. (2014) from the University of Illinois are one of the developers of hot carbonate-based capture with their Hot-CAP process. Hot-CAP is a hot potassium carbonate capture process that utilizes sorbent crystallization and high-pressure stripping. Absorption takes place at atmospheric pressure and a temperature of 60–80 °C. After absorption, the solution is cooled to ~35 °C and led to a crystallization reactor, where solid potassium bicarbonate (KHCO₃) crystals are filtered to produce a bicarbonate slurry. The CO₂-rich bicarbonate slurry is then led to a high-pressure stripper, where desorption occurs at a temperature of 140–200 °C and a pressure of 6–40 bar. Lowest reboiler duties are achieved with high stripping temperature, high carbonate concentration and high carbonate-to-bicarbonate rate. With solutions of 30–50 wt.-% K₂CO₃ concentration and 80 % carbonate-to-bicarbonate rate, reboiler duties around 1.8 GJ/tCO₂ have been achieved in bench-scale evaluations. Advantages of Hot-CAP process are low-cost and non-degradable solvent, low volatility and corrosivity, and possibility for high temperature desorption. Challenges include slow absorption rate, unfavourably low

desorption pressure of KHCO_3 of <10 bar (high stripping pressure reduces the required stripping heat), handling of the slurry regarding fast cooling demand and possible fouling, and availability of strippers suitable for handling slurry at high pressures.

In their laboratory- and bench-scale techno-economic analysis Lu et al. (2014) calculated an LCOE of \$120/MWh for a Hot-CAP process including transportation and storage, causing a 60 % LCOE increase compared to non-CCS operation (c.f. MEA \$139/MWh & 85 % increase). The process lacks demonstration in relevant environment and currently reaches only a TRL of 4. Further demonstration has not been planned.

4.3.5 Hot Potassium Carbonate process by Stockholm Exergi

Starting from the autumn of 2019, a Hot Potassium Carbonate technology has been under demonstration in post-combustion capture at Stockholm Exergi's biomass-fired KVV8 unit, located in Värtan, Sweden. The technology is based on a Sargas process, which is a simplified version of a Benfield process developed to remove acidic compounds (e.g., CO_2 and H_2S) from various industrial gases. The HPC process configuration is relatively simple: compressed flue gas is led to an absorber where CO_2 and H_2O react with hot potassium carbonate solvent to form bicarbonate. The bicarbonate is led to an unpressurized desorber column where it regenerates back to carbonate releasing the CO_2 and the H_2O . The carbonate is then circulated back to absorption after energy recovery. Previously, the technology has been commercially operated in Stockholm at a gas refinery from 1971 to 2011. It has also been trialled in pilot-scale carbon capture operation with coal-fired flue gases at a CHP-plant in Värtan during 2007–2008. (Levihn et al. 2019.) The technology is at commercial level in industrial gas purification processes, but in carbon capture HPC has been demonstrated only at pilot-scale (TRL 6).

In the demonstration project at Värtan, around 700 kg of CO_2 is captured per day, while expectedly reaching a capture rate of 80–95 %. The programme includes practical tests, simulations, and a feasibility study to evaluate possibilities for larger scale carbon capture operation at Värtan. The company estimates that CO_2 capture cost at Värtan, including

capture, treatment, and storage, is around 100 € (1000 SEK) per CO₂ tonne. (Bioenergy International 2019b; Nohrstedt 2019.) Full-scale carbon capture operation at Värtan could be achieved by 2025 (Stiernstedt 2019).

4.3.6 DMX by IFPEN

DMX, which is based on 1, 3-dipropyl-7-methylxanthine, is a liquid-liquid phase separating process developed by IFPEN for post-combustion capture applications. Upon absorption the solvent divides into two immiscible liquid phases, of which the CO₂-rich phase is separated and led to regeneration. Advantages of the process are high absorption capacity (0.1–1 mol_{CO₂}/mol_{solvent}), low regeneration energy (<2.5 GJ/tCO₂), high degradation resistance, non-corrosive solvent, and low operation costs compared to conventional processes. (Broutin et al. 2017.)

The DMX process has been evaluated as a part of IFPEN's OCTAVIUS (Broutin et al. 2017) and VALORCO (Dreillard et al. 2017) projects in mini-pilot facilities, where it has showed good promise with flue gases from coal-firing and from blast furnace processes. In IFPEN's OCTAVIUS project (Broutin et al. 2017), where DMX process was used to capture CO₂ from coal-firing flue gases at mini-pilot scale, a capture cost of 42.6 €/tCO₂ was reached. The process caused an efficiency loss of 9.3 %-points. DMX outperformed MEA-based capture, which reached a capture cost of 56.5 €/tCO₂. Based on data collected from related literature, IEAGHG (2019a) estimates a capture cost of 39 €/tCO₂ for DMX capture in coal-firing.

As part of the European 3D project DMX is currently being demonstrated at industrial scale capturing 0.5 tCO₂/hr from blast furnace exhaust gases at Dunkirk, France (Broutin et al 2018; IFPEN 2019). TRL of the process is currently at 4–5 (IEAGHG 2019a), increasing to 7 after successful demonstration at Dunkirk.

4.4 Water-lean solvents

Water-lean (or non-aqueous) solvents have been developed to reduce the high energy-intensity that is characteristic to conventional aqueous solvents. This high energy-intensity is a result of regeneration of large volume flows that mainly consist of water. By using solvents that have lower specific heat values than water the amount of regeneration energy can be reduced. (Heldebrandt et al. 2017). The principle of operation with water-lean absorbents is otherwise same as with other liquid absorbent capture processes. The most advanced water-lean solvents are mainly based on organic liquids and amine blends. IEAGHG (2019a) estimates that the TRL of water-lean solvents is currently at 5, while having an upward development trajectory and a medium (10–30 %) LCOE reduction potential compared to benchmark 30 wt. % MEA capture.

4.4.1 eCO₂Sol by RTI

The eCO₂Sol (researched under the name NAS) is a novel non-aqueous solvent developed by the Research Triangle Institute (RTI) for post-combustion applications. RTI has researched multiple non-aqueous solvent formations, mainly based on hydrophobic diluents and sterically hindered amine blends. Advantages of the process are low regeneration energy requirement (potentially 2.0 GJ/tCO₂), high stability, high loading capacity, and low corrosivity. (Zhou et al. 2018; RTI 2020.) Characteristic to all amine containing solvents, the solvent-based amine emissions present a challenge that must be overcome in the pursuit of further technology scale-up (Tanthana et al. 2018).

NAS-5 formulation of the solvent was demonstrated at small pilot-scale at 250 kW coal-fired Tiller pilot plant. For a capture rate of 90 % an L/G ratio of 2.5 was found to be the most optimal, resulting in a reboiler duty of 2.3 GJ/tCO₂. Properties of very low corrosivity and low volatility were also measured for the solvent. (Zhou et al. 2018.) Other pilot-scale demonstration was conducted at the NCCC where 1 tCO₂/d was captured from coal-fired flue gases (RTI 2020). In bench-scale evaluation, a precursory formulation of

the solvent (NAS-3) reached a capture cost of \$47/tCO₂ (vs. MEA \$57/tCO₂), when excluding TS&M costs (Lail 2016).

The solvent is currently under demonstration in coal-firing at 12 MW scale at the Technology Centre Mongstad in Norway with a capture capacity of 24 tCO₂/d. Successful demonstration at TCM will increase the TRL of eCO₂Sol from 5 to 7. The solvent is expected to be ready for commercial demonstration in 2021. (RTI 2020.)

4.5 Solid adsorbents

Carbon capture with solid adsorbents is based on chemical or physical adsorption, where particles of the adsorbate substance (CO₂) bind to the surface of the adsorbent. Commonly fixed bed reactors are used for solid adsorbents but also other bed configurations, such as rotating beds and fluidized beds, have been studied. Typical adsorbent materials are activated and porous carbons, zeolites, carbonates, amine supported materials and metallic organic frameworks. In chemical adsorption (chemisorption) the particles bind to the surface due to strong chemical bonds, whereas in physical adsorption (physisorption) the bonding takes place due to weak physical van der Waals forces between the molecules. Physisorption occurs at lower temperature levels and at a faster rate compared to chemisorption but is also typically not as selective. Due to better selectivity properties chemisorption is more suitable when purity of CO₂ is emphasized. Since adsorption applications do not require regeneration of large solvent flows as liquid adsorbents do, energy requirements are often significantly lower. Adsorption-based capture processes are categorized depending on the cyclic process method. Currently, the most mature processes are based on pressure-swing adsorption and temperature-swing adsorption, but also alternative methods such as electrical-swing adsorption have been researched. (IEAGHG 2019a; Nakao et al. 2019.) Solid adsorbent processes currently reach a TRL of 6 in carbon capture. Based on the development in other industries (e.g., natural gas purification), a straightforward technology scale-up can be expected for solid adsorbent processes in carbon capture as well. (IEAGHG 2019a.)

4.6 Pressure-swing adsorption

Pressure-swing adsorption (PSA) processes use a pressure difference as a driving force of adsorbent regeneration, meaning that the CO₂ is released from the sorbent via pressure reduction. PSA can offer rapid and low-energy regeneration for physisorption applications, where weak physical binding forces occur and only low regeneration energy is needed. However, typically two or more adsorption/desorption cycles are required to achieve high (>95 %) CO₂ purity. (IEAGHG 2019a.) Pressure-difference is typically generated by pressurising the feed-side gas, but also outlet-side vacuum can be used as a driving force of desorption, in which case the process is referred to as vacuum-swing adsorption (VSA). Single stage VSA process would however require high vacuum levels to reach high CO₂ purity. By combining pressurised feed-side gas and outlet-side vacuum, a more efficient but also costly VPSA cycle can be created. In post-combustion capture the chances of PSA/VSA limit to small scale applications (<50 MW) due to the weak scalability of the fixed bed processes. Higher potential lies in processes with high CO₂ concentrations and smaller flow rates, such as in IGCC's and in various industrial processes like in cement and refinery industries. (Bui et al. 2018.) In PSA pilots with coal flue gases, mostly utilizing zeolite sorbents, reboiler duties of >2.3 GJ/tCO₂ have been achieved. Development of PSA has not reached industrial scale, but some pilot-scale demonstration has been conducted, indicating that PSA processes have reached a TRL of 6. (IEAGHG 2019a.) Some demonstration experiments based on pressure-swing adsorption are reviewed below.

4.6.1 13X VSA by the National University of Singapore

Krishnamurthy et al. (2014) from the National University of Singapore conducted a pilot plant study for a vacuum-swing adsorption process by using synthetic flue gases with a CO₂ concentration of 15 %. Adsorption took place in columns packed with zeolite-based 13X adsorbent developed by Zeochem. With a single-stage and four-step VSA cycle they reached a capture rate of 86 % and CO₂ purity of 96 %, whereas the energy consumption of the system was measured at 472 kWh (=1.7 GJ) per CO₂ tonne.

4.6.2 Rapid PSA by the University of South Carolina

Ritter et al. (2015) from the University of South Carolina conducted a bench-scale (TRL 5) techno-economic analysis for a rapid PSA process based on 13X adsorbent material. The process can reach >90 % capture rate with >95 % CO₂ purity. Cycle time is 30 seconds, which is significantly higher compared to conventional PSA processes with ~300 second cycle times. A capture cost of \$39.7/tCO₂ and a COE increase of 52.7 % was calculated for the process.

4.7 Temperature-swing adsorption

Temperature-swing adsorption (TSA) processes utilize a temperature difference for sorbent regeneration, meaning that the CO₂ is released via temperature increase. TSA is typically used in chemisorption applications due to the strong chemical bonding forces, which require more regeneration energy. Compared to PSA, conventional TSA is more energy-intensive and occurs at a slower rate. However, advanced TSA processes have also been developed, such as the VeloxoTherm process reviewed below. (IEAGHG 2019a.) Conventional TSA processes take place in packed bed reactors, but fluidized bed configurations with better mixing properties have been developed to speed up the process, though also resulting in lower CO₂ loadings on average (Bui et al. 2018).

4.7.1 VeloxoTherm by Svante

One of the leading developers of TSA is Svante (ex-Inventys) with their VeloxoTherm capture process, which is an intensified rapid cycle temperature swing adsorption process developed to reach a capture rate of 90 % in post-combustion applications. The process consists of structured adsorbents fixed into a rotating frame, which is divided into adsorption and regeneration zones. A full cycle of adsorption, regeneration and cooling takes approximately 60 seconds, occurring at a rate 40–100 times faster than a conventional TSA process. Regeneration is done by using low-pressure steam at a temperature swing range of 40–110 °C. Regeneration energy requirement of the process

is estimated to be even less than 1.5 GJ/tCO₂. (CCJ 2011; XPRT n.d.). Based on data collected from related literature, IEAGHG (2019a) estimates a capture cost of is 41 €/tCO₂ for VeloxoTherm in coal-firing.

VeloxoTherm is currently being demonstrated at Husky Energy's Pikes Peak South heavy oil site located in Saskatchewan, Canada, where 30 tonnes of CO₂ is captured per day from a once-through steam generator and utilized in enhanced oil recovery. The company aims to commercialize the technology after successful demonstration. (ERA n.d.). If successful, the Pikes Peak South project can be seen to advance the TRL of VeloxoTherm from 6 to 7.

4.7.2 Dry-sorbent process by KIER & KEPCO

Korea Institute of Energy Research (KIER) and Korea Electric Power Corporation (KEPCO) have developed a dry-sorbent process with temperature-swing regeneration for post-combustion capture applications. Advantages of the process are high loading capacity, non-volatility, low corrosivity and lack of waste streams (Yi 2017). Both sodium- and potassium carbonate sorbents have been researched as sorbent bed material. A process with potassium carbonate bed material and bubbling fluidized bed carbonator and regenerator configurations have been demonstrated at 10 MW_e scale at coal-fired Hadong power plant located in Korea. A capture rate of 80 % with >95 % product-CO₂ purity has been achieved in the experiments. (Park et al. 2014.) According to Lockwood (2016) the process could potentially reach a capture cost of \$30 per CO₂ tonne. IEAGHG (2019a) estimates TRL of technology at 6, which may shortly progress to 7 if further demonstration is conducted at Hadong power plant.

4.8 Membranes

Membranes are thin selective barriers through which some compounds pass more easily than others. Membranes can be used either to capture CO₂ from various gas mixtures or to capture N₂ to increase the concentration of CO₂ in combustion air or in flue gases to

facilitate the capture of CO₂. Membrane capture has several advantages such as modular and compact nature of the equipment, simplicity, lack of regeneration, waste streams and phase changes, as well as low energy consumption. (Wilcox, 2012; IEAGHG 2019a.) Nakao et al. (2019) consider membrane capture to be one of the most promising capture technologies from the point of view of capital and operational costs.

The capture process is driven by a pressure difference over the membrane. The process is more efficient when the pressure difference across the membrane is high, meaning that with mixtures of low CO₂-concentration (i.e., low partial pressure of CO₂) the capture process can be challenging. In combustion processes concentration of CO₂ in the flue gases is relatively low at around 3–15 %, which is problematic for sole membrane capture systems. Post-combustion capture applications might have to utilize feed-side compression, permeate-side vacuum pumping, and larger membrane areas to create efficient capture in low-pressure flue gas conditions, which significantly increase capture costs. (IEAGHG 2019a; Nakao et al. 2019.) To reduce costs in conditions where partial pressure of CO₂ is low, high membrane permeability should be preferred over high selectivity (Nakao et al. 2019).

In pre-combustion capture applications, the concentration of CO₂ in the syngas mixtures is higher compared to combustion flue gases, making the capture conditions more suitable. In high-pressure conditions there is no need for compressors or vacuum pumps, which expectedly results in significant cost reductions compared to post-combustion capture applications. In these conditions both permeability and selectivity of the membrane should be focused upon. (Nakao et al. 2019.)

Several membrane materials are applicable for carbon capture, such as polymers, microporous organic polymers, fixed site carrier membranes, mixed matrix membranes, carbon molecular sieve membranes and inorganic membranes. Membrane material choice depends on factors like capture conditions and desired operational properties, lifetime, stability, and selectivity of the membrane. For example, polymer-based membranes typically provide good separation performance with low cost but weak stability, which

means poor resistance to impurities and challenging conditions like high pressure and temperature. Inorganic membranes are better at withstanding challenging conditions but have more complex module construction and thus higher cost. (He 2018.)

4.8.1 Polaris membrane by MTR

MTR is one of the leading developers of membrane capture with their commercially available high-permeable and CO₂-selective Polaris membrane, suitable for pre- and post-combustion processes. (MTR 2020a.) Material of the Polaris membrane is based on thin-film composite polymer structures (Figueroa et al. 2008). Gen-1 Polaris membranes have reached commercial-scale and have been used, for instance, in natural gas applications and refineries. Gen-2 Polaris membranes are more permeable compared to Gen-1, which reduces capital cost of the system since the required capture area is smaller. Gen-2 membranes have been demonstrated in several pilot-scale projects, for example at National Carbon Capture Center at 1 MW_e scale capturing 20 tCO₂/d from coal-derived flue gases. Development of Gen-3 membranes with even higher permeability is currently at laboratory-scale. (Merkel 2018.)

Power requirement for a two-stage Gen-2 Polaris membrane post-combustion capture with CO₂ selective flue gas recycling is estimated to be as low as 277 kWh/tCO₂ (= 1 GJ/tCO₂) with a capture rate of 80 % (Baker et al. 2018). Based on data collected from related literature, IEAGHG (2019a) estimate capture costs to be 47 €/tCO₂ in coal-firing and 80 €/tCO₂ in gas-firing for MTR's Polaris membranes. However, it is noted that the calculations were done for a capture rate of 90 % in conditions of relatively low CO₂-concentration and that the cost benefits of membrane capture emerge in hybrid processes, partial capture or combustion air enriching. (IEAGHG 2019a.) A capture cost of 30 \$/tCO₂ is considered feasible for scaled-up Gen-2 membranes (Merkel 2018).

A large pilot-scale post-combustion capture project designed to capture 140 tonnes of CO₂ per day in coal-firing at Wyoming Integrated Test Center is currently underway. The project aims to successfully operate a partial post-combustion capture process based on

Gen-2 Polaris membranes, while reaching a capture rate of ~70 % and a capture cost of ~40 \$/tCO₂. (MTR 2020b.) Successful demonstration at Wyoming ITC will advance TRL of Polaris membranes in carbon capture from 6 to 7–8.

4.8.2 Membrane-sorbent hybrid system by MTR & TDA

MTR and TDA Research have developed a hybrid carbon capture system combining MTR's Polaris membranes and TDA's mesoporous carbon sorbent based on physical absorption. The hybrid process is developed to reach a 90 % capture rate in post-combustion applications. Polaris membranes and TDA's sorbent have been separately evaluated at various pilot-scale projects, whereas the hybrid system has been evaluated at bench-scale (TRL 5) with coal-fired flue gases at Western Research Institute, capturing 20–40 kgCO₂ per day. A capture cost of \$35.5/tCO₂ has been calculated for the process based on these preliminary evaluations. (NETL 2018; IEAGHG 2019a.) Further demonstration will be conducted at 1 MW scale at TCM in Norway, where the process is designed to capture 20+ CO₂ tonnes per day from industrial flue gases (NETL 2018), which will advance TRL of the technology to 7.

4.9 Electrochemical separation

Whereas most capture technologies utilize thermal cycles to catch and release the CO₂ electrochemical separation technologies utilize electrochemical potential difference (e.g. fuel cells, electrodialysis) or electrochemical cycles (e.g. pH swings, redox reactions). Rheinhardt et al. (2017) summarize the desired properties of an electrochemical capture system as following: small potential difference in capture and release for low energy consumption and costs, rapid transfer kinetics, binding constant tunability, insensitivity to O₂ and H₂O, use of low cost and stable electrolytes, and lack of highly reactive intermediates. They state that none of the methods currently available can fulfil all these desired properties.

Electrochemical CO₂ separation has been successfully demonstrated in laboratory conditions thus reaching a TRL of 4, but industrial-scale demonstration with fuel cells is soon taking place (FCB 2016), which will advance the TRL significantly. IEAGHG (2019a) predicts that electrochemical separation is among the most potential technologies for widespread deployment in the next 5–10 years and that it has high potential for cost reduction. They estimate a high LCOE reduction potential (31 %) for fuel cell based electrochemical separation capture compared to a benchmark 30 wt. % MEA capture process.

Fuel cells, which produce electricity and thus increase the power output of the facility, are one of the most potential methods of electrochemical CO₂ separation. Fuel cells with recognized potential on carbon capture are molten carbonate fuel cells (MCFC's) and solid oxide fuel cells (SOFC's). The most promising techno-economic performance properties have been achieved by combining the fuel cells with various hybrid-cycles (e.g., IGCC, NGCC and NGFC). Depending on the purity of the oxidizer stream, further CO₂ purification might be required by using other capture methods such as cryogenic separation or membranes. (IEAGHG 2019b.)

MCFC's can concentrate the CO₂ from a gas stream, like combustion flue gases. Flue gas, which functions as an oxidizer, is fed to the cathode side and hydrogen/syngas to the anode side. On the cathode side O₂ and CO₂ form carbonate (CO₃⁻²), which travels through the electrolyte layer and reacts with hydrogen on the anode side forming CO₂ and H₂O. The CO₂ is captured from the anode side exhaust gas by separating the moisture and possible hydrogen remains. SOFC's are suitable for non-combustion processes. Chemical energy of a gaseous fuel (e.g., syngas, hydrogen, methane) is converted to electricity by using regular air as oxidizer. CO₂ from the fuel is separated either before or after the fuel cell. (IEAGHG 2019b.)

IEAGHG (2019b) conducted a techno-economic analysis for fuel cells combined with carbon capture by using multiple literature-based hybrid-cycle case arrangements and reference cases. The best performance was achieved with a hybrid cycle consisting of a

NGCC power plant equipped with an atmospheric pressure MCFC and cryogenic capture technology. With a capture rate of 72 % the case resulted in a capture cost of 33.5 €/tCO₂.

4.9.1 SureSource MCFC by FuelCell Energy

FuelCell Energy is one of the leading developers of the fuel cell capture technology, with their SureSource MCFC technology. In theory, by capturing 90 % of the CO₂ from a typical coal plants flue gas stream with fuel cells, the power output could be increased by 80 % while the overall cost of electricity would only increase by 33 %. In addition, NO_x emissions are reduced by 70 %. (FuelCell Energy n.d.) FCE's SureSource technology will soon be demonstrated at 3 MW pilot-scale at coal- and gas-fired Plant Barry located in Alabama, targeting to reach a capture rate of 90 %. The demonstration is conducted under a joint-development agreement by ExxonMobil and FuelCell Energy. (FCB 2016.)

4.10 Status, performance and potential of the reviewed post-combustion carbon capture technologies

The most relevant information regarding the carbon capture technologies assessed in the literature review are summarized in this section by presenting key technologies and developers, status of the technologies, ongoing or near-future demonstration projects, as well as essential energy requirement and capture cost. Additionally, the potential of various carbon capture technologies is roughly assessed.

The key technologies assessed in the literature review, as well as the developers and maturity of these technologies, are presented in Table 4.2.

Table 4.2. The key carbon capture technologies and developers assessed in the literature review. TRL level indicates maturity of the technology on a scale of 0–9. Higher TRL indicates higher maturity.

Capture method	Key technologies and developers		TRL (after ongoing or near-future demonstration)
Aqueous amines	EFG+	Fluor	9
	PZ+AMP	-	6
	KS-1	MHI	9
	KS-21	MHI	7 (8)
	CANSOLV	Shell	9
Aqueous ammonia	Aq. NH ₃	CSIRO	6
	CAP	GE	6
Aqueous carbonate	UNO MK 3	CO2CRC & Uno Technology	6
	Hot-CAP	University of Illinois	4
	HPC	Stockholm Exergi	6
Liquid-liquid separating	DMX	IFPEN	4–5 (7)
Water-lean solvents	eCO2Sol	RTI	5 (7)
Pressure-swing adsorption	VSA with 13X	National University of Singapore	5–6
	Rapid PSA with 13X	University of South Carolina	5
Temperature-swing adsorption	VeloxoTherm	Svante	6 (7)
	Dry-sorbent	KIER & KEPCO	6 (7)
Membranes	Polaris	MTR	6 (7–8)
	A membrane-sorbent hybrid system	MTR & TDA Reseach	5 (7)
Fuel cells	SureSource MCFC	FuelCell Energy	4 (7)

Of the reviewed technologies, only the amine-based EFG+, KS-1 and CANSOLV have reached commercial-scale operation (TRL 9). Most of the other reviewed technologies have at least some demonstration experience in realistic conditions from various pilot-scale projects (TRL 6), while many technologies are also facing larger industrial-scale demonstration in the near-future, as seen in Table 4.3.

Table 4.3. Ongoing and planned demonstration projects for the carbon capture technologies reviewed in the literature review.

Ongoing and planned demonstration		
EFG+	-	In commercial operation with 27 licensed plants
KS-1	-	KS-1 in commercial operation (e.g., NRG Petra Nova, Texas, 4776 tCO ₂ /d)
KS-21	-	Both solvents demonstrated in biomass-firing at Drax Power Station in UK with a capture capacity of 300 tCO ₂ /d
CANSOLV	-	1 MtCO ₂ /a at coal-fired Boundary Dam power plant in Saskatchewan, Canada
UNO MK 3	-	Preliminary plans for demonstration in natural gas power generators
HPC	-	0.7 tCO ₂ /d in biomass-firing at Stocholm Exergi's KVV8-unit in Stockholm, Sweden
DMX	-	0.5 tCO ₂ /h from blast furnace exhaust gases at Dunkirk, France (3D project)
eCO2Sol	-	24 tCO ₂ /d in coal-firing at 12 MW scale at TCM, Norway
VeloxoTherm	-	30 tCO ₂ /d from exhaust gases of a once through stream generator at Husky Energy's Pikes Peak South heavy oil site in Saskatchewan, Canada
Dry-sorbent process	-	10 MW _e demonstration at coal-fired Hadong power plant in Korea
Polaris membrane	-	140 tCO ₂ /d in coal-firing at Wyoming ITC in Wyoming, US
A membrane-sorbent hybrid system	-	20+ tCO ₂ /d in 1 MW scale with industrial flue gases at TCM, Norway
SureSource MCFC	-	3 MW demonstration at coal- and gas-fired Plant Barry in Alabama, US

Most of the carbon capture demonstration projects are conducted at fossil fuel -fired facilities. Of the reviewed technologies only MHI's KS-1 and KS-21 solvents and Stockholm Exergi's Hot Potassium Carbonate process are taking part in demonstration where biogenic CO₂ is captured. However, all the presented demonstration projects are essential in advancing the maturity of the technologies also from the perspective of BECCU/BECCS.

Performance of the reviewed technologies regarding energy requirement and capture cost are summarized in Table 4.4.

Table 4.4. Energy requirement and capture cost of the reviewed technologies.

Technology		Energy requirement per CO ₂ tonne	Capture cost per CO ₂ tonne	
			Solid fuel	Gaseous fuel
Liquid absorbents	MEA	3.3–3.7 GJ ¹	44 € ²	64 € ²
	PZ+AMP	2.5 ² ; 3.2 GJ ³	34 € ²	56 € ²
	KS-1	2.6 GJ ⁴	\$59 ⁵	-
	KS-21	2.6 GJ ⁶	\$55 ⁵	-
	CANSOLV	2.3 ⁷	-	-
Multi-phase absorbents	Aq. NH ₃	2.5 GJ ⁸	\$53 ⁸	-
	CAP	2.2 GJ ⁹	-	-
	UNO MK 3	2.0–2.5 GJ ¹⁰	\$45 ¹¹	-
	Hot-CAP	1.8 GJ ¹²	-	-
	DMX	<2.5 GJ ¹³	39 € ²	-
Water-lean solvents	eCO2Sol	2.3 GJ ¹⁴	\$47 ¹⁵	-
		2.0 GJ (exp.) ¹⁴		
Solid adsorbents	PSA	>2.3 GJ ²	\$40 ¹⁶	-
	VSA	1.7 GJ ¹⁷	-	-
	VeloxoTherm	1.5 GJ ¹⁸	41 € ²	-
Membranes	MTR Polaris	1.0 GJ ¹⁹	47 € ²	80 € ²
			\$30 (exp.) ²⁰	
Hybrid systems	Membrane-sorbent	-	\$36 ²	-
Electrochemical separation	NGCC-MCFC hybrid-cycle	-	-	34 € ²¹

Ref: 1) GCCSI in Svendsen 2014; 2) IEAGHG 2019a; 3) Rabensteiner et al. 2016; 4) Yagi et al. in IEAGHG 2019a; 5) Carroll 2017; 6) Tanaka et al. 2018; 7) Singh & Stéphenne 2014; 8) Li et al. 2016; 9) Augustsson et al. 2017; 10) Smith et al. 2014; 11) UNO 2014; 12) Lu et al. 2014; 13) Broutin et al. 2017; 14) Zhou et al. 2018; 15) Lail 2016; 16) Ritter et al. 2015; 17) Krishnamurthy et al. 2014; 18) CCJ 2011; 19) Baker et al. 2018; 20) Merkel 2018; 21) IEAGHG 2019b

From the reviewed technologies only amine-based EFG+, KS-1 and CANSOLV have reached commercial operation. Cost estimates for the other capture technologies are mainly based on pilot-scale operation or preliminary studies conducted in laboratory conditions and thus the estimates for the more immature technologies may not be as realistic as the ones from commercial-scale operation. Many of the emerging technologies are however taking part in large-scale industrial demonstration projects in the near-future,

which will provide important information on the techno-economic performance of these technologies in relevant conditions.

Regeneration is generally the most energy-intensive phase of carbon capture processes. Since liquid absorbents require regeneration of large solvent flows the energy requirements are often high, typically varying between 2.5–4.0 GJ/tCO₂. With multi-phase absorbents the CO₂-rich solvent can be more easily extracted, which decreases the regeneration flows and thus lowers the energy requirement. Energy requirements of multi-phase absorbents generally vary between 1.8–2.5 GJ/tCO₂. Also, adsorption-based technologies have generally low energy requirements due to the more efficient regeneration. For instance, the VeloxoTherm TSA process is estimated to reach a reboiler duty as low as 1.5 GJ/tCO₂. Processes without the need for regeneration can reach even lower energy requirements, like MTR's two-stage Gen-2 Polaris membrane process with CO₂ selective flue gas recycling that has estimated power consumption of around 277 kWh/tCO₂ (= 1 GJ/tCO₂).

The reviewed technologies currently reach capture costs of 34–80 €/tCO₂. On average the capture cost ranges around 40–60 €/tCO₂. Current state-of-the-art technology of IEAGHG – 40 wt. % PZ+AMP solution with 2:1 molar ratio – reaches a capture cost of 34 €/tCO₂ in coal-firing according to IEAGHG's literature-based estimates. Some other emerging technologies, such as fuel cell hybrid cycles have also reached considerably low capture costs similar to PZ+AMP. Despite the promising results, these are still high-risk technologies that lack the maturity to be considered as state-of-the-art technologies. Many emerging technologies are currently striving to achieve a capture cost of 30 \$/tCO₂ – a target set by, for instance, the US Department of Energy aiming to accelerate the deployment of carbon capture technologies (Ryser 2020).

Performance of the capture technologies is highly dependent on the application. For example, membranes perform weakly in low CO₂ concentration applications with high capture rate, whereas in high CO₂ concentration applications they become one of the most

potential capture technologies available, which also explains the relatively high capture costs estimated by IEAGHG for membrane capture in Table 4.4.

When assessing techno-economic performance of capture technologies it is important to understand differences between theoretical estimates and experimental data. Theoretical estimates often provide information on the maximum potential, whereas experimental data presents the current state of the technology. Theoretical performance estimates can be seemingly promising for some immature technologies and these estimates are often not even remotely reached in the initial demonstration projects at realistic conditions. However, these initial projects generally aim to validate the proper function of technology rather than to optimize techno-economic performance, which is improved in further demonstration projects.

4.10.1 Potential of carbon capture technologies

Most of the reviewed technologies reach roughly similar techno-economic properties and there are no clear standout technologies that have emerged over the others. Each technology has its specific advantages and challenges, and primarily, capture environment, feed gas composition and end-use application of the captured CO₂ determines the most suitable technology for various applications. The applicability is determined by factors like scale, energy requirement, form of energy required, desired capture rate and CO₂ purity, waste stream handling, equipment size, and most importantly, cost. It can be expected that future development of carbon capture technologies will include multiple different methods of carbon capture for various applications. If any major technological breakthroughs do not occur, it is unlikely that a single technology would take over the whole carbon capture market.

Post-combustion capture with liquid absorbents is currently the most mature method of carbon capture available, with lots of commercial-scale demonstration to prove its credibility. It is considered as one of the low-risk technologies with the most realistic cost estimates available. More advanced versions of the absorbents with proven feasibility are

constantly being developed, which will expectedly improve the techno-economic properties of these absorbents. Conventional absorbents, such as the previous state-of-the-art technology MEA, suffer from obvious shortcomings such as high energy-intensity and harmful nature to equipment and environment. Despite the high technological maturity, the conventional absorbents are being displaced by more advanced absorbents like advanced amines and multi-phase absorbents.

In addition to absorption-based capture, many other emerging technologies have shown great promise in preliminary and pilot-scale assessments. Many of these technologies have not yet reached large industrial-scale demonstration, which makes it difficult to realistically assess their true potential. For example, fuel cell hybrid cycles have shown very promising techno-economic performance in preliminary assessments but are still considered as high-risk technologies since demonstration in realistic conditions has not yet been conducted. Industrial-scale demonstration is however underway for both technologies, as well as for many other emerging carbon capture technologies, meaning that the true potential of these technologies can be more accurately assessed in the near-future.

In their report on emerging CO₂ capture technologies IEAGHG (2019a) ranked the emerging CO₂ capture technologies based on the potential of widespread deployment for the near future. The ranking is presented on Figure 4.2. It is based on to a scoring system taking into account each technology's demonstration level, cost reduction potential, experience from other sectors, component availability, retrofitting compatibility and requirement for further research.

SCORE	POST COMBUSTION CAPTURE TECHNOLOGIES	OXYFUEL PROCESSES	PRE-COMBUSTION CAPTURE TECHNOLOGIES
19	Amine based liquid absorbents		
18	Electrochemical separation		
17	Solid sorbents (PSA, VPSA, TPSA); calcium looping		H ₂ separation membranes; CO ₂ separation membranes; solid sorbents
16	Liquid-liquid separating, non-aqueous and non-amine; amino acid and other mixed salt; solid sorbent (TSA)		Chemical liquid absorbents
15	Catalysts and other activators	Chemical looping combustion	
14	Precipitating processes; membranes; membrane contactors; cooling processes		Sorbent enhanced water gas shift
13		Oxyfuel gas turbines; high temperature air separation membranes	
12	Ionic liquids	Pressurised solid oxyfuel combustion	
11			Clathrates

Figure 4.2. Carbon capture technologies ranked by their potential for widespread deployment in 5–10 years from 2019 onwards. Higher score indicates greater potential. (IEAGHG 2019a.)

According to IEAGHG’s technology ranking the highest potential for widespread deployment lies in post-combustion technologies. From these technologies, the highly mature amine-based absorbents rank the highest, closely followed by electrochemical separation (e.g., fuel cells) and adsorption-based capture, which are yet to prove their feasibility in large-scale industrial operation. Membranes and solid sorbents reach good potential in pre-combustion applications, whereas the still immature oxyfuel processes rank notably lower compared to post- and pre-combustion technologies. Based on related literature IEAGHG (2019a) summarize the challenges of widespread carbon capture deployment as following: high cost, investment risk of the initial projects due to weak investment returns, lack of infrastructure regarding transportation and storage of CO₂, long duration of the projects, lack of related legislation as well as unclear policymaking regarding carbon capture.

5 DESCRIPTION OF THE PILOT-SCALE CARBON CAPTURE EXPERIMENTS

Experimental part of this thesis is focused on the carbon capture experiments that were conducted as part of VTT's BECCU project between August and October of 2020. Three absorption-based post-combustion capture technologies were tested at pilot-scale by using synthetic gas mixtures, biogenic flue gases and raw biogas. The tests were conducted by using a 50 kW circulating fluidized bed (CFB) pilot combustor located at VTT's facilities in Jyväskylä, Finland. Objective was to validate proper function of the technologies in realistic conditions and to gain information about capture performances with various CO₂ sources. Additionally, some CO₂ was captured, compressed and bottled for further research regarding CO₂ utilization via Fischer-Tropsch synthesis. The utilization experiments are not however reviewed in this thesis.

The tested carbon capture technologies were:

- Enhanced soda scrubbing process by VTT,
- Enhanced water scrubbing process by CarbonReUse Finland,
- Kleener liquid – a novel capture absorbent by Kleener Power Solutions.

Compared to more mature amine absorbents these technologies use more eco-friendly capture solvents, which supposedly do not cause any harmful emissions to the environment or to the captured CO₂ stream. It is estimated that the solvents are also not as volatile as amines and could require less energy in the capture process, at least when compared to conventional amines like MEA.

Schedule, content and objectives of the experiments are presented in Table 5.1. As seen from the table, not all technologies were tested with all the CO₂ sources.

Table 5.1. Schedule, content and objectives of the carbon capture experiments.

Week	CO ₂ source	Tested technologies	Test objectives
#36	Synthetic gas mixtures	VTT Soda CarbonReUse	<ul style="list-style-type: none"> • Verifying proper function of the test equipment • Testing capture performance with modifiable gas compositions
#37	Flue gas from combustion of pine chips	VTT Soda CarbonReUse Kleener liquid	<ul style="list-style-type: none"> • Post-combustion capture in realistic flue gas conditions • Technology performance comparison
#38	Flue gas from combustion of washed straw	VTT Soda CarbonReUse	<ul style="list-style-type: none"> • Post-combustion capture in realistic flue gas conditions • Technology performance comparison • Effect of another biomass type on capture performance
#40	Flue gas from combustion of spruce bark & raw biogas	VTT Soda	<ul style="list-style-type: none"> • Post-combustion capture in realistic flue gas conditions • Effect of another biomass type on capture performance • Performance of VTT's soda process in biogas purification

The technologies were tested by using capture equipment built inside two shipping containers, which ensure effective mobility of the equipment. CarbonReUse's technology was tested by using their self-constructed pilot-scale capture container, whereas VTT's soda solution and the Kleener liquid were both tested in a capture container built by VTT. The two containers were placed outdoors next to VTT's 50 kW CFB-pilot facility (Figure 5.1) and the containers were connected to the flue gas line of the CFB.



Figure 5.1. The carbon capture technologies were tested by using capture equipment built inside two shipping containers. The 50 kW CFB-pilot is located in the building behind the containers.

The tested technologies and test arrangements are more specifically reviewed below.

5.1 Enhanced soda scrubbing process by VTT

In the enhanced soda scrubbing process developed by VTT, an aqueous sodium carbonate (Na_2CO_3) solution is used to capture CO_2 via chemical absorption. Originally, the process has been developed for biogas purification applications, but potential has been recognized also in post-combustion carbon capture. The process has been previously experimented in synthetic biogas purification at laboratory-scale by VTT (TRL 4). Via the discussed experiments TRL of the process advanced to 5.

The process includes a novel technical improvement to enhance the slow absorption kinetics of soda-based carbon capture. Instead of using a conventional large-sized absorption column that are typically used in absorbent capture, an ejector is used to mix the flue gas and the solvent flows. Efficient mixing properties of the ejector improve dissolution of CO_2 into the solvent, thus enhancing absorption rate. Furthermore, the improved absorption rate decreases size of the absorption equipment, which could

expectedly lower the capital cost of the equipment compared to conventional absorption columns.

5.1.1 Sodium carbonate as CO₂ absorbent

Sodium carbonate (commonly known as soda) can be used to capture CO₂ via chemical absorption. Soda can be used as an aqueous liquid solution (or possibly slurry), reacting with CO₂ and water to form sodium bicarbonate (Eq. 6).

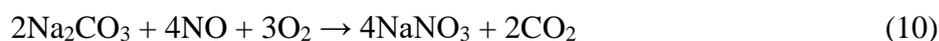
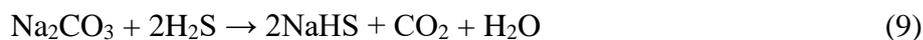
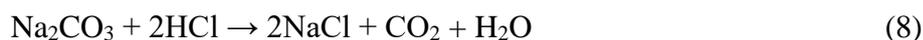


Due to low solubility of sodium carbonate and bicarbonate into water, unwanted solvent precipitation may occur with high soda concentrations. The risk of precipitation limits the soda concentration of the solution unless solid- or slurry-mode operation is desired, which requires more complex process configuration with specific solid handling equipment.

Previous research on using soda as CO₂ absorbent has been conducted e.g., by Knuutila et al. (2009). In their model-based study, they studied feasibility of carbon capture in coal-firing by using a sodium carbonate-bicarbonate slurry. For a capture rate of 90 % by using a 30 wt. % soda solution they calculated a reboiler heat duty of 3.2 GJ/tCO₂ for the process. They conclude that in carbon capture soda has advantages like eco-friendly and non-corrosive nature, stability and low sorbent cost. However, a significant drawback of soda-based capture, when used in a conventional absorption column, is the slow absorption rate, which is why the process requires large-sized capture equipment.

Soda is not as sensitive to various impurities as the more conventionally used amines are. Impurities may cause degradation of soda, but without leading to formation of harmful compounds such as nitrosamines and nitramines that occur with amine absorbents. Soda could possibly be even used to remove some impurities alongside carbon capture. Soda

may react with impurities that are commonly present in flue gases and biogas according to the reactions presented in Equations 7–11.



Non-regenerable compounds that are formed in reactions with impurities can be removed from the process via a purge stream. The purge stream also removes some soda from the process, creating a need for make-up soda. The purge stream is expectedly small and thus not a lot of make-up soda is required. Additionally, the soda solution does not require any performance enhancing additives, which some carbonates (e.g., K_2CO_3) often require to reach high capture performance.

5.1.2 Description of the enhanced soda scrubbing process

In this process configuration a soda concentration of 8 wt. % was used. The process was operated with a volumetric L/G (liquid-to-gas) ratio of ~1 l/l. Flue gas and solvent flow rates were both around 8–12 NI/min. A schematic flow diagram of the enhanced soda scrubbing process is presented in Figure 5.2.

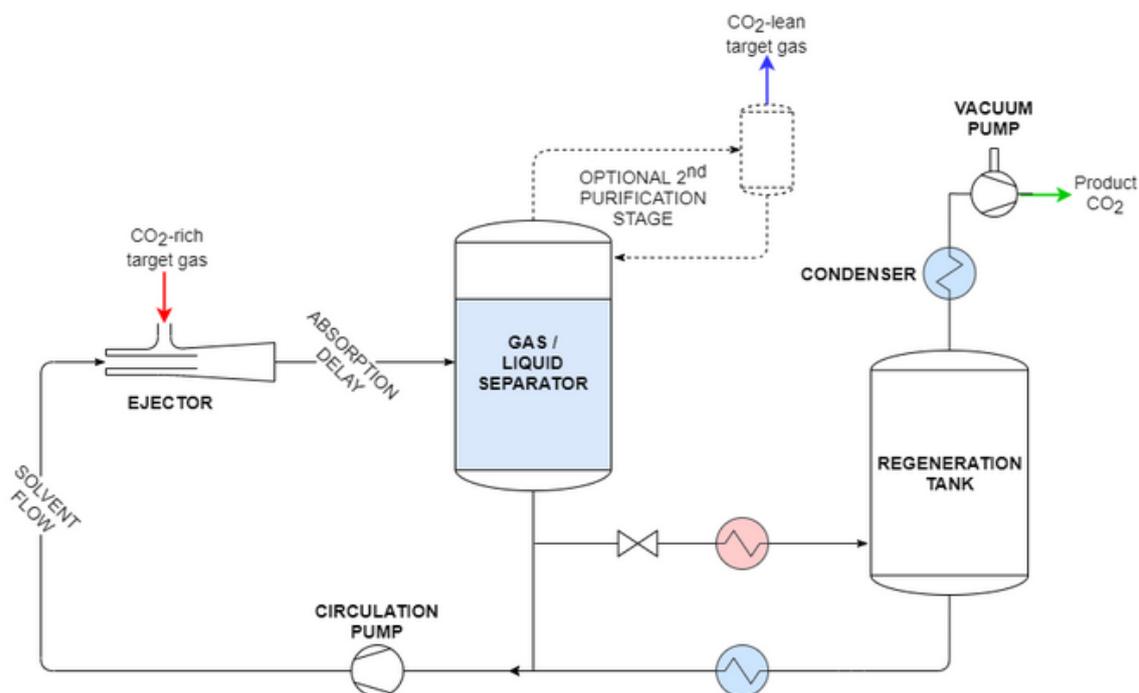


Figure 5.2. A schematic flow diagram of VTT's enhanced soda scrubbing process.

Solvent flow and CO₂-rich target gas are mixed at atmospheric pressure by using an ejector. Majority of the CO₂ dissolves into the solvent and reacts with soda and water via chemical absorption to form sodium bicarbonate (NaHCO₃). The solution is led through a delay tank to achieve a sufficient residence time for the absorption reactions to occur, which in this configuration is around one minute. Non-dissolved gases, mainly consisting of N₂ and O₂, are removed at a gas/liquid separator. The removed gas can be led through a second purification stage, which can be used, for instance, in biogas purification to produce high quality biomethane. About a fourth of the absorption cycle flow is led to a regeneration cycle, where the CO₂-rich solvent is regenerated at a pressure of 0.2–0.5 bar and a temperature of 60–80 °C. In the experiments the regeneration conditions were around 0.25 bar and 65 °C. Low-pressure-conditions are created with a vacuum pump, which enables low-temperature desorption. In this configuration heat source of regeneration was resistance heating by using electricity, which is not an optimal heat source regarding performance but easy to implement at this scale.

In these experiments, the process configuration was built rather for system validation than to reach optimal performance properties. In future development, the performance could be further improved by using a more optimal regeneration heat source, like waste heat. Additionally, higher soda concentration and higher absorption pressure could expectedly improve performance of the process.

5.2 Enhanced water washing process by CarbonReUse Finland

CarbonReUse Finland has scaled-up the enhanced water washing capture process developed by Kuopanportti & Linnanen (2014). In the process, regular water is used to bind CO₂ from the target gas via physical absorption. The absorbent water is regenerated via flash evaporation (flashing) by using pressure reduction. Water-washing is a mature technology in gas purification such as in biogas upgrading. However, it is a novel concept in post-combustion carbon capture. Previous evaluations on the process have been conducted e.g., by Linnanen (2012) and Teir et al. (2014).

5.2.1 Water as CO₂ absorbent

Advantages of using regular water as CO₂ absorbent are simplicity, low-cost solvent and eco-friendly nature compared to chemical absorbents. Since chemicals are not used, degradation and solvent-based emissions do not occur, and additive solvent is not required. The biggest disadvantage is the low solubility of CO₂ into water in conditions of low CO₂ partial pressure, which is why water washing requires larger solvent volume flows compared to chemical solvent processes. CO₂ solubility can be improved by absorbent water cooling and by increasing absorption pressure. However, the solvent mass flows are still up to ten times higher than in conventional amine solvent processes (Suomalainen & Arasto, cited in Teir et al. 2014), requiring around 830 tonnes of water per captured CO₂ tonne (Linnanen 2012). Water-soluble impurities must be removed from the target gas prior to the capture process. For instance, SO₂ and HCl react with water forming sulphurous acid (H₂SO₃) and hydrochloric acid (HCl), which are strongly acidic compounds that would cause harm to the equipment.

5.2.2 Description of the enhanced water scrubbing process

The capture equipment used in this test configuration is designed for flue gas flow rate of around 160–170 NI/min. The process is fully electric. Majority of the required electricity is consumed in flue gas compression and solvent and coolant flow pumping. Schematic flow diagram of the enhanced water scrubbing process is presented in Figure 5.3.

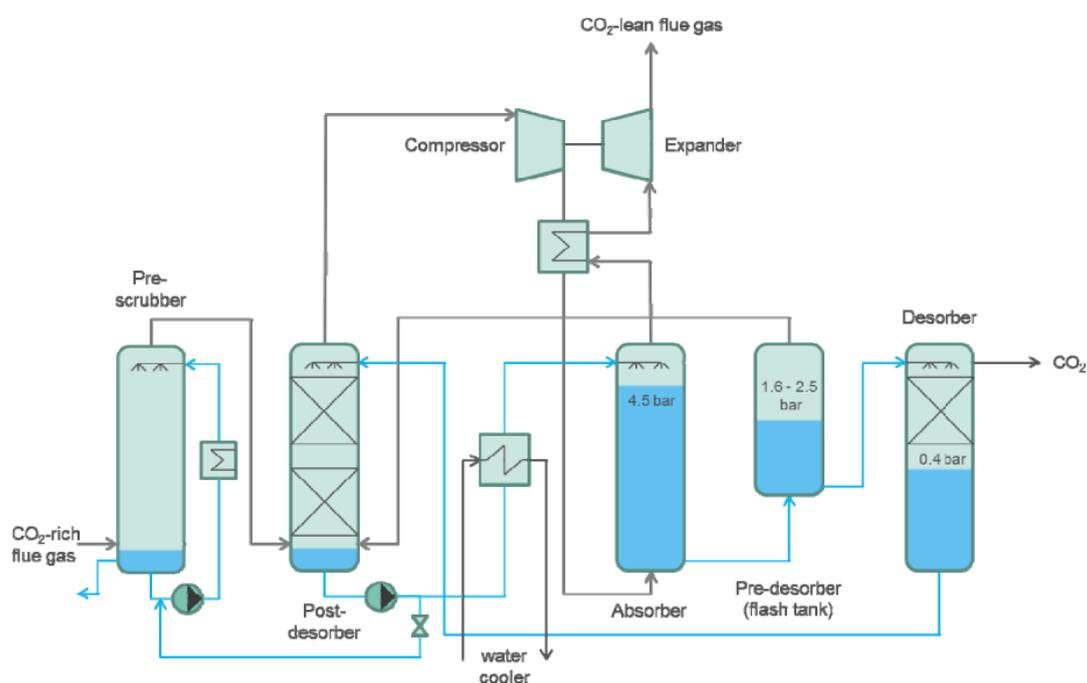


Figure 5.3. A schematic flow diagram of the enhanced water scrubbing process. (Teir et al. 2014.)

Prior to entering the capture cycle, flue gas is scrubbed in a packed-bed counter-flow water scrubber to remove water-soluble impurities. The flue gas is then led to a packed-bed post-desorber column, where it flows upwards against a water stream led from desorber at atmospheric pressure. In the post-desorber, the CO₂ which remains in the water after desorption is stripped into the flue gas flow. The post-desorber is an important technical improvement compared to conventional water scrubbing processes, since it increases CO₂ loading capacity of the water and improves CO₂ capture rate.

After the post-desorber the CO₂-rich gas stream is compressed and led through a heat exchanger, where it releases heat into a stream of CO₂-lean gas. The compressed CO₂-

rich gas stream is led to an absorption tank, where the gas is fed from the bottom into the solvent water. Before entering the absorption tank, the water stream that is entering the absorber is cooled to around 5 °C by using a heat pump to improve CO₂ solubility. The heat pump is not required if there is cool water available, for instance, during cold seasons. The gas flow is led through a fine bubble diffuser, which turns the flow into a stream of numerous small bubbles, thus improving the dissolution of the gas to the water. The gaseous CO₂ transfers into a liquid phase, binding it into the water via physical absorption. Absorption tank is at an elevated pressure of 4–5 bar since higher absorption pressure improves the solubility of CO₂ into water. Majority of the CO₂ from the gas flow is absorbed into the water, but also some unwanted compounds, such as N₂ and O₂, dissolve to the stream. Non-dissolved CO₂-lean gas, mainly consisting of N₂, is removed from the cycle from the top of the absorption tank after going through an expander to generate mechanical energy for compression of the CO₂-rich gas stream.

A pre-desorber is used decrease the amount of unwanted compounds in the product CO₂ stream. In the pre-desorber the pressure of the water is lowered to around 1.6–2.5 bar, which releases most of the N₂ and O₂ from the water, without releasing CO₂. The stripped gases are led to the post-desorber. The CO₂ is stripped and captured from the water in a desorber. A vacuum pump is used to achieve a regeneration pressure of around 0.4 bar for desorption.

5.3 Kleener liquid by Kleener Power Solutions

Kleener Power Solutions is a Finnish company specialized in utilization of power plant waste streams with special expertise on ash handling. They have developed a novel CO₂ capture absorbent called the Kleener liquid, which is also a derivative from the company's ash handling expertise. In manufacturing of the Kleener liquid, power plant ashes are used, offering also a great option for ash utilization. The Kleener liquid is an alkaline solution that captures CO₂ via chemical absorption. Due to patent-related reasons chemical composition of the absorbent is not further specified. Regeneration of the liquid

is done by heating the solution. Regeneration temperature can be reduced by using a vacuum pump to create low-pressure regeneration conditions.

According to Kleener (2021), absorption capacity of the Kleener liquid is 150 times higher compared to regular water. The company estimates that a 50 % reduction in investment cost could be achieved with their capture technology compared to amine-based capture processes. Energy consumption is estimated at 2.6 GJ/tCO₂ and capture cost at 29 €/tCO₂. The estimates are calculated to be comparable with results of the CO₂stCap Project conducted by SINTEF.

In the pilot tests, the Kleener liquid was demonstrated by using VTT's capture equipment with similar process parameters regarding solvent and flue gas flow rates and regeneration conditions (Reviewed in Section 5.1.2). Kleener Power Solutions is conducting their own research to find the most cost-effective formula for the Kleener liquid. In the pilot tests, the Kleener liquid was used as a diluted solution that was not optimized, for instance, to achieve high absorption capacity. Therefore, the results from these test runs do not necessarily present the true performance of the Kleener liquid. Also, the Kleener liquid was only tested in one test run (pine chips combustion), meaning that evaluation of Kleener liquid's performance is more limited compared to VTT's and CarbonReUse's technologies, as there is less test data available.

5.4 50 kW CFB pilot combustor

The experiments were conducted by using VTT's 50 kW CFB pilot combustor. With the pilot combustor, the carbon capture technologies can be tested in realistic flue gas conditions while still maintaining good control over the process conditions. The process conditions can be modified, for instance, with air staging and separately controlled electrically heated and water/air-cooled zones. The combustor is controlled via an automation system equipped with automatic data-logging. Schematic structure of the CFB pilot is presented in Appendix I.

5.5 Flue gas purification

The CFB pilot is equipped with a bag filter to remove particulate matter emissions. In majority of the combustion tests, the flue gas was also purified by using a separate packed bed counter-flow water scrubber. The scrubber was provided by CarbonReUse to remove water-soluble impurities like SO₂ and HCl, which would otherwise dissolve into the absorbent water in CarbonReUse's process. VTT's soda process was also tested with flue gases that were led directly from the combustor without the water-scrubbing stage. Effect of the water-scrubber on flue gas composition seen in Table 5.2. The table presents composition of the flue gas at the end of the flue gas line before the scrubber and at a point after the scrubber before entering the carbon capture processes.

Table 5.2. Mean flue gas composition (wet gas) before and after the water-scrubber in test runs with pine chips and washed straw.

Flue gas source		Pine chips		Washed straw	
Component	Unit	Before	After	Before	After
H ₂ O	vol-%	8.8	1.6	11.9	1.8
O ₂	vol-%	5.2	6.0	5.8	6.7
CO ₂	vol-%	12.7	12.4	12.2	12.8
CO	ppm	2	2	15	20
N ₂ O	ppm	0	1	1	3
NO	ppm	47	53	150	148
NO ₂	ppm	0	0	0	0
SO ₂	ppm	2	1	8	0
NH ₃	ppm	1	1	1	0
HCl	ppm	0	0	1	0

The water-scrubber removed majority of the highly water-soluble impurities like SO₂ and HCl from the flue gas stream. More insoluble impurities like CO, NO, N₂O as well as CO₂ passed through the scrubber, thus being present during the carbon capture processes. Additionally, most of the water in the flue gas condensed before entering the capture systems.

5.6 Measurement arrangements

Measurement arrangements were planned to provide the necessary data to assess the performance of the tested technologies, including flue gas and solvent flow rates, flue gas compositions at various process stages as well as composition of the captured CO₂.

The pilot combustor is equipped with a FTIR-spectrometer to measure flue gas composition. Measurement point of the FTIR was located between primary and secondary cyclones. Since the FTIR does not measure O₂ level, it was measured by using a ZrO₂ sensor. A conventional on-line analyser was also connected to the flue gas duct between the gas cooler and bag house filter to measure flue gas composition. Composition of the captured CO₂ flows were measured by using Gaset Dx4000 FTIR with a 2.6 m path length. Synthetic gas mixtures were created by mixing carbon dioxide (99.9 %), instrument nitrogen (99.999 %) and purified compressed air with two mass flow controller units manufactured by Environics Ltd.

In VTT's container CO₂ concentration was measured in the range of 0–50 vol-% by using ETG MCA 100 Bio with an interval of five seconds. Gas samples were taken automatically through a sample gas sequencer GWB Model 228-4 manufactured by J.U.M. Engineering Ltd. Gas sampling interval was about three minutes per sampling line with 1 l/min gas flow.

CarbonReUse's container was equipped with their self-developed digital interface that was used to control the process, such as to modify absorption and desorption conditions. The interface was also used to review and log various process parameter values like absorbent and flue gas pressure, temperature and flow rates at different process stages.

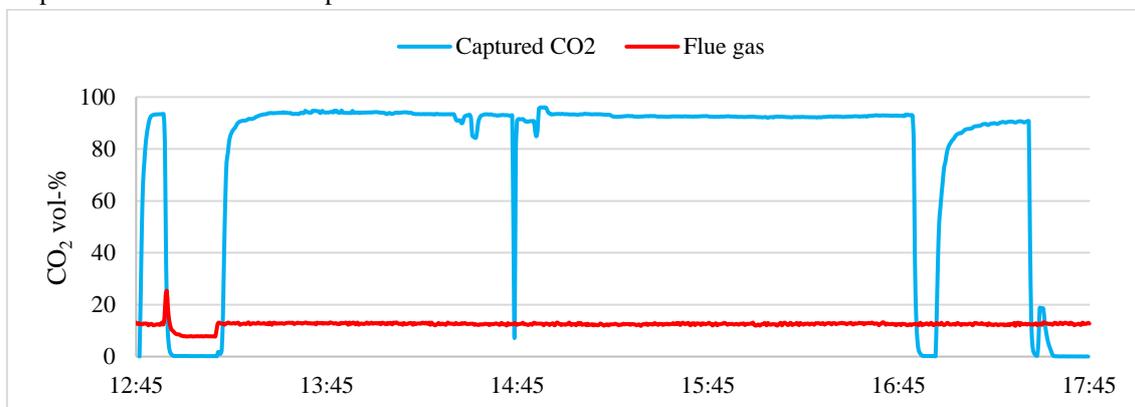
During the experiments, some minor technical problems emerged that caused temporary reduction in carbon capture performance, short interruptions or rescheduling. However, any major difficulties were avoided, and all the planned test runs were successfully executed. On average, the carbon capture processes were kept running for around 3–12 hours at a time and therefore experience from long-term carbon capture operation was not achieved in these test runs.

Multiple different measuring devices were used in the test runs, emerging a possibility for instrument errors. Since the capture processes were not fully automatic and human input was required for process operation the possibility of human error was present. However, any detrimental errors would have been most likely noticed in real-time via various measurements and such errors did not occur in the test runs. The measurement data and results have also been processed manually, which poses a risk of human error in data processing.

5.7 Data processing

Data gathered from the tests was processed manually. To facilitate data processing, the individual test runs were drawn into graphs as in Figure 5.4, which presents measured CO₂ levels (vol-%) of the flue gas and the captured CO₂ during CarbonReUse's carbon capture process in the pine chips combustion tests.

Figure 5.4. CO₂ level (vol-%) in flue gas and captured CO₂ during CarbonReUse's capture process in pine chips combustion on 8th of September 2020.



From the above-like graphs suitable stabilized test periods were chosen over which flue gas and captured CO₂ mean compositions were calculated. The compositions are presented as gas component mean values. The time periods have been selected manually from each test run. Length of the periods vary from 5 minutes to multiple hours depending on the length of the measurements. On average, the periods are rather short, around 10–30 min, as long-term steady-state operation was not one of the primary objectives in

these test runs. For instance, from Figure 5.4, a period of 13:30–14:00 was chosen as it provides a stabilized data from CarbonReUse’s capture process in that test run.

Capture rate presents how much of the CO₂ from the gas that enters the capture system is recovered into the captured product gas. The capture rates are calculated by using two different methods due to differences in flow rate measurement arrangements between the two containers. For VTT’s container – that was used for soda solution and the Kleener liquid – the capture rate is calculated via mass balances, by using properties of the CO₂-rich inlet flue gas flow and the CO₂-lean outlet flue gas flow (Eq. 12). For CarbonReUse’s process the capture rate is calculated by using properties of the CO₂-rich inlet flue gas flow and the captured CO₂ flow (Eq. 13).

$$CR = \frac{x(CO_2)_{in} \dot{v}_{in} - x(CO_2)_{out} \dot{v}_{out}}{x(CO_2)_{in} \dot{v}_{in}} \quad (12)$$

Example: $CR (VTT, \text{pine chips}) = \frac{13,2\% \cdot 11,2 \text{ l/min} - 3,3\% \cdot 9,5 \text{ l/min}}{13,2\% \cdot 11,2 \text{ l/min}} = 79\%$

$$CR = \frac{x(CO_2)_{captured} \dot{v}_{captured}}{x(CO_2)_{in} \dot{v}_{in}} \quad (13)$$

Example: $CR (CarbonReUse, \text{pine chips}) = \frac{94,0\% \cdot 15,9 \text{ l/min}}{13,5\% \cdot 144,9 \text{ l/min}} = 76\%$

The capture rates are calculated by using data from stabilized capture processes.

6 TEST RESULTS

As part of the BECCU-project carbon capture was tested with three different capture technologies by using different CO₂ sources: synthetic gas mixtures, flue gases from biomass combustion as well as raw biogas. Main objectives of the tests were to verify proper function of the technologies, evaluate capture performance and assess the effects of various gas compositions and impurities on the capture processes. Results from the tests are presented in this chapter.

6.1 Synthetic gas mixtures

Carbon capture was tested with synthetic gas mixtures during weeks #36 and #38. Objective of the test runs was to ensure proper function of the test equipment before the combustion tests, while also providing preliminary data on capture performance. With synthetic mixtures the gas composition was easily modified, enabling to test the capture performance with various gas compositions, such as with low and high CO₂ concentrations and different oxygen levels. In tests, the synthetic gas mixtures were mainly used to imitate typical flue gas compositions. The Kleener liquid was not tested in these test runs.

VTT's soda process was tested with three synthetic gas mixtures with different CO₂ and O₂ levels. Test parameters and results are presented in Table 6.1.

Table 6.1. Results from synthetic gas mixture tests done with VTT's soda process. Test date: 15th of September 2020.

Parameter	Unit	Test #1	Test #2	Test #3
CO ₂ in inlet	vol-%	15	15	10
O ₂ in inlet	vol-%	5	0	5
Flue gas inlet flow	l/min	8	8	8
Soda solvent flow	l/min	10	10	10
L/G ratio	l/l	1.25	1.25	1.25
CO ₂ after absorption	vol-% (dry)	3.0	2.9	2.4
CO ₂ in captured gas	vol-% (dry)	-	96.7	96.7
O ₂ in captured gas	vol-% (dry)	-	0	0
Capture rate	%	83	84	86

Both capture rate and purity of the captured CO₂ reached a similar level in all three synthetic gas test runs with VTT's soda process. A capture rate of 83–86 % was reached, with CO₂ purity of 96.7 vol-% (dry).

CarbonReUse's process was tested using two synthetic gas mixtures with CO₂ levels of 15 vol-% and 30 vol-% and an O₂ level of 5 vol-%. Test parameters and results are presented in Table 6.2.

Table 6.2. Results from synthetic gas mixture tests done with CarbonReUse's process. Test date: 3rd of September 2020.

Parameter	Unit	Test #1	Test #2
CO ₂ in inlet	vol-%	15	30
O ₂ in inlet	vol-%	5	5
Flue gas inlet flow	l/min	160	120
Product gas flow	l/min	17	44
CO ₂ in captured gas	vol-% (dry)	95.1	98.3
O ₂ in captured gas	vol-% (dry)	0.6	0.5
Capture rate	%	74	86

With synthetic gas mixture containing 15 vol-% of CO₂ a capture rate of 74 % was obtained, whereas the CO₂ purity in dry product gas was 95.1 vol-%. With a 30 vol-% CO₂ mixture both the capture rate and the CO₂ purity improved significantly to 86 % and 98.3 vol-%, respectively.

6.2 Pine chips combustion

During week #37, carbon capture was tested with flue gases from CFB combustion of pine chips. These test runs were conducted with all three capture technologies, enabling to compare performances of the technologies with a same flue gas source. Mean compositions for inlet flue gas and product are presented in Table 6.3.

Table 6.3. Mean compositions (wet) for flue gas and captured CO₂ in pine chips combustion. Inlet flue gas composition is measured after the water scrubber.

Technology		CarbonReUse	Kleener	VTT Soda
Test date		8.9.2020	9.9.2020	8.9.2020
Measuring period		13:30–14:00	18:42–18:47	20:10–20:20
Flue gas				
H ₂ O	vol-%	1.8	1.8	1.6
O ₂	vol-%	5.4	5.6	5.8
CO ₂	vol-%	12.8	13.7	12.9
CO	ppm	3	3	3
N ₂ O	ppm	0	0	1
NO	ppm	52	54	54
NO ₂	ppm	0	0	0
SO ₂	ppm	1	0	1
NH ₃	ppm	1	0	1
HCl	ppm	0	0	0
Captured CO ₂				
H ₂ O	vol-%	3.2	1.0	3.3
O ₂	vol-%	0.0	0.0	0.3
N ₂ O	ppm	1	0	0
NO	ppm	0	0	0
CO ₂	vol-%	94.1	93.3	92.7
CO ₂ (dry)	vol-%	97.1	94.2	95.9
Capture rate				
CR	%	72–76	69–71	74–79

CO₂ concentration in wet flue gas was around 12–14 vol-%. Amount of impurities was low, mostly consisting of ~50 ppm of NO. All three technologies produced roughly similar product gas compositions, with CO₂ concentrations around 94–98 vol-% in dry product gases. NO did not end up in the product gases. Following capture rates were achieved: 72–76 % (CarbonReUse), 69–71 % (Kleener) and 74–79 % (VTT).

6.3 Washed straw combustion

During week #38, carbon capture was tested with flue gases from washed straw combustion to test the effect of a more impure biomass. Compared to wood-biomass, agro-biomass generally contains higher amount of impurities like sulphur and chloride.

The Kleener liquid was not tested in these test runs. Mean compositions for inlet flue gas and product gas are presented in Table 6.4.

Table 6.4. Mean compositions (wet) for flue gas and captured CO₂ in washed straw combustion. Inlet flue gas composition is measured after the water scrubber. The Kleener liquid was not tested.

Technology		CarbonReUse	VTT Soda
Test date		15.9.2020	14.9.2020
Measuring period		15:34–17:30	16:15–16:32
Flue gas			
H ₂ O	vol-%	1.8	1.8
O ₂	vol-%	6.6	6.3
CO ₂	vol-%	13.0	13.3
CO	ppm	20	19
N ₂ O	ppm	3	7
NO	ppm	148	173
NO ₂	ppm	0	0
SO ₂	ppm	0	0
NH ₃	ppm	0	0
HCl	ppm	0	0
Captured CO ₂			
H ₂ O	vol-%	3.1	1.8
O ₂	vol-%	0.4	0.5
N ₂ O	ppm	18	3
NO	ppm	0	0
CO ₂	vol-%	93.0	94.9
CO ₂ (dry)	vol-%	96.0	96.6
Capture rate			
CR	%	64–70	78–83

Composition of the flue gas was roughly similar as in the pine chips tests. This was partly because of the water-scrubber, which removed the water-soluble impurities like SO₂. CO₂ concentration in wet flue gas was at similar level at ~13 vol-%. In dry product gases CO₂ concentrations were 96.0 vol-% (CarbonReUse) and 96.6 vol-% (VTT) – also similar to the results in the pine chips tests. A capture rate of 64–70 % was achieved with CarbonReUse’s process, whereas VTT’s process reached a rate of 78–83 %.

Biggest difference in flue gas composition occurred in CO and NO levels, which were roughly seven and three times higher, respectively. However, either of these compounds did not end up in the product gases due to their low solubility. Some N₂O (3–7 ppm), which is roughly as soluble into water as CO₂, was also present in the flue gas. Some of it ended up in the product gases: 18 ppm in CarbonReUse's process and 3 ppm in VTT's process.

6.4 Spruce bark combustion

A third biomass type, spruce bark, was tested in week #40. This test run was only done by using VTT's soda process. Also, the water-scrubber was not used to purify the flue gas prior to carbon capture. Mean compositions for inlet flue gas and product gas are presented in Table 6.5. The compositions are calculated over different time periods as there was no simultaneous composition measurements for the gas streams in this test run.

Table 6.5. Mean compositions (wet) for flue gas and captured CO₂ in spruce bark combustion. In this test run carbon capture was only done by using VTT's technology and without the flue gas water-scrubber.

Technology		VTT Soda
Test date		28.9.2020
Measuring period		14:41–15:10 (captured CO ₂) 15:15–15:23 (flue gas)
Flue gas		
H ₂ O	vol-%	2.6
O ₂	vol-%	6.3
CO ₂	vol-%	13.3
CO	ppm	36
N ₂ O	ppm	2
NO	ppm	219
NO ₂	ppm	0
SO ₂	ppm	0
NH ₃	ppm	1
HCl	ppm	0
Captured CO₂		
H ₂ O	vol-%	2.3
O ₂	vol-%	0.2
N ₂ O	ppm	0
NO	ppm	0
CO ₂	vol-%	94.4
CO ₂ (dry)	vol-%	96.5
Capture rate		
CR	%	88–90

In the spruce bark combustion higher levels of NO and CO occurred in the flue gas. Otherwise, the composition was fairly similar to the previous combustion tests. Compared to the pine chips tests, the amount of NO was around four times higher at 219 ppm, whereas the amount of CO was roughly twelvefold at 36 ppm. However, this did not seem to have any effect on the capture performance of VTT's soda process. Composition of the captured CO₂ was similar as in other tests, reaching a CO₂ purity of 96.5 % in dry product gas. Additionally, any NO or CO did not end up in the product gas. A capture rate of 88–90 % was achieved, which was highest of all the test runs. Presumably, the improvement

in capture rate occurred because in these test runs the soda process was operated with a higher L/G-ratio of 1.5–1.6 compared to the other test runs with an L/G ratio of 1.0–1.2.

6.5 Raw biogas

During week #40, VTT's soda process was tested in raw biogas purification. The raw biogas was delivered by Metener Ltd. In these test runs the process was operated by using also a second absorption stage (See Section 5.1.2) to produce higher purity methane. Mean compositions of raw biogas, purified biogas and captured CO₂ are presented in Table 6.6.

Table 6.6. Mean composition of raw biogas, purified biogas and captured CO₂. Test date: 30th of September 2020.

		Raw biogas (wet)	Purified biogas (dry)	Captured CO ₂ (dry)
Measuring period		10:09–10:20	9:35–9:40	13:19–13:30
CH ₄	vol-%	57.1	95.3	6.3
CO ₂	vol-%	41.2	2.0	93.6
H ₂ O	vol-%	0.8	-	-

The raw biogas consisted of 57.1 vol-% of methane, 41.2 vol-% of CO₂ and some moisture. The purified biogas (dry) consisted of 95.3 vol-% of methane and 2.0 vol-% of CO₂. The captured CO₂ (dry) consisted of 93.6 vol-% of CO₂ and 6.3 vol-% of methane. CO₂ capture rate of 97–98 % was achieved with the soda process in biogas purification, which was significantly higher than in the combustion tests. Presumably, the capture rate improved due to the high CO₂ level of raw biogas (~41 vol-%) and because a higher L/G ratio, at around 3.6–4.2, was used in this test run.

7 EVALUATION OF PERFORMANCE, SCALABILITY AND APPLICABILITY OF THE TESTED CARBON CAPTURE TECHNOLOGIES

In the carbon capture tests, all of the three tested technologies were proven functional in post-combustion carbon capture by using pilot-scale equipment. However, as discussed in the literature review, numerous carbon capture technologies are currently emerging in the carbon capture market. Therefore, potential of VTT's, CarbonReUse's and Kleener's technologies on this growing but already contested market depend on techno-economic performance, scalability and applicability. In this chapter, these matters are evaluated and compared to other carbon capture technologies that were studied in the literature review.

7.1 Performance

Performances of the tested technologies are evaluated by assessing purity of the captured CO₂, capture rate, energy consumption, chemicals, additives and waste-streams as well as economic performance. As the tests were conducted at pilot-scale with configurations that were not optimized for high performance but rather for proof-of-concept, it can be assumed that results achieved in these test runs could be improved after further development.

7.1.1 CO₂ purity

Purity of the captured CO₂ is essential when assessing performance of carbon capture technologies. Generally, high purity is desired since impurities can cause challenges in CO₂ transportation, utilization and storage (Reviewed in Section 3.2.1). Higher purity CO₂ is also more valuable. Furthermore, if additional purification of the captured CO₂ is required, the overall capture cost increases. However, the required purity depends on the application of the captured CO₂ and if high purity is not required, it is often more cost-effective to produce or capture CO₂ with lower quality.

Based on the literature review results most capture technologies that are currently in development reach CO₂ purities of >95 %. Some capture technologies, like the commercial Fluor EFG+ and Shell CANSOLV, reach CO₂ purities of >99 %. Test performances of VTT's, CarbonReUse's and Kleener's technologies regarding purity of the captured CO₂ are presented in Table 7.1.

Table 7.1. Mean CO₂ purities (vol-% in dry gas) achieved with VTT's, CarbonReUse's and Kleener's technologies in the pilot-scale carbon capture tests.

CO ₂ source	CarbonReUse	Kleener	VTT Soda
Synthetic gas 15 vol-% CO ₂	95.1	-	96.7
Synthetic gas 30 vol-% CO ₂	98.3	-	-
Pine chips	97.1	94.2	95.9
Washed straw	96.0	-	96.6
Spruce bark	-	-	96.5
Raw biogas	-	-	93.6

The tested technologies reached roughly similar performance regarding CO₂ purity. The results are in align with other carbon capture projects conducted at development-scale. CarbonReUse's enhanced water scrubbing process achieved purities of 96.0–97.1 vol-% in the combustion tests. With a synthetic gas mixture containing 30 vol-% of CO₂, the purity improved to 98.3 vol-%. The Kleener liquid, which was tested by using VTT's ejector equipment, achieved purity of 94.2 vol-% in pine chips combustion. VTT's soda process reached purity levels of 95.9–96.7 vol-% in the flue gas test runs and 93.6 vol-% in raw biogas purification. The source of CO₂ had little effect on CO₂ purity since the flue gas compositions between the different test runs were very similar.

During the pine chips and the washed straw tests samples of captured CO₂ were compressed and bottled from each process. Compositions of the samples were analyzed by using a gas chromatograph. The results are presented in Table 7.2.

Table 7.2. Composition of the captured CO₂ samples (dry).

Technology		CarbonReUse	CarbonReUse	Kleener	VTT Soda
Flue gas source		Pine chips	Washed straw	Pine chips	Pine chips
CO ₂	vol-%	93.3	92.1	97.1	97.6
H ₂	vol-%	0	0	0	0
O ₂	vol-%	1.8	2.5	0.8	0.5
N ₂	vol-%	4.8	5.3	2.1	1.9
CO	ppm	0	0	0	0
CH ₄	ppm	1	2	<5	<5
C ₂ H ₆	ppm	1	0	0	0
N ₂ O	ppm	2	12	0	0

The compositions somewhat vary from the FTIR measurements presented in Chapter 6. For instance, CO₂ purity with CarbonReUse's technology is significantly lower on these results, which may have been caused e.g., by air leaks in the CO₂ compression line.

In addition to CO₂, the captured gases consisted mainly of N₂ and O₂. In the washed straw tests also some N₂O ended up in the gas with CarbonReUse's technology, presumably since N₂O is roughly as soluble into water as CO₂. Other impurities that were present in the flue gas streams, like NO or CO, did not end up in the product gases. The effect of SO₂ or HCl on the capture processes could not be determined in these test runs as the amount of these compounds in the feed gases was very low or non-existent. Based on these results, the tested technologies do not cause solvent-based emissions, which is often a problem, for instance, with conventional amine-based absorbents.

7.1.2 Capture rate

Capture rate presents how much of the CO₂ from the gas that enters the capture system is recovered into the captured product gas. Often post-combustion carbon capture technologies are designed to capture around 90 % of the CO₂ present in the feed gas stream. During development phase lower capture rates are often achieved as can be seen with the technologies studied in the literature review. Commercial carbon capture technologies, such as Shell's CANSOLV and MHI's KM CDR, have reached capture rates of around 90 % in industrial-scale operation. However, in biogenic carbon capture,

the capture rate does not have as significant role as in fossil-based CCS applications. All excess fossil-based CO₂ emissions are harmful, whereas biogenic CO₂ emissions are climate-neutral in the long run. Therefore, focus in biogenic carbon capture and utilization applications should be on affordable capture cost and CO₂ purity rather than on high capture rate as it is more beneficial to achieve decent capture rate with affordable technology than high capture rate with expensive technology.

Test performance of VTT's, CarbonReUse's and Kleener's technologies regarding capture rate is presented in Table 7.3. The capture rates are calculated by using data from stabilized processes.

Table 7.3. Capture rates achieved with VTT's, CarbonReUse's and Kleener's technologies in the pilot-scale carbon capture tests.

CO ₂ source	CarbonReUse	Kleener	VTT Soda
Synthetic gas 15 vol-% CO ₂	74	-	83–86
Synthetic gas 30 vol-% CO ₂	86	-	-
Pine chips	72–76	69–71	74–79
Washed straw	64–70	-	78–83
Spruce bark	-	-	88–90
Raw biogas	-	-	97–98

All three technologies achieved promising results regarding capture rate, which are in align with other development-scale carbon capture experiments. CarbonReUse's water-scrubbing process achieved capture rates of 64–76 % in the combustion tests and 86 % by using synthetic gas with CO₂ level of 30 vol-%. The Kleener liquid reached capture rates of 69–71 % in the pine chips combustion tests, whereas VTT's soda process reached capture rates of 74–90 % in the combustion tests and 97–98 % in raw biogas purification.

Capture rate with the Kleener liquid and VTT's soda process could possibly be improved by modifying solvent concentration, absorption conditions or L/G ratio. Higher solvent concentration emerges a risk of solvent precipitation, which should be avoided as it can cause uneven flow conditions or even clogging. Higher absorption pressure would presumably improve absorption rate but also increase operational costs since compression

would be required. Higher L/G ratio would also increase operational costs as process energy consumption, like required pumping power, would increase.

In CarbonReUse's water-scrubbing process the absorption capacity is already fairly optimized by using absorbent water cooling, flue gas compression and a novel post-desorber column. Presumably, there are not many options to further improve the capture rate other than increasing CO₂ concentration of the feed gas if it can be done in a cost-effective way.

7.1.3 Energy consumption

CarbonReUse's enhanced water scrubbing process is fully electrically operated. Electricity is required for flue gas compression, circulation and vacuum pumps and heat pump, if it is required. The fully electric process offers good process control and adjustability like rapid start-ups, shutdowns and process parameter changes. However, electricity is generally more expensive than low-heat steam or waste heat that is often available in power plants or other industrial facilities. Many absorbent capture processes aim to utilize heat in absorbent regeneration. Since CarbonReUse's process is fully electric, heat sources cannot be utilized. Feed water temperature is also a significant factor affecting energy consumption in CarbonReUse's process. An external source of cold water would reduce or eliminate the need for a heat pump in absorbent cooling and therefore lower the energy consumption. According to previous evaluation by Linnanen (2012), with a feed water temperature of 5 °C power requirement of the process would be 0.34 MWh/tCO₂. If a feed water temperature of 15 °C is used, the power requirement increases to 0.40 MWh/tCO₂. According to Teir et al. (2014), the power requirement is at a similar level to the power losses that occur in amine-based capture processes.

The ejector process, which was used for VTT's soda solution and the Kleener liquid, requires both electricity and heat. Electricity is required for circulation and vacuum pumps. In this process configuration, also regeneration was done with electricity by using resistance heating, as it was easy to implement at this scale for proof-of-concept.

However, from an economic point-of-view, such configuration is not in any way efficient. In a more optimal configuration, low-grade heat should be used for regeneration due to being more cost-effective choice compared to electricity.

7.1.4 Chemicals, additives and waste-streams

CarbonReUse's enhanced water scrubbing process does not require any chemicals or additives since regular water acts as CO₂ absorbent. After reaching stationary operation, the process does not require additional water either. However, over long-time operation some impurities may dissolve into the absorbent water flow. If such accumulation of impurities occurs, some water must be replaced with make-up water. Presumably, any water removed from CarbonReUse's process does not require specific wastewater treatment as the amount of contaminants is low since the flue-gas is purified from water-soluble impurities before entering the capture process.

VTT's soda process utilizes an aqueous sodium carbonate solvent to absorb CO₂. During operation, the process may require some make-up soda depending on flue gas composition and process conditions, which affect degradation of the solvent. As discussed in Section 5.1.1, soda may react with some impurities that commonly occur in flue gases. The non-regenerable compounds that are formed in these reactions could be removed from the process via a purge stream. The make-up soda requirement is determined by the amount of soda that is removed from the process via this purge stream. VTT's soda solution and the Kleener liquid are alkaline and before disposal, the solutions must be neutralized by using a suitable acid. Additionally, the neutralized solutions could be utilized, for instance, as fertilizers.

Due to patent-related reasons chemicals or additives used with the Kleener liquid are not elaborated.

7.1.5 Economic performance

Economic performances of the technologies derive from investment costs and operational costs. Investment costs mainly consist of manufacturing and installation of the capture equipment and it is affected mainly by the size and complexity of the design, used materials and required labour. Operational costs consist of energy consumption, use of chemicals and additives, waste treatment, labour and maintenance.

Compared to chemical absorbent processes CarbonReUse's process requires relatively large-sized equipment because of the large mass flows caused by weak CO₂ absorption properties of regular water. According to Suomalainen & Arasto (cited in Teir et al. 2014), the solvent mass flow is up to ten times higher than in conventional amine solvent processes, requiring roughly 830 tonnes of water per captured CO₂ tonne. Teir et al. (2014) evaluate that for a small-scale capture facility (~50 ktCO₂/a) the investment cost is at similar level as in amine-based capture plants. They also note that at large scale (>1MtCO₂/a) some extra costs could emerge as the size of the equipment would expectedly grow very large. Operational costs of the process derive mainly from electricity consumption (Reviewed in Section 7.1.3). Since the process can be automated and operated remotely, it can be expected that effect of labour costs is low.

The novel ejector technology developed by VTT could possibly reduce size of the absorption equipment compared to conventional absorption columns due to efficient mixing of solvent and feed gas. However, due to lower CO₂ absorption capacities VTT's and Kleener's capture solvents require higher flow rates and therefore expectedly larger capture equipment than, for instance, amine absorbents. In the pilot tests, the ejector process was operated with a volumetric L/G ratio of ~11/1. With amine-based absorbents, such as MEA and PZ/AMP, the ratio is significantly lower at around 2–4 l/m³ (Rabensteiner et al. 2016). However, L/G ratio of the ejector process could possibly be reduced with more optimized equipment and process conditions. Further research is required to evaluate the investment cost of the ejector equipment. Operational costs of VTT's and Kleener's capture processes derive mainly from energy consumption

(Reviewed in Section 7.1.3). Other essential factors are make-up chemicals and waste treatment requirements.

The economic performance of the technologies is not assessed based on the pilot test results since capture configurations used in the tests were not optimized for cost-efficient performance but rather for proof-of-concept operation. Therefore, economic assessment based solely on the pilot test data would not provide relevant information about economic performance of these technologies. To evaluate economic performance further assessment with more optimized configurations is required, for instance, by using simulation-based studies. Additionally, it is essential to recognize the most suitable applications for each technology, as the performance is dependent on the operating environment. Some possible applications for each technology are discussed below.

7.2 Scalability and applicability

To achieve the highest potential regarding economic performance VTT's and Kleener's capture technologies require heat integration to achieve efficient use of energy in absorbent regeneration. Therefore, these technologies are most suitable for applications where there are utilizable heat sources available. However, heat integration may reduce energy generation efficiency of the facility. If possible, the most benefit would be achieved by utilizing waste heat as the negative economic effect derived from energy consumption in carbon capture would be minimal. Applicability to waste heat utilization is supported by the fact that both solvents can be regenerated at relatively low temperature level at around 60–80 °C when a vacuum pump is used to create sub-atmospheric conditions at around 0.2–0.5 bar. There are utilizable heat sources often available in energy production processes and other energy-intensive industrial processes, which can be seen as the most suitable processes for VTT's and Kleener's capture technologies. In the absence of utilizable heat sources, also a heat pump could be used to provide heat for regeneration. Both VTT's and Kleener's solvents could possibly be also utilized to remove some common flue gas impurities alongside carbon capture, although in the expense of higher solvent degradation. These alkaline solvents can react with some

common impurities (e.g., SO₂) and form non-regenerable compounds that could be collected and utilized, for instance, as fertilizers. However, further research is required to examine the applicability of impurity removal as it was not tested in the pilot tests.

CarbonReUse's process is fully electric and it does not benefit from heat integration. On the other hand, it is not dependent on heat integration either. Many carbon capture processes are often developed by using heat integration as a default, meaning that CarbonReUse's technology could provide a viable solution for applications, which lack utilizable heat sources or otherwise seek a simple and fully electric process. Since heat integration is not required the process offers a more modular nature compared to conventional absorbent processes. The process is also fairly simple as it requires only electricity and water, which facilitates retrofitting as there is no need for large process modifications in the original process. Since cooling of absorbent water increases capture efficiency of the process, an external source of cold water or utilizable cooling loads would be beneficial regarding process economics, as the heat pump would not be necessarily required. During cold seasons, the cooling load could be reduced or eliminated by using natural water sources such as lakes, rivers or seas. Due to the large mass flows caused by low absorption capacity of water, the capture equipment is larger compared to chemical absorbent processes, which can act as a restricting factor at larger scale if there are strict space limitations. As the CO₂ is captured via physical absorption, the process is more effective with feed gas of high CO₂ concentration, as was seen in the pilot tests. Therefore, if CO₂ concentration of the feed gas could be increased by using a cost-effective method (e.g., membranes) performance and process economics could be improved. However, further research is required to evaluate feasibility of such hybrid processes. Based on the discussed factors, CarbonReUse's enhanced water-scrubbing process could provide a viable carbon capture solution for industries seeking a simple and modular turnkey solution for carbon capture. A significant advantage is that the process does not use any chemicals, making it suitable for chemically sensitive applications like food- and beverage industry. The process could be also applicable for carbon capture in biogas upgrading, where water scrubbing is already a mature technology.

8 SUMMARY

Capture and utilization of biogenic CO₂ emissions (BECCU) could provide sustainable value chains to replace conventional fossil-based production of various products like fuels, materials and chemicals. Potential of BECCU is high especially in areas with strong bioeconomies, where biogenic emissions of bioenergy production and other biomass utilizing industries could be harnessed to provide feedstock for CCU value chains by using carbon capture technologies.

Numerous carbon capture technologies based on different phenomena are currently under development. Amine absorbents are the most mature capture method available, as amines perform well especially in large-scale fossil-based CCS applications, where high capture rate is important. However, amine absorbents often suffer from harmful solvent-based emissions, high energy-intensity and sensitivity to impurities, although these challenges have been reduced with more advanced formulations. In addition to amines, there are many other capture technologies emerging, such as multi-phase absorbents, solid sorbents, membranes, and fuel cells. Many of these technologies are facing industrial-scale demonstration in the near-future. Capture technologies that are approaching industrial-scale operation are at quite similar level regarding performance. Technologies studied in the literature review currently reach capture costs of 34–80 €/tCO₂ and on average the capture cost is around 40–60 €/tCO₂ in post-combustion capture. There does not seem to be any clear breakthrough technologies that would emerge over the other technologies cost-wise. Each technology has its own strengths and challenges, and the most suitable capture technology for different applications is presumably determined by the capture environment, feed gas composition and how the CO₂ is used after capture. The capture rate is not as significant in bio-CCU as it is in fossil-CCS, and the focus should primarily be on developing affordable technologies that can capture CO₂ with high purity.

As part of VTT's BECCU project three novel absorption-based technologies were tested in post-combustion capture by using pilot-scale equipment. The tested technologies were an enhanced water scrubbing process by CarbonReUse, an enhanced soda scrubbing

process by VTT and Kleener liquid – a novel capture absorbent by Kleener Power Solutions, which was tested by using VTT's novel ejector equipment. The pilot tests were conducted by using synthetic gas mixtures with different CO₂ levels and biogenic flue gases from a 50 kW CFB-pilot combustor. VTT's soda process was also tested in purification of raw biogas. All three technologies were proven functional in post-combustion capture at realistic conditions, while reaching promising performances that are in align with other similar-scale carbon capture projects. The three technologies reached roughly similar performance in biomass combustion tests achieving captured CO₂ purity of 94–97 vol-% and capture rates of 64–90 %. VTT's soda process was also proven functional in purification of raw biogas, reaching a capture rate of 97–98 %, while producing streams of 95 vol-% CH₄ and 94 vol-% CO₂. During the biomass combustion tests, captured CO₂ streams from each technology were compressed, bottled and analyzed by using gas chromatography. Based on the analysis, any solvent-based emissions did not end up in the captured CO₂ streams. In addition to the CO₂, the captured gas streams consisted mainly of N₂ and O₂. Small amount of N₂O (2–12 ppm) ended up in the captured CO₂ stream with CarbonReUse's water-scrubbing process. The capture equipment used in the pilot tests were built rather for proof-of-concept than for optimal performance and therefore performance of the technologies could possibly be improved after further development with more optimized equipment.

As numerous technologies are currently emerging in the carbon capture market, potential of VTT's, Kleener's and CarbonReUse's technologies depend on techno-economic performance, scalability and applicability. A significant advantage of these technologies is that the capture processes do not cause any harmful emissions, which is often a problem with the more mature amine absorbents. Regarding process economics, VTT's and Kleener's chemical absorbent technologies could be suitable for applications where inexpensive low-grade heat could be utilized in solvent regeneration. The aqueous soda solution and the Kleener liquid can be regenerated at a relatively low temperature level of 60–80 °C when a vacuum pump is used to create sub-atmospheric regeneration conditions, meaning that, for instance, waste heat sources could be utilized in solvent

regeneration. Soda and the Kleener liquid could possibly be even suitable to remove some common flue gas impurities like SO_2 while forming compounds that could be recovered and utilized as fertilizers. CarbonReUse's fully electric process uses regular water without any chemicals to capture CO_2 and it offers a more modular and a fairly simple carbon capture solution with easy retrofitting. The water-scrubbing process could be possibly suitable for chemically sensitive industries such as the food and beverage industry and industrial facilities that seek an easily retrofittable turnkey solution for carbon capture. Due to the large solvent flows that occur in the process, equipment size can act as restricting factor at large-scale. Since the CO_2 capture occurs via physical absorption, the process is more effective in applications where high CO_2 concentrations occur. Capture performance is improved by using cool absorbent water ($\sim 5^\circ\text{C}$) and therefore utilizable sources of cold water or other cooling loads would be beneficial regarding process economics.

In the pilot tests the tested carbon capture technologies were proven functional in realistic conditions while achieving promising capture performance. However, the capture cost is often the most significant factor when evaluating competitiveness of the technologies in the carbon capture market. Evaluation of process economics – which is also highly dependent on the capture environment – requires more work to unravel the realistic commercial potential of these technologies.

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APPENDIX I: Schematic structure of the 50 kW CFB pilot

