1 Introduction

It is now generally accepted that the anthropogenic emissions of so called greenhouse gases (e.g. methane, carbon dioxide) are affecting the climate on earth. The quantitatively largest emission is that of carbon dioxide: world wide 30 giga tonnes CO_2 were emitted in 2010, while China alone emitted 7.2 giga tonnes [1]. The longtime trend of the atmospheric carbon dioxide concentration shows a steady increase from values around 325 ppm in 1972 to values around 389 ppm in 2010 [2]. It is accepted that this development causes negative changes of the world climate [3]. Consequently, the reduction of further emissions is an important environmental, social, political, and also technological issue. A major source of carbon dioxide emissions is the power generation in coal fired power plants. Different strategies for the mitigation of the carbon dioxide emissions are presently investigated. Favorable options are first a reduction of the energy consumption by means of consumer awareness or more energy efficient consumer products and second an increase of the efficiencies of the electricity generation in the power plants. However, both options have limitations, and consequently other strategies are investigated for the mitigation of the carbon dioxide emissions e.g. the use of renewable energy or the carbon capture and storage strategy that allows a complete avoidance of carbon dioxide emissions from fossil fired power plants. Hence, the carbon capture and storage is a potential technology for the short- to midterm, especially if technologies for the carbon capture with low energy penalties are developed. However, there are still political, technical, safety and environmental issues concerning the carbon dioxide transport and storage which have to be overcome. Different carbon capture technologies, which can be classified in post-combustion, pre-combustion and oxyfuel firing, are currently under investigation. Figure 1.1 illustrates the different carbon dioxide capture strategies.

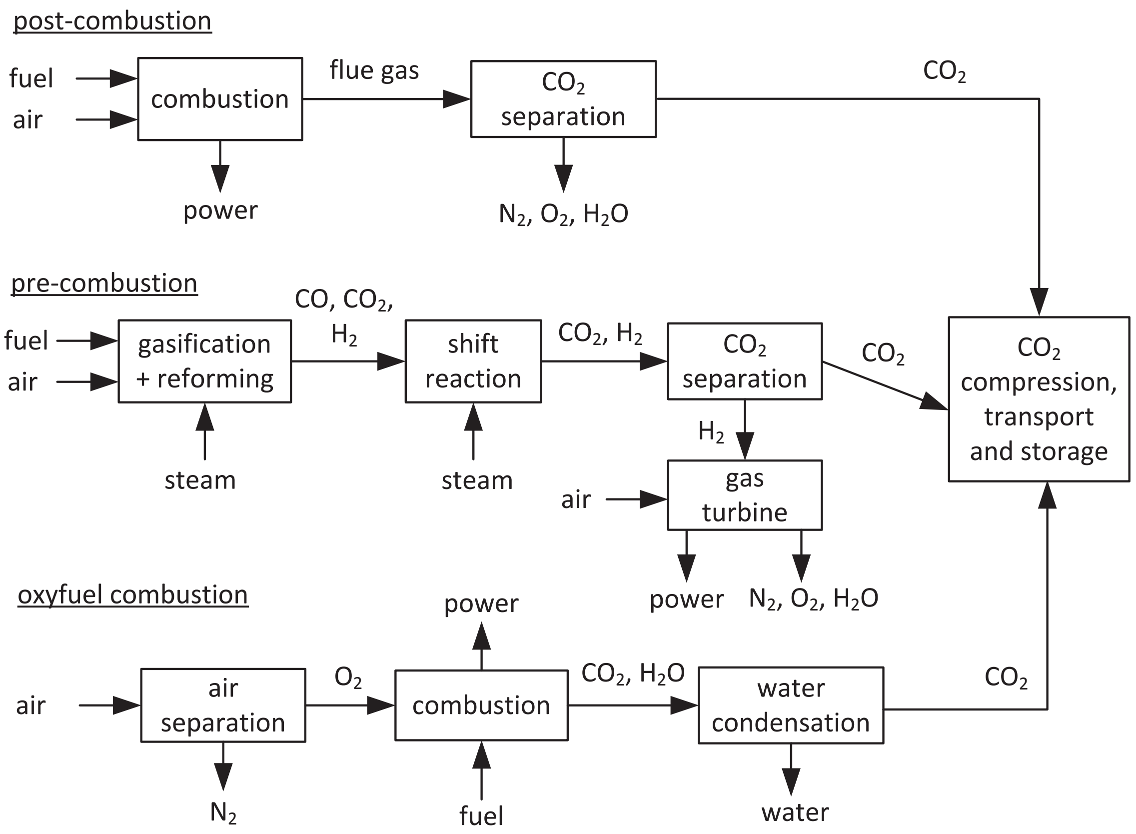

Figure 1.1: Different strategies for carbon dioxide capture after [4]

Post-combustion capture is a downstream treatment of the flue gas released from a conventional combustion of a fossil fuel in air. The carbon dioxide is removed e.g. by scrubbing with methanolamine or in a carbonate looping process. The adsorbent is subsequently regenerated in a desorber where the carbon dioxide is released. With the pre-combustion process the fuel is converted to hydrogen and carbon dioxide via gasification, steam reforming and shift reaction. The carbon dioxide is removed and the hydrogen is used for power generation. In the oxyfuel firing the fuel is converted in a nitrogen-free atmosphere to avoid the dilution of the carbon dioxide with nitrogen in the flue gas. One option is to produce pure oxygen in an air separation unit, and convert the fuel in a mixture of oxygen and the recycled flue gas i.e. carbon dioxide. The flue gas mainly consists of carbon dioxide and steam, which can be easily separated by condensation of water. A novel process, which also avoids the dilution of the carbon dioxide with nitrogen, is the so called chemical looping combustion [5]. Generally, the process consists of two reactors: in the air reactor the solid oxygen carrier is laden with oxygen, while in the fuel reactor the oxygen carrier supplies the oxygen for fuel combustion. This process has the potential to enable a carbon capture at low energy penalties.

Interconnected fluidized bed reactors have a long history (e.g. FCC crackers) and are recently investigated for the application in novel carbon capture technologies i.e. carbonate looping and chemical looping combustion. The carbonate looping is a post combustion technology which uses a solid for the removal of carbon dioxide from the flue gas (e.g. [6]). In the first reactor (carbonizer) the calcium oxide particles react at 600 - 700°C with the carbon dioxide to form calcium carbonate. The solids are subsequently transferred to a second reactor (calciner) where the calcium carbonate is calcined to calcium oxide in an endothermic reaction at around 900°C and the carbon dioxide is released. The calcium oxide is recycled to the first reactor and the carbon dioxide can be sequestrated.

In the chemical looping combustion process the solid oxygen carrier is laden with air oxygen at 850 to 950°C in the air reactor. Subsequently, the solids are transferred to the fuel reactor where they are reduced at 850 to 950°C and supply the oxygen for the fuel conversion [7]. This process has, due to the avoidance of the energy intensive air separation in a cryogenic air separation unit, the potential to enable the carbon dioxide separation with lower energy penalties [8,9]. Generally, some challenges arise from interconnecting fluidized bed reactors which must be considered for the design and operation of the facilities. In the above mentioned examples large quantities of solids circulate between the reactors but at the same time no gas from one reactor should enter the other. Furthermore, the solids must be separated from the gas flows and be returned to the system in order to avoid the loss of large quantities which have to be made up with fresh material. If coal as fuel is introduced in the chemical looping combustion process this leads to a mixing of the coal/ash and the oxygen carrier. The fluid mechanical issues which are relevant for the realization of the chemical looping process using interconnected fluidized beds are

- control and stability of the operation
- transport of a sufficient amount of solids from one reactor to the other for oxygen and heat transfer (circulation rate)
- gas and pressure sealing between the reactors
- attrition of the solids which leads to the generation of fines which are lost from the system
- gas solids separation and solids recovery
- fluidization, avoidance of agglomeration
- entrainment of coal with the oxygen carrier to the air reactor

- loss of unconverted fuel with the flue gas
- removal of the ash introduced with the coal

Scope of this work

In the present work a novel design for a system of interconnected fluidized beds for the chemical looping combustion of coal which applies a two-stage stationary fluidized bed as fuel reactor is investigated. The focus is on the fluid mechanical issues arising from interconnecting fluidized beds. Experimental investigations were conducted in both a cold flow model and in an electrically heated hot facility which have been planned, constructed and commissioned within this work. Two different oxygen carrier materials are tested: a natural ore and a synthetic oxygen carrier prepared within this work. The operational behavior of the fluidized bed system is intensively studied which comprises e.g. the measurement of the circulation rates in both facilities, the evaluation of the effect of two-stage design on the fuel conversion and the oxygen carrier loss from the test facility.

A second key point of this work is the attrition occurring in the fluidized bed system. The attrition propensity of the two oxygen carriers was assessed in lab-scale tests. Since no model for attrition occurring inside the riser can be found in literature this attrition source was investigated using a circulating fluidized bed system. Finally, flowsheet simulation is applied to simulate the attrition occurring in the chemical looping facility. The simulation results i.e. the attrition-induced oxygen carrier loss rates are compared with the values measured during experiments. Furthermore, the simulation approach is applied to the simulation of attrition occurring in a large scale unit. Finally, considerations for the large scale application of the reactor design investigated here are discussed.

After the introduction in Chapter 1 the second chapter provides a review on literature that is relevant for this work. First the basics of chemical looping combustion and the operational results obtained by other groups for continuous operation with solid fuels are discussed. Second, the two examples of the industrial application of interconnected fluidized beds are summarized followed by a summary of fluid mechanical investigations conducted with cold flow models of various chemical looping combustion designs. Finally, the basics regarding the attrition occurring in a fluidized bed process and the flowsheet simulation approach are presented. Chapter 3 describes the experimental set-ups and the applied measurement techniques. Furthermore, the strategy for the investigation of attrition occurring in the riser of a circulating fluidized bed and the approach for the simulation of attrition occurring in the chemical looping combustion process. In Chapter 4 the experimental and theoretical results are summarized and discussed. Finally, Chapter 6 gives a summary of the work.

2 State of the Art

2.1 Chemical looping combustion (CLC)

Chemical looping combustion (CLC) is a technology that allows the inherent separation of CO_2, which is generated by the combustion of fossil fuels. It basically consists of two reaction zones, the so called air reactor and the fuel reactor, together with a solid oxygen carrier which circulates between the two zones. The basic process scheme is shown in Figure 2.1. In the air reactor the oxygen carrier is oxidized, i.e. the gaseous oxygen is chemically bound to the solids. The solids are then transferred to the fuel reactor zone, where a fossil fuel is converted to carbon dioxide and steam. The oxygen required for the fuel conversion is supplied by the oxygen carrier which is reduced and subsequently returned to the air reactor to be regenerated. The advantage of this concept is, that the combustion products carbon dioxide and steam are not diluted by the air nitrogen. Consequently, after condensation of the steam an almost pure carbon dioxide stream is obtained from the fuel reactor zone whereas oxygen depleted air leaves the air reactor zone. The basic process principle was already developed and patented in 1954 by Lewis and Gilliland [10]. The latter system already involved two interconnected fluidized beds and an oxygen carrier, and it was developed for the application of a solid fuel. At that time, however, the intended application of the process was the production of a pure CO_2 product steam. The application of the principle for carbon capture was first proposed by Ishida and Jin [11] in 1987. Afterwards, various concepts were developed by different groups. The range was from rotating fixed bed reactor (for gaseous fuels) [12] over an alternating operation of two fixed bed reactors, which are either operated with air or the gaseous fuel [13], to interconnected reactor systems (e.g. [14]). However, not before 2005 the first demonstration of the chemical looping combustion process in a continuous plant was published in open literature by Lyngfelt and Thunman [15] using methane as fuel.