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Optimisation of Carbon Capture and Utilisation Value Chains

Tryfonas Pieri

A thesis submitted to the University of Huddersfield in partial fulfilment of the requirements for the degree of Doctor of Philosophy

October 2021

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Contributions T.P: Conceptualization, methodology, software, validation, formal analysis, investigation, resources, data curation, writing—original draft preparation, visualization.

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Contributions T.P: Methodology, validation, formal analysis, resources, data curation.

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- iv. Angelis-Dimakis A., Pieri T., Nicacio I., Vyrkou A., Arampatzis G., Dedousis P., Liew ZB., Sim CY, and Yusup S. (2021). Carbon Capture Utilization Potential in Malaysia, presented at the 17th International Conference on Environmental Science and Technology, Athens, Greece, 1-4 Sep.
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- i. **Pieri T.,** Nikitas A., and Angelis-Dimakis A. (2021). Public acceptance of carbon capture and utilisation products in the UK. Submitted to *Energy Research & Social Science*. Under Review
- Pieri T. and Angelis-Dimakis A. (2021). Classification and characterisation of carbon dioxide sources and capture technologies. Submitted to *Carbon Capture Science & Technology*. Under Review

Optimisation of Carbon Capture and Utilisation Value chains

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List of abbreviations AEEA: Aminoethylethanolamine AMP: 2-amino-2-methylpropanol AMPD: 2-amino-2-methyl-1,3, propanediol APFBC: Advanced circulating pressurized fluidised bed combustion APTES: 3-aminopropyltriethoxysilane Ar: Argon ASU: Air separation unit **BEC: Bare elected cost** BFBC: Bubbling fluidised bed combustion **BOF:** Basic oxygen furnace CaCO₃: calcium carbonate **CAPEX:** Capital expenditure CaSiO₃: Wollastonite CCS: Carbon capture and storage CCU: Carbon capture and utilization CDU: Crude distillation unit CFB: Fluidised bed combustion CFBC: Circulating fluidised bed combustion CFCs: Chlorofluorocarbons CH₄: Methane CHP: Combined heating and power CO: Carbon monoxide CO₂: Carbon dioxide COS: Carbonyl sulphide **CPI:** Consumer price index CRU: Catalytic reforming unit DEA: Diethanolamine DETA: Diglycolamine DGA: Diglycolamine **DIPA:** Diisopropanolamine

DME: Dimethyl ether DRI: Direct reduction iron EAF: Electric arc furnace ECBM: Enhanced coal bed methane EGR: Enhanced gas recovery EGS: Enhanced geothermal systems ENCAP: Enhanced Capture of CO₂ EOR: Enhanced oil recovery EPC: Engineering, procurement, and construction ESA: Electric swing adsorption ESP: Electrostatic precipitator FCC: Fluid catalytic cracking FCF: Fixed charge factor FGD: Flue gas desulphurisation unit (FGD) GHG: Greenhouse gas H₂: Hydrogen H₂CO₃: Carbonic acid H₂O: Water H₂S: Hydrogen sulphide HBI: Hot briquette iron HCOOH: Formic acid IGCC: Integrated gasification combined cycle IGCC: Integrated gasification combustion cycle K₂CO₃: Potassium carbonate LCOE: Levelized cost of electricity MAP: Modified atmosphere packaging MCFC: molten carbonate fuel cells MDEA: Methyl diethanolamine MEA: Monoethanolamine MeOH: Methanol MgSi₂O₅(OH)₄: Serpentine MgSiO₄: Olivine

MIG: Metal Inert Gas N₂: Nitrogen N₂O: nitrous oxide Na₂CO₃: Sodium carbonate NGCC: Natural gas combined cycle NGCC: Natural gas combined cycle NOx: Nitrogen oxides O&M: operating and maintenance O₂: Oxygen **OPEX:** Operational expenditure PC: Pulverised coal PCC: Pulverised coal combustion PE: Polyethylene PEC: Polyethylene carbonate PEI: Polyethyleneimine PFBC: Pressurised fluidised bed combustion **PP: Polypropylene** PPC: Polypropylene carbonate PSA: Pressure swing absorption RAC: Recycled aggregate concrete **ROI:** Return on investment SC: Sterling coolers SCPC: Supercritical pulverised coal SCR: Selective catalytic reduction reactor SMR: Steam methane reforming SMR: Steam methane reforming SO₂: Sulphur dioxide SO₃: Sulphur trioxide Syngas: Synthetic gas TASC: Total as spent cost TDS: Total dissolved solids TEA: Diisopropanolamine

TEPA: Tetraethylenepentamine TGRBF: Top gas recycling blast furnace TOC: Total overnight cost TPC: Total plant cost TRL: Technology readiness level TSA: Temperature swing absorption USCPC: Ultra-supercritical pulverised coal VLE: vapour liquid equilibrium line VSA: Vacuum swing adsorption VTSA: Vacuum and temperature swing adsorption (DRI)-Midrex: Direct reduction iron (SRI)-COREX: Smelting reduction iron

Abstract

This PhD thesis identifies, examines and characterises all parts of the carbon capture and utilisation (CCU) value chain to assess its potential to be used as a CO₂ emission mitigation option and, by extension, support global warming mitigation efforts. It puts CCU value chains in the context of global warming mitigation by establishing the relationship between increasing CO₂ emissions, global warming and the efforts of the European Union to reduce them. CCU value chains can be defined as the process of generating profit by capturing CO₂ from CO₂-emitting sources and transporting it to CO₂ receivers for utilisation, within a process or the production of commercial products. The examination of CCU value chains starts by identifying the chain's individual steps followed by a breakdown of the steps in four sections that make up the chain: utilisation, CO_2 sources, CO_2 capture and CO₂ transportation. Each section is introduced by discussing its purpose, process and limitations within the chain, followed by a characterisation of the key elements and identifying and specifying factors that could be used in optimisation. Utilisation happens at CO₂ receivers where CO₂ is sold for profit and utilised in a process or for the production of commercial products; CO₂ sources produce the CO₂ emissions; CO₂ capture technologies capture CO₂ at the source and prepare it for transportation; and CO₂ transportation is responsible for delivering CO₂ at the receiver for utilisation. Numerous attempts have been made in the past aimed at optimising individual steps of the chain, and various attempts have been made to integrate approaches and achieve optimisation for more than one of the steps, but these have proved difficult because of their high complexity. This PhD thesis chose a different and simpler approach that requires fewer variables and provides a quick and reliable holistic solution to propose optimised regional CCU value chain schemes by integrating all steps of the CCU value chain. It was concluded that CCU value chains show high potential for CO2 emission mitigation if they are rigorously assessed, tailored and optimised for a specified region before application.

The novel contributions of the thesis are:

- Knowledge base of CO₂ receivers and their characterization
- Knowledge base of CO₂ sources and their characterization

- Framework for the matching of CO₂ sources with CO₂ capture technologies based on their compatibility
- Models for estimating CO₂ capture cost
- Algorithm and business model for CCU value chain optimisation

The first four concepts have been integrated within an algorithm, the main novelty of the thesis, which optimizes the implementation of CCU value chains, and a business model that proposes realistic CCU schemes in a given region. The developed algorithm and business model can map the CO₂ sources and receivers in a specified region and select the sets of optimal solutions based on the optimisation preference of the user for the development of CCU value chains by matching CO₂ sources and receivers based on (i) the technological compatibility and maturity of technologies, (ii) CO₂ capture costs, (iii) CO₂ transportation costs, (iv) CO₂ utilisation costs and (v) profit within a defined project lifetime. The algorithm and the business model have been validated using real life examples (industry level, regional level, and national level) and have been also implemented in an online platform for enabling symbiotic value chains for solid waste management (the development of which happened as part of the Interreg V-B "Balkan Mediterranean 2014-2020" SWAN project where we as part of the University of Huddersfield were invited as experts in industrial symbiosis field, but which was outside the scope of this thesis). The application and validation of the algorithm and business model in these areas demonstrate the strengths of the novel concepts and their potential to commercialise CCU value chains and contribute to global warming mitigation, and also to be used in areas other than CCU value chain optimisation.

Chapter 1: What is CCU?

1.1 Introduction

Carbon capture and utilisation (CCU) describes the value chain for the production of commercial products that utilise carbon dioxide captured from industrial activities. The value chain involves the capture of CO₂ from a designated source with the use of a compatible carbon dioxide capture technology that purifies and compresses CO₂ to the required standards of the selected transportation method and transports the purified CO₂ to a designated receiver for utilisation to be sold for profit. CCU aims to reduce the carbon dioxide atmospheric abundance by preventing the release of anthropogenic emissions to the atmosphere while simultaneously producing profit.

This introductory chapter sets the context of the following chapters by establishing (i) the motivation for research by demonstrating the potential of CCU value chains related to global warming, (ii) the scope, aims and novelty of the thesis by providing a brief background of CCU and (iii) the structure of the thesis by presenting the research questions that guided the research.

1.2 What is global warming?

Global warming is defined as the unusually rapid increase of the earth's average surface temperature [1]. It has been observed that since the years 1951-1980, which were set as a baseline for the earth's average surface temperature, the earth's global average temperature has increased by 1°C. Figure 1 shows the temperature profile for the years between 1880 and 2020 with the period of 1951-1980 as the baseline. It can be seen from Figure 1 that, before the baseline years, the temperature profile fluctuated between 0 and -0.5°C, but from the year 1980 and onwards a sharp constant increase is observed with the highest increase in year 2016 peaking at 1.02°C. NASA (2021) suggests that this increase in temperature implies that global warming is taking place and justifies it with the following evidence obtained from earth-orbiting satellites and other technological advances [2]:

- Warming of oceans: Annual 0.3°C increase since 1969
- Shrinking of ice sheets in Greenland and Antarctica: 279 billion tons of ice in Greenland and 148 billion tons of ice in Antarctica are lost per year, for the years between 1993-2019
- Glacier retreat in Alps, Himalayas, Andes Rockies Alaska and Africa

- Decrease of snow cover and earlier melting of snow in Northern Hemisphere over the past five decades
- Global Sea level rise by 20 cm over the last century
- Declining Arctic Sea ice
- Extreme events: Record high temperature increasing and record low temperature decreasing in the United States
- Ocean Acidification due to increased absorption of CO₂ since the industrial revolution by 30%



Figure 1: The anomaly of the global average temperature between 1880 and 2020: Adapted from [3], [4]

1.2.1 What causes global warming?

Global warming is caused by the enhanced greenhouse effect. The earth's natural greenhouse effect is vital for life on earth, because it keeps the average surface temperature at 15°C instead of -18°C, which would be the temperature if no greenhouse effect was in place. Earth reflects about 30% of the energy radiated from sun and absorbs the remaining 70% through land, ocean and atmosphere. In the atmosphere, certain greenhouse gases, like carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and water (H₂O), have the ability to trap solar radiation in the form of heat, part of which they radiate back to space, but mostly towards earth. The enhanced greenhouse effect, responsible for global warming, is caused because of the increasing amounts of these gases in the atmosphere, caused by anthropogenic emissions. Methane is released through industrial activities like the production and transportation of coal, natural gas and oil and through agricultural activities like raising livestock, land use and decay of organic waste. Nitrous oxide is released through agricultural activities and land use, combustion of fossil fuels, combustion of solid waste and water treatment. Water vapour is released from natural causes. Carbon dioxide is released mostly by burning fossil fuels like coal, natural gas and oil, by burning solid waste, trees and as a by-product of chemical reactions [1], [3], [4].

These are the most threatening greenhouse gases, and their effect can be estimated according to three factors: (i) their ability to trap heat (radiative efficiency), (ii) how long they stay in the atmosphere (lifetime) and (iii) how much there is in the atmosphere (abundance). The effect of each greenhouse gas can be put into perspective to make comparisons using radiative forcing (RF, W/m²), a concept that quantifies the strength of the effect greenhouse gases have, based on the three factors listed above. Although nitrous oxide has a radiative efficiency 216 times higher than that of CO₂ and methane has a radiative efficiency of 26.4 times higher than that of CO₂, CO₂ has the largest radiative forcing amongst the three (CO₂=1.6, CH₄=1, N₂O=0.7) because it has the largest abundance [4], [5]. This means that CO₂ poses the biggest threat for global warming.

The total U.S. greenhouse gas emissions in 2019 consist of 80% carbon dioxide, 10% methane and 7% nitrous oxide (Figure 2). 35% of these emissions was due to transportation, 31% due to electricity



Figure 2: Total U.S. greenhouse gas emissions in 2019 [4]

Figure 3: Industry share of U.S. GHG emissions in 2019 [4]

production, 16% due to industry and the rest from residential and commercial processes and other non-fossil fuel combustion related processes (Figure 3) [4].

Evidence for the threat of increasing anthropogenic CO₂ emissions can be drawn from ice cores in Greenland, Antarctica and tropical mountain glaciers [2]. The results presented by Nasa [2] show that for the past 800,000 years (with baseline set as 1950) the CO₂ atmospheric level never exceeded 300 ppm and fluctuated between about 170-300 ppm. A sharp increase can be observed between the years 1950 and present that appears horizontal, increasing from 300 ppm to slightly above 400 ppm. NASA (2021) states with 95% probability that the increase in CO₂ is related to human activity that started in 1950 [2]. The CO₂ abundance in 1950 was 300 ppm and the highest abundance recorded before 1950, reaching today an abundance of slightly above 400 ppm, making it an all-time record in such a short period of time.

1.2.2 Global actions to tackle global warming

The European Union (EU) in 2011, following the Paris climate agreement, proposed the Roadmap for 2050 as a plan to reduce the overall levels of Greenhouse Gas Emissions (GHG) [6]. The Roadmap aims to achieve an 80% reduction below the 1990 values through a series of milestones from 2011 until 2050, 40% by 2030, 60% by 2040, and 80% by 2050. The European Commission's 2011 Energy Roadmap plan towards a low carbon economy consists of three main pillars: (a) a wider implementation of renewable energy sources, (b) promotion of low carbon energy supply options and (c) implementation of energy saving measures. The targets of the first pillar are promoted through the renewable energy directive, tailored to each country's starting point. The third pillar's targets are promoted through a framework of the Energy efficiency directive, the Energy Efficiency Plan. The second main pillar, promotion of low carbon energy supply options, includes nuclear power or conventional fossil fuels supported by carbon capture, which makes Carbon Capture and Utilization (CCU) one of the main pillars of the current European environmental policy and waste management strategy [6].

The EU has put in place two mechanisms to ensure the success of their plan [6]:

- National emissions reduction targets covering 55% of EU's greenhouse gas emissions from houses, agriculture, waste, and transport.
- The EU Emissions Trading System (EU-ETS) that allows the trading of emission rights, covering 45% of EU's greenhouse gas emissions from the power and industry sectors.

The European Union's 45% estimate of CO_2 emissions from large scale facilities of the power and industry sectors agrees with the United States' 47% estimate of CO_2 emissions from electricity generation and industry. This means that carbon capture and utilization value chains have a theoretical potential to mitigate about 45% of the global CO_2 emissions.

1.3 CCU as a mitigation option

1.3.1 The current CO_2 life cycle

Before anthropogenic activity became a source of CO_2 emissions, CO_2 would only be emitted from natural sources (animals, decomposition of organic matter, volcanic eruptions) and the large natural CO_2 sources, oceans and forests. CO_2 would be emitted naturally to the atmosphere, but it would also be stored back into forests through respiration and photosynthesis, and oceans through other natural processes [7]. This means that there are three natural CO_2 storage units, forests, oceans and atmosphere. After the industrial revolution, and especially after the year 1950, anthropogenic CO_2 emissions were released on top of natural CO_2 emissions, as indicated by Figure 4, which illustrates the global fossil fuel consumption from 1800 to 2019 for coal, oil and gas. This is the origin of anthropogenic CO_2 emissions shown in Figure 5, which summarises the current CO_2 life cycle. Raw material with carbon stored in it is extracted from the earth/underground and releases CO_2 as a byproduct through fossil fuel production and combustion and other industrial processes (discussed in Chapter 3). The additional anthropogenic CO_2 released into the atmosphere is absorbed by the same CO_2 natural storage units (forests, oceans and atmosphere) and is slowly becoming saturated in CO_2 . Forests and oceans are unable to absorb CO_2 at a higher rate, causing the accumulation of CO_2 in the



Figure 4: Global fossil fuel consumption [13]

atmosphere. Therefore, the additional anthropogenic emissions are responsible for the increasing atmospheric CO₂ abundance, which contributes to global warming.



Figure 5: Current CO₂ life cycle

1.3.2 The CCU value chain

Carbon capture and utilisation describes the process of preventing the release of CO₂ emissions to the atmosphere by capturing CO₂ from industrial activities and converting it into products [8]. The CCU value chain consists of six fundamental processes shown in Figure 6: CO₂ emission from a source, CO₂ capture, purification, compression, transportation and utilization or storage. In the case of CO₂ storage, the process has a different name, carbon capture and storage (CCS). CCS has the same aim as CCU, but it describes a very different process of preventing the release of CO₂ emissions to the atmosphere. CCS describes the processes involved in the geological storage of captured carbon dioxide instead of its utilisation for the production of commercial products. CCS and CCU have a lot



Figure 6: The steps of the CCU value chain

of differences (which are beyond the scope of this PhD thesis) but CCU has a clear advantage over CCS, its ability to generate profit by CO₂ utilisation into commercial products.

The CCU value chain can be thought of as having four major steps, because capture, purification and compression of the CO₂ stream take place at the same facility. In the context of CCU, sources are industrial activities that produce CO₂ and are characterised by industry, size and CO₂ stream type (Chapter 3). The capture of CO₂ is achieved by applying a compatible capture technology to a CO₂ source that is characterised by separation principle, maximum achievable CO₂ purity, technology readiness level and cost associated with processed flowrate of CO₂ (Chapters 4 and 5). Transportation is achieved by any of the available transportation options, onshore or offshore via pipeline, truck tankers, railroad tankers or ship tankers. Each transportation has unique operating conditions, different costs and each one offers its unique advantages based on transportation distance, transportation infrastructure and flowrate (Chapters 6 and 7). Utilisation and profit generation are achieved at the receiver, which are characterised by industry, process, permanent utilisation, temporary utilisation, technology readiness level and CO₂ demand (Chapter 2). This explains the CCU value chain from the perspective of matching a single source with single receiver, but CCU value chains do not consist of individual sources and receivers only, but rather a large number of sources and receivers that make up a region that requires optimisation to connect them in a network that produces value.

1.3.3 The future CO_2 life cycle

The potential of CCU value chains can only be realised in a scenario where CCU value chains have achieved commercialisation. For that to happen, there should be a framework that points to a clear plan in implementing such complex network configuration that will produce technically and economically feasible solutions (Chapters 9 and 10). The framework can be developed through optimisation of CCU value chains that deals firstly with (i) the examination and assessment of the technical and economic aspects of each step of the chain to determine how each process is carried out and what is the optimal set of conditions to carry out each process; and (ii) with the feasibility assessment of CCU value chain development, a problem of a much larger scale, when compared with the problem of a single source and a single receiver, which involves source-capture technology matching, transportation selection and infrastructure development and source-receiver matching (Chapters 9 and 10). Optimisation of CCU value chains from this perspective could provide

recommendations and a clear plan that facilitates the understanding of the optimisation problem on a larger regional scale that could lead to commercialisation by penetrating the free market.

Figure 7 shows the CO_2 life cycle in a scenario where CCU value chains have achieved commercialisation. In this scenario two new CO_2 storage units are created, CO_2 products with permanent storage and CO_2 products with temporary storage. The wider the acceptance of such products, the higher the production of permanent utilisation products will be and the larger the avoidance of CO_2 emissions to the atmosphere. This is further discussed in Chapter 2. Before continuing to the rest of the PhD thesis, the main research questions that guided the research must be established.



Figure 7: Future CO₂ life cycle

1.4 CCU research questions

This research aims to answer if and how it is possible to mitigate CO₂ emissions via CCU value chains. To answer this question the research asks further questions: What are CCU value chains, what are their components and how they are related to each other? Is it possible to optimise CCU value chains and if yes, how they can be commercialized and achieve CO₂ emission mitigation? The structure of this PhD thesis is explained through the following research questions, starting from the macro problems of CCU value chains and moving onto micro problems, concerning the individual parts of the CCU value chain. The questions asked in the following section are answered in the respective chapter and section, which is denoted in each set of questions. Additionally, the CCU research questions section can be used as a navigation guide for the upcoming chapters.
1.4.1 CCU value chain potential

The research starts with the objective to answer if CCU value chains can mitigate CO₂ emissions. To answer this question, one must first understand: (1) what CCU value chains can offer, (2) what are their components and how they are related to each other; and (3) can CCU value chains mitigate CO₂ emissions, if they can be commercialised by optimising and developing them when a satisfactory level of understanding is achieved? This is discussed in Chapters 8, 9 and 10.

1.4.2 Understanding the problem on a regional scale

The next step would be to understand and visualize the problem on a larger regional scale and how the individual steps of the CCU value chain are related and connected. The question that needs to be answered is (4) what are the optimisation problems of CCU value chains. More insight could be drawn by studying previous optimisation approaches and case studies (5) to investigate (a) the solutions they are offering; (b) if the current solutions is the reason that they have not yet been commercialised; and (c) if they can be improved or executed in a new way to bridge the gap. Before dealing with the big picture macro problems, micro problems concerning the individual steps of the chain must be addressed and answered first.

1.4.3 Sources

Starting from the first step of the value chain, the source of emissions, the first obvious question to ask would be (6) which are the available CO₂ sources that offer the possibility of capturing CO₂ from them? For example, an obvious CO₂ source would be cars, but it is not practically feasible to capture CO₂ from cars. It would also be useful (7) to group CO₂ sources into categories that show similarities, in terms of production method, quantity and purity of CO₂ and the stream composition of each source. Knowing the size of the source and the emission factor ratio based on the amount of product produced could facilitate the matching of sources and receivers; this is discussed in Chapter 3.

1.4.4 Capture

The next step would be to establish a conventional way to capture CO₂ from the available sources. This means that a capture technology might exist that can be applied to each source or there are several capture technologies that show high potential and offer optimal results in terms of technical or economic characteristics but are compatible with only specific sources. Therefore, the questions to be answered are (8) how CO₂ can be captured, what technologies are available, and if they can be categorised through shared similarities. The operation principle, the maturity, the cost and the purity that can be achieved can be analysed to facilitate the optimisation and development of CCU value chains; this is discussed in Chapters 4 and 5.

1.4.5 Transportation

Once CO₂ is captured, it must be transported to the receiver for utilization. What are the available options and is there a best way to do it? Is there an optimal transportation method or there is an optimal solution based on the region or maybe based on flowrate and distance for the matching between source and receiver? In other words, (9) what are the available transportation options, how can we categorize them, what are the optimal transportation conditions and are they any impurities that may cause additional problems? (10) what is the cost of each option and how can we analyse and assess cost to minimise transportation costs? These are discussed in Chapters 6 and 7.

As explained earlier, transportation requires purification and compression that happens at the capture facilities. For purification, it must be made clear (11) what needs to be removed and at what level and for compression, (12) why it is needed and how much is needed for each type of transportation.

1.4.6 Receiver

The purpose of the receiver in the CCU value chain is to absorb CO₂ and store it, either permanently or temporarily. The questions to be answered are therefore (13) which are the available receivers and how is CO₂ utilised to be turned into a product and what product is it made to? Can we categorize them, and if we can (14) what is the size of each receiver and is there a most effective receiver in terms of utilization? (15) Can receivers accept any CO₂ purity or are there constraints regarding purity or the level of impurities? (16) Are there any necessary modifications for the process to accept captured CO₂ and if yes, at what cost? (17) How mature is each technology? Knowing the ratio that CO₂ is produced to the amount of product produced would aid in the matching of sources and receivers.

1.4.7 Aims and novelties

This research aims to answer if and how it is possible to mitigate CO_2 emissions via CCU value chains. This will be achieved by answering the above research questions to prepare a knowledge base of CO_2 receivers and their characterization, a knowledge base of CO_2 sources and their characterization, a framework for the matching of CO_2 sources with CO_2 capture technologies based on their compatibility and models for estimating CO_2 capture costs. The novelties will be integrated to develop an algorithm and a business model that propose the optimal set of solutions of technically feasible and profitable combinations based on a set of ranked variables such as utilisation, profit, initial investment and more.

1.5 Chapter 1 conclusions

This chapter serves as an introduction to the thesis providing a brief background on CCU and discusses the research motivation by establishing the connection between what is global warming, how it is caused and the potential of CCU value chains highlighted by the plans of the European Union to include it as a major pillar in the Roadmap to 2050. It shows the big picture of a future without CCU and future with CCU, demonstrating what it can be achieved. It also provides the scope and aims of the research and how to achieve commercialisation via optimisation. Research questions that guide the research are explained providing the structure of the thesis and a guide to upcoming chapters, starting from Chapter 2, which focuses on permanent and temporary utilisation of CO₂.

Chapter 2: Utilisation options for CO₂

2.1 Permanent Utilisation

 CO_2 utilisation is the last step of the CCU value chain and takes place at the receiver. Receivers can be grouped into types of industry and further into the type of process in each industry. These two sections (2.1 and 2.2) present the industries which provide permanent and temporary utilisation options. Each section concentrates on the individual processes of each industry and explains how CO_2 is utilized in each process. The objective of these two sections is to perform a thorough literature review and develop an updated catalogue of all CO_2 receivers, with their main characteristics (receiver maturity and conversion factor of CO_2), which is one of the novel contributions of this thesis.

2.1.1 Carbon mineralisation

Mineral carbonation of calcium carbonate and magnesium carbonate

Mineral carbonation is the process of producing magnesium and calcium carbonate by reacting CO₂ with calcium or magnesium silicates. The process converts CO₂ and minerals to construction materials and mimics the natural process of chemical rock weathering that permanently stores CO₂. Mineral carbonation utilises minerals such as olivine (MgSiO₄), serpentine (MgSi₂O₅(OH)₄) and wollastonite (CaSiO₃) or industrial solid waste such as fly ash and brine. The reactions are presented by equations 1,2 and 3 [9].

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$$
 -89 kJmol⁻¹_{CO₂} (1)

$$Mg_{3}Si_{2}O_{5}(OH)_{4} + 3CO_{2} \rightarrow 3MgCO_{3} + 2SiO_{2} + 2H_{2}O - 64 \text{ kJmol}_{CO_{2}}^{-1}$$
(2)

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \qquad -90 \text{ kJmol}_{CO_2}^{-1} \quad (3)$$

The reaction is exothermic and thermodynamically favoured at low temperature but too slow. Instead, the metal is extracted from the solid utilising an extracting agent such hydrochloric acid or molten salts by dissolving the mineral in an aqueous solution to release metal ions. CO₂ is also dissolved in solution to form carbonic acid (H₂CO₃) which reacts with the released metal ions to form carbonates [8], [9], [10], [11]. For the production of calcium carbonate and magnesium carbonate low concentration CO₂ streams can be utilised.

Bauxite residue treatment

Red mud is produced during the Bayer process, when extracting alumina from bauxite to produce aluminium. Red mud contains a mixture of minerals and sodium hydroxide which makes it highly

alkaline and hazardous and makes its disposal difficult. Red mud can be treated with concentrated CO₂ to reduce the pH (13.5 to 10.5) of the slurry and turn it into a soil amendment product for acidic soils, road base or building materials. The CO₂ treatment carbonates red mud and permanently stores CO₂ [10]. Bauxite residue treatment can utilize 0.75t_{CO2} per tonne of product and can improve the handling and dusting of red mud while at the same time can reduce the cost of disposal or even produce revenue from selling it as soil amendment.

Total dissolved solids (TDS) removal from deep saline reservoirs

The large-scale sequestration of CO_2 in deep saline reservoirs may lead to the extraction of high TDS brine because of the increased pressure in the reservoir, which is not safe to dispose to the environment or applied for other potential uses and requires treatment. The major TDS are sodium, calcium and magnesium salts and are usually treated using conventional desalination processes, which face scaling, fouling, corrosion, and high energy consumption challenges due to the significantly higher concentrations compared to sea water. One alternative solution is treatment with ammonia/carbon dioxide, which might be able to utilise captured CO_2 [12], [13].

Concrete curing and conditioning

Natural carbonation of concrete in air is quite slow but it was found to improve its mechanical properties and reduce the shrinkage after drying. Concrete carbon-curing and carbon-conditioning is the process of curing fresh concrete and recycled aggregate concrete respectively with CO₂ to strengthen and improve mechanical and durability properties of concrete. The strengthening of concrete with CO₂ is inspired by natural carbonation and happens as calcium hydroxide in concrete undergoes the following chemical reaction with added CO₂ to form calcium carbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
 -74 kJmol⁻¹ (4)

The large calcium hydroxide forms calcium carbonate, which is smaller and fills voids in the cement paste, giving concrete a higher density and less water absorption. For accelerated concrete carbonation 100% pure CO₂ is required but lower purities are also acceptable [14], [15], [16] [17]. Concrete curing can utilize low purity CO₂ and has the ability to utilise 0.12t_{CO2} per tonne of product produce. The process can be easily retrofitted and offers many benefits to producers in energy and water savings [10].

2.1.2 pH control

Wastewater treatment

CO₂ can be used for pH reduction in wastewater treatment. Industries such as iron and steel production, textile and dying industries, pulp and paper industries and power plants produce alkaline wastewater as a by-product (pH 11.4). CO₂ can be used as a buffer to decrease pH levels from 11.4 to 5 for the safe disposal of wastewater [10], [18]. This process requires high CO₂ concentration.

Pulp and paper production

 CO_2 is used in the production of pulp and paper to regulate and stabilize pH and reduce $CaCO_3$ dissolution. The addition of CO_2 improves runnability and reduces steam consumption, wash water (during pulp washing), defoamer agent and pitch dispergents volume, which effectively reduces maintenance costs. Enzymes are added to the process to produce brighter pulp with less bleaching chemicals and the CO_2 pH stabilizing properties increase their effectiveness because they work at a narrow pH range around 7 [9], [19].

2.1.3 Enhanced fossil fuel recovery

Enhanced oil recovery (EOR)

CO₂ is used in enhanced oil recovery (EOR) when the underground pressure of the well is insufficient to continue extracting oil. Depending on the pressure of the reservoir and weight of oil, high concentration CO₂ is used for CO₂ flooding or CO₂ flooding with water to increase the wells' pressure or lower the viscosity of oil. CO₂ EOR applications help recover 5 to 40% of oil. Some of the CO₂ used returns to the surface with oil and is separated and re-injected in the well [10], [8], [18]. It is an option with large scale application in the US with initial operation since 1986 and large storage potential with the additional benefit from oil revenue.

Enhanced coal bed methane recovery (ECBM)

Coal bed methane is the geological transformation of peat to anthracite coal in underground coal seams that generates a mixture of methane and trace quantities of light hydrocarbons, nitrogen and CO₂. The mixture is stored in liquid phase at high pressures in the micro-pores of the coal surface and up to 50 % can be extracted using conventional extraction by dewatering and reducing the pressure in the coal bed. High or low concentration CO₂ can be used in enhanced coal bed methane recovery to release more methane by adding CO₂ in the coal to be adsorbed by the porous coal surfaces and

displace methane [10], [18]. ECBM can utilise low concentration CO_2 streams at a ratio of $2t_{CO2}$ of per tonne product and generate revenue from the increased production of natural gas.

Enhanced gas recovery (EGR)

Similarly to EOR, supercritical CO₂ can be injected in natural gas reservoirs to displace natural gas and facilitate its recovery [20], [21], [22]. Natural gas reservoirs have the ability to store more CO₂ compared to depleted oil reservoirs (almost twice as much) but EGR is not as mature as EOR and it is a high cost process. It has risks associated with field contamination due to the possible mixing of stored gas and injected CO₂ that could degrade gas production [20].

2.1.4 CO₂ as chemical feedstock

Methanol production (liquid fuels)

Methanol is used as fuel for internal combustion engines and in the production of formaldehyde, which is converted to many other products. The conventional methanol production process is via synthesis gas from steam methane reforming using natural gas via the following reaction that takes place at 260°C. This reaction can utilise captured CO₂ to increase methanol production.

$$CO + 2H_2 \rightarrow CH_3OH$$
 -90.77 kJmol⁻¹ (5)

An alternative way to produce methanol is via the following reaction that utilises high concentration captured CO₂ and hydrogen from water hydrolysis.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$
 -49.16 kJmol⁻¹ (6)

In the case of methanol used for the production of formaldehyde the storage is going to be permanent because of formaldehyde products but when methanol is used for energy production then the storage is temporary with an indirect mitigation effect for reducing the consumption of fossil fuels [9], [18], [22], [23].

Polymer production, Polycarbonate

Polymers are long carbon chains consisting of a repeating unit (monomer) derived from petroleum. The most widely used ones are polyethylene (PE) used in the production of plastic bags, milk bottles and film wrap, and polypropylene (PP) used in the manufacture of automotive components, textiles and banknotes. High concentration captured CO₂ can be added to the monomers to produce new ones called polypropylene carbonate (PPC) and polyethylene carbonate (PEC). Polycarbonates are produced with CO₂, an epoxide which is a polycarbonate forming monomer and a zinc-based catalyst. Depending on the type of epoxide used the polymer can have different properties like hard, soft, transparent or opaque. Polycarbonates have high strength, high impact resistance, they are light and mouldable and could potentially replace existing polymers in enhanced oil recovery, coatings, packaging, laminates, injection moulding, extrusion and blow moulding. [10], [11], [18]. Polymer processing utilization has the potential to produce a variety of chemicals and materials for many everyday uses like polymer coatings, plastic bags laminates surfactants, automotive and medical components. These products have the ability to utilize CO₂ with a ratio of 0.5-1.5 per amount of product.

Polymer production, Polyurethane production

In a similar way as the incorporation of captured CO₂ in the production of polymers to polycarbonates, captured CO₂ can be chemically fixed in polyurethane. Polyurethanes are bulk plastics with high impact protection and cushioning uses that can be used for the production of polyurethane foam [11], [21].

Carbamate production

Carbamates are produced by the reaction of CO₂ with N-nucleophiles and have a range of uses including pesticides, polymers, replacement for phosgene reagent (extremely toxic) in organic synthesis and precursors to isocyanates, which are used in the production of polyurethane [11], [24]

Sodium carbonate (soda ash, soda Solvay)

Carbon dioxide is used in the production of sodium carbonate (Na_2CO_3) [18], [21], [22], [24]. Sodium carbonate is used as a water softener, a strong base and in the manufacture of soda lime glass which is produced by heating sodium carbonate and sand (SiO₂) at high temperatures [18].

Low TRL CO2 uses for chemical synthesis

Some products that can theoretically utilise CO₂ are organic acids, alcohols, esters and sugars [10]. CO₂ can be used in the production of polyacrylates, in synthesis of drugs as intermediate, as a respiratory stimulant and in the production of fertilizers [8], [22], [24].

2.1.5 Other Uses

Working fluid in Enhanced geothermal systems EGS

 CO_2 has two uses in EGS, as a circulating heat exchange fluid that eliminates the need of a circulation pump and as a working fluid in supercritical CO_2 power cycle to recover geothermal heat [10]. CO_2 ends up stored by diffusion in the rock surrounding the reservoir.

Steel manufacture

CO2 can be used as bottom stirring agent in BOF furnaces, as a fluid for dust suppression and for injection to metal casting [10], [22].

2.1.6 Conclusions

Permanent utilisation products are the foundation of CCU value chains because they are the ones that provide a solution for the continuous increase of CO₂ abundance in the atmosphere. Every chemical reaction encountered in literature for permanent utilisation of CO₂ was exothermic, meaning that these processes do not require an energy supply, therefore no additional emissions are created. All efforts must be focused on supporting the utilisation of CO₂ by these products.

2.2 Temporary Utilisation

Temporary utilisation refers to products that only store CO₂ temporarily, meaning the emissions will be eventually emitted back to the atmosphere. This happens because of the nature of the products, (e.g. farming produce) which will release CO₂ once they are digested, or biofuels that will emit CO₂ when they are burned.

2.2.1 Enhanced growth of vegetables and plants

Greenhouse horticulture

Greenhouse horticulture processes allow for better quality products because of the accurate control of growing conditions, such as humidity, temperature and CO₂ concentration. CO₂ enrichment has been found to enhance the growth rate of fruit, vegetables and flowers which increases production yields. This can be achieved by adding pure or captured CO₂ in optimal concentrations [10], [18], [25]. This utilisation option is considered to be only temporary because any food product will be digested to produce CO₂ when consumed [26].

Algae and kelp cultivation

Algae is cultivated to produce lipids used in the production of biochemicals and pharmaceuticals, protein for animal feed, biomass for solid fuel and organic fertilisers and carbohydrates to produce biodiesel and bioethanol. It is grown in tanks, ponds or tubular bioreactors using water or wastewater, sunlight and carbon dioxide. Algae lives on a high concentration of CO₂ and NO₂ which act as key nutrients to convert CO₂ to sugars via photosynthesis. CO₂ is added in bioreactors to increase production yields and help overcome the economic barrier making it cost competitive with crude oil. Kelp in seawater can also be used in a similar way as algae [8], [9], [10], [11], [13], [18].

Algae cultivation shows very high potential for the scale of utilisation with a conversion factor of 1.8 t_{CO2}/t_p as it can offer a variety of products like algal oil which can be injected in existing crude oil refineries or for the production of biofuels and biogas that can displace fossil fuels (see Figure 4). None of these uses can be considered permanent but CO₂ used for the production of biofuels can have an indirect effect on the consumption of fossil fuels which produce CO₂ by avoiding the consumption of the fuel they replace and effectively avoiding those CO₂ emissions [10].

2.2.2 Carbon mineralisation

Baking soda

Baking soda is another variant of CO₂ mineralization that is produced by adding CO₂ to sodium-rich brine. The product is called sodium bicarbonate and can be used industrially as feedstock for bioalgae fuel production [10]. If baking soda is used in food the storage is only going to be temporary but if it is used for fuel production, it will have an indirect mitigation effect as described in the previous section.

Desalinated water mineralisation

Desalted and soft water produced from desalination plants is not healthy for direct consumption because it lacks minerals. This is solved by water conditioning with a remineralization process, by adding limestone and CO₂ to water [18]. The water will be used for consumption therefore this product stores CO₂ temporarily and eventually releases it to the atmosphere.

2.2.3 pH control

Sugar production

One of the steps of sugar production is carbonation which follows liming, i.e. the addition of lime (CaO) to neutralize acids in cane beets, precipitate organic acids and keep foreign matter in suspension to be later filtered. CO_2 is added as part of the carbonation process to reduce pH to 9 and remove all traces of lime and other impurities during the precipitation of lime to calcium carbonate (CaO₃) via a two stage carbonation process [13], [27].

$2.2.4 \text{ CO}_2$ as chemical feedstock

Urea production

Urea is a solid, inorganic, fossil-derived nitrogen fertilizer produced on an industrial scale for over 40 years. CO₂ capture urea yield boosting plants have been operational for over 20 years, making it a

mature technology with the ability to utilize 0.75t_{CO2} per tonne product. Urea is produced from ammonia and CO₂ (high concentration) in a two-step process where synthetic ammonia reacts with CO₂ to produce ammonium carbamate and then urea via dehydration. The process proceeds via the following two reactions, first one exothermic and the second one endothermic, summarised by reaction 9.

$$2NH_3 + CO_2 \rightarrow H_2NCOONH_4 \tag{7}$$

$$H_2NCOONH_4 \rightarrow (NH_2)2CO + H_2O$$
(8)

$$2NH_3 + CO_2 \leftrightarrow H_2NCOONH_4 \leftrightarrow (NH_2)2CO + H_2 - 133.5 \text{ kJmol}^{-1}$$
(9)

The final urea product is a granulated solid that reacts with water when applied to release nutrients in land and CO_2 to the atmosphere [10], [11], [18], [28].

Methanol production (liquid fuels)

In the case of methanol used for the production of formaldehyde, the storage is going to be permanent because of formaldehyde products, but when methanol is used for energy production then the storage is temporary with an indirect mitigation effect for reducing the consumption of fossil fuels. Methanol and formic acid production show high potential because of their high conversion factors with 1.4-14 and 3.1 t_{CO2}/t_p respectively. Methanol has a high TRL of 8 and formic acid has a low TRL of 2 but they both have the ability to displace fossil fuels similarly to algae products.

Methane production

Water hydrolysis can be achieved by solar power or from surplus power from the electric grid. Under different conditions compared to the reaction above, CO₂ and hydrogen can proceed via the following reaction to produce methane:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
 -165 kJmol⁻¹ (10)

The process is called hydrogen to synthetic methane gas [22], [29].

Formic Acid production (liquid fuels)

High concentration captured CO_2 can be used to produce formic acid (HCOOH) and oxygen via the electrochemical reduction of CO_2 with water (H₂O) through a series of the following three chemical reactions with an overall heat of reaction of -32 kJmol⁻¹ [10], [30], [31]:

$$CO_2 + H_2O + 2e^- \to HCOO^- + OH^-$$
 (11)

$$2H_2 0 \to 4H^+ + 4e^- + 0_2 \tag{12}$$

$$\mathrm{H}^{+} + \mathrm{HCOO}^{-} \rightarrow \mathrm{HCOOH}$$
(13)

Formic acid is a hydrogen carrier and can be used as a liquid fuel because it has the ability to release hydrogen [10]. Liquid fuels store CO₂ temporarily but reduce the consumption of fossil fuels.

2.2.5 Food industry

Beverage carbonation

Beverage carbonation involves the dissolution of high purity CO₂ in beverages like soft drinks, beer and wine [8], [9], [10], [18], [22]. This is a temporary storage solution as CO₂ will be released after digestion and when consuming the carbonated beverage.

Food processing, preservation, and packaging

CO₂ is used as a shielding gas in the food packaging industry for modified atmosphere packaging (MAP) and controlled atmosphere packaging to extend the shelf life by its ability to inhibit growth of bacteria [10], [22]. CO₂ will be released when the packaging is opened.

Coffee decaffeination (supercritical CO2)

The decaffeination of coffee involves the extraction of caffeine from coffee beans using supercritical CO₂ which is preferred because it is non-toxic and inert [10], [18], [22].

Dry ice production

 CO_2 is used for the production of dry ice (solid CO_2) for temperature control of food during transportation. It is usually used in pellet form for the refrigeration of ice cream, meat and frozen food. It is also used for the production of moulded substances and chill aluminium rivets [9], [18], [22].

Refrigeration

 CO_2 is also used for chilling and freezing in the form of a cryogenic fluid (liquid CO_2) [9]. All food industry related uses require a 99.9% pure CO_2 [32]

2.2.6 Working fluid

Welding (shield gas)

Carbon dioxide is used in MIG (Metal Inert Gas) welding systems as an inert shielding gas, to prevent oxidation of the weld metal [9], [10], [18], [21], [22]. CO₂ is cheaper than argon and helium and the least expensive option, making its use common in the automotive industry [18], [33]. Captured CO₂ can be used but must have a high concentration.

Fire suppression

CO₂ is used in industrial fire suppression systems and fire extinguishers because it reduces the oxygen level so that combustion cannot take place [9], [10], [21], [22].

Supercritical CO2

Supercritical CO₂ has many uses as a working fluid. It is used in the extraction of flavours and fragrances, dry cleaning, coffee decaffeination, as a heat exchange fluid in enhanced geothermal systems (EGS) and supercritical CO₂ power cycle in EGS and nuclear power generation plants [10], [18].

Power generation

Supercritical CO₂ is used for power generation in supercritical CO₂ power cycles instead of water or steam. This concept can also be applied in nuclear plants [10].

Extraction

 CO_2 can be used for the extraction of flavour and fragrance concentrates and de-caffeination of coffee [18].

Cleaning, Semi-conductor cleaning

Supercritical CO₂ has the ability to remove impurities by avoiding the use of water because of its chemical (dissolving of alcohols, fluorinated hydrocarbons, oil) and physical (rapid diffusion, low viscosity, low surface tension) properties that allow it to reach and dissolve a range of chemicals. For these reasons it can replace chlorofluorocarbons (CFCs) used for semi-conductor cleaning which include digital and analogue integrated circuits, transistors diodes and solar cells [18]. It can also be used for cleaning printed circuit boards during manufacturing [10].

2.2.7 Other temporary uses

Supercritical CO₂ can be used as a substitute for conventional clothes dry cleaning solvents [18]. CO₂ has other temporary uses in the metal industry as chilling agent for shrink fitting of parts and hardening sand cones and moulds [10]. Additionally, it has uses in pneumatics as a powering source for hand tool and paintball guns and as an aerosol can propellant [10], [22]

2.2.8 Conclusions

Temporary uses, although they cannot store CO_2 and stop its emission, can be useful in supporting the development of CCU value chains because they increase the demand of CO_2 which contributes

to the infrastructure and ecosystem of CCU value chains. Additionally, as the literature review showed, every chemical reaction encountered for temporary utilisation of CO₂ was exothermic, meaning that no energy supply is required, which does not contribute to additional emissions during the utilisation process.

2.3 Receiver optimisation information

Consultation with industrial CO_2 emitters has helped to reach a conclusion that the most important factors about CO_2 receivers that anyone interested in CCU value chains should know are, type of utilization, CO_2 purity requirements, technology readiness level and conversion factor (flowrate of CO_2).

2.3.1 Utilization: Permanent or not permanent

Utilization refers to the nature of the product, if it is a permanent or a temporary utilization option. Not all utilization technologies avoid the emission of CO_2 by storing it permanently. CO_2 receivers utilising captured CO_2 as feedstock are related to non-permanent utilization and avoid the direct emission of CO_2 , as CO_2 will be eventually released to the atmosphere at the end of the product's life [10], [21].

2.3.2 CO₂ purity requirements: Low or high purity

The most important attribute on a micro level for receivers is the purity of CO₂ that they can accept. Different CO₂ receivers require different CO₂ concentrations depending on the product and process. Products involving the consumption of CO₂ for food products have very high purity requirements with a minimum of 99.8 % CO₂ and additional limits on other possible impurities. Chemical processes also require as a feedstock almost pure CO₂. Receivers such as algae cultivation, mineral carbonation, concrete curing and enhanced coal bed methane can operate at lower CO₂ concentrations [10]. For some of the processes it was not possible to specify the minimum required purity, but a concentration of the highest purity will be assumed. The gathered data are illustrated in Table 1.

Table 1: Purity requirements for identified receivers

Receiver group	Receiver type	Purity	Reference
Enhanced growth of	Greenhouse horticulture	Varies	[13]
vegetables and plants	Algae and kelp cultivation	5-22%	[13], [10]
Carbon mineralization	Magnesium carbonate production	-	-
	Calcium carbonate production	-	-
	Bauxite residue treatment	>85%	[13], [10]
	Baking soda	-	-
	Desalinated water mineralisation	-	-
	TDS removal from deep saline	High	[13]
	reservoirs		
	RAC and concrete curing	Low	[13], [10], [14]
pH control	Wastewater treatment	High	[13]
	Pulp and paper production	-	-
	Sugar production	-	-
CO ₂ as a chemical	Urea production	High	[13], [10]
feedstock	Methanol production	High	[13], [10]
	Methane production	High	[13]
	Polycarbonate production	High	[13], [10]
	Polyurethane production	High	[13], [10]
	Formic acid production	High	[10]
	Carbamate production	-	-
	Sodium carbonate	-	-
	Low TRL uses	-	-
Enhanced fossil fuel	EOR	High	[13], [10]
recovery	ECBM	Varies	[13], [10]
	EGR	-	-
Food industry	Beverage carbonation	99%	[32]
	Food processing, preservation	99%	[32]
	and packaging		
	Coffee decaffeination	99%	[32]
	Dry ice production	99%	[32]
	Refrigeration	99%	[32]
Working fluid	Welding (shield gas)	-	-
	Fire suppression	-	-
	Supercritical CO ₂	-	-
	Power generation	-	-
	Enhanced geothermal systems	High	[10]
	Extraction	-	-
	Cleaning	-	-
	Dry cleaning of clothes	-	-
Industrial uses	Steel manufacture	-	-
	Metal working	-	-
	Pneumatics	-	-

2.3.3 Technology readiness level (TRL): How mature the technology is

The next important aspect is TRL which shows the maturity of a technology. Technology readiness level is a rating scale of 1 to 9 that clearly communicates if a certain technology is ready to be used in a plant. TRL does not convey accurate information on the risk, cost or timeframe for a certain technology but rather measures the technical risk of a specific technology that is to be introduced in a specific plant at the present time [34].

- TRL 1: Basic principles: Basic principles have been established
- TRL 2: Invention and research: Investigation of phenomena, acquisition of new knowledge, correction, integration of previous knowledge
- TRL 3: Proof of concept: Demonstration
- TRL 4: Bench scale: Laboratory demonstration
- TRL 5: Pilot scale: Undergoing testing to demonstrate specific aspects of the design
- TRL 6: Large scale: Undergoing full scale testing
- TRL 7: Inactive commissioning: Work, testing and factory trials
- TRL 8: Active commissioning
- TRL 9: Operations: The technology is used in an active facility

TRL can be used as a factor when selecting the optimal match between sources and receivers and a more mature technology would always be more desirable than a technology with lower maturity. Most of the identified receivers have a TRL above 7 which shows that most receivers are technologically mature and ready to be used in CCU value chains. The gathered data on TRLs are illustrated in Table 2.

Table 2: TRL for identified receivers

Receiver group	Receiver type	TRL	Reference
Enhanced growth of	Greenhouse horticulture	9	[13]
vegetables and plants	Algae and kelp cultivation	4-7	[13]
Carbon mineralization	Magnesium carbonate production	4	[21]
	Calcium carbonate production	4	[21]
	Bauxite residue treatment	7-9	[13]
	Baking soda	6	[35]
	Desalinated water mineralisation		
	TDS removal from deep saline reservoirs	9	[13]
	RAC and concrete curing	7-8	[13]
pH control	Wastewater treatment	9	[13]
	Pulp and paper production		
	Sugar production		
CO2 as a chemical	Urea production	9	[13]
feedstock	Methanol production	7-8	[13], [21]
	Methane production	6-8	[13]
	Polycarbonate production	7	[13]
	Polyurethane production	7	[13]
	Formic acid production	2	[21]
	Carbamate production		
	Sodium carbonate	7-8	[21]
	Low TRL uses		
Enhanced fossil fuel	EOR	9	[13], [21]
recovery	ECBM	7	[13]
	EGR	7	[21]
Food industry	Beverage carbonation	9	[35]
	Food processing, preservation, and packaging	9	[35]
	Coffee decaffeination	9	[35]
	Dry ice production	9	[35]
	Refrigeration	9	[35]
Working fluid	Welding (shield gas)	9	[35]
	Fire suppression	9	[35]
	Supercritical CO ₂	3	[35]
	Power generation	9	[35]
	Enhanced geothermal systems	4	[35]
	Extraction	9	[35]
	Cleaning	9	[35]
	Dry cleaning of clothes	9	[35]
Industrial uses	Steel manufacture	9	[35]
	Metal working	9	[35]
	Pneumatics	9	[35]

2.3.4 Conversion factor

Global CCS Institute (2011) has produced some estimates as to how big some of the mentioned receiver industries are expected to be, but the estimates cannot be used for predicting the size of individual receivers because these are per industry and do not indicate the region that the assumptions were based on [10]. Therefore, a way is needed to estimate the magnitude of individual receivers involved in CCU value chains at any region. The estimated required CO₂ of a receiver can be used to match a receiver to a compatible source, and CO₂ flowrate is one of the major criteria for CCU value chain development. To account for the amount of CO₂ that would be required for each source Table 3 was developed, gathering information from literature to specify the amount of CO₂ required per unit product produced. This value is a conversion factor (amount of CO₂ required per unit produced) that can produce estimates for the annual CO₂ requirements of any receiver by specifying the annual production of the receiver.

Algae and kelp cultivation, methanol and methane production show very high potential as temporary storage receivers that have the ability to displace fossil fuels because of the high conversion factors ranging from 1.65 to 2.75 and high TRLs. Permanent storage receivers that show high utilization potential are bauxite residue treatment, polycarbonate, polyurethane production, EOR and ECBM for their high conversion factors ranging from 0.5 up to 10 and their high TRLs that are all above 7.

Table 3: Conversion factors for identified receivers

Receiver group	Receiver type	C.F	Reference
Enhanced growth	Greenhouse horticulture	Ind0.6	[13]
of vegetables and		kgCO ₂ /hr100m ³	
plants	Algae and kelp cultivation	1.65-1.83	[10], [13]
Carbon	Magnesium carbonate production	0.5	[10]
mineralization	Calcium carbonate production	0.5	[10]
	Bauxite residue treatment	0.3-0.35	[10]
	Baking soda	0.52	[10]
	Desalinated water mineralisation	3	[18]
	TDS removal from deep saline reservoirs	0.024	[13]
	RAC and concrete curing	0.12	[10]
pH control	Wastewater treatment	3	[18]
	Pulp and paper production	-	
	Sugar production	-	-
CO ₂ as a chemical	Urea production	0.735-70	[10], [18], [11]
feedstock	Methanol production	1,4-14	[10], [18], [11], [13], [9]
	Methane production	2.75	[13]
	Polycarbonate production	0.2-0.5	[10], [18], [9]
	Polyurethane production	0.5-10	[10], [18], [9]
	Formic acid production	3.1	[10]
	Carbamate production	-	-
	Sodium carbonate	3	[18]
	Low TRL uses	-	-
Enhanced fossil	EOR	0.5t/barrel	[10]
fuel recovery	ECBM	2	[10]
	EGR	-	-
Food industry	Beverage carbonation	8	[18]
	Food processing, preservation, and packaging	8	[9]
	Coffee decaffeination	10	[18]
	Dry ice production	-	-
	Refrigeration	-	-
Working fluid	Welding (shield gas)	10	[18]
	Fire suppression	-	-
	Supercritical CO ₂	10	[18]
	Power generation	-	-
	Enhanced geothermal systems	-	-
	Extraction	-	-
	Cleaning	-	-
	Dry cleaning of clothes	10	[18]
Industrial uses	Steel manufacture	-	-
	Metal working	-	-
	Pneumatics	-	-

2.4 Chapter 2 Conclusions

Returning from the micro problems of the characteristics of receivers to the macro problems of how they fit in the bigger picture, the CO₂ life cycle with CCU must be recalled.

The reason that CO_2 atmospheric abundance is rising within the current CO_2 lifecycle is due to increasing anthropogenic emissions. The system of absorbing CO₂ naturally is saturated in CO₂, and it is impossible to absorb CO₂ at a higher rate. Accumulation of CO₂ is unavoidable, and the additional amount of CO₂ stays in the atmosphere. If CCU value chains are implemented, two new categories are created and added to the existing CO2 life cycle. The first one is temporary storage, which will store CO₂ temporarily and eventually release it again. This does not render them irrelevant because some products that exist in this category, such as biofuels, contribute to reducing burning of fossil fuels, therefore effectively decreasing the actual amount of fossil fuel used. The amount of CO_2 released stays the same, but the amount of new CO₂ released is decreased by the amount of fossil fuels replaced by biofuels accordingly. This category creates an enclosed recirculation loop shown by Figure 7, going from the temporary storage block to join the stream from underground to the anthropogenic CO₂ emissions. The recycling stream recycles the same amount of CO₂ with the associated CO₂ emissions from fossil fuels to produce and distribute biofuels, displacing the emissions from fossil fuels. Additionally, non-permanent CO₂ utilization options should be introduced in the CCU value chain even though is not permanent, because it can facilitate the viability and development of the CCU value chain and can also contribute to the seasonal shortage of CO₂.

The second and most important new category is CCU products made up of the permanent CO₂ storage uses. This category creates a new storage capacity that can potentially be as big as the needs of the products from this category. This category would be at its biggest in the ideal scenario were all CCU products have replaced their alternative non-CCU products. This is defined as an ideal scenario because it is unlikely that the developed CCU value chains would be able to produce the amounts that the market demands and it is even more unlikely that even if the product is available at such quantities, everyone will decide to replace the non-CCU products with their alternative CCU products.

Chapter 3: Where is CO₂ coming from?

3.1 Introduction

Carbon dioxide sources are the first step of the CCU value chain and without them there would be no reason for developing CCU value chains in the first place. To be able to capture CO₂ from them, it is initially necessary to understand and comprehend why and how CO₂ is emitted; therefore, carbon dioxide sources must be identified, analysed, and characterised. The first step in doing so is to list them in groups of industries and collect data in terms of:

- (a) What purpose does the CO₂ emitting process serve?
- (b) How is CO₂ generated and released to the atmosphere?
- (c) What is the concentration of CO₂ exiting the process?
- (d) What is the magnitude of the CO₂ emitted in comparison to the product?

Understanding how CO₂ is emitted and at what purity can assist in the capturing process, so that a specific source is matched with the optimal CO₂ capture technology. Knowing the amount of CO₂ released to the atmosphere by each process can help in the matching of CO₂ sources with CO₂ receivers so that supply and demand is managed.

This chapter presents the results of a literature review which gives an outline for the major and most common CO₂ sources to provide information on how CO₂ is generated and emitted in each of those sources, at what purity and what magnitude in relation to the product. The CO₂ sources are grouped in tables for various industry types identifying the process, sub-process, purpose, CO₂ source, reason, purity and quantity for CO₂ emission in each process. The original contribution of this chapter is the creation of a homogeneous up-to-date catalogue of carbon sources (Table 8 to Table 14), with all the above information in one place, answering Questions (a)-(d). This will allow to form the next link of CCU value chains with carbon capture technologies (sources to carbon capture).

3.2 Heat and power generation

3.2.1 Boilers

Boilers are furnaces used to generate heat and energy by combusting a variety of fuels. To combust a different type of fuel, a boiler with a different design is required. Boilers can be grouped in three types according to the state of the fuel they are using, solid fuel-fired, oil-fired and gas-fired. Solid fuel fired furnaces are used in firing plants to generate heat energy by combusting crushed or ground hard coal, brown coal or wood in the combustion chamber of a furnace. Oil-fired furnaces are used to generate heat by combusting oil in the combustion chamber of a boiler and they can utilise a steam turbine to generate electricity. Finally, gas-fired furnaces are used in firing plants to generate heat energy by burning combustible gases in boilers such as natural gas, industrial gas or blast furnace gas with the use of a gas turbine [36].

3.2.2 Coal-fired Electric Generating units

Coal fired electricity generating units burn crushed coal in coal boilers. Different types of coal and boilers exist and each one results in different boiler efficiencies and differences in electricity production (Table 4). The exhaust gas of coal fired electric generating units and therefore the CO₂ purity and stream composition of coal fired generating units is affected by the type of coal and boiler used as well.

Table 4: Typical characteristics of the most commonly used coal ranks. Adapted from: [37]

Coal rank	Higher Heating value (HHV)	Typical Coal	Coal Delivered for U.S Electric Powe	er Production in 20	008
	Range defined by ASTM	moisture	Total Coal Quantity Delivered	Average Ash	Average sulphur
	D-388 (Btu/lb)	Content	Nationwide (1,000 tons)	Content (%)	content (%)
Bituminous	>10,500	2-16	463,943	10.6	1.68
Subbituminous	>10,500 and <8,300	15-30	522,228	5.8	0.34
Lignite	<8,300	25-40	68,945	13.8	0.86

Stoker fired coal combustion boiler

Stoker firing coal combustion is the oldest coal firing design and now obsolete due to newer designs that have higher efficiencies and more advantages. The stoker-fired coal boiler operates by burning crushed coal on a grate. The heat produced is used to produce steam that generates electricity through a steam turbine. Only a few stoker-fired boilers are still in use and nowadays are more likely to be used to burn solid biomass at municipal solid waste combustion facilities [37].

Pulverised coal combustion (PCC) boiler

The pulverised coal process produces steam to turn a steam turbine and generate electricity through a generator. Heat is produced by combusting powdered (pulverised) coal while suspended in the boiler's combustion chamber. Combustion is achieved with the use of burners that can have either a wall-fired or tangential-fired positioning. The walls of the boiler's combustion chamber are fitted with tubes filled with water that turns into steam from the heat produced during the combustion of pulverised coal. Steam is separated from water and sent to a steam turbine and the products of coal combustion (flue gas) are vented to the atmosphere after they have passed the air pollutant emissions control [37]. Combustion of flue gas is responsible for the emission of CO₂ and for other impurities.

Supercritical and ultra-supercritical steam cycles

Sub-critical, supercritical and ultra-supercritical terms refer to the steam's operating conditions and to some extent to the type of boiler used to meet the conditions. Sub-critical steam conditions require water to be separated from steam, whereas supercritical and ultra-supercritical steam do not, as it is a single-phase fluid. Supercritical steam cycle operating conditions have 4-6% higher efficiency compared to sub-critical conditions [38]. Steam cycle operating conditions are summarised in Table 5.

Table 5: Conditions of pulverised coal combustion steam cycles [38]agrees with [39]

Conditions	Sub-critical	Supercritical	Ultra-supercritical
Pressure (bar)	150-180	245	245
Temperature (°C)	540-565	540-570	600

Cyclone coal combustion boiler

Cyclone coal combustion boilers operate by burning crushed 4-mesh size coal in suspension, to produce high-temperature flames that circulate in a cyclonic pattern. This technology was developed as an alternative to pulverised coal combustion, as it requires less processing for coal preparation. Existing cyclone boilers were installed before 1981 and no more are expected to be built because of the high NO_x emissions [37].

Fluidised bed combustion boiler

Fluidised bed combustion is an alternative process that is able to burn lower rank coals with low NO_x emissions. The fluidised bed combustion process produces high pressure steam to turn a steam turbine and generate electricity through a generator. Heat is produced by combusting crushed coal and sorbent (limestone) in a fluidised bed system in atmospheric or pressurised boilers. The bed design can utilise a bubbling or a circulating fluidised bed (bubbling fluidised bed combustion (BFBC), circulating fluidised bed combustion (CFBC)). In the case of a pressurised fluidised bed, combustion takes place at 10-15 bar pressure and 800 to 900°C temperature which produces less NO_x compared to PCC and increases the efficiency of a carbon capture system due to the pressurised fluidised bed's high pressure. Second generation PFBC systems, also called advanced circulating pressurized

fluidised bed combustion (APFBC), turn coal feed to fuel gas and char which are then combusted to produce steam [37]. The source of CO₂ emission is the flue gas produced from coal combustion.

Coal gasification

Coal gasification is used by IGCC plants for power generation and involves the gasification of coal into a mixture of carbon monoxide (CO) and hydrogen (H₂) (referred to as synthetic gas or syngas), which can be combusted to generate heat and steam, and in return to generate electricity [37]. CO₂ is produced during the gasification of coal which results in a gaseous mixture of CO₂, CO and H₂ and some other impurities. The gaseous mixture passes through a gas cleaning process to obtain syngas for combustion and the rest of the flue gas is vented to the atmosphere [38].

3.2.3 Combined gas and steam power station

Combined gas and steam power plants utilise a combination of gas turbines and steam turbines that can operate with natural gas, syngas from coal gasification or oil. The turbines drive electric generators that produce electricity. The turbines' exhaust gases are captured by a heat recovery system generator that creates steam and drives a steam turbine to produce electricity [36], [37], [38], [40], [41].

Integrated Gasification Combined Cycle plants

Integrated gasification combined cycle plants (IGCC) use gasifiers to convert coal or petroleum coke, petroleum residuum, biomass or a blend of these fuels into fuel gas called syngas, a mixture of hydrogen and carbon monoxide. Syngas is sent to a shift reactor to convert carbon monoxide to carbon dioxide and more hydrogen. CO₂ is then separated from the mixture and hydrogen is used as fuel in the gas turbine [37], [38], [39], [41].

Natural Gas Combined Cycle

A natural gas combined cycle power plant (NGCC) uses natural gas to run a combustion turbine which produces electricity by turning an electric generator using the pressurised hot gases produced from the combustion turbine. The hot gases exiting the combustion turbine pass through a heat exchanger to recover heat by producing steam [39].

3.2.4 Combined heating and power stations

Combined heating and power stations consist of three stages:

- (i) Power generation
- (ii) Heat recovery
- (iii) Heat utilization

In the first stage, a heat engine, called prime mover, generates electricity. The major types of prime movers are internal combustion engines, steam turbines, gas turbines and combined cycle gas turbines. Due to the variety of prime movers, a combined heating and power station (CHP) can utilise different types of fuels such as diesel oil, natural gas or landfill gas. Each fuel generates a different heat demand and CO₂ emissions.

In the second and third stages, heat is captured from the prime mover, by heat recovery equipment usually in the form of steam, hot water or heating processes to utilise the captured energy. The major heat recovery equipment are heat exchangers for internal combustion engines, steam generators for gas turbines or absorptions chillers in the case that the CHP plant has to provide chilled water [36], [42].

3.2.5. Gas turbine plants

Gas turbines are used for electricity generation by driving generators and are usually used with waste heat boilers for heat recovery purposes. The gas turbine flue gas composition is similar to that of gas fired furnaces as they both burn similar fuels, usually gases (landfill gas, biogas, natural gas) [36].

3.3 Metal industry

3.3.1 Iron and steel production

Iron and steel production comprises three sub-processes [43]:

- (i) Iron making produced via blast furnace, smelting reduction or direct reduction routes, essential for steel making and manufacturing.
- Steel making where crude steel is produced in a basic oxygen furnace or in an electric arc furnace; and
- (iii) Steel manufacturing where steel is casted/made into semi-finished steel products (slabs, billets, blooms).

Figure 8 Illustrates the three sub-processes and possible routes of steel production in the iron and steel industry and each of the processes is explained in the upcoming section



Figure 8: The three sub-processes of the iron and steel industry [43]

Although there are three main routes of crude steel production, the products of each one can be classified into two distinctive products that differ in steel quality, BOF crude steel and EAF crude steel [44]. BOF crude steel is made entirely of new iron ore, and it does not contain any alloy elements carried from recycled steel, therefore it is used for products that require higher material standards, like sheets for car manufacturing. EAF crude steel contains alloys carried over from recycled steel that cannot be separated and, therefore, is considered to be of lower quality and is used in the manufacturing of products that require lower material standards like concrete reinforcing bars [44].

BOF crude steel

BOF crude steel is made of liquid raw iron (hot metal when liquid or pig iron when solid) in a basic oxygen furnace where it gets its name from [43], [44]. The basic oxygen furnace blows pure oxygen on pig iron to remove a large part of its carbon content [45].

Blast furnace (BF)

The blast furnace route is the conventional route for steel production and accounts for 65% of the global amount of steel produced [46]. This route requires coke, lump ore, sintered iron ore and

pelletized iron ore as the raw material for the blast furnace or top gas recycling blast furnace (TGRBF) to produce liquid raw iron [43], [44], [45], [46]. CO₂ is emitted from the fuel used in the stoves but additional emissions result from the carbon content of coke and coal used in the blast furnace gas, which is transferred in the blast furnace gas [44].

Smelting reduction iron (SRI)-COREX

The smelting reduction iron or COREX route is a recent alternative to the blast furnace route that eliminates the need of coke and sintered iron ore and uses coal as a source of energy and pellets and lump iron ore as an iron source to produce liquid raw iron [44], [45], [46].

Coke

Coke is produced by coal pyrolysis in an oxidation-free atmosphere (absence of air) at temperatures between 1150-1350°C where volatile organic compounds, tar and sulphur are removed [43], [45]. The CO₂ emissions in the coke production process are caused by the fuel used for under-firing which is blast furnace gas in integrated plants and coke oven gas in stand-alone plants [44].

Sintered iron ore

Sintering is the process of re-using waste raw materials of the iron and steel plants [47]. Sintered ore is produced by mixing ores, additives, recycled sinter and limestone in a mixing drum utilising coke breeze as a heating fuel [44], [45], [48]. The fuel used for the sintering process in the production of sintered iron ore is responsible for the CO₂ emissions, recycling raw materials and in calcination of limestone as lime is required in the process [44].

Pelletized iron ore

Pelletisation of iron is the process of improving the iron content of iron ore and shaping it to 9-16 mm balls by mixing it with limestone or dolomite (fluxing agents) and bentonite or organic binders (binding agents) [44], [49]. This process does not emit CO₂.

Basic oxygen furnace

The fuel used in the basic oxygen furnace is responsible for the CO_2 emissions. Additionally, CO_2 is emitted in the basic oxygen furnace gas as the carbon content of liquid iron is reduced [44].

Casting and finishing

BOF and EAF type steel share similarities in the final steps of steel production, during the casting into semi-finished shapes. Molten steel is shaped into slabs, blooms or billets via the continuous casting

or ingot casting method (old one) which then undergo surface preparation to remove surface defects before proceeding into shaping and rolling [47]. Fuel used in the casting, rolling, surface treatment and further processing of steel results in CO₂ emissions [44].

EAF crude steel

EAF crude steel is made from scrap iron or directly reduced iron (sponge iron or hot briquetted iron (HBI)) in an electric arc furnace where it gets its name from [43], [44], [50]. The CO₂ emissions during this process result from the fuel used and the carbon from electrodes and scrap that is oxidised in the EAF [44].

Direct reduction iron (DRI)-Midrex

Direct reduction iron route uses a mixture of pellets or lump ore with fine ore as an iron source and natural gas as a reducing agent to achieve oxygen removal (reduction) and produce direct reduction iron [45].

Electric arc furnace (EAF)

The electric arc furnace pre-heats ferrous scrap from steelworks, steel manufacturers, consumer scrap and direct reduction iron (iron source) with lime or dolomitic lime (flux agent) to make EAF steel. The CO₂ emissions result from the fuel used, carbon from electrodes and scrap oxidised in the EAF furnace [44].

3.3.2 Aluminium production

Aluminium is predominantly produced by the Hall-Heroult process utilising aluminium oxide produced from bauxite ore via the Bayer process. The Bayer process refines bauxite ore to aluminium oxide (alumina) and is dissolved in an electrolytic cryolite solution in the Hall-Herroult process, where with the use of carbon cathodes and anodes, electric current passes through the solution and reduces aluminium oxide to aluminium and carbon dioxide via the following chemical reaction which requires 6.23 kWh/kg_{Al} [51], [52], [53]:

$$2Al_2O_3 + 3C \leftrightarrow 4Al + 3CO_2 \tag{14}$$

Air is introduced above the aluminium oxide solution for cooling purposes, because it melts at 1000°C. A process gas containing CO₂, SO₂ and other impurities is generated and has to be treated before being released to the atmosphere. Due to the large air flow required for cooling, the CO₂ concentration in the flue gas is approximately 1% vol [51], [52]. The capture of CO₂ at concentrations as low as 1%vol CO₂ would require large equipment that increases costs. Therefore, the process has

to be modified to allow for a larger CO_2 concentration of 4%, which is suggested to be the optimal CO_2 concentration [51], [52].

3.4 Stone and clay industry

3.4.1 Lime production

The production of lime happens in the lime kiln through calcination of limestone, dolomite or other natural minerals. About 90% of lime is produced in a rotary lime kiln by heating limestone to undergo the following chemical reaction.

$$CaCO_3 \rightarrow CaO + CO_2$$
 +178 kJ mol⁻¹ (15)

The thermal content of the fuel used to heat the kiln, the type of kiln, content and mineralogic form of the feed and quality of the lime produced affect the emissions produced in lime kilns [36], [54], [55].

3.4.2 Cement production

In the production of cement, limestone and additives such as clay, ash or sand are pre-crushed and turned into fine raw meal by dry or wet grinding in a ball mill and then homogenized by air fluidization. Most of the raw meal is de-carbonized at 1400°C in a rotary kiln (cement kiln) or at 900°C if the process is modern and utilises a pre-calciner, using coal, oil and waste material as fuel to provide heat. This is where clinker minerals are formed to be used for the production of cement. This is also where the CO₂ emissions happen, 50% due to the calcination of limestone and 40% due to fuel combustion to provide the required heat in the cement kiln (the remaining 10% is due to transportation and handling) [36], [50], [56], [57]. Cement is then prepared by mixing and grinding of clinker, gypsum and other additives.

3.4.3 Brick production

Bricks are manufactured by crushing and mixing raw materials to make clay which is then shaped accordingly. The bricks undergo a drying process and then are placed in a tunnel oven at temperatures between 900 and 1300°C. The CO₂ emissions are caused by the fuel used for the oven's burner [36].

3.4.4 Glass production

In the production of glass, raw materials such as sand, soda, limestone and additives (nitric acid) are crushed, mixed and fed to a batch or continuous melting furnace, which operates at temperatures up to 1500°C to produce a mixed conglomerate. The type of products includes hollow and flat glass.

The furnace design and firing process varies considerably and the process uses natural gas, fuel oil and electricity as an energy supply source which are responsible for the CO₂ emissions [36].

3.5 Chemical and petrochemical industry

3.5.1 Refineries

A refinery's purpose is to separate hydrocarbons (crude oil) into different fractions using atmospheric and vacuum distillation, cracking, reforming and a variety of other processes [58]. A summary of the processes and products involved is illustrated in Figure 9. All the processes mentioned above are energy intensive and thus justify the high energy consumption of refineries as the second highest industrial consumer of energy in the U.S and therefore a significant greenhouse gas (GHG) emission source, especially of CO₂ as it is 97% of a refinery's emissions [59]. The largest greenhouse gas emission sources in a refinery are stationary combustion sources and are responsible mostly for CO₂ emissions and small amounts of CH₄ and N₂O. Stationary combustion sources include processes that satisfy the refinery's heat, steam and power requirements, such as boilers, process heaters,



Figure 9: Flow diagram illustrating the major processes of a refinery [58]

combustion turbines and flares [58], [59]. The rest of the major CO₂ emission sources are related to non-combustion processes, such as cracking, regeneration of cat cracker catalyst (coke burn off) CRU unit, steam methane reforming for hydrogen production, asphalt blowing stills and coke calcining units [58], [59]. The share of emissions in a refinery is shown in Table 6.

Table 6: Share of CO₂ emissions by process in a refinery. Adapted from: [58]

Source	Percent of refinery CO ₂ emissions (%)
Oil and gas fuel firing of furnaces and boilers	65
Regeneration of cat cracker catalyst	16
Flares	<3
Methane steam reforming to make hydrogen	2
Incineration and effluent processes	1
Power (55% imported)	13

Process heaters

Oil firing furnaces, oil firing boilers, gas firing furnaces and gas firing boilers are a major part of a refinery and are responsible for 65% of CO₂ emissions in refineries. The largest process heaters are associated with atmospheric and vacuum crude oil distillation units and the catalytic reforming unit if one is present [59], [60], [61].

Flares

Flares are safety devices used by refineries for cases such as process upsets, equipment malfunctions and start-up and shut-down procedures [59].

Fluid catalytic cracking (FCC)

Fluid catalytic cracking has replaced previously used thermal catalytic cracking and is the process where the bottom products of the atmospheric distillation unit (CDU) are converted to lighter products such as high-octane gasoline, diesel and fuel oil [62]. Newer FCC use zeolite catalysts with particle size of about 100 μ m and temperatures between 480-540°C to break down the CDU's vapor feed [58], [63]. As this process takes place, coke is produced and deposited on the catalyst causing it to deactivate. For this reason, the catalyst is constantly regenerated by combusting the accumulated coke (coke burn-off), producing CO₂, and small quantities of CH₄ and N₂O [59], [62]. Combustion of coke is one source of CO₂ emissions in this process, but additional emissions are caused from heaters that provide energy to reach the FCC unit's required temperature. Those will be similar to combustion related processes mentioned before.

Catalytic reforming units

The purpose of catalytic reforming units in a refinery is to produce aromatic compounds (benzene) by reacting gasoline and naphtha in the presence of a catalyst. During this process coke deposits on the catalyst and it must be burned off to reactivate the catalyst, releasing CO₂ during coke burn-off [59].

Hydrogen production

Hydrogen in a refinery is produced by a process called steam methane reforming (SMR) where natural gas is reformed over a catalyst using steam to produce syngas, a mixture of Hydrogen (H₂) and carbon monoxide (CO). CO reacts with steam in a water-gas shift reaction to produce CO₂ and H₂ [52], [62], [64]. The process proceeds via the following two chemical reactions:

$$CH_4 + H_2O \rightarrow CO + 3H_2 + 206 \text{ kjmol}^{-1}$$
 (16)

$$CO + H_2O \rightarrow H_2 + CO_2$$
 -41 kjmol⁻¹ (17)

 CO_2 coming from reaction 16 (about 55% mol) is mixed with flue gas from the combustion of PSA and refinery's fuel gas for supplying energy to reaction 15 resulting to a final flue gas with CO_2 concentration of about 24 mol% [52]. Alternative emissions of CO_2 from the SMR process come from syngas (15-35% v/v), PSA off gas (40-50% v/v), FTR furnace flue gas (5-20% v/v) and regenerator off-gas (95-99% v/v) in the case of solvent-based purification [60].

Asphalt blowing stills

Asphalt flux is oxidised by bubbling air through it at 260°C in a vessel called a blowing still for 1 to 10 hours. The flue gas produced from this process contains organic particulates, gaseous hydrocarbons, polycyclic organic matter, reduced sulphur compounds and significant quantities of CH_4 and CO_2 that are combusted to CO_2 and SO_2 [59].

Coke calcining units

Coke calcining units are used to produce premium grade coke by burning off impurities present in coke. During coke calcination a process gas is produced due to coke pyrolysis in low oxygen conditions. The process gas is combusted in the presence of air using an afterburner and the combustion of process gas generates CO₂ emissions, mostly due to the volatile content of the coke used in the process [59].

3.5.2 Natural gas processing

Natural gas usually contains impurities, sometimes in significant levels, and therefore has to undergo processing to meet the required standards. Typical impurities that have to be removed are hydrogen sulphide (H₂S) and carbon dioxide (CO₂), this process is referred to as gas sweetening. H₂S has to be brought down to trace levels as it is highly corrosive and toxic to biological organisms and CO₂ concentration can vary between 0.2 to 20% by volume, but the usual specification is less than 2% by volume. Removal of CO₂ takes place by amine or membrane separation and this results in the final product and a flue gas consisting of 1-4% CH_x and 96-99% CO₂ by volume [54], [65], [66].

3.5.3 Industrial hydrogen, ammonia and synfuel production

Hydrogen production

Hydrogen can be produced from fossil fuel feedstock such as natural gas, oil, coal, petroleum coke, naphtha, methane and other hydrocarbons. Fossil fuels are required to generate syngas, a mixture of H₂ and CO. CO is oxidised to CO₂ through the water-gas shift reaction and hydrogen is obtained by separating CO₂ from the mixture using chemical based solvent absorption techniques or pressure swing adsorption. Different types of fossil fuels require different reactions to produce syngas, therefore the most suitable for each type of fuel is utilised [65], [67]. Table 7 lists the process that each type of fuel can utilise.

Steam reforming (SMR, steam methane reforming)

Steam reforming is the most frequently used process for hydrogen production and typically involves natural gas, therefore referred to as steam methane reforming. It is an endothermic process and the production of syngas is achieved at 800-900°C with the use of a nickel based catalyst. Steam reforming can also utilise naphtha or light hydrocarbons [65]. The general chemical reaction for steam reforming is highly endothermic and is presented by reaction 18 [68]:

$$C_n H_m + n H_2 O \rightarrow nCO + (n + 1/2 m) H_2$$
 (18)

 Table 7: Available routes for hydrogen production. Adapted from: [65], [67]

Fuel	Technology (Current)	Technology (Under development)
Natural gas/methane	Steam reforming	-
Naphtha	Steam reforming	Partial oxidation
Methane	-	Partial oxidation
Coal	Gasification of solid fuel (partial oxidation)	-
Petroleum coke	Gasification of solid fuel	-
Gas & liquid hydrocarbons	-	Autothermal reforming

Partial oxidation

Partial oxidation involves the reaction of fossil fuels, typically naphtha and methane with pure oxygen (requires oxygen separation unit) at high pressures. Although the process is exothermic, heat can be supplied by burning up feedstock to reach temperatures around 1250-1400°C, at which syngas is produced [65]. The general chemical reaction for partial oxidation is slightly exothermic and is presented by reaction 19 [68]:

$$C_n H_m + 1/2 nO_2 \rightarrow nCO + 1/2 mH_2$$
 (19)

Auto-thermal reforming

Auto-thermal reforming generates syngas by utilising gas and liquid hydrocarbons through a combination of reactions (17) and (18) [65], [67]. The process takes place in two reactors. The first reactor, through a partial oxidation reaction, provides the required heat for the endothermic steam reforming reaction in reactor 2, where steam is supplied [65]. Auto-thermal reforming has no direct CO₂ emissions as all of the heat released is internal [65].

Gasification of solid fuels

Production of hydrogen using gasification of solid fuels involves coal or petroleum coke to produce syngas, followed by the water-gas shift reaction and CO₂ separation. Gasification of such fuels is achieved with the use of gasifiers that have varying configurations and the most frequently used is the entrained flow system. Gasification of solid fuels shares similarities with partial oxidation with the difference that steam is added.

CO2 reforming

In the scenario where syngas with high CO/H_2 ratio is desirable, like in the Fisher-Tropsch reaction, steam can be substituted with CO_2 in both reactions 17 and 18 or used with steam [68].

Ammonia production plant

Ammonia is the precursor for the manufacture of a variety of products and is synthesised via the Haber-Bosch process where nitrogen (N₂) reacts with hydrogen (H₂) to produce ammonia. This requires the production of hydrogen to synthesise ammonia, and it is manufactured as mentioned in the hydrogen production process above. Due to challenges associated with transporting hydrogen to ammonia production plants, hydrogen is instead produced onsite using natural gas (predominantly) or coal [63], [65], [67], [69]. The CO₂ emissions from ammonia plants are related to the onsite production of hydrogen.

Synthetic fuel production

Synthetic fuels are synthetic diesel, jet fuel, synthetic gasoline, naphtha, dimethyl ether (DME), methanol (MeOH) and they are produced using a small portion of the global production of syngas. The production of synthetic fuels usually utilises coal. The CO_2 emissions result during the gasification of coal to make syngas, where some of the CO in the syngas mixture has to be removed in the form of CO_2 to increase the H₂/CO ratio (typically 0.7 to desired 2) that favours the production of synthetic fuels [65].

3.5.4. Ethylene oxide

Ethylene oxide is industrially produced via the direct oxidation route where ethylene and oxygen react in a catalytic reactor between 200 and 300°C temperature and 10-30 bar pressure in the presence of silver oxide catalyst. The reaction produces CO₂ as a by-product and therefore it has to be removed from the reactor gas stream with the use of physical sorbents (Benfield process, cryogenic separation techniques) [65].

3.5.5 Sources with limited information and emissions

Other CO₂ sources with limited information and emissions are the production of carbon black, synthetic rubber, biogas, bioethanol, beer, wine, during the incineration of waste and thermal gas, and pyrolysis of waste.

3.6 Sources' Optimisation information

3.6.1 CO₂ emitting sources summary

Table 8 to Table 13 present information on the process, sub-process, product, CO₂ emission source, purity and amount of CO₂ produced in relation to the amount of product produced (emission intensities) for the industries and individual CO₂ emission sources, summarizing the answers to questions (a)-(d) set at the beginning of this Chapter. The last table, Table 14, presents a summary of all CO₂ emitting process with their respective CO₂ purities and emission intensities. Table 14 can be used as a database for storing the major and most frequently encountered CO₂ emitting sources with their respective purity and emission intensity information. It can be used for (i) mapping CO₂ sources in any region using publicly available databases, which provide the location of industries and their activity; (ii) optimising source/capture technology matching; and iii) optimising source/receiver matching.

Table 8 summarises and presents the highlights of the CO₂ emitting sources under the heat and power generation industry. It illustrates the purpose and name of the sub-process and process that emits CO₂. It shows the origin of CO₂, if the process involves combustion and what type of fuel it utilises. Finally, it shows the CO₂ purity and emission intensity of the output stream. Table 9 is an extra list that shows the emission intensities of different fuels that can be used a substitute if the actual emission intensity of a process was not identified by the literature review. Table 10 summarises and presents the highlights of the CO₂ emitting sources under the metal industry. It illustrates the industry, process, sub-process and type of product and the exact source of CO₂ and whether it was or a product of combustion or produced in another process during the production of the specified product. Finally, it shows the CO₂ purity and emission intensity of the output stream of each process. Table 11 summarises the CO₂ emitting processes listed under the stone and clay industries with their respective CO₂ purity and emission intensity of the output stream. Table 12 summarises and presents the highlights of the CO₂ emitting sources under the chemical and petrochemical industries. It illustrates the industry, process and sub-process name, the origin of CO₂ emission and if it is related to combustion or not. Finally, it shows the CO₂ purity and emission intensity of the output stream of each process. Table 13 presents the CO₂ purities and emission intensities of CO₂ sources with limited information and emissions. Table 14 lists the stream purities and emission intensities for all CO₂ emitting processes.
Process	Purpose	Type of turbine	Heat recovery	Sub-process	CO ₂ source	Combustion	Fuel	CO2 %	Reference	Emission Intensity Mt _{co2} /Gwh	Reference
Solid fuel-	Heat		No	Coal-fired	Boiler's	Yes	Coal	12-14 vol	[63]		
fired furnace				Wood-fired	furnace		Wood	No CO2 reported	[36], [63]		
Oil-Fired furnace	Electricity	Steam turbine	No	Oil-fired			Oil	11-15	[36], [63]		
Gas-fired				Gas-fired			natural gas	7-11	[36], [63]		
furnace							industrial gas	9-11	[36]		
							blast furnace gas	9-11	[36]		
Coal-fired Electric		Steam turbine	No	Stoker fired coal combustion	Boiler	Yes	Coal	15-18	[36]		
Generating				Cyclone coal combustion				15-18	[36]		
units				Pulverised coal (supercritical and ultra.) combustion				15-18	[36]	0.750	[70]
				Fluidised bed combustion				15-18	[36]	0.750	[70]
Combined		Gas and	Waste heat	NGCC	Gas turbine	Yes	Natural gas			0.350	[70]
gas and steam power station		steam turbine	boiler	IGCC	Syngas separated	No	Coal gasification to syngas Oil	12-14 vol	[63]	0.74175	[71]
Combined	Electricity	Gas	Waste heat		Gas turbine	Yes	Natural gas	10	[36]	0.37059	[72]
heating and power	and heat	turbine	boiler or exhaust				Landfill gas	13	[36]		
stations		Steam turbine	gases		Internal combustion engine		Oil	7-8	[36]		
Gas turbine		Gas	Waste heat	Gas turbine plants	Gas turbine	Yes	Natural gas	3-11	[36], [63]	0.7629	[72]
plants		turbine	boiler	Gas turbine plants			Oil	3-11	[36], [63]		

Table 8: Heat and power generation CO₂ source

Fuel	Emission factor	(t _{co2} /t)
Gasolines	Normal [regular]	3.183
	Super [midgrade/plus]	3.185
	Super Plus [premium]	3.141
Fuel	CO2-emission factor	(t CO2/TJ)
hard coal	Egg coal, England	95.913
	Anthracite, Ibbenbüren	96.828
Lignite	"Rekord" brand briquettes, Lusatian mining district	98.478
briquettes	Briquettes, Rhineland district	99.036
	Gaskombinat (gas production combine), Schwarze Pumpe	100.294
	Briquette factory, Lauchhammer	98.489
	Briquettes, Lusatian mining district	96.854
	Lignite coke	109.6
	Lignite tar	82.937
	Lignite tar oil	78.631
	Lignite semi-coke	100.22
Town gas	Coal gasification	56.62
	High-temperature lignite coking	59.965
	Coal-dust gasification	119.812
	Pressurized natural gas reforming	66.387
	Pressurized oil cracking	88.126
Fuel gas	Lignite-based "winkler" gas	126.701
	Lignite-based generator gas	123.99
	Lignite-based carbonisation gas	118.439
	Lignite-based water gas	130.972
Natural gas and	Natural gas L	55.4-559
associated gas	Natural gas H	55.2-57.3
	Diesel fuel	74
	Refinery gas	54.6-65.4
	LP gas	64.0-66.6
	light fuel oil	74
	petroleum coke	94.6-95.7
	heavy fuel oil	79.0-81.3
	Coke oven gas	40.3-41.8
	blast furnace gas	254.9-272
	basic oxygen furnace gas	188.6-195.1

Table 9: Emission factors per fuel type. Adapted from [73]

Table 10: Metal industry CO₂ sources

Product	Process	Type of metal		Sub-process	CO2 source	Combustion	CO2 %	Reference	Emission intensity (tCO2/tprod)	Reference
Iron	BOF crude	Liquid raw	Raw material	Coke	Fuel used for under-	Yes	12-25	[60], [50]	0.482-0.5	[54], [44]
and	steel	iron/pig		production	firing (COG/BFG)					
steel		iron		Iron ore	Fuel used&recycled	Yes and No	5-10	[60], [50]	0.2-0.25	[47], [44]
production			Conventional	Sintering	material Fuel used in	Voc and No	12 20		1 55	[4.4]
			route	Blast furnace	stoves&coke	res and no	12-30	[30], [43], [60], [47], [50]	1.55	[44]
			Toute	TGRBF	Fuel used in	Yes and No	35%	[45]	1.55	[44]
			Smelting	Tencored	Fuel used	Yes	25- 35%	[45]	1.55-1.79	[44], [43]
			iron (Corex)	Hismelt	Fuel used	Yes	25- 35%	[45]	1.55-1.57	[44], [74]
		BOF crude steel		Basic oxygen furnace	Fuel used&liquid iron	Yes and No	10-40	[60], [36]	0.11	[47]
	EAF crude	Direct		DRI iron					0.65	[43]
	steel	reduction		(Midrex)						
		iron		DRI iron					0.53	[43]
				(Hysla)						
		EAF crude		Electric arc	Fuel used electrodes scraps	Yes and No			0.058-0.08	[43], [47]
	Casting	Crude	Steel	Hot rolled	Fuel used	Yes			0.1	[44]
	finishing	processing	steps	Cold rolled	Fuel used	Yes			0.05	[44]
				Coated steel	Fuel used	Yes			0.05	[44]
Aluminium production	Aluminium production	Alumina to aluminium		Hall-Heroult process	Aluminium oxide reduction to Al (Modified from 1% to 4%)	No	4	[52], [51]		

Table 11: Stone and clay industry CO₂ sources

Process	CO2 source	Combustion	Fuel	CO2 content %	Reference	Emission intensity (tCO ₂ /trod)	Reference
Cement production	Limestone calcination and fuel used	Yes and No		14-40	[36], [57], [60]	1.1	[66]
Ceramics production							
Brick production	Fuel used	Yes		3-5	[36]		
Glass production	Fuel used and electricity	Yes	Natural gas, fuel oil	35-45	[36]		
Lime production	Limestone calcination and fuel used	Yes and No		20-32	[36], [66], [60], [50]	1.6	[66]

Table 12: Chemical and petrochemical industry CO₂ sources

Industry		Process	Sub-process	Sub-process	CO2 source	Combustion	Fuel	CO ₂ content %	Reference	Emission intensity	Reference
Major refinery CO2 emitting	Combustion related	Process heaters			Fuel used	Yes	Gas	3-9	[52], [63], [60]		
processes							011	7-12			
		Furnaces			Fuel used	Yes	oil and gas	13	[61]		
		Boilers			Fuel used	Yes	oil and gas	13	[61]		
		Combustion turbines			Fuel used	Yes		3	[61]		
		Asphalt blowing stills			Blowing still flue gas	Yes					
		Flares			Fuel used	Yes		13	[61]		
Minor refinery CO2 emitting	Non combustion	Fluid catalytic cracking			Coke combustion	No		8-20	[61], [52], [69], [60], [50]		
processes	related	Catalytic reforming units			Coke burn-off	No					
		Sulphur recovery vents			Amine scrubbers (H2S) removal	No					
		(H2S removal) Hydrogen plants	Syngas	CO oxidation to	Chem. Absorp./Press. swing	No		40-100	[69], [61]	8.62	[67]
		Coke	generation	602	Coke calcination(pyrolysis)	No					
Natural gas processing		Gas sweetening		Removal of CO2	Amine or membrane separation	No		2-99	[65], [63],		
Hydrogen	Steam reforming	Natural gas/methane	Syngas generation	CO oxidation to CO2	Chem. Absorp./Press. swing adsorp.	No		15-100	[69], [63], [61]	8.62	[67]
	Ū	Naphtha	Syngas generation	CO oxidation to CO3	Chem. Absorp./Press. swing adsorp.	No		15-20	[63]	10.5	[67]
	Gasification of solid fuel	Coal	Partial oxidation	Syngas generation		No		15-20	[63]		
		Petroleum coke		Syngas generation		No		15-20	[63]		
Ammonia production	Haber-Bosch	Hydrogen production	Steam reforming	Syngas generation		No		18-99	[63],	1.15-1.5	[65], [69]
			Excess air reforming	Syngas generation		No		18-99		1.15-1.5	
			Partial oxidation	Syngas generation		No		18-99		1.5-2.6	
Synthetic fuel		Syngas production		coal gasification		No					
Ethylene oxide				CO2 as a by- product	Physical sorbent separation	No		8	[63]		

Table 13: Sources with limited information and emissions

Product	Process	CO ₂ source	CO ₂ content %	Reference	Emission intensity (tCO ₂ /tprod)	
Carbon black			2.4-4.9	[66]	1.9-5.25	[66]
Synthetic rubber					2-3.5	[66]
Waste disposal	Waste incineration		10-12			
	Waste pyrolysis					
	Thermal gas incineration					
Biogas production		During purification	99	[13]		
Bioethanol		Fermentation	100,100	[13],[75]	0.82 kg/L	[75]
Beer and wine production		Fermentation	100	[13]		

Table 14: Stream purities and emission intensities conclusions for all CO₂ emiting processes

	CO2 %	Reference	Emission intensity	Reference
Coal-fired furnace	12-14 vol	[63]	95.913	[73]
Wood-fired furnace	No CO ₂ reported	[36], [63]		
Oil-Fired furnace	11-15	[36], [63]		
Natural gas-fired furnace	7-11	[36], [63]	55.2-55.9	[73]
Industrial gas-fired furnace	9-11	[36]		
Blast furnace gas-fired furnace	9-11	[36]	254.9-272	[73]
Stoker fired coal combustion	15-18	[36]	95.913	[73]
Cyclone coal combustion	15-18	[36]	95.913	[73]
Pulverised coal combustion	15-18	[36]	95.913	[73]
Fluidised bed combustion	15-18	[36]	95.913	[73]
Natural gas combined cycle (NGCC)			55.2-55.9	[73]
Integrated gasification combined cycle (IGCC) coal	12-14 vol	[63]	56.62	[73]
Integrated gasification combined cycle (IGCC) oil				
Natural gas-fired gas turbine (CHP)	10	[36]	55.2-55.9	[73]
Landfill gas-fired gas turbine (CHP)	13	[36]		
Oil-fired internal combustion engine (CHP)	7-8	[36]		
Natural gas-fired gas turbine	3-11	[36], [63]	55.2-55.9	[73]
Oil-fired gas turbine	3-11	[36], [63]		
Coke production	12-25	[60]	0.482-0.5	[54], [44]
Iron ore sintering	5-10	[60]	0.2-0.25	EPA, 2012, [44]
Blast furnace	12-30	[36], [43], [60], [47]	1.55	[44]
TGRBF			1.55	[44]
Tencored			1.55-1.79	[44], [43]
Hismelt			1.55-1.57	[44], IEA, 2011
Basic oxygen furnace	10-40	[60], [36]	0.11	EPA, 2012
DRI iron (Midrex)			0.65	[43]
DRI iron (Hysla)			0.53	[43]
Electric arc furnace			0.058-0.08	[43], EPA, 2012
Hot rolled steel			0.1	[44]
Cold rolled			0.05	[44]
Coated steel			0.05	[44]
Hall-Heroult process	4	[52], [51]	0.482-0.5	[54], [44]
Cement production	14-40	[36], [57], [60], [75]	0.83-1.1	[66], [75]
Ceramics production				
Brick production	3-5	[36]		
Glass production	35-45	[36]		
Lime production	20-32	[36], [66], [60]	1.6	[66]
Process heaters	3-9	[52], [63], [60]		

Process heaters	7-12			
Furnaces	13	[61]		
Boilers	13	[61]		
Combustion turbines	3	[61]		
Asphalt blowing stills				
Flares	13	[61]		
Fluid catalytic cracking	8-20	[61], [52], [69], [60]		
Catalytic reforming units				
Sulphur recovery vents (H2S removal)				
Hydrogen plants	40-100	[69], [61]	8.62	[67]
Coke calcining units				
Gas sweetening	2-99	[65], [63],		
Natural gas/methane	15-100	[69], [63], [61], [75]	8.62	[67]
Naphtha	15-20	[63]	10.5	[67]
Coal	15-20	[63]		
Petroleum coke	15-20	[63]		
	18-99	[63]	1.15-1.5	[65],
Steam reforming		[05],		[69]
Excess air reforming	18-99		1.15-1.5	[65],
Partial oxidation	18-99		1.5-2.6	[69]
Syngas production	18-99		1.5-2.6	
Ethylene oxide	8	[63]		
Carbon black	2.4-4.9	[66]	1.9-5.25	[66]
Synthetic rubber			2-3.5	[66]
Waste incineration	10-12			
Waste pyrolysis				
Thermal gas incineration				
Biogas production	99	[13]		
Bioethanol	100	([13] [75]	0.82 kg/L	[75]
Beer and wine production	100	[13]		

3.7 Chapter 3 Conclusions

The literature review about the industrial sources of CO₂ was performed to create a list of the existing CO₂ sources and understand the characteristics and the processes involved in the generation of CO₂, which could be potentially used in an automated mapping and matching procedure. CO₂ sources were grouped by industry and then to various sub-processes depending on the process or route towards the desired product. Most CO₂ sources involve the combustion of fossil fuels, such as coal, wood, oil, natural gas, industrial gas, blast furnace gas, landfill gas and coke oven gas. These types of sources result in gaseous product stream containing mainly N₂ (from air used in combustion), CO₂ and water (products of combustion) and some other minor impurities. The characteristics of the output streams of each process vary based on the nature of the fuel used, the process where it was used giving gaseous streams of varying temperatures, pressures, CO₂ content and impurities. Some CO₂ sources do not involve combustion of fossil fuels but rather the production of CO₂ as part of a process like the generation and then oxidation of syngas to produce CO₂/H₂ streams or fermentation, gas sweetening and biogas purification that result in pure CO₂ streams. The rest of the sources involve both the combustion of fossil fuels and production of a CO₂ stream like iron ore sintering, coke calcination, lime calcination and most iron production routes. Such processes produce individual output streams, one coming from fuel combustion and the other coming from the process generating CO2. This means that CO2 industrial sources can be grouped into three categories based on their output streams, CO_2/N_2 , CO_2/H_2 and pure CO_2 as a by-product.

Although the literature review gathered the most important information that will help with the optimisation of source/capture technology matching and source/receiver matching, it was not possible to gather any data regarding important parameters of such streams such as pressure and temperature. The importance of these parameters is discussed in the following chapter that deals with the question of how to capture CO_2 .

Chapter 4: How to capture CO₂

4.1 Introduction

Carbon dioxide capture technologies aim to separate carbon dioxide from CO₂ industrial sources. As detailed in the previous section there are many industrial CO₂ sources with different characteristics and therefore a variety of CO₂ capture technologies exist to enable capture from every source. Literature classifies carbon dioxide capture technologies based on when and how combustion takes place. The categories are:

(a) Pre-combustion

Carbon dioxide capture by pre-combustion processes involves the separation of CO_2 from synthesis gas (syngas, mixture of CO/H_2) streams that have been treated to CO_2/H_2 mixtures. The separation takes place before combustion (of hydrogen and production of power) occurs, hence "pre" [57], [76], [77], [78], [79]. The characteristics of typical streams that utilise pre-combustion are high pressures between 200 and 600 psi, mainly consisting of H₂, clean from pollutants and CO_2 content between 15-40% [76], [79].

(b) Post-combustion

Carbon dioxide capture by post-combustion refers to the process of capturing CO₂ from gaseous mixtures (flue gas) produced by fossil fuel combustion using air. This group of capture processes is referred to as "post" because CO₂ is captured after the combustion of fuels, hence post [8], [57], [76], [77], [79]. The characteristics of typical flue gases that utilise post-combustion are low pressures around atmospheric, high temperature around 47-180°C, NO_x, SO_x and particulate matter with a CO₂ content between 3 and 33% [76], [77], [79]. The oxygen source for combustion is air.

(c) Oxy-fuel combustion

Carbon dioxide separation by oxy-fuel combustion is the process of capturing CO₂ from gaseous mixtures (flue gas) produced by fossil fuel combustion in pure oxygen that was separated from air. The term "oxy" comes from oxygen, which is used during combustion to produce a flue gas

stream consisting mainly of CO₂, water and traces of NO_x, SO_x and particulate matter. The only required purification in this case is the removal of impurities with the use of electrostatic precipitator units (ESP), flue gas desulphurisation units (FGD) that remove particulate matter and drying and compression processes to remove water content and prepare CO₂ for transportation conditions [8], [57], [76], [77], [78], [79]. The oxygen source for combustion is pure oxygen separated from air in an air separation unit.

4.2 Origins of CO₂ capture

Carbon dioxide capture was first used in natural gas processing and captured CO₂ was used in commercial scale for enhanced oil recovery which was profitable for almost the past 40 years [80]. Natural gas can be found in three types of wells, oil wells, gas wells, and condensate wells. It consists mainly of methane and exists in different forms depending on the source, dissolved or free and always with the associated hydrocarbons and impurities at various mixtures. The possible associated hydrocarbons like ethane, propane, butane, i-butane and pentanes plus. The possible impurities are water vapour, helium, nitrogen, mercaptans (R-SH), carbonyl sulphide (COS), carbon disulphide and the most important ones, hydrogen sulphide (H₂S) and carbon dioxide (CO₂) [81], [82]. There are two variants of raw natural gas, sour gas containing hydrogen sulphide and other sulphide compounds, and sweet gas, raw natural gas with only CO₂.

Natural gas needs to be processed to meet the stringent gas pipeline specifications and this happens in four major steps, oil and condensate removal, water removal, separation of associated hydrocarbons and sulphur and carbon dioxide removal. In the first step oil is separated from natural gas using gravity separators or low temperature separators. Water is also removed to avoid the formation of hydrates which results in processing equipment and pipeline damage. It is removed using glycol dehydration or solid-desiccant dehydration, which are both techniques used for water removal in captured CO₂ dehydration processes, further discussed in Chapter 6. The next step separates the associated hydrocarbons, because they are valuable by-products that can be sold at a higher price if sold separately and not left in the natural gas mixture. The heavier hydrocarbons (not ethane) are separated by absorption and, if it is economical, ethane is separated using cryogenic processes. Each hydrocarbon is recovered to its base component using fractionation at different boiling points. Finally, hydrogen sulphide is removed because it causes corrosion to processing equipment and gas pipelines. CO₂ is also removed because it has no calorific value, which improves the quality of natural gas and minimises environmental impact. Sulphur compounds are removed because they produce sulphur oxides during combustion, which pollute the environment and can cause health related problems [81], [82].

Hydrogen sulphide, sulphur compounds and carbon dioxide are all removed in the same process. Not all hydrogen sulphide removal processes remove CO₂, but all CO₂ removal processes remove hydrogen sulphide and sulphur compounds. This is illustrated by Table 15 which lists the gas removal processes for natural gas [81]. The processes used for natural gas processing that can separate CO₂ are sorted by literature according to the solvent (chemical solvents, physical solvents, specialty solvents) and separation principle (distillation and gas permeation). Chemical solvents used for the removal of CO₂ are monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), methylediethanolamine (MDEA) and sterically hindered amines. Physical solvents include propylene carbonate, fluor solvent, dimethyl ether of polyethylene glycol (DEPG), rectisol process which uses methanol, n-mehtyl-2pyrrolidone (NMP) and selexol. Distillation can have two, three or four stage column systems and gas permeation includes only membranes. There is only one specialty solvent that is used for carbon dioxide capture, sulfinol [81], [82]. The processes mentioned are discussed in more detail in the following sections because they are the same processes used for CO₂ capture. A method is being used by the natural gas processing industry to make quick estimates as to which

process is best suited and most economical in each case based on the conditions of the natural gas in the well [81]. This method involves a selection procedure, where the process conditions must be first determined. The conditions required are the temperature, pressure and flowrate of CO₂ as well as its inlet stream concentration and desired concentration in the outlet stream. Then its inlet and outlet partial pressures can be estimated.

Table 15: Separation categories and processes for the Natural gas processing industry

Category	Process
Chemical solvent	MEA, DEA, DIPA, MDEA and sterically hindered amines.
Physical solvents	Propylene carbonate, fluor solvent, DEPG, rectisol, NMP and selexol.
Distillation	Two, three or four stage column
Gas permeation	Membranes
Specialty solvent	Sulfinol

Finally, using the graph in Figure 10 and the estimated inlet and outlet partial pressures the optimal process on the given set of conditions can be selected.

Table 16 can be very helpful in making quick judgements for the processes. It can be observed that amines offer the lowest CO₂ concentrations for low concentration input streams and physical solvents with amines offer the lowest concentrations for high concentration input streams. Gas

permeation offers low concentration for both high and low concentration input streams. Physical solvents work best at moderate to high input concentration streams but do not offer as low concentrations as gas permeation and amines



Figure 10: Natural gas processes for gas removal [81].

Process			Ga	ises rem	oved	
		CO ₂	H_2S	RHS	COS	CS ₂
Solid bed	Iron sponge		\boxtimes			
	Sulfa-treat		\boxtimes			
	Zinc oxide		\boxtimes			
	Molecular sieves	\boxtimes	\boxtimes	\boxtimes	\boxtimes	\boxtimes
Chemical solvents	MEA (monoethanolamine)	\boxtimes	\boxtimes		\boxtimes	\boxtimes
	DEA (mythylDiethanolAmine)	\boxtimes	\boxtimes		\boxtimes	\boxtimes
	MDEA (MethylDiethanolAmine)		\boxtimes			
	DGA (DiGlycolAmine)	\boxtimes	\boxtimes		\boxtimes	\boxtimes
	DIPA (DilsoPropanolAmine)	\bowtie	\boxtimes		\boxtimes	
	Hot Potassium Carbonate	\boxtimes	\boxtimes		\boxtimes	\boxtimes
Physical Solvents	Fluor solvent	\boxtimes	\boxtimes	\boxtimes	\boxtimes	\boxtimes
	Shell Sulfinol	\bowtie	\boxtimes	\boxtimes	\boxtimes	\boxtimes
	Selexol	\bowtie	\boxtimes	\boxtimes	\boxtimes	\boxtimes
	Rectisol		\boxtimes			
Direct Conversion of	Claus		\boxtimes			
H ₂ S to sulfur	LO-CAT		\boxtimes			
	SulFerox		\boxtimes			
	Stretford		\boxtimes			
	Sulfa-Check		\boxtimes			
	NASH		\boxtimes			
	Gas Permeation	\boxtimes	\boxtimes			

Table 16: Table for the selection of carbon dioxide removal process. Adapted from: [81]

The method used by the natural gas industry for selecting the best suited and most economical separation process in each case, based on the conditions of the natural gas in the well, can be used as a guide to develop a similar selection process for each CO₂ emitting source, based on quick estimates for the optimal carbon dioxide capture technology selection. This was the original aim of the literature review on carbon dioxide capture technologies. However, this was not possible due to the limited amount of available information compared to the natural gas processing industry. Thus, the literature review, presented in the following sections, has classified and characterised the carbon dioxide capture technology can reach and what is its technology readiness level (TRL). The outcomes of the literature review are later used to develop a method to guide the matching of sources to a compatible capture technology, which is the original contribution of this chapter and is illustrated in Table 36. Combining this information with factors such as purity, TRL and later on (in Chapter 5), capture cost, can lead to the selection of the optimal carbon dioxide capture technology for each case.

4.3 CO₂ capture technologies

The literature review showed that there is a large number of carbon dioxide capture technologies, which were classified by literature as pre-combustion, post-combustion, oxy-fuel combustion and chemical looping. Presenting the capture technologies in this manner aids in the description of how oxygen is provided to a combustion process. Thambimuthu et al. [57] and Spigarelli & Kawatra [76] state that carbon dioxide sources can be grouped into two output stream types CO₂/N₂ and CO₂/H₂, which is in agreement with the literature review on CO₂ industrial sources, but it only applies to power related sources and excludes non-power related sources. This renders this classification non-inclusive. The literature review also showed that CO₂ capture technologies use various separation principles, such as absorption, adsorption, cryogenics, membranes, combustion in pure oxygen, hybrid processes and novel technologies.

The following section classifies CO₂ capture technologies by the separation principle and not by how CO₂ is provided to the process. Capture technologies are classified in such way to demonstrate how each capture technology works and what options are available. Separation principles are broken down to groups of solvents or materials depending on the separation principle and then to sub-groups to list all the available options for solvents or materials. This allows to make observations about the compatibility of capture technologies to sources, which could not be possible without using

the proposed classification and instead using the classification proposed by literature as pre, post and oxy.

4.3.1 Absorption

Carbon dioxide capture by absorption takes place in an absorption column where the gas stream comes into contact with the liquid stream containing the chemical or physical solvent. The solvent is selective towards CO_2 and during their contact it is absorbed to the solvent via physical or chemical absorption. After CO_2 has been removed from the gas mixture the solvent regeneration process follows to release the captured CO_2 and recycle the solvent.

Chemical solvents

Absorption by chemical solvents refers to the process where a gas is separated from a gas mixture stream with the use of a chemical solvent (liquid absorbent). The chemical solvent is selective towards CO₂ and absorbs CO₂ via acid-base neutralisation reactions that take place at a certain kinetic rate and at certain capacity, which are unique characteristics of each different solvent. Chemical solvents should also have negligible vapour pressure and high chemical and thermal stabilities to be suitable for regeneration. When CO₂ is absorbed by the solvent, it passes through a heat exchanger to increase its temperature and then through a stripper where is contacted with steam, causing CO₂ to desorb. The regenerated solvent is recycled for more CO₂ separation and CO₂ is regenerated by cooling the steam/CO₂ mixture to water and gaseous CO₂. The captured CO₂ is of high purity and it can then be compressed to liquid phase [50], [76], [77], [78], [79], [83].

Several chemical solvents have been developed for chemical absorption and can be grouped into two generations [50]:

1st generation: Monoethanolamine (MEA), MDEA, KS-1

2nd generation: Aminoethylethanolamine (AEEA), Tetraethylenepentamine (TEPA), Diethanolamine (DEA), Triethanolamine (TEA), Diisopropanolamine (DIPA), Polyethyleneimine (PEI), 3aminopropyltriethoxysilane (APTES), Diethyltriamine (DETA), Diglycolamine (DGA), Amino acids, piperazine, 2-amino-2-methyl-1,3,propanediol (AMPD), 2-amino-2-methylpropanol (AMP)

Physical solvents

Absorption by physical solvents is carried out similarly to absorption with chemical solvents. In this case the physical solvent (liquid absorbent) is selective towards CO_2 by physical methods like solubility, surface area of the interface and operating conditions and not by chemical reactions. This means that separation of CO_2 by absorption with physical solvents favours high CO_2 partial pressures

and low temperatures (as it follows Henry's law) [76]. The solvent can be regenerated by two methods and the most appropriate one is selected based on the characteristics of the gas stream to be separated. The first is method is using flash desorption by reducing the pressure (flashing/degassing) of the pressurised CO_2 loaded solvent and the second is by stripping which includes regeneration by pressure reduction and further regeneration of solvent in a stripper using N₂ or heating [50], [57], [76], [84]. Table 17 lists the CO_2 capture technology options using absorption.

Absorption type	Solvents	Solvent names		
Chemical solvents	Alkanolamines	MEA, AMP, DEA, MDEA, AEEA, TEPA, TEA, DIPA, DETA, DGA, KS-1		
	Amino acids	Glycine, alanine, dimethyl glycine, diethyl glycine, sterically hindered amino acids		
	Ammonia	-		
	Aqueous piperazine	-		
	Polyethyleneimine	-		
	APTES	-		
	AMPD	-		
	AMP	-		
Physical solvents	DEPG	Selexol and Coastal AGR processes		
	NMP	Purisol process		
	Methanol	Rectisol process		
	Propylene	Fluor process		
	carbonate			
	Glycol	-		
	Glycol carbonate	-		

Table 17: CO_2 capture technologies using absorption

4.3.2 Adsorption

Chemical adsorbents

Separation of CO_2 by chemical adsorption (chemisorption) refers to the process of CO_2 reacting with the exposed surface of a solid (e.g. metal oxides, alkali metal salts, hydrotalcites, double salts) via a reversible chemical reaction. For example one mole of CO_2 will react with one mole of CaO at 650°C to produce $CaCO_3$ and then reverse the reaction at 850°C in a carbonation reactor to regenerate CaO and produce a concentrated stream of CO_2 [76], [77], [78], [79].

Physical adsorbents

The process of CO_2 separation by physical adsorption (physisorption) is similar to chemical adsorption but no chemical reactions are involved. A solid that is selective towards CO_2 is used, which adsorbs CO_2 to its surface area by physical interactions. Desorption and regeneration of adsorbent is required as the next step and is achieved by pressure swing or temperature swing [57], [76], [77].

Adsorbent modification

The premise of CO₂ separation by adsorbent modification is that the surface area of physical adsorbents can be modified to improve their characteristics towards CO₂ adsorption. By adding basic groups (e.g., amine groups, metal oxides) on physical adsorbents, CO₂ selectivity and capacity are improved. More examples are summarised in Table 18 [77].

Adsorption type	Adsorbents	Adsorbent names
Chemical adsorbents	Metal oxides	CaO, MgO
	Metal salts from alkali metals	Lithium silicate, lithium zirconate, magnesium oxide, calcium oxide
	Hydrotalcites and double salts	-
Physical	Coal	-
adsorbents	Activated carbon	-
	Zeolites	-
	Zeolitic imidazolate frameworks	-
	Graphite nanoplates	-
	Functionalized graphite nanoplates	-
	Molecular sieves	-
	Carbon nanotubes	-
	Graphite nanoplatelets	-
	Pressure vacuum swing adsorption	-
	Metal organic frameworks	-
	MCM-41	-
	Layered double hydroxides	
Adsorbent	Addition of basic groups on physical adsorbents	-
modification	Molecular baskets	-
	Nitrogen rich carbon	-
	Amine modified layered double hydroxides	-
	Porous carbons	-
	Adsorbents based on the central composite design	-

Table 18: CO₂ capture technologies using adsorption

Adsorbent regeneration process

Adsorbent regeneration is an integrated part of CO₂ separation by adsorption as it is the step that results in purified CO₂. Regeneration can be achieved in a single bed adsorption unit via five different adsorbent regeneration processes [57], [76], [77], [78]:

- (i) Pressure swing adsorption (PSA), pressure is reduced for desorption to take place
- (ii) Temperature swing adsorption (TSA), temperature is increased at constant pressure
- (iii) Vacuum swing adsorption (VSA), desorption takes place at pressures below atmospheric
- (iv) Electric swing adsorption (ESA), the solid adsorbent is heated via the joule effect to achieve desorption

(v) Vacuum and temperature swing adsorption (VTSA), a combination of vacuum and temperature swing adsorption

4.3.3 Cryogenics

Cryogenic distillation is a separation process that takes place in a distillation column at very low temperatures and high pressures to separate gases from gaseous mixtures based on their boiling point. Cryogenic conditions achieve separation by a series of compression, cooling and expansion steps that directly produce liquid CO₂ without the use of any reagents [79], [83]. Various routes have been proposed for CO₂ separation by cryogenic distillation. One involves the de-sublimation of CO₂ on the surface of heat exchanger fins and using high pressures to recover it, and an alternative one utilises dynamically operated packed beds to recover CO₂ from the packing material via de-sublimation [76], [77]. Another cryogenic separation approach involves a cryogenic liquefaction and separation system consisting of a two-stage compression, two-state refrigeration and a two-stage separation system. More novel approaches include other technologies like sterling coolers and molten carbonate fuel cells (MCFC) [77].

4.3.4 Membrane separation

Carbon dioxide separation using membranes is a simple, clean continuous process with compact, easy to operate and scale up equipment. Membrane separation works by filtering out unwanted components and letting CO₂ pass based on the membrane's permeability and selectivity. Permeability and selectivity describe the membrane's performance, which depends on membrane material and gas stream characteristics (velocity, molecular weight, kinetic diameter). Altering temperature, pressure and polymer concentration during membrane synthesis allows for some control over permeability and selectivity. The process is driven by pressure and therefore is not suitable for gas streams with low pressures and low CO₂ concentrations [57], [76], [77], [79], [83].

Inorganic membranes

Inorganic membranes can be classified into two categories, porous and non-porous membranes. Porous membrane systems consist of a top thin layer that acts as the membrane. The membrane can be made of zeolite, silicon carbide, carbon glass, zirconia, titania or alumina. The top thin layer is supported on different substrates such as α -alumina, γ -alumina, zirconia zeolite or porous stainless steel, which provide mechanical strength and offer minimal mass transfer resistance [76], [77]. Dense inorganic membranes consist of a thin layer of metallic membrane such as palladium and its alloys or

solid electrolytes such as zirconia. Other types of dense inorganic membranes are liquid-immobilised membranes where the membrane is filled with a permselective liquid to block certain compounds and the recent attempts to develop dense molten carbonate selective membranes that allow CO₂ separation at high temperatures [77].

Polymeric/organic membranes

Polymeric membranes can be grouped into glassy and rubbery and operate via the solution-diffusion mechanism, achieved by using a non-porous film (listed in Table 19 under polymeric membranes) [77]. Mixed matrix membranes incorporate polymeric membranes and nano-sized inorganic particles to enhance the physical, thermal and mechanical characteristics of polymeric membranes and achieve high performance CO_2 separation (ionic liquid membranes consisting of 20% DEA immobilised in 25.4 µm microporous polypropylene supports) [77]. Hollow fibre membranes and membrane contractor systems are also grouped under polymeric and organic membranes.

Table 19: CO₂ capture technologies using membranes

Membrane category	Membrane type	Membrane name
Inorganic membranes	Porous	Zeolite, silicon carbide, carbon, glass, zirconia, titania, alumina
	Dense	Palladium and its alloys, solid electrolytes
Polymeric/organic	Glassy or rubbery	Polyacetylenes, polyaniine, polyarylene ethers, polyarylates, polycarbonates,
membranes		polyetherimides, polyethylene oxide, polyimides, polyphenylene oxides,
		polypyrroles, polysulfones, amino groups
Mixed matrix	Mixing membrane	Ionic liquid membrane
membranes	material	
Hollow fibre	Asymmetric	Polyvinylidene difluoride
membranes	hollow fibre	
	membranes	
Membrane	-	-
contractor systems		

4.3.5 Combustion in pure oxygen

Oxy-fuel combustion

Oxy-fuel combustion replaces combustion with air (80% nitrogen) and combusts fossil fuels with pure oxygen (95-97%) instead to produce a stream containing oxygen, nitrogen, argon, NO_x, SO₂ and water, as impurities in varying concentrations, depending on the fuel and combustion process used, and CO₂ content of 95-99%. The process takes place in three steps consisting of an air separation unit, combustion and a CO₂ purification unit [38], [85], [86], [87], [88]. The technology is discussed in more detail in the following section, 4.4.1.

Chemical looping

Chemical looping combustion

CO₂ capture by chemical looping combustion involves the separation of CO₂ from gaseous mixtures (flue gas), produced by fossil fuel combustion achieved with oxygen provided by an oxygen carrier (metal oxide). The process takes place by oxidising an oxygen carrier (metal) in an air reactor using air and then reducing the oxygen carrier in a fuel reactor to provide oxygen for fuel combustion. The products of combustion in the fuel reactor are CO₂, H₂O and lower oxide and/or metal. Water is removed by condensation and CO₂ is liquefied through a series of compressions. The metal oxide is recycled back to the air reactor to be re-oxidised [57], [76], [77], [79].

fuel + metal oxide $\rightarrow CO_2 + H_2O + lower oxide(and, or metal)$ (20)

lower oxide(and, or metal) + $0_2 \rightarrow$ metal oxide (21)

Chemical looping reforming

Chemical looping reforming uses modified versions of the concept of chemical looping combustion on processes involving the generation of hydrogen and capture of CO_2 from natural gas. This created two new processes called chemical looping auto-thermal reforming (CLR(a)) and chemical looping steam reforming (CLR(s)). The CLR(a) process uses the same cycle as chemical looping combustion to achieve partial oxidation of fuel resulting in the production of H₂ and CO instead of CO₂ and water. The CLR(s) process uses a waste stream of H₂/CO₂ as an energy source for conventional steam reforming [89]. Table 20 lists the processes for combustion in pure oxygen with their respective source of oxygen.

Table 20: Capture technologies using pure oxygen

Process type	Oxygen source
Oxy-fuel combustion	Cryogenic distillation
Chemical looping combustion	Metal oxygen carrier
Chemical looping reforming	Metal oxygen carrier

4.3.6 Novel technologies

Novel CO₂ capture technologies include processes such as molten carbonate with almost 100% selectivity towards CO₂, aqueous alkaline fuel cells that can separate CO₂ both from air and flue gases, electrochemical pumps, which use carbonate and proton conductors, and chemical looping approaches [77].

Hybrid processes

Carbon dioxide separation by hybrid processes involves the integration of two or more of the more conventional standalone technologies mentioned before in this section. Hybrid carbon dioxide separation processes are developed to offer a potential alternative that may be superior to standalone processes by overcoming their disadvantages. These hybrid technologies can be grouped to absorption based, adsorption based, membrane based and cryogenic based. The most suitable hybrid technology can be identified by assessing the concentration, temperature and pressure of the flue gas and the desired specifications of the product [90]. A list of various hybrid technologies presented by [90] follows in Table 21.

Unfortunately, it was not possible to collect information on the operating characteristics of each individual technology such as pressure, temperature, impurity incompatibility and CO₂ concentration because they are rarely reported.

Main separation principle	Process name	
Absorption based	Membrane contactor	Membrane contactor stripper
		Absorber-membrane contactor
		Membrane contactor(absorber)-
		membrane contactor (stripper)
	Absorption-adsorption	-
	Absorption membrane	Series arrangement
		Parallel arrangement
Adsorption based	Adsorption-catalysis	-
	Adsorption-catalysis-membrane	-
	Adsorption-cryogenic	-
	Adsorption-membrane	-
	Adsorption-hydrate	-
Membrane based	Membrane-cryogenic	Liquid CO ₂
		Solid CO ₂
	Membrane-absorption	-
Low temperature based	Cryogenic-hydrate	-
	Low temperature-membrane-	-
	cryogenic	
	Low temperature-absorption	-

Table 21: Hybrid capture technologies

4.3.7 Technology readiness level of capture technologies

Table 22 lists the technology readiness level (TRL) of the most popular capture technologies.

Separation principle	Capture technology	TRL
Chemical absorption	Amines 1 st generation	9
	Amines 2 nd generation	6-7
	KS-1, ammonia, K ₂ SO ₃	6-7
Physical absorption	Rectisol, selexol, purisol, fluor (propylene carbonate)	9
Physical adsorption	Adsorber beds	5
	Temperature, pressure, vacuum swing adsorption	5
Cryogenics		6-9
Oxy-fuel combustion	Power generation	7-8
	Industrial applications	6-7
Calcium looping		6-7
Membranes	Organic/inorganic (natural gas, syngas, high purity CO ₂)	8-9
	Organic/inorganic (low purity CO ₂)	5-6

Table 22: Technology readiness level of CO₂ capture technologies. Adapted from: [50]

4.4 Most popular carbon capture processes

This section presents the technological characteristics of the most popular capture technologies along with data from industry that show technological compatibility with certain CO₂ emitting sources. The technological compatibility is presented in a table to be used: (a) for quick selection estimates of compatible capture technologies with certain sources and (b) for the selection of the optimal capture technology, along with the CO₂ purity, TRL of capture technologies and capture cost (presented in chapter 5), based on compatibility with source, purity constraints by the receiver, and capture cost based on CO₂ demand by the receiver.

$4.4.1 \text{ CO}_2/N_2 \text{ streams}$

The most popular separation technology for what the literature has termed as post-combustion capture (CO_2/N_2 streams) is separation by absorption using chemical solvents and more commonly MEA. Another alternative for post-combustion capture is oxy-fuel combustion. The other capture technologies and processes have not been applied or studied to the degree that these technologies have, and this is highlighted by the number of studies and amount of information available in literature.

General process using chemical absorption processes

Before the CO₂ capture process, the stream that contains CO₂ goes through a pre-treatment process to remove impurities, like particulate matter, SO_x and NO_x, which can vary according to the CO₂ source. Figure 11 shows a typical block flow diagram of a generic chemical absorption process for carbon capture [91]. On the first part of the process (absorber), the stream containing CO_2 , illustrated by flue gas (in this case a power related source), enters the bottom of the absorption column, where it is brought into contact with the chemical solvent (usually MEA) [91]. CO₂ is absorbed to the chemical solvent (lean loading solution) as described in section 4.3.1. At this point CO₂ has been separated from the flue gas stream and is absorbed on the lean-loading solution (MEA) which is now the rich solution. The rich solution has to go through a heat exchanger to increase its temperature and then to the second part of the process, the top of a stripper to separate CO_2 from MEA, and regenerate MEA to be pumped to the top of the absorber and be used again to separate more CO_2 . The reboiler of the stripper produces steam that flows upwards and comes in contact with the rich MEA solution in a co-current flow fashion and releases CO₂ by breaking the bonds between CO₂ and MEA. Steam carries CO₂ with it to the top and to the condenser, where steam returns to the stripper as reflux and CO_2 with a typical purity of 99% exits the top of the stripper. Both absorber and stripper are fitted with trays or packing with either random or structured configuration to maximise contact. This type of process can control the amount of CO₂ captured from the flue gas stream and is most



Figure 11: Typical block flow diagram of a generic chemical absorption process [91]

commonly set to 90% for economic reasons, so that 90% of CO₂ ends up in the product stream, termed the CO₂ capture efficiency. Chemical absorption solvents technology are ideal for capturing CO₂ at low to moderate CO₂ content between 3 and 20% [76], [78], [79], [91], [92]. More details on the mechanism of chemical absorption using amines and other chemical solvents are available in [76] and [92].

Disadvantages of chemical absorption solvents

Although MEA and chemical absorption processes are the most commonly used technologies because of their effectiveness and performance, there is one major drawback, the high energy requirement and the associated high cost in the reboiler during solvent regeneration [91]. For example, when a chemical absorption capture system is installed at a power plant, the thermal efficiency of the power plant drops by 29.3 to 38.5% [78]. This issue has been addressed by i) modifying and improving the technology process, ii) optimising operational parameters and iii) development of new solvents [91]. The development of new solvents is straightforward, the modification of the process involves different blends of chemical solvents, but for the sake of exploring the MEA and chemical solvents technology process, in general, the optimisation of operational parameters will only be discussed in this section.

Three factors influence the energy requirements of the reboiler during solvent regeneration: the pressure of the reboiler, the CO₂ in the lean-loading solution and the concentration of MEA (chemical solvent) used [91]. The factors cannot be altered to a great extent to reduce the energy requirement considerably and are limited by the main goal, which is not to just capture CO₂, but to capture CO₂ at the desired specifications for transportation, which for pipelines are usually at least 95% purity and 110 bar. Various studies for the CO₂ in the lean-loading solution recommend different optimal values. The higher the MEA concentration the higher the CO₂ capacity of the solvent is, resulting in decreased solvent flowrate and lower energy requirements, but problems arise in process equipment erosion and solvent degradation [91]. Therefore, a concentration of 20-30% MEA is used with the remaining being water [92]. A higher reboiler pressure will reduce the energy requirements for the process, but it will increase the auxiliary power requirements to compensate for the higher pressure [91]. Table 23 lists the possible impurities in the output stream when amine or MEA capture technologies are used on various CO₂ emitting sources and

Table 24 lists the maximum obtained CO₂ purity when amine or MEA capture technologies are applied to various CO₂ emitting sources.

Component (ppmv)	MEA Refinery Stack	MEA Cement Plant	Cement Kiln	Coke Production	Lime Production
CO ₂ %(v/v)	99.6	99.8	99.0	99.4	99.52
N ₂ % (v/v)	0.29	0.0893	-	-	-
СО	1.2	1.2	1620	701	2000
Ar	11	11	-	-	-
H ₂ O	640	640	-	-	-
NO _x	2.5 (NO ₂)	0.86 (NO₃)	3330	16.90	1100
SO _x	1.3 (SO ₂)	<0.1 (SO ₂)	4410	3030	1800
CO	1.2	1.2	-	-	-
O ₂	35	35	-	-	-
CH ₄	-	-	-	206	-
Cl	0.41	0.41	65.7	26.8	-
Ash	-	5.7	-	-	-
Hg	-	0.00073	0.1	-	-
As	0.29	0.0029	-	-	-
Se	1.2	0.0088	-	-	-
VOC	-	-	-	96.9	-
ТОС	-	-	81	-	-

Table 23: Possible impurities from amine and MEA capture technologies applied to various CO₂ sources. Adapted from [93]

Table 24: Possible CO₂ purities from amine and MEA capture technologies applied to various CO₂ sources [93]

Capture technology	Real/simulation	CO ₂ Source	CO ₂ v/v %
Amine	Real	Pulverised Coal	99.8
MEA	Real	Pulverised Coal	99.7
MEA	Real	Refinery stack	99.6
MEA	Real	Cement plant	99.8
MEA	Real	Cement kiln	99
MEA	Real	Coke	99.4
		production	
MEA	Real	Lime production	99.52

Oxyfuel

As previously mentioned, oxy-fuel combustion replaces combustion with air with combustion in pure oxygen to achieve a cleaner flue gas that requires considerably less processing and preparation before transportation. The process takes place in three major steps, oxygen separation in the air separation unit (ASU), followed by combustion in the boiler and a series of processes that removes present impurities and compresses CO₂ to transportation conditions. The process is outlined in Figure 12, which represents a possible oxy-fuel combustion power plant with an air separation unit (ASU), selective catalytic reduction reactor (SCR), electrostatic precipitator (ESP) and flue gas desulphurisation unit (FGD) [76].





ASU

The air separation unit's function is to separate oxygen from air and can be achieved with the use of cryogenic distillation, pressure swing adsorption or membranes. The most common air separation technology is cryogenic distillation where oxygen is separated from nitrogen by liquifying air to achieve separation by boiling point in a distillation column and can produce oxygen of 95.5% purity [9], [77], [85], [86], [94], [95], [96]. Oxygen separation by membranes is achieved with the use of polymer membranes or ion transport membranes that offer high selectivity towards CO₂. However, to reach high purity CO₂ streams, the use of cascade membrane reactors is required or the application of hybrid processes by combining cryogenic distillation units or pressure swing adsorption [86]. For oxygen separation using pressure swing adsorption there is a limited amount of information.

Combustion

Combustion takes place in regular air-combustion boilers. Steam side temperatures and pressure capabilities are similar and fuels such as pulverised coal, oil, natural gas and biomass can be used [9], [85]. To transition from air combustion to pure oxygen combustion, 80% of the flue gas exiting the boiler must be recycled to increase the concentration of inert gases and to control combustion temperature, as the transition changes the concentration of inert gases (80% N₂ replaced with 80% CO₂), density and heat transfer. Recirculation of the flue gas also decreases significantly NO_x emissions [85], [86], [94], [95], [96], [97].

CPU

The CO₂ purification unit uses a series of processes, such as SCR, ESP, FGD, to control SO₂ and particulates, to avoid their accumulation in the boiler and CO₂ product stream. No control is usually required for NO_x as it is reduced by the flue gas recirculation unit [85], [86]. The CO₂ purification unit dries and compresses CO₂ to applicable standards. Initially CO₂ is dried by compression and cooling, where most of the water is removed. Further drying is required via absorption by hygroscopic liquids, reactive solids or adsorption by activated solid desiccant. Finally, condensation by pressurising CO₂ to intermediate pressure and cooling to -50° C removes volatile components by simply venting them off. Non-volatile impurities are separated by distillation to achieve the desired CO₂ purity [85], [86], [95], [96]. Table 25 shows the level of possible impurities present in oxy-fuel combustion capture technologies and

Table 26 lists the maximum CO₂ purity that can be achieved from various oxy-fuel capture technologies applied on different CO₂ emitting sources.

Component		Composition (mol%)	
	Raw flue gas	Standard drying and volatile removal	Air products process
CO ₂	71.5	95.8	96.3
N ₂	14.3	2.0	2.0
O ₂	5.9	1.1	1.1
Ar	2.3	0.6	0.6
SO ₂	0.4	0.5	-
NO	0.04	0.01	-
H ₂ O	5.6	0.0	-

Table 25: Possible stream composition from various oxy-fuel combustion capture processes. Adapted from: [86]

Table 26: CO_2 purities from various sources using oxy-fuel combustion

Capture technology	Real/simulation	CO ₂ Source	CO ₂ v/v %	Reference
Oxy fuel (double flashing)	Real	NG	96	[86]
Oxy fuel (double flashing)	Real	Coal	97	[86]
Oxy fuel (double flashing)	Real	PC	95.84	[93]
Oxy fuel (double flashing)	Real	PC	96.3	[93]
Oxy fuel (double flashing)	Real	PC	96.7	[93]
Oxy fuel (distillation)	Real	Coal	99	[86]
Oxy fuel (distillation))	Real	PC	99.94	[93]
Oxy fuel (distillation)	Real	PC	99.93	[93]
Oxy fuel (distillation))	Real	PC	>99.95	[93]
Oxy fuel (LINDE)	Real	PC	>99.9	[93]
Oxy fuel (air products)	Real	PC	>99.9	[93]
Oxy fuel (distillation)	Real	NG	99	[86]

$4.4.2 \text{ CO}_2/\text{H}_2 \text{ streams}$

The next two popular capture technologies, Selexol and Rectisol, are most frequently used for capture in IGCC plants, where syngas is converted to CO₂/H₂ streams and CO₂ is removed to produce energy by combusting H₂. This is illustrated by Figure 13. Because CO₂ capture is applied before combustion, these two technologies fall into the category of pre-combustion capture [76].



Figure 13: Block flow diagram for absorption by physical solvents [76].

As mentioned in Section 4.3.1, Selexol uses the solvent DEPG and Rectisol uses methanol, and both are physical solvents. Physical solvents rely on physical properties and the solubility of CO₂ in the solvent which increases at high partial pressures (concentration of gases) and low temperatures [76]. Figure 14 shows the block flow diagram of a Selexol process applied at a natural gas treatment plant to remove H₂S and CO₂. The description for the removal of H₂S will be omitted to focus on how the process works for CO_2 . The stream containing CO_2 (in this case natural gas) is brought into contact with DEPG in an absorption column at 450 psi and 0-5°C, which forces CO₂ to be absorbed by the solvent. The rich solvent is fed into two stages of flash desorption where the pressure is decreased to atmospheric or slight vacuum and most of the CO₂ desorbs. The stream is fed to the last stage of solvent regeneration, a CO₂ stripper where a pure CO₂ stream is achieved ready to be processed for transportation [76], [82]. The Selexol process can capture over 95% of the present CO₂ [82]. The Rectisol process works similarly to the Selexol process but uses methanol instead of DEPG. The different solvent requires 700 psi in the absorber and very low temperatures between -30 and -100°C and is regenerated at a similar fashion as the Selexol process through a series of flash desorption units [76]. Examples of the CO₂ purities the two processes can achieve are shown in Table 27.

Γable 27: Possible CO₂ stream impurities fo	Selexol and Rectisol applied to	IGCC power plants.	Adapted from: [93]
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Component	Selexol	Rectisol	SEWEGS
(ppmv)			
CO ₂ %(v/v)	98.1	95-98.5	>99
N₂ % (v/v)	0.0195	<1	<1
H₂ % (v/v)	1.5	0.002	<1
Ar	178	150	<1
H ₂ O	378	0.1-10	500
H₂S/COS	1700	0.2-20	1-5000
CH ₄	112	100	<1
CO	1300	400	<1
CH₃OH	-	20-200	-
Ash	1.2	-	-
NH ₃	38	-	-
Cl	17.5	-	-
Hg	0.068	-	-
As	0.0033	-	-
Se	0.01	-	-



Figure 14: Block flow diagram of a Selexol process applied at a natural gas treatment plant [82]

Table 28 lists the maximum possible CO_2 purity for Selexol, Rectisol and SEWEGS capture technologies applied on IGCC CO_2 emitting sources. The rest of the impurities can be regulated at the required levels. Since they are not as important as CO_2 , they were omitted for clarity. Table 29 summarises the maximum CO_2 purities achieved for the most popular CO_2 capture technologies in each of the three main capture technology categories.

Table 28: Selexol and Rectisol CO₂ purity results

Capture technology	Real/simulation	CO ₂ Source	CO2 v/v %	Reference
Selexol (dual stage)	Simulation	IGCC	97.2-97.6	[98]
Selexol (dual stage, unintragrated)	Simulation	IGCC	97.3	[98]
Selexol standard	Real	IGCC	98.1	[86]
Selexol advanced	Real	IGCC	99.7	[86]
Selexol	Real	IGCC	98.1	[93]
Rectisol	Real	IGCC	95-98.5	[93]
Rectisol standard	Real	IGCC	95	[86]
SEWEGS	Real	IGCC	>99	[93]
Rectisol advanced	Real	IGCC	>98.5	[86]

Table 29: Summary of captured CO₂ stream purities from various capture technologies applied on various CO₂ sources

Capture technology	Real/simulation	CO ₂ Source	CO ₂ v/v %	Reference
Selexol (dual stage)	Simulation	IGCC	97.2-97.6	[98]
Selexol (dual stage, unintragrated)	Simulation	IGCC	97.3	[98]
Selexol standard	Real	IGCC	98.1	[86]
Selexol advanced	Real	IGCC	99.7	[86]
Selexol	Real	IGCC	98.1	[93]
Rectisol	Real	IGCC	95-98.5	[93]
Rectisol standard	Real	IGCC	95	[86]
SEWEGS	Real	IGCC	>99	[93]
Rectisol advanced	Real	IGCC	>98.5	[86]
Oxy fuel (double flashing)	Real	NG	96	[86]
Oxy fuel (double flashing)	Real	Coal	97	[86]
Oxy fuel (double flashing)	Real	PC	95.84	[93]
Oxy fuel (double flashing)	Real	PC	96.3	[93]
Oxy fuel (double flashing)	Real	PC	96.7	[93]
Oxy fuel (distillation)	Real	Coal	99	[86]
Oxy fuel (distillation))	Real	PC	99.94	[93]
Oxy fuel (distillation)	Real	PC	99.93	[93]
Oxy fuel (distillation))	Real	PC	>99.95	[93]
Oxy fuel (LINDE)	Real	PC	>99.9	[93]
Oxy fuel (air products)	Real	PC	>99.9	[93]
Oxy fuel (distillation)	Real	NG	99	[86]
Amine	Real	PC	99.8	[93]
MEA	Real	PC	99.7	[93]
MEA	Real	Refinery stack	99.6	[93]
MEA	Real	Cement plant	99.8	[93]
MEA	Real	Cement kiln	99	[93]
MEA	Real	Coke production	99.4	[93]
MEA	Real	Lime production	99.52	[93]

4.5 Source-capture matching method

By reflecting on the classification and characterisation of CO_2 sources from Chapter 3 Sections 3.2-3.6 and the conclusions from Section 3.7 regarding the three categories of CO_2 output streams $(CO_2/N_2, CO_2/H_2$ and pure CO_2 as a by-product), it would be sensible to ask if it is possible to do what the natural gas processing industry did to select the most suitable capture technology for each different CO_2 source. It can be done for CO_2 capture from natural gas because there is already an established selection method, which was developed due to the necessity to avoid CO_2 emissions, and the use of CO_2 in enhanced oil recovery, which was a straightforward option to utilise CO_2 and have profit at the same time. But even though there is an established selection method for natural gas processing, it would be tedious and time consuming to find the specific conditions and data from each different natural gas source and even then, the data are not probably going to be available. So, the answer should be No (within the time frame and scope of this research). The same applies for the rest of the CO_2 sources because that makes it even more difficult for other CO_2 sources. For the rest of the sources there is no economic incentive yet to develop such an approach, similar to what has been used for the natural gas processing industry.

However, the issue stays and there is still a need for a robust method that quickly selects a suitable capture technology for any available CO₂ source and a need to commercialise CO₂ receivers to create an economic incentive, to facilitate the development of a similar selection process for each source. This is presented in the following section, where every example of carbon capture technologies found in literature was grouped and sorted in terms of CO₂ source and capture technology to create a database of all sources and capture technologies that are compatible and have been applied to them. Successful application of a specific capture technology to a source means that the necessary engineering design has been performed, the specific technology and source are compatible, and design optimisation in terms of technologies were added to a database (of tables), which was created and filled during the literature review of sources and capture technologies. The compatible match was added to a database when a capture technology was applied to a CO₂ source in real life or a design was created through simulation. In the following sections, Table 30 to Table 35 list the CO₂ capture technologies that are compatible with all the CO₂ sources identified in Chapter 3.

4.5.1 Heat and power

The literature review showed that CO₂ sources from the heat and power generation industry, even though they all involve combustion, are compatible with most capture technologies that fall into the post combustion and oxy-fuel combustion categories. For example, CO₂ from all sources utilising coal (PC, SCPC, USCPC, CFB), and natural gas combustion cycle sources have used chemical absorption or oxy-fuel combustion technologies. Gas-fired furnaces and CHP sources have used capture technologies from all three categories, post, pre and combustion with pure O₂, like chemical absorption, physical absorption, chemical adsorption, calcium looping and cryogenics gas fired furnaces. IGCC sources showed that they are only compatible with physical absorption and specifically with Selexol, Rectisol and Purisol technologies. The compatible technologies are listed in Table 30.

Source	Separation technology	Process	Reference
Gas-fired	Chemical absorption	1 st generation solvents	[50]
furnaces		2 nd generation solvents	[50]
		Chilled ammonia	[50]
	Physical absorption	Rectisol	[50]
		Selexol	[50]
	Chemical adsorption	K ₂ CO ₃	[50]
	Calcium looping		[50]
	Cryogenics		[50]
PC	Chemical absorption	Amine based	[74]
		Cansolv	[99], [100]
		MEA	[9]
	Oxyfuel combustion		[9], [101], [87]
SCPC	Chemical absorption	Econamine FG+	[102]
		MEA	[102]
		Amine	[102], [100]
		Advanced amine	[102],
		KS-1	[102]
		Cansolv	[102], [103], [100]
	Oxy-fuel combustion		[102], [74], [103]
	Gas separation membranes		[103]
USCPC	Chemical absorption	MEA	[9]
		KS-1	[9]
		Amines	[74]
	Oxy-fuel combustion		[74], [104]
CFB	Chemical absorption	Amines	[74]
	Oxy-fuel combustion		[9]
	Chemical looping		[9]
IGCC	Physical absorption	Selexol	[101], [87], [9], [86], [8]
		Rectisol	[87], [86], [8], [104]
		Purisol	[86], [104]
NGCC	Chemical absorption	Econamine FG+	[102]
		MEA	[102], [99], [63]
		Amine	[102], [100]
		Advanced amine	[102]
		KS-1 Canaalu	[9]
	Oxy fuel compustion	Calisoly	[100]
СНР	Chemical absorption	1 st generation solvents	[50]
GII		2 nd generation solvents	[50]
		Ammonia	[50]
	Physical absorption	Selexol	[50]
	i nysical absorption	Rectisol	[50]
	Chemical adsorption	K ₂ CO ₃	[50]
	Calcium looping	25	[50]
	Cryogenics		[50]

Table 30: List of CO_2 capture technologies compatible with heat and power CO_2 sources

4.5.2 Metal industry

The CO₂ emissions from the metal industry are created due to both combustion related processes and as a by-product. Coke production and smelting reduction iron processes involve the production of CO₂ only through combustion related processes and blast furnace and TGRBF processes involve CO₂ emissions from both combustion related processes and as a by-product. The literature review showed that smelting reduction iron and coke production usually use absorption technologies, both chemical and physical, and coke production can also utilise chemical adsorption with K₂CO₃. Blast furnace processes utilise both chemical and physical absorption and inorganic porous membranes. TGRBF processes use chemical absorption and inorganic porous membranes but no physical absorption processes. They can also use hydrate crystallization and physical absorption. The compatible technologies are listed in Table 31.

Source	Separation technology	Process	Reference
Blast furnace (BF)	Chemical absorption	MEA	[45]
		KS-1	[45]
		Other amines	[45]
		Advanced solvents	[45]
	Physical absorption	Selexol	[45]
	Inorganic porous membranes	Carbon	[45]
Top gas recycling	Chemical absorption	MEA	[45]
blast furnace	Inorganic porous membranes	Carbon	[45]
(TGRBF)	Hydrate crystallization		[45]
	Physical adsorption	PVSA	[45]
Smelting reduction	Chemical absorption	MEA	[45]
iron (COREX)	Physical absorption	Selexol	[45]
Coke production	Chemical absorption	1 st generation	[50]
		2 nd generation	[50]
		Ammonia	[50]
	Physical absorption	Rectisol	[50]
		Selexol	[50]
	Chemical adsorption	K ₂ CO ₃	[50]

Table 31: List of CO₂ capture technologies compatible with the metal industry's CO₂ sources

4.5.3 Stone and clay

Cement and lime production produce CO₂ emissions by fuel combustion processes and as a byproduct, but literature showed that they use completely different capture technologies. Cement production utilises most of the chemical absorption technologies, physical absorption, cryogenics, chemical adsorption and all the processes with combustion in pure oxygen. Lime production on the other hand utilises only physical adsorption processes. The compatible technologies are listed in Table 32.

Source	Separation technology	Process	Reference
Cement	Chemical absorption	1st generation	[50]
		2nd generation	[50]
		Ammonia	[50]
		MEA	[105]
		Amines	[8], [86]
		Alkaline solvent	[8], [86]
		Ionic liquids	[8], [86]
	Physical absorption	Rectisol	[50]
		Selexol	[50]
	Chemical Adsorption	K ₂ CO ₃	[50]
	Chemical looping	Calcium looping	[50]
	Cryogenics		[50]
	Oxy-fuel combustion		[105] [45], [8]
Lime production	Physical adsorption	VSA	[86]
		PVSA	[86]

Table 32: List of CO₂ capture technologies compatible with the stone and clay industries' CO₂ sources

4.5.4 Chemical and petrochemical

Sources from the chemical and petrochemical industries mostly involve the emission of CO₂ resulting as a by-product and they usually produce medium to high CO₂ concentrations. Only major refinery CO₂ emitting processes emit CO₂ via combustion related processes and the CO₂ concentration in the flue gas is always low. Despite those differences, all CO₂ sources from the chemical and petrochemical industries are compatible with chemical absorption, physical absorption, chemical adsorption, calcium looping and cryogenics. Emissions from combined stack in refineries can only utilise postcombustion and oxy-fuel combustion technologies, whereas methanol and DME production can only utilise physical absorption technologies. FT-liquids can use chemical absorption technologies and it can be assumed to be able to use the compatible capture technologies of hydrogen production since they are similar. Natural gas production can utilise chemical absorption, physical absorption and membranes. The compatible technologies are listed in Table 33.

Source	Separation technology	Process	Reference
FCC	Chemical absorption	1st generation	[50]
		2nd generation	[50]
		Ammonia	[50]
	Physical absorption	Rectisol	[50]
		Selexol	[50]
	Chemical Adsorption	K2CO3 PSA	[50]
	Calcium looping		[50]
	Cryogenics		[50]
Utilities	Chemical absorption	1st generation	[50]
		2nd generation	[50]
		Ammonia	[50]
	Physical absorption	Rectisol	[50]
		Selexol	[50]
	Chem.Adsorp.	K ₂ CO ₃	[50]
	Calcium looping		[50]
F	Cryogenics Chaminal abaa matian	1-1	[50]
Furnaces	Chemical absorption	Ist generation	[50]
		Ammonia	[50]
	Physical absorption	Porticol	[50]
		Solovol	[50]
	Chem Adsorn	KaCOa	[50]
	Calcium looning	N2CO3	[50]
	Cryogenics		[50]
Hydrogen	Chemical absorption	1st generation	[50]
,		2nd generation	[50]
		Ammonia	[50]
		Amine	[50]
	Absorption	Rectisol	[50]
		Selexol	[50]
	Chem.Adsorp.	K ₂ CO ₃	[50]
	Calcium looping		[50]
	Cryogenics		[50]
Ammonia	Chemical absorption	1st generation	[50]
		2nd generation	[50]
		Ammonia	[50]
		Amine	[8], [86]
	Physical absorption	Rectisol	[50]
		Selexol	[50]
	Chem.Adsorp.	K ₂ CO ₃	[50]
			[50]
Ethylopo	Cryogenics Chamical absorption	1st concration	[50]
ovide	chemical absorption	2nd generation	[50]
UNICE		Ammonia	[50]
	Physical absorption	Rectisol	[50]
		Selexol	[50]
	Chem.Adsorp.	K ₂ CO ₃	[50]
	Calcium looping		[50]
	Cryogenics		[50]
Combined	Post-combustion		[45]
stack	Oxy-fuel combustion		[45]
Methanol	Physical absorption	Selexol	[9]
DME	Physical absorption	Rectisol	[9]
		Selexol	[9]
FT-Liquids	Chemical absorption	Amine	[9]
Natural gas	Membranes	Polymeric	[8], [86]
processing		Inorganic	[57]
		Hybrid	
	Physical absorption	Selexol	[77], [57],
		Rectistol	[86], [87]
	Chemical absorption		[57] <i>,</i> [86]

Table 33: List of CO_2 capture technologies compatible with the chemical and petrochemical industries' CO_2 sources

4.5.5 Sources with limited information and emissions

Biogas production generates high concentration CO₂ emissions during the purification process and is only compatible with chemical absorption and physical absorption processes. The compatible technologies are listed in Table 34. Some other references do not include the level of detail in CO₂ sources and capture technologies and for this reason they are reported in a separate table, Table 35.

Table 34: List of CO₂ capture technologies compatible with biogas production CO₂ sources

Source	Separation technology	Process	Reference
Biogas production	Chemical absorption	Amines	[86]
	Physical absorption	Selexol	[86]
		Polyethylene glycol	[86]

Table 35: Examples of sources and capture technologies compatibility from literature

Source	Separation principle	Process		Reference
Power	Absorption	Amine based solvent, alkaline solvent,	Post	[8], [77], [86], [93], [91]
plants	chemical solvent	ionic liquids, amino acids, ammonia		
	Membranes	Porous, polymeric, inorganic, hybrid	Post	[8]
	Physical adsorbents	Zeolites, activated carbon, PSA, VSA	Post	[8], [86]
	Combustion not in air	Oxy-fuel, chemical looping,	Оху	[8]
Syngas	Combustion not in air	chemical looping reforming		
production				
IGCC	Absorption	Selexol, rectisol, Purisol, SEWGS	Pre	[8], [86], [93]
	physical solvent			
Iron	Absorption	Amine based solvent, alkaline solvent,	Post	[8], [86]
and steel	chemical solvent	ionic liquids		
	Adsorption solid	PSA, VSA		[86]
	sorbent			
	Combustion not in air	Oxy-fuel	Оху	[8]
Cement	Absorption	Amine based solvent, alkaline solvent,	Post	[8], [93]
industry	chemical solvent	ionic liquids		
	Combustion not in air	Oxy-fuel	Оху	[8]
Oil	Absorption	Amine based solvent, alkaline solvent,	Post	[8], [86]
refineries	chemical solvent	ionic liquids		
Natural gas	Membranes	Polymeric, inorganic, hybrid	Post	[8], [57] , [86]
sweetening	Absorption	Selexol, Rectisol	Pre	[77], [57], [86], [87]
	physical solvent			
	Absorption chem.solv.			[57], [86]
Ammonia	Absorption	Amine based solvent (MEA)	Post	[8], [86]
production	chemical solvent			
Biogas	Absorption chem.solv	Amine based solvent	Post	[86]
production	Absorption phy.solv	Selexol(type), plyethylene glycol	Pre	[86]
Lime	Adsorption	PSA, VSA	Post	[86]
production	solid sorbent			
Refinery	Absorption chem.solv	Amine based solvent	Post	[93]
4.5.6 Compatibility table

Table 30 to Table 35 contain all of the examples of CO₂ capture technologies applied to sources from literature so far. The examples were combined to a single table to form the source-capture compatibility table, Table 36. Table 36 lists vertically capture technologies per separation principle and solvent or material and horizontally the CO₂ sources per industry and sub-process. The compatibility between a source and a capture technology is marked by a shaded square. It can be observed from Table 36 that most of CO₂ sources are compatible with more than one capture technology type but there are some exceptions, such as the USCPC and IGCC processes, lime production and three sub-processes of the chemical and petrochemical industry.

The purpose of this table is not to replace any detailed engineering design but to serve as a method that quickly points out the most prominent candidates of capture technologies for a particular source based on previous published studies. This is only the first part of the matching method. Once the most prominent options are identified, the next step would be to use the technology readiness level (Table 22) to assess the technological maturity of the capture technology for the particular source that it is applied to. The third and final step is fully explored in Chapter 5, where cost models for most of the capture technologies have been developed to incorporate the economic aspect and not just the compatibility and TRL factor. Therefore, once the matches are ranked based on TRL, the final and more informed decision would be made by the investment and operating and maintenance cost of the capture technology.

4.6 Chapter 4 conclusions

The literature review on CO₂ capture provided insight into the available capture technologies in terms of how they emerged and how they were initially used, how CO₂ is captured, the maximum reported CO₂ purity and TRL for each type of capture technology and finally examples of compatibility between CO₂ sources and CO₂ capture technologies. Using the information collected in Table 22, Table 29 and Table 36, a matching method for sources and capture technologies was developed to account for compatibility and technological maturity which will be fully developed in the next chapter that covers the final parameter for capture technology selection, the cost of CO₂ capture.

Table 36: Source-capture technology compatibility table

Capture technology	Brocoss													Indu	istry-	-Soui	rce										
Capture technology	Process		Pow	erar	nd he	at ge	enerat	ion		Me	etal i	indus	stry	Sto	one			Ch	emic	al ar	nd petro	ochemi	cal ir	ndustr	γ		Other
Separation principle	Solvent/material	Gas-fired furnaces	PC	SCPC	USCPC	CFB	IGCC	NGCC	CHP	BF	TGRBF	COREX	Coke	Cement	Lime	FCC	Utilities	Furnaces	Hydrogen	Ammonia	Ethylene oxide	Combined stack	Methanol	DME	FT liquids	Natural gas proc.	Biogas production
Oxy-fuel combustion	Oxy-fuel																										
	1st gen																										
	2nd gen																										
	MEA																										
	KS-1																										
	Amine																										
Chamical abcorntion	Adv.Amine																										
	Econ FG+																										
	Cansolv																										
	Ammonia																										
	Ionic liquids																										
	Alkaline solvents																										
	КНСОЗ																										
	Selexol																										
	Rectisol																										
Physical absorption	Water quench																										
	Polyethelyne glycol							_																			
	Purisol																										
	Fluor															_											
Physical adsorption	VSA											_															
	PVSA		_												_												
Chemical looping	Calcium loping																										
	Polymeric																										
Membranes	Inorganic																										
memoraneo	Hybrid																										
	Gas separation																										
Hydrate crystalization																											
Cryogenics																											

Chapter 5: The cost of CO₂ capture

5.1 Introduction

In the previous chapter, it has been established that the aim of CO₂ capture technologies is to separate CO₂ from industrial sources to produce a concentrated CO₂ stream. IPCC (2005) states that in the context of CO₂ capture from power plants, capture technologies impose large energy penalties that increase fuel consumption, solid wastes and environmental impact in contrast with the same power plants without CO₂ capture [9]. These reasons put a high priority on the optimization of capture technologies so that future development will minimise energy requirements and improve the efficiency of power plants to overcome these issues [9]. The CO₂ capture costs are influenced by the applied capture technology, its technical design, as well as operation and financial factors. This means that to use capture cost estimates, a specific context is required that relates the source to the capture technology, otherwise comparison would not be possible. Spigarelli & Kawatra [76] confirm IPCC [9] by verifying that extensive work has been done for CO₂ capture because of the very high costs, which are estimated to be in the range of 70-90% of the total cost of a carbon capture and storage investment. This renders CO₂ capture costs the highest cost in CCS and by extension CCU, and the biggest obstacle to overcome before CCU value chain commercialization is achieved.

Apart from continuing research to improve CO₂ capture processes, the most efficient way to address this issue and help with the commercialisation of CCU value chains is to quantify capture costs and incorporate them in the process of CCU value chain formulation and optimization. At this point it is possible to quantify capture costs only from detailed design, but it is difficult to reach to that point because one has neither the choice nor luxury to explore it, since it first requires the implementation of CO₂ utilization. At this point, detailed design is rarely implemented because it is not viewed as a whole or a system due to its high complexity, and it can only be viewed as a system when complexity is reduced. It is like painting a picture, one must first start with the broader context of the picture (the individual steps of the chain), specify the subjects and how they are connected and how they influence each other. Only then can one focus on individual subjects and start increasing the resolution and detail on each subject until the picture (CCU value chains in a regional level) is finished. Capture cost estimation is something very detailed, which can only be realized after everything has fallen into place, but in order for everything to fall into place a low-resolution design must be developed with reduced complexity. At this point there is no tool that enables someone to quantify a rough capture cost estimation (or a "low-resolution estimation"). The development of a method for low-resolution capture cost estimation is the first step into visualising and starting to plan carbon capture and utilisation routes on a regional level with different types and many sources and receivers and not just where an obvious opportunity exists (like in the natural gas processing industry) but in areas where there is potential, it is not straightforward and becomes easier only when the right navigation tools become available.

5.2 Capture cost elements and metrics

The capture cost elements and metrics presented in this section are derived from carbon capture and storage (CCS) through application on power plants, which is the most popular source that offers the highest potential. They are used to demonstrate previous work on the matter and develop a better understanding of how costs can be estimated. They serve as the foundation on which the models developed later in Section 5.4 are built. The following section outlines the elements of carbon capture and storage (CCS) costs which can also apply for CCU. They are presented in terms of CCS because the only literature available on carbon capture costs is regarding CCS, which was applied earlier than CCU and was more popular than CCU until recently. Additionally, the only available CO₂ capture costs are related to the power generation industry because it is the largest CO₂ emitting industry and therefore efforts were initially concentrated on that industry.

5.2.1 Elements of CCS cost

Capital cost

The bare elected cost (BEC) of a carbon capture (CC) project is a value estimated by the contractor to complete the project that includes the cost of all the required equipment, materials and labour. BEC can be rated according to the level of detail ranging from simplified, least detailed to finalized, most detailed. BEC serves as the core for costing CC projects as other costing elements are estimated as a percentage of this value [50], [106].

$$BEC = Equipment + Material + Labour$$
(22)

Engineering, procurement and construction (EPC) cost is the BEC cost including the cost of fees for additional engineering services that are estimated as a percentage of BEC. EPC cost includes direct and indirect costs related to project management, engineering, facilities, equipment and labour. This is an optional cost measure and is used only by some organisations [74], [106].

Additional engineering services =
$$(...)$$
 % × BEC (23)

111

EPC = BEC + Additional engineering strvices (24) Total plant cost (TPC) is a term that includes BEC, additional engineering services and contingency costs. The contingency costs of a project are included to account for the risks associated with technological maturity, performance and regulatory difficulties and can be estimated as a percentage of BEC or EPC according to the level of detail [50], [74], [106].

$$Contingency \ cost = BEC \times (...)\% \ class$$
(25)

$$Total \ plant \ cost = EPC + contingency \ cost$$
(26)

Total overnight cost (TOC) includes the owner's cost and all components of total plant cost. The owner's cost covers the rest of components of capital cost that are not included in BEC or EPC, such as feasibility studies, surveys, land, insurance, permitting, finance transaction costs, pre-paid royalties, initial catalyst and chemicals, inventory capital, pre-production (start-up), other site-specific items unique to the project. Owner's costs do not include interest during construction [50], [74], [106].

$$Total overnight cost = Total plant cost + owner's cost$$
(27)

Total capital requirement (TCR), sometimes referred to as total as spent cost (TASC), is the sum of all costs mentioned before, [50], [74], [106].

Total capital requirement

= Total overnight cost + interest during construction

Operating and maintenance cost

Fixed O&M costs

Fixed operating and maintenance (O&M) costs are independent of plant size and consist mostly of operating and maintenance labour components. Other components include administrative and support labour, maintenance materials property taxes and insurance. Fixed O&M costs can be estimated as follows using straightforward relationships [106]:

Operating labour: Based on specified hourly labour rates (\$/h) and working hours in a year

Maintenance labour: 40% of total maintenance cost

Administrative and support labour: 30% of operating and maintenance labour

Maintenance materials: 60% of total maintenance cost (which is 1-10% of total plant cost)

Property taxes insurance: Included in capital charge factor. Other sources use 1-2% of total plant costs.

(28)

Variable O&M costs

Variable operating and maintenance costs include components that are directly proportional to the amount of electricity generated (fuel, chemicals, flue gas clean-up systems). This includes fuel, other consumables, waste disposal, CO₂ transport, CO₂ storage, by-product sales and emissions tax. All variable O&M costs are estimated as the unit cost of the element times the annual quantity based on electricity generated [106].

5.2.2 Carbon dioxide capture cost metrics

Levelized cost of electricity

Levelized cost of electricity (LCOE) is a metric indicating the price that electricity should be sold to be profitable enough based on a specified return on investment (ROI) and project lifetime. This is estimated by incorporating all expenses involved with producing a certain amount of electricity per year for a specified project lifetime and ROI. TCR is levelized by the fixed charge factor (FCF) (includes ROI and project life) and fixed and variable O&M costs [101], [106], [107]. Therefore, LCOE serves as an indicator for the potential profitability of a specific project and allows comparison between projects with different plant sizes and electricity generation technologies, assuming project lifetime and ROI are the same and TCR costs are estimated in similar ways. LCOE is calculated using two equations depending on the costs and annual net electricity produced of the plant. If they are constant over the project life, equation 29 is used; if they are not constant, equation 31 is used [87], [102], [106], [108].

$$LCOE\left(\frac{\$}{MWh}\right) = \frac{(TCR)(FCF) + FOM}{(MW)(CF \times 8766)} + VOM + (HR)(FC)$$
(29)

where FCF is shown by equation 30 and the parameters of Equation 28 are shown by Table 37

$$FCF = \frac{r(1+r)^{T}}{(1+r)^{T} - 1}$$
(30)

Table 37: Parameters of Equation 29

Parameter	Definition	Unit
TCR	Total capital requirement in the base year of the analysis	\$
FCF	Fixed charge factor	Fraction
FOM	Fixed O&M	\$/year
MW	Net power output of the plant	MW
CF	Capacity factor (this value multiplied by the total number of hours in a year, times MW gives the net annual electricity generation	Fraction
VOM	Variable O&M costs, excluding fuel (feedstock) costs	\$/MW
HR	Net power plant heat rate	MJ/MWh
FC	Fuel cost per unit energy	\$/MJ

The fixed charge factor component uses an assumed project life (T) and an interest rate (r) to obtain the total annualized capital cost that must be recovered from electricity sales. FCF values can vary depending on where interest rate is applied, on before-tax or after-tax basis [106].

$$LCOE = \frac{(TCR)(FCF_L) + l_1(FOM)}{(MW)(CF_L \times 8766)} + l_2VOM + l_3(HR)(FC)$$
(31)

where I_1 , I_2 , I_3 are levelisation factors.

First-year cost of electricity

The first-year cost of electricity is identical to LCOE with the only difference that inflation rates and cost escalation rates are assumed to be zero for the first year of operation [106], [107].

Cost of CO2 avoided

The cost of CO₂ avoided metric quantifies the average cost of avoiding a unit of CO₂ per unit of useful product (in this case electricity produced) by comparing a plant with carbon capture to a reference plant of similar type and size, without carbon capture. This metric is equal to the price of CO₂ emission tax and includes costs of capture, transportation and storage, otherwise CO₂ will not be avoided. This is similar to saying that if a unit of CO₂ is avoided then an equivalent unit of money is saved from CO₂ emission taxes, and is available to be used for capture, transportation and storage [106], [107], [109]. The cost of CO₂ avoided for power plants can be estimated using the following equation [9], [101], [102], [108], [109]:

$$Cost of \ CO_2 avoided \ (\frac{\$}{tCO_2}) = \frac{(LCOE)_{CCS} - (LCOE)_{ref}}{(tCO_2/MWh)_{ref} - (tCO_2/MWh)_{CCS}}$$
(32)

Cost of CO2 captured

The metric of cost of CO₂ captured covers only the cost of capturing and producing CO₂ as a chemical product. Unlike the cost of CO₂ avoided metric, that has the same units but different meanings, cost of CO₂ captured excludes transportation and storage costs; therefore it always has a smaller value, [106], [107], [109]. The cost of CO₂ captured for power plants can be estimated using the following equation [102], [108], [109]:

$$Cost of CO_2 captured \left(\frac{\$}{tCO_2}\right) = \frac{(LCOE)_{CCS} - (LCOE)_{ref}}{(tCO_2/MWh)_{captured}}$$
(33)

where tCO_2/MWh captured is the amount of CO_2 produced minus emitted.

Cost of CO2 abated

This metric quantifies the cost of minimising CO₂ emissions by modifying the process of producing electricity in any way, changing generators, fuel, region, country, and utility system, anything that

changes the current situation to one with lower CO₂ emissions, including CCS [109]. This can be estimated using the following equation [108], [109].

$$Cost of CO_2 Abated(\frac{\$}{tCO_2}) = \frac{(NVP)_{low-c} - (NVP)_{ref}}{(tCO_2)_{ref} - (tCO_2)_{low-c}}$$
(34)

where NPV= Net present value cost and tCO₂=mass of CO₂ emitted per year

Energy penalty and efficiency penalty

The energy penalty metric estimates the power output difference between a power plant with CC and a similar reference power plant without CC. This shows the decrease in power output in the case that a certain power plant applies a carbon capture technology. This is estimated using the following equation [108].

$$Energy \ penalty$$
(35)
= 100 $\left(\frac{Power \ output \ without \ CCS - Power \ output \ with \ CCS}{Power \ output \ without \ CCS}\right)$

The efficiency penalty metric estimates the decrease in efficiency between a reference power plant without CC and a similar power plant without CC. This decrease is caused by the application of capture technologies and can be estimated using the following equation [108].

$$Efficiency \ penalty \qquad (36)$$

= Efficiency without CCS(%) - Efficiency with CCS (%)

5.2.3 Conclusions

The cost of CO₂ abated and the energy efficiency penalty are metrics related to the costs of minimising CO₂ emissions and the efficiency of capturing CO₂ rather than its quantification. The LCOE, first-year cost of electricity and cost of CO₂ approach the CO₂ capture process as an investment opportunity and do not quantify the cost of capturing, transporting and storing/utilizing. On the contrary, an amount of money is estimated that would be available for those purposes, without specifying any of the individual components or providing any insight on how CO₂ would be captured, transported and stored/utilized and their associated costs. Although this might be used in a scenario where the objective is to reuse CO₂ from just one source by looking at many CO₂ receivers, it is not convenient or useful when the objective is to reuse CO₂ in a system consisting of several CO₂ sources and receivers, because the viability of that system lies in knowing and minimizing individual costs (capture, transportation, storage/reuse) through optimization. Therefore, the individual quantification of each cost of the CCU value chain is necessary.

The only metric that quantifies the cost of CO_2 capture is "cost of CO_2 captured" that excludes transporting and storing or utilizing. Cost of CO_2 captured is expressed as \$/t_{CO2} and can be estimated using equation 32 [102], [108], [109]. It is estimated by dividing the difference of LCOE of power plants with and without CO_2 capture by the ratio of the amount of CO_2 captured per amount of electricity produced. Since LCOE is involved, it means that the related costs are levelized by the FCF factor which integrates project lifetime and ROI in the metric, which additionally makes it only relevant to power related CO_2 sources. This excludes non-power related sources, which, as demonstrated in Chapters 3 and 4, are also important and should be used in CCU value chains. Although the cost of CO_2 capture can quantify the price that electricity should be sold to be profitable enough based on TCR costs, project lifetime, ROI and amount of CO_2 captured per amount of product, it still does not quantify the actual cost of capturing CO_2 from a source and does not reflect on the

type of source, CO_2 capture technology used, or the annual amount of CO_2 captured. Therefore, a method to isolate and quantify such costs is necessary.

5.3 Classification and quantification of costs

5.3.1 Data extraction

This section suggests and presents an alternative method to quantify CO₂ capture costs based on the nature of the source, capture technology used and annual amount of CO₂ captured. When CCS cost metrics are reported in literature, capture cost elements are reported as well. The capture cost elements reported usually include the capital costs of both the plant and CO₂ capture plant and if a reference case is provided, then the capital cost of capture can be estimated by subtracting the cost of the reference case from the cost with capture. Annual O&M costs are sometimes reported too or otherwise can be estimated by assuming to be equal to a percentage of capital costs. This will quantify the capital and O&M costs of a specific case. Chapter 4 provides information about the type of the source and capture technology used, which will allow the categorization of costs based on principle of separation. The annual amount of CO_2 captured is also reported, which can be used to adjust the cost of capture based on the required size of the capture plant. The objective of this method is to develop capture cost models for TCR and O&M, based on the amount of CO₂ captured, by extracting capture cost, annual amount of CO_2 captured and CO_2 capture technology data from literature. The values are standardized in terms of currency, year and inflation, sorted by CO₂ capture technology type and source type and plotted as a function of the annual amount of CO₂ captured for each CO₂ capture separation principle. The above procedure will produce a graph that its shape will

A thorough literature review was performed to identify studies that presented capture costs using real data, simulations, economic assessments or literature reviews to be screened for several variables and factors associated with the extraction of the required data for the analysis. The major ones are presented in Table 38, which also indicates whether the study reported the data mentioned in the first column. The variables and factors are:

• Source type

- Year
- Separation principle
- Compression
- Amount of CO₂ captured
- Project lifetime
- Working hours per year

Constant/current

- Plant capacity/output
- Capital cost
- O&M cost
- Cost of CO₂ captured
- Cost of CO₂ avoided
- LCOE

Currency

Table 38: Extracted data	for the estimation o	f carbon capture costs

Parameters	[110]	[87]	[102]	[110]	[50]	[00]	[111]	[112]	[74]	[112]	[114]	[100]	[75]	[115]	[116]	[101]	[105]	[103]	[30]	[117]	[112]	[0]
Source type		DR	DR	DR	Both	[<u>]</u>],	DR	Both		DR			[75] DR	DR	DR	DR		[105], DR	[33]	Both		Both
Senaration principle	V	v	v	v	v	v	v	N	v	v	NER	v	v	N	N	v	v	v	N	v	N	v
Compression	v	v	v	v	v	v	N	N	v	v	v	v	N	N	v	v	v	v	v	N	IN	v
	F	v	Y	N	v	F	N	N	F	v	v	F	v	N	Y	v	v	v	v	N		v
Currency	Y	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Y	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ		Ŷ
Year	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ	N	Ŷ	Ŷ	N	Ŷ	Ŷ	N	Ŷ	Ŷ	Ŷ		Y.
Constant/Current	Co	Co	Co	Co	Co	N	N	Co	N	Co	Cu	Cu	Ŷ	N	Co	Co	Со	N	Cu	N		Co
Project lifetime	Y	Y	N	Y	Y	N	Ν	N	Y	Y	Y	N	Y	Y	N	Y	Y	Y	Y	Ν		N
Annual Working Hours	Y	Y	Y	Y	Y	Y	Ν	Ν	А	Y	Y	А	Ν	Y	Ν	Ν	Ν	Ν	Ν	Ν		Ν
Reference Plant Capacity	Ν	Y	Y	Y	Ν	Ν	Ν	Ν	Y	Y	Ν	Y	Y	Ν	Ν	Y	Ν	Y	Ν	Ν	Y	Y
Reference Capital cost	Ν	Ν	Y	Y	Ν	Y	Ν	Ν	Y	Y	Y	Y	Y	Ν	Ν	Y	Y	Y	Y	Ν	Y	Y
Reference O&M cost	Ν	Ν	Ν	Y	Ν	Y	Ν	Ν	Y	Y	Y	Y	Y	Ν	Ν	А	Y	Ν	Ν	Ν	Ν	Ν
With Capture Plant Capacity	Y	Y	Y	Y	Ν	Ν	Y	Ν	Y	Y	Ν	Y	Y	Ν	Y	Y	Y	Y	Y	Y	Y	Y
With Capture Capital cost	Y	Y	Y	Y	Y	Y	Ν	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Ν	Y	Y
With Capture O&M cost	Y	Y	Ν	Y	Y	Y	Ν	Ν	Y	Y	Y	Y	Y	Ν	Y	А	Y	Ν	Ν	Ν	Ν	Ν
Cost of CO ₂ captured	N	Ν	Y	Ν	Ν	Ν	Ν	N	Ν	Ν	Ν	Y	Ν	Ν	Ν	Ν	Y	Y	Ν	Y	Y	Y
Cost of CO ₂ avoided	Ν	Y	Y	Ν	Ν	Ν	Ν	Ν	Y	Y	Ν	Y	Ν	Ν	Ν	Y	Y	Y	Ν	Y	Y	Y
LCOE	Ν	Y	Y	Ν	Ν	Y	Y	Ν	Y	Y	Ν	Y	Ν	Ν	Ν	Y	Ν	Ν	Ν	Ν	Y	Y

The source type indicates whether data are for power related, non-power related or both. The separation principle defines if the type of capture technology used was specified. The amount of CO_2 capture indicates if the annual amount of CO_2 captured is directly reported or if it can be estimated. Currency, base year, constant/current, project lifetime and working hours per year are the data required to standardize cost for a fair comparison. The base year indicates the year of the reported costs, constant or current indicates if inflation is included, and working hours per year specify the annual number of hours that the plant operates, in case it might be needed for the quantification of annual production that relates to costs or emissions. Plant capacity or plant output, capital cost and O&M costs are needed just for the CO_2 capture plant if the data are directly reported. This is rarely the case and therefore data for both the reference plant and the plant with CO_2 capture are required to work out the difference between the two. Plant capacity or output indicates whether data directly report the annual amount of CO_2 avoided and LCOE are not required for this study, but they were included as reference. The data required for the analysis are capital cost of capture (TCR, TOC or TPC), annual O&M costs (M\$/yr) and annual amount of CO_2 captured (Mt_{co2}/yr).

5.3.2 Capital cost of CO₂ capture

The capital cost in a common currency is required for the whole project but only for CO_2 capture facility, excluding the capital cost of the other plant.

As demonstrated in the previous section, capital costs can be expressed in different terms where each one includes certain costs. While screening studies for capture costs, the term expressing the costs was noted to ensure that the data gathered are comparable. Additionally, the way capture costs were expressed is also important because they are rarely reported directly in millions of monetary units of a currency but rather in amount of monetary units per amount of product produced.

EE [50] reports the CO₂ capture costs as TPC directly in pounds (M£). Kuramochi et al. [110] report CO₂ capture costs as TCR in \notin/t_{CO2} y which were converted to M€ by multiplying by the annual amount of CO₂ captured. The rest of the studies report CO₂ capture costs as TCR in amount of money per amount of product produced (\$/kW) for a case with and without CO₂ capture [9], [74], [100], [101], [102], [103], [105], [113]. TCR costs in \$/kW were converted to \$ by multiplying \$/kW by the plant's capacity (kW). The reference case without CO₂ capture was subtracted from the case with capture to determine the absolute cost for CO₂ capture only. IEA [74] and Barker et al. [105] reported capital costs as TOC.

$5.3.3 O&M cost of CO_2 capture$

O&M cost for capture is required as an annual cost for operating and maintenance in M\$/y. Certain studies report annual O&M costs directly in amount of money per year in dollars or euros but will be standardized in a following step, Section 5.3.5 [50], [105], [113]. IEA (2011) reports annual O&M costs as 4% of TOC [74]. Kuramochi et al. (2012) report O&M costs as a percentage of TCR [45]. NETL [100] reports annual O&M costs as fixed and variable O&M costs in \$/MWh which were converted in \$/y by multiplying by plant capacity (MW) and working hours per year. The rest of the studies ([9], [101], [102], [103]) do not report annual O&M costs but a 6% of TCR was assumed. The assumption of 6% of TCR costs for O&M costs is an average value based on assumptions made in other studies [45], [103], which assume O&M costs from 2 to 12% for various capture technologies.

5.3.4 Annual amount of CO₂ captured

Certain studies report annual CO₂ emissions of a plant with and without CO₂ capture in kg_{CO2}/MWh ([74], [100], [103]). In this case the annual amount of CO₂ emitted was calculated by multiplying kg_{CO2}/MWh by plant capacity (MW) and working hours per year (assumed 8760 hours if it was not reported). The amount of CO₂ captured was calculated by subtracting the annual CO₂ emission of the plant with capture from the plant without capture. ZEP [113] and Davison et al. [101] report the amount of CO₂ captured in t_{CO2}/MWh, which was converted to the annual amount of CO₂ captured by multiplying by plant capacity (MW) and working hours per year. Kuramochi et al. [110] do not report annual amount of CO₂ captured but it is estimated using plant size, capture rate and CO₂ emission intensities from Chapter 3. The rest of the studies report the annual amount of CO₂ captured directly in Mt_{CO2}/y [9], [50], [102], [105].

5.3.5 Financial structure and standardization of data

The extracted cost data were standardized to constant USD2018 prices [119]. The method adjusts for inflation of the reported currencies to 2018 prices using local consumer price index (CPI) values and then converting currencies to USD₂₀₁₈ using market exchange rate data from the World Bank [120]. The selected studies usually report cost data in US dollars, British pounds or Euro. A base year was always provided, and it was specified whether inflation was included. For US dollars and British pounds, it was easy to find CPI values which are based on location because it is a country-based index, but for costs reported in Euros, it was not possible to find CPI values because there was no indication of country and instead the costs were converted to USD of the base year and then adjusted for inflation to USD2018 using USD CPI. Cost data in current values were standardized for inflation of

currencies to 2018 prices using local CPI values by dividing the CPI₂₀₁₈ by 100 and multiplying by the current price and then converting currencies to USD₂₀₁₈ using market exchange rate data from the World Bank [120], [121].

5.3.6 Sorting of data

The extracted data include information on the source type and capture technology and ideally a model can be developed for each type of source using all available and compatible capture technologies. Because of the lack of enough data this was not possible. Instead of developing a model for each capture technology applied on every source, the data were sorted per source type and capture technology, and a model was developed for each source and capture technology, if enough data were available. The sorted data can be found in the appendix section 1, Table 103 to Table 112.

Source type

The extracted data were sorted according to the classification of source types (presented in Chapter 3) for non-power related sources (metal industry, fluid catalytic cracking (FCC), combined stack, cement industry, hydrogen, ammonia, ethylene oxide production and synthetic fuel production) and power related sources (pulverised coal (PC), integrated gasification combined cycle (IGCC), supercritical pulverised coal (SCPC), ultra-supercritical pulverised coal (USCPC), natural gas combined cycle (NGCC), gas-fired furnaces, combined heating and power station (CHP), fluidised bed combustion (CFB)). To develop models for these sources, it was required that there were enough data (at least 10 data points), which covered a reasonable range of flowrates (usually 0-7 Mt_{co2}/yr or at least 0-2 Mt_{co2}/yr) so that they were spread and not stacked. For these reasons it was only possible to develop models for the metal industry, cement industry, fluid catalytic cracking, IGCC, SCPC, USCPC and NGCC.

Capture technology

The cost data from each source were sorted according to the classification of capture technologies per separation principle, chemical absorption, physical absorption, oxyfuel combustion, chemical adsorption, chemical looping, cryogenics, inorganic membranes and hydrate crystallization (presented in Chapter 4). Again, the criteria for developing models for these capture technologies was that there were at least 10 data points and covered a reasonable range of flowrates so that the data were spread and not stacked. Therefore, it was not possible to develop models for chemical adsorption, chemical looping, cryogenics, inorganic membranes and hydrate crystallization CO₂ capture technologies because there are fewer than 10 pieces of data for each of them that cover a

very small range of about 0-0.8 Mt_{CO2}/y (3.8-5.5 for inorganic porous membranes). For the rest of the capture technologies (chemical absorption, physical absorption and oxyfuel combustion) there were many available data that covered a wide range of flowrates from 0 to 6.7 Mt_{CO2}/y , meaning that a cost model can be developed. This also shows that these three types of capture technologies have been used more frequently and can be applied for a wide range of annual amounts of CO₂ captured and sources.

5.4 Model development

Numerous regression analyses were performed and assessed to develop a model that best predicts the investment cost and O&M cost based on amount of CO₂ captured. A power regression analysis was used to develop a model that predicts the total capital requirement (TCR) and annual operating and maintenance cost (O&MC) (dependent variables) based on the annual amount of CO₂ captured (independent variable). The proposed models are presented in the following section.

5.4.1 TCR and O&M models of capture cost based on separation principle

Data were split based on the separation principle used in each case into three categories, chemical absorption, physical absorption and oxyfuel combustion. The data group includes data from various CO_2 sources (SCPC, NGCC, gas-fired boilers, CHP, USCPC, sub-PC, CFB, metal industry, cement industry and chemical and petrochemical industry). Regarding chemical absorption, there were many data points that covered a decent range of flowrates between 0-6.7 MtCO₂/yr. The analysis showed that the curve that best described the data has the form of $y = ax^b$ (power curve model), where a and b are constants calculated from regression (Figure 15 and Figure 16/Summary in Table 39 and Table 40).

For physical absorption, the data points covered a decent range of flowrates between 0-6.4 MtCO₂/yr and included data from various non-power related CO₂ sources like the metal industry, cement industry, chemical and petrochemical industry and only IGCC from power related sources. The analysis showed a curve of the shape of $y = ax^b$ where a and b are constants calculated from regression (Figure 17 and Figure 18/Summary in Table 39 and Table 40).

For the oxy-fuel combustion capture technology, there were fewer data points, still covering a decent range of flowrates between 0-6 MtCO₂/yr. This data group includes data from sources that include combustion like SCPC, USCPC, CFB, PC&NGCC and chemical and petrochemical industry and cement industry. The power model that was proposed by the regression analysis is presented in Figure 19 and Figure 20 and summarized in Table 39 and Table 40.



Figure 15: Estimation of TCR cost based on the amount of CO₂ captured for chemical absorption



Figure 16: Estimation of O&M cost based on the amount of CO_2 captured for chemical absorption



Figure 17: Estimation of TCR cost based on the amount of CO₂ captured for physical absorption



Figure 19: Estimation of TCR cost based on the amount of CO_2 captured for oxy-fuel combustion







Figure 20: Estimation of O&M cost based on the amount of CO_2 captured for oxy-fuel combustion

5.4.2 TCR and O&M models of capture cost based on the source type

It was also decided to categorize the data points based on the type of the source and, for those sources that had an appropriate number of data points, specify the model that best described their profile. The different CO₂ sources of the metal industry, including blast furnace, top gas recycling blast furnace (TGRBF), smelting reduction iron and raw material production, were all grouped under metal industry because there were not enough data to develop a model for each one individually. There were 20 points of data that covered a range of flowrates between 0-6.4 MtCO₂/yr. Some data points are stacked, because the authors of the references cited compare different capture technologies applied on the same CO₂ source. This data group includes various capture technologies like chemical absorption, physical absorption, inorganic porous membranes, physical adsorption, calcium looping and cryogenics. The power model that was proposed by the regression analysis is presented in Figure 21 and Figure 22 and summarized in Table 41 and Table 42.

For the cement industry, data from the pre-calciner and from the entire cement plant were grouped together, because there were not enough data to develop a model for each one individually. There were 13 points of data that covered flowrates between 0-1.4 MtCO₂/yr although some data points are stacked. This data group includes various capture technologies like oxy-fuel combustion, chemical looping, chemical absorption, physical absorption and cryogenics. The power model that was proposed by the regression analysis is presented in Figure 23 and Figure 24and summarised in Table 41 and Table 42.

There were 18 points of data for FCC that covered flowrates between 0-1 MtCO₂/yr which is restrictive for the analysis, but it shows that is a relatively small CO₂ source when compared to power related ones. Although some data points are stacked, it was done intentionally by the reference to compare different capture technologies applied on the same CO₂ source. This data group includes various capture technologies like chemical absorption, oxy-fuel combustion, chemical adsorption, physical absorption, calcium looping and cryogenics. The power model that was proposed by the regression analysis is presented in Figure 25 and Figure 26 and summarized in Table 41 and Table 42.



Figure 21: Estimation of TCR cost based on the amount of CO_2 captured for metal industry



Figure 22: Estimation of O&M cost based on the amount of CO_2 captured for metal industry



Figure 23: Estimation of TCR cost based on the amount of CO_2 captured for cement industry







Figure 25: Estimation of TCR cost based on the amount of CO_2 captured for FCC



Figure 26: Estimation of O&M cost based on the amount of CO_2 captured for FCC

The power-related sources was the category with the most available data. There were 57 data points for IGCC, 65 for SCPC, 23 points of data for NGCC and 16 for USCPC. All of them covered a range greater than 4.5 MtCO₂ (from 0-4.5 MtCO₂ to 0-6.7 MtCO₂). For IGCC, the data set includes only physical absorption capture technology (mainly Selexol), whereas for SCPC includes chemical absorption, oxy-fuel combustion and gas separation membranes capture technologies. For NGCC the data set include only chemical absorption (mostly MEA) and for USCPC it combines chemical absorption and oxy-fuel combustion capture technologies. The power model that was proposed by the regression analysis is presented in Figure 27 to Figure 34 and Table 43 and Table 44.



Figure 27: Estimation of TCR cost based on the amount of CO2 captured for IGCC



Figure 28: Estimation of O&M cost based on the amount of CO2 captured for IGCC



Figure 29: Estimation of TCR cost based on the amount of CO_2 captured for SCPC



Figure 30: Estimation of O&M cost based on the amount of CO_2 captured for SCPC



Figure 31: Estimation of TCR cost based on the amount of CO_2 captured for NGCC



Figure 32: Estimation of O&M cost based on the amount of CO_2 captured for NGCC



Figure 33: Estimation of TCR cost based on the amount of CO_2 captured for USCPC



Figure 34: Estimation of O&M cost based on the amount of CO_2 captured for USCPC

5.4.3 Model validation

The regression analysis in all cases was forced to go through 0,0 (0.000001, 0.000001) because the cost to capture zero amount of CO_2 is zero. The shape of all models in the range that the data represent (0-6.7 Mt) seems to be of a positive straight line, but the equations are of the form of $y = ax^b$ where a and b are constants calculated from regression with most of the exponents being close to 1. Further analysis was done to the obtained model to determine its statistical characteristics like R^2 value, p-value and standard deviation. The R^2 value, which signifies the accuracy of the model, is high in all cases with the lowest being 0.823 and highest 0.986 and shows that all models would produce accurate predictions. The p-value, which signifies the statistical significance of the model, is significantly small in all cases and allows to demonstrate that the model is statistically significant by

rejecting the null hypothesis. Standard deviation signifies the error of the model and is reported to account for the deviation of each model's predictions. All data are summarized in Table 39 to Table 44. A detailed list of the data used in the model development can be found in the Appendix section 1, Table 103 to Table 112.

	Chemical	Physical	Oxyfuel
	Absorption	Absorption	Combustion
Equation	y=218.4x ^{1.025}	y=164x ^{1.113}	y=143.8x ^{1.316}
R ² value	0.823	0.828	0.963
p-value	1.06×10 ⁻⁴¹	9.38×10 ⁻²¹	7.55×10 ⁻²⁸
Error (SD)	378.68	793.65	476.02

Table 39: Statistical analysis of TCR costs models per separation principle

Table 40: Statistical analysis of O&M costs models per separation principle

	Chemical	Physical	Oxyfuel
	Absorption	Absorption	Combustion
Equation	<i>y</i> =12.03 <i>x</i> ^{0.94}	y=9.185x ^{1.015}	y=8.824x ^{1.113}
R ² value	0.859	0.869	0.94
p-value	6.43×10 ⁻⁴⁷	1.03×10 ⁻²³	2.14×10 ⁻²²
Error (SD)	22.01	47.55	24.92

Table 41: Statistical analysis of TCR costs models per source type (non-power sector)

	Metal Industry	Cement Industry	FCC	
Equation	y=113.9x ^{1.156}	<i>y</i> =335.5 <i>x</i> ^{1.49}	y=515.3x ^{1.53}	
R ² value	0.986	0.985	0.99	
p-value	6.57×10 ⁻²⁰	2.54×10 ⁻¹²	2.87×10 ⁻¹⁸	
Error (SD)	456.23	113.85	105.83	

Table 42: Statistical analysis of O&M costs models per source type (non-power sector)

	Metal Industry	Cement Industry	FCC	
Equation	<i>y</i> =6.05 <i>x</i> ^{1.11}	y=17.96x ^{1.249}	y=21.89x ^{1.255}	
R ² value	0.980	0.957	0.982	
p-value	1.68×10 ⁻¹⁸	1.49×10 ⁻⁹	2.5×10 ⁻¹⁶	
Error (SD)	25.47	26.65	5.91	

Table 43: Statistical analysis of TCR costs models per source type (power sector)

	IGCC	SCPC	NGCC	USCPC	
Equation	y=77.66x ^{1.373}	y=106.86x ^{1.388}	y=192.9x ^{1.434}	<i>y</i> =93.0 <i>x</i> ^{1.39}	
R ² value	0.918	0.957	0.949	0.983	
p-value	1.8×10 ⁻²⁵	7.75×10 ⁻⁴⁵	1.08×10 ⁻¹⁵	9.43×10 ⁻¹⁵	
Error (SD)	822.35	380.91	229.70	451.34	

Table 44: Statistical analysis of O&M costs models per source type (power sector)

	IGCC	SCPC	NGCC	USCPC	
Equation	y=5.59x ^{1.15}	y=8.06x ^{1.173}	y=10.53x ^{1.186}	y=5.13x ^{1.136}	
R ² value	0.881	0.954	0.921	0.97	
p-value	5.3×10 ⁻²²	9.54×10 ⁻⁴⁴	1.35×10 ⁻¹³	7.11×10 ⁻¹³	
Error (SD)	47.82	22.27	13.66	16.27	

5.5 Interpretation of model to the real world

Until now it has been demonstrated that there is a need for a robust method of estimating CO₂ capture costs because it is one of the biggest obstacles, since it is the largest cost hindering the development and commercialization of CCU value chains. The method of development, presentation and statistical analysis of low-resolution CO₂ capture costs models has also been demonstrated. What is missing is how this method is relevant and how it can be implemented to aid the development of CCU value chains.

5.5.1 Capture technology cost comparison

The development of cost estimation models for each of the most popular CO₂ capture technologies allows for a cost comparison to identify the technology with the lowest cost both for initial investment and operating and maintenance of capture plants. A cost comparison was performed by plotting the developed models from Table 39 and Table 40 for flowrates between 0.25-6 Mt_{CO2}/y, and comparing the magnitude of TCR and O&M costs, presented in Table 45. As it can be observed from Table 45, the capture technology with the lowest cost per amount of CO₂ processed for both capital and operating and maintenance costs and for all flowrates is oxy-fuel combustion, then physical absorption, followed by chemical absorption as the most expensive option. Table 45 also shows that the O&M cost for the capture technologies under study on average is about 18 times less (18.7, 18.5 and 17.8 for chemical absorption, physical absorption and oxy-fuel combustion respectively) than the TCR (assuming the fitted curve approximates a straight line because of the exponents being close to 1). Of course, this comparison ignores important parameters such as technology readiness level and maximum achievable CO₂ purity and focuses solely on cost.

	TCR Cost	(M\$)		0&1	M Cost (M\$,	/y)		TCR / C	0&M (ratio)
Flowrate	Chemical	Physical	Oxyfuel	Chemical	Physical	Oxyfuel	Chemical	Physical	Oxyfuel
(Mt _{CO2} /y)	absorp.	absorp.	comb.	absorp.	absorp.	comb.	absorp.	absorp.	comb.
0.25	52.7	35.1	23.2	3.3	2.2	1.9	16.1	15.6	12.3
0.5	107.3	75.8	57.8	6.3	4.5	4.1	17.1	16.7	14.2
0.75	162.6	119.1	98.5	9.2	6.9	6.4	17.7	17.4	15.4
1	218.4	164.0	143.8	12.0	9.2	8.8	18.2	17.9	16.3
3	673.4	557.0	610.5	33.8	28.0	30.0	19.9	19.9	20.4
5	1136.8	983.6	1195.6	54.6	47.0	52.9	20.8	20.9	22.6
6	1370.4	1204.8	1519.9	64.8	56.6	64.8	21.1	21.3	23.4

Table 45.	Cost com	narison	hetween	Chemical	absorption	Physi	cal absorp	tion and	Oxv-	fuel	combustion
TUDIE 4J.	COSt COM	punsonn	DELWEEN	Chenneur	ubsorption	, , , , , , , , , , , , ,	un absorpt	uon unu	UAy-	juei	combustion

5.5.2 How can the models be used?

The required data used for the development of the models introduced some limitations to the models in the sense that the data used were gathered from various sources and standardized in order to process them and use them. Capital costs were reported in different currencies and sometimes they did not cover the same costs because, as was mentioned in Section 5.2.1, capital costs reported do not always include the same cost components, as certain variants exist. Additionally, compression was sometimes not included and costs were reported in various currencies and base years. O&M costs were not always reported in amount of money per year and had to be converted using assumptions and in other cases they were not directly reported but instead reported as estimates using percentages of capital cost which were always specified by the source. The annual amount of CO₂ captured was not always reported and sometimes had to be estimated from plant capacity and annual working hours.

Nevertheless, the developed models are simple equations that only require the annual amount of CO₂ to be captured to estimate the capital cost of capture and the annual O&M cost of capture. Although the extracted data differed slightly and were standardised to allow for the development of the models, the models can provide quick, reasonably accurate estimations, with statistical significance. This allows for the cost estimation for any CO₂ source or any one of the most popular capture technologies using either one of the models developed specifically for sources or capture technologies, something which was not possible until now. The models were developed in such way that they allow for total capital cost estimation per project based on annual amount of CO₂ to be captured and annual O&M cost estimation to allow flexibility for various project lives.

5.6 Chapter 5 Conclusions

As mentioned in Chapter 4, the capture cost estimation models complete the last part of the sourcecapture technology matching method. This means that according to the CO₂ source, a list of compatible capture methods is created which then uses the technology readiness level and cost estimates from capture cost models as factors to select the most beneficial capture technology. Once the capture technology is selected, it can then undergo a detailed design followed by an optimisation that will most likely produce the most desirable result. The most desirable result is defined by the needs of the one interested to invest in a capture technology, which means that it can be a low or high TRL technology with a low or high cost, if the options allow it. This method fills a big gap in the development of CCU value chains by addressing one of the biggest obstacles and providing a quick, reliable and low-resolution cost estimation that has the potential to dictate the development of CCU value chains.

The next step was to address transportation in terms of technological feasibility to set transportation conditions and standards, and economical estimation to develop a method for estimating transportation costs in a similar way to what was achieved in Chapter 5.

Chapter 6: How to transport CO₂

6.1 Introduction

The next step of the CCU value chain is transportation, which poses an important question – how is CO_2 best transported? This is not a question that can be answered easily because CO_2 is a gas and must be compressed to a liquid before transportation, in contrast to liquids or solids, which are ready to be transported and exist in a confined shape and space. Therefore, the optimal transportation conditions for the available means of transportation (onshore and offshore pipelines or storage tanks loaded on various types of vehicles that use different transportation infrastructure – roads/trucks, ships/sea, trains/railway) must be investigated first. The optimal conditions for each type of transportation are chosen based on efficiency, techno-economic and health and safety reasons. Impurities are present in captured and compressed CO_2 streams and have an effect on the transportation conditions which, if not altered accordingly, can cause corrosion and damage to equipment. This means that transportation conditions are directly influenced by the impurities present in captured CO_2 streams and therefore certain limits must be placed on each type of impurity to ensure that transportation is efficient and safe.

This chapter focuses on the process of compressing and dehydrating CO₂ after capture, in other words the optimal transportation conditions (temperature and pressure for each type of transportation) and on the effect of impurities during transportation and their limit to ensure safe and efficient transportation. Chapters 6 and 7 do not include an original contribution of the thesis and are based on a literature review. However, they are important for the understanding of the entire CCU value chain and will contribute to the algorithm and business model development. More specifically, Chapter 6 examines the suitable transportation conditions per transportation type and the estimation of the cost.

6.2 Transportation conditions

Carbon dioxide is favoured to be transported in the dense phase or supercritical phase at a pressure of 7.38 MPa and higher and a temperature below 20°C [122], [123], [124], [125]. Dense and supercritical phases are favoured because they increase density, which makes it easier to move a dense liquid in comparison to a gas and maximises the amount of CO₂ transported per unit volume, making it cost effective. Additionally, dense and supercritical phases allow for a more efficient and safe transportation by keeping CO₂ and impurities in a single phase, which prevents damage to valves, pumps and compressors. This means that compression is necessary to keep the components in a single phase for cost effectiveness and that certain limits for impurities must exist to ensure that the components stay in a single phase and do not interfere with transportation. Figure 35 shows the phase diagram for CO₂. Table 46 shows the recommended transportation conditions by various sources.



Figure 35: Phase diagram of CO₂ [124]

Table 46: Recommended transportation conditions by various sources

Pressure	Temperature	Reference	Transportation
Above 7.38 MPa	Below 20°C	[124]	Pipeline
50-80 MPa	Above 0°C	[125]	Pipeline
50-100 Bar	-	[122]	Pipeline
71.3 Bar	-10-25°C	[126]	Pipeline

6.2.1 Effect of impurities on transportation

As concluded in Chapters 3 and 4, various carbon dioxide capture technologies exist that utilise different separation principles and can be applied to a range of CO₂ sources. This means that different capture technologies applied at different sources will result in an output stream with different impurities and varying levels of impurities, each unique to the capture technology, source and process [127]. Cole et al. [125] chose Lee et al.'s [128] analysis to show the impurities present in captured CO₂ streams from coal fired plants using CO₂ captured by MEA. Lee et al. [128] show that the impurities present in such CO_2 capture streams include SO_2 , SO_3 , HCl, mercury, NO_x and water. Wettenhall et al. [127] presented the possible impurities in CO₂ capture streams from adsorption, calcium looping, membrane, oxyfuel combustion and pre-combustion capture technologies, which include O₂, N₂, Ar, H₂, CO, H₂S and CH₄ (Table 47). They also report the possible contaminants from pre-combustion, post-combustion and oxyfuel combustion, which are O₂, N₂, Ar, H₂O, NO_x, SO₂, SO₃, CO, H₂S and COS, H₂ and CH₄ (Table 48) (Wettenhall, Race, & Downie, The effect of Co2 Purity on the development of Pipeline Networks for Carbon Capture and storage Schemes, 2014). These are some of the most common impurities found in captured CO₂ streams and therefore various studies exist on the effect of these impurities during transportation. These studies suggest that the presence of contaminants in captured CO₂ streams affects phase behaviour, density, viscosity and compressibility during transportation. Consequently, as contaminants affect fluid properties, they affect the operating conditions of the transportation system (pipelines) and the design [123].

Scenario	Scenario Component (all values % by volume)								
Number		CO ₂	O ₂	N_2	AR	H_2	CO	H_2S	CH_4
1	REF	100	-	-	-	-	-	-	-
2	CO2 MEM1	93	-	7	-	-	-	-	-
3	CO2 MEMe	97	3	-	-	-	-	-	-
4	ADS1	90	1	9	-	-	-	-	-
5	ADS2	95	-	5	-	-	-	-	-
6	Ca LOOP (also OXY-like)	95	1	2	2	-	-	-	-
7	OXY1	90	6	3	1	-	-	-	-
8	OXY2	96.5	0.5	2.5	0.5	-	-	-	-
9	PR H2 MEME	98	-	-	-	2	-	-	-
10	H2 MEME	96	-	1	-	1	0.5	1.5	-
11	CH4-RICH	98	-	-	-	-	-	-	2
12	ULCOS	96	-	0.5	-	-	3.5	-	-

Table 47: Possible	impurities in CO ₂ co	pture streams fron	n various capture	technologies. Ada	pted from	: [127]
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Component (vol%)	Pre-combustion Min	Max	Post-combustion	Max	Oxyfuel min	Max
CO ₂	95.6	99.7	99.8	99.97	85	99.94
SOx	-	-	0.001	0.01	0.007	2.5
NO _x	-	-	0.002	0.01	0.01	0.25
H₂S	0.01	3.4	-	-	-	-
CO	0.03	0.4	0.001	0.002	-	-
Ar	0.03	1.3	0.003	0.045	0.01	5.7
O ₂	0.03	1.3	0.003	0.03	0.01	4.7
N ₂	0.03	1.3	0.021	0.17	0.01	7
H ₂	0.002	1.7	-	-	-	-
CH ₄	0.035	2	-	0.01	-	-
Hydrocarbons	-	-	0.003	0.01	-	-
HCN	-	0.0005	-	-	-	-
NH₃	-	0.003	-	0.05	-	-
CH₃OH	-	0.02	-	-	-	-

Table 48: Possible impurities in CO₂ capture streams from various capture technologies. Adapted from: [123]

6.2.2. Phase behaviour

Different contaminants have different effects on the phase behaviour of the captured CO₂. Contaminants with a critical temperature below that of CO₂ will form a second phase above that of pure CO₂ and those with critical temperature above that of pure CO₂ will form a second phase below that of CO₂. This is illustrated by Table 49 and Figure 36, where binary mixtures of CO₂ and one contaminant were used along with the Peng Robinson equation of state to produce a phase diagram. As can be observed from Figure 37, all contaminants increased the critical pressure of the mixture and contaminants with lower critical temperature than that of pure CO₂ decreased the critical temperature of the mixture and contaminants with critical temperature higher than that of pure CO₂ decreased the critical temperature of the mixture. This agrees with the work of Wang et al. [129] who calculated phase envelopes for CO₂, CO₂ mixtures, which illustrate that contaminants with critical temperatures and pressures above that of pure CO₂ produced a phase envelope below and those critical temperatures and pressures below that of pure CO₂ produced a phase envelope above. In conclusion, the addition of impurities to the mixture will require higher pressure to keep the mixture in the supercritical phase [123], [129].

Figure 36 shows also the phase envelope for CO₂ composition streams of 87%, 96% and 99% purity and clearly illustrates that the critical pressure (minimum pressure for single phase behaviour) increases with decreasing purity. Since CO₂ is preferred to be transported in the dense or supercritical phase, it is important to understand the effect of contaminants on phase behaviour because the operating conditions during transportation are altered and narrowed making it more difficult to operate efficiently and in single phase without causing damage to equipment.

	Molecular	Critical	Critical pressure	Effect on phase envelope
	Weight	temperature (°C)	(bar)	
Hydrogen	2	-240	13.0	
Nitrogen	28	-147	33.9	
Carbon monoxide	28	-140.35	35.0	
Argon	40	-122.4	48.7	Phase envelope above CO ₂
Oxygen	32	-118.6	50.4	
Methane	16	-82.8	46.0	
Carbon dioxide	44	31.0	74.1	
Hydrogen sulphide	34	100.1	89.4	
Sulphur dioxide	64	157.7	78.8	Phase envelope below CO ₂
Nitrogen dioxide	46	157.9	101.0	

Table 49: Relative critical pressures of key impurities and their effect on the phase envelope. Adapted from: [123]



Figure 36: Phase diagram for binary mixtures of CO_2 and $2mol\% H_2$, H_2S and NO_2 [123]









Figure 37: Phase envelope of the CO_2 mixture changing with gas composition [9]

6.2.3 Density

Wettenhall et al. [127] explain that in general the density of CO₂ decreases at lower pressures and higher temperatures, but it is not linear, and a sharp discontinuity is observed at the vapour liquid equilibrium line (VLE) during the phase change from liquid to gas. Figure 39 shows the density profile with pressure for pure CO₂. The addition of contaminants with lower critical temperatures and pressures than that of pure CO₂ have been found to move the discontinuity to higher pressures and the addition of contaminants with higher critical temperatures and pressures than that of pure CO₂ have been found to move the discontinuity to higher pressures and the addition of contaminants with higher critical temperatures and pressures than that of pure CO₂ has been found to move the discontinuity to lower pressures [123]. This is illustrated by Figure 38. It can be concluded that pipeline capacity can be improved by decreasing the amount of contaminants with lower critical temperature and pressure than that of pure CO₂ and lowering the inlet temperature of the stream.



Figure 39: Density profile with varying pressure for pure CO_2 and binary mixtures of $CO_2/4$ mol H_2 and $CO_2/4$ mol NO_2 [123]



Figure 38: Density profile with varying pressure for pure CO_2 (using Peng Robinson equation of state) [123]

6.2.4 Viscosity

The general trend for the viscosity of pure CO₂ is that it increases at higher pressures and lower temperatures with a sharp discontinuity at the VLE and liquid phase. The addition of contaminants does not affect the viscosity of the mixture in the gaseous phase, but it dramatically affects it in the supercritical phase. Once again, the contaminants with higher critical temperature and pressure than that of pure CO₂ will increase the viscosity of the mixture and contaminants with lower critical temperature and pressure than that of pure CO₂ will increase the viscosity of the mixture and contaminants with lower critical temperature and pressure than that of pure CO₂ will decrease the viscosity of the mixture. This is illustrated in Figure 40. Low viscosity is preferred during the transportation of captured CO₂ as it reduces the flow resistance of the mixture in the pipeline [123].



Figure 40: Viscosity Vs Pressure graph for pure CO₂ and binary combinations of CO₂/4mol H₂ and CO₂/4mol NO₂ at 5°C and 30°C [123].

6.2.5 Corrosion

Cole et al. [125] have reviewed the few available studies on the corrosion of pipelines during captured CO₂ transportation and concluded that the reason for corrosion in pipelines during the transportation of captured CO₂ is the presence of water. This happens because CO₂ will form an acid in the presence of water, causing corrosion, and the presence of other contaminants exaggerates the acidification and lowers the pH, effectively accelerating corrosion. Corrosion can still occur in the presence of water below a certain threshold and even in the absence of water, but research in this subject is still underdeveloped [125]. Cole et al. [125], de Visser et al. [130] and Onyebuchi et al. [122] agree that no corrosion will occur if water content is kept below 600 ppm and in supercritical phase, avoiding the formation of an aqueous phase. The aqueous phase forms when the water content passes the

solubility limit of the transportation conditions and its formation is facilitated by the presence of other impurities.

Cole et al. [125] suggests that transportation of captured CO₂ in pipelines can take place only under four regimes:

- (i) Very low contaminant levels and extremely low water level: Related to CO₂ transportation for EOR.
- (ii) Low contaminant levels and water level below the solubility content: Limited gas conditioning or a limited source of H₂O in pipeline.
- (iii) Low contaminant levels and water content above the solubility content: No gas conditioning or significant changes to pipeline operational conditions during transportation and or additional source of H₂O in the pipeline.
- (iv) Moderate contaminant levels and water content above solubility limit: Limited gas conditioning or no conditioning by choice.

Regime A is the only regime that ensures zero to minimal corrosion rates because of the stringent requirements on impurities and transportation conditions to keep supercritical CO₂ in a single phase and in absence of an aqueous phase. McGrail et al. [131] and de Visser et al. [130] agree to a maximum water content limit of 600 ppm. Regimes B, C and D will suffer from corrosion because they take place in the presence of water and other contaminants, especially if an aqueous phase forms because of H₂O exceeding the solubility limit. Additionally, the corrosion rate will accelerate in the presence of HNO₃, HCl, NO_x, SO_x and H₂S, even at very low levels, because they significantly lower the pH (as low as 3.2) by segregating in the aqueous phase and forming acids. O₂ presence can also cause significant corrosion. Corrosion can still take place if H₂O exceeds a certain critical value even if an aqueous phase is not present, that is how strict the requirements must be to avoid corrosion [122], [125].

This means that corrosion will always take place if H₂O content is not kept under 600 ppm and in the aqueous phase, all other regimes will suffer from corrosion. The rate of corrosion that regime B will suffer is still not clear, but regimes C and D will suffer significant corrosion and a coating technology or a monitoring and repair program will be required [125].

6.2.6 Achieving compression conditions

Martynov et al. [132] developed a thermodynamic model to estimate the power requirements and cost for the available compression processes, which prepare captured CO₂ streams to transportation conditions. Along with the presentation of their model they also present possible compositions of captured CO₂ streams from oxyfuel combustion, pre-combustion and post-combustion, available in Table 50, and they explain that the choice and design of the process and compressors is tailored to the unique characteristics of each of the streams and required transportation conditions.

Table 50: Average compositions of captured CO_2 streams from oxy-fuel combustion, pre-combustion and post-combustion. Adapted from: [132]

Component		Oxy-fuel		Pre-combustion	Post combustion
(ppm _v)	Raw/dehumidified	Double flashing	Distillation		
CO ₂ (% v/v)	85.0	96.78	99.3	98/07	99.8
O2 (%v /v)	4.7	1.2	0.4	-	0.015
N ₂	5.8	1.6	0.2	0.02	0.045
Ar	4.47	0.4	0.1	0.018	-
NO _x	100	150	33	-	20
SO ₂	50	36	37	700	10
SO ₃	20	-	-	-	-
H₂O	100	-	-	150	100
СО	50	-	-	1300	10
H ₂ S	-	-	-	1700	-
H ₂	-	-	-	15000	-
CH_4	-	-	-	110	-
Bubble-point	-54.5	14.8	23	16	23
temperature					

The three available compression approaches are:

- (i) Centrifugal compressors: Internally geared, centrifugal compressors or trains of single-staged compressors are combined with inter-stage cooling (up to 10 stages) to reach pressures up to 200 bar.
- (ii) Supersonic shockwave compression: Shock-wave compressors are used in single or two stages to compress large volumes of CO₂ at high pressure ratios with the additional benefit of high discharge temperature that can be used for heat integration purposes. This is a novel technology.
- (iii) Compression combined with liquefaction and pumping: Gas phase centrifugal compressors are utilised to bring the pressure at transportation conditions by compressing to an intermediate point where the mixture is liquified and then pumped to the final pressure using

liquid pumps. The premise of this compression approach is that liquid pumps consume less energy and are less expensive than gas compressors.

Kolster et al. [133] modelled four variations of compression and purification units of captured CO₂ streams utilising only centrifugal compressors to estimate the capital and operational costs of captured CO₂ streams from oxy-fuel combustion and post-combustion capture processes. The variations involve a compression process followed by a dehydration process, which agrees with Kemper [134], who states that dehydration units are required following up the compression process as most of the water is removed during compression and removes a load from the main dehydration unit [133], [134].

The four models are:

- (i) 6-stage CO₂ compression and dehydration: Centrifugal compressors with 6 stages of interstage cooling and flash system are used to bring the mixture to 120 bar pressure. Between stage 3 and 4 a dehydration system is used to produce a dry mixture for stage 4.
- (ii) High purity double flash with heat integration: Centrifugal compressors with 6 stages of interstage cooling and flash system is used to bring the mixture to 120 bar pressure. This variation is similar to the 6-stage compression and dehydration process, with two additional flash distillation processes at -27 and -54°C, respectively, with the three following intercooling stages, without flash systems. This process results in a mixture with higher CO₂ purity and less water.
- (iii) Low purity double flash without heat integration: This variation is almost identical to the high purity double flash with integration with the exception that the captured CO₂ stream is of lower purity and there is no heat integration used between the two flash systems at –27 and -–54°C. This process results in a lower purity CO₂ mixture.
- (iv) Compression and purification unit with a 6-stage distillation column: This variation is similar to the high purity double flash with heat integration with the exception that there are three flash distillation units between the dehydration unit and the compression stage 4. This results in the highest purity CO₂ mixture.

Centrifugal compressors with inter-stage cooling is the more simple and conventional choice for compression of captured CO₂ streams to transportation conditions [124], [132], [133].

This choice of compression approach can be used for oxy-combustion, pre-combustion and postcombustion capture technologies and it can be designed to the specific characteristics of the captured CO₂ stream and required transportation conditions. The simplest variation consists of 6 compressors with inter-stage cooling and can be up to 10 because it is impossible to increase the pressure of the mixture to the required final pressure in one step and the temperature rise will be too high. For these reasons, in the first three stages the mixture is compressed and cooled with water at 20°C, after each cooling stage water condenses out and it is removed before the mixture is fed into the next stage. Removing water during interstage cooling reduces the load of the main dehydration system, which minimises the water content of the mixture at the required transportation level. The process is repeated until it reaches 30 bar pressure at the end of stage 3, which is then fed to a dehydration system. The dehydrated mixture exiting the dehydration system goes into 3 more stages of compression and inter-stage cooling using propane as a refrigerant until it exits stage 6 at 120 bar (can be up to 200 bar) and 33-46°C depending on the capture technology used. The process is illustrated by Figure 41.



Figure 41: Flow diagram of compression and dehydration process with inter-stage cooling [133]
6.2.7 Dehydration

Kemper et al. [134] presented a list of various dehydration processes that can be utilised in CO_2 capture systems but most of them cannot achieve low enough water levels and they were not considered for examination. Molecular sieves and triethylene glycol (TEG) were included in the examination because they are the most efficient technologies and the choice of the industry at the moment [134]. The conclusions of the examination were a preliminary assessment of operating conditions and capital and operating and maintenance costs. It shows that dehydration using TEG and molecular sieves technologies can achieve water levels of 550 ppm up to <10 ppm (TEG 30 ppm, solid bed desiccants <1 ppm, which is in the desired range for transportation [135]. The capital cost for dehydration units is not affected by the target water content, but by the volume of the gas to be processed. High presence of inert contaminants (N₂, Ar, H₂, CH₄) will increase capital costs. Hence, vendors suggest that the design for dehydration units should be for <1 ppm water with the use of a continuous water content monitoring systems, which is essential because manual monitoring would not be sufficient. A list of the dehydration technologies is presented in Table 51.

Technology	Description
Cooling	Compressor inter-stage cooling
Joule Thomson cooling	Adiabatic cooling via gas expansion
Refrigeration	Gas cooling with refrigerant
Turbo expansion	Isentropic cooling with gas expansion
Supersonic separation	Gas expansion to supersonic velocity in a Laval nozzle and subsequent
	separation of the formed liquid droplets in a cyclone
Solid desiccants	Silica gel
	Activated alumina
	Molecular sieves (synthetic zeolite aluminosilicates, types 3A and 4A
Liquid desiccants	Methanol
	Glycerol
	Triethylene glycol
	Other glycols
Membranes	Still in research and development

Table 51: List of availabl	e dehydration	technologies	[134
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6.2.8 Conclusions

Carbon dioxide transportation is favoured to be in the dense phase or supercritical phase at a pressure of 7.38 MPa and higher and a temperature below 20°C. Some of the most common impurities found in captured CO₂ streams are O₂, N₂, Ar, H₂O, NO_x, SO₂, SO₃, CO, H₂S and COS, H₂ and CH₄. Different contaminants will have different effects on the phase behaviour of the captured CO₂. Some contaminants increase critical temperature and some other decrease it.

All contaminants increase the critical pressure of the mixture. Contaminants affect density as well and it is suggested to decrease contaminants with lower critical temperature and pressure than that of pure CO₂ and lower the inlet temperature of the stream to improve pipeline capacity. Contaminants with higher critical temperature and pressure than that of pure CO₂ will increase the viscosity of the mixture and contaminants with lower critical temperature and pressure than that of pure CO₂ will decrease the viscosity of the mixture. Water content should be kept under 600 ppm to avoid damage to transportation equipment due to corrosion. Compression is required to prepare the stream for transportation conditions and is achieved by stage compression and inter-stage cooling. The process is followed by dehydration where necessary if the compression stage does not remove water to the required level. The most efficient dehydration technologies are dehydration using TEG and molecular sieves. Limited gas conditioning and processing compromises transportation efficiency and causes damage to equipment.

6.3 Pipeline transportation

CO₂ transportation is more efficient and cost effective in the dense phase, liquid or preferably in supercritical fluid phase as [105] and [136] suggest, which agrees with what it has been concluded from the previous section. After CO₂ is captured from a source with an appropriate capture technology, the stream has a high CO₂ content, low concentration of impurities but the water content exceeds the transportation limits. The stream requires treatment before it reaches transportation conditions, which is achieved via compression and water removal (dehydration) steps that effectively increase pressure and remove water. CO₂ can then be transported onshore via pipeline, trucks or railway and offshore via ship and pipelines. Recommendations for transportation conditions and impurity limits for pipeline transportation have been researched by the Dynamis project, which provides recommendations for maximum allowable concentrations of impurities from precombustion capture technologies [126].

6.3.1 Recommendations for CO2 transportation via pipeline

de Visser et al. [126] have investigated the maximum allowable concentration of impurities for pipeline transportation. The assessment was focused on captured CO₂ from pre-combustion technologies (CO₂/H₂ streams) and draws knowledge from the European project Enhanced CAPture of CO₂ (ENCAP) to provide recommendations for transportation conditions and limits for impurities, ensuring that there are no severe effects from corrosion, hydrate formation, free water formation and health and safety due to toxic impurities and that transportation operates under acceptable

safety risks. The limitation of this study in the context of CCU is that it covers captured CO₂ only from pre-combustion technologies and excludes CO₂ from other capture technologies with different impurities. The study also concentrates on pipeline transportation, therefore it does not cover any additional restrictions that might apply for other types of transportation such as truck, railroad and ship tankers [126].

CO₂ transportation via pipeline must take place at pressures above 71.3 bar and temperatures between -10 and 25°C. The reason is to keep CO₂ above its critical pressure in order to keep water in the soluble region (which is between -10 and 25°C for up to 1300 ppm) and avoid free-water formation. Addition of H₂S was found to increase water solubility but at the recommended levels of H₂S the effects are negligible. By contrast, addition of CH₄ at proportions of 5% showed a decrease in water solubility by 30% [126]. Hydrogen sulfide was limited to 200 ppm because it is toxic, and 200 ppm serve as a reasonable margin for health and safety considerations. Carbon monoxide limit was set to 2,000 ppm by applying a safety factor of 5. Condensable gases which includes N₂, Ar and H₂ are recommended to be kept under 4% vol as proposed by the ENCAP project.

Although the Dynamis project does not cover captured CO₂ from all possible capture technologies, CO₂ sources or transportation types it is the most extensive study on the subject of CO₂ transportation, considering transportation conditions in terms of design, economics and health and safety, and therefore it should be used as an indication for the rest of the CO₂ sources, capture technologies and transportation types.

6.3.2. Transportation conditions and impurity limits

The Dynamis project [126] recommendations for maximum allowable concentrations for pipeline CO₂ transportation ensure safe, durable, effective and efficient transportation by considering technical and health and safety factors. It recommends i) CO₂ quality and limits for impurities adjusted for safety, toxicity and technical reasons and ii) conditions for pipeline transportation which are temperature of less than 30°C and pressure of 100 bar [130]. The recommended impurity limits are presented in Table 52.

Component	Concentration	Limits	Limitation
H ₂ O	500 ppm	Max	Technical: Below solubility limit of H ₂ O in CO ₂
H₂S	200 ppm	Max	Health and Safety considerations
CO	2000 ppm	Max	Health and Safety considerations
SO _x	100 ppm	Max	Health and Safety considerations
NO _x	100 ppm	Max	Health and Safety considerations
O ₂	S <4% vol, EOR 1000ppm	Max	Technical: Range for EOR
CH_4	S <4% vol, EOR <2% vol	Max	Proposed by ENCAP project
N ₂	<4% vol	Max	Proposed by ENCAP project
Ar	<4% vol	Max	Proposed by ENCAP project
H ₂	<4% vol	Max	As low as possible because of its energy content
CO ₂	>95.5%	Min	Balanced with other components at their maximum allowable values

Table 52: Transportation recommendations for maximum allowable concentration for pipeline CO₂. Adapted from: [130]

Previous applications

There are many examples of previous application of pipelines for the transportation of CO₂ from projects in the United States, Canada, Brazil, Saudi Arabia, United Arab Emirates, China, Australia and Europe [122], [137], [138], [139], [140], [141]. The projects were implemented mainly for enhanced oil recovery (EOR) and storage and previous experience shows that CO₂ pipeline transportation has a lower risk of leakage when compared to natural gas transportation, and is a cost-effective and reliable means of CO₂ transportation, which shows that it is a well-established type of transportation [142]. The projects vary in size ranging from 0.06 to 27 Mt/y and distance 1.9-808 km and demonstrate the versatility of pipeline transportation.

Operating pressure and temperature

The operating conditions of CO₂ transportation via pipeline should be above the critical point of pure CO₂ (74 bar and 31°C) in the supercritical phase but, as discussed in Section 6.3.1, pressure and temperature should be altered to keep the mixture in supercritical phase [122]. Operating temperatures of pipelines are also affected by the temperature of the surrounding soil [143]. The pipeline material that is usually used is carbon steel with seamless seams because it is the most economical option but it is prone to corrosion in the presence of free water [140], [144]. The recommended transport conditions via pipeline from the Dynamis project are a stream temperature of less than 30°C and pressure of 100 bar [130]. Operating conditions from other projects are illustrated in Table 53.

Table 53: Operating conditions	from various	projects of CO ₂	transportation	via pipeline
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Pressure (bar)	Temperature (°C)	Reference
50-145	-	[122]
86 <	-	[143]
100-130	27	[144]
72-200	-	[140]
150-200	5	[145]
140	49 max	[146]
100-150	15-30	[141]
73.8	Below 20	[124]
50-80	Above 0	[125]
71.3	-10-25	[126]

6.3.3 Conclusions

The pressure and water limits for pipeline transport are achieved via a series of cooling and compression steps called compression inter-stage cooling and knockout, which serve both as a compression and dehydration process. If the stream requires further dehydration to meet the recommended concentrations, then an extra dehydration process utilising triethylene glycol or molecular sieves is recommended by [134] and [135]. The operating conditions for pipeline transportation must be above the critical point of pure CO₂ which is 74 bar and 31°C. Literature showed that in different projects these conditions may vary. Transportation pressures have been reported in the range of 5-200 bar and temperatures in the range of 0-49°C. The Dynamis project optimal recommendations suggest a temperature below 30°C and a pressure of 100 bar. For stream compositions their recommendations suggest a CO₂ purity larger than 95.5% vol and water content of less than 500 ppm which ensures that it stays below its solubility level in CO₂.

6.4 Offshore transportation

6.4.1. Ship transportation

 CO_2 transportation by ship takes place in the liquid phase for efficiency and economic reasons. Because CO_2 can be liquefied at a range of pressures, there are many suggestions and examples at different conditions for different applications. Seo et al. [147] present the findings of various studies that proposed the optimal conditions based on their individual tasks and range from 5.18 bar and – 56.6°C to 26 bar and –10°C, but only a few of the studies considered all the aspects of the supply chain. The liquefaction pressure affects the characteristics of the cargo tanks, the physical volume of the tank and the volume of CO_2 the tank can hold as density changes. This includes the material and cargo tank design. The findings are presented in Table 54. They performed a life cycle cost (LCC) for each of the seven liquefaction pressures including the cost of the liquefaction system, storage tanks, ship (CO₂ carrier) and pumping system and the results of the sensitivity analysis showed that the optimal liquefaction pressure for CO₂ transportation by ship was 15 bar and -27.7°C [147].

Liquefaction pressure (bar)	Density (kg/m³)	V _{Tank} (m ³)	V _{Hold} (m ³)	V_{Hold}/V_{Tank}
6	1159	10,600	28,200	2.7
15	1064	11,500	29,500	2.7
25	990.6	12,400	42,600	3.5
35	926.6	13,200	52,00	4.0
45	864.4	14,200	62,500	4.5
55	784.9	15,600	78,200	5.1
65	649.4	18,900	105,700	5.6

Table 54: Cargo tank characteristics for increasing liquefaction pressures for 12.3t of CO₂. Adapted from: [147]

There are two possible scenarios for ship transportation. The first one is explained by Seo et al. [147] and involves the capture of CO₂ from a source near a port where it is directly liquefied to ship transportation conditions on site. The second one, explained by Engel et al. [148], involves the capture of CO₂ from more than one sources where individual streams are pre-compressed and transported by onshore pipelines to a port for ship transportation. Then, CO₂ can either be stored underwater in an injection well via pipeline or be offloaded to a shore-based facility with intermediate buffer storage before transporting it onshore for utilisation. The transportation procedure is outlined by the following processes presented in the order in which they are executed.

Liquefaction system

The first step of liquefaction is the dehydration of the captured CO₂ stream to a water content of 50 ppm. This is achieved by compressing the stream multiple times to 35 bar and with the use of inter stage cooling, dehydration is achieved by water condensation followed by a duplex regenerative adsorption column [136]. Liquefaction systems are responsible for liquefying gaseous CO₂ that has been captured to maximize density and the amount of CO₂ transported per tank volume. This is achieved by increasing pressure and reducing temperature if necessary. These systems can be classified in two categories, open systems and closed systems. Open systems are the simplest and use CO₂ as a refrigerant where it is compressed and expanded and closed systems are more efficient and utilise external refrigerants. Four prominent liquefaction systems exist, the Linde Hampson system, a dual pressure Linde Hampson system, a pre-cooled Linde Hampson system and a closed system with the latter two showing higher performance [136], [147], [148].

Storage tanks

Transportation of CO₂ by ship is a batch process but capture and liquefaction are continuous processes and therefore there is a need for buffer storage between liquefaction and loading the ship. Storage tanks or buffer tanks are essentially cylindrical or spherical pressure vessels that keep CO₂ at the required high pressure and their design is well established. Their size varies according to the capacity of the CO₂ carrier and studies have suggested a factor of 1.2 or 1.5 times the size of the CO₂ carrier [136], [147].

CO2 carrier

CO₂ has been previously transported by ship for use in beverages and food processing industry but in much smaller scale, compared to what is needed for CCS and CCU, in the range of 2-3 Mt/yr. The ammonia producer Yara International produces CO₂ as by-product and trades it to Western Europe using two 1.8 Mt reconditioned LPG tankers. Anthony Veder, a gas shipping company, uses a 1.25 Mt LPG tanker that doubles as a CO₂ carrier and IM Skaugen, a shipping company, has six 10,000 m³ CO₂ carriers [136], [147], [149]. A design has been proposed to contain 3,000-6,000 m³ cylindrical tanks arranged horizontally as pairs to a total capacity of 20,000-40,000 m³. Another design consists of cylindrical tanks, vertically arranged to allow for a more close-packed arrangement of tanks for a total capacity of up to 100,000 m³. Wettenhall (2014) agrees, stating that two 30,000 m³ carriers are currently being developed, with 7,500 m³ vessels [127]. The suggested vessels are Type C tanks (i.e. insulated cylindrical, bi-lobe or tri-lobe shaped tanks that can be fully or partially pressurized) which have the advantage of minimising boil-off-gas (BOG), because some ships lack BOG processing facilities.

Pumping system offshore offloading

The pumping systems consist of a unit of intermediate storage tanks where CO_2 is stored to be prepared for storage or transportation via pipeline. CO_2 is prepared for pipeline transportation via a pump and a heat exchanger where CO_2 is compressed to the required pipeline pressure and a heat exchanger is used when it is necessary to increase the temperature in order to avoid hydrate formation and freezing in the pipeline [147]. The conditions vary based on the well [136].

Offloading for onshore transportation

Offloading for onshore transportation is achieved via conventional loading/unloading arms to liquid storage tanks for buffer storage [136].

6.4.2 Offshore pipelines

Designing offshore pipelines for CO₂ transportation is very similar to designing pipelines for transporting hydrocarbons, assuming the stream operates in non-corrosive conditions [150]. Although offshore pipeline transportation is a mature technology, the existing design experience for transporting over long distances is not as developed and extensive [122]. Offshore pipelines are made from carbon steel, they are protected from external corrosion by anticorrosion coatings and sacrificial bracelets and a concrete coating is added for extra protection and hydrodynamic stability. Offshore pipelines are manufactured for various water depths from shallow at 100 m depth to deep at 1,000 m depth. As water depth increases the pipelines and required coatings thickness increase too. They operate at higher pressures and lower temperatures than onshore pipelines and usually cost between 40 and 70 percent more. Transportation via offshore pipelines starts to be economically competitive at large transportation distances for 250 km and 3 Mt/y up to 400 km and 9 Mt/y because ship transportation is more expensive over such distances and flowrates. Ship transportation on the other hand is considered to be more flexible as it can easily adapt to changes in volume, location and be repurposed when the project ends [9], [122], [151], [152].

 CO_2 transportation by ship takes place in the liquid phase for efficiency and economic reasons. The liquefaction pressure affects the physical volume of the tank and the volume of CO_2 the tank can hold, the material and cargo tank design as density changes. The optimal liquefaction pressure for CO_2 transportation by ship was estimated to be 15 bar and $-27.7^{\circ}C$. CO_2 transportation by ship takes place in five stages, i) liquefaction and dehydration, ii) temporary storage in onshore tanks, iii) loading on to CO_2 carrier, iv) temporary offshore storage and v) offshore offloading. CO_2 transportation has been used in the past by the food industry to transport 2-3 Mt_{CO2}/yr but LNG ships are available that can handle 1.25 Mt.

Offshore pipelines are competitive at large transportation distances for 250 km and 3 Mt/y up to 400 km and 9 Mt/y. They operate at higher pressures and lower temperatures than onshore pipelines and usually cost between 40 and 70 percent more.

6.5 Alternative transportation

6.5.1 Railroad tankers

 CO_2 can be transported by railroad tankers using cryogenic railroad tank cars which are optimized for CO_2 transportation. The tanks are made from carbon steel designed to hold CO_2 in the liquid or gas phase with a temperature range of –40 to 50°C, they can have a nominal volume of up to 60 m³ and

are charged and discharged via a hydraulically operated bottom valve. This type of transportation might be considered in the case where the source and receiver have access to a railroad, they are linked, and the railroad is able to support the required volumes to be transported. The cost for transportation via railroad tankers is more than double compared to pipeline and for these reasons it is unlikely to be considered for large scale CCU projects [9], [153], [154].

6.5.2 Truck tankers

Information for CO₂ transportation using truck tankers can be drawn from the transport of liquid CO₂ for the food and beverage industry around the world where it is used for beer and soft drinks production. CO₂ is transported using trucks equipped with specially designed storage units with varying capacity and similar characteristics. TOMCO2 systems design three types of tanks for truck transportation, truck mounted, CO₂ ISO containers and portable CO₂ storage fleet units. The truck mounted tanks are available in 2.5, 3, and 3.5 tonne sizes, and they can hold CO₂ at a maximum of 23.8 bar. The liquid CO₂ ISO containers are made of carbon steel and store CO₂ at a maximum pressure of 24 bar between –40 and 93.3°C and come in sizes of 17 and 19.2 tonne. The portable CO₂ storage fleet units were designed for temporary onsite storage and therefore they are equipped with pressure build and refrigeration systems and come in large storage capacities for 60 and 70 tonne options [154], [155]. The larger capacity and temporary storage capabilities of portable CO₂ storage fleet units sets them apart from the rest of the smaller scale options and makes them competitive for large scale transportation of CO₂.

6.6 Chapter 6 Conclusions

CO₂ transportation can be grouped into onshore and offshore transportation. The onshore transportation options are pipelines and track and railway tanker carriers. Offshore transportation offers the options of ship tank carriers and offshore pipelines. Each type offers certain advantages according to the situation that is applied.

Onshore transportation

The conventional means of CO₂ transportation is pipelines because they can carry large flowrates of CO₂ for large distances. It takes place in the dense phase, liquid or preferably in supercritical fluid phase, above 71.3 bar and between -10° C and 25°C. Pipeline transportation is the most researched, reliable, efficient and tested technology for years, driven by EOR, and it is easier to build or use

existing infrastructure and find information on policies. Additionally, costs can be estimated more accurately as there are many models available in literature, which follows on the next chapter.

Truck tankers are the conventional way of pure CO₂ transportation for the food industry as they serve that purpose better because of lower volume demand. The research for transportation of captured CO₂ using truck tankers is still under development but information for procedures, policies and costs can be drawn from the food industry as the two processes are similar. Specially designed tanks are available in portable storage tanks with pressure build and refrigeration systems in 60 and 70 tonne capacities that store CO₂ at 24 bar between –40 and 93.3°C. On the other hand, CO₂ transportation using railroad tankers has not been applied before and there is almost no literature about it. Although it is possible and specially designed tanks exist, this option is limited by the access of source and receiver to the railroad network, if they are linked and the if the required capacity for CO₂ transportation can be supported by the railroad.

Offshore transportation

 CO_2 transportation by ship takes place in the liquid phase and the optimal transportation conditions range from 5.18 bar and -56.6°C to 26 bar and -10°C. Ship transportation is a multistage process that prepares CO_2 and stores it temporarily before is loaded to the ship and after it is unloaded. Previous examples of CO_2 ship transportation show that ships have a 1.8 Mt_{CO2} capacity and it has been used in the past to transport CO_2 at much smaller scale in the range of 2-3 Mt/yr for the beverage and food industry.

Offshore pipelines are not as developed and mature as onshore pipelines, but they are similar to hydrocarbon pipelines, and they cost 40 to 70% more than onshore pipelines because they are placed and designed for greater depths. Transportation via offshore pipelines starts to be competitive at large transportation distances for 250 km and 3 Mt/y up to 400 km and 9 Mt/y because ship transportation is more expensive over such distances and flowrates. Ship transportation on the other hand is considered to be more flexible as it can easily adapt to changes in volume, location and be repurposed when the project ends.

Onshore pipelines have the most application examples and therefore are the most researched means of CO₂ transportation. The Dynamis project provides recommendations for minimum CO₂ concentration and maximum impurity limits for pipeline transportation.

The recommendations do not necessarily apply to all capture technologies and all means of transportation. Due to the lack of other studies focusing on the rest of the capture technologies and

transportation means to this extend, for the scope of this project it will be assumed that it applies to all other types of capture technologies and transportation.

In this chapter, transportation has been assessed in terms of technological options and conditions, but the search for the optimal transportation option for each specific situation continues in the next chapter, which addresses the factor of cost in the process for the selection of the optimal CO₂ transportation type.

Chapter 7: The cost of CO₂ Transportation

7.1 Introduction

In Chapter 6 the available transportation methods with their respective conditions and procedures were presented. This chapter builds upon this information to discuss and present the available corresponding transportation cost models from literature, to aid with the planning and development of CCU value chains. Similar to Chapter 5, cost models can help choose the most economical route and transportation method, when it is not obvious if a source should be matched with one or multiple receivers. For this to become possible, transportation cost estimation models available from literature have been reviewed to identify the available cost models and, amongst the available models, one model for each transportation method is selected, to provide quick and reliable low-resolution solutions.

7.2 Pipeline cost

Knoope [156] performed a state-of-the-art review for 14 techno-economic models that predict the cost for CO₂ transportation using pipelines by either relating pipeline diameter or mass flowrate to costs. The 14 models were found to produce inconsistent predictions for a fixed diameter of 0.76 m with large differences for capital and levelized costs in the range of 0.6-1.6M€₂₀₁₀/km. The large discrepancies were attributed to one or a combination of the following factors: topographic conditions, geographical regions, assumptions used for project lifetime, interest rate and capacity factor, materials used (coating steel, insulation), level of detail and additional costs for auxiliary equipment, presented in Table 55. Similarly, to the capture cost model development in Chapter 5, the review identified the characteristics and assumptions of each of the models and further categorized them in five groups: (i) linear cost models, (ii) models based on the weight of the pipelines, iii) quadratic equations, (iv) CMU models and (v) models based on flowrates (Table 55). The models were then analysed by plotting graphs of cost against the outer diameter and against the mass flow for two different lengths and three different mass flowrates according to: (a) which variable they relate costs to, (b) pipeline diameter or (c) mass flowrate, as shown in Table 56 [156]. The three mass flowrates are 50, 150 and 750 kg/s and they are named DEMO, COM and TRUNK respectively (Table 56). The review also provides an analysis for models used to predict the O&M costs of pipelines, O&M costs of pumping stations and capital costs of pumping stations.

Table 55: Factors affecting the capital cost of pipelines [156]

Factor	Example
Topographic conditions	Terrain
Geographical regions	Labour, right of way
Assumptions used	Project lifetime, interest rate, capacity factor
Materials used	Type of steel, coatings, insulation
Level of detail	
Kind of costs incorporated	Compressors, pumping stations etc

Table 56: Analysis of models

Plot	Diameter	Length	Mass Flow
	(m)	(km)	(kg/s)
Cost vs outer diameter	0.1-1.3	25	50
			150
			750
Cost vs mass flow	-	25	0-800
	-	300	

7.2.1 Linear cost models

The review identified three linear cost models for the cost estimation of CO₂ pipelines, [157], [158], [159] and they all use a linear cost relationship of the following form (equation 37):

$$I = C \times D \times L \times F_T \times F_C \times F_R \tag{37}$$

where I is the investment cost (\in), C the constant cost factor (\in /m²), D is the diameter (m), L the length of the pipe (m), F_T is a correction factor for different terrains, F_C is a correction factor for following or not following corridors, and F_R is a correction factor for different regions.

Each model uses different values for the constant cost factor derived from their own estimations and use different correction factors based on the characteristics of the pipeline to be build [156].

7.2.2 Models based on the weight of the pipelines

The first cost model to relate the investment cost of CO₂ pipelines to the weight of the pipeline was developed by Gao et al. (2011) for China and is illustrated by Equation 38 [160].

$$I = W_{steel} \times \frac{P_p}{f_m}$$
(38)

where *I* is the investment cost (\in), W_{steel} is the weight of the pipeline (kg), P_p is the price of the steel pipeline (\notin /kg) and f_m is the fraction of material cost in the total pipeline costs.

Equations 39 and 40 are used to calculate the weight of the pipeline (W_{steel}).

$$W_{steel} = 0.02466t \times (OD - t) \times L \tag{39}$$

where OD is the outside diameter of the pipeline (mm), *L* is the length of the pipeline (m) and *t* is the wall thickness of the pipeline (mm) estimated using Equation 40

$$t = \frac{p_{max} \times OD}{2 \times S \times F \times E} \tag{40}$$

where *t* is the wall thickness of the pipeline (mm), p_{max} is the maximum operation pressure of the pipeline (15.3 MPa), OD is the outside diameter of the pipeline (mm), *S* is the minimum yield stress (483 MPa), *F* is the design factor (0.72) and *E* is the longitudinal joint factor (1).

The model can be used for other parts of the world, if it is adapted to the characteristics of a certain region. For example, the fraction of material costs for the Chinese market is 50%, but when it is adapted for the USA market it decreases between 22 and 34% because of higher labour costs.

Another weight-based model developed by Piessens et al. (2008) uses a more detailed estimation of pipeline investment costs for the materials, illustrated by Equation 41, and three additional components for cost of labour, right of way and damages, and miscellaneous costs [161]. The model of Piessens et al. (2008) is shown by equation 42:

$$I_{material} = L \times St \times FP \times \left(\frac{\pi \times 7,850}{4}\right) \times (OD^2 - (OD - t^2))$$

$$-16 \times OD \times \ln(L) \times L$$
investment set for the metariclused
(41)

where I_{material} is the investment cost for the material used

 $I = I_{material} + I_{Labour} + I_{Row \& damages} + I_{Miscellaneous}$ (42) where $I_{material}$ is the investment cost of material, I_{Labour} is the investment cost of labour, $I_{Row \& damages}$ is the investment cost of right of way and damages, and $I_{miscellaneous}$ is the investment cost of miscellaneous costs

Pipeline thickness is used only by weight-based models.

7.2.3 Quadratic equations

A study of the onshore and offshore transportation of CO₂ using pipelines by the IEA GHG report 2002 considered three types of carbon steel and developed the following model shown by equation 43 [156], [162].

 $I = (a_1 \times L + b_1 + (a_2 \times L + b_2) \times OD + (a_3 \times L + b_3) \times OD^2) \times F_T \times F_R$ (43) where *I* is the investment cost (M \in_{2010}), a_1 , a_2 , a_3 , b_1 , b_2 and b_3 are constants, *L* is the length (m), *OD* is the outer pipeline diameter (m), F_T is a correction factor for different terrains and F_R is a correction factor for different regions.

Parker [163] focused on assessing the costs of hydrogen infrastructure by analysing the construction costs of natural gas, oil and petroleum pipelines. Parker [163] developed equations for estimating the investment cost of each category involved, materials, labour, right of way and miscellaneous costs and, by adding them, developed an equation for the total investment costs (equation 44). The analysis of Parker was later used in the cost assessment of CO₂ pipelines by other papers [164], [165].

 $I = (996,820 \times D^2 + 441,912 \times D + 223,522) \times L + 545,537$ (44) where *I* is the total investment cost (ξ_{2010}), *D* is the diameter (m) and *L* is the length (km)

7.2.4 CMU (Carnegie Mellon University) model

McCoy and Rubin [143] developed a model that estimates the total construction costs (total investment) of CO₂ pipelines by formulating individual cost estimation equations for cost of material, labour, right of way and miscellaneous costs, for various regions. The model is illustrated by equation 45.

$$I = bL^{a_6} \times D^{a_7} \times a_8 \tag{45}$$

where I is the total construction costs (\in_{2010}), L is the length (km), D is the diameter (m), a_6 , a_7 , a_8 are constants for each cost category and b is calculated using equation 46

 $\log(b) = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_5X_5$ (46) where a_{0-5} are constants for each cost category and X_{1-5} are binary values for one of the USA regions used in the study

7.2.5 Models based on flowrates

The review identified six models that are based on mass flowrates [156]. The first one was a model developed for predicting the costs of onshore CO₂ pipelines, which assumed a linear relationship between the cost of onshore CO₂ pipelines and length and diameter and analysing data using linear regression, shown by equation 47 [166]. The model was later updated by Dahowski et al. (2009) (equation 48) using more recent data to develop cost supply curves in China [167].

$$I = 68,719 \times m^{0.5} \times L \tag{47}$$

$$I = 77,854 \times m^{00.4055} \times L + 595,704 \tag{48}$$

where *I* is the investment cost of onshore CO₂ pieplines (\in_{2010}), *m* is the mass flowrate (kg/s) and *L* is the length of the pipeline (km).

Ogden et al. (2004) used data from Skovholt (1993) on investment cost estimations for onshore CO₂ pipelines for various pipe diameters. By analysing the series of processes involved in the production of H₂ with CCS, they derived an equation for the estimation of capital cost of CO₂ pipelines as a function of diameter. The equation was then reformulated to depend on mass flowrate and length, shown by equation 49 [156].

$$I = C_0 \times \left(\frac{m}{m_0}\right)^{0.48} \times \left(\frac{L}{L_0}\right)^{0.24} \times L$$
⁽⁴⁹⁾

where *I* is the investment cost (\in), C_0 is the base cost per unit (1052 \in_{2010} /m), *m* is the mass flowrate (kg/s), *L* is the length (m) and L_0 and m_0 are the length and mass flowrate base cases equal to 100,000 m and 185 kg/s respectively.

McCollum and Ogden [164] used the average of six models to propose a new model that predicts the investment cost of onshore CO₂ pipelines and eliminates the factor of pipeline diameter in the equation to become equation 50.

$$I = 24.7 \times m^{0.35} \times L^{1.13} \tag{50}$$

where *I* is the investment cost (ε_{2010}), *m* is the mass flowrate (kg/s) and *L* is the length of the pipeline (m)

Serpa et al. [162] used the previously mentioned quadratic equation model developed by the IEA GHG report (2002), simplified it by making assumptions and substituting an equation containing mass flowrate for OD, to develop a model for estimating the investment costs of onshore CO₂ pipelines Equation 51.

$$I = (\beta m^{\gamma} + a_0) \times F_T \times L \tag{51}$$

where *I* is the investment cost ($M \in_{2010}$), a_0 is a constant, F_T is a correction factor the terrain type, *L* is the length (km), *m* is the mass flowrate (Mt/y), γ is the mass flowrate exponent, and β is calculated using equation 52.

$$\beta = \alpha_1 \times \left(\frac{8 \times f_{Darcy} \times L}{\rho \times \pi^2 \times \Delta P}\right)^{\frac{2}{5}}$$
(52)

where f_{Darcy} is the Darcy friction factor, ρ is the density (kg/m³) and ΔP is the overall pressure drop (Pa)

Chandel et al. [165] used the Parker [163] model to develop a mass flow-based model to estimate the levelised cost of CO₂ pipelines per tonne of CO₂ transported which includes capital costs, energy costs, O&M costs and all the costs associated with required pumping stations. They estimated the costs for varying diameter sizes and pipeline lengths to construct a mass flowrate-based equation, Equation 53 [156].

$$LC = L \times e^{-3.47 + \frac{35.8}{m} - 0.17 \times \ln(m)}$$
(53)

where *LC* is the levelized cost of onshore CO₂ pipeline per tonne CO₂ transported (\leq_{2010}/t), *L* is the pipeline length (km) and *m* is the mass flowrate (kg/s).

7.2.6 Conclusions

The literature review on pipeline cost models showed that there are five groups of pipeline models, which show large discrepancies between them that are attributed by one or a combination of the several factors. Linear cost models require many correction factors and diameter calculation. Models based on the weight of pipelines use many factors that are influenced by the region that the pipeline is applied and require diameter calculation too. Models based on quadratic equations use many

constants, correction factors and diameter calculation. The CMU model uses many constants and requires diameter calculation. Correction factors, constants and diameter make the cost estimation tedious and complicated to be calculated for such purposes. On the other hand, models based on flowrates require only the length of the pipeline and flowrate, which are both straightforward parameters that can be obtained effortlessly from supply and demand and location of CO₂ sources and receivers.

7.3 Model comparison and model selection

Following the above conclusions, Knoope [156] has also presented a review of equations for diameter calculation for the models that rely on diameter directly. All the reviewed cost models, except models that relate pipeline weight to costs, underestimate the CO₂ pipeline investment cost, mainly because cost models use as their basis natural gas pipelines, while CO₂ pipelines have higher material requirements, and most cost models are based on pipelines constructed in the 1990s and early 2000s. The various models cost estimations are also inconsistent with each other due to different factors as explained earlier.

7.3.1 Capital costs model selection

Knoope [156], after a general cost comparison of the cost estimation models for pipelines, states that it is not straightforward as to which of the models is best to use for cost comparison, but suggests linear and weight-based models, because they are the only ones that include parameters that have physical or economic meaning. Weight-based models produce the most accurate results because they are based on the cost of natural gas pipelines and the rest of the models produce underestimated estimations. The models were further compared to diameter-based models and mass flow-based models.

Having in mind the purpose of this PhD thesis, which is the optimisation of CCU value chains (and not a model which predicts pipeline costs more accurately), the question still remains: "Which model should be chosen to best serve the purpose of this PhD research?". Apart from weight-based models, the rest have been developed by fitting data to obtain the highest R² value (similar to the approach followed in Chapter 5). Amongst these models, the mass flowrate models, and specifically the models developed by Dahowski et al. [166], Dahowski et al. [167] and McCollum and Ogden [164], are the most straightforward ones because they require only the mass flowrate and length of the pipeline, and the pipeline diameter is not needed. Although this means that it is difficult to find out what assumptions have been used for pressure drop, temperature, roughness height, pipeline diameter etc and, as a consequence, it is not possible to tailor the design to a specific situation, the Dahowski et al. [166] model has other merits that are applicable in the way that cost estimations are going to be used in the scope of the case study. The biggest advantage is that the only two parameters needed for the pipeline cost estimation are mass flowrate and pipeline length, which will be specified by the case study, so the calculation is straightforward. As mentioned before, pipeline cost models in general underestimate costs and the Dahowski et al. [166] model has the highest cost estimations, when compared for 25 km pipeline between 0 and 800 kg/s, and the second highest cost estimations when compared for 300 km pipeline between 0 and 800 kg/s. It also shows linear relation with respect to length, meaning that costs increase with length of pipeline, while data show that between 0 and 50 km costs decrease with length of pipeline. Thus, this model might overestimate cost that will compensate with the general trend of models that underestimate cost. However, this is not true after the pipeline has exceeded a length of 50 km. For the reasons stated above the Dahowski et al. [166] is chosen for capital cost pipeline estimation in the scope of this research.

 $I = 68,719 \times m^{0.5} \times L$ (54) where *I* is the investment cost of onshore CO₂ pieplines (ξ_{2010}), *m* is the mass flowrate (kg/s) and *L* is the length of the pipeline (km).

7.3.2 O&M costs of CO_2 pipelines

The study of Knoope [156] shows that several studies developed ways of accounting for CO₂ pipeline operating and maintenance cost. Some use a fixed amount regardless of the pipeline specifications, one study developed a linear model, but most studies use a percentage of the capital costs to account for operating and maintenance costs in the range of 1.5% to 4%. For the scope of this study, a percentage of 4% of the capital cost will be used, because it is a straightforward calculation and will provide the highest cost estimation. If the cost estimation provides the highest cost, then when CO₂ is sold it would produce less profit, and if the route is profitable the likelihood of the route to be viable increases.

7.3.3 Capital costs for pumping stations

Knoope [156] identified and reviewed five models from literature for the estimation of pumping station capital costs and five models for the estimation of operating and maintenance costs of pumping stations.

IEA GHG [162] and Chandel et al. [165] developed models that relate the capacity of the pumping station in MW_e to the capital cost which are illustrated by equations 55 and 56. This type of model

will require the inlet pressure, pressure drop across the pipeline and distance between pumping stations respectively.

$$I_{pump} = (W \times 12 + 0.71) \times 10^6$$
(55)

$$I_{pump} = (W \times 23 + 0.15) \times 10^6 \tag{56}$$

where I_{pump} is the capital cost of the pumping station and W is the capacity of the pumping station (MW_e).

The other three models use a fixed amount of capital cost either expressed in $M \in_{2010}/MWe$, $M \in_{2010}/200$ km or just $M \in_{2010}$ per project. The model of Element Energy [159] uses an estimation of 5 $M \in_{2010}/MWe$ with an uncertainty of 0.8-8 $M \in_{2010}/MWe$. Wildenborg et al. [168] propose an estimation of 50 \in_{2010}/m and 10 $M \in_{2010}/200$ km. Piessens et al. [161] use a fixed capital cost 38.6 $M \in_{2010}$ regardless of the magnitude of the project, number of pumping stations and required capacity of pumping stations [161].

Since simple mass flowrate models will be used for the estimation of capital costs of CO_2 pipelines, and the calculation of diameter was omitted to obtain robust answers without compromising accuracy, for the purpose of this study the only model to be considered will be the model of Wildenborg et al. [168]. This model is robust, since it does not require the conditions of the pipeline, and flexible, because it states that a pumping station will be required after 200 km with a capital cost of 10 M \in_{2010} and a capital cost of 50 \in_{2010}/m for the remaining length of pipeline if it does not exceed 200 km.

7.3.4 Operating and maintenance costs for pumping stations

O&M costs for pumping stations are split to fixed O&M costs and energy costs. O&M costs are usually expressed as a percentage of capital cost in the range of 1.5-5%. The energy costs vary with time because they are affected by electricity price, hours of operation and the amount of electricity the pumping station consumes [156]. Most of the models presented in Section 7.3.3 use equation 55 to estimate energy costs and equation 57 to estimate the capacity of the pumping station required by equation 57, but all use slightly different values for density, efficiency and pressure difference [156]. Piessens et al. [161] use a different set of equations to estimate the size of the pumping station that takes into account the potential energy difference between the inlet and outlet streams:

$$W = \frac{m}{\rho} \times \left(\frac{P_{final} - P_{cut-off}}{\eta_{booster}}\right)$$
(57)

where W is the capacity of the pumping station (MW_e), m is the mass flowrate (kg/s), ρ is the density of captured CO₂ (kg/m³), P_{final} is the outlet pressure of the pumping station, P_{cut-off} is the inlet pressure of the pumping station (MPa) and η_{pump} is the pump efficiency.

For the scope of this study the cost of energy of pumping stations will be omitted to reduce the amount of case specific information required. To compensate for its absence a 5% of the capital cost (highest % used in literature) will be used to account for the O&M cost of pumping stations.

7.3.5 Conclusions

For the scope of this thesis, which is to provide quick and reliable low-resolution solutions to facilitate the optimisation and development of CCU value chains, the most straightforward and not underestimating cost estimation models were selected. For the capital cost estimation of pipelines, the model of Dahowski et al. [166] was selected, which is a simple but effective model that omits the calculation of the pipeline diameter and uses only the transportation distance and flowrate of captured CO₂. For pipeline O&M costs, a percentage of 4% of the capital pipeline cost is assumed, which is a straightforward calculation that estimates the highest cost. For the capital cost of pumping stations, the model of Wildenborg et al. [168] was chosen, which recommends 50 ϵ_{2010} /m and 10 M ϵ_{2010} /200 km. For the O&M costs of pumping stations a percentage of 5% of the capital cost of pumping stations will be assumed which accounts for the highest O&M costs from literature.

Pipeline capital costs

$$I = 68,719 \times m^{0.5} \times L \tag{58}$$

where *I* is the investment cost of onshore CO₂ pieplines (\leq_{2010}), *m* is the mass flowrate (kg/s) and *L* is the length of the pipeline (km)

Pipeline O&M costs

$$PO\&M = I \times 0.04 \tag{59}$$

where PO&M is the annual O&M cost for onshore pipelines (€2010/yr)

Pumping stations capital cost if pipeline is larger than 200km

$$PS = 1000L \times 50 \tag{60}$$

where *PS* is the investment cost of CO₂ pipeline pumping stations (\in_{2010}) and *L* is the length of the pipeline (km)

Pumping stations O&M costs if pipeline is larger than 200 km

$$PSO\&M = PS \times 0.05 \tag{61}$$

where PSO&M is the annual O&M cost for pipelines pumping stations (ε_{2010} /yr)

The above cost models are expressed in constant ξ_{2010} . To convert and standardize the cost models to ξ_{2018} the cost models must include an extra factor that multiplies the estimated value by a conversion factor. The conversion factor is obtained using the currency data available from the World Bank, found in the Appendix section 2 Table 113 [120]. ξ_{2010} are first exchanged to ξ_{2010} and then inflated to ξ_{2018} . The conversion factor for the above models becomes 1.527 (to exchange from ξ_{2010} to ξ_{2010} divide ξ_{2010} by 0.754, to exchange from ξ_{2010} to ξ_{2018} multiply by (117.579/100)).

7.4 Shipping Cost

Only a few sources in literature were identified mentioning CO₂ shipping costs and they did not expand to explain in detail the method used to estimate cost, but they rather focused on presenting assumptions and generic values that used in their cost estimation and comparing shipping costs to other means of CO₂ transportation.

Only one study focused on explaining the method of cost estimation, which performed a literature review and gathered data of each individual shipping process from previous CO₂ shipping projects, compared and analysed them to develop a model for estimating shipping costs [169].

Shipping costs are not as straightforward as other transportation costs because shipping of CO₂ happens in multiple steps. The various costs involved with their respective steps are i) liquefaction, ii) temporary storage, iii) loading and unloading, iv) ship cost and v) gasification. It was found that pressure and ship capacity are the most influencing factors for ship transportation. Liquefaction costs and gasification costs increase with decreasing inlet pressure and temporary storage costs and ship costs increase with higher transportation pressures. The higher the transportation capacity the higher the cost because larger equipment will be required. Distance only influences operating and maintenance costs because it only increases fuel consumption.

7.4.1 Shipping cost review

For the estimation of shipping CAPEX, Kang et al. [170] used Aspen HYSYS to estimate liquefaction costs, input from oil tankers to estimate ship construction costs and manufacturing and material costs to estimate temporary storage tank costs [170]. For the estimation of annual OPEX a percentage of 5% of CAPEX was assumed. Gao et al. [160] only considered the CO₂ tanker cost and assumed 70M RMB for a 3,600 m³ ship and 6.5M intermediate storage of 3,000 m³ tanks for CAPEX. For OPEX a percentage of 4.7% of the CO₂ was assumed. ZEP 2011 does not mention any details on how the cost was estimated, but only some assumptions for the ship cost, interest rate and project lifetime for CAPEX and some assumptions for OPEX.

Kjarstad et al. [171] presented a cost comparison between ship and pipeline CO₂ transportation [171]. The data are presented in Figure 42 and Figure 43, illustrating the cost in ϵ/t_{CO2} for distances between 50 and 500 km, and cost in ϵ/t_{CO2} between 300 and 1200 km for annual volumes of 0.5, 1, 2, 5, 10 and 20 Mt_{CO2}. It can be observed from the figures that the cost of CO₂ shipping decreases at larger volumes and is not affected by distance except between 300-400 km, 600-700 km and 1000-1100 km [171]. ZEP [172] presented a cost comparison between offshore, onshore pipeline and ship CO₂ transportation. The data are illustrated in Table 57 and

Table 58 and show the transportation cost of CO_2 in \notin/Mt_{CO2} for 180, 500, 750 and 1500 km for 2.5 and 20 Mt_{CO2}/a . It can be observed that the cost decreases with increasing amounts of CO_2 and that it almost stays constant with increasing distance, confirming the observations made from the previous reference. Therefore, it can be concluded that ship transportation cost decreases at higher transportation capacities and that distance is not a big factor for ship transportation.



Figure 42: Cost profile (in €/tCO2) as a function of distance for pipeline and ship transportation [171]



Figure 43: Cost profile (in \notin /tCO₂) as a function of distance for pipeline and ship CO₂ transportation [171]

The few examples of cost comparison above do not provide a satisfactory level of shipping cost estimation. Element Energy [169] is the only study that analysed the costs of shipping CO₂ for each individual process of the CO₂ shipping chain as explained in ship transportation literature review. The study presents various references from literature that report cost estimates for every process of the shipping chain for capital expenditure (CAPEX), operational expenditure (OPEX) and energy requirements sections. The methodology and conclusions for cost assumptions that were used in the model are presented in the following section.

Table 57: CO_2 transportation cost comparison for 2.5 Mt/a for onshore pipelines, offshore pipelines and ship in \notin /MtCO₂ Adapted from: [172]

Distance (km)	Onshore pipeline	Offshore pipeline	Ship	Liquefaction (ship)
180	5.1	9.3	8.2	5.3
500	n.a	20.4	9.5	5.3
750	n.a	28.7	10.6	5.3
1500	n.a	51.7	14.5	5.3

Table 58: CO_2 transportation cost comparison for 20 Mt/a for onshore pipelines, offshore pipelines and ship in \notin /MtCO₂ Adapted from: [172]

Distance (km)	Onshore pipeline	Offshore pipeline	Ship (with liquefaction)
180	1.5	3.4	11.1
500	3.7	6.0	12.2
750	5.3	8.2	13.2
1500	n.a	13.2	16.1

7.4.2 Liquefaction

For liquefaction cost, it was found that the cost is a function of transportation pressure. It increases with decreasing pressure and increases even more if CO₂ is not pre-pressurized. This is illustrated by Table 59 which shows the cost estimates from literature presented by Element Energy [169] for CAPEX along with Specific CAPEX £/tCO₂year, fixed annual OPEX as percentage of CAPEX and energy requirements per tonne of CO₂ liquified kWh/tCO₂ for various transportation pressures, inlet pressures and mass flowrates.

Table 60 shows the cost assumptions used in the Element Energy (2018) model for transport pressure, inlet pressure, specific CAPEX, fixed annual OPEX and energy requirements.

Transport	Inlet pressure	Flowrate	Capex	Specific CAPEX	Fixed OPEX/y	Energy
pressure	(bar)	(Mtpa)	(M£)	(£/tCO ₂ /a)	(%of CAPEX)	(kWh/tCO ₂)
Low P	2	1.1	18.4	16.8	N/A	80.3
Low P	2	1.1	19.1	17.4	N/A	80.2
Low P	2	1.1	23.1	21.1	N/A	143.2
Low P	2	1.1	22.6	20.6	N/A	87.0
Low P	1.8	1	21.3	21.3	N/A	130.5
Med P	1.8	1	16.6	16.6	N/A	104
High P	1.8	1	10.6	10.6	N/A	88
Low P	1	10	N/A	N/A	N/A	106.3
Low P	70	0.8	6.3	7.9	N/A	N/A
Low P	70	0.8	9.9	12.4	N/A	N/A
Low P	75	3	27.2	9.1	10%	42
Low P	100	10	N/A	N/A	N/A	17.3
Low P	100	6.2	23.7	3.8	5%	14.4

 Table 59: Liquefaction cost estimates from literature. Adapted from: [169]
 [169]

Table 60: Liquefaction cost assumptions used in the Element Energy 2018 model. Adapted from: [169]

Transport pressure	Inlet pressure	Specific CAPEX (£/tCO ₂ /a)	Fixed OPEX/y (%of CAPEX) (%)	Energy (kWh/t)
Low P	Pre-pressurised	9.8	10	24.6
Low P	Non-pressurised	19.5	10	104.2
Med P	Pre-pressurised	7.6	10	19.6
Med P	Non-pressurised	15.1	10	83.1
High P	Pre-pressurised	4.9	10	16.6
High P	Non-pressurised	9.7	10	70.3

For the scope of this thesis, it is assumed that captured CO_2 will be pre-pressurized as it will be transported up to the temporary storage tanks by pipelines. Additionally, it is assumed that it will be transported at medium pressure around 15 bar, as this pressure was identified by the literature review to be the optimal transportation pressure.

7.4.3 Temporary storage

Element Energy [169] showed that the specific CAPEX (in £/tCO₂) and annual OPEX are a function of storage pressure and they increase with increasing pressure, shown in Table 61 and Table 62. For the scope of this thesis, the medium pressure will be considered in the cost model as it was found to be the optimal transportation pressure (15 bar), as suggested by Element Energy [169].

 Table 61: Temporary storage cost estimates from literature. Adapted from: [169]

Transport pressure	Capacity	CAPEX	Specific CAPEX	OPEX/y
	(t _{CO2})	(M£)	(£/t _{co2})	(%of CAPEX) (%)
Low P	12,310	5.9	482	5
Med P	12,310	9.8	795	5
High P	12,310	37.8	3.073	5
Low P	14,285	12.3	550	5

Table 62: Storage assumptions used in Element Energy 2018 model. Adapted from: [169]

Transport pressure	CAPEX per t _{CO2} of storage capacity	OPEX/y
	(£/t _{CO2})	(% of CAPEX) (%)
Low P	516	5
Med P	795	5
High P	3,073	5

7.4.4 Onshore ship loading and unloading (same cost)

Element Energy [169] showed that onshore ship loading and unloading have the same cost and Table 63 illustrates the annual CAPEX per tonne of CO_2 loaded/unloaded (\pounds_{2017}/t_{CO2} year) and annual OPEX as a percentage of CAPEX reported by literature.

Table 64 shows the annual CAPEX and OPEX that was used in the model of Element Energy [169], the assumptions of which can be used directly as they fit the scope of this thesis.

Table 63: Loading cost estimates from literature. Adapted from: [169]

Flowrate (Mtpa)	CAPEX (M£)	Specific CAPEX (£/(t _{CO2} /a)	OPEX/a (% of CAPEX) (%)
3	8.4	2.8	2
6.2	6.3	1.02	25
8.1	57.0	7.03	2
10	4.6	0.46	1
3	2.6	0.88	1
0.8	0.9	1.07	5
0.8	1.3	1.68	4

Table 64: Loading cost assumptions used in Element Energy 2018 model. Adapted from: [169]

Specific CAPEX	OPEX/a	
(£/(t _{co2} /a)	(% of CAPEX) (%)	
1.4	3	

7.4.5 Ship cost

The data presented by Element Energy [169] show that ship construction CAPEX is both a function of capacity and pressure. Figure 44 shows the data collected by Element Energy [169] from literature in a graph of construction cost (\pm M) for ship capacity in t_{CO2} ranging from 2 Mt to 50 Mt for low, medium and high pressures. Table 65 shows also two models developed to estimate the construction cost for low and medium pressures for capacities between 0 and 60 Mt_{CO2}. Table 65 shows the CAPEX cost data used in the same model, and Figure 45 presents the data for fixed OPEX as a percentage of CAPEX. Table 66 shows the fixed OPEX as a percentage of CAPEX, harbour fees per trip cycle and daily fuel consumption for various ship capacities that were used in their model [169].



Figure 44: Ship CAPEX values from literature [169]

Table 65: Ship CAPEX values use	in Element Energy 2018	model. Adapted from: [169]
---------------------------------	------------------------	----------------------------

Capacity	CAPEX low pressure	CAPEX medium pressure	CAPEX high pressure
(t _{CO2})	(M£)	(M£)	(M£)
2,000	12	26	52
4,000	17	37	74
6,000	21	45	90
8,000	25	52	104
10,000	28	58	117
20,000	42	N.A	N.A
30,000	53	N.A	N.A
40,000	61	N.A	N.A
50,000	69	N.A	N.A

In Figure 45 Element Energy [169] presents the data found from literature for fixed OPEX as a percentage of CAPEX. Table 66 shows the fixed OPEX as a percentage of CAPEX, harbour fees per trip cycle and daily fuel consumption for various ship capacities that were used in their model [169]. As

previously mentioned, CAPEX is a function of ship capacity and pressure, and it was found in the literature review of CO₂ ship transportation that the optimal transportation pressure is 15 bar which close to medium pressure and the only example of previous application was a ship transporting 2 Mt. For these reasons for the scope of this project the data regarding medium pressure and ship capacity of 2 Mt will be used.

Сара	city F	ixed	OPEX/y	Harbour	fees	Fuel consumption
(Mt _{co}	₅₂) (9	%of CAF	PEX) (%)	(£/cycle)		(MWh/d)
2	5			6,486		233
4	5			7,413		240
6	5			8,340		248
8	5			9,267		256
10	5			10,194		263
20	5			14,829		301
30	5			19,464		339
40	5			24,099		377
50	5	j.		28,743		415

Table 66: Ship OPEX used in the model of Element Energy 2018, Adapted from: [169]



Figure 45: Ship fixed OPEX from literature: [169]

7.4.6 Gasification

The gasification cost data used by Element Energy [169] are presented in Table 67.

Table 67: Onshore gasification cost assumptions used in the model of Element Energy 2018 [169]

Transport pressure	CAPEX	OPEX
	(£/(t/a))	(£/t _{co2})
Low P	0.83	0.33
Med P	0.78	0.31
High P	0.5	0.23

7.4.7 Conclusions

Based on the above data, conclusions from the literature review and assumptions stated the following equations can be formulated to estimate capital and operating costs for CO_2 ship transportation.

Liquefaction capital cost = $7.6 \pm 2017/(tCO_2/a) \times (annual flowrate)$

Annual O&M = 10% of capital cost

Energy requirements = 19.6 kWh/tCO₂

Storage capital cost = 795 £₂₀₁₇/tCO₂

Annual O&M = 5% of capital cost

Storage should be 1.2-1.5 time the size of the CO₂ carrier, literature review

Unloading costs = $1.4 \pm \frac{2017}{(tCO_2/a)}$

Annual O&M = 3% of capital cost

Ship construction = $26 M f_{2017}$

Annual Ship O&M = 5% of capital cost

Harbour fees = $6,486 \pm_{2017}$ /cycles

Energy requirements = 233 mWh/day

For 2 Mt and medium pressure

Gasification Capital costs = $0.78 \pm 2017/(tCO_2/a)$

Annual $O&M = 0.31f_{2017}/tCO_2$

For low pressure

Energy requirements were omitted to simplify calculation of cost estimation and because no data on energy requirements per process were available.

Distance was not included in the calculations/equations, since the literature review shows that between 300 and 1200 km the cost of CO_2 per tonne changes only by 5 \in . The assumptions used in

the Element Energy [169] model assume a distance of 600 km. Additionally, the function of distance can be incorporated into the model by including the energy requirements of the ship per day and estimating the number of days for a ship's transportation cycle.

Capital costs = Liquefaction costs + loading/unloading costs + gasification costs + ship construction + Storage

Capital costs = (7.6 + (2×1.4) + 0.78 + (795×2×1.5)) +(26×10⁶)

Capital costs = 2396.16 $\pm_{2017}/(tCO_2/a) + (26x10^6) \pm_{2017}$

$$Total shipping capital costs = 2396.16t_{CO2} + 26 \times 10^6$$
(62)

where t_{CO2} is the annual amount of CO_2 to be transported

Annual Operating and maintenance costs = $((7.6 \times 0.1) + (795 \times 0.05) + (1.4 \times 0.03) + (0.31)) + 26 \times 10^{6} \times 0.05$

Annual Operating and maintenance costs =
$$40.862 \pm_{2017}/(tCO_2/a) + 1.3 \times 10^6 \pm_{2017}$$

Annual
$$0\&M \ costs = 40.862t_{CO2} + 1.3 \times 10^{6}$$
 (63)

where t_{CO2} is the annual amount of CO_2 to be transported

The above cost models are expressed in constant \pounds_{2017} . To convert and standardize the cost models to $\$_{2018}$ the cost models must include an extra factor that multiplies the estimated value by a conversion factor. The conversion factor is obtained using the currency data available from the world bank found in the appendix section 2 Table 113. Pounds 2017 are first inflated to pounds 2018 and are then exchanged to dollars 2018 and the conversion factor for the above models becomes 1.364.

7.5 Alternative transportation cost

7.5.1 Truck tankers

Information for CO₂ transportation using truck tankers can be drawn from the transportation of liquid CO₂ for the food and beverage industry around the world, where it is used for beer and soft drinks production. CO₂ is transported using trucks equipped with specially designed storage units with capacity of 60 and 70 tonnes [154], [155].

Research conducted by Hooper & Murray [173] in the United States collected current real-world data for operational costs of motor carriers by interviewing motor carriers to prepare a high-level benchmarking tool for motor carriers, public sector agencies and transportation impact assessments. The research included data from 178,926 truck-tractors, 4,773 straight-trucks, and 360,434 total trailers and analysed the size of operation, type of operation, equipment, alternative fuels and fuel efficiency. This analysis for operational costs covers the costs of fuel, truck lease or purchase payments, repair and maintenance, insurance premiums, permits and licenses, tires, tolls, driver wages and benefits. The reported total average marginal cost per mile for 2017 was \$1.691 and \$1.05/km when converted to per kilometre [173].

Although the data provided from Hooper & Murray [173] are generic trucking cost data, they were used for the scope of this PhD thesis because there are no other available data for the truck transportation of CO₂ specifically. This decision, therefore, assumes the use of rented trucks fitted with specially designed tanks of 60 tonne capacity. This assumption eliminates capital costs. The operating and maintenance cost for truck tanker transportation will be estimated using the average marginal cost per mile data of Hooper & Murray [173].

Annual cost estimation based on annual flowrate and routes

The annual cost of transportation via truck can be estimated by dividing the annual amount of CO_2 to be transported to the receiver by the transportation capacity of the truck (60 t), which is the number of routes per year, multiplied by the double of the distance (km), accounting for the return trip to the source, multiplied by the transportation cost per km.

$$TO\&M = \frac{t_{CO2}/y}{60t_{CO2}} \times 2D \times 1.05$$
(64)

The above cost model is expressed in constant $$_{2017}$. To convert and standardize the cost models to $$_{2018}$ the cost models must include an extra factor that multiplies the estimated value by a conversion factor. The conversion factor is obtained using the currency data available from the world bank found in the appendix section 2 Table 113. Dollars 2017 are inflated to dollars 2018 and the conversion factor for the above models becomes 1.024.

7.5.2 Railroad tankers

On the other hand, CO₂ transportation using railroad tankers has not been applied before and there is almost no literature about it. Although it is possible and specially designed tanks exist, this option is limited by the access of source and receiver to the railroad network, if they are linked and the available capacity for CO₂ transportation of the railroad. There are no reviewed models for cost estimation, but sources suggest that it is double the price of pipeline transportation. Due to these limitations, this option will not be considered for the scope of this PhD thesis, and where a pipeline option is not competitive, transportation by truck tankers will be considered since it is a similar option with more flexibility on routes.

7.5.3 Offshore pipelines

Offshore pipelines are not included in this research for two reasons: (a) accurate models or data for the development of such models are not available in literature and (b) from the few examples of cost estimations that were found in literature it can be concluded that offshore pipeline transportation offers an alternative to ship transportation with a much higher cost about 50% more when compared to ship transportation with much less flexibility and only competitive at much higher transportation capacities and distance.

7.6 Chapter 7 Conclusions

For the scope of this PhD thesis the available options are onshore transportation using pipelines, and truck tankers and offshore transportation using ship tankers. The conventional means of CO₂ transportation is pipelines because it is the most researched, reliable, more efficient and a tested technology for years. For these reasons it is easier to build or use existing infrastructure and find information on policies. Additionally, costs can be estimated more accurately as there are many models available in literature. For the scope of this research the selected models were chosen in order to provide quick and reliable low-resolution solutions because they are straightforward. The models make high-cost estimations compared to other models from the same category, which compensates for the underestimated estimations compared to the more accurate but much complicated alternatives. The review towards the understanding of CCU value chains continues on the next chapter, where the optimisation problems of CCU value chains are addressed and identified.

Chapter 8: CCU Business Model

8.1 Optimisation problems

The analysis so far gave answers to what CCU value chains can offer and has identified and characterised four fundamental steps (CO₂ source, capture, transportation, receiver/utilisation). The next and last step towards understanding the CCU value chain and finally developing an optimisation method, is to answer how those steps are related to each other from a systemic point of view. In order to do so, previous CCU value chain optimisation approaches were studied, to highlight the relationship between the four fundamental steps through four optimisation problems, which were identified. The aim of this chapter is to present the identified optimisation problems and demonstrate their complexity through the introduction and visualisation of the fundamental steps of CCU value chains in an imaginary potential CCU region. The chapter also highlights how to achieve a holistic optimisation and presents a summary of each of the previous chapters with their respective conclusions and the decisions, which were taken as a final conclusion to start the development of an optimisation approach. The developed optimisation approach is explained through the development, application and validation of an algorithm and business model, in Chapters 9 and 10.

8.1.1 The steps of CCU value chain

The CCU value chain consists of six major steps, CO₂ source, CO₂ capture, CO₂ purification, compression, transportation and utilization or storage, but it can be visualised as having four fundamental steps because capture, purification and compression of the CO₂ stream can be grouped into a single step. This is illustrated in Figure 46.





All the steps mentioned above have been extensively studied in literature in terms of technical and economic characteristics and have also been implemented, demonstrating the feasibility of the CCUS value chain. Patricio et al. [13], Reiter & Lindorfer [174] and Pieri et al. [6] have presented methods

for characterising CO₂ industrial sources. Yan & Zhang [175] presented a state-of-the-art research and development review of CCUS value chains that covers the studies published between 2014 and 2017 [175]. They demonstrate that many papers have been published considering carbon capture (post, pre, oxy, chemical looping), transportation, storage, utilization and even policy and economic assessments and CCUS as a whole. Additionally, they present a table with all the world-wide largescale CCS or CCU projects that were currently operating, were in early development, advanced development or in construction. In the case of the CCS value chain there is no opportunity for large economic profit for the source (except CO₂ tax avoidance), since CO₂ is stored underground and it is not sold as a by-product. On the other hand, CCU value chains can generate profit for sources by selling CO2. A CCU value chain can therefore be considered feasible if CO2 is being utilised and generates profit and can be considered optimised when utilisation and profit are maximised. Wu et al. [176] explain that there are complex interactions between capture, transportation and storage activities within a CCS chain. The interactions are even more complex in the case of CCU, because of the characteristics of each individual receiver. Optimizing a route for a single source and a single receiver has considerably fewer decisions to be made compared to the optimization of a CCU value chain within a region containing many sources and many receivers, each with varying characteristics. The reason is that for a single source and a single receiver, decisions have to be made just between the pre-determined route and then the economic and utilisation performance of the route can be estimated, whereas in the optimization of a region, routes have to be developed based on the regional economic and CO₂ utilisation performance.

8.1.2 Visualizing a potential CCU region

In order to understand the optimisation problems of CCU value chains, one has to first visualize a potential region. A potential region can be thought of as a square with a random number of sources and receivers with different characteristics – sources with different types of CO₂ streams and emission intensities, and receivers with different needs in terms of purity and flowrate. The sources and receivers have also a random distance between them that may or may not be divided by any type of landform like rivers, mountains or even sea. Figure 47 displays an imaginary region with sources (displayed as circles) and receivers (displayed as squares) and uses two classes to portray the required purity of receivers, shaded high purity and non-shaded low purity. The size of circle or square illustrates the size of source or receiver. Chapters 2, 3 and 4 have covered the knowledge required to characterise sources and receivers in terms of type, magnitude and stream purity and

methods to capture and utilize CO_2 for any type of source or receiver. Chapter 6 covers how CO_2 can be transported and Chapters 5 and 7 propose ways that capture costs and transportation costs can be estimated to aid with cost minimization.



Figure 47: Imaginary potential region for CCU application (where circles represent sources, squares represent receivers, shading represents high purity and the size is relative to CO_2 supply or demand

Previous review papers have identified three key questions that hinder the development of CCU value chains [177]

- (i) How should CO₂ sources and sinks be matched?
- (ii) How can the total CCUS network cost be minimized?
- (iii) How can the total CO2 emissions reduction be maximized?

The first question which is the most natural one to ask is about the characteristics of the sources and receivers available in the selected region. Which sources can be matched with which receivers? The second question refers to the cost of CO₂ capture and transportation infrastructure, and how should the CCU network be designed so that the transportation of the selected matches is feasible, covers demand or supply and at the same time minimises costs. The third question is about CCU as a mitigation option asking how the CO₂ emissions can be minimized so that maximum CO₂ utilization is achieved from the region to have maximum CO₂ mitigation results.

8.1.3 Which are the optimisation problems?

The individual optimisation problems exist between each of the four steps of the CCU value chain illustrated above in Figure 46. As Tapia et al. [177] explain, these problems can be thought of as problems related to CO₂ capture, transportation and utilization or storage, and this is what literature was focused on the most. Several models and approaches (which are presented in the next section, Section 8.2) were developed, focusing to optimise selected parts of each problem but each one on its own [177]. The optimisation approaches addressed those problems individually and did not focus on all problems with a single approach. Several approaches for individual problems exist, but not one integrated approach that optimises and supports the development of CCU value chains. Some studies developed methods that focus on more than one problem at the same time but did not attempt to integrate many mathematical models into one that targets all problems simultaneously. The answer to this problem might lie in a multi-stage approach where the output of each model is used as the input of the next one [177].

8.1.4 Capture problem

Carbon dioxide capture technologies are energy intensive processes and for this reason previous CO₂ capture optimisation approaches focused on energy models. These energy models were developed for power plants and aimed at target optimisation from two perspectives: (a) estimating power losses due to CO₂ capture; and (b) minimising power losses due to CO₂ capture. The first type of model estimates how much electricity from the plant is going to be used for capture and the second type focuses on capturing the optimal amount of CO₂ based on sink/receiver availability to minimise power losses. This problem was named the source retrofitting problem [177].

For example, Tan et al. [178] developed a graphical pinch methodology for power plants to determine how much additional power is required for a minimal CCS retrofit, which at the same time ensures that the sectoral carbon footprint is kept within targets. Building on their previous work, Tan et al. [179] developed integer programming models that optimise the planning of carbon capture retrofits by minimising the carbon footprint of a specified sector. The models estimate the additional compensatory power required for the carbon capture retrofit of each plant and estimate their respective additional emissions and emission reductions from the CC retrofit to select which plants are to be retrofitted. The models can also specify which capture technology (oxy-fuel, postcombustion, pre-combustion capture) is to be applied by assigning an aggregated cost limit on the cost of capture and constraints that limit incompatible matches of power plants and capture technologies.

The models developed for this type of optimisation only consider power plants and therefore cannot be used for any of the other sources or, if it is possible to be used, they have to be modified. Most importantly the capture selection procedure, if available at all, lacks in terms of cost estimation, process conditions and performance details. As discussed in Chapters 4 and 5, there are many available options of varying costs and there are compatibility restrictions between certain capture technologies and certain CO₂ sources. One other aspect that this type of model does not consider is the transportation of CO₂ to the available sinks/receivers, which is the second optimisation problem in the CCU value chain.

8.1.5 Transportation problem

The CO₂ transportation problem has been tackled by the available models focusing on pipeline infrastructure, aiming to reduce transportation costs by determining and optimising the network configuration. The result will be a network layout to deliver CO₂ effectively at an optimal transportation cost. This problem was named the transportation infrastructure development problem [177].

For example, Middleton and Bielicki [180] developed a scalable infrastructure model for carbon capture and storage (SimCCS) that focuses on the optimal design of pipeline networks between certain CO₂ sources and reservoirs. The model selects arcs and pipeline capacities to form hubs and routes that minimise construction costs and environmental impact by avoiding areas with higher cost of construction. The SimCCS model has the ability to take advantage of economies of scale, topography and social impact factors. Sun and Chen [181] use a combination of databases and mixed integer programming to design pipeline networks for CCUS projects that take into consideration pipeline topology structure, distance and CO₂ quantity. Databases are responsible for handling source-sink matching, route and hub formation and the mixed integer programming to carbon mitigation targets.

This type of model does not take into consideration technical aspects during the development of the optimised networks, such as operating conditions, climatic conditions or environmental policies or, in the case of storage, the geophysical characteristics of storage reservoirs [177]. Previous CO₂ transportation models also do not consider the other options of CO₂ transportation, which are
discussed in Chapter 6. The alternative methods of transportation can contribute to regional optimisation of CCU value chains by offering lower cost solutions for shorter, lower volume distances as opposed to pipelines. By omitting the inclusion of other transportation options, the optimisation potential of a region is limited in terms of CO₂ utilisation potential and cost minimization.

8.1.6 Utilisation problem

The CO₂ utilisation problem was considered mainly for storage options and was approached by developing models that dealt with the question: "which sources should be matched with which sinks?". The models propose matchings based on the characteristics of sources and sinks, but mainly for power plants and storage reservoirs without considering capture or transportation. The models use characteristics of storage reservoirs, such as the capacity, injectivity rates, injectivity limits, and geographical constraints to schedule CO₂ balances between sources and sinks. The limitation of these models is that they only consider the flowrate and quantity, but they are useful for providing high-level quick insights to source-sink matches before any detailed engineering design. Therefore, this problem was named the source-sink matching problem. Some of these optimisation tools were extended to include a purity constraint for uses other than storage [177].

For example, Tan et al. [182] developed a continuous time optimization model for source-sink matching with the objective to maximize CO₂ emission reduction for power plants by considering the size and lifetimes of sources and sinks. Tapia and Tan [183] developed a fuzzy mixed integer linear program that focuses on regional CO₂ emission reduction between CO₂ sources and geological sinks while at the same time accounts for technical risk associated with uncertainties in sink parameters like storage and injectivity. Mohd Nawi et al. [184]proposed an algebraic pinch analysis method that approaches the source-sink matching problem from the concept of total site CO₂ integration. The concept works by capturing CO₂ of certain purity and distributing it to sinks or CO₂ utilisation facilities based on their purity requirements through one or multiple centralised CO₂ mixing plants.

Although previous utilisation models consider the purity of sources and receivers, they do not consider capture or transportation of CO₂ and make decisions entirely on the purity and availability/demand of sources and receivers. This type of approach can be problematic in the sense that a source and a receiver are allowed to be matched even if they are separated by large distances or even have geographical or technological constraints. This can greatly limit the optimisation of CCU value chains by allowing more possibilities in the matching stage.

8.1.7 Integration problem

Certain optimisation approaches developed models that can address more than one problem at a time. Tapia & Tan [185] developed a model for revamp of source-sink matching, where the process can be updated when new sources or sinks are available. Tan et al. [186] developed a model that integrates the energy planning problems and the source sink matching problem.

Hasan et al. [187] developed a source-sink matching model with simultaneous selection of capture process and materials, transportation, maximising profit and CO₂ utilisation, but for EOR and storage only. Al-Mohannadi et al.'s [188] model addresses source-sink matching and infrastructure development, but with pipelines as the only transportation option and without discussing capture options. D'Amore et al. [189] developed a model focusing on the source-sink matching problem while simultaneously considering various capture technologies and pipeline and ship transportation, but for coal and gas power plants for storage options only. The model also includes societal risks during CO₂ transportation. Lee et al. [190] developed an algorithm that designs an optimal CCS infrastructure from a set of given inputs for power plants with pipelines, ship and track as a transportation option while minimising risk.

In conclusion, although some models managed to integrate more than one of the functions discussed above, they still provide a limited optimisation approach in one way or another, leaving a lot of room for improvement to consider all important aspects of CCU value chain optimisation that can contribute to better optimised solutions.

8.2 Previous optimisation approaches

Tapia et al. [177] wrote a state-of-the-art literature review covering the development of methods for CCUS optimization as a CO₂ management strategy. The literature review presents an overview of CCUS systems and their technological options, planning of CCS, integration of CCU and CCS and the environmental impact of CCU options. The literature review focuses on a discussion about previous CCS and CCU optimisation approaches, including several models, and presents the problems to be solved and the approaches used so far. Tapia et al. [177] demonstrated that in the past, optimisation of CCS and CCU value chains has been approached by pinch analysis, mathematical programming and miscellaneous methods and showed the advantages and limitations of each one. Mathematical programming models have been used to deal with energy models (focusing on energy losses during CO₂ capture), pipeline infrastructure design (economic and technical aspect) and the matching of sources and sinks [177]. Pinch analysis tools have been applied to CCS systems with multiple CO₂

sources, capture technologies and sinks and function by determining the best CCS retrofit, optimal source-sink matching and maximizing CO₂ utilization. Tapia et al. [177] group numerical simulation and P-graph approaches into miscellaneous methods and continue to explain that they were used to investigate the flow characteristics of reservoirs or to optimize injection schemes, and that the p-graph approach has been additionally used in the optimization of source-sink matching [177]. In their review they grouped studies according to their optimisation approach and explained the aspect of the CCS/CCU value chain the study was optimizing.

Similar studies have been published by Tapia et al. [186], Zhang et al. [151], Zhang et al. [191] and d'Amore & Bezzo [189], who reviewed a large number of studies investigating the optimisation of CCS and CCU value chains as part of their approach to develop an optimisation model [186], [192], [193], [191]. Tapia et al. [186] developed a discrete-time mixed integer linear programming (MILP) model that deals with the source-sink matching problem and plans CO₂ utilisation for various EOR projects from a single source. They performed a literature review and studied 25 models that dealt with the source retrofitting problem, transportation infrastructure development, source-sink matching and integration of tools. Those models used mathematical programming, pinch analysis and miscellaneous methods in their optimisation approach. Similarly, Zhang et al. [191] studied 25 previously developed models that dealt with all four optimisation aspects using pinch analysis and mathematical programming approaches. Their output was the development of a MILP that considering sources, capture technologies, pipelines as a transportation medium, storage and utilisation sites and designs CCUS supply chains by minimising costs. Zhang et al. [192] developed a MILP model that targets the optimisation of infrastructure development and more specifically the development of a pipeline network based on the distance and geographical location of the available sources and sinks in the area. They studied nine previous optimisation models that tackle infrastructure development and source-sink matching. d'Amore & Bezzo [193] chose the mathematical approach method utilising a MILP to develop a framework to aid in the design of CCS network by tackling three problems at the same time, capture, transportation and sequestration/storage. The literature review for the development of this model included eight models that focused on the development of transportation infrastructure and integrated tools that focused on more than one problem. Table 68 to

Table 72 present all the available reviewed literature studies on model development by the studies mentioned above (using [171] as a basis and enhanced by [186], [192], [193], [191]). The table shows that, based on the problems listed, there are four aspects/issues of the CCUS value chain that

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literature has dealt with: the retrofitting of sources with the appropriate capture technologies; the development of CO₂ transportation infrastructure to deliver CO₂ effectively to storage areas and receivers; the optimization of source-sink matching; and the integration of individual models to develop a model that has the ability to perform more than one optimization function. Although the following optimisation approaches provide a solution to the problem they address, they have a common disadvantage when it comes to CCU value chain optimisation: the models are too complicated to be integrated and thus not capable to deal with all issues at the same time and provide a single approach towards the optimisation of CCU value chains. Table 68 sorts the optimisation approaches that are related to CO₂ capture, which aim to estimate the optimal amount of CO₂ to be captured. Although it can be useful to know the optimal amount of CO₂ to be captured from each source, there are other more important issues to be solved beforehand, like:

- (i) What are the optimal sources to be considered in terms of technical, economic and emission reduction performance?
- (ii) What is the optimal capture technology in terms of technical and economic performance?
- (iii) What is the optimal transportation method in terms of technical and economic performance?
- (iv)What is the optimal disposal method in terms of technical and economic performance?

Table 69 sorts the optimisation approaches that are related to CO₂ transportation, and it appears to focus mainly on pipelines and storage options. In the context of CO₂ utilisation, it would be useful to have other transportation options to cover a variety of sources, receivers and distances because there are purity and quantity constraints restricting the compatibility of sources and receivers.

Table 68: CO₂ Capture related models

Source	Aspect	Approach
[194]	Early approach for CO ₂ capture in power generation: Taiwan	Mathematical programming models
[195]	Early approach for CO_2 capture in power generation: Greece	Mathematical programming models
[196]	Uncertainty analysis based on energy demand	Mathematical programming models
[197]	Hybrid methods in energy planning	Mathematical programming models
[179]	ILP model for retrofit selection	Mathematical programming models
[198]	Integration of CO ₂ capture with biofuels	Mathematical programming models
[199]	Integration of CO ₂ capture with nuclear energy	Mathematical programming models
[200]	Selecting power plants for CCS retrofitting	Mathematical programming models
[201]	Planning for power plant retrofit	Mathematical programming models
[202]	Power system planning for identifying carbon, cost, land and water footprint	Pinch analysis tools
[178]	Retrofit selection for power generation	Pinch analysis tools
[203]	Automated targeting based on minimum compensatory power requirement	Pinch analysis tools
[204]	Site selection: Analytic network process (ANP)	Miscellaneous methods

Table 69: CO₂ Transportation related models

Source	Aspect	Approach
[205]	Early approach for CO ₂ allocation: Pipeline distribution problem	Mathematical programming models
[180]	Pipeline infrastructure models: SimCCS static framework	Mathematical programming models
[206]	Pipeline infrastructure models: SimCCS Time dynamic framework	Mathematical programming models
[181]	Assessing economics of CO ₂ transportation: Single stage	Mathematical programming models
[207]	Assessing economics of CO ₂ transportation: multi-stage	Mathematical programming models
[208]	Transportation design: pipeline sizing	Mathematical programming models
[177]	Transportation design: operating conditions	Mathematical programming models
[197]	Development of large-scale network infrastructure	Mathematical programming models
[192]	CCS infrastructure in Qatar	Mathematical programming models
[209]	Infrastructure cost minimization in the UK	Mathematical programming models
[210]	Model for the optimal EU-wide transportation network CCS	Mathematical programming models
[211]	Pipeline infrastructure and pressure drop: Site targeting	Pinch analysis tools
[212]	Method for determining the characteristic of an optimal CCS pipeline network	Miscellaneous methods
[193]	Source-sink matching and transportation infrastructure development	Miscellaneous methods
[213]	4-step methodology for estimating length, cost and time framework in CCUS	Miscellaneous methods
	pipeline network development	
[214]	Transportation for CCS deployment: Minimum cost approach	Miscellaneous methods

Table 70: CO₂ Storage related models

Source	Aspect	Approach
[192]	Source-sink matching models considering temporal constraints: discrete time scheduling of storage	Mathematical programming models
[182]	Source-sink matching models considering temporal constraints: continuous time scheduling of storage	Mathematical programming models
[191]	Source-sink matching: injection rate, capacity limitation and temporal constraints	Mathematical programming models
[215]	Source-sink matching models considering temporal constraints: continuous time scheduling of storage	Mathematical programming models
[183]	Accounting for storage uncertainties in CCS	Mathematical programming models
[186]	Accounting for temporal uncertainties in CCS	Mathematical programming models
[216]	Source-sink matching and grid energy balance	Mathematical programming models
[217]	Addressing CO ₂ allocation for each time period for enhanced coal-bed methane recovery	Mathematical programming models
[218]	Source-sink matching in CCS: Single period	Pinch analysis tools
[219]	Source-sink matching in CCS: multi-period	Pinch analysis tools
[220]	Managing CO ₂ storage capacities: Carbon storage composite curves	Pinch analysis tools
[186]	Meeting storage requirements for deep saline aquifers as back up storage: Model	Miscellaneous methods
[221]	Optimum CO ₂ injection scheduling: Extended dynamic model	Miscellaneous methods
[222]	Storage development: Genetic algorithm	Miscellaneous methods
[223]	Source-sink matching: P-graph methodology	Miscellaneous methods
[224]	Source-sink selection: Simultaneous under geographic constraints	Miscellaneous methods

Table 71: CO₂ utilization related models

Source	Aspect	Approach
[225]	EOR scheduling: discrete time	Mathematical programming models
[226]	ECBM injection allocation and scheduling	Mathematical programming models
[227]	Gas field development: CO ₂ quality constraint	Mathematical programming models
[177]	Oil field development	Mathematical programming models
[228]	Novel pinch analysis: Total site carbon planning	Pinch analysis tools
[177]	Total site targeting for CO ₂ utilization	Pinch analysis tools
[229]	Generic carbon cascade analysis (GCCA): analogous to water network synthesis	Pinch analysis tools
[230]	Source-receiver matching using purity constraints	Pinch analysis tools
[231]	Non-dominated sorting genetic algorithm (NSGA): Best Injection scheme with CCS and EOR	Miscellaneous methods

Table 72: Integrated tools

Source	Aspect	Approach
[185]	Revamp framework for CCUS systems	Mathematical programming models
[232]	Integrated framework for CCS: Technical improvements	Mathematical programming models
[187]	Multiscale engineering framework: CCUS supply chain	Mathematical programming models
[233]	Integrated process model: EOR operations	Mathematical programming models
[234]	Carbon integration: Water network design approach in static settings	Mathematical programming models
[188]	Carbon integration: Water network design approach in multi-period settings	Mathematical programming models
[235]	CO ₂ utilisation with heat integration	Mathematical programming models
[189]	European supply chain optimisation for CO_2 capture, transportation and sequestration	Mathematical programming models
[190]	CCS infrastructure programming optimizing trade-off amongs cost, environmental impact and	Mathematical programming models
	downside risk	
[236]	Multiperiod stochastic programming model for CO ₂ capture, transport and storage in Korea	Mathematical programming models
[237]	Updated han and Lee, 2013: technoeconomic, environmental and risk	Mathematical programming models
[238]	CO ₂ management networks: P-graph methodology, genetic algorithms	Miscellaneous methods

8.3 Previous case studies

Consequently, a literature review was performed focusing on published studies that applied the models developed on real life case studies, in order to validate the developed approach, dealing with the CCS and CCU value chain, in order to assess their approach and applications and identify potential gaps in the literature.

8.3.1 Review of case studies

Minh & Hoang Anh [239] used a subset of Howells et al.'s [240] OseMOYSYS model (open-source modelling system for long-run integrated assessment and energy planning), and applied it to two scenarios in Vietnam. The scenarios involved the CO₂ capture from gas and oil-fired power plants in Vietnam and utilisation for EOR using ship. Their study also addresses issues in CCUS such as financial and political barriers, policies and environmental issues.

d'Amore & Bezzo [193] presented a MILP time dependent model for the optimisation of the European CCS supply chain. The model considers capturing up to 70% of available CO₂ for a period of 20 years considering pre- and post-combustion capture technologies for the sources available in the IEA (2002) emission sources database using pipelines and ships for transportation.

Ravi et al. [241] developed a MILP model for the optimization of the CCS supply chain network costs and applied it in the Netherlands for various scenarios. The model considers sources, storage sites and post-combustion capture technologies to develop supply chain networks with minimised total costs.

Arnette [242] modified previous mathematical models to develop a multi-objective optimization model that determines the optimal combination of renewable energy and CCS as a tool for reducing carbon emissions. The case study considers CO₂ capture from coal plants using post-combustion capture technologies and pipelines as a transportation means for storage.

Agrali et al. [243] developed a MIP model for CCS optimization by minimising overall costs. The model is targeted at thermal power plants that operate under the cap-and-trade system and it was applied in Turkey for two power plants with the options of storage, EOR and soda carbonation using pipelines as a transportation option.

Zhang et al. (2018) proposed a MILP model for the optimization of CCUS value chains that integrates selection of CO₂ sources, CO₂ capture, pipeline infrastructure and selection of storage sites and EOR [191]. The model was applied in China and optimizes the value chain by minimising the annualized net cost and therefore assessing the economic feasibility for a selected region.

Wu et al. [176] developed an inexact CCS optimization model that plans CO₂ emission capture, transportation and storage in a region under uncertainty and has the potential to address source-sink matching issues while considering many types of CO₂ sources and storage regions.

Middleton et al. [244] developed a framework for optimizing the CCS value chain pipeline network that can also be used to any network optimization problem. The framework was applied in a case study capturing CO₂ from coal-fired plants and transporting CO₂ to storage sites using pipelines. Tapia et al. [186] proposed a model that combines two MILP models to optimize the capturing of CO₂ and EOR operations, allocating CO₂ to EOR according to supply and source-sink matching considering the injectivity and capacity of sinks. The model considers power plants and natural gas fields for storage using pipelines as a transportation type.

Amit et al. [245] have developed a methodological framework for CCS that was applied in India, which optimizes source-sink matching by identifying CO₂ sources and grouping them in clusters based on their geographical location and annual emissions. The clusters are then matched to a storage location using four different techniques to calculate the optimal storage location based on distance. The cluster-sink matching creates a transportation infrastructure consisting of pipelines which then enables the estimation of transportation costs

d'Amore et al. [189] proposed a MILP model for the design of risk constrained CCS supply chains in terms of total cost minimisation, considering the capture, transport and storage problems. The model was applied in Europe utilising CO₂ from coal and gas-powered power plants for storage using onshore pipelines, offshore pipelines and ships. The model considers risk mitigation measures which they found that it can facilitate the policy makers in their decision-making process.

Santibanez-Gonzalez [246] proposed a stochastic MILP model that aims to minimise the construction, capture, transportation, storage and emission costs. The model was applied in Brazil for the cement industry using pipelines for transportation.

8.3.2 Conclusions

The case study literature review is summarised in Table 73 to facilitate the assessment of the models and conclusions. Table 73 shows that these case studies mainly consider power plants as sources for CO_2 (10 out of 14 consider power plants). From the 14 case studies only six mention what type of capture technology is used and only three consider more than one option. The most common capture technology used is post-combustion capture. From the 14 case studies, 13 include pipelines as a transportation option, three consider ship as well and only one truck tankers. Out of 14 case studies, 13 mainly consider storage and only six consider EOR as well. The only two that offer more utilisation options are Argali et al. [243], which also considered beverage carbonation, and Mohd Nawi et al. [184], which considered beverage carbonation, EOR, methanol production and a chemical plant (no more information is available).

Therefore, it can be concluded that certain gaps exist in the previous optimisation approaches and case studies. The gaps lie in the limited options for CO₂ sources, capture technologies, types of transportation and utilisation, and this produces models with limited optimisation potential. It is clear now that a model that can truly develop value chains with minimised costs and maximised utilisation must consider all available options for every step of the value chain, and such a model has not been identified in literature so far.

Table 73: Case study litarature review

Reference	Year	CCU/ CCS	Type of sources	Type of receivers	Capture technology	Transportation	Approach	Case study	Region	Eco.Ass	Envi.Ass.	Social.Ass	Policies
[247]	2017	CCS	Coal, gas, oil, cement, steel, refinery, fertilizer	Storage	Skips	pipeline	Computation al method	Yes	India	-	-	-	-
[193]	2017	CCS	IEA (2002) and JRC 2016 databases	Storage	Post, pre, oxy	Pipeline, ship	MILP	Yes	Europe	Yes	-	-	Yes, Slightly
[189]	2018	CCS	Coal and gas power plants	Storage	Post, pre, oxy	Pipeline, ship	MILP	Yes	Europe	-	-	Societal risk	-
[241]	2017	CCS	Netherlands Government's pollutant release database	Storage	Post	Pipeline	MILP	Yes	Netherlands	Yes	-	-	-
[242]	2017	CCS	Coal plants	Storage	Post	Pipeline	Multi- objective	Yes	Appalachianmo untain.region	Yes	-	-	-
[244]	2012	CCS	Coal-fired plants	Storage	Suitable for coal, not mentioned	Pipeline	MIP	Yes	US Midwest	-	-	-	-
[246]	2017	CCS	Cement	Storage	Skips capture part	Pipeline	SMILP	Yes	Brazil southeastern	Yes	-	-	-
[243]	2018	Both	Lignite-fired power plants	Storage, EOR, soda	Skips	Pipeline	MIP	Yes	Turkey	Yes	-	-	-
[191]	2018	Both	Coal-fired power, cement, iron & steel	Storage, EOR	Post combustion	Pipeline	MILP	Yes	China, northeastern	-	-	-	Yes
[176]	2015	CCS	Coal, gas fired plants, IGCC, coal to Chemicals/gasification liquids, oil refinery, iron & steel, cement	Storage, EOR	Post, oxy, pre, industrial separation.	Pipeline, tanker truck.	ICCSM(inexac t optimisation model)	Yes	China	Yes	-	-	-
[186]	2016	CCUS	Power plants, natural gas fields	Storage, EOR	Skips	Pipeline	MILP(continu ous)	Yes	Adapted from elsewhere	-	-	-	-
[248]	2018	Both	Power generation, coal, chemical, oil and gas	Storage, EOR	Skips	Pipeline	Business model	Yes	China	Yes	-	-	Yes
[239]	2017	Both	Coal, gas	EOR	Skips	Pipeline, Ship	Model/scenar ios	Yes	Vietnam	-	Slight env.impa ct assess.	stakehol ders	Yes
[228]	2015	CCUS	NG, coal, refinery, oil	Beverage, methanol, EOR, chemical plant	Skips	skips	Algebraic pinch analysis	Yes	Hypothetical	-		-	-

8.4 The CCU business model

8.4.1 The business model approach

Alternatively, Yao et al. [248] have approached CCUS as a business opportunity instead of a mathematical problem, and explain that the lack of a business model hinders the development of CCU value chains and thus their commercialisation too. They explain that business models are developed spontaneously from business activities, but this is not likely to happen with CCUS because there is no profit to be made, and companies are not engaging with it because there are not enough incentives from government. Another reason is that the CCUS value chain involves the collaboration of many industries, including many different technologies across a big industry chain, which have to co-exist symbiotically for a long time, and adds this extra complexity to the optimisation.

Yao et al. [248] underline that there is an urgent need for the development of a CCUS business model, and they have proposed four and applied them to identify the most appropriate one for China. They define the term business model as "a structural template that describes the organisation of a focal firm's transactions with all of its external constituents in factor and product markets". They explain that emphasis is given on the structure of the business with regards to stakeholders rather than its administrative structure. They address four entities, capture, transportation, storage and utilization, and define them as follows.

- Capture cost: The cost of retrofitting power plants with CO₂ capture technology, compression equipment and pump costs. Each component has an investment and operating and maintenance cost. An additional component that accounts for the electricity lost during CO₂ capture is also added.
- Transportation cost: It is defined by the flowrate of CO₂ and distance to be transported, which is estimated using a suggested model for CO₂ pipeline cost estimation.
- Storage: It is assumed that only depleted oil reservoirs are used, and the only costs are capital costs which include the costs of screening and site evaluation, injection equipment and drilling for onshore injection wells and O&M costs which include daily expenses, consumables, surface and subsurface maintenance.
- Utilization: Utilization only covers EOR and includes capital and O&M costs. Capital costs include the costs of injection and production, and O&M costs include general expenses, surface and subsurface maintenance costs, electricity cost and CO₂ cost.

8.4.2 Business model 1: Vertical Integration model

The first business model proposed is called the Vertical Integration model and was designed for China, because it is better suited for China's State-owned enterprises, as most private companies are discouraged from entering this industry because of the high CO₂ capture costs, maturity of technology and uncertainty of policy incentives [248]. This business plan assumes that CO₂ capture, transportation and storage/EOR are one state-owned entity. The state-owned enterprise is based on receiving 80% of the total investment from the capital market, receiving a subsidy from Government to cover CO₂ storage costs and to generate profit from the carbon trading market by selling emission quotas and oil generated from EOR. Figure 48 illustrates the vertical integration model and, as can be observed, CO₂ sources (power plants), are also state owned because they receive profit from the power grid company for selling electricity to the consumer.



Vertical integration model

Figure 48: Vertical integration model [248]

8.4.3 Business model 2: Joint Venture model

The joint venture business model is proposed as an upgrade to the vertical integration model by promoting collaboration among sectors to accelerate and extend the development of CCUS value chains. The joint venture business model proposes that, instead of a state-owned enterprise, a joint venture is formed between the capture, transportation and storage companies with 40%, 30% and 30% shares respectively, with a long-term purchase and sale agreement. The joint venture receives 80% of the total investment from the capital market, subsidy from government for CO₂ storage and

profit from selling CO₂ emission quotas to the carbon trading market and CO₂ for enhanced oil recovery. In this model, the power plant does not belong to the state-owned enterprise or joint venture and receives profits from selling electricity to the power grid company and CO₂ to the joint venture (CO₂ capture company). The CO₂ user receives profit from selling oil. Figure 49 illustrates the joint venture model.



Figure 49: Joint Venture model [248]

8.4.4 Business model 3: The CCS operator model

The CCS operator model is inclined towards a more market-driven business model where the CO₂ source (power plant), CO₂ sink (EOR) and storage are independent entities, which rely on a CCS operator for the distribution of CO₂. Since the CCS operator handles all distribution of CO₂, it is responsible for CO₂ capture from the power plant and transportation to EOR and other CO₂ users as well as storage, and therefore receives the 80% of total investment costs from an investor. Each entity deals with the CCS operator and the CCS operator receives profit from selling CO₂ to EOR and other CO₂ users and additionally receives subsidy from government for CO₂ storage. The CCS operator pays the CO₂ source (power plant) for buying CO₂. The capture source (power plant) receives profit from selling market. EOR and other CO₂ users receive profit from selling goods to the consumer. Figure 50 illustrates the CCS operator model.



Figure 50: The CCS operator model [248]

8.4.5 Business model 4: CO₂ Transporter model

The CO₂ transporter model is the one closest to free market and, as Yao et al. (2018) state, it approaches a vertical disintegration model "which is the typical form of development in growing industries". In this model the CO₂ capture company (power plant), CO₂ transporter and CO₂ user/storage are independent entities each doing their own part in the CCUS value chain. The capture company receives an investment from the capital market and is responsible to capture CO₂ from the CO₂ source (power plant) and cover the equipment and O&M costs of capture. It makes profit by selling captured CO₂ to the CO₂ user or storage facility and by selling CO₂ emission quota to the carbon trading market. The CO₂ user buys the captured CO₂ at an agreed long-term price and makes profit by the product it provides to the consumer. The CO₂ storage facility is able to operate by the subsidy provided by the government to store captured CO₂. The CO₂ transporter receives 80% of the total investment from the capital market and is responsible for transporting captured CO₂ to the CO₂ user. The CO₂ transporter profits by charging the CO₂ user for the services it provides. This model is only feasible when the price of oil or the product sold by any other CO₂ user has to be higher than the break-even price for EOR or the CO₂ user. Figure 51 illustrates the transporter model.



Figure 51: CO₂ Transporter model [248]

8.5 Decisions for optimisation

By identifying the gaps in literature (i.e. not considering all options of every step, difficulty and complexity to integrate individual optimisation models, lack of business CCU models), this PhD thesis proposes an algorithm and a business model with a holistic approach that considers all three optimisation issues (source retrofitting, source-sink matching, transportation infrastructure) and optimises and develops CCU value chains in terms of their utilisation and economic performance. By revisiting the previous chapters, Chapters 2-7, the following conclusions and decisions were made to facilitate the development of an algorithm and a business model towards the optimisation of CCU value chains.

8.5.1 CO₂ Receivers

The available CO₂ receivers were listed in Chapter 2, categorized per industry and presented as temporary and permanent utilization choices. A process description was presented for each receiver based on its product and on how CO₂ is utilised. Personal communication with industrial stakeholders involved in CCU value chain development revealed that the most important factors in optimisation of CCU value chains for receivers are: (a) the utilization potential of the receiver in terms of temporary or permanent utilization; (b) the technology readiness level of the receiver; (c) the size of the receiver

(magnitude of production and conversion factor); and (d) the minimum required purity of the receiver.

Information on the retrofitting of receivers before accepting captured CO₂ are required too, regarding (a) any specific contaminants that should be avoided; (b) any process modifications that are required; and (c) how much it would cost for these modifications. Unfortunately, this information is not available, and it was omitted from the PhD thesis. This level of detail can be dealt with when the recommendations of this study are implemented, and the issues arise in real life.

The information gathered so far for the scope of this PhD thesis was used as follows. All identified receivers are important and vital for the optimisation of CCU value chains, because even if they cannot store CO₂ away permanently, they can contribute to seasonal CO₂ shortages and in the development and commercialisation of CCU value chains by contributing to the region, supporting permanent utilization receivers and biofuels, which are the ones actually contributing to CO₂ emissions mitigation. Therefore, the characteristics of all identified receivers were specified so that they can be used as variables/factors in the process of scouting and matching with CO₂ sources.

8.5.2 CO₂ Sources

Chapter 3 lists all the available CO₂ sources and categorizes them per industry, listing also the processes that emit CO₂. Personal communication with industrial stakeholders interested in CCU value chain development revealed that the most important factors in optimisation of CCU value chains for sources are: (a) how CO₂ emissions are produced, which dictates the stream composition of the emitted CO₂; (b) what capture technology is best to be used in terms of technical and economic reasons; and (c) what is the size of the source (magnitude of production and emission intensities), which is directly related to the amount of CO₂ that can be captured.

The information gathered so far in the scope of this PhD was used as follows. All identified sources were taken into consideration because they are an integral part of the CCU value chains, and it is the starting point and the reason to develop CCU value chains in the first place. Therefore, the characteristics of all identified sources was specified, so that they could be used as variables/factors in the process of scouting and matching with CO₂ receivers.

8.5.3 CO₂ Capture

Chapter 4 demonstrated how CO_2 can be captured, starting from its origins in natural gas processing. It explained how each available technology works to capture CO_2 by categorizing capture technologies based on their separation principle. A connection was then made between the source

and origin of CO_2 emissions and the capture process used for the source, as proposed by literature, but it was abandoned because it only covered power related sources. Another connection was then made to the selection of capture technologies for the natural gas processing industry, but it required many detailed data that were not possible to be gathered. Therefore, a compatibility table was developed from examples from literature with all the capture technologies that have been applied on each source. Technology readiness level information was also gathered for all major capture technologies (chemical absorption, physical absorption, physical adsorption, cryogenics, oxy-fuel combustion, calcium looping and membranes). In Chapter 5, capture cost models for all major capture technologies were developed to estimate capital costs and annual operating and maintenance costs for CCU projects. A capture technology matching method was also developed, which selects the best option for each source based on the regional characteristics, compatibility table, technology readiness level and capture cost models. This method is introduced and demonstrated in the following chapter, Chapter 9. Additionally, in Chapter 4, the CO₂ purity that can be achieved by the major capture technologies was specified along with general stream composition impurities that would help in the process of matching CO₂ sources with CO₂ receivers, as purity is an important parameter. This matching method has the ability to select the optimal capture technology based on a region and estimate the CO₂ purity from a source, to facilitate the source and receiver matching process.

8.5.4 CO₂ Transportation

The available transportation options were discussed in Chapter 6 and categorized in onshore and offshore transportation options. The optimal transportation conditions were discussed along with the most important impurities, their limits and reasons for their limitations. Chapter 7 proposed models from literature that can estimate transportation costs in such way that are in line with the scope and purpose of this PhD thesis, and explained how cost can be analysed per transportation method in terms of distance, pressure and transportation volume/flowrate. This allows the simultaneous cost estimation between all sources and all receivers and all available options to select the most economical transportation type.

8.5.5 Algorithm and Business Model

Based on the literature review on optimisation problems, approaches and previous case studies, along with the novelties of this research and conclusions so far, it was decided that optimisation of CCU value chains would be approached by developing an algorithm. The algorithm would follow the multi-stage approach that it was deemed as one of the most promising approaches for CCU optimisation. The algorithm would not be based on any of the models encountered in literature, but rather on the conclusions of the literature review and novelties of this research. The main idea describing the algorithm on a macro level is to include all possible theoretical solutions in the decision process of matching sources and receivers, and do not eliminate any possible matches until it is specified by the algorithm. The algorithm would start from CO₂ sources, where all sources are matched with all receivers to form individual routes between them, which will would later be evaluated for technical compatibility and economic viability. These would be called the theoretical solutions. At this point, the optimal capture technology would be assigned to each source and the complexity and number of theoretical solutions to technically feasible solutions. On the next stage, the economic viability of each of the technically feasible solutions would be estimated to provide the cost of each solution and reduce the matches to technically and economically feasible solutions. Finally, matches for the region would be selected based on the utilization flowrate and cost between the source and receiver matches, since all the remaining combinations are economically feasible.

The CCU value chain problem starts from CO₂ sources, for which the geographical location and CO₂ emissions of the source is defined. The optimal capture technology and cost of capture is determined by the source-capture technology matching method. The output purity of the source is also known, since the capture technology has already been defined. On the other side of the problem, the location, required CO₂ flowrate and purity of the receivers are defined. The solution to this problem lies in satisfying as much of the required CO₂ flowrate of the receivers as possible and not in capturing the maximum CO₂, because there would be no use to capture it if it cannot be utilized. So up to this point, the source retrofitting problem has been tackled and the remaining problems (transportation infrastructure development and source-sink matching) are tackled in the same step. The transportation cost estimation models, CO₂ purities and required flowrates are used to select the most economical matches that offer the highest utilization for the specified region. The proposed algorithm is introduced and explained in Chapter 9, which provides the solution for the optimisation of CCU value chains.

The proposed algorithm would provide optimisation to the CCU value chain. However, the development of a business model would be the answer to commercialisation, by introducing the algorithm in the market. To guide the development of a business model tailored to the requirements of the proposed algorithm, out of the four business models mentioned in section 8.4, the CO₂

transporter model is chosen. The reasons are because it simplifies the complex interactions across the big industrial value chain by giving each individual entity a role to fulfil within the industrial chain, but also the responsibility to deliver their services/product from the previous step to the next. This model amongst the four is the one closest to free market, which as discussed in section 8.4.5 approaches a vertical disintegration model, a typical form of development in growing industries. Because of the individuality of all entities, it has the potential to provide value to all entities that decide to participate through their own initiative.

8.6 Chapter 8 Conclusions

The conclusions and decisions made in Section 8.5 are used in Chapter 9 to develop three individual steps that address each of the three optimisation problems of CCU value chains. The three individual steps are integrated into a single algorithm that is marketed using a business model presented in Chapter 9.

Chapter 9: Algorithm and Business model development

9.1 Algorithm and business model

Following the conclusions from Chapter 8 regarding the three identified optimisation problems, the integration problem and the need of a business model, a multistage approach was chosen to be used in the optimisation of CCU value chains, which utilises a business model to help with their development and commercialization. The proposed optimisation and commercialization method (consisting of an algorithm and a business model) is based on three steps. Each step was developed independently, based on the problems identified from the literature review, and aims to provide holistic solutions in the sense that every available source, receiver, capture technology and transportation method is taken into consideration and analysed in terms of availability, technological maturity, compatibility and cost. The aim is to provide optimal solutions in terms of maximum CO₂ utilization and minimum cost that can be achieved in a region. The three steps are interconnected using a database, developed for: (a) storing and retrieving the gathered data; and (b) implementing the optimisation through queries and external algorithms. The business model specifies the responsibilities of the involved entities, which ensures the smooth running of the project and its commercialisation. The proposed algorithm and business model map CO₂ sources and receivers within a specified region and select the sets of optimal solutions based on the optimisation preference of the user for the development of CCU value chains. The matching of CO₂ sources and receivers is based on: (i) the technological compatibility and maturity of technologies; (ii) CO₂ capture costs; (iii) CO_2 transportation costs; (iv) CO_2 utilisation costs; and (v) profit within a defined project lifetime.

The algorithm is presented using an imaginary region that aids in the presentation, development, simulation and demonstration of the proposed optimisation and commercialization method. An imaginary region is used due to the lack of data required to perform a real-life scenario application and demonstration, because of the volume and availability of required data and lack of time to gather the data within the timeframe of this research.

The imaginary region starts with a simple scenario to demonstrate how the algorithm and business model work on a micro level, while the complexity increases with each section, similar to one of real regions to demonstrate how everything functions on a macro level.

9.1.1 Step 1. The capture problem

The desired outcome of the "capture problem" is a method that matches sources to the optimal capture technology in terms of compatibility, technological maturity and minimum cost. The output of this step is a table of the identified sources with their respective annual CO₂ emissions from a region, each one matched with all the available compatible capture technologies with their respective TRLs, maximum achievable CO₂ purities and capture cost.

Source-capture options (with TRL and purity)

To demonstrate the problem, an example of an IGCC power generation plant of 1 GWh annual electricity production named "IGCC power plant 1" is used. To produce the desired output, the algorithm requires the data shown in Table 74, i.e. the industrial CO₂ source's name, annual production, process type and name (as defined in Table 1-Table 3 from Chapter 2). The algorithm uses the source process type and name and the source-capture compatibility table (Table 36, Chapter 4) to determine the compatible capture technologies. Then, based on the capture technologies, the algorithm draws data from Table 8-Table 13 (from Chapter 3, showing the emission intensity of the process), Table 22 (from Chapter 4, showing the TRL of each capture technology) and Table 24 to Table 29 (from Chapter 4, showing the maximum possible purity from each capture technology).

Annual CO2 emission estimation

The source's annual CO₂ emissions are estimated using Equation 65 in Mt_{co2}/y .

$$S_{ae} = S_{ap} \times S_{ei} \tag{65}$$

where S_{ae} is the source's annual emission, S_{ap} is the source's annual production and S_{ei} is the source's emission intensity.

Table 74: Input table

Required input data	Input data
Source Industry name	PC power plant 1
Source Industry type	Power generation
Source process name	Pulverised Coal
Source annual production	1 GWh

Capture cost estimation

The total capital required (TCR) for the capture of a source's CO₂ is estimated in M\$₂₀₁₈, based on the separation principle of the capture technology, using an equation derived in Chapter 5 and illustrated in Table 39 (equation 66). The annual operating and maintenance cost of a source's capture facility is estimated in M\$₂₀₁₈ /y, based on the separation principle of the capture technology, using an equation derived in Chapter 5 and illustrated in Table 40 (equation 67). The total cost of capture for a source is estimated by adding TCR of capture and the O&M cost of capture for a project life of 25 years, which was the most common assumption encountered during the literature review for carbon capture projects.

$$TCR = 164S_{ae}^{1.113}$$
 (66)

where *TCR* is the total capital required in M\$₂₀₁₈ for capture and S_{ae} is the source's annual emission

$$0\&M = 9.185S_{ae}^{1.015} \tag{67}$$

where O&M is the annual operating and maintenance cost of capture in M_{2018}$ and S_{ae} is the source's annual emission

Optimal capture technology selection

The output of this first step for one source is illustrated in Table 75. The same algorithm can be applied to more than one source, and the output of Table 75 would still look the same but with more rows corresponding to the number of CO₂ sources and the compatible capture technologies for each source. Finally, the algorithm chooses the optimal capture technology by using as criteria in order of importance, a) the TRL, b) the cost (over a project lifetime of 25 years) and c) the purity that can be achieved. For this example, the optimal carbon capture technology is shaded in Table 75.

Table 75: Optimal capture technology selection

Input data				Output data							
Source industry name	Source Industry type	Source process name	Source annual production GWh	Source's emission intensity Mt _{C02} /GWh	Source's annual CO ₂ emission Mt _{CO2}	Compatible capture technology	TRL	Purity	Project's Total capture cost M\$ ₂₀₁₈	Capital cost M\$ ₂₀₁₈	O&M cost M\$ ₂₀₁₈
PC power plant 1	Power generation	IGCC	1	0.75	0.75	MEA	9	99.7	392.11	162.62	229.49
PC power plant 1	Power generation	IGCC	1	0.75	0.75	Amine	9	99.8	392.11	162.62	229.49
PC power plant 1	Power generation	IGCC	1	0.75	0.75	Oxy-Fuel	7-8	99.95	258.61	98.45	160.16

9.1.2 Step 2. The transportation problem

The desired outcome of the "transportation problem" is to propose the transportation infrastructure for the region. The transportation infrastructure must be optimised in terms of technical aspects (outlined in Chapter 6), so that it is carried out efficiently and safely, and economic aspects so that it is achieved at the minimum cost. Assuming all transportation options are of equal maturity, because they have all been implemented in the past, then the optimal transportation option between a source and a receiver can be judged solely on the cost of each option.

To demonstrate the problem, an example of a potential receiver is required (Table 76), combined with the outcome of the source-capture technology step. The receiver's required data are the receiver's industry name, process name and its annual product production. The algorithm using the receiver process name draws data from Table 3 from Chapter 2 (that shows the conversion factors for each process), Table 2 in Chapter 2 (that shows the TRL of the process) and Table 1 in Chapter 2 (that shows the required purity of the receiver).

Table 76: Potential receiver example

Required input data	Input data
Receiver Industry name	Enhanced oil recovery 1
Receiver process name	Enhanced oil recovery
Receiver Industry type	Permanent
Receiver annual production	2000 barrels
Receiver minimum required purity	High (assuming 99%)
Receiver TRL	9

Receiver annual CO2 requirement

The receiver's annual CO₂ requirement is estimated using equation 68 in Mt_{co2}/y :

$$R_{ar} = R_{ap} \times R_{cf} \tag{68}$$

Distance estimation

To estimate the distance between a potential match, the algorithm uses the source's and receiver's locations and the available road network to provide a realistic estimation, and not the shortest (straight) distance. This means that if a truck option is chosen, the estimation would be very realistic, and in the case a pipeline is chosen it is going to have a slightly overestimated distance because there might be certain alternative routes for the pipeline, but it is still a decent estimation because a landform (e.g., mountain) might block the passage of a pipeline while at the same time a truck can use a road on a mountain. The algorithm also checks if transportation requires an offshore option by checking if the two locations are separated by sea. If it does require an offshore option, it calculates

the distance from the source to the nearest port, then the straight distance from port to port and the distance from the port to the receiver. The data required are shown in Table 77.

Table 77: Required data for transportation distance estimation

Required input data	Input data
Receiver Industry name	Enhanced oil recovery 1
Receiver Industry longitude	
Receiver industry latitude	
Source Industry name	IGCC power plant
Source Industry longitude	
Source industry latitude	

Transportation cost estimation

Onshore

Pipeline

Pipeline TCR (\$2018)

$$I = 1.527 \times 68,719 \times m^{00.5} \times L \tag{69}$$

Pumping station TCR (\$2018)

$$PS = 1.527 \times 1000L \times 50 \tag{70}$$

Pipeline O&M (\$2018/y)

$$PO\&M = 1.527 \times I \times 0.04$$
 (71)

Pumping stations O&M ($$_{2018}/y$)

$$PSO\&M = 1.527 \times PS \times 0.05 \tag{72}$$

Truck

O&M truck costs $(\frac{2018}{y})$

$$TO\&M = \frac{Mt_{CO2}/y}{6 \times 10^{-5} Mt_{CO2}} \times 2D \times 1.05 \times 1.024$$
(73)

Offshore

The algorithm checks if the two locations are separated by sea and if so, it develops a route based on the source's location and the nearest port where transportation will take place by onshore transportation (pipeline or truck). The route continues from the source's nearest port to the receiver's nearest port via offshore transportation (ship or pipeline). From the receiver's nearest port, it is transported to the receiver via onshore transportation.

Total shipping capital costs =
$$2396.16t_{CO2} + 26 \times 10^6 \times 1.364$$
(74)Annual $0\&M \ costs = 40.862t_{CO2} + 1.3 \times 10^6 \times 1.364$ (75)

where t_{CO2} is the annual amount of CO_2 to be transported.

Optimal type of transportation selection

The output of this step is illustrated in Table 78 and Table 79. The example from Table 77 and Table 78 refers to the instance of estimating the transportation cost for an onshore case, but the same algorithm can be applied to estimate the transportation cost for an offshore case where it requires three transportation costs, two onshore and one offshore. The transportation cost estimation step can be used for more than one source, and the outputs of Table 78 and Table 79 would still look the same but with more rows corresponding to the number of CO₂ sources and their respective compatible CO₂ receivers. Finally, the algorithm will choose the optimal transportation technology solely on the lowest transportation cost over a project life of 25 years (denoted as shaded in Table 78 and Table 79).

Onshore transportation only options													
Input data						Output data							
Source industry	Source	Source	Receiver	Receiver	Receiver	Exchange flowrate	Pipeline	Pipeline Total	Pipeline Capital	Pipeline O&M			
name	longitude	latitude	industry name	longitude	latitude	(Mt _{CO2/y})	distance km	transportation cost	cost	cost M\$ ₂₀₁₈			
								M\$ ₂₀₁₈	M\$ ₂₀₁₈				
PC power plant 1	-	-	EOR 1	-	-	0.75	100	18.18	9.09	9.09			
Source industry	Source	Source	Receiver	Receiver	Receiver	Exchange	Truck distance	Truck Total	Truck Capital cost	Truck O&M			
name	longitude	latitude	industry name	longitude	latitude	flowrate (Mt _{CO2/y})	km	transportation cost	M\$ ₂₀₁₈	cost M\$ ₂₀₁₈			
								M\$ ₂₀₁₈					
IGCC power plant 1	-	-	EOR 1	-	-	0.75	100	67.2	-	67.2			

Table 79: Selection of the optimal offshore transportation type (example)

Offshore	transportati	on options												
Input data	9						Output data							
Source	industry	Source	Source	Receiver	Receiver	Receiver	Exchange flowrate	Pipeline	Pipeline	Total	Pipeline	Capital	Pipelin	e O&M
name		longitude	latitude	industry name	longitude	latitude	(Mt _{CO2/y})	distance km	transportation	cost	cost		cost M	\$ _{2018y}
									M\$ ₂₀₁₈		M\$ ₂₀₁₈			
PC power	plant 1	-	-	EOR 1	-	-	0.75	50	9.09		4.54		4.54	
Source	industry	Source	Source	Receiver	Receiver	Receiver	Exchange flowrate	Truck distance	Truck	Total	Truck Cap	ital cost	Truck	0&M
name		longitude	latitude	industry name	longitude	latitude	(Mt _{CO2/y})	km	transportation	cost	M\$ ₂₀₁₈		cost M	\$ ₂₀₁₈
									M\$ ₂₀₁₈					
PC power	plant 1	-	-	EOR 1	-	-	0.75	50	33.6	33.6 -		33.6	33.6	
Source in	dustry	Source	Source	Receiver	Receiver	Receiver	Exchange	Ship distance	Ship Total		Ship Capital cost		Ship O&M	
name	name lo		latitude	industry name	longitude	latitude	flowrate (Mt _{CO2/y})	km	transportation of	cost	M\$ ₂₀₁₈		cost M	\$ ₂₀₁₈
									M\$ ₂₀₁₈					
PC power	plant 1	-	-	EOR 1	-	-	0.75	200	36.36		3.1		33.27	
Source	industry	Source	Source	Receiver	Receiver	Receiver	Exchange flowrate	Pipeline	Pipeline	Total	Pipeline	Capital	Pipelin	e O&M
name		longitude	latitude	industry name	longitude	latitude	(Mt _{CO2/y})	distance km	transportation	cost	cost		cost M	\$ ₂₀₁₈
									M\$ ₂₀₁₈		M\$ ₂₀₁₈			
PC power	plant 1	-	-	EOR 1	-	-	0.75	50	4.54		2.27		2.27	
Source	industry	Source	Source	Receiver	Receiver	Receiver	Exchange flowrate	Truck distance	Truck	Total	Truck Cap	ital cost	Truck O&M	
name		longitude	latitude	industry name	longitude	latitude	(Mt _{CO2/y})	km	transportation	cost	M\$ ₂₀₁₈		cost M\$ ₂₀₁₈	
									M\$ ₂₀₁₈					
IGCC pow	er plant 1	-	-	EOR 1	-	-	0.75	50	16.8		-		16.8	

9.1.3 Step 3. The utilisation problem

The desired outcome of the "utilisation problem" is a method that matches sources to the optimal receiver in terms of compatibility, technological maturity, minimum cost and maximum regional CO₂ utilisation. The output of this step is a table of the identified sources with the matched receivers and corresponding annual CO₂ exchanged quantity from a region. Each combination includes all the available compatible capture technologies with their respective TRLs, maximum achievable CO₂ purities and capture cost. The output of this sorting step provides the optimal source to receiver combinations for a specific region. It is presented initially as an independent procedure, but for a regional analysis the previous two steps should be performed, with a different sequence of events which is introduced in Section 9.2.

The sorting selects the best combinations of sources and receivers, based on the user preference from a list of pre-defined criteria: utilisation flowrate, cost of investment, O&M costs, total cost over project lifetime and profit, which are estimated over the project life. The highest ranked criterion dictates how optimisation will be approached, and the rest guide the decision if the first criterion is ambiguous. A list of the profitable combinations is created and sorted per receiver to illustrate the profitable combinations for each receiver. Based on the scores of the criteria, the optimal matching for each receiver is selected and the rest of the variables are used when a decision cannot be made using the highest ranked priority.

The procedure starts with the sorted list of profitable matches and assigns the receivers to their best match, according to the priority that has been given to the variables. All profitable matches for each receiver are ranked and the best match of each receiver is picked and stored in a list. The list is checked for any sources that might have been matched with more than one receiver. If no sources are matched with more than one receiver then that list contains the optimal solutions for the region, based on the priority given to the variables.

In the case where a source or sources have been matched with more than one receiver, a new list is created for each one of the sources. The list for a specific source contains the profitable combinations of receivers that are matched with that source and the next best profitable match of each receiver. According to the number of receivers present in the table, there is the same number of combination scenarios, where each receiver is matched with that source and the others are matched with their second-best match. For each scenario, the score for the highest ranked criterion is calculated (e.g. utilization, cost) and the scenario with the best performance (e.g. maximum utilization, minimum

cost) is selected. The same procedure is applied for the second source that has been matched with multiple receivers. Every time this procedure is done for sources matched with multiple receivers, each list that has been created is checked top to bottom for sources that might have been matched with more than one receiver. If a source is matched with more than one receiver at any point, the same procedure is applied and continues to be applied until no source is matched with more than one receiver. The only case where this is allowed is if the source has enough flowrate to satisfy both (or more) receivers. When no source is matched with more than one receiver, or it fully satisfies all receivers matched to it, the profitable combinations are stored in a list that illustrates the optimal solutions of the region.

At the end of the sorting algorithm, it is possible for sources and receivers that have already been matched to not supply or utilise CO₂ to their maximum potential. For these sources and receivers, the source-sink matching method is reapplied to produce a new set of profitable matches where the sorting algorithm will indicate the optimal profitable matches. This process is repeated until no profitable matches are indicated by the source-sink matching method.

9.1.4 Commercialization: Business model and cost/profit allocation

As discussed in Chapter 8, CCU value chains are very complex because they require the collaboration of many industries across a big industrial value chain. Their commercialisation depends on the development of a business model. This thesis proposes to market the algorithm through the business model discussed and selected in Section 8.5. Therefore, the transporter model is used as a guide to develop a business model tailored to the requirements of the proposed algorithm.

This business model's main purpose is to use as much CO_2 as possible and is based on the use of CO_2 as raw material. For the business model to be successful it must provide value to all entities involved along the value chain, from the capital market and CO_2 source to the consumer.

Sources

The CO₂ sources are considered to be individual entities and are responsible for providing receivers with the agreed annual CO₂ flowrate. Their responsibilities include building and running the required facilities for capturing CO₂. Sources can choose to provide their own investment costs or receive the investment from the capital market with the responsibility of paying the agreed return on investment. Sources receive profit by selling CO₂ to the CO₂ receiver/user and at the same time provide value to their business by reducing their CO₂ emissions. Additionally, if the carbon trading market is in place, they can make extra profit.

Receivers

 CO_2 receivers are considered to be individual entities and are responsible for providing the consumer with a quality product that has reused CO_2 and has stored it permanently, temporarily or has indirectly contributed to the reduction of CO_2 emissions. If the receiver requires a modification in their process to accept captured CO_2 , they can provide their own investment costs and benefit from the investment or receive investment from the capital market. The receiver modification costs are not taken into consideration for the scope of this research because there are no available data or information to specify the required modifications or estimate their cost. The CO_2 receiver receives profit by selling a product to the consumer, which allows the consumer to use a product that reduces CO_2 emissions and at the same time provides value to the CO_2 source by reusing their CO_2 emissions.

Transportation

The CO_2 transporters at this stage are considered as one entity, since it is still unknown who is going to provide this service because there are no fixed interested parties, but they are separated based on the type of transportation they offer, since CO_2 transporters are responsible for transporting the agreed annual amount of CO_2 from source to receiver. They are also responsible for building (if needed), running and maintaining the required facilities. The transporters can choose to provide their own investment or receive investment from the capital market with the responsibility of paying the agreed return on investment. Transporters receive profit from the corresponding stakeholder for transporting the captured CO_2 (in this thesis, it was initially assumed that the source is responsible for the transportation expenses) and at the same time providing value to their business by contributing to the reduction of CO_2 emissions.

Capital market

The capital market, if interested, is considered as one entity and is responsible to provide the investment for any of the other entities involved including CO₂ sources, receivers and transporters. The capital market provides value to the interested entity and the development of CCU value chains and in return receives an agreed return on its investment.

Consumer

The consumer is responsible for the CO_2 emissions emitted in the first place; therefore, it receives direct value by contributing to the reduction of CO_2 emissions just by consuming alternative CO_2 products. The alternative CO_2 products must be of equal quality (both technical and impact to health

related) to the conventional products that they replace. The quality assessment of alternative products and the comparison to commercial products is out of the scope of this research and in some instances not applicable because some of the products are new products and do not replace any previous ones. A questionnaire conducted within the context of this PhD research regarding the public acceptance of CCU value chains and their respective commercial products, with 266 participants, demonstrates that the majority of the respondents show a willingness to support the research and development of such schemes.

Agreed selling price

The balance between the value chain is maintained by the agreed selling price between each source/receiver match. It is estimated in such way that profit is generated from each source/receiver match. If profit is ensured between each match, then it means that every entity provides value to the CCU value chain and receives value from it.

The agreed selling price of CO_2 is estimated based on the break-even price of the source, or minimum selling price of CO_2 , and the break-even price of the receiver, or maximum buying price of CO_2 . If the break-even price for the source is lower than the break-even price for the potential receiver (P_{BES} < P_{BER}), the proposed symbiotic scheme is economically viable. An agreed selling price for the CO_2 can be proposed as the average value of the two break even points (P_{BES} + P_{BER})/2.

In the case where the break-even price for the source is greater than the break-even price for the potential receiver (P_{BES}>P_{BER}), then an agreed price cannot be determined with the existing economic figures and the assumptions made. In this case, a trade-off analysis can be performed, assessing alternative options for the transportation or storage costs (full responsibility for the waste source/full responsibility for the waste receiver/split cost between the two involved parties). The comparison can be then used again, to calculate the new break-even prices. If an agreed selling price still cannot be determined, then the symbiotic scheme under investigation is characterized as non-economically viable and is rejected. This concept has already been implemented in the SWAN platform, discussed in Chapter 10.

Source break-even price calculation

The source break-even price is calculated as follows:

The total capture cost for a source over the project life can be defined as the initial capital cost and the O&M cost over the project life:

$$Capture \ cost = Capture \ capital \ cost + Capture \ O\&Mcost$$
(76)

The capture capital cost can be estimated using one of the developed models according to the separation principle:

Capture capital cost(\$)

= price per tonne
$$CO_2$$
 per year $\left(\frac{\$}{TCO_2 y}\right) \times amount(TCO_2 y)$

The capture O&M cost can be estimated using one of the developed models according to the separation principle:

= % of capture capital cost \times Capture capital cost \times project life The transportation cost can be defined as the initial investment cost and the O&M cost over the project life:

= Transportation capital cost + Transportation O&Mcost The transportation capital cost and transportation O&M cost can be estimated using the models from literature, using the respective model for each transportation type, defined in Chapter 7.

The revenue that can be generated over the project life of a source can be defined as follows:

$$Revenue = Selling Price of CO_2 \times flow rate \times project life$$
(80)

The net profit generated over the project life from selling captured CO_2 can be defined as the revenue minus the total capture capital cost over the project's life.

$$Net \ profit = Revenue - Capital \ cost - 0\&M \ cost$$
(81)

For the source's break-even price, net profit can be assumed to be equal to zero, which can be substituted into equation 81 to become:

$$Revenue = Capital \cos t + 0\&M \cos t \tag{82}$$

Therefore, when substituting equation 82 into equation 81 and rearranging for zero profit, the source break-even price is:

$$\therefore Break even Price of CO_2 Source = \frac{Capital cost + 0\&M cost}{flow rate \times project life}$$
(83)

Receiver break-even price calculation

The receiver break-even price can be calculated in a similar way to the source's break-even price calculation, where the capital cost would normally include any modification costs required by the receiver to accept captured CO_2 and the O&M cost would include the gasification cost of captured CO_2 (liquid to gas, transportation). As mentioned before these costs are not incorporated in the scope of this research and therefore they are not included in the break-even price calculation. The only costs considered are the commercial price of CO_2 and selling price of captured CO_2 .

(77)

Capital cost = Modification cost

O&*M* cost = gasification cost

The revenue for the receiver break-even price can be defined as the difference in cost to transition from commercially produced CO_2 to captured CO_2 , expressed as follows:

$$Revenue = (Commercial Price of CO_2$$
(84)

- Selling Price of recycled CO_2) × Q × project life

The net profit can be expressed as before, revenue minus the total capital cost which in this case will be equal to zero:

$$Net \ profit = Revenue - Capital \ cost - 0\&M \ cost$$
(85)

which becomes:

$$Net \ profit = Revenue - 0 - 0 \tag{86}$$

For the break-even price calculation, net profit is equal to zero, therefore substituting equation 84 in equation 86 gives:

Break even Price of
$$CO_2$$
 Receiver = Commercial Price of CO_2 (87)

Useful cost metrics

Return on investment (ROI) is a useful indicator for evaluating the efficiency of an investment, defined as the profit received at the end of a specified period relative to the investment made initially. It can be used as an optimisation parameter for the sorting algorithm. ROI calculation is illustrated by equation 88:

$$ROI = \frac{Net \ profit \ at \ the \ end \ of \ project \ life}{Investment \ cost} \times 100$$
(88)

Payback period is another useful indicator for evaluating the efficiency of an investment, defined as the period of receiving the initial investment cost relative to annual net profit. Payback period calculation is illustrated by equation 89. Payback period can also be used as an optimisation parameter by the sorting algorithm.

$$Payback \ period = \frac{Initial \ investment}{Annual \ net \ profit}$$
(89)

9.2 Algorithm Integration

The individual parts presented in Section 9.1 only approach the individual problems that they were designed to solve, but in the state presented in Section 8.1 cannot provide any optimisation solutions

on a regional level. Figure 52 demonstrates how the three steps and the business model have been integrated to develop an approach that can propose optimised CCU value chains on a regional level. Additionally, the individual steps require a database to function and produce the desired outcomes. Therefore, a database was built, with the current literature review and its limitations in mind. The database and the algorithm consist of options that are currently available, but also with the potential to expand and develop as new information is added to increase the current options it can offer.



Figure 52: Block flow diagram of the integrated algorithm

9.2.1 Block flow diagram

The following section presents the integration of the three steps and the business model, described in Section 9.1, to develop an algorithm that is able to optimise and propose CCU value chains on a regional level. The block flow diagram illustrates the integration and explains how the algorithm operates. It lists the required data (input data) and outlines the steps of the algorithm and the output of the algorithm.

The integrated algorithm consists of four major parts:

- (i) Regional mapping: Creation of a database that stores the regional data under assessment
- (ii) Technical matching: Matching sources with receivers based on technical characteristics
- (iii) Cost estimation: Estimation of all costs along the project's life and identification of profitable matches
- (iv) Sorting algorithm: Selection of the optimal source-sink combinations based on the users' preferences.

Regional Mapping: Source retrofitting

The first part of the algorithm creates a database that stores the data of the region under assessment. This database will be used by the algorithm for all the remaining processes to make computations and provide the user with the respective outcomes based on the user's preference.

The required data for sources are the names of industries, locations, annual production and each source's process name. Based on the source's process name, sources are assigned their respective purity (Table 10-Table 14/Chapter 3), emission intensities (Table 10-Table 14/Chapter 3) and compatible capture technologies (Table 36/Chapter 4). The required data for receivers are the names of industries, locations, annual production and each receiver's process name. Based on the receiver's process name, receivers are assigned their respective receiver type (Section 2.1.2-1.3), purity (Table 1/Chapter 2), TRL (Table 2/Chapter 2) and conversion factor (Table 3/Chapter 2). Table 80 shows an example of the required data.

Table 80: An example of the required data for sources and receivers

Sources	Receivers
Industry name	Industry name
Latitude	Latitude
Longitude	Longitude
Production (annual)	Production (annual)
Source industry type	Receiver process name
Source process name	Receiver type
Source CO ₂ purity	Receiver purity
Source emission intensity	Conversion factor
Source compatible capture technology	TRL

When the database is ready, all sources are matched with all receivers to create a list of the theoretical combinations. In theory, all sources can provide any receiver with captured CO₂ and therefore the theoretical combinations are defined as a source that can provide captured CO₂ to any receiver regardless of the receiver's required purity and cost of capture and transportation. Later on, this list is filtered based on purity, utilisation, cost and profit to pinpoint the optimal solutions. After all sources are matched with all receivers, each combination is assigned a flowrate that the source will provide the receiver. That flowrate is specified as the minimum flowrate between the source's CO₂ emissions and the receiver's potential for CO₂ reuse. The source-capture technology matching method is then applied, as demonstrated in Section 9.1, using the minimum flowrate instead of the source's maximum flowrate, to select the optimal capture technology for each source based on compatibility, TRL, cost and purity.
The output of this step is a list of all the sources and receivers matched together with their assigned optimal capture technologies and the data associated with the selected capture technology. Figure 53 shows the block flow diagram of the first step of the algorithm.



Figure 53: Block flow diagram of the first part of the algorithm

Technical matching: CO2 flowrate

The second part of the algorithm (Figure 54) reduces the list of theoretical combinations to the technically feasible combinations. The algorithm uses the generated list of theoretical combinations and checks for combinations where the purity of receiver is equal or higher than that of the captured CO₂ from the source. Combinations where the purity of the source is lower than that required by the receiver are discarded because they are incompatible. The output of this part of the algorithm is a reduced version of the theoretical combinations list, to a shorter list of only technically feasible combinations. The list of technically feasible combinations is used later, in conjunction with the estimation of transportation costs, capture costs, receiver costs and agreed selling price, to reduce the list to the technically feasible and profitable combinations.



Figure 54: Block flow diagram of the second part of the algorithm

Transportation Cost estimation

The third part of the algorithm (Figure 55) estimates the cost of transportation via all the available options between each combination of source and receiver and specifies the optimal transportation method, based on the option with the lowest cost. It takes the list of the technically feasible combinations and using an external algorithm (Google Application Programming Interface - Google API), it specifies if a combination requires onshore or offshore transportation and estimates the realistic distance between them based on the available road infrastructure. Using the estimated distance and the minimum flowrate specified between the source and the receiver, it estimates the transportation cost for each option (initial investment and annual O&M and the total cost over the project lifetime). The option with the least cost is the selected transportation type. The output of this step is the selection of the optimal transportation type for each of the combinations under assessment.



Figure 55: Block flow diagram of the third part of the algorithm

Sorting algorithm

The purpose of the sorting algorithm (Figure 56) is to formulate a list of the technically and economically feasible combinations of sources and receivers based on the profitable combinations and the agreed selling price of CO₂ between each source and receiver. From the list of technically feasible and economically feasible combinations, it selects the combinations that reflect the user's needs (maximum utilisation, maximum profit, minimum cost). The algorithm is designed to run until the receivers are fully satisfied (receivers receive the largest annual flowrate that they can), or they have been matched with sources that ensure a maximum CO₂ supply based on what the region can offer. The sorting algorithm requires the technically feasible and profitable combinations list, which

is obtained by estimating the agreed selling price between each combination using the maximum CO_2 buying price of the receiver and minimum CO_2 selling price of the source, as outlined in section 9.1.4.



Figure 56: Block flow diagram of the fourth part of the algorithm

9.2.2 Database

The database stores data for sources, receivers and transportation purposes. Figure 57 presents the database entity relationship diagram. The tables named "Sources" and "Receivers" include the regional data that need to be inserted by the user, which make up the foundation of the optimisation process. The rest of the tables correspond to the data that are already stored in the database. They draw information from the tables and cost estimation models developed and gathered for this research. The optimisation is made possible through queries in the database.

Sources

The "Source" table holds the region-specific information of the involved industrial sources, the entries are the industry name of the source, latitude, longitude, annual production of the source's product and the source's process name. By selecting the source process name the database fills the information from the rest of the tables, source process attributes, capture technology attributes and separation principle attributes. The source process name is connected to the source process attributes table with a one-to-one connection through the primary key of source process name, because there is only one set of characteristics that can describe the source process name. The source process attributes table includes the entries for source industry type (power generation, metal industry, etc.), the CO₂ purity of the source and the source's emission intensity, which describe the source process name.

The source process attributes table is connected to the compatible capture technologies table via a one-to-many connection from source process name to a foreign key called source process name, because there can be several compatible capture technologies with one source process name. The compatible capture technologies table acts as a bridge table between the source process attributes and separation principle attributes tables that are connected with a many-to-many relationship. The compatible capture technologies table holds the entries for the compatible capture technologies with each specific source process name, separation principle and separation process. The separation principle is used as a second foreign key to connect the compatible capture technologies table to the separation principle attributes table with a many-to-one relationship, because many separation principles have one unique set of separation principle attributes. The separation principle attributes table holds the entries for the data regarding each separation principle, using the separation principle TRL, purity, capture capital cost factor, capture capital cost power, capture O&M cost factor and capture O&M cost power for each separation principle.

Receiver

The receivers' table holds the region-specific information of the involved industrial receivers; the entries are the industry name of the receiver, latitude, longitude, annual production of the receiver's product and the receiver process name. By selecting the receiver's process name the database fills the information from the receiver process attributes table. The receiver process name is connected to the receiver process attributes table with a one-to-one connection through the receiver process name, because there is only one set of receiver process attributes that can describe the receiver process name. The receiver process attributes table holds the entries for receiver type, receiver purity, conversion factor and TRL.

Transportation

The terrain compatible transportation type table holds the entries for the terrain type and transportation type. By specifying the terrain type (onshore, offshore) the allowed transportation types according to that terrain are specified as well. The terrain compatible transportation type is connected to the transportation type attributes table with a many-to-one connection through transportation type as foreign key, because there is only one set of attributes that can describe the transportation type. The transportation type attributes table holds the entries for the constants required by the transportation cost estimation models which are specific for each transportation type.



Figure 57: Entity relationship diagram for database

Queries:

1. <u>Theoretical combinations:</u>

Combine every [Industry Source Name, Sources] entry with every [Industry Receiver Name, Receivers] entry.

2. Minimum flowrate between source and receiver:

For each entry:

- a. For Source multiply Production annual by Conversion factor (CO₂ annual emissions)
- b. For Receiver multiply Production annual by Emission intensity (CO₂ annual consumption)
- c. Choose smallest value (Minimum flowrate between source and receiver)

3. <u>Capture Technology Selection:</u>

For all Sources

- a. Compute minimum flowrate between source and receiver to the power of Capture Capital Cost Power and multiply by Capture Capital Cost Factor (Capture capital cost).
 Compute for all available separation principle entries
- b. Compute minimum flowrate between source and receiver to the power of Capture O&M power, multiply by Capture O&M Factor and multiply by Project lifetime (Capture O&M cost). Compute for all available separation principle entries
- c. Add Capture capital cost and Capture O&M cost (Total Capture cost)
- d. Choose largest value of TRL. If there is more than one solution, choose smallest value for Total Capture Cost. If there is more than one solution, choose highest purity. If there is more than one solution, choose first entry (Optimal Capture Technology)

4. <u>Technically Feasible Combinations:</u>

a. Compare all purity entries from the Optimal Capture technology of each source with all Receiver purities

 Keep combinations that Purity of Optimal Capture technology is equal or higher than Receiver Purity

5. Distance estimation:

a. For all technically Feasible combinations ask Google Maps API for Terrain Type and distance based on Terrain type (Distance)

6. Transportation Cost Estimation

- For all pipeline entries compute Minimum flowrate between source and receiver to the power of TCR power and multiply by Exchange Factor, by TCR Constant 1 and Distance. (Pipeline Capital Cost)
- b. For all pipeline entries multiply the estimated Pipeline Capital Cost by O&M Constant 1 and by Project life. (Pipeline O&M cost)
- c. For all pipeline entries multiply distance TCR Constant 1 and TCR Constant 2. (Pumping Stations Capital Cost)
- For all pipeline entries multiply Pumping stations Capital Cost by O&M constant 1 and Project life (Pumping Station O&M Cost)
- For all pipeline entries add Pipeline Capital Cost, Pipeline O&M cost, Pumping Stations
 Capital Cost, Pumping Station O&M Cost. (Pipeline Cost)
- For all truck entries divide Minimum flowrate between source and receiver by O&M Constant 1 and multiply by O&M Constant 2, O&M Constant 3, Distance, Exchange Factor and Project life. (Truck Cost)
- g. For all Offshore entries execute a to f twice, firstly for source to port distance and secondly port to receiver distance but replace distance with the appropriate distance specified from Google Maps API.
- h. For all offshore entries multiply Minimum flowrate between source and receiver by TCR Constant 1. Add TCR Constant 2. Multiply by Exchange Factor. (Ship capital cost)
- For all offshore entries multiply Minimum flowrate between source and receiver by O&M Constant 1. Add O&M Constant 2. Multiply by exchange Factor and Project life. (Ship O&M Cost)

7. <u>Transportation Selection:</u>

- a. For all onshore entries select the smallest value. (Transportation Cost)
- b. For all offshore entries select smallest value for source to port Transportation Cost.
 Select smallest value for port to receiver Transportation Cost. Add Source to Port transportation cost, Port to Receiver Transportation Cost, Ship Capital Cost and Ship O&M Cost. (Transportation Cost)

8. Source CAPEX and OPEX:

- a. For all remaining entries add Capture Capital Cost and Transportation Capital Cost
- b. For all remaining entries add Capture O&M and Transportation O&M
- c. For all remaining entries add Capture Cost and Transportation Cost

9. <u>Minimum CO₂ selling price:</u>

 For all remaining entries add Capture Cost and Transportation Cost (Total Cost), and divide by the product of Minimum Flowrate between Source and Receiver and Project life. (Source break-even price)

10. <u>Receiver Capex:</u>

a. For all remaining entries multiply Minimum Flowrate Between Source and Receiver by the Average Price of commercial CO₂. (Maximum CO₂ buying price)

11. Technically Feasible and Profitable Combinations:

- a. For all remaining entries subtract Minimum CO₂ selling price from Maximum CO₂ buying price
- Keep the Source/Receiver combinations where value is positive (Technically Feasible and Profitable Combinations)

12. Sorting algorithm

- a. Execute Sorting algorithm as outlined in Section 9.1.3
- b. When solutions are specified re-run the sorting algorithm until there are no matches.

9.3 Chapter 9 conclusions

Chapter 9 presents the development of the main novelty of this PhD thesis, a multi-step approach to optimise and commercialise CCU value chains. The approach aims to minimise CO₂ emissions by assessing matched CO₂ sources and receivers based on: (i) technological compatibility and maturity of technologies; (ii) CO₂ capture costs; (iii) CO₂ transportation costs; (iv) CO₂ utilisation costs; and (v) profit within a defined project lifetime, to propose and select optimised source-receiver combinations within a specified region. This is achieved through an algorithm and a business model. The algorithm integrates the three solutions, which were developed and presented in Chapter 9 for each of the optimisation problems identified from the literature review presented in Chapter 8. The algorithm handles the optimisation planning of CCU value chains while the business model ensures that the optimisation and planning of CCU value chains is executed in a way that everyone receives value.

Chapter 10: Algorithm Validation

10.1 Introduction

Chapter 10 presents the validation of the developed algorithm, through its application in four different case studies. The first one, presented in Section 10.2, is based on an imaginary region, in order to demonstrate the functionalities of the entire algorithm in one case, from data collection to business model development. The other three cases, presented in Section 10.3, are based on real-life examples, and aim at further validating certain functionalities of the algorithm and dealing with uncertainties and lack of data, issues that arise in real life situations.

10.2 Algorithm Validation

The algorithm is demonstrated initially through an imaginary region (similarly to Chapter 9) in order to highlight all different steps and how they are integrated. The purpose of the case study is set to be the development of regional CCU value chains between the mapped CO₂ sources and CO₂ receivers. The proposed CCU value chains from the algorithm and business model's outcome must be optimised in terms of maximum allowed regional utilisation.

10.2.1 Visualisation of problem/region

The imaginary region has three CO₂ sources and three potential receivers. For simplicity, it involves only onshore transportation options. The locations for sources and receivers are assigned at random but their corresponding characteristics are drawn from real cases (sources and receivers) to depict a realistic scenario.

The sources were picked from three different industrial types, with varying magnitudes, to demonstrate the variety of the collected data and options that are provided by the algorithm and business model. Similarly, receivers were picked from three different industrial types at varying magnitudes for the same reasons.

10.2.2 Data preparation for data base

The simulation starts by visualising a region consisting of three sources and three receivers. Figure 58 illustrates the sources (represented with circles) and receivers (represented with diamonds) of the region with their approximate distance at scale. Two of the sources are relatively close to each other and seem to be competitive and a smaller source is present much further away. A receiver is present

at the centre of the region, almost at equal distance from every source. Another receiver is present closer to source A but slightly further from source B and at much larger distance from the small source C. Finally, a third receiver is present relatively close to the small source C, at a much larger but almost equal distance from sources A and B.



Figure 58: Imaginary region under study (where circles represent sources, diamonds represent receivers, size is relative to CO_2 supply or demand and placement is relative to distance)

Table 81 shows the sources of the imaginary region under assessment. Three types of sources from different industries were selected, a PC power plant from the heat and power generation industry, a blast furnace from the metal industry and a pre-calciner from the cement industry. Each CO₂ source was assigned a reasonable annual production to match the CO₂ emissions of real plants, identified in Chapter 5.

Industry	Туре	Emission Intensity	Production	Emissions
Name		(t/t)	(Mt/y)	(Mt/y)
Source A	PC	0.74	5 (GWh/y)	2.52
Source B	BF	1.5	3.8	5.70

1.1

0.37

Table 81: Sources of the imaginary region under assessment

Source C

Total

Cement

Similarly, three receivers from different industries were selected with varying purity and CO_2 requirements. One algae cultivation receiver was selected from the enhanced growth of vegetables

0.41

8.62

and plants, one beverage carbonation plant from the food industry, and one EOR plant from the enhanced fossil fuel recovery industry. The receivers were assigned their respective characteristics from Tables 1-3/Chapter 2, and sources were assigned their respective characteristics from Tables 5-11/Chapter 3. The receivers of the imaginary region are shown in Table 82. Source and receiver location data were omitted since they are imaginary.

Industry Name	Туре	Purity (%) TRL		C.F (t/t)	Production (Mtproduct/y)	Demand (Mt/y)
Receiver A	Algae	22.0	7	1.83	1	1.83
Receiver B	Bev.Carb.	99.9	9	8	0.4	3.20
Receiver C	EOR	95.0	9	0.5	10000000	5.00
Total						10.03

Table 82: Receivers of the imaginary region under assessment

10.2.3 Source-capture technology matching method

The regional database is complete when the sources and receivers are identified, mapped and characterised as specified in Section 9.1.1. The theoretical combinations are then created, by matching all sources with all receivers and specifying the minimum flowrate for each match, as explained in Section 9.2, and presented in Table 83.

Source	CO ₂ Emissions	Receiver	CO ₂ Demand	Minimum flowrate
	(Mt/y)		(Mt/y)	(Mt/y)
Source A	2.52	Receiver A	1.8	1.80
Source A	2.52	Receiver B	3.2	2.52
Source A	2.52	Receiver C	5.0	2.52
Source B	5.70	Receiver A	1.8	1.80
Source B	5.70	Receiver B	3.2	3.20
Source B	5.70	Receiver C	5.0	5.00
Source C	0.41	Receiver A	1.8	0.41
Source C	0.41	Receiver B	3.2	0.41
Source C	0.41	Receiver C	5.0	0.41

Table 83: Shared flowrate specification between source and receiver

Following the process specified in Section 9.1.1, once the minimum flowrate between each match is specified, the total capture cost over a project life of 25 years, investment cost and O&M cost over project life were estimated and the optimal capture technology was selected based on three decision variables. The variable with the highest priority is set to be TRL, followed by total cost and purity. The estimated costs and characteristics for all the options of each match are shown in Table 84 with the selected capture technology highlighted. For example, the second/fifth/eighth row shows the selected capture technologies for all theoretically feasible combinations of source A.

Source	Receiver	Flowrate	Source	Compatible Capture	Purity		Total Cost	Capital Cost	O&M Cost
			Туре	technologies	(%)	TRL	(M\$ ₂₀₁₈)	(M\$ ₂₀₁₈)	(M\$ ₂₀₁₈)
А	А	1.83	PC	Oxy-fuel	99.9	8	735.9	311.6	424.3
A	А	1.83	PC	MEA	99.8	9	921.5	398.9	522.6
Α	А	1.83	PC	Amine	99.8	9	921.5	398.9	522.6
Α	В	2.52	PC	Oxy-fuel	99.9	8	1102.3	485.2	617.1
А	В	2.52	PC	MEA	99.8	9	1280.2	563.2	717.0
Α	В	2.52	PC	Amine	99.8	9	1280.2	563.2	717.0
Α	С	2.52	PC	Oxy-fuel	99.9	8	1102.3	485.2	617.1
А	С	2.52	PC	MEA	99.8	9	1280.2	563.2	717.0
Α	С	2.52	PC	Amine	99.8	9	1280.2	563.2	717.0
В	А	1.83	BF	MEA	99.8	9	936.5	405.8	530.8
В	А	1.83	BF	Amine	99.8	9	936.5	405.8	530.8
В	А	1.83	BF	KS-1	99.8	9	936.5	405.8	530.8
В	А	1.80	BF	Selexol	99.0	9	745.3	321.33	424.04
В	В	3.20	BF	MEA	99.8	9	1617.0	719.5	897.5
В	В	3.20	BF	Amine	99.8	9	1617.0	719.5	897.5
В	В	3.20	BF	KS-1	99.8	9	1617.0	719.5	897.5
В	В	3.20	BF	Selexol	99.0	9	1346.2	598.52	747.73
В	С	5.00	BF	MEA	99.8	9	2502.2	1136.8	1365.3
В	С	5.00	BF	Amine	99.8	9	2502.2	1136.8	1365.3
В	С	5.00	BF	KS-1	99.8	9	2502.2	1136.8	1365.3
В	С	5.00	BF	Selexol	99.0	9	2159.7	983.55	1176.18
С	А	0.41	Cement	Oxy-fuel	99.9	8	125.2	44.0	81.1
С	А	0.41	Cement	MEA	99.8	9	212.5	85.4	127.1
С	А	0.41	Cement	Amine	99.8	9	212.5	85.4	127.1
С	А	0.41	Cement	Selexol	99.0	9	149.7	59.15	90.60
С	А	0.41	Cement	Rectisol	99.0	9	149.7	59.15	90.60
С	В	0.41	Cement	Oxy-fuel	99.9	8	125.2	44.0	81.1
С	В	0.41	Cement	MEA	99.8	9	212.5	85.4	127.1
С	В	0.41	Cement	Amine	99.8	9	212.5	85.4	127.1
С	В	0.41	Cement	Selexol	99.0	9	149.7	59.15	90.60
С	В	0.41	Cement	Rectisol	99.0	9	149.7	59.15	90.60
С	С	0.41	Cement	Oxy-fuel	99.9	8	125.2	44.0	81.1
С	С	0.41	Cement	MEA	99.8	9	212.5	85.4	127.1
С	С	0.41	Cement	Amine	99.8	9	212.5	85.4	127.1
С	С	0.41	Cement	Selexol	99.0	9	149.7	59.15	90.60
С	С	0.41	Cement	Rectisol	99.0	9	149.7	59.15	90.60

10.2.4 Technically feasible combinations

The technically feasible options are filtered out, as explained in Section 9.2.1, and are illustrated in Table 85. The matches that are not technically feasible because they cannot meet the required standards appear shaded and were discarded. The full list of technically feasible combinations is shown in

Table 86 and is used as the input for the next step, transportation cost estimation.

10.2.5 Transportation cost estimation

The next step requires the distance estimation between each of the technically feasible combinations, but since this is a simulation using an imaginary region, the distance between each of the combinations was pre-determined and the use of google maps API was omitted. The straight distance between each combination is shown in Table 87 (using

Table 86), along with the realistic distance imitating the real length of the road network by multiplying the straight distance by a factor of 1.04 (assuming an increase of 4%). Using the realistic distance of each of the technically feasible combinations, the total transportation cost over a 25-year project life, transportation capital cost and O&M cost over a project life of 25 years was estimated for each of the available transportation options. The cheapest option for each matching was selected and highlighted in Table 88. In all cases transportation by pipeline was selected because of its significantly lower cost, which is mainly influenced by flowrate. For combinations CA and CB where flowrate was much lower compared to the rest of the combinations (0.4 compared to 1.8 Mt_{CO2}/y) truck transportation was competitive, but pipelines transportation offered a slightly lower option.

Table 89 shows the technically feasible combinations with their respective selected capture technologies and transportation methods along an economic breakdown of capture cost, transportation cost and total project cost in capital costs, O&M costs and total cost over the project lifetime.

Source	Receiver	Purity	Flowrate	Source	Compatible	Purity	TRL	Total	Capital	0&M	Technically
		(%)	(mt _{co2} /y)	Туре	technologies	(%)		(M\$ ₂₀₁₈)	(M\$ ₂₀₁₈)	(M\$ ₂₀₁₈)	Feasible?
Α	Α	22.0	1.83	PC	MEA	99.8	9	921.5	398.9	522.6	Yes
А	В	99.9	2.52	PC	MEA	99.8	9	1280.2	563.2	717.0	No
А	С	95.0	2.52	PC	MEA	99.8	9	1280.2	563.2	717.0	Yes
В	Α	22.0	1.83	BF	Selexol	99.0	9	745.4	321.3	424.0	Yes
В	В	99.9	3.20	BF	Selexol	99.0	9	1346.2	598.5	747.7	No
В	С	95.0	5.00	BF	Selexol	99.0	9	2159.7	983.6	1176.2	Yes
С	Α	22.0	0.41	Cement	Selexol	99.0	9	153.7	60.8	92.9	Yes
С	В	99.9	0.41	Cement	Selexol	99.0	9	153.7	60.8	92.9	No
С	В	95.0	0.41	Cement	Selexol	99.0	9	153.7	60.8	92.9	Yes

Table 85: Theoretical combinations with their respective optimal capture technologies (TRL>Cost>Purity)

Table 86: Technically feasible combinations with their respective optimal capture technologies (TRL>Cost>Purity)

Source	Receiver	Purity	Flowrate	Source	Compatible	Purity	TRL	Total	Capital	0&M	Technically
		(%)		Туре	technologies	(%)		(M\$ ₂₀₁₈)	(M\$ ₂₀₁₈)	(M\$ ₂₀₁₈)	Feasible?
А	А	22.0	1.83	PC	MEA	99.8	9	921.5	398.9	522.6	Yes
А	С	95.0	2.52	PC	MEA	99.8	9	1280.2	563.2	717.0	Yes
В	А	22.0	1.83	BF	Selexol	99	9	745.4	321.3	424.0	Yes
В	С	95.0	5.00	BF	Selexol	99	9	2159.7	983.6	1176.2	Yes
С	А	22.0	0.41	Cement	Selexol	99	9	153.7	60.8	92.9	Yes
С	В	95.0	0.41	Cement	Selexol	99	9	153.7	60.8	92.9	Yes

Table 87: Straight distance between each combination

		Distance	Real	Distance
Source	Receiver	(km)	(km)	
А	А	50		52
А	В	45		46.8
А	С	105		109.2
В	А	65		67.6
В	В	40		41.6
В	С	100		104
С	А	70		72.8
С	В	35		36.4
С	С	40		41.6

Table 88: Transportation selection

		Real Distance	Flowrate	Capture Cost	Capture Cost	Capture O&M	Transportation	Transportation	Transportation Cost	PS		PS
Source	Receiver	(km)	(Mt/y)	Total (M\$ ₂₀₁₈)	Capital (M\$ ₂₀₁₈)	(M\$ ₂₀₁₈)	Туре	Cost total (M\$ ₂₀₁₈)	Capital (M\$ ₂₀₁₈)	Capital	0&M	0&M
А	А	52	1.83	921.5	398.9	522.6	Pipeline	23.57	7.32	3.97	7.32	4.96
А	А	52	1.83	921.5	398.9	522.6	Truck	83.87	-	-	-	-
А	С	109.2	2.52	1280.2	563.2	717.0	Pipeline	55.14	18.19	8.34	18.19	10.42
А	С	109.2	2.52	1280.2	563.2	717.0	Truck	246.56	-	-	-	-
В	А	67.6	1.83	745.4	321.3	424.0	Pipeline	30.80	9.60	5.16	9.60	6.45
В	А	67.6	1.83	745.4	321.3	424.0	Truck	110.84	-	-	-	-
В	С	104	5.00	2159.7	983.6	1176.2	Pipeline	66.67	24.40	7.94	24.40	9.93
В	С	104	5.00	2159.7	983.6	1176.2	Truck	465.92	-	-	-	-
С	А	72.8	0.41	153.7	60.8	92.9	Pipeline	22.29	4.89	5.56	4.89	6.95
С	А	72.8	0.41	153.7	60.8	92.9	Truck	26.74	-	-	-	-
С	В	36.4	0.41	153.7	60.8	92.9	Pipeline	11.14	2.45	2.78	2.45	3.47
С	В	36.4	0.41	153.7	60.8	92.9	Truck	13.37	-	-	-	-

Table 89: Technically feasible combinations with their respective optimal capture technologies and transportation types

Source	Receiver	Capture Cost Total (M\$ ₂₀₁₈)	Capture Cost Capital (M\$ ₂₀₁₈)	Capture O&M (M\$ ₂₀₁₈)	Туре	Transportation Cost total (M\$2018)	Transportation Cost Capital (M\$2018)	Transportation O&M Cost (M\$2018)	Project total (M\$ ₂₀₁₈)	Total investment (M\$ ₂₀₁₈)	Total O&M (M\$ ₂₀₁₈)
А	А	921.5	398.9	522.6	Pipeline	23.6	11.3	12.3	945.1	410.2	534.9
А	С	1280.2	563.2	717.0	Pipeline	55.1	26.5	28.6	1335.4	589.8	745.6
В	А	745.4	321.3	424.0	Pipeline	30.8	14.8	16.0	776.2	336.1	440.1
В	С	2159.7	983.6	1176.2	Pipeline	66.7	32.3	34.3	2226.4	1015.9	1210.5
С	А	153.7	60.8	92.9	Pipeline	22.3	10.4	11.8	176.0	71.2	104.7
С	В	153.7	60.8	92.9	Pipeline	11.1	5.2	5.9	164.8	66.0	98.8

10.2.6 Agreed selling price/business model

Table 89 is the input for the next step, which is the calculation of the agreed selling price, as explained in Section 9.1.1 using 57.9 M\$ $_{2018}$ /Mt_{CO2} (50 $_{2016}$ /t_{CO2}, a price for the average price of commercial CO₂ per tonne provided by personal communication with industrial partners involved in CO₂ trading and located at the port of Antwerp) as the price for the seasonal average price of commercial CO₂ per tonne. Table 90 shows the technically feasible and profitable combinations with their respective costs, source break-even price, receiver break-even price and profitability. It can be observed that the higher the flowrate the higher the project costs, with O&M costs being larger than capital costs in all cases. Table 91 shows the agreed selling price, specified as the average between the source break-even price and receiver break-even price the profit made by the source, receiver, per Mt, total profit made over the project life of a 25-year period, net profit, ROI and payback period. All combinations look very promising, with a payback period of under 7 years and with some of them being as low as 4 years (3.8), and an ROI of 166% to as high as 400%.

Table 90: Technically feasible and profitable combinations

Source	Receiver	Flowrate (Mt/y)	Capture Cost Total	Туре	Transportation	Project total (M\$2018)	Total investment	Total O&M (M\$2018)	Source _{bep} (M\$/Mt)	Receiver _{bep} (M\$/Mt)	Profitable
		((0000 00001 (11192018)	((11, 2018)	((¢)	(¢/	
A	A	1.83	921.5	Pipeline	23.6	945.1	410.2	534.9	21.0	57.9	Yes
А	С	2.52	1280.2	Pipeline	55.1	1335.4	589.8	745.6	21.2	57.9	Yes
В	А	1.83	745.4	Pipeline	30.8	776.2	336.1	440.1	17.0	57.9	Yes
В	С	5.00	2159.7	Pipeline	66.7	2226.4	1015.9	1210.5	17.8	57.9	Yes
С	А	0.41	153.7	Pipeline	22.3	176.0	71.2	104.7	17.2	57.9	Yes
С	В	0.41	153.7	Pipeline	11.1	164.8	66.0	98.8	16.1	57.9	Yes

Table 91: Project cost metrics

Source	Receiver	Agreed Selling price	Source profit	Receiver profit	Project profit per Mt	Total project profit	Net profit	ROI	Payback period
		(M\$ ₂₀₁₈ /Mt)	(M\$ ₂₀₁₈ /Mt)	(M\$ ₂₀₁₈ /Mt)	(M\$ ₂₀₁₈ //Mt)	(M\$ ₂₀₁₈)	(M\$ ₂₀₁₈)	(%)	(years)
А	А	39.5	18.5	18.5	36.9	1661.8	716.7	174.7	6.2
A	С	39.6	18.4	18.4	36.7	2314.3	978.9	166.0	6.4
В	А	37.4	20.5	20.5	41.0	1874.2	1098.0	326.7	4.5
В	С	37.9	20.1	20.1	40.1	5015.0	2788.6	274.5	5.1
С	А	37.6	20.4	20.4	40.8	417.8	241.8	339.4	4.3
С	В	37.0	20.9	20.9	41.9	429.0	264.1	400.1	3.8

10.2.7 Sorting algorithm

The last step is to select the optimal combinations based on the set priority of the variables (selected by the user), which in this case were specified in the following order: (i) of amount of CO₂ utilised; (ii) total profit; and (iii) total investment cost (any of the cost metrics from Table 91 could have been used instead in any order). The sorting algorithm begins by selecting the optimal option for each of the sources and then rating the remaining options in descending order, based on the set of optimisation variables. This is shown in Table 92 where the optimal options for each source are highlighted. If receivers are matched with multiple sources, then as presented in Section 9.1.3, the value for the highest ranked criterion is calculated. Assuming that in this case the objective is maximum utilization, and beginning with the first receiver that is matched with more than one source, receiver C, Table 93 was generated to calculate the change in that criterion (flowrate in this case). The source that shows the largest difference in the flowrate was chosen as the optimal combination for this receiver, so that the decrease in flowrate would be minimized. The rest of the sources were discarded and assigned with their second most optimal combination. If they were matched with a receiver that is matched to more than one source, they will compete again for the specific receiver. Similarly, Table 94 shows the optimal combinations for receiver A and Table 95 shows the optimal combination for receiver C, as receiver C was assigned to source C after Table 94 matched source C with receiver C. The final and optimal solutions (combinations are BC and AA) are illustrated in Table 96 and discussed in Section 10.2.8.

Source	Receiver	Flowrate (Mt/y)
А	А	1.80
А	С	2.52
В	А	1.83
В	С	5.00
С	А	0.41
С	С	0.41

Table 92: Optimal combination for each source

Table 93: Competing sources for receiver C

Source	Receiver	Flowrate	ΔF
		(Mt/y)	(Mt/y)
В	А	1.83	3.17
В	С	5.00	
А	А	1.80	0.72
А	С	2.52	
С	А	0.41	0.00
С	С	0.41	

Table 94: Competing sources for receiver A

		Flowrate	ΔF
Source	Receiver	(Mt/y)	(Mt/y)
А	А	1.80	1.80
С	А	0.41	0.00
С	С	0.41	

Table 95: Second table for sources competing for receiver C

		Flowrate	ΔF
Source	Receiver	(Mt/y)	(Mt/y)
В	С	5.00	5.00
С	С	0.41	0.41

Table 96: Solutions

Source	Туре	Receiver	Туре	Flowrate (Mt/y)
В	Blast furnace	С	EOR	5.00
А	Pulverised coal	А	Algae	1.83
			0: -	

10.2.8 Discussion

Presentation of solution

The recommended solutions from the algorithm and business model involve two combinations, the matching between source A and receiver A and the matching between source B and receiver C. The first combination involves source A, a pulverised coal powerplant producing 2.52 Mt_{co2}/y and receiver A, an algae production plant with the capacity to utilise 1.83 Mt_{co2}/y . This combination results in a total utilisation of 1.83 Mt_{co2}/y . The second combination involves source B, the blast furnace of a steel plant producing 5.7 Mt_{co2}/y and receiver C, an enhanced oil recovery plant with the capacity to utilise 5 Mt_{co2}/y . This combination results in a total utilisation of 5 Mt_{co2}/y . The sources in the region produce 8.62 Mt_{co2}/y and the receivers have the capacity to utilise 10.03 Mt_{co2}/y , enough to be theoretically able to utilise all of the emissions. The recommended solutions have the potential to achieve a regional utilisation of 79.2% and generate \$3.00 billions of profit within the project lifetime. The utilisation potential of the solutions is the result of the prioritization of the optimisation variables. The optimisation potential can be increased and is discussed later in the capture technology selection and sorting algorithm sections. The solutions are illustrated in Table 97.

Table 97: Algorithm and business model solutions

Industry	Туре	Emissions	Industry		Demand	Flowrate
Name		(Mt/y)	Name	Туре	(Mt/y)	(Mt/y)
Source A	PC	2.52	Receiver A	Algae	1.83	1.83
Source B	BF	5.70	Receiver C	EOR	5.00	5.00
Source C	Cement			Beverage		0
		0.41	Receiver B	Carbonation	3.20	
Total		8.62	Total		10.03	6.83

Capture technology selection

Table 98 shows the capture technology options for the combinations of sources A and B. The prioritization of optimisation variables for the selection of capture technology was set in descending order as TRL, total cost and purity. This approach ensures low-cost solutions with high reliability and, as can be observed from Table 98 and Figure 59, both capture technology choices offer a reliable option with TRL 9 but not always the lowest cost. A completely different solution would have been produced if the prioritization of the optimisation variables was set to total cost, purity and TRL in descending order, or purity, total cost and TRL in descending order. The optimal option for the first combination in that case would be oxy-fuel combustion that offers a slightly lower but still reliable TRL 8 with significantly lower (20.1%) total cost and higher purity that could make the source compatible with receiver B, a food industry receiver that requires a very high purity of 99.9%. This could potentially increase the utilisation percentage of the region so that source A provides receiver B with its surplus CO₂ emissions. Changing the prioritization of the optimisation variables and comparing them to the capture technology options of source C from Table 84, would make the captured CO₂ of source C compatible with receiver B, effectively increasing the utilisation potential of the region.

Source	Receiver	Flowrate	Source	Compatible Capture	Purity	TRL	Total Cost	Capital Cost	O&M Cost
			Туре	technologies	(%)		(M\$ ₂₀₁₈)	(M\$ ₂₀₁₈)	(M\$ ₂₀₁₈)
А	А	1.83	РС	Oxy-fuel	99.9	8	735.9	311.6	424.3
A	А	1.83	PC	MEA	99.8	9	921.5	398.9	522.6
А	Α	1.83	PC	Amine	99.8	9	921.5	398.9	522.6
В	С	5.00	BF	MEA	99.8	9	2502.2	1136.8	1365.3
В	С	5.00	BF	Amine	99.8	9	2502.2	1136.8	1365.3
В	С	5.00	BF	KS-1	99.8	9	2502.2	1136.8	1365.3
В	С	5.00	BF	Selexol	99.0	9	2159.7	983.55	1176.18

Table 98: Capture technology options for sources A and B



Figure 59: Proposed regional solutions (where circles represent sources and diamonds represent receivers)

Transportation

Table 98 shows the transportation options and cost estimations for each of the technically feasible combinations. The optimal transportation option in all cases is pipeline transportation. The reason that pipeline transportation is always preferred is due to the transportation distance and CO₂ flowrate. Combinations C/A and C/B have a shorter transportation distance (less than 40 km) and much lower CO₂ flowrate (almost 4.5 times lower) when compared to the rest of the combinations. For these two combinations, pipeline transportation and truck transportation have comparable and almost equal costs, which demonstrates that truck transportation becomes competitive and useful at low flowrates and short distances.

Agreed selling price

Table 90 and Table 91 show the technically feasible and profitable combinations of the region along with the source break-even price, receiver break-even price and agreed selling price, which dictates the share of profits between source and receiver. The business model allows the involved parties to negotiate how profits are split. In this case the profits are equally shared between sources and receivers, but for example this can be changed so that all profits go to the source since there are no modification costs from the receiver's side and all risk is taken by the source which has to invest in capture technologies and pay for transportation. This would justify the shift of profits towards the source's side.

Optimisation algorithm

Table 90 and Table 91 are the inputs of the sorting algorithm, because they provide all the cost metrics and information, which can be used as optimisation variables for the technically feasible and profitable combinations. In this case the sorting algorithm was completed in only one run because

two of the receivers were fully satisfied, and there were no technically feasible combinations involving receiver B because of its high purity requirements. The region cannot reach a higher CO₂ utilization percentage with the current ranking of prioritization variables. The CO₂ utilization percentage can only be increased if the prioritization variables for the selection of capture technologies are altered as explained previously in this section. Looking at Table 99, which shows the cost metrics of the technically feasible and profitable combinations, it can be observed that combinations AA and BC happen to offer both the highest CO₂ utilisation and the highest total project profit. If the prioritization optimisation variables of the sorting algorithm are changed, the profit potential, ROI or payback period could improve but it could significantly compromise the CO₂ utilisation percentage of the region.

Source	Receiver	Flowrate	Project profit per Mt (M\$ ₂₀₁₈ //Mt)	Total project profit (M\$ ₂₀₁₈)	Net profit (M\$ ₂₀₁₈)	ROI (%)	Payback period (years)
А	А	1.83	36.9	1661.8	716.7	174.7	6.2
А	С	2.52	36.7	2314.3	978.9	166.0	6.4
В	А	1.83	41.0	1874.2	1098.0	326.7	4.5
В	С	5.00	40.1	5015.0	2788.6	274.5	5.1
С	А	0.41	40.8	417.8	241.8	339.4	4.3
С	В	0.41	41.9	429.0	264.1	400.1	3.8

Table 99: Flowrate and cost metrics of the technically feasible and profitable combinations,

10.3 Application and validation in real case studies

In order to further validate the proposed algorithm and business model, the following section presents the three real life case studies, where these have been implemented.

- (i) In order to validate the applicability of the algorithm and its compatibility with real data, the algorithm has been implemented into a web-application, the SWAN platform. It is a demonstration of the algorithm, specifically in the utilisation of the sorting algorithm adapted for solid waste (more than one waste types), instead of gases, with the transportation being only performed by trucks.
- (ii) In order to validate the results from an industrial standpoint, the algorithm was applied in five industrial plants across Europe, to assess their carbon capture potential. This has demonstrated the applicability of the source and receiver characterisation, presented in Chapters 2 and 3, as a source and receiver mapping method and the validity of the algorithm's outcome.

(iii) In order to validate the results from a regional standpoint, the algorithm is applied in Malaysia, in order to estimate the national CCU potential from biogenic source. The results confirmed the findings which have been established with the two previous applications

10.3.1 SWAN Platform Development

Introduction

Most of the functions presented for the optimisation of CCU value chains have been implemented in the development of the SWAN platform. The SWAN Platform is an integrated suite of on-line resources and tools that identifies, formulates and assesses industrial symbiosis schemes for the reuse of solid waste as secondary raw material. The platform has been developed as part of the Interreg V-B "Balkan Mediterranean 2014-2020" SWAN project (acronym of "a digital Solid Waste reuse plAtform for BalkaN"). The project focused on the creation of links between industrial partners in the Balkan-Mediterranean region, leading to the development of an ecosystem that will develop local and transnational symbiotic schemes. The University of Huddersfield was not a member of the SWAN consortium, but we were invited as experts in the industrial symbiosis field to contribute to the platform development. The platform is currently fully operational (www.swanplatform.eu) and the University of Huddersfield has recently received a second round of funding to expand its capabilities for the reuse of liquid waste [249], [250].

Approach

The SWAN platform approaches waste management schemes by proposing industrial symbiosis through one-to-one solid waste reuse value chains. It borrows and integrates some characteristics of previous waste management methodologies to map regions and run simulations to optimise matches on a regional level. This is achieved using the developed technical matching algorithm that screens technically feasible options and reduces the options down to economically feasible options based on the preference of the industrial users. Additionally, the platform can be used as a monitoring system that stores solid waste sources and potential receivers and interested parties can share technical and financial information and/or participate in solid waste reuse value chains. The platform uses and adapts, where necessary, the approach presented in Sections 9.1 and 9.2 to map the suitable solid waste sources and receivers, and applies the technical and economical matching to propose the optimal regional combinations based on the preferences of industrial users.

Development

The SWAN platform uses a novel method to propose solid waste value chains. The main differences between the CCU value chains and the solid waste reuse schemes are:

- (i) There are more than one waste types of interest in the solid waste case, whereas in the CCU schemes the only waste stream that can be reused is CO₂.
- (ii) Pipelines cannot be considered for the transportation of solid waste streams.
- (iii) Since the solid waste reuse is a batch process, there is need to check the seasonal availability/matching between sources and receivers and to potentially add temporary storage facilities, before or after transportation.

Having that in mind, the algorithm proposed in Chapter 9 and demonstrated in Chapter 10 has been adapted to the specific characteristics of the SWAN case studies. It is beyond the scope of the thesis to present in detail the SWAN algorithm and the SWAN platform functionalities. However, the following notes highlight the major similarities that can lead to the validation of certain algorithm components.

The SWAN platform formulates the proposed symbiotic schemes by following a three-step approach: (a) mapping and characterising the waste source and receivers; (b) identifying the list of technically feasible combinations; and (c) assessing the viability of the combinations and formulating the list of economically feasible symbiotic schemes.

For the first step, the sources' and receivers' categorisations are based on the guidelines and the characteristics presented in Table 80 (Chapter 9). The database of best practices is similar to the receivers' optimisation information (Section 2.3) and sources' optimisation information (Section 3.6), but tailored for solid waste management purposes.

For the second step, the technical matching is performed in two stages: a literature based technical matching (based on a database of best practices), and a region-specific matching (based on the actual flows recorded in the database). The first stage differentiates the SWAN algorithm from the matching process, presented in Chapter 9, due to the fact of having multiple waste streams of interest. The second stage of the technical matching applied is similar to the technical matching presented in Section 9.2.1 (based on purity constraints, minimum value of exchanged flow). As previously discussed, an extra check is performed for the seasonal availability of each stream and the requirement for waste storage. If yes, an extra cost component is added in the economic matching part. Finally, the distance is estimated based on the available road network, identically to the method

presented in Section 9.2.1., but only trucks are considered, as this is the only available option for solid waste transportation, unlike CO₂ which is in the gas or liquid phase and therefore has more options.

In the third step, the economically feasible symbiotic schemes are identified, using the method explained in Section 9.1.4 for the agreed selling price by estimating the source break-even price and receiver break-even price. The only difference is that the cost of storage is included in the receiver total cost calculation, since the process cannot be continuous and temporary storage of solid waste need to be accounted for.

Figure 60 presents the list of economically feasible solutions as formulated automatically using the SWAN platform. The platform is identical (with adapted properties due to the nature of solid waste) to Table 90, which is the output of the of the proposed algorithm presented in Section 9.2.2.

	Technically Feasible Solutions Excel CSV Print Column visibility v										
Show 10 🗢 entrie	ihow 10 ¢ entries Search:										
Source Industry Name î↓	Receiver Industry Name î↓	European Waste Stream Type î↓	Straight Distance (Km) ↑↓	Driving Distance (Km) ↑↓	Collection Cost î↓	Trasportation Cost î↓	Break Even Price Source ↑↓	Break Even Price Receiver ↑↓	Is Economically Feasible 11		
"ECONOMIDES METAL RECYCLING LTD "	Vasilikos Cement Plant	7.4Plastic wastes Non- hazardous	40.63	52.10	0	203.2	20.32	333.33	숀 Feasible		
"ECONOMIDES METAL RECYCLING LTD "	C.E.I Cyprus Environmental Industries Ltd	6Metallic wastes, ferrous Non- hazardous	0.45	0.82	0	7078.5	0.16	0	A Not Feasible		

Figure 60: List of Economically Feasible Solution (screenshot from SWAN Platform – www.swanplatform.eu [250]

The SWAN platform uses web application architecture to provide a service that is accessible through a web browser. Web applications have the benefits of lower IT costs and reduced complexity with easier and more ergonomic upgrades as they happen only on the web and not on multiple individual computers. When the algorithm is applied in a given region, the platform's output is a list of one-toone technically feasible and economically viable combinations of solid waste sources and solid waste receivers, similarly to the "technically feasible and profitable combinations" from the first part of the sorting algorithm in Section 9.2.1. Each set of combinations includes regional source and receiver specific data as well as transportation, cost estimation and return on investment data that are accessible by everyone involved in the platform. Unlike the proposed optimisation for CCU value chains, the SWAN platform does not utilise this optimisation function of the sorting algorithm, but rather allows each individual industry to select or negotiate with the options that are presented. Some of the proposed criteria are return on investment, payback period, environmental and waste management strategy of the company or even storage availability.

The SWAN platform also utilises a similar business model to the one presented for the optimisation of CCU value chains, with the same types of stakeholders (waste source, waste receiver, transporter, consumer and capital market) (See also Section 9.1.4). The SWAN Platform is fully functional, includes details of more than 500 industrial plants from four countries (Greece, Albania, Bulgaria and Cyprus) and has been already applied in two of these countries to propose solid waste reuse schemes. The application of the platform in the real-life cases has confirmed that the number/type of input data requested is satisfactory for the identification of the new values chains. The time required for the completion of the algorithm in a regional level varies (from a few seconds to 5 minutes) and depends on the number of sources and receivers.

Conclusions

In conclusion, the development of the SWAN platform demonstrates the application and validations of the following parts of the presented algorithm and business model from Sections 9.1 and 9.2:

- (i) Receiver optimisation information (Section 2.3) and source optimisation information (Section 3.6) for the development of the database of best practices that acts as the foundation for the formulation of technically feasible combinations.
- (ii) Transportation cost estimation (Section 9.1.2) of the available road network is used by the SWAN platform.
- (iii) Economical matching is done using the method explained in Section 9.1.4 for the agreed selling price by estimating the source break-even price and receiver break-even price.
- (iv) Business model which aims at providing value to all involved entities from the waste source to the consumer.

10.3.2 Assessing the CCU potential of an industrial plant

Introduction to project

The developed algorithm has been applied in a collaborative project between the University of Huddersfield, Imperial Consultants (ICON), the engineering consulting services of Imperial College London, and a multinational company and leading supplier of refractory products, systems and services. The objective of the project was to assess the CCU potential of the company's plants in

Europe, with the aim to reduce its CO_2 emissions through the application of CCU value chains. The expected deliverable was a technoeconomic analysis that proposes and justifies the selection of technically feasible and profitable CCU value chains.

The participating company has plants in multiple locations spread in multiple countries. It was decided to assess five plants in three different countries. The data are presented in Table 100, without the details of the plants (due to the confidentiality agreement) but it is highlighted that the plants under question were significant producers of CO₂ at a regional level. Moreover, the results presented are limited for the same reason. However, the main generic findings and conclusions as well as the algorithm validation points are highlighted and illustrated in the following sections.

The approach for assessing CCU value chain options was applied in each region individually with a one-to-one matching basis. The outcome was a list of technically feasible and economically viable options with technical and economic description and justification for the proposed options, which fully or partially satisfy the CO₂ emissions of the source. The CO₂ emitting company could choose any one of the proposed solutions, either being driven by profit or CO₂ utilisation maximisation.

Table 100: Plants under assessment

Plant Name	Country	Emissions (t _{CO2})
Plant 1	Country 1	270,000
Plant 2	Country 1	181,000
Plant 3	Country 1	77,500
Plant 4	Country 2	53,000
Plant 5	Country 3	175,000

Methodology

The output was achieved by first visualizing each individual region through characterisation and mapping of sources and receivers. The mapping was executed by first specifying the characteristics of receivers (Chapter 2/Table 1-Table 3) and sources (Chapter 3/Table 8- Table 14) and then identifying the relevant matches by searching through databases. The identification of relevant sources and receivers was done manually, using our critical thinking and experience by (i) looking through the European Pollutant Release and Transfer Register (E-PRTR); (ii) obtaining geographical content from Google Earth about industrial CO₂ receivers; and (iii) scanning the area around each plant in a 5 km radius using Google Maps. The mapping process of sources and receivers is not covered by the algorithm and business model from Chapter 9, but the method used in the context of this case study demonstrates the additional potential of the literature review performed on sources and receivers in Chapters 2 and 3.

According to the procedure of the algorithm presented in Section 9.1.1, the capture cost was estimated, and the optimal capture technology was selected based on TRL and cost. Following the procedure of the algorithm from Section 9.1.2, the available transportation types with their respective conditions that suited each unique case were specified, and the transportation distance and cost were estimated. A list of technically feasible and profitable combinations was prepared for each source, based on the procedure described in Section 9.1.3.

The proposed list of technically feasible and profitable options was followed by a list of assumptions that were used for the technical matching and economic analysis of the case study, along with a list of assumptions based on the business model presented in Section 9.1.4 to demonstrate to the involved entities how costs and duties are assigned/allocated within the value chain. Finally, a sensitivity analysis was performed using the margin for profit, CO₂ price and project lifetime as variables to assess the economic feasibility of the potential CCU value chains. The variables deemed the most uncertain were the following three and were varied as:

- Margin for profit: 0, 10, and 20%
- CO₂ price: 40, 50, 60, 70 and 80 €/t_{CO2}
- Project lifetime: 15, 20 and 25 years

The project's sensitivity analysis confirms that the assumptions used in Section 10.2 were in a reasonable range (CO₂ price of $50 \notin /t_{CO2}$, Project Lifetime 25 years and Margin for profit: 0%). However, it also indicates that the results can be highly affected by the assumptions made. The values that the industrial partner proposed as more reasonable for the formulation of business models was margin for profit equal to 20%, a project lifetime of 15 years and a CO₂ price that varies depending on the carbon market.

Output

The output of the study was a set of solutions for each individual region with a list of all the mapped sources and receivers and the technically feasible options along with their respective capture technology selection, capture cost estimation, transportation cost estimations and the respective sensitivity analysis of each set of options. The output was complemented with the top-ranking options, technical information for sources, receivers and transportation options along with institutional support and consultation support for CCU value chain projects for each individual region. Seven different alternative CCU schemes were identified as technically and economically feasible out

of the 140 technically feasible combinations assessed. Only three of the five studied plants were included in the final list as potential CO_2 sources. It should be also mentioned that in all seven cases the distance between source and receiver did not exceed 35 km, and in six of the seven cases, the two industries were closer than 25 km.

Since the sorting algorithm was not utilised for the proposal of the optimal solutions, the CO₂ emitting company can use the outcome of the consultancy as they see fit. The outcome was not influenced by the sorting algorithm on purpose to allow the company to assess all possible options, understand the required procedures, how they work, how they are executed, how they should be executed and how they fit with each other, and then decide on their own and choose the options that align with the company's plans and vision.

Conclusions

This consultancy project was the first official application of the proposed algorithm and business model from Chapter 9, demonstrating its potential and validity although it was not utilised to its full extent. The project highlighted the literature review performed on all aspects of the CCU value chain, the usefulness of the gathered data for the characterisation of sources and receivers, capture technology selection, capture cost estimation and transportation estimation as well the potential of source and receiver characterisation information for the mapping of sources and receivers. Most of the parts of the algorithm were applied and assessed, demonstrating the validity of all aspects of Chapter 9 and a tailored version of the business model that best suited the scope of the project.

10.3.3 Case study: CCU potential in Malaysia

Introduction

A collaborative research project has been developed with the Universiti Teknologi PETRONAS (UTP) in Malaysia, aiming to assess the carbon capture utilization potential from biogenic sources in Malaysia. A data collection was performed by two undergraduate students as part of their final year project with the aim to apply and test the developed algorithm for CCU value chain optimisation. The collaborative research was followed by a peer-reviewed publication [251].

The development of such a case study was proposed by colleagues in UTP, as Malaysia is in need of CO_2 emissions reduction strategies because of the rapid increase of CO_2 emissions from 1990 to 2019 where they increased by more than four times. The need right now is even more urgent because Malaysia has entered the Paris agreement which specifies a 45% decrease by 2030, with 2005 as a base year. Certain actions have been taken with the deployment of two commercial carbon capture

and storage (CCS) projects which are currently active, but the potential of carbon capture and utilisation to complement the actions/effect of CCS has not been considered yet.

Approach

Initially, to gain an understanding of the CCU potential of the region, the appropriate data were collected, guided from Section 2.3 for receivers and Section 3.6 for sources. Since Malaysia (Figure 61) is separated by the South China Sea into two regions, Peninsular Malaysia, and Borneo's East Malaysia, the mapping methodology was applied in two separate regions since they are geographically separated by sea. These two regions were considered independent and matchings between the two regions were excluded from the analysis.

The focus of the study was on the power generation industry and especially on biogenic carbon sources of the two Malaysian regions. The mapping in the East Malaysia region specified 81 biomass related CO₂ emitting sources, which consist of empty fruit bunch (EFB), wood chips, chicken manure and POME biogas, adding to a total of 3.5 MtCO₂/y. Six potential CO₂ receivers were identified, three of which are methanol production plants, two are urea production plants and one algae production plant. For the West Malaysia region 144 biomass related CO₂ emitting sources were identified, consisting of 32 EFB, 104 POME biogas, three wood chip and five landfill gas power plants, which produce a total of 3.4 MtCO₂/y. There are also six available CO₂ receivers in the region consisting of sugar and urea production plants.



Figure 61. Mapping biogenic CO₂ sources in Malaysia

Methodology and outcomes

The CCU potential case study was completed and further examined by applying the algorithm proposed in Chapter 9 (Sections 9.1 and 9.2), utilising the sorting algorithm, the source and receiver characterization, capture technology selection and cost estimation, transportation selection and cost estimation along with the proposed business model to present the technically feasible and profitable combinations of the two regions. This allowed the selection of the optimal symbiotic scheme combinations for both regions.

In the East region the optimal combinations consisted of one dominant receiver (a urea manufacturer) utilising a total of almost $0.8 Mt_{CO2}$ per year from 20 sources located within both short and long distances (3.8-400 km). The optimal transportation method was by truck. Another four combinations between two receivers and four sources were identified, which contribute to the utilisation of $0.06 Mt_{CO2}$ per year. The optimal transportation method was again by truck.

By contrast, in the West region it was not possible to develop any symbiotic schemes because of the magnitude of the sources' CO_2 emissions. A small cluster of sources in close proximity was identified and could potentially form a CO_2 hub that could be used to transport CO_2 using any onshore or offshore option to a receiver.

The University partners and collaborators provided us with a data set containing the technically feasible combinations of the two regions to perform the analysis. Each source was then matched with a compatible capture technology and the minimum flowrate (between source and receiver) was specified, which allowed the estimation of capture costs. Separation of CO₂ with chemical absorption was selected to satisfy sources and receivers with its high TRL and high CO_2 maximum purity and the requirements of the case study. The next step was to estimate the transportation costs, which was done by utilising the transportation cost models for pipeline and truck transportation and the SWAN platform to estimate the driving distance between source and receiver combinations. The profitable combinations were then selected among the technically feasible combinations, and the CO₂ selling price was specified using the source and receiver break-even prices. The West region did not exhibit any potential. Finally, the sorting algorithm, aiming for maximum utilisation, maximum profit and minimum total cost, provided the optimal combinations for the East region. The results are summarised in Table 101 and Table 102. Table 101 shows the exchanged quantity between source and receiver, the straight and driving distance (as estimated by the SWAN platform), the total cost over a project life with a 25-year period for capture and transportation by pipeline and truck, and the source and receiver break-even prices. Table 101 demonstrates that transportation by truck is

competitive with pipeline transportation and offers a lower cost solution for low transportation volumes for both short and long distances. This is evident in row one where the exchanged flowrate is about 0.7 Mt_{CO2} per year, compared to row two where the exchanged flowrate is 0.08 Mt_{CO2} per year and total transportation costs for pipeline transportation are 13.5 and 40.2 $M\$_{2018}$ respectively. It is also evident that the capture cost is the highest cost and increases with increasing exchanged flowrate.

Additionally, Table 101 demonstrates the ability of the sorting algorithm to allow multiple sources to be matched with one receiver if there is enough CO₂ demand by the receiver, which was not possible to be demonstrated in Section 10.2.7. Table 102 shows the agreed selling price specified as the average between the source break-even price and receiver break-even price, the profit made by the source, receiver and per Mt_{CO2} sold, total profit made over the project life of a 25-year period and certain cost metrics (i.e. net profit, ROI and payback period).

Conclusions

In this case study, all parts of the algorithm have been used, and once more it demonstrates the potential, applicability, and validity of both the algorithm and business model

Table 101: Technically feasible and profitable combination for the East Malaysian region

Source industry name	Receiver industry name	Flowrate	Straight	Driving	Capture	Total transportation	Total	Project	Source	Receiver
		(t/y)	distance	distance	Cost Total	cost (pipeline)	transportation	total	(bep)	(bep)
			(km)	(km)	(M\$ ₂₀₁₈)	(M\$ ₂₀₁₈)	cost truck (M\$2018)	(M\$ ₂₀₁₈)	(M\$/Mt)	(M\$/Mt)
Sipitang (Sabah Forest) Biomass Plant	Sabah Ammonia Urea (SAMUR)	661440	3.8	11.9	346.9	13.5	7.08	354.0	21.4	57.9
Olive Energy (Mukah) Biomass Plant	Asean Bintulu Fertilizer	8422	105.7	143.5	5.0	40.2	1.08	6.1	28.9	57.9
Untung Ria Sdn. Bhd.	Petronas Methanol Labuan 2	33280	98.1	171.6	19.0	66.5	5.12	24.1	28.9	57.9
Selangau POM Biomass Plant	Asean Bintulu Fertilizer	11136	111.5	150.5	6.6	44.6	1.50	8.1	29.0	57.9
Mukah Green Energy Plant	Asean Bintulu Fertilizer	8004	124.5	168.6	4.8	46.8	1.21	6.0	29.9	57.9
STF Agriculture Sdn. Bhd.	Sabah Ammonia Urea (SAMUR)	147	148.0	180.7	0.1	33.6	0.02	0.1	33.9	57.9
Eksons Biomass Energy Sdn. Bhd.	Sabah Ammonia Urea (SAMUR)	24960	246.7	413.0	14.3	148.1	9.24	23.6	37.8	57.9
SSB - Kapilit POM Biomass Plant	Sabah Ammonia Urea (SAMUR)	2088	229.8	385.5	1.3	87.0	0.72	2.0	38.7	57.9
Cash Horse Biomass Plant	Sabah Ammonia Urea (SAMUR)	8352	269.6	418.1	5.0	117.0	3.13	8.1	38.8	57.9
Seguntor Bioenergy Biomass Plant	Sabah Ammonia Urea (SAMUR)	8004	291.3	442.9	4.8	122.9	3.18	7.9	39.7	57.9
Kina Biopower Biomass Plant	Sabah Ammonia Urea (SAMUR)	8004	293.3	445.2	4.8	123.6	3.19	8.0	39.8	57.9
IOI Bio-Energy Plant	Sabah Ammonia Urea (SAMUR)	10440	293.5	457.0	6.2	133.7	4.27	10.4	40.0	57.9
Evergreen Intermerge Biomass Plant	Sabah Ammonia Urea (SAMUR)	4176	276.2	457.7	2.5	113.6	1.71	4.3	40.7	57.9
TSH Bio-Energy Plant	Sabah Ammonia Urea (SAMUR)	8352	284.2	482.0	5.0	134.9	3.61	8.6	41.1	57.9
QL Tawau Biogas Sdn. Bhd.	Sabah Ammonia Urea (SAMUR)	17088	291.7	502.8	9.9	164.0	7.70	17.6	41.3	57.9
Seo Energy Sdn. Bhd.	Sabah Ammonia Urea (SAMUR)	835	298.4	458.8	0.5	94.5	0.34	0.9	42.2	57.9
Potensi Gaya-Sg Burung POM Biomass Plant	Sabah Ammonia Urea (SAMUR)	4872	300.8	503.3	2.9	128.0	2.20	5.1	42.2	57.9
Leluasa Biomass Steam Plant (KLK)	Sabah Ammonia Urea (SAMUR)	7656	315.4	532.3	4.6	146.5	3.65	8.2	42.9	57.9
Kwantas Biomass Plant	Sabah Ammonia Urea (SAMUR)	6821	317.2	534.5	4.1	144.0	3.27	7.3	43.1	57.9
LDEO Energy Plant	Sabah Ammonia Urea (SAMUR)	835	315.9	532.4	0.5	109.6	0.40	0.9	44.8	57.9
Felda-Sahabat Biomass Plant	Sabah Ammonia Urea (SAMUR)	5220	395.4	625.9	3.2	161.0	2.93	6.1	46.6	57.9
Nilam Permata POM-Biomass Plant	Sabah Ammonia Urea (SAMUR)	4176	390.4	634.2	2.5	157.4	2.37	4.9	47.1	57.9
Kembara Sakti POM-Biomass Plant	Sabah Ammonia Urea (SAMUR)	4176	396.6	643.1	2.5	159.6	2.41	4.9	47.4	57.9
Jerangan Bestari POM-Biomass Plant	Sabah Ammonia Urea (SAMUR)	4176	413.0	652.8	2.5	162.0	2.44	5.0	47.7	57.9

Source industry name	Receiver indusry name	Agreed	Selling	Source profit	Receiver profit	Project profit per	Total project	Net profit	ROI (%)	Payback
		price (M\$2	₂₀₁₈ /Mt)	(M\$ ₂₀₁₈ /Mt)	(M\$ ₂₀₁₈ /Mt)	Mt (M\$ ₂₀₁₈ //Mt)	profit (M\$ ₂₀₁₈)	(M\$ ₂₀₁₈)		period (years)
Sipitang (Sabah Forest) Biomass Plant	Sabah Ammonia Urea (SAMUR)		39.7	18.2	18.2	36.5	655.7	301.7	458.6	5.5
Olive Energy (Mukah) Biomass Plant	Asean Bintulu Fertilizer		43.4	14.5	14.5	29.0	9.1	3.1	559.9	4.5
Untung Ria Sdn. Bhd.	Petronas Methanol Labuan 2		43.4	14.5	14.5	29.0	36.1	12.1	541.1	4.6
Selangau POM Biomass Plant	Asean Bintulu Fertilizer		43.4	14.5	14.5	28.9	12.1	4.0	556.3	4.5
Mukah Green Energy Plant	Asean Bintulu Fertilizer		43.9	14.0	14.0	28.0	8.8	2.8	566.7	4.4
STF Agriculture Sdn. Bhd.	Sabah Ammonia Urea (SAMUR)		45.9	12.0	12.0	24.0	0.2	0.0	655.2	3.8
Eksons Biomass Energy Sdn. Bhd.	Sabah Ammonia Urea (SAMUR)		47.8	10.1	10.1	20.1	29.9	6.3	600.5	4.2
SSB - Kapilit POM Biomass Plant	Sabah Ammonia Urea (SAMUR)		48.3	9.6	9.6	19.2	2.5	0.5	645.3	3.9
Cash Horse Biomass Plant	Sabah Ammonia Urea (SAMUR)		48.3	9.6	9.6	19.1	10.1	2.0	623.6	4.0
Seguntor Bioenergy Biomass Plant	Sabah Ammonia Urea (SAMUR)		48.8	9.1	9.1	18.2	9.8	1.8	630.2	4.0
Kina Biopower Biomass Plant	Sabah Ammonia Urea (SAMUR)		48.8	9.1	9.1	18.1	9.8	1.8	630.7	4.0
IOI Bio-Energy Plant	Sabah Ammonia Urea (SAMUR)		48.9	9.0	9.0	17.9	12.8	2.3	628.0	4.0
Evergreen Intermerge Biomass Plant	Sabah Ammonia Urea (SAMUR)		49.3	8.6	8.6	17.2	5.1	0.9	647.4	3.9
TSH Bio-Energy Plant	Sabah Ammonia Urea (SAMUR)		49.5	8.4	8.4	16.8	10.3	1.8	638.4	3.9
QL Tawau Biogas Sdn. Bhd.	Sabah Ammonia Urea (SAMUR)		49.6	8.3	8.3	16.6	21.2	3.6	628.4	4.0
Seo Energy Sdn. Bhd.	Sabah Ammonia Urea (SAMUR)		50.0	7.9	7.9	15.7	1.0	0.2	683.8	3.7
Potensi Gaya-Sg Burung POM Biomass Plant	Sabah Ammonia Urea (SAMUR)		50.1	7.8	7.8	15.7	6.1	1.0	654.8	3.8
Leluasa Biomass Steam Plant (KLK)	Sabah Ammonia Urea (SAMUR)		50.4	7.5	7.5	15.0	9.6	1.4	651.8	3.8
Kwantas Biomass Plant	Sabah Ammonia Urea (SAMUR)		50.5	7.4	7.4	14.8	8.6	1.3	654.8	3.8
LDEO Energy Plant	Sabah Ammonia Urea (SAMUR)		51.4	6.5	6.5	13.1	1.1	0.1	701.8	3.6
Felda-Sahabat Biomass Plant	Sabah Ammonia Urea (SAMUR)		52.2	5.7	5.7	11.3	6.8	0.7	682.0	3.7
Nilam Permata POM-Biomass Plant	Sabah Ammonia Urea (SAMUR)		52.5	5.4	5.4	10.8	5.5	0.6	688.9	3.6
Kembara Sakti POM-Biomass Plant	Sabah Ammonia Urea (SAMUR)		52.6	5.3	5.3	10.5	5.5	0.5	691.0	3.6
Jerangan Bestari POM-Biomass Plant	Sabah Ammonia Urea (SAMUR)		52.8	5.1	5.1	10.2	5.5	0.5	693.3	3.6

Table 102: Cost metrics for the proposed combinations of the East Malaysian region

10.4. Chapter 10 conclusions

Chapter 10 presents how the main novelty of this PhD thesis functions, how the developed algorithm selects the optimal set of solutions to propose optimised CCU value chain schemes that aim at CO₂ emission minimisation. The functionality of the algorithm is demonstrated with a simulation and a case study due to the lack of real data because of time constraints and limited availability of data. Its relevance and applicability are validated with the SWAN platform development, which was largely based on the concepts discussed in Chapter 9. The application of the main idea behind this algorithm and business model might not be limited only within the area of CCU value chains but could be tailored to other areas of Supply Chain Management such as solid waste management schemes, as demonstrated with the development of the SWAN platform. The algorithm's results are validated on an industrial level with its application on five industrial plants across Europe and on a regional level with a case study in Malaysia. This does not only validate the algorithm and business to support CCU value chains.
Chapter 11: Future CCU value chains

11.1 Introduction

Even though the proposed algorithm and business model have been applied as demonstrated in Chapter 10, gaps exist in certain areas. They can only be filled in the future when the commercial application of CCU value chains is employed on a larger scale and new information and data emerge. By researching and investigating such information, new ideas will be developed that could update and improve the algorithm and business model.

11.2 Progress made in the current work

This section establishes the progress made in the current work by summarising the main findings and novelties of the thesis and prepares for the next section dealing with research areas that can improve the algorithm and business model.

11.2.1 Receivers

CO₂ receivers can be characterised by their most important factors, utilisation type (permanent, temporary), purity requirements (minimum CO₂ purity), technology readiness level and conversion factor (amount of CO₂ utilised per unit product). The literature review examining carbon dioxide receivers' production processes revealed that permanent utilisation options include carbon mineralisation that stores CO₂ into minerals, pH control for pH stabilization at desired levels via CO₂ addition, enhanced fossil fuel recovery by CO₂ injection, CO₂ as a chemical feedstock for the production of useful chemicals and fuels and other industrial processes. Temporary utilisation options share some of the industries that utilise CO₂ permanently, carbon mineralisation, pH control and CO₂ as chemical feedstock. Although they share these industries, the products of temporary storage in these industries are different and do not offer permanent CO₂ storage. The unique industries of temporary utilisation options include enhanced growth of vegetables and plants by absorbing CO₂, food industry, CO₂ as a working fluid and other temporary uses. Data for the rest of the receiver factors were collected from various sources and were compiled into a comprehensive up to date catalogue of receivers to create a receiver knowledge base to be used in the development of the proposed algorithm and business model for the optimisation of CCU value chains.

By looking at the bigger picture in a scenario where CCU value chains have been commercialised, it can be concluded that the commercialisation of CCU value chains has the ability to change

dramatically the current CO₂ life cycle by creating two new CO₂ storage units. Permanent utilisation products can be seen as the foundation of CCU value chains because they provide a solution for the continuous increase of atmospheric CO₂ abundance. Temporary utilisation options on the other hand, although they cannot store CO₂ permanently, can contribute to the infrastructure and ecosystem of CCU value chains by increasing CO₂ demand and decreasing fossil fuel demand. Permanent and temporary utilisation options are two of the main contributors of CCU value chain impact and sustainability because their size determines the utilisation potential of a region, and technical and economic aspects determine the satisfaction of the involved entities (sources, capture companies, transportation companies, receivers and the general public).

11.2.2 Sources

The literature review examining CO₂ sources showed that sources suitable for carbon dioxide capture consist of industrial processes and can be grouped by industry into the heat and power industry, metal industry, stone and clay industry and chemical and petrochemical industry. They were further categorised to the exact emission source within a process and sub-process of a specific product. Most industries produce CO₂ via combustion of fossil fuels that results mainly in N₂, CO₂ and water and some other impurities. Processes involving syngas production and its oxidation produce CO₂/H₂ streams. Other industrial processes like fermentation, gas sweetening and biogas purification result in pure CO₂ streams produced as a by-product. This means that CO₂ industrial sources can be grouped into three categories based on their output streams, CO₂/N₂, CO₂/H₂ and pure CO₂ as a by-product. Important factors of CO₂ sources that could be used in CCU value chain optimisation include CO₂ purity, emission intensity and compatibility with CO₂ capture technologies. The grouping and characterisation factors of sources were compiled into a comprehensive up to date catalogue of CO₂ sources to create a source knowledge base to be used in the development of the proposed algorithm and business model for the optimisation of CCU value chains. Compatibility with CO₂ capture technologies is addressed in the next section, Section 11.2.3.

11.2.3 Capture technologies

Carbon dioxide capture can be characterised by separation principle, technology readiness level, maximum achievable purity and cost. Separation principles include absorption with chemical or physical solvents, adsorption with chemical and physical adsorbents, cryogenics, membrane separation with polymeric and inorganic membranes, combustion in pure oxygen with oxy-fuel combustion and chemical looping, and novel hybrid technologies. The most popular capture technologies are chemical absorption and especially absorption with MEA, oxyfuel combustion and physical absorption with Selexol and Rectisol technologies. Chemical absorption and oxyfuel combustion are compatible with CO₂/N₂ streams and physical absorption is compatible with CO₂/H₂. The associated technology readiness level and maximum achievable purity have been assigned to each capture technology to create a knowledge base for capture technologies.

Due to the lack of capture cost estimation models in literature, a meta-analysis was performed to bridge the gap. The meta-analysis of CO₂ capture costs of this PhD research presented the capture cost metrics from the standpoint of heat and power generation industry and extracted, standardized and sorted capital and O&M capture cost data from various sources, related to the amount of CO₂ captured per source and capture technology. A regression analysis was then performed using the meta-analysis data to develop capture cost models for capture technologies and sources based on just one variable, CO₂ flowrate.

The literature review on CO₂ capture technologies also revealed that there is an established capture technology selection method for natural gas processing, which requires the temperature, pressure, CO₂ flowrate, inlet stream concentration and desired outlet concentration of the process stream. Although it is a very useful method for the natural gas processing industry that could potentially be applied to other CO₂ sources, it was not considered in this PhD research because of time constraints associated with identifying the relevant data for each industrial process within the project's time frame. An alternative method was suggested involving the characteristics of capture technologies from the capture technology knowledge base and the development of a source-capture compatibility table from examples of sources matched with certain capture technologies. The selection method was enhanced by introducing a third factor (other than TRL and maximum achievable purity), capture cost, which could be easily estimated by specifying flowrate.

11.2.4 Transportation

The literature review focusing on transportation of CO₂ revealed that it can take place via onshore and offshore transportation using pipelines, railroad tankers, truck tankers and ship tankers. Each transportation type has unique transportation conditions that relate to the transportation type's favourable phase and therefore they have to be altered accordingly. Each CO₂ stream has different impurities, level of impurities, density and viscosity, which are all factors affecting phase behaviour. Finally, appropriate compression and dehydration are required to avoid corrosion and prepare for transportation. The process of each transportation type and unique transportation conditions were presented followed by a review of transportation costs. The literature review showed that the selection procedure of transportation options mainly involves the consideration of maturity, distance and CO₂ flowrate. The conventional means of CO₂ transportation is by pipeline because it is the most researched, reliable and efficient technology. Other technologies were also considered for their individual strengths that could contribute to CCU value chain optimisation, like truck tankers for their efficiency and low cost with small CO₂ flowrates and maturity with the food industry for years, and ship tankers with their cost effectiveness for offshore transportation. Railroad tankers were excluded because of their low maturity and lack of infrastructure, and offshore pipelines for their high cost and low maturity. For the scope of this research the requirements for the selection of transportation cost estimation models were quick and reliable, low resolution cost models.

11.2.5 Algorithm and business model

As demonstrated in Chapter 8, CCU value chains have very complex interactions between each step of the CCU value chain and for this reason a completely new approach was selected to tackle the optimization of CCU value chains. Existing models (discussed in Chapter 8) were not used because, although they have the potential to provide users with highly detailed solutions, it is very difficult, and in some cases impossible, to gather the data required by such models. Tan et al. [179] developed a method for estimating the optimal method and optimal amount of CO₂ to be captured from power plants based on cost. The model uses a plethora of parameters that need to be specified in order to provide the desired outcome. These are removal ratios, relative power losses and compensatory power losses for each one of the available capture technologies, and assumptions for cost of electricity for power plants with and without capture technologies, which additionally is only possible for power plants [179]. Sun and Wenying [207] developed a MILP model for pipeline infrastructure development model for EOR and ECBM that uses a database of sources and sinks (which might not be suitable for a holistic optimization and or appropriately updated) and utilizes information about location, area, shape, emissions, storage potential and other, which additionally requires a utilization target to be set, further increasing the complexity of optimization. Additionally, such solutions involve the difficulty of integrating individual optimization models, which makes them unable to provide meaningful holistic solutions, unless integrated.

A balance between low-level and high-level detail should be aimed so that it is low-level enough to be simple, quick and reliable and at the same time accurate to make decisions based on regional targets but not high-level so that operations become complex enough to make the integration of optimization problems impossible (as it is currently). Therefore, a solution with a lower level of detail was pursued to reduce the amount of data required and to allow the integration of individual optimization problems into the algorithm and business model proposed in Chapter 9 (capture problem, transportation problem, utilization problem, commercialization and integration through the algorithm and database), and applied and validated in Chapter 10 (with the development of SWAN platform, industrial consultancy and the case study in Malaysia). The proposed algorithm and business model provide low resolution and holistic solutions (which select the sets of optimal solutions based on the optimisation preference of the user for the development of CCU value chains by matching CO₂ sources and receivers based on (i) the technological compatibility and maturity of technologies, (ii) CO₂ capture costs, (iii) CO₂ transportation costs, (iv) CO₂ utilisation costs and (v) profit within a defined project lifetime), at their current state, but have the potential to be further developed into a tool with better capabilities.

11.3 Gaps and future research

The level of detail and accuracy of the algorithm and business model can be significantly improved by investigating the following five areas over the initial period of the application of CCU value chains: (i) receivers, (ii) sources, (iii) capture technologies, (iv) transportation and (v) policies regarding CCU value chains. The improvements discussed in these five areas cannot be implemented at the moment because they are based on the application and commercialization of CCU value chains. The proposed algorithm and business model can be improved by adding new functionalities, information and data, which will become available upon the commercialization and collected during the period of application.

11.3.1 Future research

Receivers

As CCU value chains start to gain popularity, industrial receivers will become more interested in substituting conventional CO₂ with captured CO₂. They will begin to investigate their options in terms of CO₂ purity and potential impurities that could pose as disadvantages for the substitution. As a result, more understanding will be gained in terms of technological compatibility of captured CO₂ with individual receivers and issues with specific contaminants. This could potentially result in the modification of the receiver's process in such way to accept captured CO₂, which by extension can increase the capital and operating costs of the receiver (influencing receiver break-even price etc.). It will also clarify the technology readiness level of each receiver. In some cases, this can cause the

rapid increase of TRL, and in some other cases (e.g. food industry) the opposite, which might demonstrate that it cannot be further improved. Conversion factors will become more accurate as receivers begin to rely more and more on captured CO₂, which by extension can improve the estimation accuracy of the algorithm for CO₂ demand. The estimation accuracy of the minimum flowrate between source and receiver (Section 9.2.1.) will increase, leading to the better allocation of supply and demand between sources and receivers and finally better optimization. Seasonal CO₂ shortages might occur but will be handled through the knowledge base for transportation procedure and transportation timing, which will be improved as practical knowledge and experience is gained through the initial design of CCU value chains and their application. As this takes place more receivers will be identified and introduced to the algorithm and CCU value chains' planning and optimization, leading to an optimization tool with increased capabilities and the ability to increase the utilization potential and viability of regions. Emphasis should be given on strengthening the relationships between the matched industries to ensure the longevity and quality of their co-operation and by extension the region.

Sources

Similarly, to CO₂ industrial receivers, sources (especially small-scale ones, not currently reporting emissions) will increase the level of detail of emission intensities so that a more accurate representation of CO₂ emissions is estimated. A more accurate estimation of CO₂ emissions will lead to a more accurate estimation of capture costs. Additionally, this will help with the matching of CO₂ sources and CO₂ receivers as both supply and demand of CO₂ will become more accurate, producing better optimized CCU value chains. The commercialization of CCU value chains will attract the interest of more potential CO₂ sources that were less popular during the current literature review, which could be added to the algorithm and CCU value chains planning and optimization, improving the capabilities of the algorithm and the optimization of regions.

Capture technologies

As discussed in Chapter 5 and observed in Chapter 10, the biggest obstacle in the commercialization of CCU value chains is capture cost, which accounts to about 70-90% of the total cost of CCU value chains. Special emphasis should be given in the research, development and improvement of such technologies to reduce costs or at least bring them to the minimum possible level and achieve maximum efficiency. Eventually, more advanced technologies will arise and TRLs of previous technologies will increase, which should be added to the algorithm to ensure it is updated according to the latest advancements. Better TRLs will provide more freedom of choice for source to capture technology matching, leading to more mature and lower cost options. As demonstrated in Chapter 5, although some procedures have been introduced to account for the cost imposed to power plants utilizing capture cost technologies, gaps were identified in the cost estimation of CO₂ capture, which were filled by the development of the presented cost models. Capture cost estimation could be improved by utilizing the data emerging from the initial application of CCU value chains to create source specific cost models for all available capture technologies, covering a relevant range of flowrates. In an ideal scenario a cost model of each capture technology should be available for every source, assuming they are compatible.

Transportation

Although there are five transportation options (pipelines onshore and offshore, truck tankers, railway tankers and ship tankers), only three of them are included in the algorithm presented in Chapter 9 and 10 (pipelines and truck tankers for onshore transportation, and ship tankers for offshore transportation) because there were gaps regarding the specifications of technical design or transportation procedures, or economic barriers due to low technological maturity and especially cost estimation models. For these reasons it is important that the less researched transportation options (railway tankers and offshore pipelines) and even current options are fully investigated and updated in terms of technical design, specification of equipment and transportation conditions and procedures. Research should also be conducted for the development of cost models for the feasible transportation options and the improvement of current models included in this PhD thesis. An analysis for the competitive range of each transportation option regarding flowrate and distance could prove very beneficial for quick estimations, although the proposed algorithm is already built with this function. For example, the algorithm can propose the most optimal transportation option in each case, but it does not provide a reason, whereas the analysis could suggest a maximum and minimum distance for which each option is optimal.

Policy making

With the beginning of CCU value chains commercialization, it is expected that the interested authorities will start scrutinizing and assessing all processes in terms of health, safety and environmental compliance to propose new policies regarding products, receivers, sources and transportation. The following section presents recommendations which would be beneficial to the efficient and safe employment of CCU value chains

CO₂ Streams

In order for waste streams to be reused in another industrial process, they must meet the End of Waste criteria (common and lawful use, non-detrimental to environment and human health, existing market). Since 2016, industrial flue gases from sectors that do not belong to the European Emissions Trading Scheme (Non-ETS sectors) are considered by the Waste Framework Directive (WFD) as emissions and not as wastes. However, that is not enough, and Castillo-Castillo and Angelis-Dimakis [252] propose further amendments to what the WFD requires, such as the classification of all gaseous effluents as recyclable by-products and the adaptation of the End-of-Waste criteria to allow for the recycling of such streams products by mineralization or other value-adding CCU processes.

Another policy-related hurdle is that in the current Emission Trading Scheme (ETS), the captured CO₂ can only be subtracted from the reporting if it is captured from a plant, reporting to ETS, and transferred/used in another plant, included in the ETS. This covers the majority of the CO₂ sources, but excludes many potential receivers (e.g. greenhouses, ethanol production), which either are not included in the ETS or are too small to report. Such issues might lead to certification and validation issues for a new symbiotic value chain.

Products

Although the receivers added in the receivers' database of the algorithm (Chapter 9) were added based on the respective literature review (Chapter 2), which presented the knowledge base of receivers along with minimum CO₂ purities, conversion factors and technology readiness levels, the safety and performance of using and consuming captured CO₂ products should be further assessed to create guidelines, procedures and policies for their production. This will provide a clearer understanding of the products' safety and utilization potential to pinpoint the products that will make difference in mitigation of CO₂ emissions and the ones that can support and sustain CCU value chains in the long run (or both).

Sources

CO₂ emitting sources are the starting point of CCU value chains and the reason to pursue CO₂ emissions reduction. To achieve reduction/mitigation, they have to be mapped before they are assessed for CO₂ capture and therefore, it is important to record emissions, study them, report them and understand them better. It would be very helpful if strict policies regarding measuring of such emissions and emissions in general were in place, so that they are reported in publicly available databases. If more public databases were available, it would facilitate the mapping process of CO₂ industrial sources, the estimation of emissions and by extension the optimization process.

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Transportation

Transporting captured CO₂ between countries could be a sensitive subject that might require regulations and new policies that support CCU value chains. Additionally, all CO₂ transportation options except onshore pipelines (which have been demonstrated for years for EOR) could benefit from further research since they have not been used extensively for the transportation of captured CO₂. Safety regulations are required for all means of transportation, offshore pipelines, truck, railway and ship tankers.

11.3.2 Algorithm Gaps

Certain gaps exist in the proposed algorithm (Chapter 9) which are known and were not just simply dismissed, but rather they were filled with the most current information and conclusions from the literature review. Those gaps exist because of the little or no application so far of specific parts of the CCU value chains, and no information or few conclusions can be drawn from literature.

The current algorithm's source-to-capture technology matching method is based on a knowledge base of examples of sources and capture technologies that were matched for real cases or simulations and demonstrate their compatibility. They could be considered enough to provide quick and reliable low-resolution solutions but certainly they could be developed to a more mature and detailed method. By investigating the compatibility of each source with every type of capture technology in terms of process conditions (temperature, pressure, concentration of components, targets), a similar matching method to the one developed for the natural gas processing industry could be developed. This method would require more information with a higher level of detail but in return it would provide a more detailed solution, which can be used to make more informed decisions for more optimized CCU value chains.

As mentioned in Section 11.2.3 Capture cost estimation models could be improved from data emerging from the initial application of CCU value chains to create source specific cost models for all available capture technologies. In an ideal scenario a cost model of each capture technology should be available for every compatible source to provide more CO₂ capture technology options

Another gap exists in the algorithm's transportation options, which currently includes only pipelines, truck tankers and ship tankers. Less researched options like offshore pipelines and railway tankers were dismissed because literature indicated that they provide less flexibility in term of ease of transportation and higher costs. These options should be further investigated in terms of cost and ease of transportation and, if proven to be useful, a full investigation should be followed to update

technical design, specification of equipment and transportation conditions and procedures. Even current options can benefit from a full investigation on these aspects.

The current distance estimation method depends on the available road infrastructure. The algorithm identifies the shortest route (based on the available road infrastructure) from the source's location to the receiver's location and utilizes that distance to provide a realistic transportation cost estimation instead of the estimation of the straight distance. The further research and placement of policies around CO₂ transportation regarding transportation conditions, procedures (e.g., ban of installing new pipelines in certain countries / use of existing network only), health and safety and transportation between countries will add restrictions to route selection. The restrictions that would emerge from such policies should be added to the method of distance estimation increases and makes the planning of routes for transportation infrastructure development easier because of terrain and policy restrictions/constraints. A more detailed distance estimation could also provide a more accurate transportation cost estimation which are both (distance and transportation costs) parameters used in the source-to-receiver matching method.

11.4 Chapter 11 Conclusions

It was stated that the main novelties of this PhD thesis have four gaps (limited source-capture matching method, limited capture technology options, limited transportation options, limited distance estimation method) that were addressed and analysed in terms of why they exist and how they could be further improved. Nevertheless, the application of the algorithm and business model constitutes a complete and viable approach towards the optimisation of CCU value chains. This research started with the purpose to answer if CCU value chains can mitigate CO₂ emissions, and to do so it identified, examined and characterised all parts of the CCU value chain. It presents a knowledge base for sources, receivers and their characterisation, a framework for matching sources with capture technologies, models for the estimation of capture costs and ways to improve them. With the development and application of the algorithm and business model presented in Chapters 9 and 10, it was demonstrated that a viable approach towards the optimisation of CCU value chains for the production of capture CO₂ products exists, which can permanently and temporarily store CO₂ emissions. This PhD thesis concludes that CCU value chains are a tool with high potential for the mitigation of CO₂ emissions, and it presents a plan to achieve the commercialisation of CCU value chains.

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Appendix 1. Extracted standardized data

A1.1 Standardized data used for the cost model of chemical absorption

CO₂ captured	TCR	0&M	Reference	CO ₂ captured	TCR	0&M	Reference
(Mt/y)	(MŞ)	(M\$/y)		(Mt/y)	(M\$)	(M\$/y)	
0.000001	0.000001	0.000001	(0,0)	3.00	543.82	25.90	[50]
0.04	73.37	2.88	[50]	3.10	448.25	26.89	[9]
0.04	67.62	2.88	[50]	3.16	993.23	39.73	[74]
0.05	48.91	1.44	[50]	3.18	503.77	20.15	[74]
0.10	76.25	4.32	[50]	3.29	595.51	23.82	[74]
0.10	50.35	1.44	[50]	3.33	1231.89	49.28	[74]
0.10	69.06	2.88	[50]	3.34	1314.86	52.59	[74]
0.20	292.05	14.39	[50]	3.38	258.10	15.49	[9]
0.20	192.78	5.75	[50]	3.54	1281.29	51.25	[74]
0.20	267.59	12.95	[50]	3.79	1103.09	44.12	[74]
0.40	146.74	7.19	[50]	3.82	1170.19	70.21	[102]
0.40	96.39	2.88	[50]	3.82	734.21	36.52	[113]
0.40	133.80	5.75	[50]	3.90	884.41	35.38	[74]
0.40	273.35	12.95	[50]	3.91	1410.90	56.44	[74]
0.40	250.33	11.51	[50]	3.96	1325.69	79.54	[102]
0.50	179.83	5.75	[50]	4.01	619.99	37.20	[103]
0.70	248.89	7.19	[50]	4.01	524.00	31.44	[103]
0.70	345.28	17.26	[50]	4.03	1128.31	45.13	[74]
0.73	158.56	9.51	[9]	4.06	347.78	20.87	[9]
0.80	139.55	4.32	[50]	4.09	1317.52	79.05	[102]
0.80	192.78	8.63	[50]	4.15	648.36	38.90	[103]
0.80	420.09	20.14	[50]	4.15	532.08	31.93	[103]
0.87	460.05	20.73	[113]	4 17	535.65	32.14	[9])
0.88	387.83	23.27	[9]	4.25	634.11	25.36	[74]
0.94	233.92	28.07	[45]	4 39	759 22	30 37	[74]
0.95	231.94	13.92	[9]	4.50	580.07	26.52	[100]
1.07	481.57	104.15	[105]	4.59	694.36	41.66	[103]
1.09	289.01	11.56	[74]	4.64	588.38	35.30	[103]
1.09	287.53	11.50	[74]	4.66	492.77	29.57	[9]
1.09	295.66	11.83	[74]	4.66	677.09	40.63	[103]
1.10	158.56	9.51	[9]	4.66	606.27	36.38	[103]
1.11	484.19	19.37	[74]	4.93	729.57	43.77	[103]
1.13	257.55	15.45	[102]	4.94	616.52	36.99	[103]
1.25	391.16	23.47	[102]	4.95	698.45	41.91	[103]
1.30	575.70	34.54	[102]	4.96	628.56	37.71	[103]
1.34	434.48	26.07	[102]	5.09	700.04	42.00	[103]
1.47	215.89	8.64	[74]	5.09	678.96	40.74	[103]
1,60	450.62	18.02	[74]	5.09	678,96	40.74	[103]
1.60	484.14	19.37	[74]	5.10	638.01	38.28	[103]
1,70	535.86	42.87	[45]	5.18	426,45	17.06	[74]
1.83	201.57	12.09	[9]	5.34	1684.42	101.07	[102]
1.84	269.46	16.17	[9]	5.52	775.51	46.53	[103]
1.84	385.46	23.13	[9]	5.52	618.38	37.10	[103]
2.09	420.04	25.20	[9]	5.58	833.15	41.66	[45]
2.20	423.76	16.95	[74]	5.58	648.01	77.76	[45]
2.20	501.04	20.04	[74]	5.50	648.01	32.40	[45]
2.25	785.12	47.11	[102]	5.59	1424.56	85.47	[102]
2.25	1034.81	62.09	[102]	6.05	1453.77	87.23	[101]
2 35	234 76	14 09	[9]	6 21	1109 11	46 71	[113]
2.35	183 17	10.99	[9]	6 44	534 53	42 76	[45]
2.36	406.99	24.42	[9]	6 44	427.62	25.66	[45]
2.50	195 56	11 72	[0]	6.44	748 3/	37.42	[45]
2.80	286.09	17.17	[9]	6.67	1295.50	62.93	[100]
2.95	1093.19	43.73	[74]	6.67	1288.13	61.31	[100]

Table 103: Standardized data used for the cost model of chemical absorption

Costs: constant USD 2018

Not TCR for: [50] TPC [74] TOC, [105] TOC,

Costs: constant USD 2018,

Not TCR for: [50] TPC [74] TOC, [105] TOC,

Chemical absorption includes: MEA, KS-1, Econamine FG+, advanced amines, cansolv, ammonia, 1st generation amines, 2nd generation amines

Sources include: Pulverised coal (PC), Supercritical pulverised coal (SCPC), Ultra supercritical pulverised coal (USCPC), Natural gas combustion cycle (NGCC), Combined heating and power plant (CHP), gas fired furnace, coke production, iron ore sintering, blast furnace (BF), Top gas recycling blast furnace (TGRBF), Smelting reduction iron, cement plant, pre-calciner, Fluid catalytic cracking (FCC), hydrogen production, ammonia production, ethylene oxide production, furnaces.

Compression is not included: [50]

A1.2 Standardized data used for the cost model of physical absorption

CO ₂ captured (Mt/y)	TCR (M\$)	0&M (M\$/y)	Reference	CO ₂ captured (Mt/y)	TCR (M\$)	O&M (M\$/y)	Reference
0.000001	0.000001	0.000001	(0,0)	3.37	1148.63	68.92	[102]
0.06	63.30	1.44	[50]	3.50	921.91	55.31	[102]
0.06	64.74	2.88	[50]	3.52	963.52	57.81	[102]
0.10	66.18	1.44	[50]	3.60	471.88	14.39	[50]
0.10	67.62	2.88	[50]	3.70	480.52	18.70	[50]
0.20	253.21	7.19	[50]	3.89	369.92	22.20	[103]
0.20	258.96	10.07	[50]	4.05	270.08	16.20	[9]
0.40	128.04	4.32	[50]	4.68	153.14	9.19	[9]
0.40	129.48	5.75	[50]	4.73	94.29	5.66	[9]
0.50	237.38	7.19	[50]	4.97	300.36	18.02	[103]
0.50	241.70	10.07	[50]	5.02	2178.65	130.72	[102]
1.00	363.98	11.51	[50]	5.04	321.82	19.31	[103]
1.00	371.18	14.39	[50]	5.39	374.23	22.45	[103]
1.38	311.04	18.66	[9]	5.44	2357.15	141.43	[102]
1.80	322.42	19.35	[9]	5.52	309.97	18.60	[103]
1.87	181.55	10.89	[9]	5.56	2469.04	148.14	[102]
2.15	242.47	14.55	[9]	5.58	1666.30	83.31	[45]
2.36	654.49	39.27	[9]	5.58	1758.87	87.94	[45]
2.37	56.39	3.38	[9]	5.64	360.80	21.65	[103]
2.38	239.83	14.39	[9]	5.81	2918.87	175.13	[102]
2.75	239.83	14.39	[9]	5.94	2224.18	133.45	[101]
3.06	317.17	19.03	[102]	6.01	259.34	15.56	[103]
3.21	401.76	24.11	[102]	6.37	2406.26	144.38	[101]
3.22	428.73	25.72	[102]	6.41	2519.94	151.20	[101]
3.29	261.22	15.67	[102]	6.44	427.62	21.38	[45]
3.31	370.06	22.20	[102]	6.44	1175.97	58.80	[45]

Table 104: Standardized data used for the cost model of physical absorption

Costs: constant USD 2018

Not TCR for: [50] TPC

Physical absorption includes: Selexol, Rectisol, PVSA

Sources include: Integrated gasification combined cycle (IGCC), CHP, gas fired furnace, coke production, iron ore sintering, BF, TGRBF, smelting reduction iron, pre-calciner, FCC, hydrogen production ammonia production ethylene oxide production Compression is not included: [50]

A1.3 Standardized data used for the cost model of oxy-fuel combustion

CO ₂ captured (Mt/y)	TCR (M\$)	0&M (M\$/y)	Reference	CO ₂ captured (Mt/y)	TCR (M\$)	O&M (M\$/y)	Reference
0.000001	0.000001	0.000001	Forced through 0,0	3.96	1089.39	43.58	[74]
0.47	104.48	26.12	[105]	4.00	1144.34	68.66	[102]
0.82	203.06	12.18	[45]	4.06	1230.93	73.86	[102]
0.94	311.89	12.48	[45]	4.14	1144.49	45.78	[74])
1.00	647.01	38.82	[45]	4.38	445.54	26.73	[103]
1.28	233.59	11.68	[45]	4.38	1337.12	53.48	[74]
1.74	692.80	13.86	[45]	4.51	441.20	26.47	[103]
3.18	564.85	22.59	[74]	4.82	523.51	6.25	[113]
3.41	907.61	36.30	[74]	5.03	487.75	29.26	[103]
3.57	1100.92	66.06	[102]	5.05	515.25	20.61	[74]
3.58	1101.68	66.10	[102]	5.09	525.35	31.52	[103]
3.60	1485.72	59.43	[74]	5.35	504.96	30.30	[103]
3.67	1150.19	46.01	[74]	5.41	552.59	33.16	[103]
3.76	1693.86	67.75	[74]	5.48	1958.19	117.49	[102])
3.78	1545.69	21.26	[113]	5.54	583.46	35.01	[103]
3.86	1000.08	40.00	[74]	5.54	673.32	40.40	[103]
3.86	1069.75	42.79	[74]	5.99	522.12	31.33	[103]
3.89	1122.36	67.34	[102])	6.01	1493.76	89.63	[101]

Table 105: Standardized data used for the cost model of oxy-fuel combustion

Costs: constant USD 2018

Not TCR for [74] TOC, [105] TOC

Oxyfuel combustion includes: Oxyfuel combustion

Sources include: PC, SCPC, USCPC, Fluidised bed combustion (CFB), pre-calciner, cement plant, FCC, combined stack of oil refineries, hydrogen production.

Compression is not included: [50]

A1.4 Standardized data used for the cost model of metal industry

Table 106: Standardized data used for the cost model of metal industry

CO ₂ captured (Mt/y)	TCR (M\$)	O&M (M\$/y)	Reference	CO₂ captured (Mt/y)	TCR (M\$)	0&M (M\$/y)	Reference
0.000001	0.00001	0.000001	Forced through 0,0	5.58	648.01	32.40	[45]
0.40	46.04	7.19	[50]	5.58	1666.30	83.31	[45]
0.80	139.55	4.32	[50]	5.58	1758.87	87.94	[45]
0.80	192.78	8.63	[50]	5.58	740.58	37.03	[45]
0.80	161.13	5.75	[50]	5.58	833.15	33.33	[45]
2.80	335.21	14.39	[50]	5.58	648.01	19.44	[45]
3.00	543.82	25.90	[50]	6.44	534.53	42.76	[45]
3.60	471.88	14.39	[50]	6.44	427.62	25.66	[45]
3.70	480.52	18.70	[50]	6.44	748.34	37.42	[45]
5.58	833.15	41.66	[45]	6.44	427.62	21.38	[45]
5.58	648.01	77.76	[45]	6.44	1175.97	58.80	[45]

A1.5 Standardized data used for the cost model of cement industry

Table 107: Standardized data used for the cost model of cement industry

CO ₂ captured (Mt/y)	TCR (M\$)	O&M (M\$/y)	Reference	CO₂ captured (Mt/y)	TCR (M\$)	O&M (M\$/y)	Reference
0.00001	0.00001	0.00001	Forced through 0,0	0.40	51.79	7.19	[50]
0.30	90.64	4.32	[50]	0.40	112.22	4.32	[50]
0.40	146.74	7.19	[50]	0.47	104.48	26.12	[105]
0.40	96.39	2.88	[50]	0.82	203.06	12.18	[45]
0.40	133.80	5.75	[50]	0.83	69.01	3.45	[45]
0.40	128.04	4.32	[50]	1.07	481.57	104.15	[105]
0.40	129.48	5.75	[50]	1.28	233.59	11.68	[45]

A1.6 Standardized data used for the cost model of FCC

CO ₂ captured (Mt/y)	TCR (M\$)	0&M (M\$/y)	Reference	CO₂ captured (Mt/y)	TCR (M\$)	O&M (M\$/y)	Reference
0.00001	0.00001	0.00001	Forced through 0,0	0.70	248.89	7.19	[50]
0.40	83.44	12.95	[50]	0.70	345.28	17.26	[50]
0.40	273.35	12.95	[50]	0.70	258.96	11.51	[50]
0.40	250.33	11.51	[50]	0.70	287.73	11.51	[50]
0.40	168.32	7.19	[50]	0.80	420.09	20.14	[50]
0.40	83.44	12.95	[50]	0.94	233.92	28.07	[45]
0.40	208.61	8.63	[50]	0.94	311.89	12.48	[45]
0.50	179.83	5.75	[50]	1.00	363.98	11.51	[50]
0.50	237.38	7.19	[50]	1.00	371.18	14.39	[50]
0.50	241.70	10.07	[50]	-	-	-	-

Table 108: Standardized data used for the cost model of FCC

A1.7 Standardized data used for the cost model of IGCC

Table 109: Standardized data used for the cost model of IGCC

CO ₂ captured	TCR (M\$)	0&M	Reference	CO ₂ captured	TCR (M\$)	O&M (M\$/y)	Reference
0.00001	0.00001	(IVI,7/Y) 0.00001	Forced through 0.0	(WIC/Y) 2.01	E / 1 0 2	21.67	[74]
0.00001	0.00001	0.00001	Forced through 0,0	3.01	541.02	21.07	[74]
1.38	311.04	18.00	[9]	3.82	514.98	20.60	[74]
1.80	322.42	19.35	[9]	3.89	369.92	22.20	[103]
1.87	181.55	10.89	[9]	4.05	270.08	16.20	[9]
2.15	242.47	14.55	[9]	4.35	632.45	25.30	[74]
2.36	654.49	39.27	[9]	4.68	153.14	9.19	[9]
2.37	56.39	3.38	[9]	4.73	94.29	5.66	[9]
2.38	239.83	14.39	[9]	4.97	300.36	18.02	[103]
2.75	239.83	14.39	[9]	5.02	2178.65	130.72	[102]
3.06	317.17	19.03	[102])	5.04	321.82	19.31	[103]
3.20	475.02	19.00	[74]	5.06	421.23	16.85	[74]
3.21	401.76	24.11	[102]	5.39	374.23	22.45	[103])
3.22	428.73	25.72	[102]	5.44	2357.15	141.43	[102])
3.29	261.22	15.67	[102]	5.52	309.97	18.60	[103])
3.31	370.06	22.20	[102]	5.56	2469.04	148.14	[102])
3.37	1148.63	68.92	[102]	5.64	360.80	21.65	[103])
3.45	363.26	14.53	[74]	5.81	2918.87	175.13	[102]
3.50	921.91	55.31	[102]	5.94	2527.28	82.36	[113]
3.52	963.52	57.81	[102]	5.94	2224.18	133.45	[101]
3.56	454.95	18.20	[74]	6.01	259.34	15.56	[103]
3.65	415.78	16.63	[74]	6.08	983.55	27.71	[113]
3.66	439.24	17.57	[74]	6.37	2406.26	144.38	[101]
3.79	187.10	7.48	[74]	6.41	2519.94	151.20	[101]

A1.8 Standardized data used for the cost model of SCPC

CO ₂ captured (Mt/y)	TCR (M\$)	0&M (M\$/v)	Reference	CO ₂ captured (Mt/y)	TCR (M\$)	O&M (M\$/y)	Reference
0.00001	0.00001	0.00001	Forced through 0,0	4.42	1219.10	73.15	[103]
1.83	201.57	12.09	[9]	4.51	441.20	26.47	[103]
2.80	286.09	17.17	[9]	4.59	694.36	41.66	[103]
3.10	448.25	26.89	[9]	4.64	1221.45	73.29	[103]
3.16	993.23	39.73	[74]	4.64	588.38	35.30	[103]
3.18	503.77	20.15	[74]	4.66	677.09	40.63	[103]
3.18	564.85	22.59	[74]	4.66	606.27	36.38	[103]
3.29	595.51	23.82	[74]	4.70	1286.04	77.16	[103]
3.33	1231.89	49.28	[74]	4.81	1289.61	77.38	[103]
3.34	1314.86	52.59	[74]	4.81	1370.66	82.24	[103]
3.57	1100.92	66.06	[102]	4.93	729.57	43.77	[103]
3.58	1101.68	66.10	[102]	4.94	616.52	36.99	[103]
3.67	1150.19	46.01	[74]	4.95	698.45	41.91	[103]
3.79	1103.09	44.12	[74]	4.96	628.56	37.71	[103]
3.80	1095.34	65.72	[103]	5.03	487.75	29.26	[103]
3.82	1170.19	70.21	[102]	5.09	525.35	31.52	[103]
3.86	1000.08	40.00	[74]	5.09	700.04	42.00	[103]
3.86	1069.75	42.79	[74]	5.09	678.96	40.74	[103]
3.89	1122.36	67.34	[102]	5.09	678.96	40.74	[103]
3.94	1084.45	65.07	[103]	5.10	638.01	38.28	[103]
3.96	1325.69	79.54	[102]	5.23	1268.02	76.08	[103]
3.96	1089.39	43.58	[74])	5.34	1684.42	101.07	[102]
4.00	1144.34	68.66	[102])	5.35	504.96	30.30	[103]
4.01	619.99	37.20	[103]	5.41	552.59	33.16	[103]
4.01	524.00	31.44	[103]	5.48	1958.19	117.49	[102])
4.03	1128.31	45.13	[74])	5.52	775.51	46.53	[103]
4.06	1230.93	73.86	[102]	5.52	618.38	37.10	[103]
4.09	1317.52	79.05	[102]	5.54	583.46	35.01	[103]
4.14	1144.49	45.78	[74]	5.54	673.32	40.40	[103]
4.15	648.36	38.90	[103]	5.59	1424.56	85.47	[102]
4.15	532.08	31.93	[103]	5.99	522.12	31.33	[103])
4.38	445.54	26.73	[103]	6.67	1288.13	61.31	[92]
4.38	1284.82	77.09	[103]				

Table 110: Standardized data used for the cost model of SCPC

A1.9 Standardized data used for the cost model of NGCC

Table 111: Standardized data used for the cost model of NGCC

CO ₂ captured	TCR (M\$)	0&M	Reference	CO ₂ captured	TCR (M\$)	O&M (M\$/y)	Reference
(Mt/y)		(M\$/y)		(Mt/y)			
0.00001	0.00001	0.00001	Forced through 0,0	1.30	575.70	34.54	[102]
0.73	158.56	9.51	[9])	1.34	434.48	26.07	[102]
0.87	460.05	20.73	ZEP	1.47	17.34	0.69	[74]
0.88	387.83	23.27	[9]	1.60	161.91	6.48	[74]
0.95	231.94	13.92	[9]	1.60	484.14	19.37	[74]
1.09	289.01	11.56	[74]	1.84	269.46	16.17	[9]
1.09	287.53	11.50	[74]	1.84	385.46	23.13	[9]
1.09	295.66	11.83	[74]	2.20	423.76	16.95	[74]
1.10	158.56	9.51	[9]	2.20	501.04	20.04	[74]
1.11	484.19	19.37	[74]	2.25	785.12	47.11	[102]
1.13	257.55	15.45	[102]	2.25	1034.81	62.09	[102]
1.25	391.16	23.47	[102]	4.50	580.07	26.52	[92]

A1.10 Standardized data used for the cost model of USCPC

CO ₂ captured (Mt/y)	TCR (M\$)	O&M (M\$/y)	Reference	CO₂ captured (Mt/y)	TCR (M\$)	O&M (M\$/y)	Reference
0.00001	0.00001	0.00001	Forced through 0,0	4.17	535.65	32.14	[9]
2.35	183.17	10.99	[9]	4.25	634.11	25.36	[74]
2.36	406.99	24.42	[9]	4.38	1337.12	53.48	[74]
2.95	1093.19	43.73	[74]	4.39	759.22	30.37	[74]
3.41	290.30	11.61	[74]	4.82	523.51	6.25	[113]
3.78	1545.69	21.26	[113]	5.05	515.25	20.61	[74]
3.82	734.21	36.52	[113]	5.18	426.45	17.06	[74]
3.91	1410.90	56.44	[74]	6.21	1109.11	46.71	[113]
4.06	347.78	20.87	[9]				

Table 112: Standardized data used for the cost model of USCPC

Appendix 2. Data for base year, CPI and exchange rates

CPI (2010)=100)			Offic US\$)	ial exchang	ge rate (LCU per
Year	US	EU	UK	US	EU	UK
1995	69.883	-	73.932	1	-	0.634
1996	71.931	-	76.040	1	-	0.641
1997	73.613	-	77.714	1	-	0.611
1998	74.755	-	79.129	1	-	0.604
1999	76.391	-	80.516	1	0.938	0.618
2000	78.971	-	81.468	1	1.083	0.661
2001	81.203	-	82.717	1	0.117	0.695
2002	82.490	-	83.974	1	1.058	0.667
2003	84.363	-	85.130	1	0.884	0.612
2004	86.622	-	86.314	1	0.804	0.546
2005	89.561	-	88.117	1	0.804	0.55
2006	92.450	-	90.281	1	0.796	0.543
2007	95.087	-	92.436	1	0.730	0.5
2008	98.737	-	95.691	1	0.680	0.544
2009	98.386	-	97.568	1	0.717	0.642
2010	100	-	100	1	0.754	0.647
2011	103.157	-	103.856	1	0.718	0.624
2012	105.292	-	106.529	1	0.778	0.633
2013	106.834	-	108.97	1	0.753	0.64
2014	108.567	-	110.551	1	0.753	0.608
2015	108.696	-	110.958	1	0.901	0.655
2016	110.067	-	112.077	1	0.903	0.741
2017	112.412	-	114.944	1	0.885	0.777
2018	115.157	-	117.579	1	0.847	0.75

Table 113: Data for base year, CPI and exchange rates [120]