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Experimental Investigation of a semi-industrial Carbonate Looping Process for scale-up

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1 Introduction

The continuous increase of CO_2 concentration in the atmosphere can be observed with the beginning of industrialization in the 18^{th} century. Since then, the CO_2 concentration has increased from pre-industrial 280 ppm to 400 ppm in 2017 [1]. The average annual increase of 0.5 ppm can be attributed to the human influence on the climate system. The current anthropogenic greenhouse gas emissions are on the highest level since the beginning of records. According to a study by the Intergovernmental Panel on Climate Change (IPCC), with a probability of over 90 % the anthropogenic greenhouse gas emissions are the main cause of climate warming and the rise in the average global temperatures. It increased by about 1 °C in the 20^{th} century [2]. The changes have comprehensive effects on humans and nature. A drastic reduction of greenhouse gas emissions is mandatory in order to counteract it.

Combustion of fossil fuels and industrial processes count to the main sources of CO_2 emissions, others are forestry and land use [3]. Different sectors are responsible for the continuous energy-related increase of CO_2 emissions. As depicted in Fig. 1.1, the power and heat production releases almost 40 % of the energy-related CO_2 emissions. The industry and the transport sectors also have a significant share.

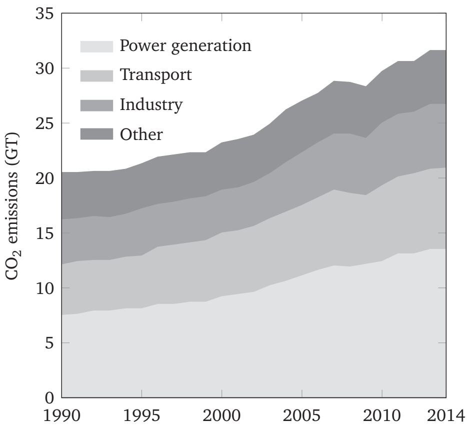

Figure 1.1: Global CO_2 emissions from 1990 to 2014 by sector [4]

At the United Nations climate conference in Paris 2015 an agreement was reached to limit global warming. The temperature increase is to be limited to 2 ° C, preferably 1.5 ° C above the level before industrialization. Furthermore, significant efforts needed to reduce emissions were also agreed. The currently assigned measures on national levels are not sufficient to comply with the concluded agreement [5]. The limitation of greenhouse gas emissions and thus the global warming to 2 ° C requires various activities in different sections. Increased energy efficiency in industry, transport and construction sectors, shutting down of less efficient coal-fired power stations, increased investments in renewable power supply, the abolition of subsidies for fossil fuel as well as the reduction of methane emissions from oil and gas production and processing are short-term actions. Nevertheless, the achievement of long-term success to meet the climate goals demands commercial availability of advanced technologies to electrify the transport and to decarbonize the power and industry sector. These technologies will be the key to succeed in the early 2020s. However, the development of electric vehicles or CO_2 capture and storage (CCS) technologies is essential [4].

1.1 The Potential of Carbon Capture and Storage/Utilization Technologies

Carbon capture and storage (CCS) or utilization (CCU) describes the industrial intent to avoid CO_2 emissions to the atmosphere in order to meet the long-term climate goals. Therefore, the CO_2 is directly separated at the location of the emissions source, e.g. coal-fired power plants or industrial processes such as cement or steel production. The separated CO_2 allows either the storage in underground facilities (CCS) or the re-utilization (CCU), e.g. in chemical industry processes.

Since the power sector is one of the largest contributors to the overall CO_2 emissions, the International Energy Agency (IEA) considers CCS to be an essential part to reduce CO_2 emissions besides efficiency improvements, the expansion of renewables, fuel switching or nuclear power. The "New Policies Scenario" defines thereby the benchmark of the IEA and depicts today's policy ambitions. At the moment, power production emits around 500 gramme CO_2 per kilowatt-hour. In the "Sustainable Development Scenario", more than 60 % of the cumulative CO_2 emission savings occur in the power sector. This scenario outlines an integrated approach to achieve the goal of 2 ° C. According to this scenario, 17 giga-tonnes of CO_2 are saved (see Fig 1.2). CCS thereby accounts for savings of 2 giga-tonnes and is an important means to decrease the emissions to 325 gramme of CO_2 per kilowatt-hour in 2040 [6].

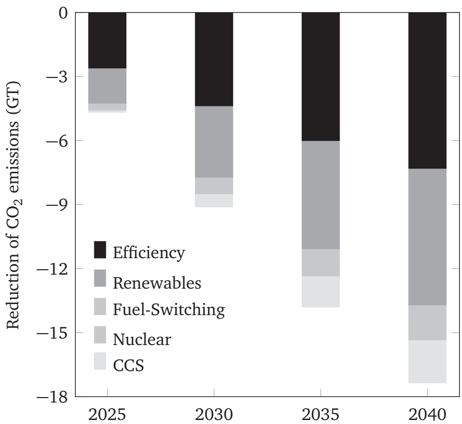

Figure 1.2: Global CO_2 emissions reduction in the "Sustainable Development Scenario" in comparison to the "New Policies Scenario" [6]

The CO_2 capture technologies can be divided into three processes: pre-combustion capture, post-combustion capture, and oxy-fuel combustion. The processes differ in the point where CO_2 is captured. It is either captured before, after or during combustion. Fig. 1.3 shows the principal scheme of the various CO_2 capture processes. Abanades et al. [7] and the IEAGHG [8] give a very detailed assessment of the development stages. Hereafter, a description and the development progress of first generation and second generation technologies based on fluidized beds is given.

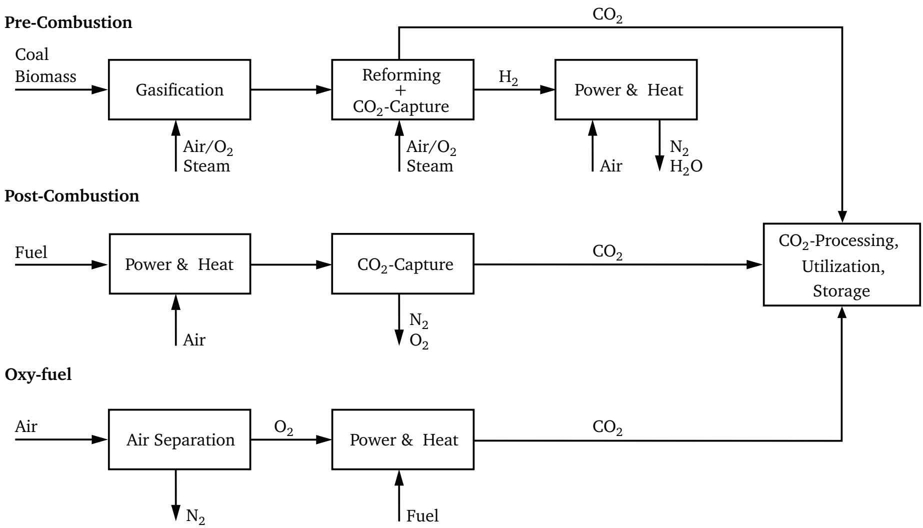

Figure 1.3: CO_2 capture processes [9]

The CO_2 capture in the pre-combustion technologies takes places before the combustion. Carbonaceous fuel is gasified or reformed. The generated product or synthesis gas mainly consists of CO_2 and H_2. The CO_2 is separated from this stream by gas scrubbing, e.g. with Selexol [10] or Rectisol [11]. Combustion of the remaining almost pure H_2 stream in a gas turbine allows heat and power production without CO_2 emissions. An example for a pre-combustion process is the Integrated Gasification Combined Cycle (IGCC) with CO_2 capture [12].

The Kemper County Energy Facility of the Mississippi Power Company has lead the way for the pre-combustion CO_2 capture processes. The construction of a 562 MW_{el} power plant using IGCC to produce power from lignite began in 2010. The plant was to capture at least 65 % of the CO_2 from the synthesis gas by physical absorption (selexol scrubbing). The annually captured 3 Mio. tonnes of CO_2 were to be used to increase the oil production by means of Enhanced Oil Recovery (EOR). For this purpose, a pipeline network of approx. 100 km was necessary to be build for the transport of CO_2 to the neighbouring oil fields. In 2017, an increase in the costs from $ 2.4 billion to an estimated $ 7.5 billion and a further delay in the commercial operation of coal became apparent. The construction of the IGCC project was officially terminated. Instead, it was announced that the fuel is switched from lignite to natural gas [13].

Post-combustion CO_2 capture processes are characterised by their ability to retrofit existing emission sources such as power and industrial plants. The flue gas comes from the combustion of fossil fuel and air and is used for heat and power production. It is led into a downstream capture plant where the CO_2 is separated from the flue gas stream. The separated CO_2 then can be process and stored or utilized depending on the application. The CO_2-depleted flue gas stream of the host plant exits the capture unit and is released into atmosphere. Exemplary post-combustion processes are based on chemical absorption, such as amine scrubbing [14, 15] and chilled ammonia [16], or limestone-based absorption like Carbonate Looping [17].

Amine scrubbing has already been realized on an industrial scale with the Boundary Dam Project by the Canadian power supplier SaskPower and the Petra Nova Project by the American NRG Energy. Boundary Dam is the first commercial full-scale application of post-combustion CCS. The capture plant uses chemical absorption and separates more than 80 % of the CO_2 of a 111 MW_{el} coal-fired power station. The captured 1 Mio. tonnes of CO_2 are used for EOR and the investigation of underground storage with liquid CO_2. With the beginning of capture operation in 2014, the readiness for commercial full-scale application was proven [18]. The second commercial application by Petra Nova started operation in 2017 and decarbonizes a slip stream of 37 % from the W.A. Parish Unit 8 with 654 MW_{el} in Houston. The process utilizes a different amine solvent. Boundary Dam uses Shell's Cansolv solvent while Petra Nova uses Mitsubishi's KS-1 solvent. The captured CO_2 of 1.6 mega-tonnes per year is used for EOR [19].

The oxy-fuel process is based on the combustion of carbonaceous with pure oxygen [20, 21], i. e. the conversion of carbon takes places in a nitrogen-free atmosphere. Thus, the products of the combustion process are almost exclusively CO_2 and H_2O. A comparably pure stream of CO_2 exits the process after condensing the steam from the flue gas. The oxy-fuel process features the inherent CO_2 capture. The variations of oxy-fuel combustion arise by the different methods to provide the oxygen. The most common possibility is the cryogenic air separation. Other approaches are membranes processes [22] or Chemical Looping Combustion [23]. Chemical Looping Combustion provides the oxygen by alternating oxidation and reduction of a solid oxygen carrier in a high temperature process.

In 2011, the oxy-fuel technology was demonstrated by energy supplier Vattenfall in the German pilot plant Schwarze Pumpe. The CO_2 capture of more than 90 % was demonstrated with a 30 MW_{th} lignite fired oxy-fuel boiler [24]. The pilot plant was built for research purposes. The amount of 1,500 tonnes of CO_2 from capture operation was sent to the storage place Ketzin. It was the first time that CO_2 captured from a power plant was stored [25]. The technological readiness ona a demonstration scale was proven with the Callide oxy-fuel project in Australia. The full chain of CCS was demonstrated by operating a 30 MW_{el} oxy-fuel boiler for more than 10,000 hours in 2014 [26, 27]. But the technology has not yet been realized in a full-scale demonstration unit. A project to build a 250 MW_{el} boiler in Jänschwalde in Germany has been cancelled [28].

The first generation CCS technologies like IGCC, amine scrubbing or oxy-fuel combustion have already reached demonstration or even commercial scale. Nevertheless, these technologies have the disadvantages of high energy requirements. So, they significantly decrease the efficiency of the power production from the upstream host plant or the total plant, respectively. As a consequence, the demand of energy is higher causing ecological and economic disadvantages in terms fuel consumption and increased CO_2 avoidance costs. In contrast, second generation CCS technologies such as Carbonate Looping (CaL) and Chemical Looping Combustion (CLC) offer economic and ecological improvements in terms of a better energetic efficiency and thus a lower penalty of the power production. These processes are currently under development to reach the next development level, the application in demonstration scale. Both high-temperature solid looping processes, the CaL [29, 30] and the CLC [31–33] have been a rapid development process from laboratory to successful operation in MW_{th} scale. The next step will be a demonstration plant in the magnitude of order around 10-30 MW_{th}. Due to the unclear political conditions and the change of the power sector towards renewable energies, the required financing to bring these processes to the next stage of maturity is challenging. However, an increase of CO_2 certificates could change the conditions and may lead to a higher demand of second generation CCS technologies.

1.3 CO_2 Processing, Transportation, Storage and Utilization

The CCS and the CCU process chains consist of processing, transport and storage or utilization of the captured CO_2. Therefore, the CO_2 captured in the aforementioned processes has to be cleaned. Typical impurities such as H_2O, O_2, Ar, N_2, SO_x and NO_x have to be limited in the process stream since they may cause complications during transport or storage, e. g. corrosion in the pipelines. The CO_2 is processed and purified after the capture on site and the technical effort depends on the applied capture technology. The minimum requirements for the purity of CO_2 and the maximum concentrations of each species depends on the further usage. However, the components should be present in concentrations that are harmless both for the health of living organisms and with regard to technical safety [34]. Various approaches exist to condition the CO_2 product whereat most are based on multistage compression, e. g. by piston or turbo compressors, with intermediate and subsequent cooling. According to Pipitone et al. [34], the processing in general consists of the following steps:

- Compression of the CO_2 product stream to 20 bar, cooling to 25 °C and separation of water
- SO_2 removal by seawater flue gas desulphurization (SFGD)
- Compression to 33 bar and separation of water
- Adsorption of remaining water content
- Final conditioning by distillation, compression and cooling to 110 bar and 25 °C

The high pressure at ambient temperature reduces the CO_2 into a fluid state and significantly lowers the transport volume. After the CO_2 purification and compression, the transport of CO_2 captured from large point sources is feasible via pipeline or ship to the storage or utilization site. Both options allow a throughput of large amounts of CO_2 captured from commercial power and industrial plants. In general, the transport depends on the required amount and the distance between CO_2 source and sink. The on- and offshore transport via pipeline at pressures of 100-200 bar is state of the art in the USA and Canada for Enhanced Oil Recovery (EOR) where a pipeline network of 6,000 kilometers already exists [35]. The transport by ship is an economic option for distances longer than 2,000 kilometers since it is more energy-intensive and requires much more expensive infrastructure compared to pipelines. Similar to the transport of liquid natural gas, the CO_2 is liquefied to 7-9 bar at -50 °C [36].

Different possibilities for CO_2 storage (CCS) are available. Geologic formations such as deep layers of sandstone soaked by salt water (saline aquifers), depleted oil or gas fields as well as coal seams are possible storage solutions. Storage in an oil or gas field is the only commercially available technology. Especially in the USA, it is common to use CO_2 as an extraction agent into depleted oil and gas fields for Enhanced Oil (EOR) or Gas (EGR) Recovery. With respect to Europe, the capacities of saline aquifers thereby exceeds the possibilities of oil and gas reservoirs as storage options [37]. For the transport and storage a CO_2 purity of 95 vol.% is sufficient [38, 39]. The advantage is that a large part of the CO_2 injected into the storages remains there and thus is removed from the atmosphere in the long term.

An alternative to storage is the utilization of the captured CO_2 (CCU). The CO_2 can continue to be used physically or chemically. Huang and Tan [40] divides the utilization into the categories of direct use (beverages, fire extinguishers or solvents) or as a raw material for the synthesis of follow-up products. There, the required purity depending on the purpose, e. g. 99.9 vol.% in the food industry [41], has to be considered. Important follow-up products are microalgae, urea, methanol and dimethyl ether. An important factor for these products is hydrogen in sufficient quality and quantity. Hydrogen can be supplied in electrolysis driven by the power from renewable energy sources and can be utilized with CO_2 for hydration of synthetic natural gas [42]. The synthetic fuel is a possibility to store excess energy from renewable sources whereby difficulties in the storage of hydrogen could be avoided [43]. However, the development of utilization technologies requires more financial efforts to develop towards maturity and commercialization.

1.4 Costs of CO_2 Capture

The economics of the CO_2 capture processes are essential for the commercial realization. The implementation of a capture unit to thermal power plants leads to additional investment efforts, operational expenses and the efficiency of the host plant is lowered. On the one hand, the specific emissions of the power generation process decrease while on the other hand, the levelized costs of electricity generation increase. To compare the different technologies, the cost of CO_2 avoided is used as the overall cost measure. It is based on the CO_2 emission rates and the levelized costs of electricity for plants with and without CO_2 capture. The result is a quantification of average costs for avoiding a ton of atmospheric CO_2 emissions while electricity is still provided [44]. It is the basis for techno-economic comparison of the different capture technologies, but this is subject to major uncertainties. Different boundary conditions impede the scientific comparison, but the results express the relations. It is noteworthy to mention that only the specific costs for the capture are considered. Additional costs arising by transport, storage and utilization must not be taken into account to compare the technologies [45]. The real CO_2 avoidance costs can only be determined by building and operating large-scale capture units included in the whole CCS chain.

The CO_2 avoidance costs for different CO_2 capture technologies are shown in Table 1.1. It shows the results of an IEA study for first generation processes [46] and for the second generation technology CaL most recent results from the SCARLET project [47]. The depicted costs refer to the capture, processing and compression and do not include transportation and storage. The last two points mentioned are strongly dependent on the location of the site and the distance to available storage capacities.

Table 1.1: CO_2 avoidance costs of different studies for various technologies.

Technology	Study	Unit	Value
Pre-combustion	IEAGHG 2014 [46]	€/t_{CO2}	87
Post-combustion	IEAGHG 2014 [46]	€/t_{CO2}	56
Oxy-fuel combustion	IEAGHG 2014 [46]	€/t_{CO2}	51
Directly Heated Carbonate Looping	SCARLET [47]	€/t_{CO2}	23

According to Junk et al. [45], the impact factors on uncertainties in the cost evaluation are the fuel price, the operating costs, the capital costs and the hours of operation (ordered after ascending uncertainty). It can be seen in Table 1.1 that the costs of the second generation technology CaL undercuts the costs of first generation technologies. The reason for the lower costs can be explained by the significant lower efficiency penalty of the power generation by the second generation technology. In 2014, the costs given by the IEA [46] drastically increased for the first generation technologies, so that second generation CCS becomes more attractive. The costs of first generation pre-combustion (+ 321 %), post-combustion (+ 63 %) and oxy-fuel combustion (+ 56 %) technologies are estimated significantly higher compared to the results three years ago [48]. As a result, the second generation technologies, such as CaL, become much more economically attractive. Based on this knowledge, the motivation and task definition for the thesis can be derived.

1.5 Research Motivation

The objective of this work is the development of the second generation CCS technology Carbonate Looping towards the next step of maturity. The feasibility of the CaL technology has been proven in laboratory up to semi-industrial scale. The technology stands on the threshold to the next step, a demonstration plant with the size of 20 MW_{th}. To take this subsequent step, a reliable data base derived from long-term operation in semi-industrial 1 MW_{th} scale is required for scaling-up the process. In contrast to already published results, the pilot operation is carried out under realistic operating conditions of later application, e. g. coal-originated flue gas, various fuels and oxy-fuel conditions in the calciner. Additionally, the required operating periods to show the stable operability and to draw conclusion of the sorbent behaviour are several tens of hours up to days. Thus, this work shows the long-term pilot operation of the CaL technology to determine the operating parameters and conditions. It provides the reliable basis for a larger-cale demonstration plant. These fundamental expertise needed for the scale-up and pre-commercialization is obtained by addressing the key challenges and demonstration the CaL technology in 1 MW_{th} scale.

Based on the results obtained from the long-term operation 1 MW_{th} scale, a process scale-up to a 20 MW_{th} pilot plant is conducted. Developed and validated scale-up tools with the help of the experimental data support the work. A detailed process layout with heat and mass balances for a design and various operating cases is elaborated to define the basis for the industrial application in demonstration scale. The data provided by this work allows the design and engineering of reactors and all required auxiliary systems, a health, safety, environment and technical risk assessment and the estimation of investment and operational costs. Finally, it provides the confidence for investments into a larger-scale unit.

1.6 Outline of the Thesis

This thesis "Experimental Investigation of a semi-industrial Carbonate Looping Process for scale-up" is the outcome from the author's work at the Institute for Energy Systems and Technology at Technische Universität Darmstadt. The results were generated within the project SCARLET (Scale-up of Calcium Carbonate Looping Technology for efficient CO_2 Capture from Power and Industrial Plants). The thesis is structured as follows:

Chapter 2 describes the fundamentals of the Carbonate Looping process. Besides the process principles, this chapter presents the chemical and mechanical properties of the sorbent. It includes the chemical equilibrium, the kinetics of the reactions, the deactivation by impurities and the abrasion of the sorbent. In addition, the fundamentals of the fluidized bed technology are shown. This technology serves to realize the process. The most important evaluation parameters of the process are introduced and finally the progress made in the recent years and the experimental results from different CaL pilot plants worldwide are summarized.

In Chapter 3, the experimental setup for the long-term pilot tests is shown. It describes the general setup of the 1 MW_{th} pilot plant and various coupling concepts. Also, this chapter gives information about the upgrades required for long-term operation under realistic conditions. It also includes the description of the relevant measurements and the uncertainty estimation. Furthermore, the utilized sorbents and fuels during pilot operation are shown.

Chapter 4 includes the results and discussion of long-term pilot operation in 1 MW_{th} scale. It describes the approach of steady-state operation and the necessary stability of operating conditions. The range of assessed parameters is given and the closure of mass and heat balances is shown. Also, the author assesses the hydrodynamic stability of various coupling concepts for the interconnection of the fluidized bed reactors and the temperature profiles. Furthermore, the chapter shows the assessment of key parameters for carbonator and calciner reactor operation and the efficiency of the process.

In Chapter 5, the CaL technology is scaled-up to a demonstration pilot of 20 MW_{th} for a host plant in France. The author elaborates a detailed plant setup and scales the process on the basis of results from pilot operation with the help of a validated process model. Various operational cases besides a design case are presented to investigate the essential parameters of the process in larger scale. The scale-up includes the heat and mass balances for the design case and the ranges for the other operational cases. Finally, a detailed thermodynamic assessment is given to show the expectations for the demonstration unit.

Chapter 6 concludes the results of this work and gives an outlook for the next step of a demonstration pilot and the future application of the technology for power generation and industrial processes.