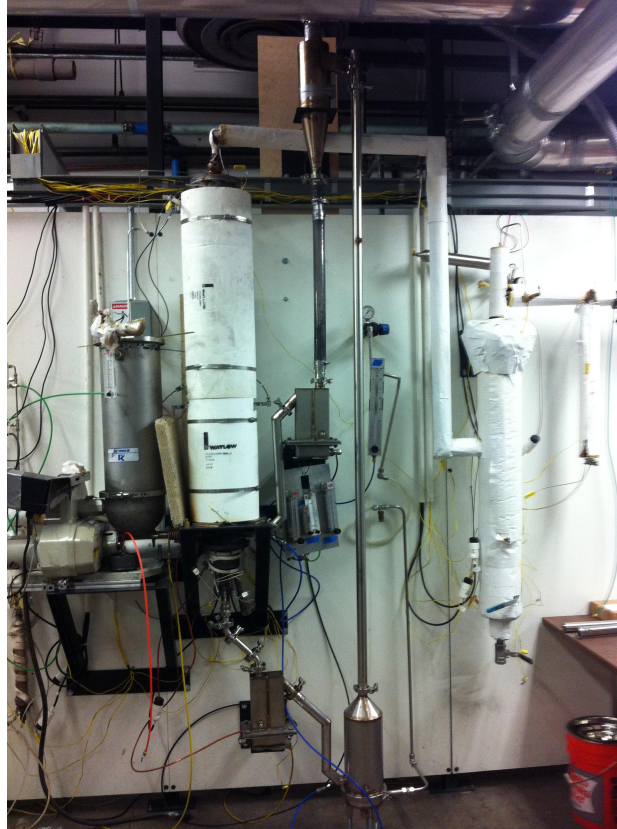




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Experimental Study of the Hydrodynamics of a Lab-scale Chemical Looping Combustion System

A study in preparation for a CLOU (Chemical Looping with Oxygen Uncoupling) system based on Copper Oxides for solid fuels

Master's thesis in Master Programme Sustainable Energy Systems

VIKTOR STENBERG

MASTER'S THESIS 2015:06

Evaluation of the Hydrodynamics of a Lab-scale Chemical Looping Combustion System

A study in preparation for a CLOU (Chemical Looping with Oxygen
Uncoupling) system based on Copper Oxides for solid fuels

VIKTOR STENBERG



CHALMERS
UNIVERSITY OF TECHNOLOGY

Department of Chemical and Biological Engineering
Division for Chemistry and Biochemistry
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2015

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VIKTOR STENBERG

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Abstract

One of the most important issues of our time is climate change originating to a great extent from emissions of carbon dioxide. There is a strong interest to decrease these emissions while at the same time be able to use the fuels that are already available to a large extent today. Among those are coal and biomass and to combust fuels such as these more sustainably, Chemical Looping Combustion (CLC) and Chemical Looping with Oxygen Uncoupling (CLOU) are two promising technologies.

This study aims to prepare the future operation of a coal-fueled CLOU-system based on a copper-based oxygen carrier on a silicon carbide support. A lab-scale Chemical Looping system is tested to measure circulation rates and pressures for varying air flows, bed materials and bed material quantities. The measured pressures and circulation rates were compared with a CFD-simulation of the system using alumina as bed material which showed that the measured pressures were overall higher than the simulated pressures. The same comparison with the simulation showed that measured circulation rates were smaller for smaller air flows but higher for higher air flows. Silicon carbide was compared to alumina in terms of circulation rate and pressure. The measured circulation rates can be used to locate suitable operation parameters for future operation in terms of flow rates, bed material characteristics and bed material quantities.

A potential problem using copper-based oxygen carriers for solid fuels is the formation of volatiles originating from devolatilization. In order to obtain a better understanding of this problem and the hydrodynamics in general for fuel introduction in the fuel reactor of the chemical looping system, a cold-flow model of a bubbling fluidized bed is used for injection of gaseous CO₂. Higher air flows for fluidization proved to result in better mixing overall and the jet velocity was shown to have a big impact on the radial mixing of the injected gas. Larger bed particles results in a better dispersion and a better mixing overall. The experimental approach is evaluated for possibilities for a future simulation of the devolatilization process in fluidized beds for solid fuels. A future study using injection of dry ice to simulate this process is evaluated and several interesting areas for further research are identified.

Keywords: CCS, CLC, CLOU, hydrodynamics, jet penetration, gas plume.

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Viktor Stenberg, Salt Lake City, Utah, June 11th 2015

Nomenclature

a	Empirical constant
C_1	Empirical constant
C_2	Empirical constant
d	Diameter of a spherical object
D	Dispersion coefficient, m^2/s
F	Force, N
h	Height, m or " (inches)
g	Gravitational acceleration constant 9.8 m/s^2
L	Radius of coal feed module, m
L_j	Penetration length, m
n	Empirical constant
ID	Inner diameter, m or "
OD	Outer diameter, m or "
P	Pressure, Pa
r	Distance in horizontal direction, m
u	Velocity, m/s
X_v	Fraction of burned volatiles, %

Greek letters

ϵ	Bed porosity
μ	Dynamic viscosity, Pas ($\text{kg}/(\text{ms})$)
ρ	Density, kg/m^3
τ	Time constant, s

Indexes

B	Buoyancy
D	Drag
dev	Devolatilization
grav	Gravitational
h	Horizontal
inter	Interstitial
mf	Minimum fluidization
mb	Minimum bubbling
Op	Operating condition
rad	Radial
standard	Standard conditions
t	Terminal
v	Vertical
0	Superficial

Dimensionless numbers

Ar	Archimedes number
Da	Damköhler number
Pl	Plume number
Re	Reynolds number

Abbreviations

AR	Air Reactor
CCS	Carbon Capture and Storage
CFD	Computational Fluid Dynamics
CFH	Cubic Feet per Hour
CLC	Chemical Looping Combustion
CLOU	Chemical Looping with Oxygen Uncoupling
CR	Circulation Rate
EDX	Energy-disperse X-Ray spectroscopy
FBG	Fluidized Bed Gasifier
FR	Fuel Reactor
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
MBS	Multiple Bubble Segregation
MFV	Minimum Fluidization Volumetric flow rate
PIMC	Pressure-induced Measurement of Circulation
SiC	Silicon carbide
SBS	Single Bubble Segregation
SEM	Scanning Electron Microscopy
SG	Specific Gravity
SLPM	Standard Liters Per Minute
XRD	X-Ray Diffraction

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1

Introduction

1.1 Context

Climate change is one of the world's biggest challenges and it has been concluded with a high certainty that most of these changes are due to human emissions of greenhouses gases to the atmosphere[1][2]. The annual temperature at the earth's surface has increased over the past 200 years and a major contributor to this increase is carbon dioxide (CO_2)[3]. The concentration of CO_2 in the atmosphere has increased from 280 ppm during the beginning of the industrialization[3] to 400 ppm in February 2015 which most likely has not been seen on the earth for 23 million years[4]. Therefore, one of the most important issues today is to decrease the emissions of CO_2 into the atmosphere.

IEA(International Energy Agency) has concluded that the energy from fossil sources (gas, oil and coal) will supply 80 % of the energy demand during the first part of the 21st century. It is also probable that a complete substitution of these technologies is not yet achievable[5]. Consequently, the development to ensure a continued supply of energy from these fuels while at the same time reducing the CO_2 -emissions globally would be a step in the right direction. A promising method to achieve decreased emissions from these sources is to use Carbon Capture and Storage (CCS). When using CCS, CO_2 is pumped down into for example underground geological formations such as depleted oil and gas fields, saline aquifers or unminable coal seams under high pressure[6]. According to an analysis of IEA (International Energy Agency) and IPCC (Intergovernmental Panel on Climate Change), CCS could account for 19 % of the total CO_2 emission reductions needed during the 21st century to stabilize the climate change at a reasonable cost[1].

In order to substantially decrease the emissions of CO_2 with Carbon Capture, large stationary sources is an area of focus. This concerns for example fossil-fueled power plants (approximately one-third of the total carbon dioxide released from fuel combustion[7]), cement manufacturing, ammonia production, iron and non-ferrous metal industry, industrial boilers, refineries and natural gas wells[6]. Along with the previously mentioned fossil energy sources, biomass is an important component for heat and power production and also a possible target for CCS-technology[8]. By using

biomass as a fuel, it is even possible to have negative net emissions of CO_2 which is likely needed to be able to meet the future climate targets[9].

However, to use this technique a stream of pure CO_2 is needed. There are several different solutions to achieve this which take place either before or after the combustion process: pre-combustion, oxy-fuel combustion and post-combustion. With pre-combustion the CO_2 is removed before the combustion is completed. This can for example be done by adding steam to produce syngas (H_2 and CO_2) from where the CO_2 can be captured[10]. One advantage with this technology is that hydrogen is produced but on the other hand there are two steps of gas separation needed. In addition, since the capture of CO_2 must be done in connection with the combustion it is not possible just to add another unit in an existing plant, instead there is a need to rebuild it[11].

Oxy-fuel combustion is combustion with pure oxygen which results in combustion with a flue gas containing CO_2 and H_2O which means that condensation is enough to obtain a good separation of CO_2 . However, retrieving the oxygen through separation of air is a very costly operation. Another issue is the high demands on the equipment which combustion with pure oxygen results in (higher temperatures are reached with no inert nitrogen available). Post-combustion involves separation out CO_2 from the exhaust gases. This can be done by absorption by a liquid solution forming a chemical compound from which the CO_2 can be removed. This technology is more well-known than the previously mentioned methods and it is easily added to an existing plant. However, this comes with a high energy penalty mainly since steam at a constant temperature is used to remove the CO_2 from the formed compound[12].

A technique that has the potential to deliver an efficiency improvement and cost reduction for CO_2 capture is Chemical Looping Combustion. This process avoids the use of a gas-gas separation technology and its energy penalties by using two interconnected fluidized beds with a circulation of an oxygen carrier between these two reactors. This is a recently developed fuel conversion technology with an inherent capture of the CO_2 . An even more novel method is CLOU (Chemical Looping with Oxygen Uncoupling) for which the carrier releases the oxygen needed for combustion once entering the reactor where the conversion of the fuel takes place[1, 8, 13].

1.2 Background

The development of CLC is so far being done with several pilot studies around the world and more research has to be conducted to make it possible to reach commercial scale which is predicted within 20 years' time[8]. An example of research within this field is oxygen carrier development. There are currently numerous alternatives and it remains to be seen which carrier will be the best suited for CLC/CLOU-operation a few years from now. Another part of the research is about obtaining a better un-

derstanding of the dynamics between the fluidizing gases, oxygen carriers and fuel. Since combustion of solid fuels has more recently become more and more interesting, the dynamics between these fuel particles in the fuel reactor and for fluidized beds in general is turning into an important area of research. As an example, the United States of America has one of the biggest coal reserves in the world[14] and it is the largest fossil-fuel resource[15]. Based on the fact that the resource is also cheap compared to other alternatives, it is likely that coal will play an important role in the American energy supply in the future. The U.S Department of Energy has shown more and more interest to continue the use coal but in a more sustainable manner.

One of the universities researching within this field is the University of Utah which is focusing on technologies with the intent to use coal as a fuel and one of these technologies is Chemical Looping Combustion. At this University the intent is to use copper which is well characterized and has proven advantages as a oxygen carrier for CLOU. Studies have been done looking at a possible support material for copper and it was shown that a form of silicon carbide works well with copper[16]. In a laboratory-scale dual-bed chemical looping system, it is then the intention to investigate different options to operate the system and to finally run the system successfully for CLOU using a solid fuel such as coal. Before this can be done, there is a need for a better understanding of the hydrodynamics for the possible areas of operation for the lab-scale system. It also requires a better knowledge about the possible issues with using copper as a carrier having a solid fuel that releases a large amount of volatiles which could pose a problem using this carrier in practice. The release of these volatiles occurs in the devolatilization process which can be investigated using a cold-flow model of a fluidized bed where solid fuel injection can be simulated using sublimation of dry ice (solid carbon dioxide). In a first part of this plan, gaseous CO_2 will be injected to establish a method for the future dry ice injection study.

1.3 Purpose

The purpose of the Thesis is to gain an increased understanding of the fluid dynamics (hydrodynamics) of fluidized beds in general and chemical looping systems in particular during cold conditions (room temperature) to pave the way for a future solid-fueled CLOU system with SiC-particles covered with copper. In order to fulfill the purpose of the Thesis, the following objectives aim to be met:

- Measure the circulation rate and pressures for the system with alumina as bed material for different air reactor flow rates and compare with a CFD-simulation.
- Perform tests with different bed materials and different amounts of these and compare the obtained results to discuss suitable properties of the bed particles.

1. Introduction

- Discuss the hydrodynamics of the CLC system based on the obtained experimental results to identify suitable settings for future operations.
- Provide a summary of the research that has been done in the area of gas plume formation originating from solid fuel devolatilization in fluidized beds.
- Discuss the hydrodynamics of the fluidized bed based on measurements during injection of gaseous CO₂.
- Discuss how the results can relate to the future study of devolatilization of a solid fuel as well as providing a better understanding of the problems connected to the gas plume formation in fluidized beds could be reduced.

2

Theory

This chapter contains the theoretical framework needed to follow the experimental procedure as well as the results. It also includes a literature review of the research has been conducted on the area of gas plume formation in fluidized beds originating from solid fuel injection.

2.1 Chemical Looping Combustion (CLC)

The CLC-system consists of two interconnected fluidized beds, the air and the fuel reactor[17]. In the air reactor, a metal oxygen carrier (further described in chapter 2.5) gets oxidized and separates the oxygen from the air and transports it to the fuel reactor where the fuel conversion process takes place. Air is used as a fluidizing agent in the air reactor while the fluidizing agent in the fuel reactor is either CO_2 or H_2O in order to avoid separation of additional compounds at the outlet of the fuel reactor. The reduced metal returns to the air reactor in this continuous closed loop system. This process therefore achieves two outlet streams: one with unreacted oxygen and nitrogen and one with CO_2 and steam. From the latter the carbon dioxide is easily separated through condensation of the steam to a highly concentrated stream of CO_2 which is ready for transport and storage[13]. The process is illustrated in figure 2.1.

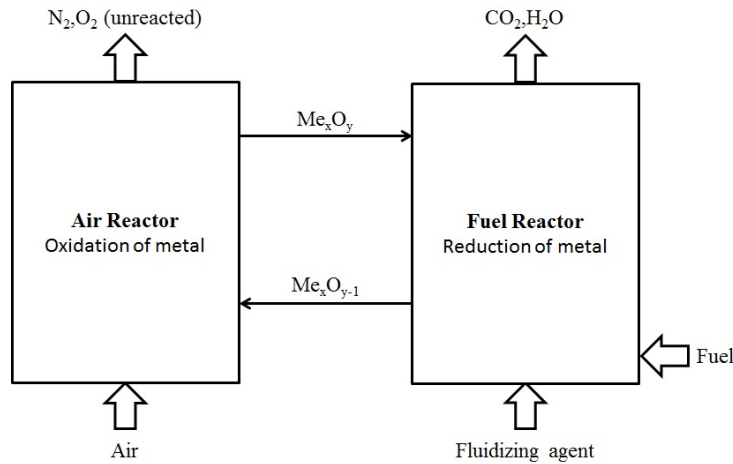
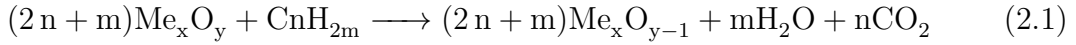


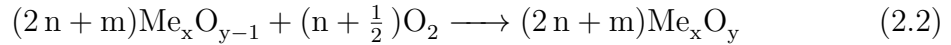
Figure 2.1: Schematic of the CLC-process with the two fluidized beds, three inlet streams and two outlet gas streams.

When the process is run with a deficit of air, reforming or gasification of the fuel is obtained which could be used to produce fuels such as hydrogen by using steam or air. CLC can be used for any type of fuel. For gaseous fuels, there is a direct reaction with the oxygen carrier. Liquid fuels are less common than solid/gaseous fuels but research on using for example heavy oils has been conducted[18]. For solid fuels the fuel can either react with the oxygen in solid form or in the form of syngas through gasification. The latter process is called syngas-CLC where the oxygen carrier reacts with the fuel in gaseous form as the gasification products (syngas) which are produced in a gasifier. Gasification means conversion of an organic or fossil fuel to CO, H₂ and CO₂ with a controlled amount of oxygen and/or steam. The gasification of the solid is used since a solid-solid reaction is slow compared to for example a gas-solid reaction.

Assuming that the fuel is in gaseous phase and reacts in a gas solid-reaction with the oxygen carrier, the reaction can be written as[13, 18]:



The flue gas leaving the fuel reactor is a mixture of the steam and carbon dioxide while the reduced metal oxide circulates to the air reactor[8]. The reaction with the incoming air and the reduced oxygen carrier in the air reactor can be described by:



The flue gas leaving the air reactor is a mixture of all the incoming nitrogen (ideally) and the unreacted oxygen (not included in the reaction above).

Reaction 2.2 is exothermic while reaction 2.1 is usually endothermic. The net amount of heat from these two reactions constitute the heat of combustion of the fuel with oxygen and fuel in direct contact[8]. The oxidation reaction with the oxygen and the oxygen carrier is always exothermic. In the fuel reactor on the other hand, the reaction is either endothermic or exothermic depending on how endothermic the reduction of the oxygen carrier is as well as what kind of fuel that is being used[19].

There is most often a temperature difference between the air reactor and the fuel reactor. In the cases when the air reactor is hotter, CLC does not result in enthalpy gains, but it achieves a separation of CO₂ and H₂O from the flue gases which represents a major cost and energy saving[13].

2.2 Existing CLC plants in the United States of America

Considering the fact that this thesis work takes place in the United States of America, it is of interest to provide a background on the conducted research in the country. At the institute for Clean and Secure Energy at the University of Utah in Salt Lake

City, CLC and CLOU has been investigated through several studies[20]. Simulations have been done in ASPEN PLUS for solid fuel-based chemical looping with a copper oxide as carrier for CLOU[16]. A simulation has also been done of a 300 kW CLOU reactor in Barracuda and a scaled cold flow model at 100 kW is being built and tested at the University of Utah[21]. There is an interest to further study the effects of devolatilization in CLC systems in cooperation with Chalmers University of Technology[22].

A clean coal technology is being developed by Ohio State University where a reactor of 25 kW_{th} has been constructed and run for more than 200 hours using iron oxides as oxygen carriers. The method which is called coal direct chemical looping (CDCL) combustion and makes it possible to have a coproduction of hydrogen and heat[23]. Furthermore, a 250 kW_{th} pilot-scale unit has been designed for the development of Syngas Chemical Looping for coal and biomass gasification[24]. At Western Kentucky University there is a current development of Cu-based oxygen carriers using aluminum oxide (Al₂O₃) and titanium oxide (TiO₂) as support material. The tests were done in a 10-kW hot-model CLC facility. At North Carolina State University, the Li Research Group is present which are researching on oxygen carriers for Chemical Looping with the target of for example gaseous fuels for power generation[25].

NETL (National Energy Technology Laboratory) has designed a 50 kW_{th} Chemical Looping Reactor. The unit is used for researchers to better understand the various experimental challenges operating the system. Alstom has conducted several projects on CLC in the United States of America. An example of this was a calcium-based CLC system for which testing has been done on a 65 kW_{th} system. Computational models and optimizing control systems have been completed as well[24]. Alstom Power Plant Laboratories is working on using limestone or metal oxides as carriers and successful initial tests have been done for Limestone Chemical Looping with a 3 MW_{th} unit[26].

2.3 Existing CLC plants worldwide

To provide a more holistic picture of research on CLC worldwide a shorter presentation is provided in this section. In South Korea, the Korea Institute of Energy Research (KIER) has set up a 50 kW unit testing Nickel- and Cobalt oxides for natural gas[27]. At the Southeast university in Nanjing, China, two units of the sizes 1 and 10 kW are in operation in Nanjing, China which use solid fuels (coal and biomass) and nickel- and iron-based oxygen carriers[28]. A small pilot scale unit of 140 kW_{th} is in operation for gaseous fuels (natural gas, CO, H₂) using ilmenite and Nickel oxides at Vienna University of Technology[29].

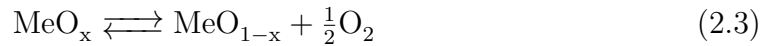
At Chalmers University of Technology in Gothenburg, Sweden, the development of CLC was initiated in 1998 and was first to demonstrate operation with a gaseous fuel for a 10 kW unit in 2003 as well as for solid fuel in 2006 and liquid fuel in 2011. Extensive testing of different oxygen carriers (more than 300) has been con-

ducted[30]. The largest operated unit is a 100 kW dual circulating fluidized-bed for solid fuels which has been operated with bituminous coal and ilmenite[28].

In Zaragoza, Spain, CSIC (Spanish National Research Council) has a 10 kW unit in operation using methane as fuel[27]. In addition, a 50 kW_{th} unit has been designed and operated for coal combustion. The designed system is to be operated both in CLC and CLOU mode for solid fuel combustion. The design consists of two interconnected circulating fluidized beds reactors[31]. At Hamburg University of Technology a 25 kW chemical looping combustion plant is located which is constituted by a circulating fluidized bed reactor using coal as a solid fuel and ilmenite as oxygen carrier[28,32]. A 1 MW_{th} chemical looping pilot plant has been constructed at the Technical University of Darmstadt. The first operational results that has been presented was for ilmenite as oxygen carrier and hard coal as fuel. It was observed that the conversion of coal resulted in production of unconverted gases at the reactor exit. These gases were later converted with a system for oxygen injection in the flue gas duct[33].

2.4 Chemical Looping with Oxygen Uncoupling

In order to obtain an efficient conversion of solid fuels in particular, CLOU has a big potential use. CLOU differs from CLC in the sense that the carrier has characteristics to spontaneously release oxygen in the fuel reactor[8]. The background for this reaction is the equilibrium behaviour of the carrier oxidation/reduction reaction. The gaseous CO₂ is favored at high temperature and low concentrations of oxygen which is the case in the fuel reactor while the high oxygen content in the air reactor favors the oxidized metal[34]. This means no need for the reaction with CO₂ and/or steam for gasification[35]. As a result, the low reactivity of for example the gasification of solid char is overcome since the reaction in this case does not take place at the active surface of the oxygen carriers[1]. Instead, the carrier releases the oxygen once it enters the fuel reactor which makes it possible to get a faster conversion of the solid fuel (see equation 2.3). CLOU can therefore be used to improve the reactivity even for other fuels and reduce the need for carrier material as well as decrease the reactor size and costs linked to that[1].



The oxygen carrier is reduced because of the lower partial pressure of oxygen in the fuel reactor and the oxygen is therefore released. In order to understand the tendency to release the oxygen, the equilibrium partial pressure has to be studied for different temperatures since the release of oxygen increases with temperature. It is however important to note that the dependency look differently for each kind of carrier[8]. The CLOU process is relatively untested and at this point it needs to be assessed in further detail for a small-scale system[1].

Examples of materials which have the ability to release some oxygen (displaying CLOU properties) are Mn combined with Ca, Mg, Cu, Ni and Fe among which Cu has the ability as a pure substance as well[8].

It is important to note that for both CLC and CLOU no gaseous compounds are allowed to follow the carriers from the air reactor to the fuel reactor or vice versa. If fuel passes to the air reactor, combustion will take place there and emissions more than air will be let out. If air passes to the fuel reactor, more components than just CO_2 and H_2O will have to be taken care of by the following separation step. This will in turn decrease the efficiency of the capture of the CO_2 . In order to understand what makes a good oxygen carrier, a summary of some of these characteristics are provided in the next section.

2.5 Oxygen carriers

The four metal oxides that were initially tested for CLC were Ni, Fe, Mn and Cu. Now more and more work has been done on combined metal oxides aiming at low cost in general and displayed CLOU properties for solid fuels. In addition to these also Co and Cd have been tested. Several low-cost materials have been used for solid fuel such as iron ore, manganese ore, ilmenite (consisting of FeTiO_3 and industrial waste materials[8, 36, 37].

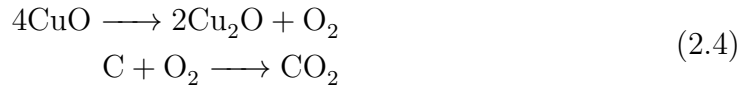
There are several characteristics of a suitable oxygen carrier (bed material)[1]:

- Sufficient oxygen transport capacity.
- Favorable thermodynamics for fuel conversion to CO_2 and H_2O in CLC. If an oxygen carrier does not contribute to complete conversion of the fuel, there will be energy losses because of unconverted fuel.
- High reactivity for reduction and oxidation reactions which should be maintained for a long period of time (in a repeated cycle) to reduce the need for bed material.
- Resistance to attrition in order to minimize the losses of bed material.
- Negligible carbon deposition which otherwise would mean a release of CO_2 in the air reactor. Carbon deposited on the oxygen carrier means decreased efficiency of the capture of CO_2 .
- Good fluidization properties (no agglomeration). Agglomeration of the bed particles lead to channeling (poorly distributed flow of the fluidizing agent over the bed) and disturbances of the solids circulation.
- Limited cost.
- Environmentally friendly as well as non-hazardous for use.

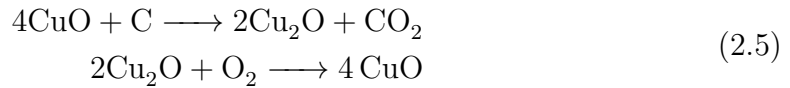
When using metal oxides directly as carriers there is a strong dependency with time since the reaction rates and above mentioned characteristics can decrease quickly with time. Therefore, more suitable choices can be found by using a combination of metal content and an inert support material. This can increase the reactivity by providing a high dispersion of the metal, durability (mechanical strength) and the fluidizability characteristics of the carrier. The oxygen carrying capacity can then be seen as a function of the metal loading and the stability of the carrier[1, 13].

In addition to the kind of carrier is used, it is important to take into account the fact that the size of the bed particles also plays an important role in the operation using the carriers. For finer particles, a more wide range of flows is possible while larger particle size means a smaller suitable flow rate interval. Apart from the size, the density of the bed material as well as the ratio between the densities of the solid and the fluid must be taken into account[38].

Cu-based materials have been proven to have high reactivities with several different supports and preparation methods which make these reliable when it comes to tests of CLC even though the performance may be higher for other alternatives. Copper has been proven to not abrade and once loaded on a suitable support it does not lose carrying capacity. In addition it is well characterized and reacts quickly under oxidation and reduction[16]. For CLOU, the looping of copper takes place between the states CuO and Cu₂O. The decomposition of the CuO (the reduction reaction) can be written as:



The oxidation reaction can be represented as:



The reduction reaction is endothermic but compared to other metals the heat needed is rather small which means that both reactors are likely to be exothermic[16]. This in turn results in less need from external heating.

In a recent study comparing several different support materials for copper and chemical looping operation, it was concluded that silicon carbide was among the tested compounds the most promising support material among the tested compounds[16]. Based on this knowledge the intent is to use copper with support of silicon carbide (SiC). A problem is the low melting point (1085°C) which may cause agglomeration problems at high temperatures[1]. Another potential problem when using copper as a carrier can be traced to the formation of volatiles originating from solid fuel devolatilization. In order to understand the background of this formation, solid fuel conversion will be explained in further detail in the following section.

2.6 Solid fuel Conversion

The conversion process of a solid fuel can be described by drying (vaporization of moisture) and devolatilization (release of volatiles) followed by oxidation of volatiles and char and finally a gasification of the char by CO_2 and steam[39]. There are several significant parameters that have an impact on devolatilization. Example of such are the kind of fuel, particle size, heating rate, superficial gas velocity (see section 2.7), gaseous environment, temperature, pressure, oxygen concentration and fragmentation of solid fuel[40]

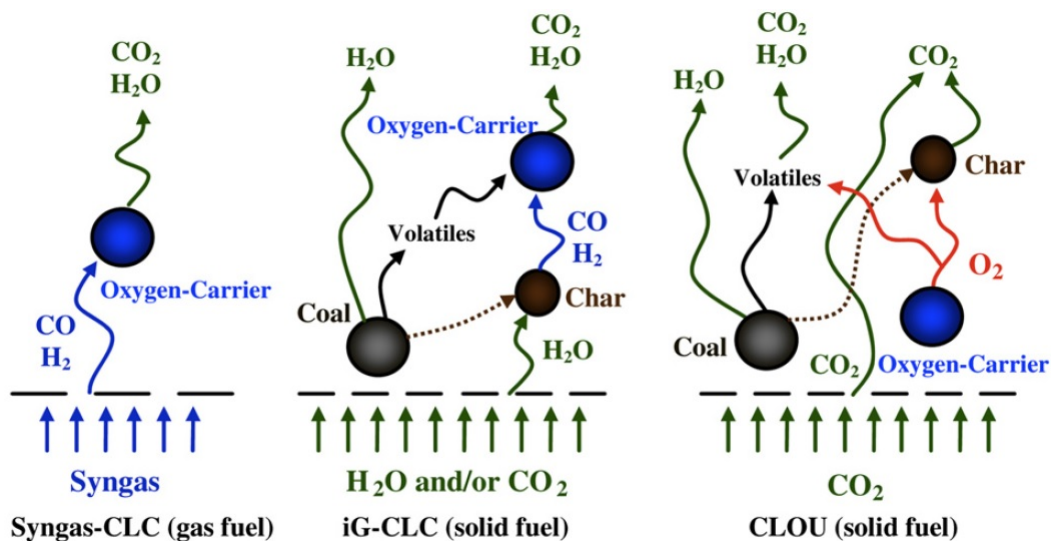


Figure 2.2: Schematic of gas conversion and solid (coal) conversion for CLC and CLOU[1].

The speed at which the different conversion processes for a solid fuel take place varies but a general guideline is that the devolatilization is very fast compared to char conversion and gasification with CO_2 and H_2 is even slower.

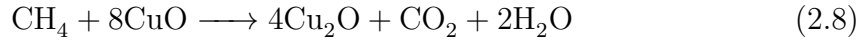
When converting solid fuels with large amounts of volatiles, large amounts of gas are formed. When using solid fuels such as coal, there is a substantial amount of volatiles being released near the feed ports. This creates large amounts of gas which rises like a plume of unburned volatiles which looks like a gas flame and the model to describe this phenomenon is often called the gas plume model. This has been proven to cause problems to the CLC-process. One problem is the conversion of char which needs to react with released oxygen. Unconverted char is a problem for the process and when the compounds released during devolatilization reacts easily with oxygen which may limit the char conversion. In addition to this reaction, it may also react with the bed particles causing unwanted reactions resulting in for example bed agglomeration.

In order to understand how the gas plume may affect the operation of the fuel

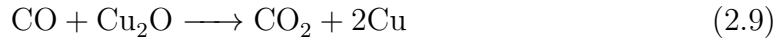
reactor, it is required to list the known reactions. First of all, the wanted reaction with cupric oxide is a release of oxygen gas forming cuprous oxide.



During combustion, volatile species will be formed and CO and CH₄ are examples of such. When these gases react with cupric oxide the result is a conversion to cuprous oxide and CO₂ which are wanted reactions.



An example of a possible reaction that could occur is CO and cuprous oxide reacting to form elemental Cu is written below in equation 2.9:



This reaction could also occur with for example CH₄. From these reactions, it is possible to see that an increased amount of volatile species in relation to the amount of cupric oxide can increase the risk of reactions such as 2.9 to occur. This is the case during devolatilization of a solid fuel which means a release of these species. Even though it is known that the presence of these species may increase the risk of formation of elemental copper and therefore also the risk of bed agglomeration, the actual outlook of the gas plume being formed is relatively unknown. Another issue with the increased concentration of volatiles species is the loss in char conversion. The gas-gas reaction with the volatiles species goes much faster than the reaction between the gaseous oxygen and the solid char particles. This can therefore lead to an accumulation of unconverted char particles in the system. Apart from the impact on the oxygen carrier and the char conversion, the plume decreases the efficiency of the CLC-process since unconverted amount of these gases escaping the bed are seen as a loss to the process. The conversion of these volatiles species depend on the mixing of these species with other reactants as well as the residence time of these species in the system[41].

There are several additional reasons for that the generation of volatiles is important to investigate further. An example is the aspect of pollutant formation which may increase at local hotspots (approximately 50 % of the overall heating value of coal comes from volatile species)[42]. Poor distribution of combustible compounds in the bed leads to the creation of reducing and oxidizing zones which in turn can affect the performance of a carrier material or lead to pollutant formation[43]. The segregation of volatile compounds in relation to gas-solids suspension may also lead to poor contact between volatile compounds and fluidized bed solids which can be when combusting there when using in situ desulphurization (more than 50 % of the sulfur in coal can be found in the volatiles) of flue gases is done with the limestone[44]. The concentration of the volatiles gases throughout the bed therefore greatly affects the efficiency of the combustion process with regards to fuel conversion, pollutants

formation as well as reliability and safety[42, 45]. When combusting high-volatile fuel, it is often reported that combustion takes place in layers from the fuel particles. There is a need to consider gas plume formation also for full-scale combustion units which have larger superficial gas velocities. One common indication of this is the measured local temperature increase just above the bed surface[42]. As a result of volatile compounds passing into the freeboard, a post-combustion is done in that region. Fuels with a high content of volatiles have also been confirmed to caused more attrition and fragmentation compared to other fuels[42].

Having described the solid fuel conversion process and the importance to better understand the impact of devolatilization in a fluidized bed, the next section provides a more in-depth description of fluidized beds.

2.7 Fluidized bed

In a fluidized bed a fluidization agent sets bed particles in motion by flowing upward and makes the different components in the reactor come in contact. The chemical looping system consists of two fluidized beds where the characterization of these beds is done by looking at the fluid dynamics.

The fluidization properties of the bed depend strongly on the shape and size of the bed material. Bed particles are classified into 4 different categories based on the behaviour of the particles that make them fluidize (here listed from smallest to largest particle size)[38]:

- Geldart Group C: The smallest particles (cohesive or very fine powders) and it is difficult to fluidize the bed because the forces caused by the gas flow are smaller than the interparticle (electrostatic) forces. The particles lift like a plug through the reactor when the gas penetrates the bed.
- Geldart Group A: Particles having a small mean particle size and/or low particle density ($< \sim 1.4 \text{ g/cm}^3$). These particles are easily fluidized already at low gas flows. A bed of Geldart A particles is likely to expand before bubbles start to appear and bubbles are formed at high gas velocities but the bubble formation is controlled and the increase in size is not substantial. If the bubbles grow to the size of the diameter of the vessel, the bubbles turn into axial slugs (coalescence of gas bubbles).
- Geldart Group B: Sandlike particles that are easy to fluidize with sizes around $40 \text{ } \mu\text{m} < \bar{d}_p < 500 \text{ } \mu\text{m}$. Bubbles form as soon as the gas velocity exceeds u_{mf} which means that $u_{mb}/u_{mf} \cong 1$ (u_{mb} represents the velocity at which bubbles are first observed) . An issue however is that bubbles can be formed at relatively low gas velocities and the size of these will increase along the bed length.
- Geldart Group D: Large particles that are difficult to fluidize which means that there is a substantial risk for channeling and bubbles growing large when

passing through the bed. Flat slugs can be observed when the bubble size approaches the bed diameter.

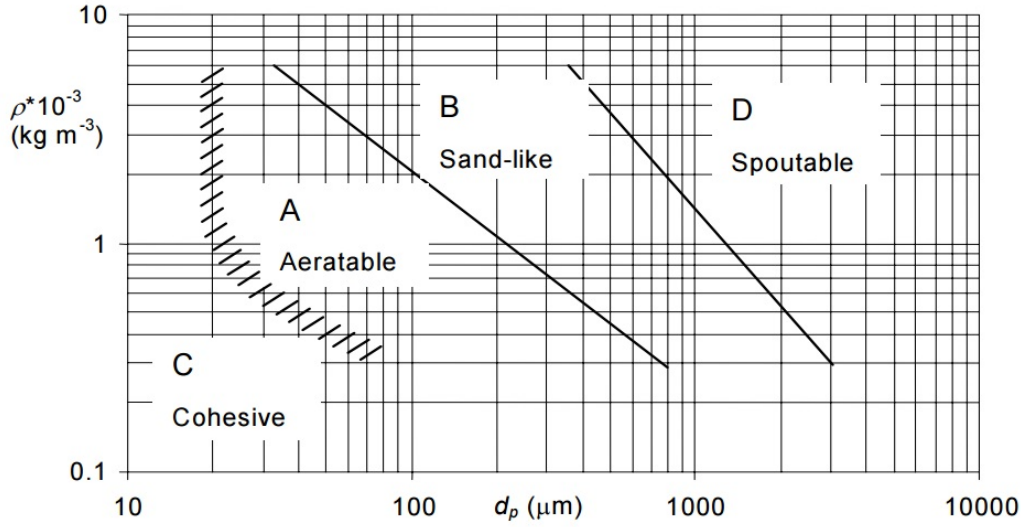


Figure 2.3: Diagram of the Geldart classification of particles[46].

These large particle beds are usually seen as undesirable for physical or chemical operations. There is for example a substantial amount of gas needed to fluidize these beds[38]. One approach that is used to fluidize with less amount of fluidizing agent is to use a spouted bed which means that only a part of the reactor is fluidized and on the other part of the reactor, the large particles falls down[41].

The fluid dynamics can be described by the velocity of the fluidization agent. In order to obtain a fluid-like behaviour of the solid particles, the velocity of the fluidization agent has to ensure that the pressure drop over the bed is equal to the weight of the particles and the fluidization agent in that section with the height h ($\Delta P = \rho g h$).

It is possible to express the minimum fluidization velocity in the following form[38]:

$$u_{mf} = \frac{Re_{mf} \mu_g}{d_p \rho_g} \quad (2.10)$$

where Re_{mf} is the Reynolds number for the minimum fluidization velocity, μ_g represents the dynamic viscosity of the gas flowing through the bed while d_p is the diameter of the particles and ρ_g is the density of the gas in the bed. An estimation of Re_{mf} is needed, the Reynolds number has to be estimated which is done with a correlation between Ar (Archimedes number) and Reynolds number.

$$Re_{p,mf} = [(C_2/(2C_1))^2 + (1/C_1)Ar^{1/2} - C_2/(2C_1)] \quad (2.11)$$

Where C_1 and C_2 are experimentally determined constants which have been determined for different operating conditions. It is important to note that the velocities

are dependent on several operation parameters such as pressure and temperature apart from the previously mentioned particle size and shape. Ar is determined by the following expression:

$$Ar = \frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu_g^2} \quad (2.12)$$

The additional parameters needed to calculate Ar are ρ_g which is the particle density and g is the gravitational acceleration. Another important parameter to be able to estimate is the terminal velocity (u_t) representing the velocity at which the drag force F_D and the buoyancy F_B is equal to the gravitational force F_{grav} of a single particle which could be seen as a particle floating in the air.

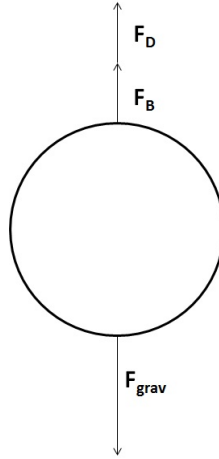


Figure 2.4: Force balance over a single particle.

In order to determine the terminal velocity there are several different correlations depending on the fluid flow characteristics. One approach suggested by Basu was that the terminal velocity of the particles should be described as[47]:

$$\left\{ \begin{array}{l} u_t = \frac{Ar \mu_g}{18 d_p \rho_g} \quad for \quad Re < 0.4 \\ u_t = \frac{(\frac{Ar}{7.5})^{0.666} \mu_g}{d_p \rho_g} \quad for \quad 0.4 < Re < 500 \\ u_t = \frac{(\frac{Ar}{0.33})^{0.5} \mu_g}{d_p \rho_g} \quad for \quad Re > 500 \end{array} \right. \quad (2.13)$$

where the Reynolds number is defined by

$$Re = \frac{u_t d_p \rho_g}{\mu_g} \quad (2.14)$$

If the fluidization agent has a velocity larger than the terminal velocity the particle starts to move upwards in the reactor. Therefore, this velocity marks an important threshold where the bed goes from being a bubbling bed (when the particles will

remain fall back into the bed and remain in the same reactor) and becoming a fast bed (when the particles leave the bed). Consequently, to maintain a fluidized bed without transporting away solids, a velocity between u_{mf} and u_t must be kept. There are 4 kinds of beds which will be discussed in further detail: Fixed/packed bed, bubbling bed, turbulent bed, fast bed and transport bed.

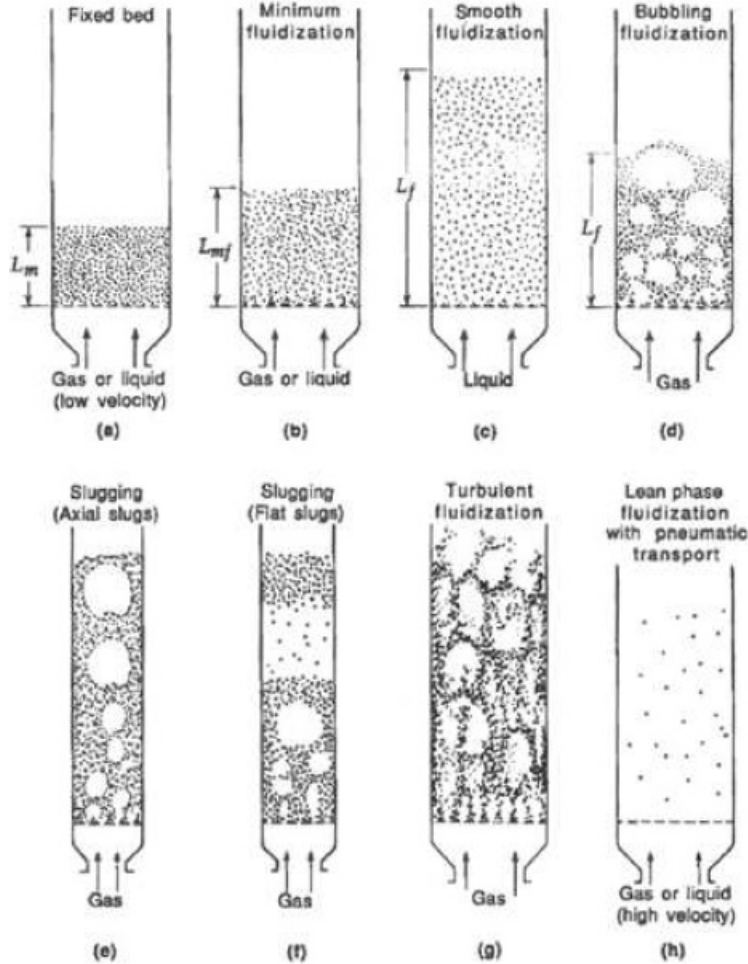


Figure 2.5: Schematic of different fluidization velocities in a fluidized bed [38].

A fixed bed ((a) in figure 2.5) represents the case of low fluidization velocities and with air carefully passing through a fixed layer of bed particles. By increasing the fluidization velocity, the pressure drop over the bed increases until the velocity u_{mf} is reached (b). At this velocity the bed starts to behave like a fluid. When the velocity is increased even more the bed reach a bubbling state (d) where the mixing is good and the flow gets turbulent. Increasing the velocity even more results in particles leaving the bed entering the freeboard region (between the dense bed and the gas stream exit)[38]. The splash zone is the region between the fixed bed and the freeboard.

When the velocity is increased over the minimum fluidization, problems with slugging start to occur. The gas that is not used for the fluidization forms bubbles which create an uneven distribution of the bed particles. At the bottom of the bed the

bubbles are small and spherical and they grow bigger and get more and more flat as they move upward. On the way upward they can also come together which means that a taller bed gives space for building up bigger bubbles. Big bubbles travel faster than small bubbles as well and the walls affect the velocity at which they rise in a similar manner. For a deep bed with small diameter, slugging can spread to cover the whole diameter of the vessel. One approach to characterize a slugging regime is to observe bubble sizes larger than 0.6 times the inner bed diameter[48]. This phenomenon can in turn lead to a decrease in the combustion efficiency as well as have a bad impact on the equipment[38]. This change in bubble sizes can be seen in (e) and (f) in figure 2.5.

When the velocity of the fluidization agent is increased over the terminal velocity u_t the upper surface of the bed disappears and there is now a turbulent flow of solids (g). At even higher velocities the solids are carried out of the bed (h) and this results in a pneumatic transport of solids in the system. The solids flow up the tube as separate particles dispersed in a gas. This flow regime can be used to prevent settling of particles (saltation) which is likely to occur at horizontal surfaces of the Chemical Looping system. This problem could also be prevented by inserting gas jets at various angles close to the horizontal surface but it is essential to consider the risk of attrition[38].

A pneumatic transport bed needs a bigger cyclone and it is said that a fast fluidized bed is used when these two units are used. A fluid bed is a turbulent fluidized bed with an inner cyclone. These two kinds of beds represent circulating fluidized beds[38].

A commonly used parameter for fluidized beds is the superficial gas velocity u_0 which represents the velocity the fluidizing agent would have had if it was flowing through an empty reactor[38]. Directly related to this velocity is the interstitial velocity which represents the velocity the fluidizing gas will have inside the bed. This velocity is directly proportional to the superficial velocity (u_0) and inversely proportional to the voidage or porosity of the bed [49].

$$u_{inter} = \frac{u_0}{\epsilon} \quad (2.15)$$

It is important to note that the velocity within the bed is higher than the superficial. It is obvious that the resistance to fluid flow through the bed is affected by the amount of particles present as well but normally the porosity is used to relate these velocities to one another.

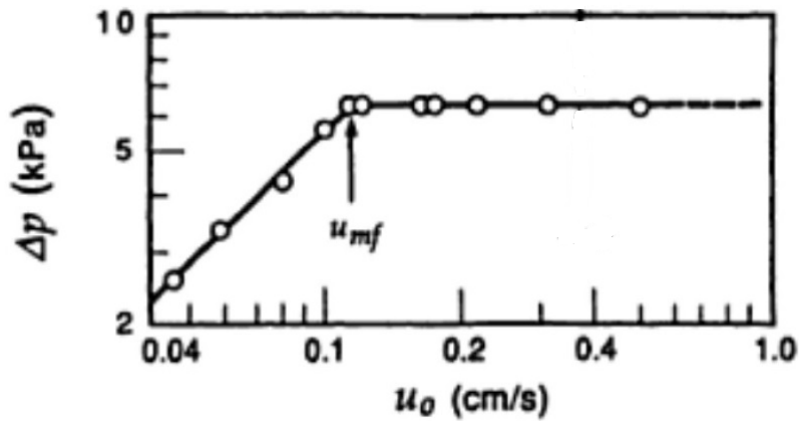


Figure 2.6: Pressure drop over a fluidized bed for different superficial velocities[38].

The pressure drop over the bed increases with u_0 up to the velocity u_{mf} when the pressure drop becomes constant which can be seen in figure 2.6. However, the figure looks slightly different depending on which kind of bed particles that are present. For Geldart particles of type B, the transition from a packed bed to a bubbling bed is more linear for a narrow bed and for a wider one the transition to a constant pressure drop is more gradual[50].

For these different kinds of beds, the conversion is in general the highest for the fixed bed since this flow is more similar to plug flow and then decreases with increasing superficial velocity (at which the flow is more similar to ideal mixing). On the other hand, beds with higher u_0 have a better efficiency when it comes to heat exchange.

There are several reasons for using a fluidized bed. Fluidized beds provide a continuous process thanks to the smooth liquid-like flow and the rapid mixing also makes it easier to have a more or less isothermal process with no reaction runaway[38]. Fluidized bed combustion is seen as an especially promising technique thanks to the fuel flexibility[42].

In the fluidized bed, the heat and mass transfer is good between the gas and the solid particles and excess heat can also be removed by extracting hot solids. Another advantage is that large flows can be used. One of the biggest disadvantages with the technology is the difficulty to describe the fluid dynamics. A trade-off with the rapid mixing is that it results in non-uniform residence times for the fuel particles. The bed material may also need to be replaced due to mechanical stresses. The bed particles themselves can cause erosion of pipes and vessel. In the case of non-catalytic operation at high temperatures, agglomeration and sintering of the bed particles is a problem for the operation of a fluidized bed[38]. It should however be noted that even at low temperatures, the bed particles can agglomerate if they get moist or tacky which may be a result of using a moist fuel for example[38].

One characteristic that can be used to understand the impact of injection of a gas into a fluidized bed is the jet penetration length. The jet penetration length L_j for an orifice in a plate be defined as the distance between the plate and the center of

the bubble at the instant it detaches from the jet[51]. Another reason for the importance to consider this length is the risk of erosion of equipment in contact with the bed particles as well as the risk of attrition of the solids. Smaller holes result in shorter jets but it also results in a larger pressure across the distributor. The jet penetration length has been proved to increase with the jet velocity[52]. It has also been shown that the jet penetration length decreases with the bed particle size. This trend is especially large for larger jet velocities[53, 54]. Interestingly enough, one of the two equations that are presented to follow the experimental data the best in Musmarra's article presents that the jet penetration length should increase with increasing particle size and the other one shows no dependence. Still, there is support showing that the penetration decreases as the diameter of the bed particles increases as in studies of Filla et al. as well. What Filla et al. presented was that larger particle size results in faster dispersion of jet momentum and as a result the penetration is smaller[51]. Zhong et al. displays that the jet penetration length increases with increasing fluidizing gas flow for several different bed materials[55].

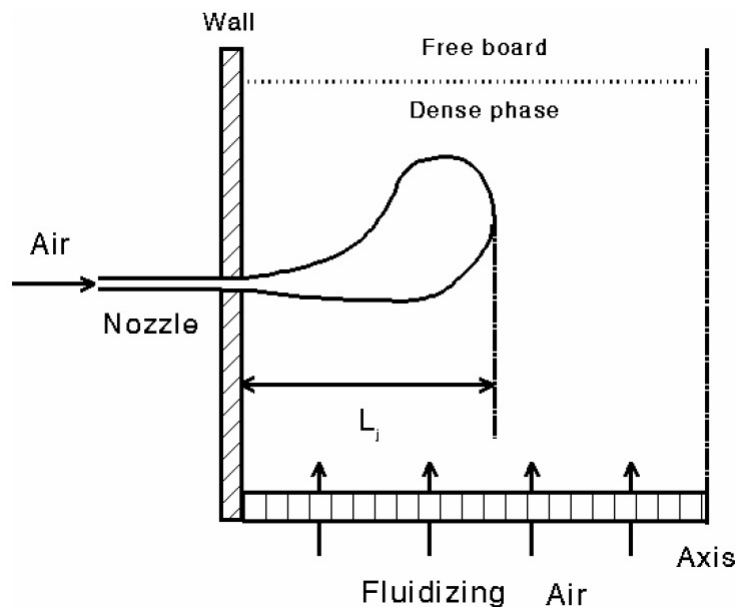


Figure 2.7: Schematic of the horizontal jet penetration length (L_j)[52].

This basic knowledge on the fluidized bed can now be applied to better understand the used CLC system. In the air reactor the velocity is high and the flow is circulating (whereas the bottom part is a low velocity bubbling bed[39]) and the expansion of the bed is large which means that the riser is tall. In the riser the velocity is higher than u_t to make sure there is circulation of oxygen carrier. The second part is the fuel reactor and the bed can for example be either circulating or bubbling depending on the system (bubbling in this case)[1]. In order to obtain an even distribution of the fluidizing agent a sufficiently high flow resistance is provided by a distribution plate. Filter cloth, compressed fibres, metal/wire plates as sandwich and using the above mentioned materials in-between are all examples of possible distributor configurations[38].

At the outlet of the air reactor, the cyclone is reached and the oxygen carriers are here separated from the air by using the air velocity's dependency on the pipe diameter. The carriers fall down into a loop seal while the air is purged out on top[38].

Loop seals are placed at the outlet of the reactors make sure that no gas is flowing into the other reactor due to pressure difference. They can be seen as small fluidized beds and the seal make sure that there is a continuous transfer of carriers to the fuel reactor while the air cannot pass the seal through the fluidized particle bed[38]. The oxygen carriers which leave the bed can be recirculated back into the fuel reactor by a second cyclone. See picture of the existing CLC system in figure 3.1.

In order to characterize the hydrodynamics of the CLC system, the circulation rate is a useful parameter. There are several proven approaches to measure the circulation rate and one of the methods for cold operation is to close a part of the chemical looping and observe the rate at which the material accumulates in a transparent tube. This approach does not work for hot operation since available materials cannot endure the high temperatures. A recently developed method presented is Pressure-induced Measurement of Circulation (PIMC) which is a technique that also works for higher temperatures[56]. The circulation rate can then be calculated by using Bernoulli's equation. The total pressure of a flow can be expressed as the sum of the hydrostatic pressure, the static pressure and the dynamic pressure in the flow. By interrupting the fluidization in a part of the system, the solids will accumulate at that part and by having two nozzles at different heights in this tube that accumulates solids inside; a dynamic pressure will be formed in these two points for the nozzles with a certain delay in time. This time delay (the time to fill the volume in the downcomer between these two mentioned points) can be used to find an estimation of the circulation rate in the same way as for cold operation.

After a description of fluidized beds and the use of fluidization in the chemical looping system, an investigation is done in the previously mentioned area of interest that is gas plume formation in fluidized beds.

2.8 Gas plume literature review

This section summarizes the research that has been done in the area of gas plume formation in fluidized beds. The words gas plume comes from the description of volatiles forming a bubble around the solid fuel particle from which they originate. The bubble consists of volatiles flowing outward in the radial direction and they are consumed at the bubble boundary. These bubbles are considered to be different from air bubbles since flow of gas through the bubble cannot occur. The size of these bubbles is determined by the rate of formation of volatiles and the rate at which the oxygen diffuses towards the bubble. The bubble exerts a buoyant force on the solid particle by elongating upwards which result in moving the solid particle upwards.

When this bubble with the solid inside reaches the bed surface, a plume-like flame is formed above the surface which is a result of a fast combustion of the bubble which then results in that the solid particle moves downwards into the bed. The process can then repeat itself with a solid particle of a smaller size but normally the amount of remaining volatiles is very small. It is important to note that there is a certain rate of formation of volatiles that is required for the described theory to be valid. If the rate of formation is too slow, the oxygen diffusion will be fast enough to consume all volatiles close to the solid fuel particle[57].

The formation of bubbles of volatiles around devolatilizing fuel particles has been confirmed experimentally in several studies [58–61]. Experimental results indicated that these bubbles could transport fuel particles towards the surface but once there, particle segregation followed where volatile compounds were released into the free-board while the fuel particles remained in the bed.

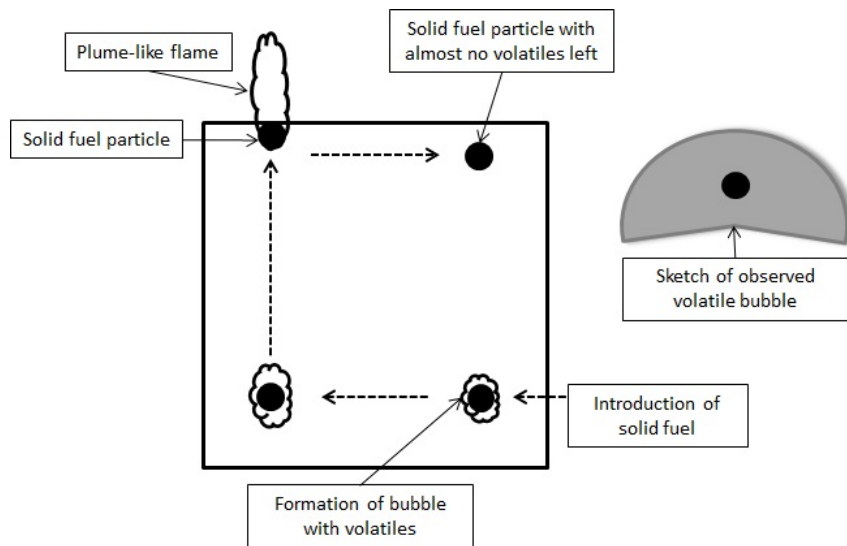


Figure 2.8: Visualization of an early gas plume model and the observed gas plume.

It is important to note that the drawing to the left in figure 2.8 only provides a very simplified image of the gas plume model. The visualization is based on the interpretation of observations made by Bruni et al.[45]. There are several publications investigating the dynamics between gas and solids in general through modelling with mass and heat balances over the bed. For the small volume around the gas injection point there are several models focusing on what the burning profile as well as the temperature profile looks like [42]. There are several important phenomena to take into consideration when describing the combustion of solid fuels with a large amount of volatiles. The fuel particle fragmentation and attrition in the bed as well as the segregation of the volatile matter and the post-combustion above the bed are all important elements when establishing a suitable model[42].

It has been determined that the position at which the volatile matter is burnt is dependent on the operating conditions such as the fluidizing velocity[42]. In order

to assess the segregation and combustion of volatile gases, a gas plume model which assumes that volatile gases form a rising plume consuming oxygen throughout the bed. The gas there is assumed to rise in a plug-flow through the bed which means that no mixing of the gas takes place in the radial direction, only in the direction of the height of the bed (for ideal plug flow) [62]. Combustion of the volatiles occurs as a diffusion flame (oxidizer and fuel source is separated so mixing limits the energy release rate [12]) at the boundary of the plume [42, 62].

When looking at the devolatilization in the bed it is important to take into account the time scale for the reaction as well as the movement of the solid fuel. One of the most commonly studied fuels is coal. The devolatilization time for coal particles is normally most a few seconds (up to 10 seconds for a 3 mm particle and less for smaller particles) [62]. The time to obtain a well-mixed bed is at least 15 seconds whereas a complete combustion of coal particles is in the time-scale of minutes. As a result, devolatilization is faster than particle mixing which in turn is faster than the chemical reaction of the particles [62]. Based on this it is possible to assume that devolatilization takes place instantaneously when entering the bed and then the volatiles rise with the same velocity as the other gases in the bed in a plug flow as plumes [62]. The devolatilized coal particles are assumed to be distributed uniformly across the bed. The volatiles in the rising gas plume reacts at the plume boundary with air which then resembles a diffusion flame [62].

By taking these assumptions into account, a single plume in the bed can be visualized as in figure 2.9.

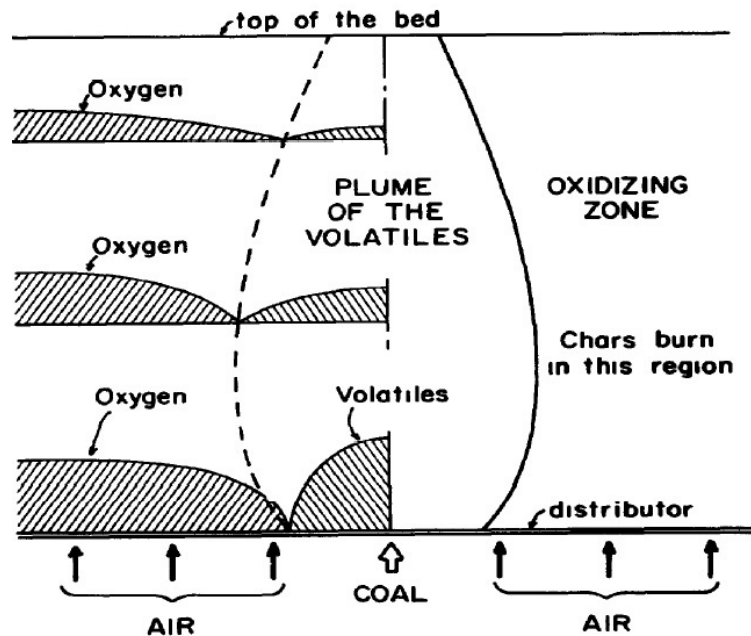


Figure 2.9: Scheme displaying the concentration of oxygen and volatiles close to the feed port (directed upwards) based on the early gas plume model [62].

It is important to note that the introduction of the solid fuel takes place in the same

direction as the fluidizing gas. Many of the early models ignored the volatiles reaching the freeboard region but since observations were made showing a temperature increase in this region it was concluded that this had to be taken into account in the model. It was also observed that the gas composition was varying significantly for different radius which meant that the distribution of volatiles in the cross section of the bed was not uniform.

Larger particles tend to stay in the bed while particles smaller than a critical size tend to be removed by elutriation[62]. Elutriation of small solid fuel particles means that the particles are removed by a fluid flow from the bed as a result of their size[63]. There is therefore two competing phenomenon: the reaction process and elutriation and to obtain an efficient combustion of the fuel, the latter has to be smaller. There appears to be a relation that larger particles are almost completely combusted in the bed (larger than $500 \mu\text{m}$) and very small particles react before they elutriate but in between these two groups of fuel particles, there is a group of coal particles that have a significant risk of being elutriated[62].

The plume model can be used to explain the effect of changing several parameters that relates to the combustion of the coal particles such as coal feed size, superficial gas velocity, excess air velocity and bed depth. The dimensionless plume group number (HD_{rad}/u_0L^2) can then be used to characterize the plume combustion dynamics independently of the use of air and the elutriation of particles. H is the bed height, D_{rad} is the radial gas dispersion coefficient and L is the radius of the coal feed module. This dimensionless number can be related to the fraction of volatiles that are burned in the bed which is represented by the parameter X_v .

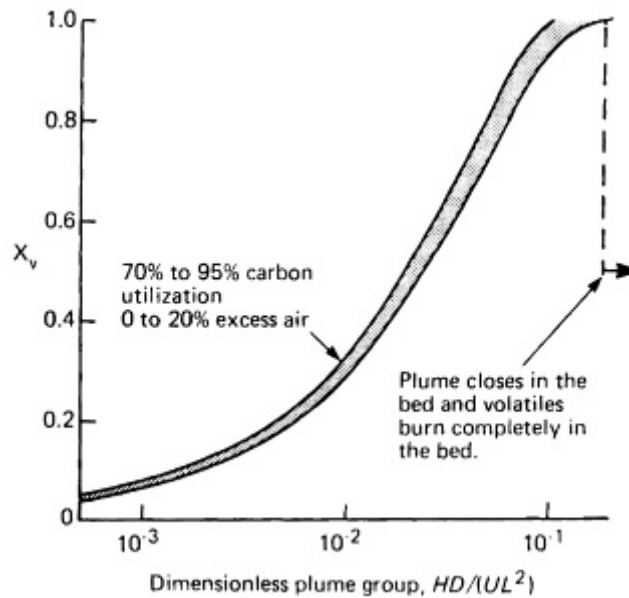


Figure 2.10: Graph of the fraction of volatiles burned in the bed for different plume group numbers[62].

The graph shows that for increasing plume group numbers, the combustion of

volatiles is complete which means for example for larger bed heights, smaller superficial velocities and more fuel feed ports (each port is then smaller)[62]. As a result of the description of the combustion of volatiles as a diffusion flame it was suggested to develop a multiple discrete diffusion flame model to take into account the movement of the devolatilizing compounds to the top of the bed as an effect of the fluidizing gas bubbles. It is important to note that none of these models take into account the hydrodynamics between the devolatilizing fuel particles and the surrounding fluidized suspension. However, the segregation of gas-emitting particles is similar to known mechanisms of mixtures of inert particles[64].

The hydrodynamics between the stream of devolatilizing compounds, the suspension of fluidized particles and the fuel particle motion was later investigated theoretically as well as through experiments. This was done at incipient fluidization (at the point of minimum fluidization velocity) and the conclusions from this study confirmed the previous indications about the bubbles of the volatiles by using x-ray imaging[44,45]. Mechanistic studies have only been done for low superficial gas velocities and only for bench scale systems[45].

Results have shown that fluidization has a big impact on introduction for gaseous fuel. It is important to point out that there appears to be two different ways the gas-emitting fuel particles could be dragged along upwards with the bubbles of formed volatiles. This could be done in patterns described as single bubble segregation (SBS) or multiple bubble segregation (MBS). SBS is the process when the first single generated volatile bubble is able to “lift” the fuel particle to the top of the bed. MBS on the other hand is a result of a stepwise motion of the fuel particle which is caused by generation of multiple volatile bubbles. It is important to note that these segregation patterns do not occur for very heavy fuel particles or very slow devolatilization rates. For these cases the fuel particle remains at the bottom of the bed where the volatiles are being formed[45].

As a result of different fluid dynamics of the fluidized bed, the bed can be divided into different parts to create an overview of the combustion process in the bed. Through models of the different combustion processes of these solid fuels, it was then possible to determine where the heat of combustion is released. There are few models which have investigated fluidized bed combustion of high-volatile fuels. In 1995 a three-phase FBC model for a high-volatile fuel considering attrition and fragmentation was presented by Irusta et al. assuming devolatilization in freeboard and bed where the relation of these are varied[65]. The results from this modelling were compared with a pilot plant with lignocellulose as a fuel and it was shown that 20-40 % of the volatiles were burned in the freeboard region. A different kind of model considering combustion of volatiles and char in bed and freeboard and by using a modified two-phase plume model for biomass combustion predicted that up to 40 % of the volatiles could burn in the freeboard region[42]. Experiments with a 4-mm-sized biomass particle fed in an incipient fluidized bed shows that the fuel particle was carried to the top of the bed in the SBS pattern in less than a second which is much

shorter than the devolatilization time. This could be seen as a confirmation that the volatile matter is likely to be released above the bed surface[45]. One measure to decrease the amount of volatile matter in the freeboard is to achieve a better oxygen mixing rate at the lower part of the bed[42].

A suggested focus from this point was instead to model high-volatile fuels in general to investigate the importance and effect of the volatile segregation, combustion and fuel attrition. The solid fuel was then divided into three parts: ash, fixed carbon and volatile matter (all fuel bound hydrogen and oxygen, including moisture). From this model it was possible to observe where in the fluidized bed the combustion of volatiles took place and the result showed that comparable amount of volatiles was combusted in the fluidized bed and in the splash zone. The model showed that the fraction of volatile matter burning in the freeboard region is not negligible. This rather simple model confirmed that the processes of solid fuel fragmentation, attrition and segregation of volatile matter and post-combustion in the region/regions above the bed are critical to find a reliable model of the system[42].

An interesting observation that was made was that the size of the bed material had an impact on the combustor performance. For more coarse particles, fewer particles are ejected and the result is less thermal feedback (hotter bed particles being ejected and then fall back into a lower situated section). It was concluded that a too large diameter of the bed material is to be avoided because of the fact that the thermal feedback in the splash zone decreases and more heat has to be extracted from the freeboard[42]. One approach to estimate the transport of the volatiles is to study the time constants for the horizontal transport across the bed via dispersion and compare this to the devolatilization time.

$$\tau_d = \frac{r^2}{2D} \quad (2.16)$$

where r is the distance in horizontal direction and D is the dispersion coefficient.

$$\tau_{dev} = ad^n \quad (2.17)$$

where d is the initial fuel particle size while a and n are experimentally determined ($a=n=1.6$) constants[66]. The devolatilization process is normally fast which means a smaller time constant and during this time, the distance that the particle is transported in the horizontal direction is short which means that a poor distribution of the volatiles across the bed. The char combustion on the other hand is a slow process compared to the dispersion which means that the char particles will be well distributed over the bed volume.

The vertical mixing should also be considered in relation to the devolatilization in the fluidized bed. There are three different possible cases: The particle remains at the free surface most of the devolatilization process, the devolatilization takes place

completely close to the feed point and the third possibility is that the particles are well distributed throughout the bed as the devolatilization takes place[39].

The first option represents the case where the transportation of fuel particles is fast compared to the devolatilization and $Da_v \ll 1$. Da is the Damköhler number relating the reaction rate and the convective mass transport rate. This includes also the case where the fuel is fed at the top of the bed and stays there. The devolatilization then takes place at the top of the bed while the remaining char is then likely to sink into the bed. In this case the amount of volatiles at the bottom of the bed is small[39].

The second case is the situation that is the most commonly experienced in practice so far which means instantaneous devolatilization. Da_v is much larger than 1. Close to the fuel feed point, the oxygen is quickly depleted and the most probable reason is that the released combustible volatile compounds such as H_2 , CO and CH_4 reacts with the oxygen since rate of char combustion has been confirmed to decrease fast with limited oxygen transfer to the particle surface. After the devolatilization the biomass in this case is carried up by the fluidizing agent to the oxidation zone where the char is exposed to oxygen[39].

In the two situations described so far, either the reaction or the mixing is dominant and devolatilization coupled with fluid-dynamics does not have to be included in the model. It is then enough to know the total release of volatile matter knowing the initial composition and distribution of the gas entering the bed mixed with the fluidizing agent coming from the distribution plate. However, few of the models consists of a quantification of the Da_v to confirm this assumption[39]. For this case it is possible to determine the decomposition of the fuel particle in the laboratory to model the devolatilization of biomass but the general case where Da_v is close to 1, the motion of the biomass particle has to be established in each position and coupled with devolatilization and size distribution which results in more complex modeling. Experimental information can then be useful to predict the distribution of the devolatilizing particles.

Apart from the transport in the vertical direction, the lateral (horizontal) mixing plays an important role, especially for larger units for which few studies have been conducted. Simulations show that the horizontal gas mixing is much slower than the axial transport which means that most of the volatiles can be found close to the feed ports[39]. Da_h should be analyzed to understand the transport in the horizontal direction. A number much smaller than 1 means that the volatiles are transported a long way and devolatilization takes place in the entire cross section. For large numbers the horizontal transport is limited and the devolatilization takes place only in the vicinity of the feed ports. The intermediate case with a number around 1 means that both processes should be taken into account at the same time. Measurements should be done for larger units at different radial positions for fluidized bed gasifiers (FBG).

Despite the available models, there is no published model that combines a structural kinetics model with diffusion effects for FBG conditions. Measured data is therefore still the basic input for FBG modeling[39]. One problem when conducting devolatilization experiments is the difficulty to observe the difference between primary and secondary conversion of volatiles. In addition to that, the secondary reactions may vary for different systems[39]. The secondary devolatilization reactions comes as a result of the components after the primary devolatilization which involves structural changes in the solid fuel[40].

Most investigations that have been done describes the global mechanisms of devolatilization. Simplified models to combine simplified hypothesis and empirical relations with the foundation in experimental data have been used repeatedly to characterize the rate and the composition of the gases released during devolatilization. The target is then to estimate the time to complete devolatilization by only looking at the rate-limiting phenomena. When estimating the time for devolatilization that time is often combined with an estimation of the drying and devolatilization altogether. The characteristic rates of these two phenomena can then be compared by investigating the Damköhler and thermal Biot numbers (ratio of heat transfer resistance inside of and at the surface of a body) for solid fuels. The devolatilization process can be represented by a first order reaction with a coefficient obeying the Arrhenius law[39].

It should be noted that dimensionless numbers are used to identify the dominant process and by doing so make it possible to simplify the description of the system. The used model must then be supported by empirical data. The composition of volatiles are estimated separately by using mass balances and empirical relations, however there is still a need for additional empirical relations to get a more correct estimation[39].

There is a substantial amount of experimental studies that have been done describing the performance of the fluidized bed combustion for different fuels but less attention has been paid to the mechanisms of the conversion of these fuels with respect to the fluidizing gas and the bed material. Further studies are needed above the behaviour of particle dispersion and gas concentrations in the bed to improve the design of for example combustion chambers for better allocation of fuel and air feed points for various fuels[43]. A rigorous description of the release of the volatiles has not been done and in particular not for a fluidized bed system for higher fluidizing velocities than the minimum fluidization. The interaction between the endogenous volatile bubbles and the exogenous volatile bubbles (as well as their cooperative influence on the fuel particle movement) has therefore not been investigated in further detail. There is a lack of investigation of a study on the devolatilization in a fluidized bed for different fluidizing conditions and it is important to understand the distribution of these gases to operate a future CLOU system with copper-based

carriers. For this reason a study is done in the area of the gas plume formation of a solid fuel in a fluidized bed. This should be done for various bed materials and fluidization velocities to get a better general understanding of the dynamics in the fluidized bed so experimental data to describe the distribution of the devolatilizing species in the bed is crucial to develop more accurate models. The experimental work has mostly been done for rectangular/quadratic fluidized beds while circular beds are more uncommon which makes the study even more interesting in that sense.

In order to study the solid fuel injection and the following devolatilization, sublimation of dry ice (solid carbon dioxide) by heating can be used to simulate the devolatilization process. The enthalpy of sublimation of dry ice is 573 kJ/kg[67]. There are a few examples of publications on attempts to use sublimation of dry ice to simulate combustion phenomena such as pyrolysis of a solid fuel[68] and the combustion of propellant gases[69]. No attempts appear to have been done more recently and none more specifically for devolatilization of a solid fuel. The method to use dry ice has an advantage over studying solid fuels directly since it is possible to use for a cold flow model and since no other reactions than the sublimation of the CO_2 would take place which means that the fluid mechanics of the phenomena could be separated from the combustion process itself[68]. Cold flow experiments such as this one also have the advantage that the experiments are relatively easy to conduct for a longer period of time[70].

Apart from just using the surrounding air for example to provide heat for the sublimation for the CO_2 , infrared radiation from an IR lamp can be used[69]. A piston could be used to excite acoustic waves in the chamber and the waves pass over the subliming dry ice. This technique was used to simulate a burning propellant (mix of fuel and oxidizer to produce thrusts) in rocket motors[69]. It would then be possible to have this at the end of the tube that supplies the dry ice to the fluidized bed. With a successful isolation of the tube, almost all of the dry ice could then sublimate at the entrance of the fluidized bed[69]. The dynamic behaviour of the dry ice is similar to the behaviour of an actual propellant but not as powerful. An observation with this comparison was that an increased pressure gave an increase in the mass flow rate both the burning of the propellant and the sublimating solid CO_2 [71].

2.9 Variable area flowmeters

When using a variable area flowmeter, a weighted float rises in a tube as the flow rate increases but the rise of the float (a cone) inside stops when the weight of the cone is as big as the drag force pulling the cone upward. The variable area flowmeters are calibrated for standard conditions and air flow, it is important to adjust for the present operating conditions in the lab. This adjustment has to be done for all flow measurements using these kind of flowmeters. The conversion from the observed value on the flowmeter and the actual flow is done by using the following formula:

$$True\ SLPM = \frac{SLPM}{\sqrt{\left(\frac{T_{Op}}{T_{Standard}}\right)(SG_{Op})\left(\frac{P_{Standard}}{P_{Op}}\right)}} \quad (2.18)$$

This formula takes into account the gas in use, the atmospheric pressure at the location of the lab, the actual temperature in the lab as well as the pressure in the system (measured after the flowmeter and described as the backpressure)[72]. Op stands for the operating conditions and standard stands for standard conditions (air is the flowing gas with pressure at 14.7 psi (101.3 kPa) and temperature at 530 °R (Rankine temperature) (21.1°C)). SG stands for the specific gravity (ratio of the density of a certain substance of a reference substance which in this case is air). This is then equal to the ratio of the molar mass of the gas flowing through the flowmeter and the molar mass of air. P_0 can therefore be formulated as the backpressure in the system added to the atmospheric pressure in the lab of 12.5 psi (86.2 kPa). Increased temperature means expansion of the gas which means less gas density. This means that the volumetric flow rate needs to be increased to supply the same drag force. Increased pressure means a higher gas density and less volumetric flow rate.

3

Methods and materials

This study consists of two main parts, the first involving the experimental work with a dual-bed chemical looping system and the second being experimental work with the bubbling fluidized bed reactor. The methods used during the study of these two parts are described here as well as the reasoning behind the choice of method. Since the project was carried out in the United States of America, customary units of the United States are often used in equipment design and all used equipment has been in U.S customary units. In order to simplify for the reader, measurements have to a large extent been converted to SI-units and if not, values in both units have been provided.

3.1 Dual-bed chemical looping system

The experimental work with the dual-bed chemical looping system is described here where the materials in the existing system as well as the setup of the experiments is provided.

3.1.1 Materials - Chemical Looping system

The system consists of two bubbling fluidized beds serving as a fuel reactor and an air reactor with a riser coming out from the top of the bed. The air reactor is connected to a cyclone which in turn is connected to a loop seal entering the fuel reactor. In the fuel reactor, there is a pipe in the middle through which particles is transported down to pass another loop seal and back to the air reactor.

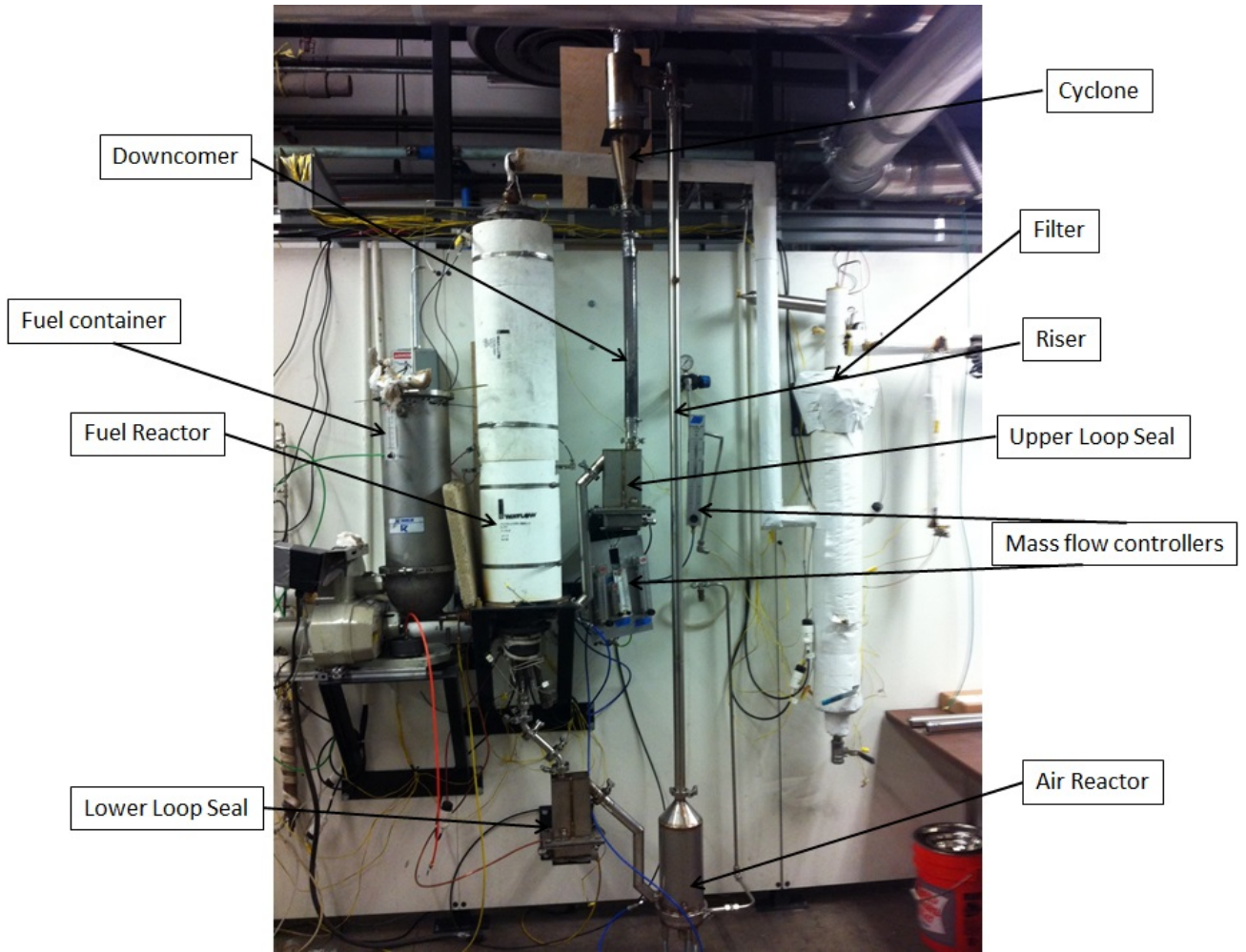


Figure 3.1: Outlook of the CLC system.

The solid fuel injection is at the bottom of the fuel reactor. The bed height in the fuel reactor is set to 254 mm (10") but can be changed since the pipe sticking up through the bed is moveable. The air reactor constitutes of a bubbling bed with a riser with a smaller diameter on top to enable particle circulation. This outline results in a bottom part with a bubbling bed and at least a fast bed in the riser. See dimensions of the cyclone, air- and fuel reactor in tables 3.1, 3.2 and 3.3. In connection between each of the metal parts, there are graphite plates to create a gas-tight seal when adding clamps to bring pieces together to prevent leaks.

Table 3.1: Dimensions of the cyclone.

	[mm]	[""]
OD	124	4.88
ID	111	4.38
Height	229	9
ID lower part	38.1	1.5

Table 3.2: Dimensions of the air reactor.

	Bubbling bed		Riser	
	[mm]	["]	[mm]	["]
OD	152	6	38.1	1.5
ID	147	5.78	34.8	1.37
Height	305	12	1970	77.5

Table 3.3: Dimensions of the fuel reactor.

	[mm]	["]
OD	114	4.5
ID	102	4
Height gasifier	1270	50
Height extra piece	88.9	3.5
Total FR height	1360	53.5
Bed height	254	10

All tubing connecting parts in the system has the size 38.1 mm (1.5") outer diameter (OD) and 34.8 mm (1.37") inner diameter (ID) apart from a few exceptions. One exception is the downcomer for the circulation rate measurement which has an inner diameter of 38.1 mm (1.5"). Two more exceptions are the connecting hoses to the pressure-dampening tank which has a 25.4 mm ID (1") and the tube between the fuel reactor and the lower loop seal which has 25.4 mm (1") OD and 22.1 mm (0.87") ID. The loop seals consist of square tubing that was used had a side length of 63.5 mm (2.5") on the outside and 57.2 mm (2.25") on the inside. The total loop seal size was in total 127 mm (5") by 63.5 mm (2.5") outside and 114 mm (4.5") by 57.2 mm (2.25") inside[73].

When the CLC system was constructed, two horizontal tube pieces were used and as a result of this, two extra air injectors had to be added to ensure that the bed particles travel in the right direction. The non-fluidized system has a maximum level of inventory of carrier material of 19 kg[41], but the system can take less because of bed expansion during fluidization. Previous testing shows that the system can operate successfully up to 14 kg of bed material. The air reactor plenum has 36 holes with a 1.59 mm diameter. The distributor plate makes sure that a sufficient pressure drop is achieved over the distributor plate and avoids the risk of uneven fluidization.

3.1.2 Materials - Bed material characteristics

During cold operation, aluminum oxide (alumina) is a frequently used bed material. The use of this substance comes from the prize as well as its fluidizing properties. The initial operation of the system has been done successfully with this bed material. Apart from this bed material, it was decided that silicon carbide was to be used because of its function as support material for future CLOU operation. The characteristics of the two bed materials that were used in the dual-bed chemical looping system are presented in table 3.4 and 3.5.

Table 3.4: Alumina density and size data where the distribution was obtained from previous sieving of the alumina.

Alumina	
Measured bed density [kg/m ³]	2080
Size distribution:	
%	Size [μm]
0	150
10	180
20	210
70	230
90	250
100	300

Table 3.5: Size and bed density of the used silicon carbide.

Silicon carbide	
Measured bed density [kg/m ³]	1519
Size [μm]	175

3.1.3 Measurements of circulation rate

There is a need to adapt several different parameters to obtain a working CLC system. This concerns finding suitable flow rates for the fluidizing agent into the following parts: AR, FR, upper lower loop seal and the horizontal tubes to prevent blockage. Apart from these, the amount of bed material that is being used can be changed as well as the kind of bed material used. Since the injectors into the horizontal tubes are only there to make the system function and were not varied during testing, the system can be seen to consist of four flow parameters. However, air flow through the fuel reactor and the loop seals was not varied during the experiments either. Suitable volume flows for these parts have been established whereas the air reactor has been proven to be able to vary the flow rate for this unit and be able to obtain variable circulation rates. The parameters that were to be varied were instead the air flow through the air reactor as well as the volume of

bed material for a selected bed material. For these chosen parameters a suitable operation window would be established which could be of great value for future tests.

The chosen flows for these locations had been assessed so operation could be carried out for a varied air flow to the air reactor. In order to characterize the result of the variation of this flow rate, the measured circulation rate and pressures would be used. Because of the fact that the circulation rate is the parameter that should be able to control depending on the oxygen demand in the fuel reactor, the assessment of possible settings to obtain certain circulation rates is important. It should be noted that it was difficult to assess if the loop seals are able to ensure that there are no leaks with gas passing through since the entire system was run with air during these tests. The status of the equipment from the start was that the CLC system had been mounted and installed so no major leaks were observed. One observation that was done was that all flows of fluidizing agents are interconnected, when changing one it was likely that another changes at the same time, therefore it was necessary to keep track of the other parameters when one of these was changed. The rate of circulation of the oxygen carriers was measured by removing the supply of fluidizing agent to the upper loop seal. This leads to an accumulation of solid material in the plastic tubing heading out on top from the loop seal up towards the cyclone in the downcomer and knowing the dimensions of the inner tube, it was possible to estimate the circulation rate by measuring the time required to fill up a certain volume of the tube.

It was observed that the height at which the circulation was measured for could affect the value on the recirculation rate. It seemed as if the rate at which the material was flowing down the downcomer decreased with the height of the bed material stuck in the downcomer already. Because of this possible impact of measurement on the process itself some intermediate times were taken to ensure that the rate was not decreasing for the last inch/inches measured. This was a trend which was observed for several measurements but no further investigation was done. When calculating the mean circulation rate, the means of the individual measured values on the circulation rate were collected (not as a sum of all individual runs and the time that was used). If the sum of all measurements would have been added up, the impact of measurements over a longer height could be higher than those over a shorter height. This should according to the author be avoided since measurements over long heights (and more quantities of bed material) could be more likely to have an intrinsic impact on the circulate while conducting the measurement.

After the first experimental matrix had been done running at 14-24 SCFM (396-680 SLPM) for the AR and keeping all the other rotameter settings constant, it was concluded that the actual flow rates differed quite substantially from the indicated flows in the rotameters. The settings to run at the correct actual flow rates were set up and a new experimental matrix was then prepared for the CLC system. The intended settings for the rotameter are indicated in table 3.7. Note that U.S customary units to indicate flows are used in this section to more clearly illustrate

3. Methods and materials

the issue with the settings of the used rotameter. A conversion table is provided here to simplify conversion to SI-units.

Table 3.6: Conversion table from U.S customary units for gas flow to SI units.

U.S customary unit	SI unit
1 SCFM = 60 SCFH (Standard Cubic Feet per Hour)	28.3 SLPM = 0.0283 m ³ /min (Standard Liters per Minute)

Table 3.7: Presentation of how the increased back pressure affected the wanted flow rates for the experimental matrix.

AR [True SCFM]	Back pressure [kPa]	Rotameter setting [SCFM]
14	34.5	12.8
16	41.4	14.3
18	62.1	15.1
20	75.8	15.8
22	103.4	16.1
24	110.3	17.2

It can be observed that the intended settings were close between some measurements points, especially for 20 and 22 true SCFM. One problem during the execution of the experimental matrix was that the float in the rotameter was fluctuating significantly for increasing flow rates. Because of the fact that the back pressure increased faster than the indicated flow rate on the rotameter, the settings to achieve an interval of actual flow rates every 2 ACFM from 14 true SCFM to 24 true SCFM ended up much closer than the previous distance of 2 SCFM. This meant that in order to differentiate between the different settings, something should be done to either dampen the fluctuations of the cone in the rotameter or a simplification to obtain reliable settings.

Several attempts were tried using a t-crossing to a tank and an addition of a needle valve after the back pressure gage but the solution that was used in the end was to install a tank which all of the flow would have to pass through. This solution is illustrated in figure 3.2.

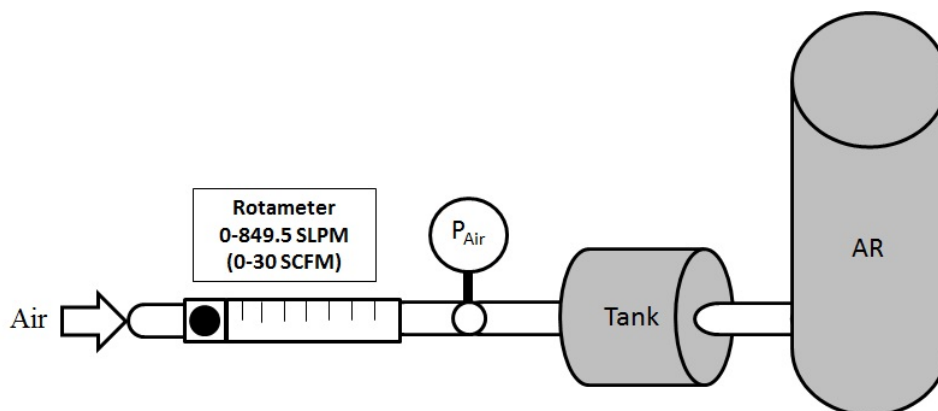


Figure 3.2: Schematic of the solution using the through-flowing of a tank to dampen the fluctuations in the rotameter.

The result of this installation was that the fluctuations decreased slightly, even though there were still significant fluctuations in the range 16-18 SCFM on the rotameter. In addition to the addition of the tank, another procedure was used when establishing the correct settings for the rotameter where the back pressure in small steps and for each new step the true flow rate was calculated using the observed value on the rotameter and equation 2.18. When operating the system, it was seen that some start-up time of a couple of minutes was needed before the found settings for the rotameter and the back pressure (or close to the found settings) were observed. It is unclear what this originated from.

When changing bed materials, the difference in densities should be considered to operate the system with the same volumetric load of bed mass. The bed density of the used alumina particles and the silicon carbide particles were measured by filling up a beaker with 1000 ml of particles and measuring the weight. This results in densities of 2.08 kg AlO/1000 ml and 1.519 kg SiC/1000 ml. This results in a density quotient of 0.73. Therefore all the amounts of silicon carbide to be inserted into the system were calculated by multiplying the quantities used of alumina and this quotient.

This resulted in a matrix that can be used for the experiments. It is important to observe that the new bed material may have other fluidization properties (apart from density) that may change the behaviour of the system even though the bed volume is the same. This can for example be how sticky they are to each other. This could therefore affect for example the dynamics of the air supply to each part of the system. Therefore, the established settings for the rotameter considering the back pressure had to be checked so the true flows in SLPM were used.

In this case the temperature in the room and the system was at room temperature or very close to it which then corresponded quite well with standard conditions. However, for a higher temperature which is the case for warm/hot operation of the

CLC system causes change in the density of the gases. In order to maintain the same velocity of the fluidizing gas in the system for the hot condition as well as for the cold condition the volumetric flow rate has to be constant and this means that the mass flow rate has to change. How it should be changed depends on the of the gases used as well as the temperature range at which the system is operated. Since this study did not continue to run for hot conditions, this was not needed to be considered at this stage.

In order to measure the circulation rate during hot conditions the plastic tube as a downcomer cannot be used. Pressure-induced Measurement of Circulation (PIMC) is a technique that can be used for measurements during warm/hot conditions. In order to use this method, it was decided that a stainless steel tube with 8-9 swage-lock fittings every 2 inches and connect these to pressure transducers. The installed transducers would then react when a certain part of the downcomer was filled with bed particles by observing an increase in pressure when there is material blocking the entrance. This change in pressure would trigger a light which would make it possible to make the same measurements as before based on time between lights are switched on and the volume of the downcomer.

3.1.4 Pressure measurements

In order to locate suitable points of operation and be able to understand the system better, pressure measurements were prepared for the lab-scale CLC-system. The locations for pressure measurements were determined by the locations used in the previous simulations of the system done by PhD student Matthew Hamilton using Barracuda. The data from the simulation is provided in section A.1.1.

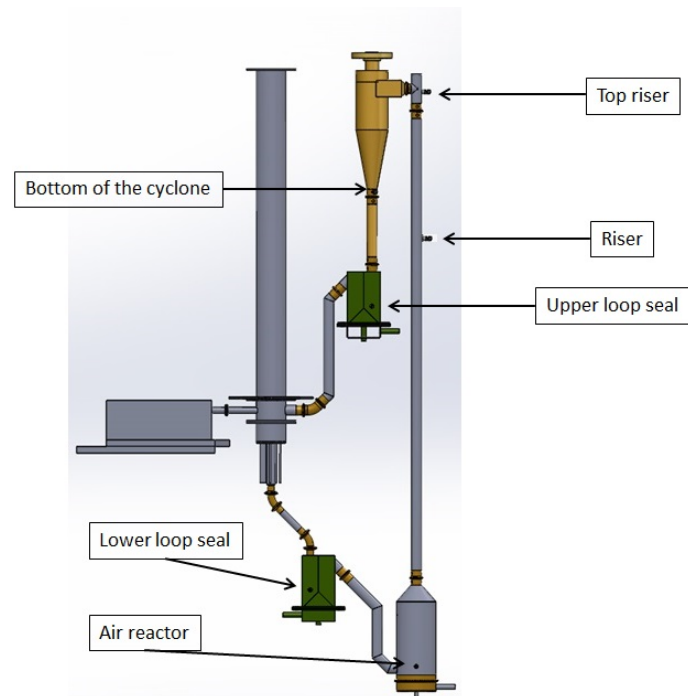


Figure 3.3: Locations of the pressure measurement in the CLC-system.

This result in six places where holes were drilled, a swagelock-connection was made with a sintered metal piece on a quarter inch tube. The idea behind this solution came up when working with the bubbling fluidized bed reactor where the measurement tube could have a porous end to the tube which allowed a small amount of gas to pass through but no bed particles (see section 3.2). The gas passing through would be enough to connect to a pressure gage to get a reading. The connected tube on the outside can be seen in figure 3.4.



Figure 3.4: Connecting tubing added to the six pressure measurement points of the system.

The stainless steel quarter inch tube and the sintered metal piece was welded at the top of the tube should also both be able to handle the high temperatures that will be reached during hot operation later on. The tubes were made with a length that made it possible to add copper wire around it to cool it down to the point where the pressure gage was connected to the tube. At this point it was chosen that plastic tubing would be added to the end of the tubes along with clamps to connect one gage to each measurement point one at a time for each run. It was decided that the tube should initially in to the center of all the chosen locations in the CLC system.

If the downcomer plastic tube would be replaced by a stainless steel tube the current configuration the system could be able to run during warm conditions (300-500°C) but probably not during hot conditions (900-1100°C). One problem that occurred while running the system at the advised flow rates for a couple of hours in total, a sandblasting effect was seen on the tubes sticking into the riser as bed particles were coming out through the tubing from the system when the pressure was monitored (see figure 3.5)



Figure 3.5: Wear observed on sintered metal piece and the stainless steel tube.

The riser is the part of the system where the velocity of the bed particles is the highest but since the position was based on where the pressure should be measured, there would be a need to install a new piece at a place close to the previous one (if not the exact same place). One alternative would be to have the tube sticking less into the tube but since the hole occurred just before the end of the end, it would be difficult to avoid having the same problem occurring again. In addition, it appeared as if the wear from bed particles was rather well distributed across the piece located inside the tube which means that the actual position of the top part of the tube would have to be outside of the inner diameter. This was the solution that was chosen, but it was seen as interesting also to investigate the impact of having the pressure measurement tube in the center of the tube versus having it located at the wall. The effect of having a flow passing by the tube could then be evaluated. This was done by placing the end of the pressure measurement tube at four locations ranging from the center of the riser tube to just outside of the inner diameter in the drilled fitting to the tube. The system was then run at three different flow rates all within the intended range of flows. This was done for both positions at the riser (see figure 3.8 and 3.9)

Table 3.8: Pressure measurements at varying positions from outside the inner tube diameter (-0.9 cm) to the center (1.8 cm) at the position at the riser.

396 SLPM		510 SLPM		623 SLPM	
Position[cm]	P [kPa]	Position[cm]	P [kPa]	Position[cm]	P [kPa]
1.8	0.69	1.8	1.62	1.8	2.68
0.9	0.69	0.9	1.74	0.9	2.74
0.0	0.69	0.0	1.74	0.0	2.74
-0.9	0.69	-0.9	1.74	-0.9	2.74

Table 3.9: Pressure measurements for varying from positions outside the inner tube diameter (-0.9 cm) to the center (1.8 cm) at the position at the top of the riser.

396 SLPM		510 SLPM		623 SLPM	
Position[cm]	P [kPa]	Position[cm]	P [kPa]	Position[cm]	P [kPa]
1.8	0.69	1.8	1.62	1.8	2.12
0.9	0.69	0.9	1.68	0.9	2.24
0.0	0.69	0.0	1.74	0.0	2.37
-0.9	0.69	-0.9	1.74	-0.9	2.37

The analysis indicates that the difference where the tube is placed does not have a significant impact on the observed pressure. A slightly smaller pressure was read for higher flow rates at both locations in the riser inside the tube compared to the wall and just outside the inner tube diameter. This indicates that having a high velocity flow of air and particles past the pressure measurement tube end induce a slightly lower pressure. The difference was considered to have a minor impact on the final result of the pressure measurement. Based on this test it was decided that the end of the tube should be put outside the inner diameter of the tube for all pressure measurements.

When running the initial testing of the CLC system the flows were larger than intended. Once it was determined that the actual flows were significantly higher than the flows displayed on the flowmeter (see further information in section 3.1.3). The new settings for the rotameters were determined and it was then clear that the flows for the upcoming tests were distinctively smaller which meant less risk of wear of the same magnitude of the equipment. After setting up the matrix to achieve the correct flows in true SCFM (SLPM), the pressures were measured using magnahelic pressure gages. The used gages showed significantly different values and after consulting the simulated values for the system were consulted for the first time to get an idea of the range that could be expected for the measurements. The values can be observed in table A.1.

In order to confirm that the magnahelic pressure is reading a correct value, a test is established using plastic tubing and the principle of a manometer.

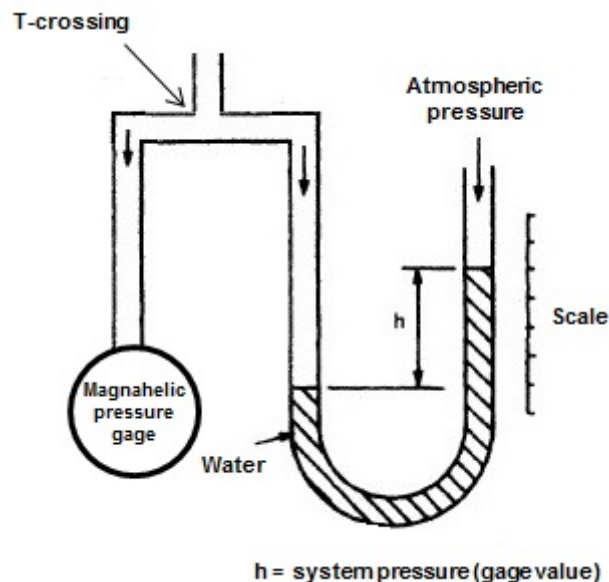


Figure 3.6: Schematic of setup for the calibration of the pressure gages.

The right side of the T-crossing was filled with water. Air was then blown through the plastic tubing with a t-crossing at the top of the picture and then the system was capped. The height of the water column formed on the right side was then observed and compared with the pressure reading on the magnahelic gage. The gages in the ranges from 0-60 inches of water (0-15 kPa) that were tried were consistently showing smaller values than what was seen by the water column. Some of the gages showed a similar deviation which indicated that something might be wrong with the execution. The source of the error was found which was that the plugging of the lower port of the magnahelic gage most likely caused a pressure increase on that side compared to atmospheric pressure. That in that case lead to that the pressure displayed by the magnahelic gage was in fact the pressure at the high end subtracted with the pressure at the lower side which was higher than the atmospheric pressure. This led to the attempt to expose the lower side of the magnahelic gage to the atmosphere and all but two gages then showed correct values and those gages were removed from the testing.

3.1.5 Experimental conditions

The experimental matrix that was decided to be used for the experiments can be seen in table 3.10.

Table 3.10: Exerimental matrix with all indicated bed material use as well as air flows in each unit in the chemical looping system.

Bed particles	Alumina	Alumina	Alumina	Alumina	SiC	SiC	SiC	SiC
Bed mass [kg]	12.5	13	13.5	14	9.1	9.5	9.85	10.2
Bed volume [liter]	6.01	6.25	6.49	6.73	6.01	6.25	6.49	6.73
AR flow rate [SLPM]	396-680 SLPM				396-680 SLPM			
FR flow rate [SLPM]	30.7							
ULS flow rate [SLPM]	13.7							
LLS flow rate [SLPM]	13.7							
FR side [SLPM]	1.42							
AR side [SLPM]	1.42							

The air flows marked for the sides are to avoid the mentioned problem with accumulation of build-up of bed particles in the horizontal tubes. In addition to these rotameter settings the purge air supply from the solid fuel feeder (which here is empty) should have a small air flow into the fuel reactor to avoid the risk of material going into that tank during operation.

3.2 Bubbling fluidized bed reactor

3.2.1 Materials - Fluidized bed

The simulation of gas plume formation is done on a separate 6.5 inch (16.52 cm) diameter acrylic tube system which is suitable for cold conditions connected to an analyzer to measure the concentration of CO₂ in the bubbling fluidized bed reactor. The acrylic vessel bed is 53" (134.6 cm) tall in total with an inner diameter of 6.5" (16.5 cm). The distributor plate is a construction of two 0.125" (3.2 mm) thick plates with two layers of high-density fabric sandwiched in between these plates. The circular plate consists of 42 holes which are evenly spaced in three rings. The ring closest to the bed center has 8 holes, all on a distance of 1" (2.54 cm) from the center. The following have distances of 1.88" (47 mm) and 2.75" (70 mm) from the center where a 0.88" (22 mm) hole is connected to a pipe and a ball valve for solids removal. A diagram with the dimensions of the distributor plate is provided in figure 3.7. For a more complete picture of the system, see figure 3.8 and 3.12.

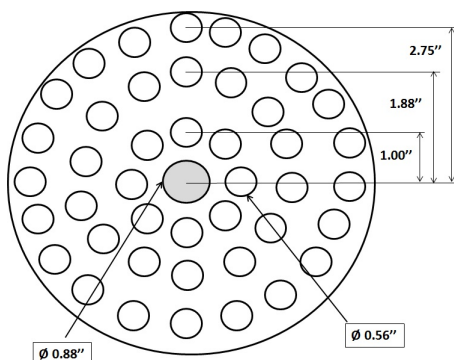


Figure 3.7: Schematic of the distributor plate.

Compressed air was used as fluidizing agent. The bed can be drained by opening a valve which lets the bed out through the bottom center part of the bed. The existing fluidized bed was cleaned up on both in- and outside to ensure good visibility through the glass as well as to remove particles that may contaminate the experiments. In order to connect the difference acrylic tube-pieces, tape was used as well as silicone once more problematic leaks were observed. The acrylic tubing can be dismantled at three places, 1.5" (3.81 cm), 13" (33 cm) and 25.5" (64.8 cm).

3.2.2 Materials - Bed material characteristics

The bed particles used for the experiments should be easily fluidized to create a bubbling fluidized bed. The three bed materials that were bought were all in the range or close to the range of the classification for Geldart particles of type B which are known to fluidize well. A more exact description of the bed particles is provided in table 3.11.

Table 3.11: Bed material for the fluidized bed system.

Soda-lime silica glass	
Density [kg/m ³]	2500
Crush resistance [psi]	14000 - 36000
Particles are 90 % round	
Size:	Size (μm)
Small	120 - 180
Medium-sized	250 - 350
Large	500 - 710

The bed material are in the rest of the report described as small, medium or large along with the size range.

3.2.3 Preparation of experiments

The first part of this testing involves setting up the system to be able to inject gaseous CO₂ into a bed, use air to obtain the sought fluidizing conditions and detect the CO₂ at different positions. In the existing system, there are already several threaded holes drilled out with caps on them spread all over the bed which in theory all were possible to use for injection as well as sampling. Most of these holes are smaller threaded holes in the size 1/8 of an inch while a few of them are a quarter of an inch in size. Considering the increased risk of leaks with more holes and caps and the times required to make new holes, the intention was to use as many of these holes as possible. Since the goal is to map the concentration of CO₂ across the whole bed, it is essential to make sure possible measurement points are well spread over the acrylic container.

It was decided that a solution of using 3 layers with 4 holes available for measurements in each layer would be used with one possible injection point under each measurement layer. This would allow for concentration measurements across the entire volume. One could argue that only two holes are needed in each layer and that the sampling tube can reach to the other side of the bed, but it was decided that having a tube crossing the whole bed would be avoided to avoid unnecessary impact on the fluidization of the bed and simplify the installation process. More holes could have been added on other angles than with an interval of 90 degrees but this was omitted at this step. The layer and injection points were spread over the bed using the general guideline that the bed should not be higher than 3 times the inner diameter. All layers should be within this height of the container and distance between these layers were decided so they were spread over the entire bed height and the possible use of old threaded holes is maximized. This means that in addition to the existing holes, new holes were drilled to create a system of 3 layers with 4 holes for measurement in each layer.

It was vital to take into consideration that since the initial testing is done with one bed material only, the bed height during fluidization was likely to be different when using other bed materials. Therefore, the used bed height was chosen slightly below the measurement points of the third layer so the measurement points during operation would be at the top of the expanded bed. It is also important to note that the inlet gas is pressurized and therefore the actual flow rate through the bed differs from the one displayed at the inlet (same as for the CLC system). When it came to piping and fittings, the NPT-standard (National Pipe thread Taper) was used. When adding new threaded holes it was important to consider that the acrylic material is brittle which means that drilling has to be done in smaller steps and threading was done with soap as lubrication of the material. Initially, the holes for the sampling tube (for the gas measurements) were of 1/8 of an inch in size while the holes for the injection were designed to be one quarter (1/4) of an inch. This was a result of the existing quarter inch hole at the bottom as well as a suitable sampling tube of the size 1/8 of an inch.

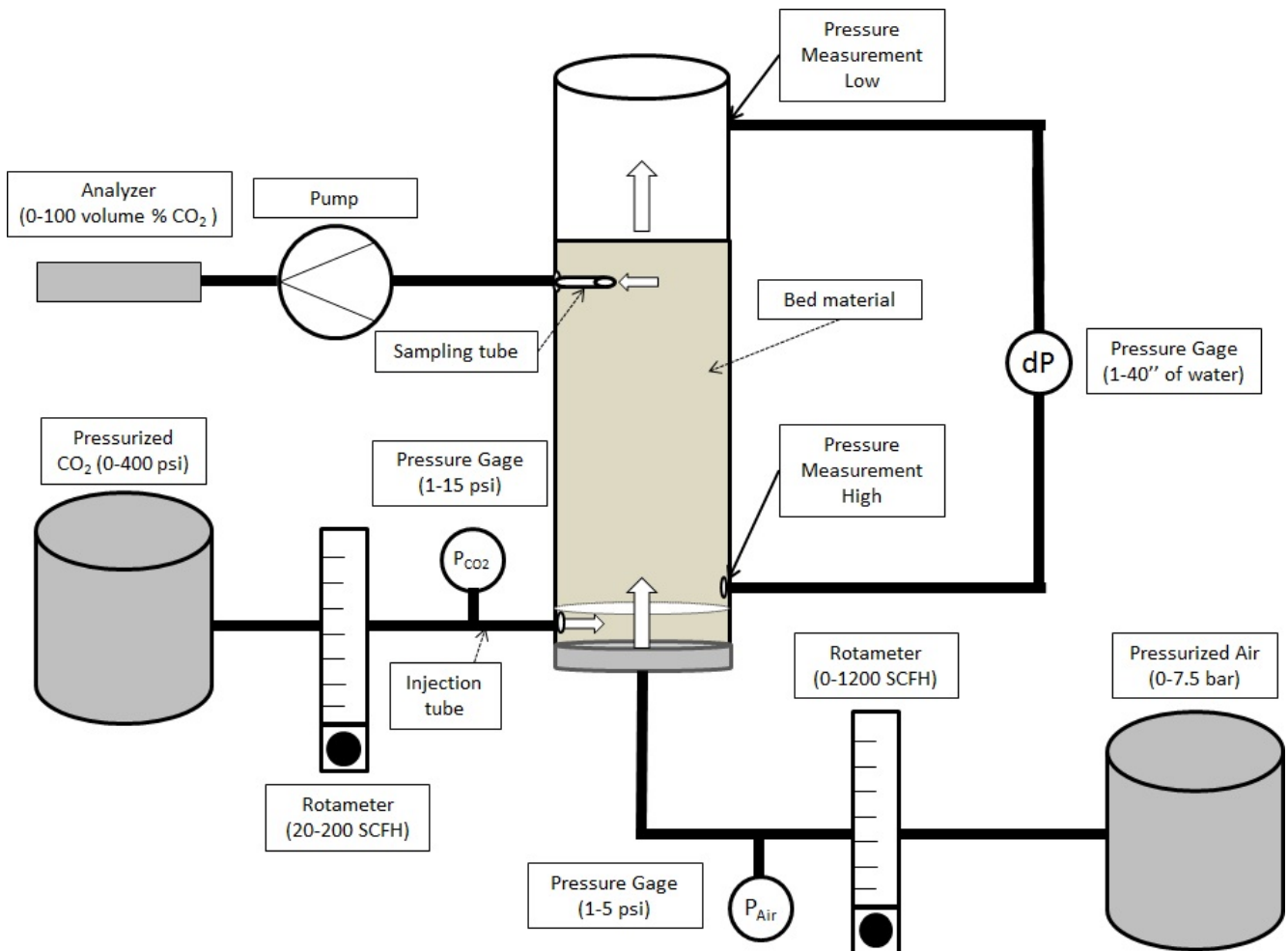


Figure 3.8: Schematic of the setup of the fluidized bed system.

One problem that had to be addressed early on was the risk of bed particles escaping

the bed and bed particles entering the outlet to the CAI-analyzer would be especially problematic. When conducting the preliminary testing, glass beads of the size 105 μm was used. This was slightly smaller than the intended bed particles for the actual experiments. A cloth was added to the tube sticking into the bed. The first cloth that was used on the existing bed material of glass spheres was not fine enough and the particles went through the cloth. A finer material was found which stopped the particles from passing through. In order to measure at different radial positions in the bed, nylon ferrules were used to connect to the fitting on the bed side to ensure that its position could be changed and it had to be possible to pull the end at the tube through the fitting.

In order to analyze the gas sample, an CAI ZRE Gas analyzer is used. The analyzer is able to indicate the percentage of CO_2 , CO , O_2 and CH_4 . The performance of the analyzer is tested by injecting CO_2 from tube to observe if the measured amount was close to 100 % which it was (102 %). It should be noted that the analyzer has an ideal range for its operation indicated by a metal ball in a glass tube which is vital to reach to get reliable data. Polyethylene piping was used to simplify the setup of the system and since no corrosive gases etc. would be used. Since the analyzer does not have an internal pump to suck out sample from the bed, an external pump had to be connected to the system. The pump could have been placed either before or after the analyzer, but because of the apparent risk of bed particles entering the sampling tube, it was decided that the pump with an internal filter would be placed before the analyzer.

Apart from this safety measurement, an additional filter was installed before the pump to decrease the risk of overloading the internal filter of the pump. The new filter seemed to cause some additional delay in the measurements, but this was still considered as the best option since the operation of the pump and the analyzer is essential to be able to run all the experiments. The delay in the system was tested by observing the time before the increase of concentration of CO_2 was observed when starting to supply CO_2 . This was tried without a fluidization agent.

A first measurement was done by injecting CO_2 and no fluidizing agent gives 3.3% at the top of the bed and one possible reason of this small amount of CO_2 can be caused by presence of air in the system since a substantial amount of oxygen is measured (around 14 %). In the bed, it is likely that air is present however, in the case where there is no fluidization and a constant supply of CO_2 , the air is likely to move upward while CO_2 should accumulate at the bottom of the bed since CO_2 has a higher density than air (1.98 kg/m^3 compared to 1.29 kg/m^3).

Possible leaks into the system were difficult to observe which made this part of the experimental work more complicated. Air could enter through tubing heading into the bed as well as tubing from the bed to the analyzer. In order to decrease this risk, bolts were tightened one by one and by observing the difference in the measured percentage of CO_2 it was possible to observe if a possible leak was found. When using 1/8 of an inch tubing it seemed as if the tube did not allow enough gas to pass through and therefore quarter inch tubings were tested. One solution

that was evaluated was a fine rolled up film which was put at the inside end of a quarter inch tube which can be seen in figure 3.9. The film stayed at its place even during pump operation and was therefore tested. This solution caused after a few minutes operation a drop in the CO_2 -concentration which was caused by bed particles entering the sampling tube. Some sand entered the pump which its filter had to take care of. This resulted in that this solution was removed from further testing.



Figure 3.9: Rolled film inside tubing.

After this test, several more solutions were tested and there were three which all gave clearly higher readings of CO_2 than the previous solutions and did not cause problems with leaks of bed material out from the system. These three solutions are presented in figure 3.10.

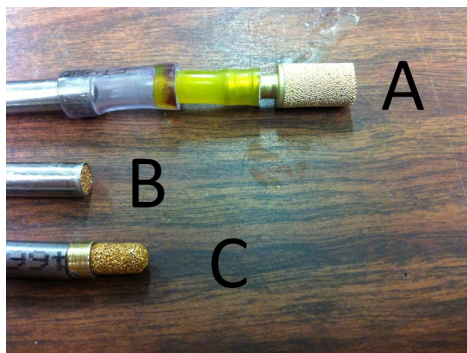


Figure 3.10: Comparison of the three quarter inch sampling tubes.

The first sampling tube (A) has two plastic tubes and an atomizer at the top end of the tube. It is important to note with this solution that both the plastic tubing and the atomizer had outer diameters that were bigger than the tube going through the fitting. The metal tube would be possible to remove through the fitting and the end piece with two plastic tubes and the atomizer could be removed from the inside after emptying the bed. A problem with this sampling tube was that it was not possible to measure close to the wall by the metal tube because of the additional plastic tubes.

The second alternative (B) was to solder a sintered metal disk to it with a smaller diameter than the tube to the end of a tube. By creating a larger inner diameter at the end of the tube it was possible to place the atomizer at the end of the tube without any welding. This solution had an advantage in relation to solution A since it was possible to measure at the wall and no need to reach into the bed after measurements to remove the end part after each measurement.

When testing sampling tube A and B it was observed that the concentration of CO_2 decreased after conducting measurements after a few minutes time. This indicated that there was a resistance for the gas to enter the sampling tube (which increases with time). One explanation would then be that the bed particles adhere to the end of the tube. A test was done above the bed and the measured concentrations for the two sampling tubes were then comparable. This indicated that bed particles seemed to adhere to the surface and make it difficult for the measurement to function properly and therefore the solution with the plastic tubes was seen as a better choice of a sampling tube. When investigating the reason for that A and B differed, it was observed that the sampled gas had less area to flow through in case B compared to A. Sampling tube B has only the cross sectional area of the inner tube. The calculated ratio in these estimated active areas for gas sampling was 16.6.

Based on these results the intended sampling tube would have a larger area which the gas could flow through while still be able to pull through the fitting. A muffler of a suitable size was then added to the end of a tube and the middle part had to be polished with a file to the same dimension of the tube (see C in figure 3.10). When comparing the active surface area of solution A and C, the estimated ratio was 2.45 which was significantly smaller than the ratio between A and B. It is important to note that the inner tube area plays an important role as well for the gas that can flow through. However, In this case all three tubes have the same inner area for the gas to flow through apart from the double plastic tubes solution which has one part that has one part with a slightly larger inner surface area.

Solution B was now compared with C for further testing. In the initial tests that were run to try out with tube B and tube C using 236 SLPM of air and 23.6 SLPM of CO_2 , the measured concentration with the tube C was almost identical to the one measured with the plastic tube B (0.38 compared to 0.35 vol-%). However a difference that could be seen was that the values measured by the plastic tube varied more than the values for the sintered sampling tube. This varied no more than 0.1 percentage point [0.3,0.4] while the plastic tube had a larger span [0.2,0.7]. There was a more significant difference between the sampling tubes at higher fluidization velocities where the values for the plastic tube were higher. The trend with a larger variation in the observed values for the plastic was seen also for these cases. Since it was difficult to decide which values on the average concentration are the most reliable for the two sampling tubes, the basics for the choice of the sampling tube was based on other factors.

A problem that was observed for both sampling tubes was the difficulty to measure the concentration at small injection flows of CO_2 since the value shown by the analyzer then becomes zero. The plastic tube has two additional drawbacks since it is not possible to measure by the wall at the side it is introduced and the values tend to fluctuate more for this sampling tube. One potential drawback that could be seen for tube C was the risk that it would be difficult to distinguish the difference between two measurement points since the largest measured concentrations of CO_2 were closer to the smaller values compared to the case of the plastic tube. However, since tube C had less variation in its measured values, this risk decreased. Thanks to less fluctuation in the concentration values and the simplicity of use, tube C was chosen for the experimental work.

One major problem during the setup of the system was leaks, especially in the bottom acrylic piece close to the threaded injection hole. Use of silicone made it possible to cover these holes. For a more extensive crack in the bottom piece, glue made specifically for acrylic was used to close this gap.



Figure 3.11: Observed crack at the bottom part of the acrylic vessel.

A magnahelic pressure gauge was added (up to 40 inches of water(9.96 kPa)) to measure differential pressure over the bed. The high pressure side was connected at two places where it was already installed. This was below the distributor plate and the low pressure side at the top of the fluidized bed. This resulted in values in the range at hand; however, the indicator was not dynamic to change from one point to the other (rather sticky). The pressure gauge fluctuated significantly during operation at higher flows which meant that it would be difficult to observe when the pressure drop over the bed would no longer increase but instead obtained a constant value. Therefore a new pressure gauge (in the same range) was installed.

Since the differential pressure now included the pressure drop over the distribution plate (which may vary with the flow of fluidizing agent), an alternative measurement point above the distribution plate was investigated. This led to the introduction

3. Methods and materials

of another hole a few centimeters above the bottom piece of the bed which was considered too short to drill through without risking getting cracks in the acrylic.



Figure 3.12: Tubing connected to the fluidized bed system.

To supply the CO_2 , a rotameter was needed to control the actual flow flowing into the bed. When flow was run through the line then, for the same pressure (200 kPa), a flow of 5 SCFM was observed. This indicates that the problem now was located between the rotameter and the bed itself. The most probable explanation that was seen was that the small space the gas is allowed to flow through limits the transportation of gas. Then, when this amount of gas is pushed through this tube, it has a substantial amount of bed material to pass through. One factor that could make the difference was the size of the particles. For the new bed material, the smallest bed particles were larger than these particles but the difference is not significant. This lead to the conclusion that in order to use the existing tubing, the range of the flow of CO_2 into the bed had to be decreased. A rotameter that was considered suitable for to supply the CO_2 range of 20-200 SCFH (9.44-94.4 SLPM). Another alternative would have been to use wider tubes but this would require a reconstruction of the system which was not advised. In addition to the rotameter, a pressure gauge was needed to calculate the actual flow considering non-standard conditions. A pressure gauge in the range 1-15 psi (6.9-103.4 kPa) was installed.

Another problem with the injection tube was the risk of bending of the tube on the fitting because of the heavy pressure gage attached to the injection tube. The threads did easily get beat up and this resulted in changing this piece a few times.

It is also important to note that a substantial amount of static charges are formed when using dielectric materials[74]. An accumulation of these charges can present a hazard for anyone in the lab but even if not directly by getting in contact with the equipment it could be indirectly by causing movement which may cause damage. The risk is in general higher for larger units but it still not to be neglected. A wire was therefore connected from the fluidized bed to a water pipe in the lab. These static charges would also affect the measurements since the bed particles tend to stick to surfaces such as the inner wall of the fluidized bed which might deteriorate visibility. These particles may also stick to pieces instead of following the surrounding flow of bed material.

The forces that were being put on the acrylic in the horizontal direction were not to be neglected either. To support the bed and to avoid having pieces falling off from the top, two threaded rods were fastened in the top metal plate of the fluidized bed.

3.2.4 Initial testing procedure

After the setup of the fluidized bed, 8 initially interesting parameters to work with were identified for the fluidized bed system:

1. Fluidizing agent flow rate

This parameter is vital when it comes to understand the fluidization of the bed during fuel introduction. Control of this flow rate is needed to ensure that the suitable bed conditions are obtained. For these experiments the velocity of the fluidizing agent has to be at least the minimal fluidization velocity to obtain a bubbling bed which therefore is important to consider when choosing the range for this parameter. It is important to note that u_{mf} is different for different bed materials and even for the same kind of bed material different sizes of bed material will alter this velocity. For smaller particles u_{mf} is smaller which means that the largest particles was be the limiting factor (can be derived from equation 2.10) to establish the highest suitable value for the range of the fluidizing agent flow rate (see parameter 6 for explanation).

2. Flow rate of injected CO₂

The rate at which the fuel is introduced is likely to have an impact on the circulation of the fuel in the bed. By injecting at a higher flow rate in a fixed bed, the CO₂ is expected to enter further into the center. Apart from the specific circulation of CO₂, it also affects the overall fluidization of the bed. The upper range was decided to be around 30 % of the flow of the fluidizing agent. This was based on that there is normally more air used to fluidize the bed than fuel injected into the bed. It is important to note that the pressure at this point is most likely not standard pressure (1 atmosphere) and it must therefore be measured to calculate the actual gas flow.

3. Radial position of CO₂-injection

The position of the injection was considered to affect the circulation of CO₂

in the bed and it could be possible to change the position in relation to the wall where the gas is injected. The position of this inlet was adjusted with a tube that was possible to slide in and out of the side wall.

4. Vertical position of CO₂-injection

Apart from the radial position, the injection point in the axial direction in was also seen as an interesting parameter to investigate. The injection points could then be spread out all over the bed.

5. Direction of CO₂-injection

In addition to the positioning of the injection, the direction in which the CO₂ is introduced was also a parameter that was considered to have an impact of the concentration of the CO₂ in the bed. A hole was drilled about 2 centimeters from the end of the tube with the same diameter as the inner diameter of the tube (3 mm) which then could be directed in the intended direction. The hole that was not in use was covered with tape during operation. Since the hole directing the flow forward it at a different position compared to the drilled hole on the side, the position of the drilled hole was moved to the place where the forward hole was for those measurements.

6. Bed particle size

The fluidization of the bed is closely related to the bed material properties and another potential parameter to change is the size of this bed material. The three different sizes of investigated bed materials are presented in table 3.11. In order to simplify an expression to describe the simplicity to fluidize the bed particles, the ratio between the drag force and the gravitational force can be used. This can be expressed as a ratio of the cross sectional area and the mass of the bed particle. The drag force is then proportional to the projected area which in turn is proportional to the cross sectional area $4\pi r^2$. The gravitational force can be written as the density times the volume of a sphere (assume 100 % spherical particles) and this ratio is therefore proportional to $1/r$. It is therefore easier to fluidize smaller particles which results in a higher ratio.

7. Radial and angular sampling point

The radial position at which the sample is extracted to the analyzer could also be varied. The sampling points would then be distributed from the wall to the other side of the bed. Measurements could also be done for different angles in relation to the injection point. Examples of angles that could be interesting to study was to the right side of the injection (at 90 degrees) and to the left side (270 degrees).

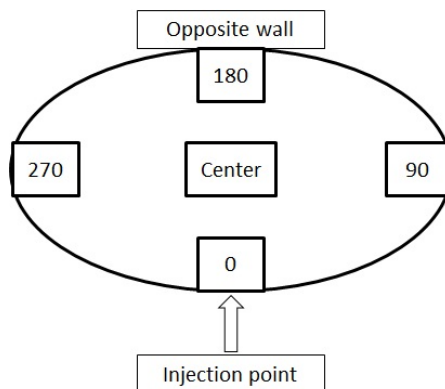


Figure 3.13: Representation of the positions in each layer in relation to the injection point.

8. Vertical sampling point

The concentration of CO_2 was expected to vary along the bed height and therefore it was considered as interesting to measure the concentration at different heights along the bed.

An investigation of all these parameters independently of each other (each parameter having three levels of measurement) would mean $3^8 = 6561$ different measurements which was not possible to conduct within the timeframe of this project. Therefore, to decrease the number of measurements needed, a baseline measurement was determined which all other measurements can be related to. One parameter was adjusted at a time within an intended range to identify the impact on the measured concentration of CO_2 for these parameters. For all these parameters, three values are spread over the range that was deemed interesting for the experiment with a baseline condition somewhere in the middle of these ranges. Note that the radial and angular sampling point was put into two separate parameters in this initial experiment. An additional note is that the lower and higher limit was just used as a way to define the range and have a base condition (see table 3.12).

It should be noted that the bed height was another parameter that could have been included in the initial testing but was removed due to the fact that other parameters seemed of more value for the purpose of this study. For all measurements, the bed heights were kept constant. The suitable bed height being used for the experiments were determined using a general guideline to have a bed height of 3 times the diameter of the bed. In this case this meant around 15 inches (38.1 cm). For a too tall bed, there is a substantial risk of slugging.

The testing was to be done with glass beads in the range between 0.15 mm and 0.605 mm (see more exact details on this material in table 3.11). The choice of using glass beads was based on the good fluidization properties and the fact that it does not scratch the acrylic tube as much as for example ilmenite and aluminum oxides[41]. The bed material that was acquired for the experimental

planning proved to fluidize much better than the bed material used during the setup of the system which showed extensive slugging during operation.

A testing procedure was established where the supply of CO₂ would be followed by a supply of fluidizing agent. It is essential to initialize in the following order since a movement of bed particles without a supply of CO₂ resulted in bed particles flowing into the CO₂ injection tube. During operation a possible adjustment of the pump could then be made to ensure that a gas flow of the suitable range it supplied to the analyzer. Connections in the system were checked for possible leaks. The measurement value was then collected with a time interval of 5 seconds after 2 minutes of time to await steady state. In the cases where the concentration was constantly increasing or decreasing during the time of measurement, the measurements were redone. This was done for the initial testing as well as for the final matrix.

Since the initial tests aimed for screening of the parameters would have a base case keeping all parameters close to the middle of their operation range, the medium-sized bed material would be used for these tests. The first test that was to be done was to get an indication on the minimal fluidization velocity. This would give an indication of a suitable range for the flow of the fluidization agent for the upcoming measurements as well. Since the minimum fluidization should occur at different flows for each bed material, the theoretical flow could be calculated to make sure that the available testing equipment could supply the required flows of air. By using the equation 2.10 and values on the empirical constants C_1 and C_2 it was possible to estimate the MFV for each of the bed materials. The other values that were used for the theoretical calculations are reported in table 3.11 and in section A.2.1. All Experimental tests are run at 70 °F (21.1 °C) for the fluidized bed system and 12.5 psi (86.2 kPa) was the estimated atmospheric pressure used for the lab located in Salt Lake City, Utah.

In order to find u_{mf} (and the setting for the volumetric flows in terms of MFV) for the initial tests, it is possible to observe and visually get an approximation when the minimum fluidization velocity has been reached. This observation can then be mainly based on a bed expansion, bubbles at the top of the bed and a circulation pattern of solid material, best seen by looking at solid particles falling down by the inner surface of the tube. Apart from the visualization, the possibility to observe when this velocity is reached was investigated by an installation of a differential pressure gauge. By using this gauge, the intention was to get an indication of the pressure drop over the fluidized bed (see figure 2.6). In the current system, a pressure gauge was already installed with a measurement point just below the distribution plate in the tube of the incoming fluidizing agent. Above the bed, another pressure measurement point could be chosen and a tube could then be connected to the differential pressure gauge. This was the practically simple solution but mark well that with this setup, the measured differential pressure would also include the pressure drop over the distribution plate. The chosen approach was to install another pressure

measurement point slightly above the distribution plate. Due to the fragility of the thin acrylic tube piece at the bottom, it was decided a hole should be prepared 1.7 cm above the bottom piece of acrylic tubing, 4.5 cm above the bottom of the vessel.



Figure 3.14: End of the tube connected to the low pressure side of the differential pressure gage.

The drawbacks with this method are the unknown impact of the cloth on the pressure measurement as well as the fact that the measurement a few centimeters above the very bottom of the bed which may have an impact on the result.

Another solution that could have been used to maintain the existing setup with the pressure gauge and avoid the installation of a new bead-safe tube into the bed, an approximation of the pressure drop over the distribution plate could have been determined. This could have been done by using an empty bed and use the intended range of flows of the fluidizing agent and record the pressure drops over the bed. Following these experiments, planned experiments could have been done and in order to observe the correct pressure drop over the bed, the obtained values could be subtracted by the values of the reference measurement with no bed material. Even though the reference measurement would be enough to run once, it would not be easy to directly interpret the read data of the pressure drop. Since the intention was to be able to observe when the pressure drop was stabilized, this method would probably not be the most effective. The measurement of the pressure drop would mostly serve to ensure that this point had been reached. The precise value and how it fluctuates for higher values was not of interest. For these reasons, this solution would be also mean additional work during the experiments. A solution to dampen observed fluctuation in the used differential pressure gages was to install pressure snubbers on both tubes entering the gages.

The examination of u_{mf} was conducted by step-wise increasing the supply of air through the distribution plate of the fluidized bed and monitoring the back pressure for the air supply and the pressure drop over the bed. When the point of MFV got closer, the interval at which values were taken were increased to

make sure that the point of interest was found with as good accuracy as possible. Once the minimum fluidization was reached the tests continued to at least double the MFV or as in the case of the largest bed particles until the available rotameter had reached its maximum flow rate. With these tests for the u_{mf} done, the initial testing plan was decided, see table 3.12.

Table 3.12: Initial testing for the nine parameters and the chosen ranges.

	Lower Limit	Base run	Higher limit
Bed particles	Medium-sized particles: 250-350 μm		
Vertical Injection point CO_2	1.5 cm from bottom	22 cm from bottom	37.5 cm from bottom
Radial injection point CO_2	Wall	4.1 cm in	Center
Injection flow CO_2 [SLPM]	14.2	23.6	47.2
Injection direction	Left/right	Forward	Up/down
Vertical sampling point	11 cm from bottom	27.5 cm from bottom	42 cm from bottom
Radial sampling point	Wall	Center	Wall 180 degrees
Angular sampling point	90 degrees	Center (no angle)	270 degrees
Fluidizing agent flow	1.5MFV	2MFV	3MFV

3.2.5 Preparation of experimental matrix

Based on the initial testing result (which is not presented in this report), the choice of the experimental conditions for the final experimental matrix were decided. Two parameters which were identified to have a great impact on the concentration were the air flow and the injection flow of CO_2 . Both these parameters were also seen as especially important to better understand the hydrodynamics of a system where a fuel is introduced in a fluidized bed which is the case in the fuel reactor. Apart from these two parameters it was decided that the geometrical position of the sampling points should be evaluated. This would then allow for a mapping of the concentration over the entire bed for different values on the previously mentioned parameter. Monitoring these different locations would make it possible to understand the transport of CO_2 within the bed.

Another parameter that was considered was the injection direction. Based on the fact that the direction for the injection of a solid fuel may vary this would seem as interesting to investigate. The direction did in the initial have an impact on the measured CO_2 . This was also interesting based on the fact that the formation of volatiles from solid fuels leads to gas expansion which should occur in all directions (not just forward in the injection direction). When it comes to relating the gas injection to a future injection of dry ice, the hypothesis was that injecting the dry ice in different directions than forward (and downwards) would be difficult if using a tube to inject the fuel unless all CO_2 would be in gaseous form before the introduction but then the test

would not serve its purpose to be able to relate to dry ice injection. Because of this reason and time limitations, this kind of study was put aside for the time being. Now it then came to decide the suitable parameter settings. A further discussion on the choice of the settings was however required.

Suitable fluidization flows of operation for the fluidized bed are approximately 2-10 MFV for a bubbling bed[41]. If the same rotameter was to be used, flow rates in the range of 2 to 5 times the minimum fluidization flow could be used for the medium sized particles. Apart from the limitations in the rotameter, too high turbulence was observed to cause leaks at the bottom of the bed and even if these leaks would be fixed continuously, operation for a long time could lead to more serious cracks in the brittle construction. This corresponds well with possible flows on the fluidizing agents in a fluidized bed as one in a fuel reactor in a CLC system. The additional 50 SCFH (23.6 SLPM) outside of the range (which was marked between 0-1200 SCFH (0-566.4 SLPM)) was still possible to set up. The three flows that were chosen were 2, 3.5 and 5MFV. In order to increase the flow at which air was used to fluidize the bed, the pressure of the available air supply was increased to 7.5 bar. In order to make tests with two different bed materials comparable, it was decided that the tests should be different for the two bed materials depending on the minimum fluidization velocity for each bed material.

Once the tests had been done for the medium-sized particles, it became clear that with the present equipment, it would not be possible to reach more than just slightly above the minimum fluidization velocity for the largest bed particles which meant that the study would be limited to the two smaller bed particles. For a user of a fluidized bed, it is vital to know what bed material can be used for a certain operating condition. This could be the availability of pressurized air for example. The understanding of what difference the bed material can make for the hydrodynamics in general and for fuel injection in particular is therefore of a big importance.

All injection of gas was decided to take place at the wall of the fluidized bed. Injection of a gas (or solids as well) is most likely to take place at the wall of the fluidized bed which then motivates that all measurements would be done at the wall of the fluidized bed.

All injections of gas would take place at the bottom of the bed since it was observed in the initial tests that injection higher up in the bed led to that no or only a small amount of injected CO₂ was detected. To have a region where no fuel is located and therefore having all the conversion and combustion of the fuel higher up in the bed would not be a good use of the available space. Having the injection point further down would also as in the case of a solid fuel with volatiles mean a longer distance before reaching the freeboard region.

The flow of CO₂ was varied based on the interest to see the effect of having less or more fuel as an input to the bed. It is very important to know what effect this quantity may have on the distribution of the fuel inside the bed which directly relates to the performance of the overall system. The range of this flow is highly dependent on the available equipment which was 20-200 SCFH (9.44-94.4 SLPM), however it was observed that 30 SCFH (14.2 SLPM) was the lowest controllable flow the rotameter could be run at. By applying high pressure of CO₂, a flow of 200 SCFH (94.4 SLPM) was approached but since the experiments will last for a longer period of time a value smaller than 200 was chosen to reduce the risk of finishing the stored quantity of CO₂ and putting too much pressure on the system. Therefore the range of 30-150 SCFH (14.2-70.8 SLPM) was chosen for the experimental matrix. The following values were chosen: 14.2, 42.5 and 70.8 SLPM. When choosing these values, the actual flow of CO₂ was not taken into account and this was done for the actual values. Since this had not been done before the measurements had been done for the first bed material, the same procedure was used for the other bed material as well.

The injection direction for CO₂ was concluded to be set to forward (into the middle of the bed) for all runs which was motivated by the fact that in order to spread the injected fuel over the whole bed in the radial direction it would in theory make the most sense to inject the fuel in that direction instead of in the axial direction or to the side walls. This is also the likely direction of the dry ice and being able to compare this data is of great interest.

The vertical (axial) sampling points were chosen for three different locations as well. The vertical sampling point plays an important role to be able to map the entire bed volume. The chosen points were at 11, 27.5 and 42 cm height from the bottom of the bed.

Apart from a mapping of the concentration of CO₂ in the axial direction, the radial direction was also needed to create a map in 2 dimensions. In order to spread these points across the entire bed, three points was distributed across the diameter of the bed, two points by the wall and one in the middle. In order to create a map in three dimensions of the concentration, the angle from the injection point should be varied as well. This results in that two additional measurement points were chosen for each vertical sampling position. These were placed at 90 and 270 degrees from the injection point.

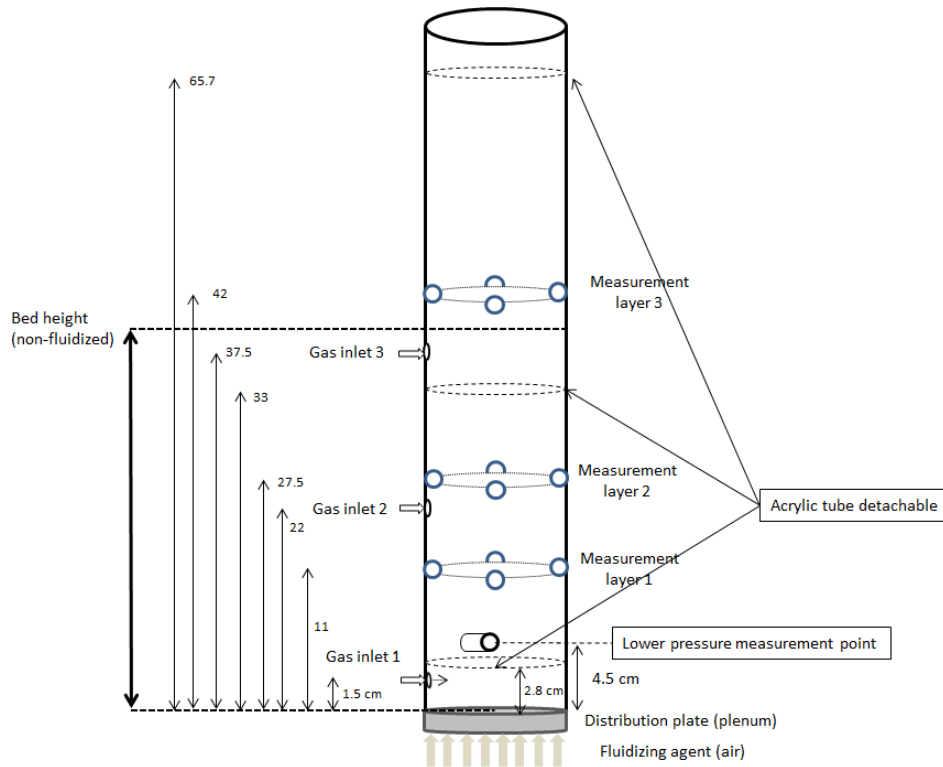


Figure 3.15: Schematic of the fluidized bed with the measurement layers, detachable parts and lower pressure measurement point.

The fluidizing air flow is a very important parameter when it comes to understand the hydrodynamics in the fluidized bed and the gas-solid interaction between the fluidizing agent, the injected CO_2 and the bed particles. During the preliminary testing of the medium-sized bed particles, the maximum flow rates that were able to reach depended on the pressure on the pressurized air and the pressure drop in the system.

It is important to note that the initial flows of CO_2 set above were set out for both bed materials, but since these flows would be in different proportion to the flow of air for the two cases, the flow of CO_2 was scaled for the second case. Therefore the flows of CO_2 for the smaller bed particles was multiplied with by the ratio between the minimum fluidization velocity of the two bed materials to scale the injection flows correctly for the larger particles.

Another rotameter was found to support the flow rates of CO_2 for the smallest particles (120-180 μm) which would be approximately one-fourth of the CO_2 -flow rates for the medium-sized particles (250-350 μm) based on the minimum fluidization velocity. The listed guidelines was followed for the experimental matrix with the aim to create a map of the concentration of CO_2 for a number of different flow rates of air and CO_2 . The total number of experiments was then equal to $2 \cdot 3 \cdot 3 \cdot 5 \cdot 3 = 270$ runs. Observe that the radial and angular sam-

pling points should be seen as 1 point in the middle and then 4 points around the cross section of the bed = 5 which means five points at each vertical position.

Since the concentration of CO₂ is measured in volume percent, the measured values are dependent on the available gas volumes. Since the flow of air and CO₂ varies, the quantity of these flows will have an impact on the acquired value. In order to be able to compare one value more precisely to the other, each value can be evaluated based on the total volume of gas flowing through the bed. The percentage of CO₂ is normalized for the flow of 2MFV and 14.2 SLPM of CO₂. To exemplify the calculation that can be done, for the case using 3.5MFV of air and 14.2 SLPM the measured volume percentage is A, this means that the scaled value is 3.5A/2. The same procedure is done for the injection flow of the CO₂. For a run with 2MFV of air and 42.5 SLPM of CO₂ measuring B vol-%, the scaled value becomes B/3. This is mentioned as the dilution effect when this is taken into consideration later in the report.

3.2.6 Experimental conditions

The chosen experimental conditions are displayed in table 3.13.

Table 3.13: Parameter settings for the experiments with injection of gaseous CO₂ in the bubbling fluidized bed reactor.

Bed particles size	120-180 μm	250-350 μm			
Vertical Injection point CO2	1.5 cm from bottom				
Radial injection point CO2	Wall				
Injection flow CO2	0.125MFV	0.377MFV	0.629MFV		
Injection direction	Forward				
Vertical sampling point	11 cm	27.5 cm	42 cm		
Radial/Angular sampling point	Wall 0	Wall 90	Wall 180	Wall 270	Center
Fluidizing agent flow	2MFV	3.5MFV	5MFV		
Sampling tube	Sampling tube C				

All notations of distances in the vertical position are measured from the bottom of the used vessel. It is important to note that the largest sized particles (500-710 μm) were still tested for the minimum fluidization velocity.

3.2.7 Dry ice injection plans

The realization that the dry ice injection would not be done within the time-frame of this project came once the alternative had been evaluated and here

follows the description of the preparation work that was done for this future study. In order to find a possible structure of a injection system for the dry ice, an estimation had to be done about the quantities of dry ice that would have to be transported into the bed. In order to inject as much mass of CO_2 into the system in solid form as in gaseous form in the initial tests, the densities of these compounds must be regarded. The density of dry ice was assumed to be 1.5 kg/liter[75] and the density of gaseous CO_2 is estimated to be 1.842 kg/m³[76] at normal temperature and pressure. A sample conversion is provided here: 1 CFM corresponds to 28.3 liters/minute. Considering the density of the gas, this corresponds to 52.1 grams/minute of CO_2 . This corresponds to a volume flow of dry ice of 35 ml/minute.

This volume would then be fed into the bed and if the current tube with an inner diameter of 3 mm would be used, the velocity would have to be as high as 4.92 m/s. The velocity is inversely proportional to the diameter squared. A new calculation can be done for a tube with a diameter of 10 mm and this give a velocity of 0.44 m/s. Another measure to decrease the velocity could be to decrease the need of mass of CO_2 into the system which is proportional to the velocity.



Figure 3.16: Sublimation of dry ice pellets[77].

Apart from the mass that should be supplied to the bed, there is also a constraint when it comes to the heat supplied to the incoming dry ice. In order to achieve a sublimation of dry ice that resembles the devolatilization of a solid fuel, the sublimation should take place just as the dry ice enters the fluidized bed. This means that the heat of sublimation should be supplied from where it is stored to the bed inlet, not more and not less. This would be difficult to accomplish in practice without an advanced cooling system.

Based on the known heat of sublimation of dry ice, it is possible to calculate the heat required to sublime the flow of dry ice. If 1 CFM is used as a basis, 29.9 kJ is the heat that should be supplied until the point it enters the bed to this amount per minute (approximately 500 W). The dry ice starts to sublime at -78.5°C which means that there is a big temperature difference

between the surroundings and the dry ice. It is therefore essential to have a well-isolated storage and an efficient transport and cooling not to heat the dry ice more than the mentioned amount.

One approach to inject dry ice into the fluidized bed is to use a long tube in which the dry ice can be inserted heading into the fluidized bed. A plunger could then be used to push the solids into the bed. The problem with this solution is that it would be restricted to smaller mass flows. Apart from this limitation, it would be practically difficult to get the dry ice into the long tube and at the same time avoid sublimation of the dry ice before injection. In addition, it would require cylinder-shaped dry ice so it could easily be pushed through the tube. Since dry ice can be ordered as in pellet or nugget shape, this could be possible, however other more technically advanced solutions were considered as well.

In order to supply a sufficient amount of dry ice and to supply it in a controlled environment to achieve the major part of the sublimation at the entrance of the bed, the idea of a feeding system with a screw and isolation on the outside of the system. With such a solution, it would be possible to change the pace at which dry ice is fed to the bed by adjusting the speed of rotation of the screw. The screw should be able to take larger pieces of dry ice in order to minimize the contact with the equipment and possible sublimation. By using a larger tank in which the dry ice can be supplied, the dry ice could maintain a low temperature and at the bottom the solids would then fall down and be pushed into the bed by the rotating screw.

Even though it is known how much heat the dry ice should receive, the actual amount is difficult to estimate. By assuming that no heat exchange takes places while the dry ice is in the first storage container, the dry ice then comes in contact within the feeding system, the screw itself and the tube entering the bed. It is then also assumed that no bed particles enter the screw. To be able to put a number on the heat exchange, it could be possible to divide the heat transfer from the outside to the tube, from the tube to the inside of the tube and to the dry ice. If isolation is used on the outside of the tube, the transferred heat will be even smaller. An assumption would be to regard the heat exchange between the surroundings and the tube as the limiting heat exchange. The heat transfer between two solids in contact and the conduction in a metal tube is likely to be good. The conduction through an isolation layer and the convective heat transport of the surrounding air is on the other hand likely to limit the heat transport overall.

Because of time and lack of resources to run the experiments within the time-frame of this project, the experimental study in this project focused instead on the injection of gaseous CO_2 and to provide a foundation for testing which can be used for future testing with injection of dry ice.

4

Results and Discussion

In this section the results from operation of the dual-bed chemical looping system are presented through measured pressures and circulation rates for varied air flows, bed material quantities and bed material type. For the bubbling fluidized bed system the characteristics of the bed are presented in form of an evaluation of the minimum fluidization velocity of the different bed materials. In addition, measured concentrations of CO₂ at various points across the system are presented for different air flows, CO₂-flows bed materials and bed amounts. These parts are followed by a discussion on how these results can be interpreted and applied for future research.

4.1 Dual-bed chemical looping system

4.1.1 Experimental verification

As a result of the initial tests without taking into account the back pressure when setting up the rotameter flow rates.

Table 4.1: Measured data to confirm assumptions of conditions at the loop seals and fuel reactor similar to standard conditions for AR flow rates with AR flow rates accounted for the back pressure.

AR [true SLPM]	396	453	510	566	623	680
AR setting [SLPM from rotameter reading]	368.2	382.2	419.1	433.3	467.3	489.9
FR setting [SLPM]	30.7					
ULS setting [SLPM]	13.7					
LLS setting [SLPM]	13.7					
FR side setting [SLPM]	1.42					
AR side setting [SLPM]	1.42					
Pressure AR rotameter [kPa]	31.0	55.2	65.5	86.2	91.4	110.3
Pressure FR rotameter [kPa]	15.2	15.2	15.2	15.2	15.2	15.2
Pressure ULS rotameter [kPa]	12.5	12.5	12.5	13.0	13.0	13.0
Pressure LLS rotameter [kPa]	17.2	18.3	18.3	19.0	20.0	21.4
FR [True SLPM]	30.7	30.7	30.7	30.7	30.7	30.7
ULS [True SLPM]	13.5	13.5	13.5	13.54	13.54	13.54
LLS [True SLPM]	13.80	13.90	13.90	13.94	14.01	14.10

This table displays how the back pressure affected the true flow rate. Since the back pressures should be taken into account to get the true flows in SLPM, the analysis of retained back pressures were needed. In table 4.1 it can be seen that the back pressure for the air reactor rotameter (denoted Pressure AR rotameter in the table) increases substantially with increasing flow rate. For low back pressures, the setting on the air reactor (which is the intended value) is close to the true value but this difference increases as the flow rate increases. The back pressure for the fuel reactor is constant and almost constant for the upper loop seal. For the lower loop seal the back pressure increases slightly with the AR flow rate.

The back pressures of the loop seals and the fuel reactor were in the order of magnitude that the value displayed on the rotameter (see values for the flows in true SLPM in the same table) was close to its true value which resulted in that these back pressures were not corrected for during the experimental work. It should be noted that this is just a sample of what the back pressures were, they varied slightly for each experiment but no retained data questioned this assumption. An important note is that all the data after this section that presents flow rate data will refer to the flow in true SLPM (not the rotameter

setting). From now on will all flow rates in the rest of the report will refer to the estimated true SLPM-value (not the rotameter setting).

4.1.2 Chemical Looping with alumina

The CLC system is run with 12.5 kg of alumina bed material for which the circulation rate was measured operating the system according to the specifications presented in the Method section 3.1.5. The parameter that was varied was the AR flow rate. The first tests were for the case where the back pressure was not taken into account which overall gave higher flow rates in the AR than intended. The corrected data is however still interesting to analyze.

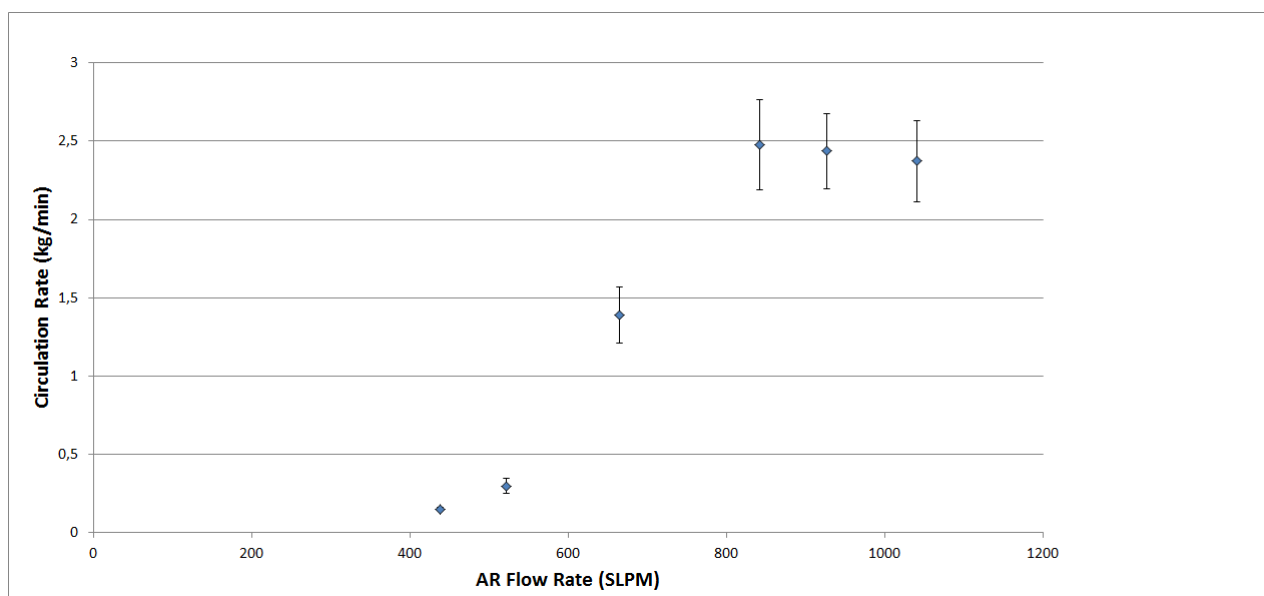


Figure 4.1: The circulation rate as a function of the AR flow rate with 12.5 kg of alumina for the CLC-system for varied AR flow rates.

For low AR flows, the circulation rate is low. When measuring these circulation rates, the accumulation of bed material was slow and difficult to observe. The increase in circulation from the first two measurement points to the third and fourth is substantial. The fact that the circulation rate increases with increasing volumetric flow rate of air through the air reactor makes is expected since higher flow should result in that more particles are carried up the riser by the gas at a higher velocity. However, the increase of circulation rate stops at around 850 SLPM where it starts to decline slightly. Nevertheless, it has to be mentioned that the standard deviation is large at these points and as a result it is difficult to assess the certainty of this trend for higher flow rates through the air reactor. The maximum recorded circulation rate of 2.48 kg/min was recorded at 842 SLPM. It is interesting to observe that increasing fluidization of the bed in the air reactor does not mean that more particles reach the

downcomer. Therefore it might be possible to operate this CLC system for a lower air supply to the air reactor and still obtain a high circulation rate.

For the second experimental matrix the back pressures of the air reactor rotameter are taken into account to compare with the simulation data provided by PhD student Matthew Hamilton using CFD-models in Barracuda. This results in data for AR flow rates in the range below flow rates examined in the previous experiment presented in figure 4.1.

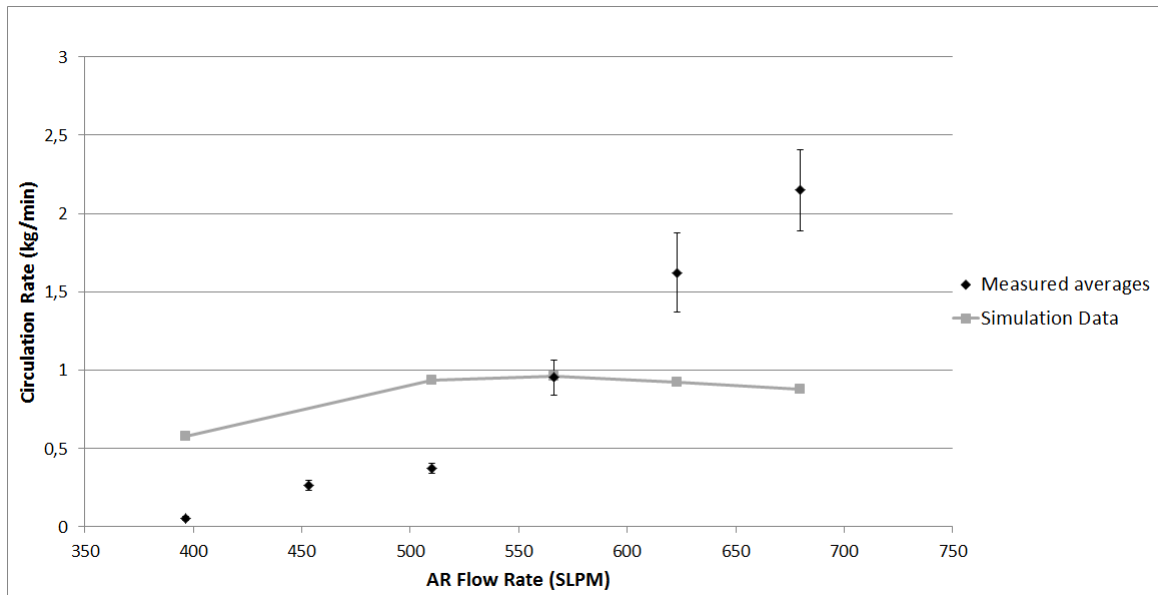


Figure 4.2: The circulation rate as a function of the AR flow rate with 12.5 kg of bed material for the CLC-system for varied AR flow rates.

The trend of the measured circulation rates are not corresponding well with the simulated circulation rates. It is however interesting to see that the simulated values correspond quite well with the overall average of the experimental values. Another observation that can be made is that the trend of the simulated circulation rates correspond rather well with the circulation rates for higher flow rates (see the last four points in figure 4.1). This could indicate that the behaviour indicated by the simulation in the real CLC system is spread out over a wider range of flows of the air reactor and also that the circulation rates (possibly as a result of that) vary more as well. That does still not explain the difference in values but since there are many parameters that come together to the final circulation rate it is come up with a reason for this difference at this point.

The experimental values show a similar trend in the values to what was seen for the smaller AR flows in the first experiment considering all measured values, there is a non-linear trend even though the interval 396-680 SLPM and in particular between 510 and 680 SLPM the trend is rather linear. The total

trend displays a non-linear dependence on the air reactor air flow. The standard error for the last two measurement points is in comparison to the first four points is large. This indicates that the value can be unreliable. One reason for that the obtained standard deviation was in general higher for higher circulation rates was that the time that the measurement took place was a few seconds. Pulsations were present for all air flow rates but the quantities arriving at the same time increased with the air flow. Therefore, not only are the fluctuations larger but also the impact of the start and stop of the measurements with the shorter time of measurement. The effects being referred to is the fact that the quantity of bed mass that arrives and makes the volume pass the mark for start and end of the measurement varies greatly.

Another possible reason for larger standard deviation for higher circulation rates is that the effect of a turned off upper loop seal may have a greater effect on the supply of bed material to the air reactor. Since no bed material is supplied from the upper loop seal to the fuel reactor during the measurement, this decreases in turn the amount of bed material that passes from fuel reactor. This decreases the pressure from the fuel reactor side on the lower loop seal which means that the differential pressure over the lower loop seal gets smaller and less bed material is pushed through to the air reactor. It is difficult to say how big this effect has on the measurements. In principal this effect should have a larger impact with increasing circulation rate and decreasing amount of bed material (the accumulating material in the downcomer constitutes a larger share of the total amount). For this reason, the quantity that was used to measure the circulation rate was much smaller for the smaller flows compared to the higher flows. Another approach that was used to avoid this effect of measurement on the system in general was to measure the circulation over a small distance in the downcomer, but yet not too small to avoid getting an unreliable value because of difficulties with a non-continuous flow. The effect of measuring a height of bed material in the downcomer for the smaller bed masses and air flows indicated that the circulation rate eventually started to decrease when measuring higher up in the downcomer.

It is clear that an increased air flow through the air reactor will make a larger share of the particles in the air reactor reach the cyclone and the upper loop seal but this is clearly not the only effect on the system since the circulation rate would then keep increasing. One possible reason for that the circulation rate reaches a maximum is that it is the increasing pressure in the air reactor that comes along with the increasing air flow. With an increased pressure in the air reactor the driving force decreases in the lower loop seal to transport particles to the AR. The driving force here consists of the pressure difference over the lower loop seal. With a small pressure difference, bed material will accumulate in the tube heading down to the lower loop seal. This will increase the pressure on that side of the loop seal and eventually result in that more bed particles are transported through this loop seal. In time, a balance will be

reached which the height of the bed material in the mentioned tube is higher than before at the lower air reactor pressure. In the event that the air reactor pressure gets high enough pressure so the entire tube up to the fuel reactor is filled with bed particles (the system is choked) and the lower loop seal could break. A pressure measurement also in the fuel reactor might have been able to provide a more complete picture but nevertheless, the measured trend for the increase in the lower loop seal along with the increase in the air reactor pressure supports this hypothesis (see figure 4.3).

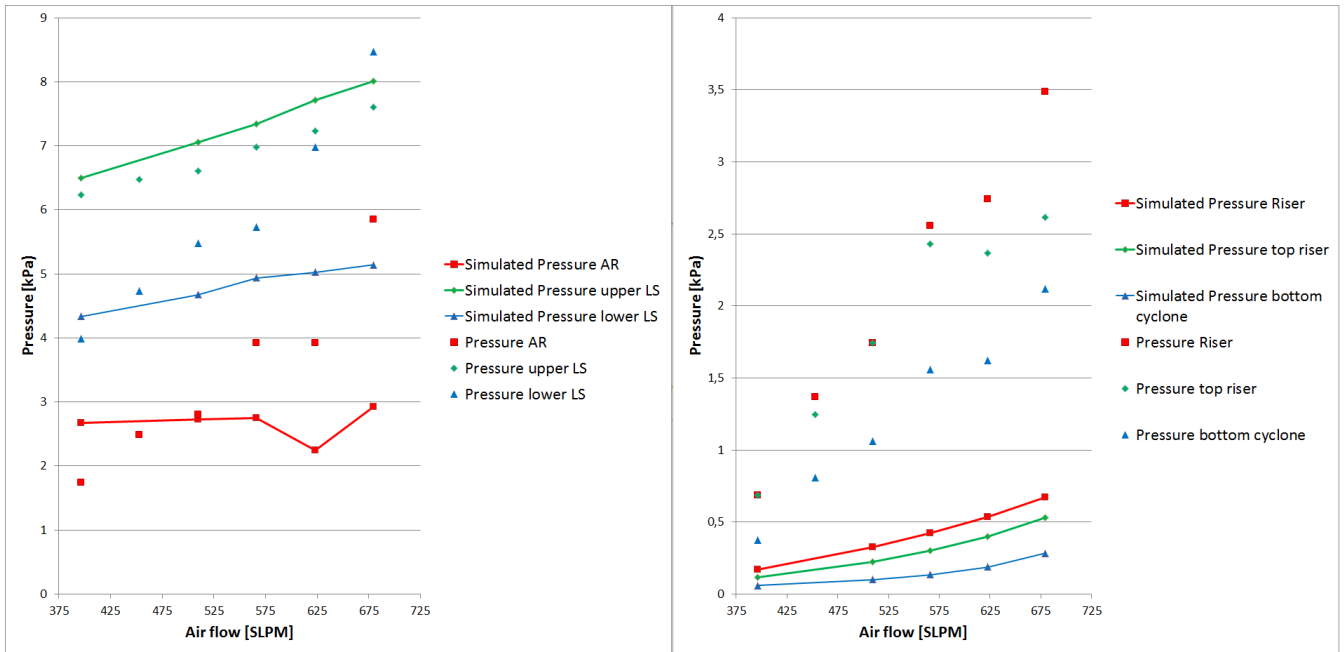


Figure 4.3: The pressure at all six measurement points with 12.5 kg of alumina for varied AR flow rates compared to simulated pressures of the CLC system.

The measured pressure can be seen to increase with the flow rate which is expected. The highest pressures are found in the two loop seals. All units apart from the upper loop seal experience at least a doubling of the pressure from 396 SLPM to 680 SLPM. It is interesting to see that the ratio between the pressure at the highest air flow rate (680 SLPM) and the lowest air flow (396 SLPM) is similar for the measured pressures in the riser and in the cyclone (3.98, 4.57 and 4.76). When comparing the measured values with the simulated values, it can be observed that the measured pressure in the air reactor is lower than the simulated pressure for lower air flows but with increasing air flow it is significantly higher. It therefore seems as if the simulation underestimates the impact of an increased air flow. It is expected that the pressure in the air reactor increases with the flow rate and this in turn increases the pressure at the parts of the system closely connected to it even though the simulation displays a smaller predicted increase. The measured pressure in the upper loop seal corresponds well with the simulated pressure for all air flows.

For the lower loop seal, the difference is small for low flow rates but there is a significant difference between the simulated and the actual pressure for higher air velocities. The substantial increase in the lower loop seal pressure is likely to depend on that for higher flow rates, more bed material is accumulated in the fuel reactor which in turn means that more bed material is accumulated in the tube heading down to the lower loop seal (see previous discussion on how air reactor pressure increases this height). If the pressure in the air reactor would have increased more slowly, it is possible that the measured pressure would have been closer to the simulated values.

During the pressure measurement, the fluctuations at the pressure gage were more prevalent in the loop seals than anywhere else in the system. A possible explanation (which also could contribute to the changes in level of bed particles in the loop seals) could be that the air supply tube to the loop seals are small which means that smaller changes in the volumetric flow rate affects the velocity more than in a tube with a larger cross section (which is the case for the air reactor for example). At both places in the riser and in the cyclone, the simulated pressure is lower than the actual for all flow rates. An increase is expected and is observed but the values are in general higher for the actual system. The pressure is also lower for the top part of the riser, just as the simulation indicated. The pressure at the bottom of the cyclone is for all measured air flows higher than the simulated values. More data is available in section A.1.

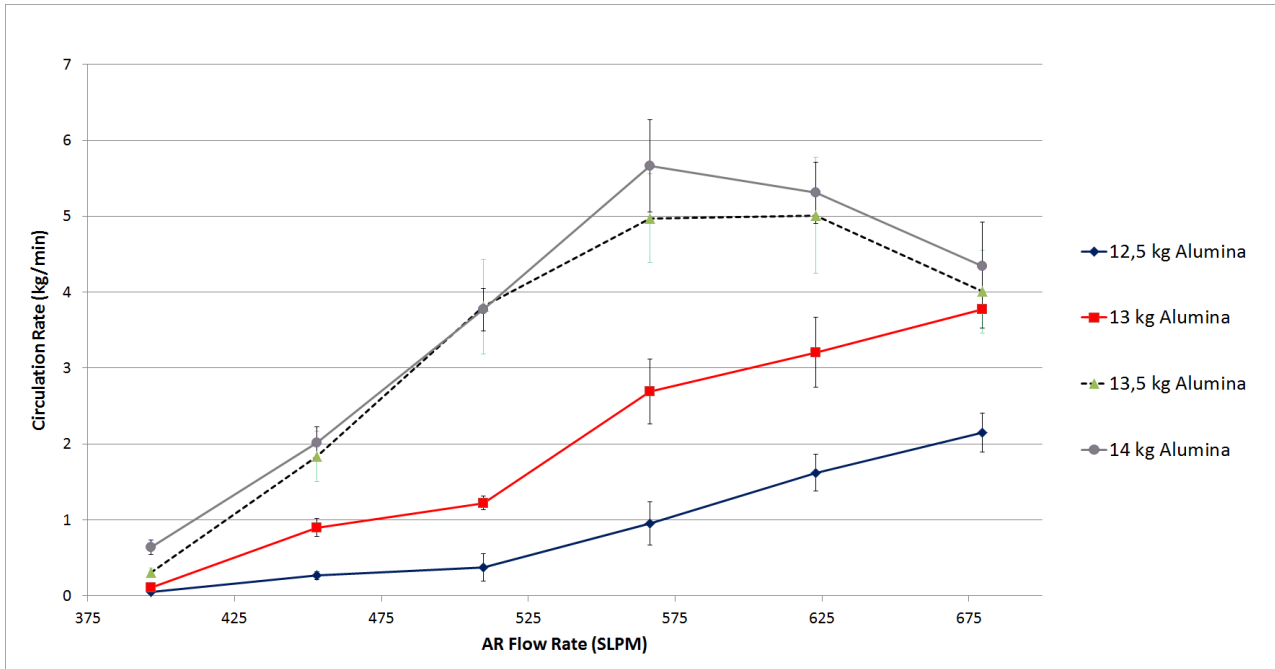


Figure 4.4: The circulation rate as a function of the AR flow rate with different amounts of bed material for the CLC-system.

It can be observed that for the studied bed masses that the circulation rates in general increase with increasing amount of alumina and with increasing air flow rate. This corresponds well with what has been seen when operating this system for lower amounts of bed material[73]. The difference between the two highest amounts is in general small for all flow rates and the most significant difference between these two bed masses and the smaller amounts are for 510 SLPM. For higher flow rates the difference between the lower and higher bed masses decreases. The maximum circulation rate of 5.66 kg/min is measured for 14 kg of alumina at 566 SLPM. A possible reason for that could be that the top of the bubbling bed in the air reactor is located higher up and closer to the riser which then could make it easier for the bed material to be transported up to the riser. It should however be noticed that the level of bed material is unknown apart from in the downcomer. It would have been interesting to see if the lower bed mass amounts (12.5 and 13 kg) would pass the higher bed masses for even higher flow rates. In this aspect it is interesting to use the observation that was made for higher flow rates than 680 SLPM for 12.5 kg of alumina. In that experiment it was seen that the circulation rate reaches a maximum of 2.48 kg/min and then started to decline. It therefore seems like the relation between the circulation rate for a certain bed mass and the flow rate has a U-shaped curve with a maximum circulation rate for a certain flow rate. The measured point of maximum increases with the bed material amount. The flow rate which is required to reach this flow rate decreases with increasing bed material quantity.

Another possible explanation for that the outlook of the curve for each bed mass are similar can be that for the lowest flow rates only the smaller particles (all particles are not of the exact same size) are transported up the riser since these have a lower terminal velocity. This could also explain why the circulation rate starts to increase faster at a certain air flow rate. Assuming that the size follows a normal distribution there will be a certain point over the average size when there is only a small amount which is larger. Once the flow reaches the point when the terminal velocity corresponds to a size of particles which most particles are smaller, then the circulation rate could then increase more substantially. The size distribution was not controlled which makes it hard to make any more conclusions on this matter.

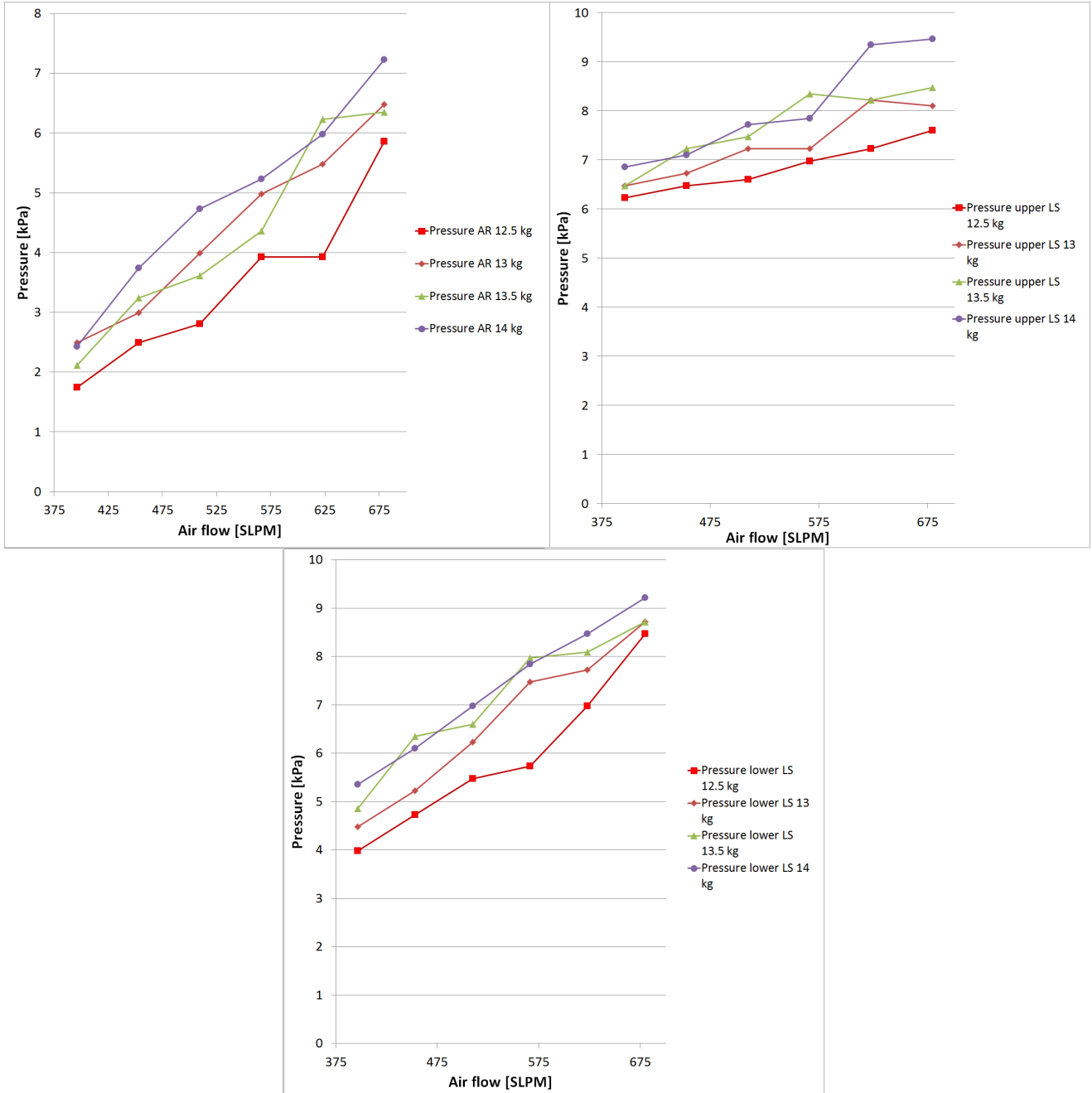


Figure 4.5: The pressure at the air reactor and in the loop seals as a function of the AR flow rate with different amounts of bed material for the CLC-system.

For the air reactor and the loop seals the pressure increases with increasing bed mass. This is according to the expectations since the level of bed material in these units is expected to be higher and therefore results in a higher pressure at the bottom of these units where the measurement tubes are placed. This trend with increasing pressure for increasing flow rates and a higher pressure for larger bed mass is consistent for all three measurement places with a few exceptions.

4. Results and Discussion

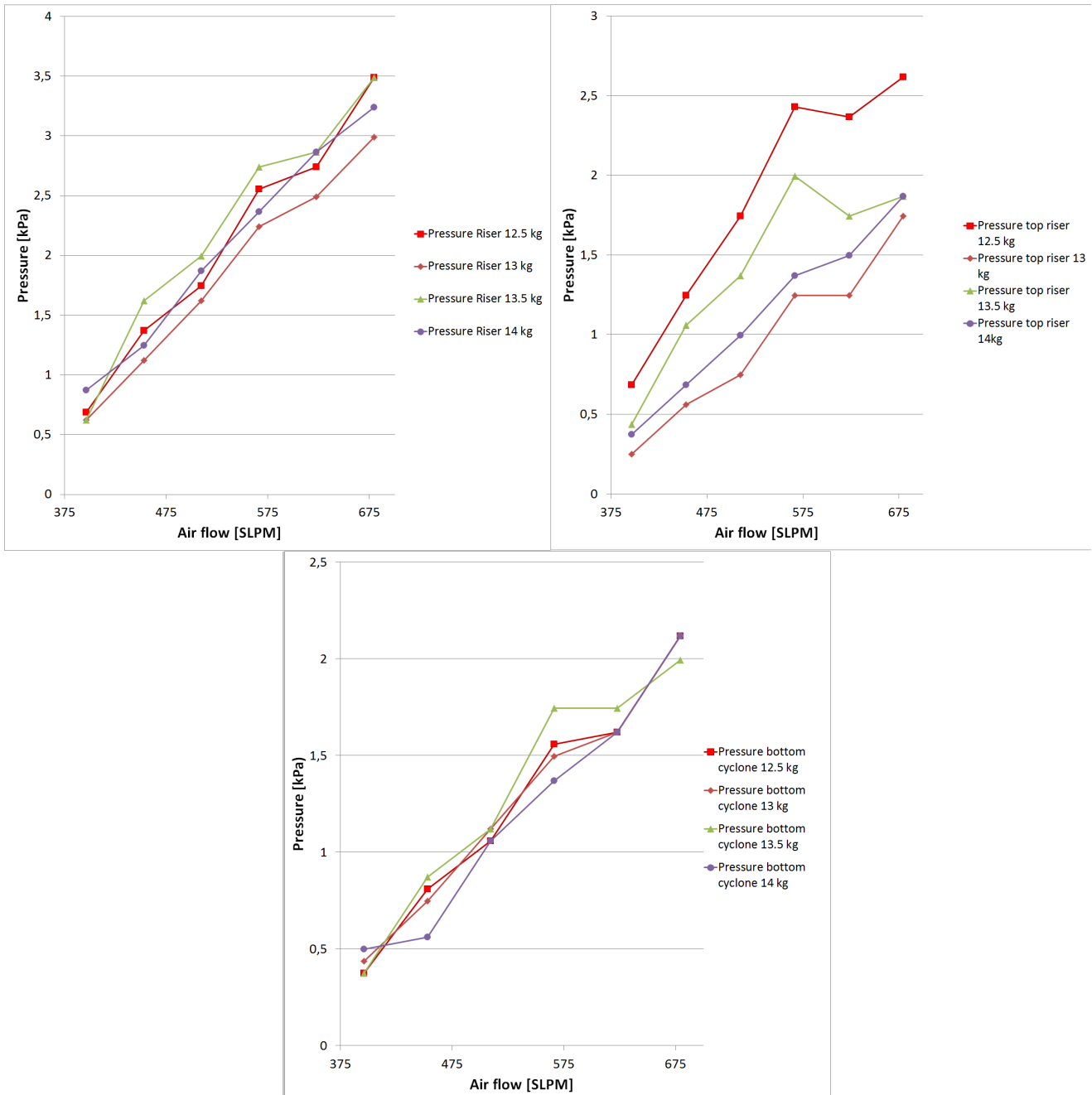


Figure 4.6: The pressure at the riser and the bottom of the cyclone as a function of the AR flow rate with different amounts of bed material for the CLC-system.

The pressure measurements for varying bed masses resulted in general in pressures that were similar for all bed masses which can be observed in figure 4.5 and 4.6. The pressure increased rather linearly with the AR flow rate. This was however not as clear for the top of the riser where the pressure was the highest for the lowest bed mass. It was surprising that the second largest bed mass had the lowest measured pressure for all air flow rates. The highest bed masses were in between these pressures. It would be interesting to repeat these measurements as well as measure the pressure for lower and higher bed masses than the ones used for these experiments.

4.1.3 Chemical Looping with silicon carbide

For the experiments with silicon carbide (SiC), the same experimental matrix was used and the results are presented in a similar way as it was for alumina. It is important to note that the used quantities of silicon carbide have the same volume as the attempts with alumina. The smallest volume corresponds to 12.5 kg of alumina, the second smallest volume to 13 kg alumina and so on.

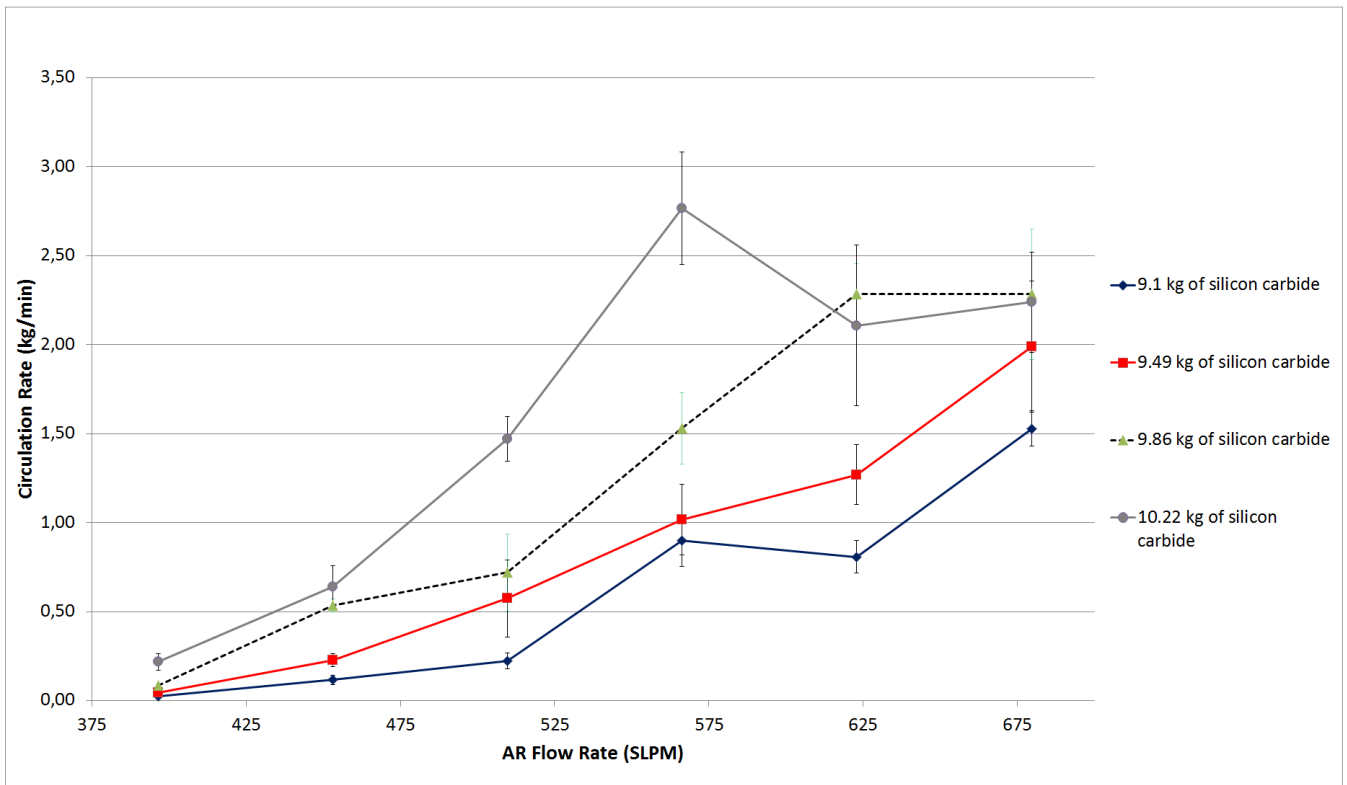


Figure 4.7: The circulation rate as a function of the AR flow rate with different amounts of bed material for the CLC-system.

When looking at how the circulation rate is affected by the amount of SiC it is clear that the trend is similar to what was seen for alumina. However, for this bed material the big difference in circulation rate at 510 SLPM occurs between the highest bed mass and the three other masses. Additionally, for the maximum fluidization of air, the value for the circulation rate is almost the same for all bed masses. The maximum circulation rate that is measured is 2.77 kg/min for 566 SLPM.

4. Results and Discussion

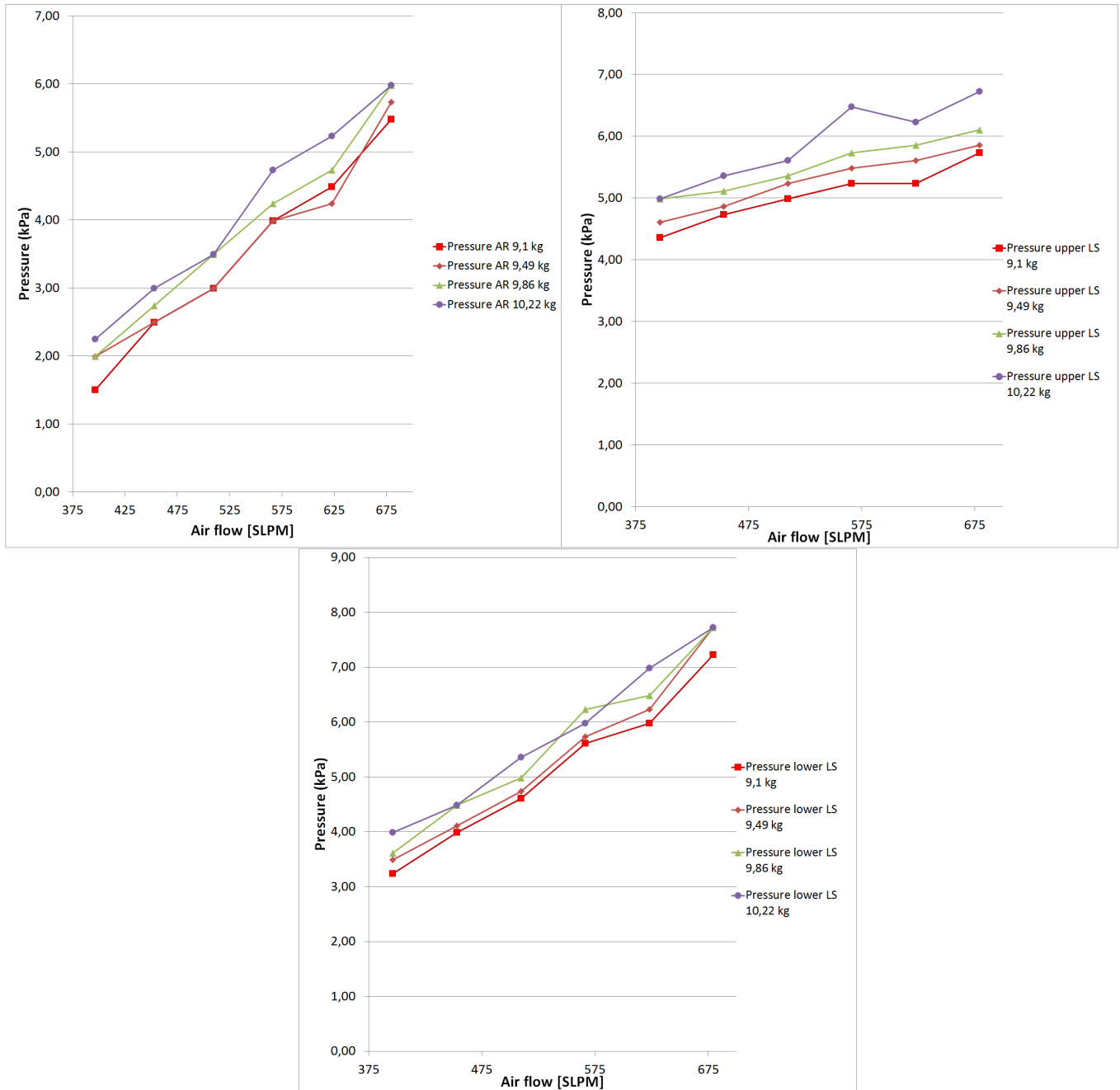


Figure 4.8: The pressure at the air reactor and in the loop seals as a function of the AR flow rate with different amounts of SiC for the CLC-system.

For the system with SiC, the pressures for the air reactor show similar trends with increasing pressure with increasing amount of bed material and air flow. The pressure is in general higher in the loop seals when using alumina as bed material but especially in the upper loop seal. One possible reason for this is the density difference. Since the volumetric load in the systems are the same, the system with alumina has more mass inside. For the same bed volumes in the loop seals and air reactor (where the bed material is collected during circulation), the pressure at the bottom where the measurement point is higher.

Recalling the pressure due to a liquid column of a constant density for example which is equal to $p = \rho gh$ makes this reasoning more stringent. This reinforces as a matter of fact the previous hypothesis that the pressure difference over the lower loop seal limits the circulation rate. When the density is higher, there is need for less bed volume to accumulate in the tube down to the lower loop seal for the same pressure on the fuel reactor side. This makes it easier for bed particles to pass to the air reactor for the same bed volume in this tube. If more bed particles can pass to the air reactor, more bed particles will reach the upper loop seal where a more significant accumulation of bed particles occurs here instead. This increase shows an important point that bed materials with too high densities might cause problems for this lab-scale CLC system. It is however unclear if this trend would continue with more accumulation in the accumulation in the upper loop seal since increasing density will also make it harder to circulate the particles from the air reactor to the cyclone. For the other three parts the density difference should not make a big difference which also can be seen in the experimental results. The pressures for the riser with the lowest amount of SiC stand out from the rest which otherwise are close to what was seen for the alumina system. For the top of the riser the trend is also the same but the values with the SiC-particles the difference between different bed material quantities is smaller.

4. Results and Discussion

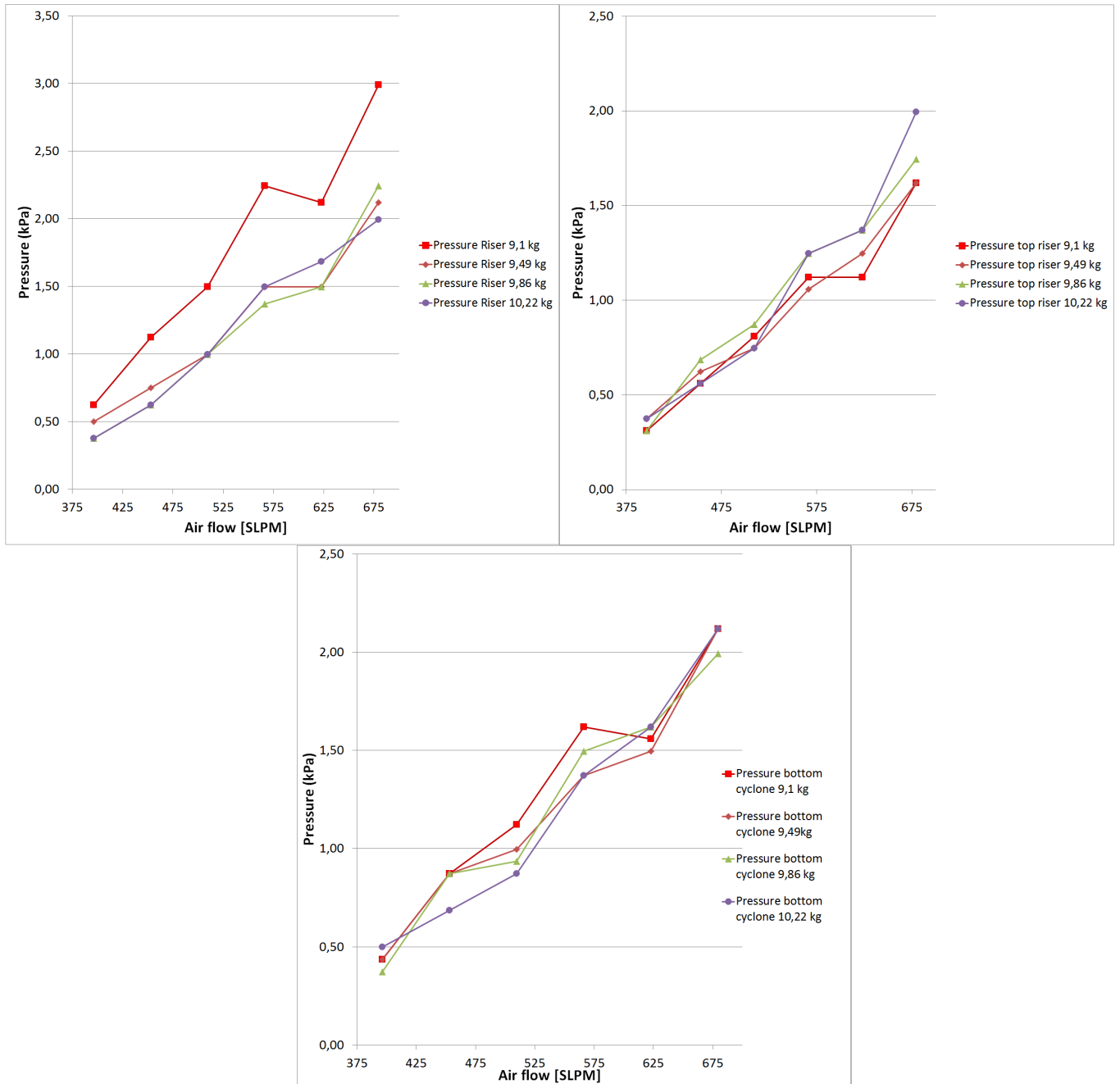


Figure 4.9: The pressure at the riser as a function of the AR flow rate with different amounts of bed material for the CLC-system.

For the bottom of the cyclone the curves are very similar regardless of the used bed mass. For the riser, the pressures are in general higher when using alumina, but the difference is not as apparent as in the upper loop seal for example. For the top of the riser the pressures are rather similar with the exception of the smallest bed mass of alumina which has a higher pressure.

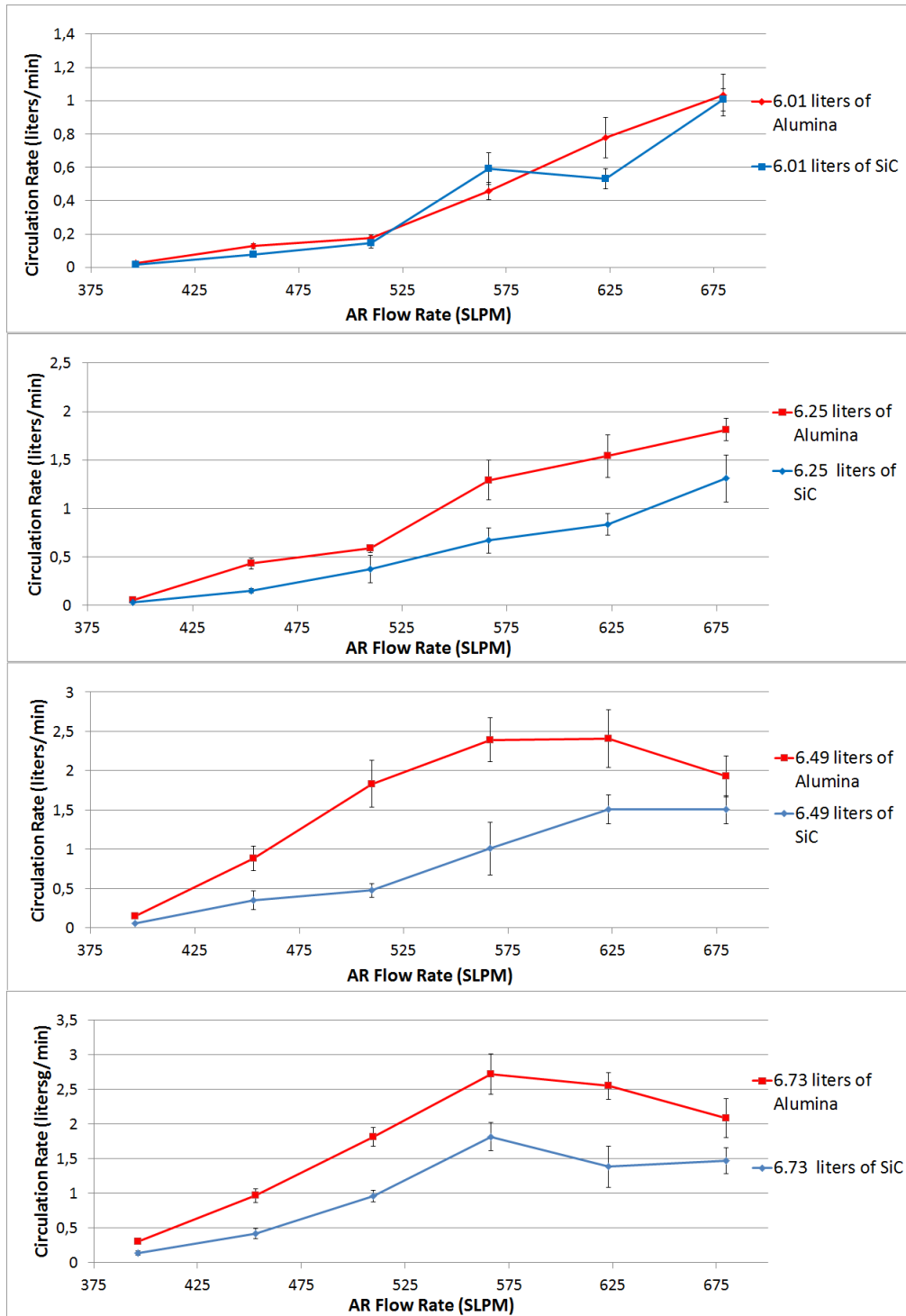


Figure 4.10: The circulation rate as a function of the AR flow rate with 6.01 and 6.25 liters of the two different bed materials.

For the smallest volume of bed material the circulation rates for the two different particles are very similar. Here the only point where the average circulation rate is higher for the SiC is found for the same volumetric content. For 6.25 liters of bed material, the difference is larger. The big differentiation between

the bed volumes occur between 510 and 566 SLPM. For both bed materials the maximum circulation rate is measured for the maximum air flow rate. For higher bed volumes, the difference appears to be getting larger between the two bed materials. However, for the largest air flow rates the circulation rate is similar. The more exact difference between the two bed materials can be seen in table 4.2.

The alumina particles have an estimated average particle size around 250 μm while the silicon carbide are sized 175 μm . The alumina particles have a higher density and therefore more mass of bed particles is inside that system. According to the equation for the terminal velocity, decreasing density means that the particles are more easily transported up the riser. This is also true for a decreasing diameter. Both these characteristics then points out that the SiC should be easier to transport up the riser but still, the circulation rate is in general faster for alumina. This is difficult to understand by just looking at these parameters. A possible reason is that the higher density helps the driving force in the lower loop seal (which has been identified as a possible bottleneck for a higher circulation of particles) to supply the air reactor with more bed material than in the case of SiC with a lower density. A possible reason for that the difference in circulation rate then becomes more apparent for higher bed volumes is that the additional bed volumes is likely to accumulate especially in the loop seals. In the air reactor the particles comes overall closer to the riser and more particles can reach is terminal velocity. In the fuel reactor the level is not likely to increase as much as in the loop seals since the tube in the middle will keep limit the bed height from becoming too tall. If the additional bed material then accumulates in the loop seals to a higher extent, the more dense material will make a bigger difference on the pressure that the accumulated bed volume puts on these units. This forces more bed material to pass through the parts of the system which seem to be limiting the circulation rate and as a result the circulation rate increases faster in the case of alumina.

Table 4.2: Comparison of the circulation rates of the two bed materials expressed as the percentage of the difference compared to the circulation rate for SiC.

Volume bed	396 SLPM	453 SLPM	510 SLPM	566 SLPM	623 SLPM	680 SLPM	Average
6.01 liters	61%	66%	21%	23%	47%	3%	37%
6.25 liters	79%	190%	56%	93%	84%	39%	90%
6.43 liters	160%	150%	286%	138%	60%	28%	137%
6.73 liters	115%	130%	88%	50%	84%	42%	85%

Apart from what could be seen in the measurement results there are other possible differences between operating with the SiC-particles compared to the alumina. The SiC-particles are to a larger extent found in fittings between units when disconnecting pieces in the system to fill up the system with more bed particles. A part of the explanation to that should be that the size is

smaller than the majority of the alumina particles. In addition, more dust was formed when preparing the solid as well as during operation. It would be interesting to see if this dust formation would decrease with the addition of the copper to the particles. It should here also be noted that the kind of SiC-particles intended for CLOU is planned to have a different porous structure and may therefore have other properties when it comes to for example dust formation.

The targeted circulation rate for future operation is determined by the kind of fuel that is in use as well as the flow of the fuel. This will determine the required supply of oxygen to the fuel reactor and as a result the required circulation rate of the oxygen carrier. When it comes to operate the chemical looping system, a suitable window of operation should be identified and one of the most important factors is that the circulation rate is stable when varying various parameters voluntarily or not. It is therefore useful to locate suitable areas of operation in terms of choice of bed material, air reactor flow rates and bed mass volume. In this case alumina is not an option for CLOU because of its formation of non-reactive copper aluminates when acting as support copper but based on the known properties of the material it gives an indication of the behaviour of a bed material of the properties of alumina.

When it comes to comparing the two bed materials at hand the standard deviation is studied which describes the reliability to obtain a certain circulation rate for a given setting. This comparison is shown in table 4.3 and it shows that the overall standard deviation is higher for alumina. However, it should be noted that the measured circulation rates are higher for alumina and if a standard deviation is calculated in terms of percentage of the deviation compared to the average circulation rate, the result is different.

Table 4.3: Comparison of the standard deviation during measurements of the circulation rate for the two bed materials.

		6.01 liters	6.25 liters	6.49 liters	6.73 liters	Average
Alumina	Sum standard deviation (liters/min)	0.34	0.65	1.39	1.05	0.86
Silicon carbide	Sum standard deviation (liters/min)	0.27	0.65	0.91	0.88	0.68
Alumina	% standard deviation	14%	12%	15%	11%	14%
Silicon carbide	% standard deviation	14%	20%	19%	16%	18%

This shows that the standard deviation from the chosen settings resulting in a certain circulation differs slightly more when using silicon carbide. This assumes that the standard deviation is independent of the range in which the circulation rate is measured. As a consequence of this observation, a bed material displaying the properties of alumina would be more suitable overall but there are more parameters that could be considered in this choice. An example

of that is the stability of the circulation rate in a certain range, that is to say that change in circulation rate is smaller for a certain change of the air reactor flow rate.

As a result of these changes with the intended range, each intended circulation rate should be looked at separately. It is then possible to locate which carrier, what bed volume and for which air flow rate this should be done for. Regarding the choice of bed volume it is interesting to observe that the percental deviation in circulation rate (from the mean value) is fairly similar for all bed volumes but slightly smaller for the smallest and the largest volume. This accentuates the statement above to adapt the choice of these parameters based on the sought circulation rate.

As an example, if the intended circulation rate is 1.5 liters per minute, the choice to operate could be to use 6.49 liters of SiC and operate within the flow rate interval of 623 to 680 SLPM. Although standard deviation is clearly observed at 623 and 680 SLPM, the circulation rate appears to be rather constant for air flows just above or just below. If the flow rate setting instead should be up towards 2.5 liters/minute, the choice of using 6.73 liters of alumina at around 623 SLPM might work well considering the small standard deviation at this point for this high circulation rate.

It is difficult to draw more complete education on the suitable size as well as density of the particles. The trend is however that the alumina has a broader range of circulation rates and a smaller standard deviation considering the percental difference and therefore a carrier with the characteristics of alumina would seem more desirable. Alumina has a higher density and a larger size. Both parameters result in theory that these particles are more difficult to fluidize. Within the used range, higher density would be preferable, but it is not sure that this trend would remain for higher densities as indicated earlier. It is however difficult to draw more complete conclusions for these two factors but an idea would be to run the system for higher bed densities and sizes of the particles. It is difficult to say what the effect of addition of copper on the final particles on the silicon support in terms of for example density and size. The density is likely to increase since copper is denser than the other component but it is not possible at this stage to relate this possible density to the one of Alumina.

Some additional notes are needed for the measurements in general. Apart from the mentioned difficulties measuring the circulation rates precisely, another factor is that the flow of bed particles into the downcomer is not evenly distributed over the entire cross section. In addition, some oil was observed in the used rotameters, most likely originating from the compressors in the building. This is especially prevalent in the rotameter for the air supply to the

air reactor. This may cause fluctuations in the air supply apart from potential contamination of the CLC system. Another possible source of error was changes in other rotameters when one of them was changed. It was clear that some of the rotameter settings were interconnected to other rotameters which made it necessary to monitor the rotameter reading. It is possible that some changes occurred without the knowledge of the author.

4.1.4 Recommendations for further research

There are several possibilities to advance from the results in this study. In order to obtain a more exact estimation of the circulation rate more attempts would have to be done in general. More precisely a measurement should be done to conclude what effect the volume of bed material in the downcomer used to measure the circulation rate has on the measured circulation rate. Another factor which may have an impact is the level of bed particles in the downcomer when the upper loop seal air flow is shut off. Since this effect is assumed to be dependent on both the bed material quantity and the air reactor flow rate, a correction for this factor may be able to be defined.

The system should be run with other bed materials and most importantly with the Cu-coated SiC-particles that aims to be used for CLOU. The system could also be run for higher air flows to the air reactor as well as using larger amounts of bed material to see where a high and reliable circulation rate with reasonable pressures in the system are present. Apart from running the system cold, the reliability of the circulation of the system should be done for higher temperatures. The long-term performance of the carriers in operation should be tested. This can be done using characterization methods such as XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy) and EDX (Energy-disperse X-Ray spectroscopy). By using XRD the changes in crystalline compounds on oxygen carrier surface can be traced. SEM and EDX can be used to trace changes in the morphology and the surface elemental composition. Apart from the carrier it would also be useful to characterize the coal fuel that intends to be used. As an example it would be of great interest to know the reactivity of the coal and in terms of the gas plume formation it would be of great value to know define how much volatiles are formed during devolatilization. It would also be useful to know sulfur content and the impact of this on the system performance.

It would be interesting to study the larger bed material amounts at even higher air flow rates to determine if the circulation rate keeps increasing. It would also be interesting to locate the height of the bed material in the tube coming down to the lower loop seal to verify the previously mentioned hypothesis. The observations made for increasing densities with increasing accumulation

in the upper loop seal rather than in the lower would be interesting to investigate further to see if a high enough the bed particles start to a higher extent accumulate in the air reactor instead for example. It could also be interesting to study what impact the size distribution of the bed material has on the circulation rate for the system as well.

The system will as indicated in the Method section be restructured to run during warm and hot operation and the part that needs to be replaced is the downcomer for a stainless tube where circulation rate can be measured. Heating will be added as well as insulation. The heating could be supplied using a external heater, the idea to insert a gaseous fuel such as natural gas or hydrogen will be considered. This may be cheaper and require less space to reach the intended high temperatures.

The system should then in time be run with a solid fuel such as coal fluidizing the fuel reactor with steam or CO_2 and running the system with SiC-particles covered with copper for CLOU. This could then provide a better understanding of how well this setup and this oxygen carrier works and potential learnings to use the same approach for a larger sized system.

4.2 Bubbling fluidized bed

In this section the results from the study on the bubbling fluidized bed are presented including a characterization of the bed and concentration measurements during injection of gaseous CO_2 .

4.2.1 Bubbling fluidized bed characteristics

The found characteristics for the fluidized bed when operating the system with different bed particles are presented in this section to provide a basis for the experiments done with injection of CO_2 and simplify the interpretation of these experiments. In the calculation of the theoretical minimum fluidization velocity, the particle size was assumed to be the mean value within the specified range of the size. The exact values of these experiments are provided in section A.2.1. By looking at the recorded differential pressure measured over the bed for the three different bed materials an estimation of the minimum fluidization velocity could be estimated (see figure 4.11 for the smallest bed particles).

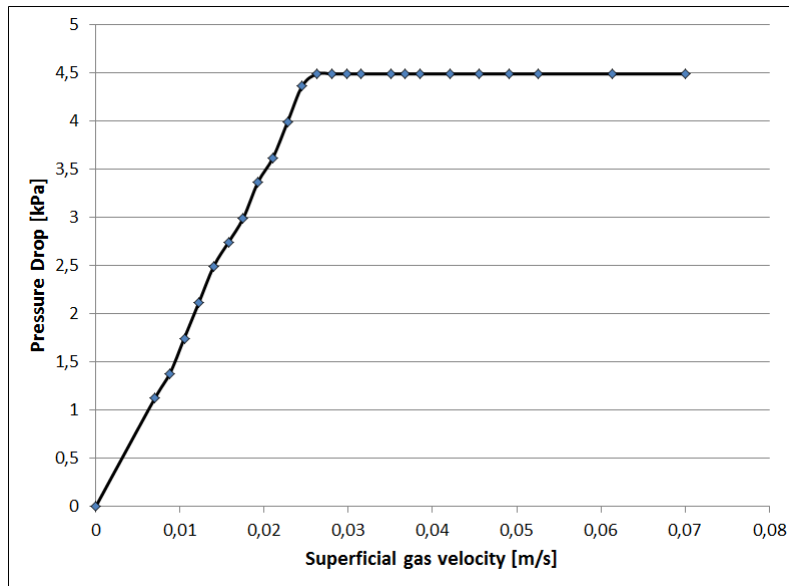


Figure 4.11: Pressure drop over the fluidized bed for different flows of the fluidizing agent for the 120-180 μm glass beads.

The smallest bed material has the lowest required flow to reach minimum fluidization and for this bed material the pressure drop over the bed increases almost perfectly linearly to 4.5 kPa where the pressure drop becomes constant. The minimum fluidization is reached at the superficial velocity of 0.028 m/s.

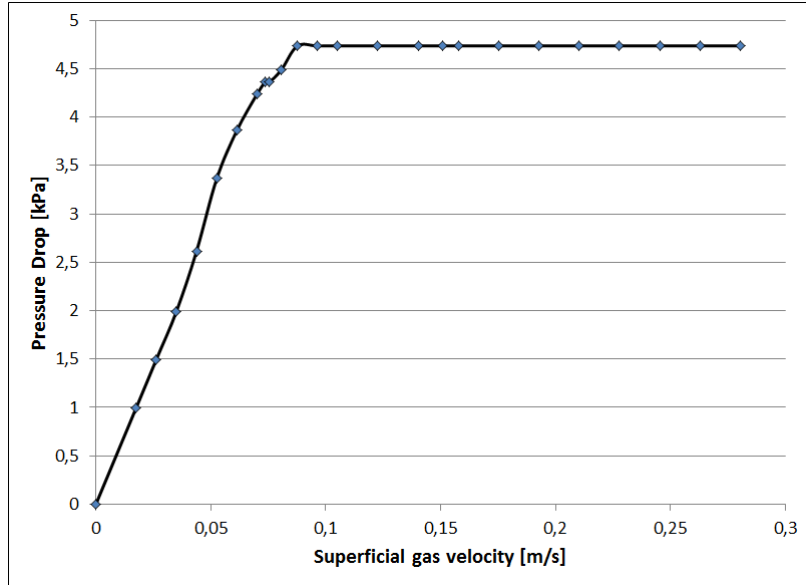


Figure 4.12: Pressure drop over the fluidized bed for different flows of the fluidizing agent for the medium-sized glass beads (250-350 μm).

For the medium-sized particles, the minimum fluidization is reached at a superficial velocity of 0.087 m/s. Just as in the case for the smallest particles, the medium-sized particles display a linear increase of the pressure drop with increasing flow of the fluidizing agent and a constant pressure drop for higher flow rates.

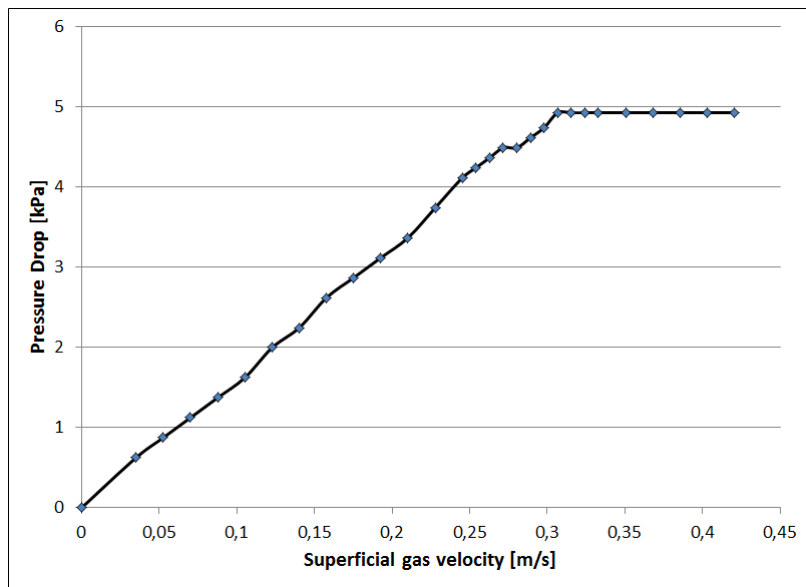


Figure 4.13: Pressure drop over the fluidized bed for different flows of the fluidizing agent for the largest glass beads used (500-710 μm).

The minimum fluidization for the large particles is reached at the superficial velocity of 0.31 m/s. The maximal pressure drops across all three beds are all

similar and so is the trend for flows both above and below the minimum fluidization. It can be observed that the pressure drop for all three bed materials corresponds well with the theoretical graph for Geldart type B particles (see section 2.7 for further information). Apart from the visual confirmation that the bed particles are easily fluidized this can be seen as a confirmation that the particles are behaving like type B particles. Since the transition from a packed bed to a bubbling bed is rather linear, the bed can be considered as narrow.

Table 4.4: Characteristics of the three bed materials relating to the minimum fluidization velocity.

Bed material	Smallest size	Medium size	Largest size
Estimated average d_p [μm]	150	300	605
Re_{mf}	0.227	1.763	12.195
Theoretical u_{mf} [m/s]	0.023	0.088	0.303
Experimental u_{mf} [m/s]	0.028	0.088	0.307

The experimental values for u_{mf} corresponds well with the calculated theoretical values for u_{mf} for all three bed materials with the biggest difference for the smallest bed material. These results were then directly applied to the experimental work with injection of CO_2 .

4.2.2 Gaseous CO_2 Injection

In this section the results from the injection of CO_2 are presented. This is done in steps where the impact of the air flow, CO_2 injection flow and the bed material on the hydrodynamics of the bed are done by comparing the measured quantities of CO_2 . An important note that applies to all comparisons between different fluidization velocities and flows of CO_2 is that since the analyzer measures the volume percentage of CO_2 at the point of measurement, the ratio between these changes. This means for example that the same quantity of CO_2 may be found in terms of mass at a certain point but for a higher flow of air, the value in percentage will be smaller. In the case of comparing 2MFV with 5MFV for example for a certain injection flow of CO_2 , the concentration of CO_2 for the case of 2MFV is A %. That means that if the amount equal to $A/2.5$ % is measured, the same share of the injected CO_2 is located there. This however assumes that the flow is equally distributed across the entire cross section. All values are presented in vol-% (without considering the dilution effect) unless explicitly mentioned that the values are scaled or that the dilution effect is taken into account.

4.2.3 Variation of fluidization flow

Here is an illustration of the concentration profile in the cross section in the direction of the injection point. Three points at each vertical position are used: at the wall where the injection of CO_2 takes place with a radial coordinate of 0, in the center at 8.26 cm and at the other side of the bed at 16.52 cm. The three vertical positions are located 11, 22.5 and 42 cm from the bottom. Note that the actual injection point has the coordinate (0,1.5). The measurement positions to the right and left are therefore not included in these plots.

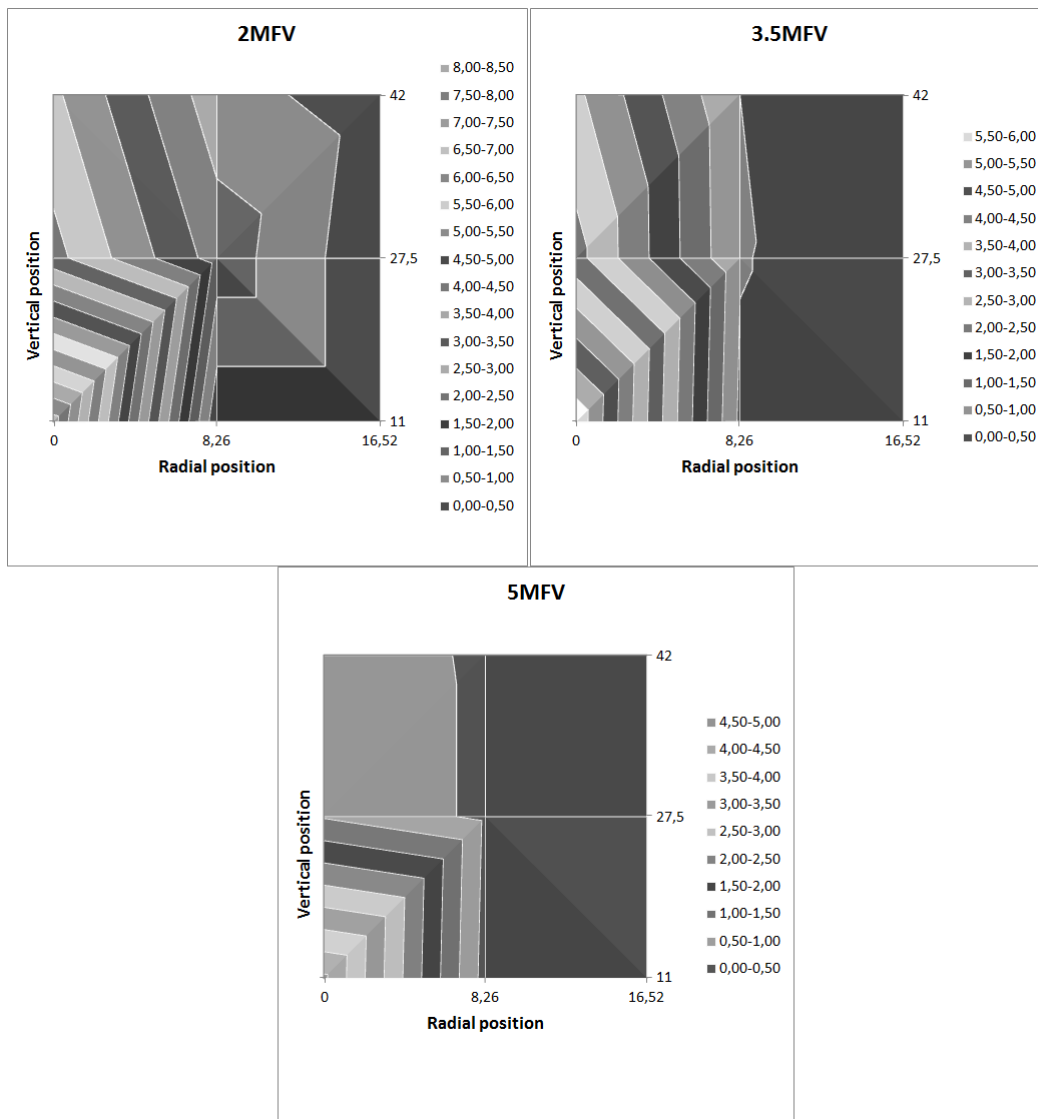


Figure 4.14: Contour plots of the concentration of CO_2 in volume-% across the cross section in the direction of the injection port for CO_2 -injection at 14.2 SLPM for the medium-sized particles (250-350 μm) for air flows in the range of 2MFV to 5MFV.

These contour plots can serve as a first indication on how the increased air flow dilutes the injected CO_2 (gradually smaller maximum concentrations measured for higher air flow rates) as well as the concentration gradient from the injection side to the opposite side. It is clear that the difference between the is substantial for this low injection flow of CO_2 . Another approach to present the measured concentrations is to use circles representing the different layers (vertical positions) and bars whose heights represent the concentration measured. The connection between the bars and the position in the bed can be done with support of figure 4.15.

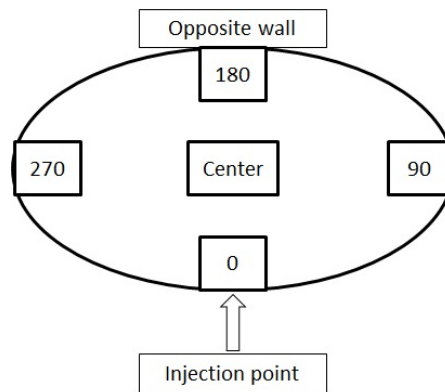


Figure 4.15: Representation of the positions in each layer in relation to the injection point.

It can be seen that the injection takes place at the bottom of the figure and each vertical position (layer) has five measurement points.

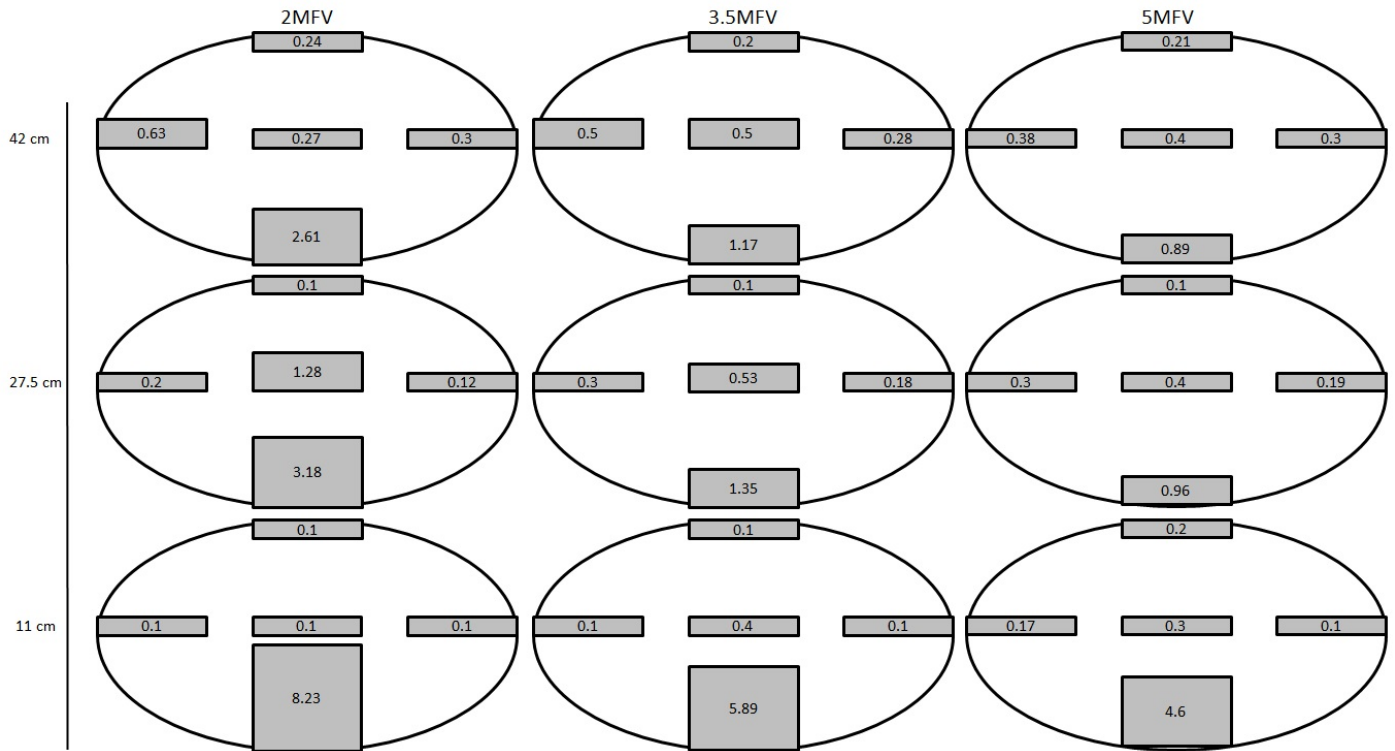


Figure 4.16: Visualization of the measured volume-% of CO_2 (not corrected for dilution) at different points in the bed for the three fluidization flows used when injecting at 14.2 SLPM for the medium-sized particles (250-350 μm).

At the lowest air flow, most of the CO_2 appears to flow upward with the fluidizing agent and gradually spread out across the cross section further up. Even at the measurement point close to the freeboard and located in the splash zone (42 cm), the concentration of CO_2 is significantly higher there than anywhere else in the cross section. An interesting observation is that the measured concentration of on the left side seen from the feed port is higher than on the right side for almost all measurements. This may depend on that the injection port is slightly to the left after observation of the threaded hole. When comparing the different flows of air for the lowest injection flow of CO_2 it can be observed that increasing fluidizing agent flow results in more radial mixing of the CO_2 . For all measured vertical cross sections the CO_2 is more spread out over all measurement points for higher fluidization flow rates. The same graphs for 42.5 and 70.8 SLPM for this bed material are provided in section A.2.3.

As mentioned earlier in the Method section, higher flow rates dilute the CO_2 to a higher extent. If this effect is considered, the measured concentration of CO_2 is in general higher for higher flow rates of air. This is be done by using the scaling operation explained earlier at the end of the Method section. The result of an aggregation the measured amount of CO_2 for different layers and for different flows of fluidizing agent considering the dilution can be seen in table 4.5. For 14.2 SLPM of CO_2 and 2MFV of air flow, the measured

amounts in vol-% are added up directly for each vertical position. For the other air flows, the ratio between the air flows are considered (see all scaled values in the Appendix section A.2.2.2).

Table 4.5: Aggregation of the content of CO₂ for different layers and flow considering the dilution of CO₂ by the air flow and the relative injection flow of CO₂ into the bed using the bed particles of the medium size (250-350 μm).

14.2 SLPM CO ₂	2 MFV	3.5 MFV	5 MFV	Sum
Vertical 11 cm	8.63	11.54	13.42	33.59
Vertical 27.5 cm	4.88	4.32	4.88	14.07
Vertical 42 cm	4.48	4.64	5.44	14.56
Sum	17.99	20.49	23.73	$\Sigma = 62.21$

A trend that is observed is that increasing flow rates results in that a higher share of the injected CO₂ is sampled in the bed. This indicates that the CO₂ stays to a higher extent in the bed rather than entering the freeboard region. It would be very interesting if a similar trend would be found in the case of the volatile gases originating from devolatilization. This could mean that the injected gas to a larger extent remains in the bed (instead of entering the freeboard) when operating at higher fluidization velocities. This could then result in a decrease in unconverted volatiles thanks to combustion of these compounds in the bed.

However, one effect that contradicts this statement is that higher fluidization velocities also means that higher velocity through the bed which in turn means less residence time in the dense bed and the splash zone before the gases reach the freeboard region. This could in turn lead to that a smaller amount of the volatiles are combusted before reaching the freeboard region. If the fluidizing gas and the CO₂ would leave the bed to the same degree for each fluidization velocity, then this would be the case, but this might not be the case. If higher flows of the fluidization agent result in a better radial mixing and circulation of the CO₂ compared to the case for the lower fluidization velocities, the CO₂ might even spend more time before reaching the freeboard region. Therefore it would be very interesting to study the residence time of the injected gas. Another aspect that would contradict the risk of increased amount of unburnt volatiles in the freeboard would be that the increased fluidization velocity results in more efficient conversion of the volatiles through better contact between the air and volatiles through improved mixing. The indications that CO₂ is in general more spread out over the bed could support this hypothesis.

By considering the dilution effects, it can be seen that the total amount of CO₂ that is measured for each layer shows that the most CO₂ is detected in the first measurement layer. This could show that CO₂ to a higher degree is located at the bottom of the bed than higher up in the bed. Another interpretation

in the case of lower flows of CO_2 is that almost none of the CO_2 is spreading to other parts of the bed other than along the wall (where the majority of the CO_2 is measured). Further up in the bed the CO_2 spreads out more across the entire cross section and this means that less CO_2 is detected at the five points of measurement that are available. When looking at the total amount of CO_2 that is observed in each layer and considering the dilution of the CO_2 , several interesting observations can be made. For the two layers higher up in the bed the difference in estimated total amount of CO_2 is much smaller. For the highest fluidization of air, the value is clearly higher than for the lower velocities in the first measurement layer. One possible explanation in this case could have been that almost all the CO_2 passes the measurement point just slightly above the injection point. The highest fluidization velocity gives the highest estimated amount of CO_2 in the first layer at 11 cm but the trend is the same at the other layers although the same amount is detected for 2MFV (4.88). This could mean that an increase in fluidization velocity actually results in that more CO_2 is located in the bed in general, not only above the feed port. When comparing for higher injection flows of CO_2 , the same trend can be seen with CO_2 to a larger extent measured in the first layer for higher air flows as well, although the trend is slightly smaller.

Another remark that should be done is that the concentration in the center of the bed is almost the same between the heights 27.5 cm and 42 cm in the cases for the higher air flows. For the lower air flows, the concentration changes still, especially for lower flows of the CO_2 . This may indicate that the CO_2 that is found at the height of 27.5 continues to flow straight upward above this measurement point. If the CO_2 does not mix with the air to the same degree as further down would therefore imply that mixing at this part of the bed is not very good. This may seem a bit contradictory since the measurements at 42 cm are clearly in the splash zone of the fluidized bed which should have a good radial mixing. However, the same trend is not observed at the measurement points at the walls which in general show that more and more CO_2 is spread to these measurement points.

When comparing the concentrations at the other side of the bed, the amounts of CO_2 are in general low for low injection flows of CO_2 but there is a small increase higher up in the bed considering the dilution of the CO_2 . The measured concentration is always higher in the middle than at the opposite side. It is also interesting to investigate if it is possible to see what the effect of air flow has on the jet penetration length. The indication that is used is the measured quantities at the first measured layer. For the lowest injection of CO_2 , there is a clear increase in the amount of measured CO_2 from 2MFV to 3.5MFV while the additional increase for 5MFV is small compared to 3.5MFV. However, if the dilution of CO_2 is taken into account, the trend is more clear. A more significant amount of the introduced CO_2 reaches the center of the bed for higher air flows. When comparing 3.5MFV and 5MFV it seems as if the jet reaches even further since the value at the opposite site increases. This

could then be used as a support that the jet penetration increases with the increasing air flow, but no complete proofs are provided with the conducted experiments. As it can be seen in figure 2.7 in the Theory section, the jet penetration length is the point which reaches the furthest into bed through injection. This study does not have access to more exact data closer to the injection point which could have given a more exact answer to how far the jet reaches through the injection itself (before the dispersion of the injected gas governs the mixing in the bed). As a result it is however difficult to assess the reason for that the concentration of CO_2 increases at the mentioned point. What can be concluded is however that more of the introduced CO_2 appears to reach further into the bed with an increased air flow.

4.2.4 Variation of CO_2 -injection flow

In order to assess the impact of the injection flows of CO_2 , comparisons have to be made between the different injection flows for the same air flows. An example of this is presented in the following graph investigating at 5MFV of air flow (see figure 4.17)

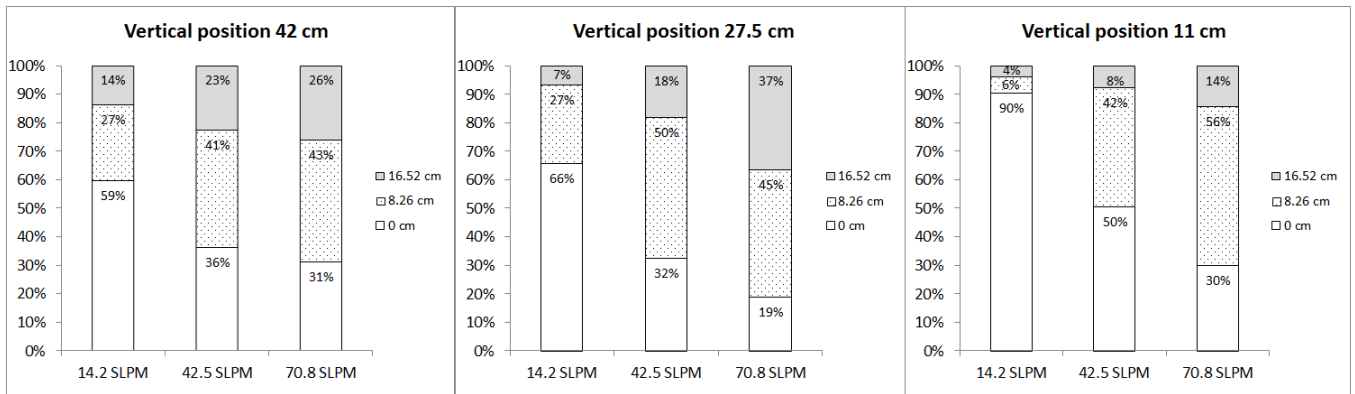


Figure 4.17: Distribution in % of the CO_2 for different radial positions from the injection point (0, 8.26 and 16.52 cm) in each vertical layer (42, 27.5 and 11 cm) when varying the injected CO_2 -flow from 14.2 to 70.8 SLPM using the bed particles of the size 250-350 μm .

For the highest fluidization that is clear that the injection flow has a big impact on the measured concentration of CO_2 . For the lowest injection flow, only 4 % of the CO_2 measured at these three points is found at the wall at the opposite side. For injection at 42.5 SLPM this share increases to the double and then to 14 % for the injection at 70.8 SLPM. The same trend is seen at this point higher up in the bed. The biggest difference is however further down in the bed. The share of CO_2 located at the center of the bed increases significantly from 6 % to 42 % of the measured CO_2 in these three points when increasing the injection flow from 14.2 to 42.5 SLPM and continues to increase also for injection of 70.2 SLPM CO_2 . The difference is smaller higher up in the bed

also for this case and even decreases slightly at 27.5 cm going from 42.5 to 70.8 SLPM. These results show that in order to disperse the injected fuel in the radial direction for lower heights, the flow has to be able to penetrate through a bed that is fluidized. This ability is described by the jet penetration length mentioned earlier in the Theory section and it has been concluded that the jet penetration length increase with the jet velocity[53].

These observations are very interesting considering the injection of a solid fuel in a fluidized bed. In order to prevent high amounts of from being concentrated close to the injection ports as a result of devolatilization, the distribution in the radial direction has to be functional. Since the radial mixing is strongly dependent on the jet penetration length as shown in these experiments, the possibility to penetrate a fluidized bed is important. These experiments have been done with a gas and in the case with a solid fuel the solid will be injected which through devolatilization creates a gas expansion. This gas expansion should in theory occur in all directions which in that case means that neglecting the surrounding flows, the gas is just as likely to expand towards the fuel port as towards the other side of the bed. It is difficult to assess what effect this has on the penetration towards the opposite side since the velocity of the formed in various directions is unknown. Considering the problems that have been observed with volatiles forming a plume rising through the bed, the penetration is likely to decrease because of this phenomenon. It is important to note here that the penetration of the solid itself has not been considered. This penetration is likely to be dependent on the same parameters as well as the size of the injected solid fuel.

The two measurement points that were not looked at in the previous figure shows some interesting results as well. It can be observed that the increased injection flow in the direction of the opposite side of the bed also increases the mixing in the direction of the measurement points located 90 and 270 degrees from the injection point. In figure 4.18, the measured amounts of CO₂ in these two points are put in relation to the total measured amount in the same layer and flow conditions are presented ranging from 14.2 to 42.5 SLPM. This analysis indicates that the increased injection flow in the direction of the opposite side of the injection point also means that a larger share of the CO₂ reaches the right and left side of the bed. The biggest difference is seen between 14.2 and 42.5 SLPM here. For the same reason as indicated as above, a successful penetration is therefore advised to obtain a wide distribution of the volatiles formed from devolatilization.

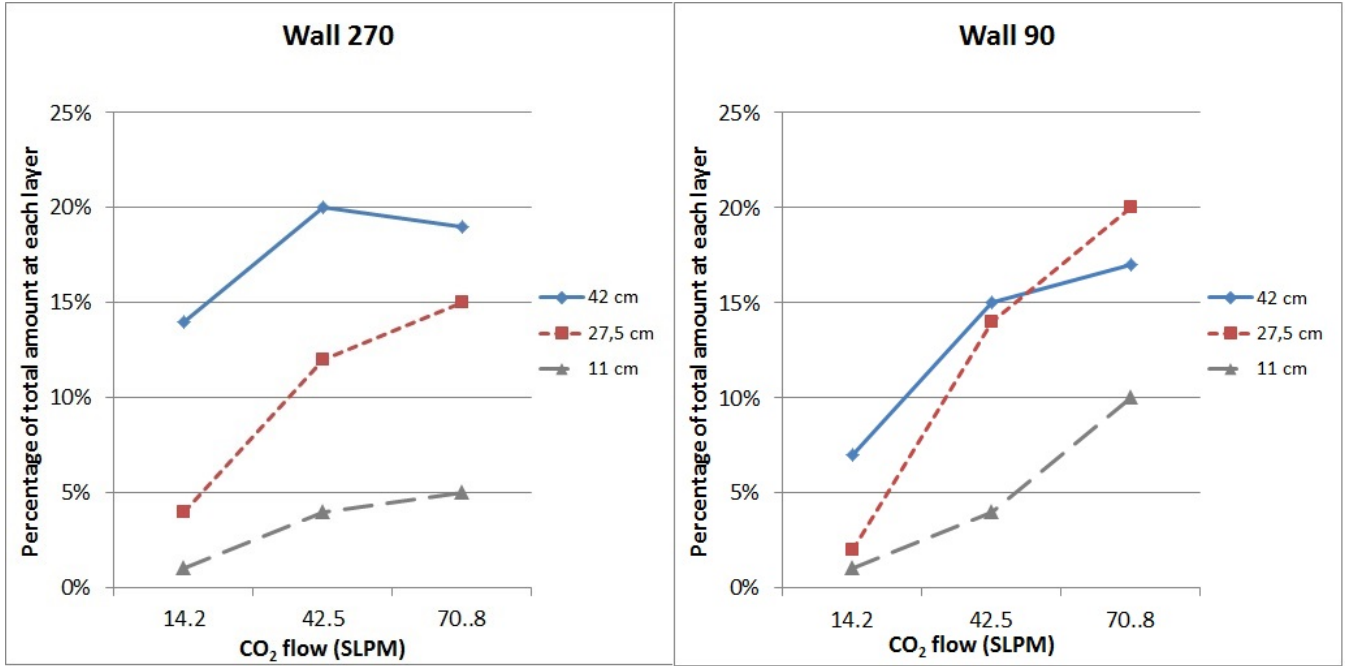


Figure 4.18: Ratio of the measured volume-% of CO₂ to the left (wall 270) and right (wall 90) to the total amount measured volume-% in each vertical layer using the 250-350 μm sized bed material.

Another interesting observation can be made by looking at the ratio between the measured volumetric percentage at the center position and the opposite side of the injection point. This ratio decreased for increasing height in all tests but one where the ratio increases between the second (27.5 cm) and the last measurement layer (42 cm). This occurs for the highest injections injection flows of CO₂ (see last two rows in table 4.6)

Table 4.6: Comparison between the measured percentage of CO₂ for the center point and on the opposite side of the bed higher up in the bed for varying air flows for the medium-sized bed particles (250-350 μm).

14.2 SLPM	2MFV	3.5MFV	5MFV
Ratio at 27.5 cm	12.83	5.33	4.00
Ratio at 42 cm	2.90	2.50	1.92
42.5 SLPM	2MFV	3.5MFV	5MFV
Ratio at 27.5 cm	2.97	2.09	2.74
Ratio at 42 cm	2.30	1.96	1.83
150 SCFH	2MFV	3.5MFV	5MFV
Ratio at 27.5 cm	1.53	1.09	1.22
Ratio at 42 cm	1.91	1.50	1.63

This indicates that a substantial amount of the CO₂ reaches beyond the center (most likely due to the high jet velocity) of the bed and then further up the

mixing in the bed transports some of the CO_2 back towards the center. This shows that in order to distribute the injected fuel over the entire bed, there is a balance between high and low injection velocities that have to be adapted to the size of the bed material properties as well as the injected fuel for example. There is no apparent explanation to this trend apart from that the flow pattern appears to be different in the splash zone for higher flow velocities. It should also be noted that the bed in general is displaced over a higher height for increasing air flows. A similar trend was not observed for the smaller bed particles.

4.2.5 Bed material variation

As a result of the substantial amount of measurements, a majority of the data for the smaller bed material (120-180 μm) is found in the Appendix section A.2.2. Nevertheless, figure 4.19 is here provided to present a general outlook on the concentration variation in the bed for different air flows.

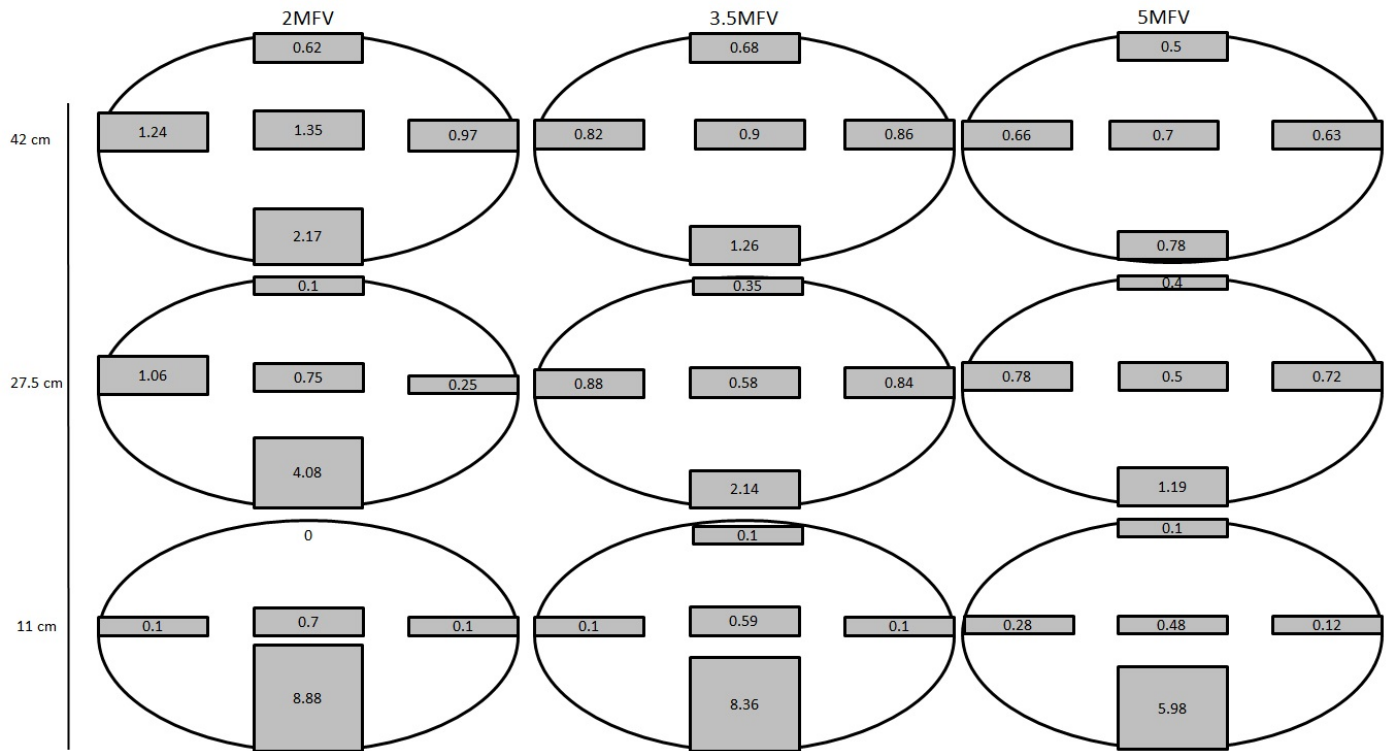


Figure 4.19: Visualization of the concentration of CO_2 in volume-% at different points (not considering dilution effects) in the bed for the three air flows used when injecting at 13.66 SLPM for the smallest particle size (120-180 μm).

For the smaller bed material (120-180 μm), there are numerous similarities between these results and the ones obtained for the medium-sized bed material (250-350 μm). The radial mixing increases in general with an increase in

the air flow. In addition, at the measurement layer at 42 cm, the measured percentages of CO₂ are in general more evenly spread over the cross section as well. Just as for medium-sized material, the most CO₂ is detected at the height of 11 cm considering the dilution effect. Considering these effects also give the same results with a least detected amount of CO₂ for maximum injection of CO₂ and minimal fluidization (2MFV).

However, there are several differences that should be pointed out. The largest amounts of CO₂ detected considering dilution effects is at 3.5MFV and with minimum injection of CO₂. A general observation is that the amount of CO₂ detected in the center of the bed is much smaller with the smaller bed particles. A summation when considering dilution effects of the total amount of CO₂ detected to the left is four times the amount detected to the right for the small bed particles. This itself is actually an indication on that the mixing (dispersion) in the bed with the smaller particles are worse than in the case of the larger particles. This deduction is made since despite the fact that the injection point leans slightly to the left, the result is a smaller difference between left and right side of the bed for the larger particles, which indicates good mixing in the radial direction of the bed.

It is also interesting to see that the amount measured at the center at the height 27.5 cm is often smaller than at the side walls (90 and 270 degrees from the injection point) which in the case with the medium-sized particles never occurred. In addition, the measured amount of CO₂ at the opposite side is in general larger for the larger particles. The amount of CO₂ by the wall of the injection point is significantly larger for the case with the higher injection flows. The reason for that the injected CO₂ spreads more for the larger sized particles appears however not to be because of a larger jet penetration length. It was shown by Musmarra and Filla et al. that smaller bed particles results in longer jet penetration length[51, 54]. The reason here appears to be that the dispersion is faster for the case with larger particles as mentioned by Filla et al.[51].

Regardless of the reason for this difference, based on this observation and the intention to spread out the injected fuel over the entire bed, small bed particles may cause more accumulation of formed volatiles in the bed close to the injection point which then would cause more problems for the system overall. Therefore, large particles should be preferred for this reason but there is naturally also a trade-off since larger-sized particles needs more fluidization and this might be a limiting factor for the system at hand. It is also important to note that too large bed particles results in less thermal feedback (see section 2.7) which means more heat extraction from the freeboard when using solid fuels.

When looking at the sum of amounts of CO₂ measured for the two systems

considering dilution of CO₂, the total amount measured at the lowest flow 4.56 SLPM (corresponding to 14.2 SLPM injection for the medium sized particles) is 60 % higher for the medium-sized particles compared to the smaller particles. For the other flow rates of CO₂, this difference is only 6 and 5 %. A possible reason for that the amount is much less for the smaller particles may be the volume of the fluidized bed itself. The flows for the CO₂-injection have been scaled for the case with the smaller particles based on that the air flows are different. Even though this relation is the same between the two experiments, the volume of gas inside the fluidized from the start is the same. At the smaller flows of CO₂, it seems as if the amount of other gases already located in the bed dilutes the CO₂ and gives a smaller value even though the relation between the flowing CO₂ and air are the same. However, this difference is present for all the fluidization velocities which make it less likely that this is the explanation since an increase of the air flow is more likely to remove these gases.

4.2.6 General observations and possible sources or error

There are several possible sources of error which mainly originates from the fact that by measuring, the process is affected. The fluidization of the bed may be altered by having tubing sticking into the bed. The minimum fluidization flow is determined by fluidizing the bed with no tubes sticking into the bed while the operation takes place with tubes. It is difficult to assess what the impact of these tubes can have on the overall result but an observation that was made when running the system at low fluidization flows such as just above MFV and with measurement tube at (27.5 cm and 42 cm) to the center of the bed was that less bubbles were observed at the top of the bed on the side where the tube was sticking in. The same observations could not be made for the fluidization velocities which were used for the experimental matrix. Another possible source of error is the exact positioning of the sampling tube. This can occur in all directions depending on how the hole is drilled and how the hole is threaded for the tube that will fit through there. Another possible source of error because was unused threaded holes with caps in the fluidized bed. The used caps leave most often a smaller volume on the inside where bed particles may end up which may alter the flow pattern in the fluidized bed. This may relate more to the cases with measurements by the wall. These volumes are however small compared to the total volume of the bed which motivates that these changes can be neglected.

A source of error when measuring the back pressure for the used rotameter for the air flow is the possible pressure drop over the tubing to this point direction under the bed. After passing the rotameter, there are two 90 degree turns before the gas reaches the pressure gage measuring the back pressure. One indication that the measurement is rather accurate is that the experimental and theoretical values for u_{mf} aligned well. When draining the bed after test-

ing, it is observed that bed particles tend to adhere to the surface of the end of the sampling tube. This observation suggest that the bed particles tend to stick to this surface, even without having the pump running, but even more so when the pump is operative. It is difficult to assess how reliable the sampling tube is to retrieve a sample that represents the actual gas mixture in the bed. Another source of concern could be the analyzer used which was not tested against a reference after the initial tests using pure CO_2 and therefore these values may have changed.

Another interesting observation that was made after the experiments without fluidization agent had been conducted was that the concentration of CO_2 remained at a more or less constant level for a few minutes before dropping more dramatically. This indicates that the flow sampled from the bed is smaller compared to the total gas volume in the bed. This also implies that it takes time to drain a non-fluidized bed from the CO_2 and that the flow of CO_2 appears to be plug-flow like. This shows that the risk of having air entering from the top is rather small since air appears not to be diluting the existing gas mixture in the system that fast, even though there are no gases flowing from the bottom of the bed. One basic hinder for that to happen is that the carbon dioxide is heavier than the air.

An interesting observation that was made during the preparation of the tests without operating with fluidization was that despite that only CO_2 was injected into the bed, no values of CO_2 -concentration higher than 80 % were recorded. One possible reason for this could be that there is some air in the bed that does not escape the bed no matter how much CO_2 is injected into the bed. Another possible reason is that there are still leaks of air into the system. A more far-fetched reason could be that the analyzer is not working properly (the flow is too small to detect all the CO_2). Since the oxygen indicator on the analyzer was proved to be working poorly when sampling air in the lab, it was not possible to get an indication on the oxygen level that the remaining amount of gas would be air (and that air mixed with the CO_2 along the way). Since only the relative quantities are of importance in these experiments, this was not seen as a source of concern for the validity of the measurements.

Since the measurement of the low pressure side of the differential pressure gauge over the fluidized bed is not at the very bottom of the bed, the actual differential pressure over the bed is most likely slightly higher. Hopefully this did not change the trend of the differential pressure with varying flow of fluidizing agent. The temperature in the lab is not controlled which means that the fluidization properties may change slightly. Another source of concern is that the bed material is exchanged several times and it is likely that other particles will end up in the bed during this process. Another possible source of error is that the use of the bed material may suffer from attrition due to its use which may affect the results of the experiments. This was not verified

during the experiment.

When it comes to directly relating the results of the fluidized bed to the fuel reactor in the CLC system, the dimensions are different, other bed particles are used and in addition the fuel reactor of the lab-scale CLC system has a tube in the middle which therefore is likely to alter the fluidization behaviour from the fluidized bed. However, the fluidized bed system can still be used to understand what factors governs the circulation of the fuel in the fuel reactor.

4.2.7 Recommendations for further research

The main future goal with this research is to use the same kind of experimental matrix and setup for injection of dry ice. This could then be done with the method indicated in the method section to control the position at which the gaseous CO_2 is released. To simulate the devolatilization process as well as possible it would be useful to look into how much volume of gas that is generated for each solid fuel kind. A similar study could then be done for the case of dry ice to know which fuels this technique might apply the most for. An important consideration for future experiments should be the differences between the dry ice and the devolatilizing solid particle. Since all of the injected dry ice will sublime, no solids remain in the fluidized bed, as opposed to the case of devolatilization where char remains in the bed which has a major impact on the fluid dynamics as well as the possible reactions in the system. If possible it would be interesting to inject solids with a similar size and properties such as density compared to the solid fuel that remains after devolatilization with the dry ice. This could then be done to observe if the same gas plume behaviour of generated gas carrying the solids upwards in the fluidized bed which has been observed for solid fuels. In order to observe the dynamics of the gas plume (volatiles bubbles with fuel particle inside), x-ray imaging could be used to observe the dynamics of fuel particles, volatiles and the bed material also for higher fluidization velocities than was attempted by Bruni et al.[45]. When comparing the results from the simulation with dry ice it would also be needed to estimate the difference in properties of CO_2 compared to the gas mixture that makes up the volatiles. This could then provide results which are more applicable for the real case scenario.

Apart from the direct focus on the simulation of the devolatilization of a solid fuel, there are, as indicated in the Method section several more parameters that could be looked into which were omitted in this thesis work. Among them is the injection direction of the gas. This could even be interesting for the simulation of devolatilization since because of the gas expansion that takes place as a result of the formation of volatiles. By injecting the gas in different directions separately or even combining these could provide a more complete picture of the fluid dynamics even without injecting the dry ice. In addition to

this alternative, the injection position in the bed could be alternated. It would then be interesting to see if the system would be able to obtain a circulation of the injected gas or gas from solid fuel conversion is found at the bottom of the bed. This study has also limited the measurements to a selected number of points which could be increased to obtain a more complete picture of the distribution over the bed. The concentration of CO_2 is in this experiment only measured at selected locations of the bed which means that this does not give a full coverage of the concentration profile of CO_2 in the bed. The system should be tested for a wider range of bed materials to get a better understanding of what impact the different bed particle characteristics have on the system overall. A more specific suggestion would be to use SiC-particles to make the results easier to relate to the future CLC system. It would also be interesting to make a new cold flow model with a more specific design and geometries of a fuel reactor in a CLC system and look at the fluid dynamics and mixing in that system.

The bottom piece in acrylic has been damaged in previous experiments as well as during these experiments and it is a vulnerable part of the equipment. Since it is not a part that is important to observe from the outside, this piece should be exchanged for a metal piece at the bottom of bed to provide better support. This could then decrease the risk of leaks at this part of the bed as well as make it possible to run the system at higher air flow rates. This could then possibly allow the same kind of gaseous injection study for the largest sized particles (500-710 μm). Apart from a new bottom plate a new rotameter would have to be found.

Even though the flows of air and CO_2 were adapted to the minimum fluidization velocity, it could be interesting to look into the impact of using the flow rates of the larger sized particles on the smaller bed particles to see how the system then operates.

A parameter that was neglected in the present setup was the bed height which was defined to 15 inches (38.1 cm). It could be interesting to investigate other bed heights.

5

Conclusions

The dual-bed chemical looping system was initially operated with alumina as bed material and the measured pressures were in general higher than the simulated pressures using this material. Based on the simulated circulation rates the measured amount was lower than expected for low air flows but higher for high air flows. Silicon Carbide was circulating well in the lab-scale system even though the values were not as high as when using alumina. One explanation appears to be that the lower density means that particles tend to accumulate in the lower loop seal which in turn seems to be limiting the circulation rate, especially at higher air flows through the air reactor. The pressures were similar for operating with both bed materials and the circulation rate increased in general with the air reactor flow rate as well as the bed material volume used. The pressure was in general higher when using alumina which to a major extent can be explained by the higher density. Higher bed volumes resulted in a higher circulation rates overall and the maximum circulation rates were found using the highest amount of bed material. The points at which the maximum circulation rate was observed decreased with the bed material quantity. It was possible to identify suitable operating points for both bed materials.

The tests on the bubbling fluidized bed showed that the theoretical minimum fluidization velocities corresponded well with the determined velocities in practice. For injection at gaseous CO_2 it was shown that larger air flows to fluidize the bed gave overall a better mixing of the injected gas in the bed. Injection of gaseous CO_2 proved that the gas penetration length has a large impact on the radial mixing of the injected gas in the lower part of the bed. The jet velocity should be high enough to spread out the injected fuel further down in the bed. Larger particles contributed to a smaller jet penetration length but despite that a better radial mixing thanks to a better dispersion of the injected gas. The literature study showed the need to study the gas plume formation and indicated for example that the fuel should be introduced at several places at the bottom of the bed to create a better mixing of the injected fuel, especially at the bottom of the bed. There is a good potential to use the established experimental setup to inject dry ice to simulate the fluid dynamics when injecting a devolatilizing solid fuel to a fluidized bed and if possible verify the observations in this study. This knowledge could then be directly applied to the final system for solid-fueled CLOU with SiC coated with copper.

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A

Appendix 1

A conversion table is provided here to simplify conversion to SI-units.

Table A.1: Conversion table from U.S customary units to SI units.

U.S customary unit	SI unit
1 SCFM = 60 SCFH (Standard Cubic Feet per Hour)	28.3 SLM (Standard Liters per Minute)
1 psi (pound square inch)	6.89 kPa

A.1 Dual-bed chemical looping system

A.1.1 Simulation data

Table A.2: Simulated pressures at six chosen locations in the CLC system for 12.5 kg alumina.

True flow rate AR [SLPM]	396.44	509.70	566.34	622.97	679.60
Simulated Pressure AR [kPa]	2.68	2.73	2.75	2.24	2.93
Simulated Pressure Riser [kPa]	0.17	0.32	0.42	0.53	0.67
Simulated Pressure top riser [kPa]	0.12	0.23	0.30	0.40	0.53
Simulated Pressure bottom cyclone [kPa]	0.06	0.10	0.13	0.19	0.28
Simulated Pressure upper LS [kPa]	6.49	7.06	7.34	7.72	8.01
Simulated Pressure lower LS [kPa]	4.33	4.68	4.94	5.03	5.14

Table A.3: Simulated circulation rates at six chosen locations in the CLC system for 12.5 kg alumina.

True flow rate AR [SLPM]	396.44	509.70	566.34	622.97	679.60
Average CR [kg/min]	0.58	0.94	0.96	0.92	0.88

A.1.2 Experimental results - Alumina

Table A.4: Results from testing with the CLC system with 12.5 kg of alumina (6.01 liters) not considering the back pressure of the air reactor rotameter.

AR flow rate [SLPM]	438.68	521.88	664.78	842.18	926.40	1041.25
Average CR [kg/min]	0.15	0.30	1.39	2.48	2.44	2.37
Standard deviation [kg/min]	0.01	0.05	0.18	0.29	0.24	0.26

Table A.5: Results from initial testing with the CLC system with 12.5 kg of alumina (6.01 liters) considering the back pressure of the air reactor rotameter.

AR flow rate [SLPM]	396.44	453.07	509.70	566.34	622.97	679.60
Average CR [kg/min]	0.05	0.27	0.37	0.95	1.62	2.15
Standard deviation [kg/min]	0.01	0.03	0.03	0.11	0.25	0.26
Pressure AR [kPa]	1.74	2.49	2.80	3.92	3.92	5.86
Pressure Riser [kPa]	0.69	1.37	1.74	2.55	2.74	3.49
Pressure top riser [kPa]	0.69	1.25	1.74	2.43	2.37	2.62
Pressure bottom cyclone [kPa]	0.37	0.81	1.06	1.56	1.62	2.12
Pressure upper LS [kPa]	6.23	6.48	6.60	6.98	7.23	7.60
Pressure lower LS [kPa]	3.99	4.73	5.48	5.73	6.98	8.47

Table A.6: Results from testing with the CLC system with 13 kg of alumina (6.25 liters) considering the back pressure of the air reactor rotameter.

AR flow rate [SLPM]	396.44	453.07	509.70	566.34	622.97	679.60
Average CR [kg/min]	0.11	0.90	1.22	2.69	3.21	3.77
Standard deviation [kg/min]	0.01	0.12	0.09	0.43	0.46	0.24
Pressure AR [kPa]	2.49	2.99	3.99	4.98	5.48	6.48
Pressure Riser [kPa]	0.62	1.12	1.62	2.24	2.49	2.99
Pressure top riser [kPa]	0.25	0.56	0.75	1.25	1.25	1.74
Pressure bottom cyclone [kPa]	0.44	0.75	1.12	1.50	1.62	2.12
Pressure upper LS [kPa]	6.48	6.73	7.23	7.23	8.22	8.10
Pressure lower LS [kPa]	4.49	5.23	6.23	7.48	7.72	8.72

Table A.7: Results from testing with the CLC system with 13.5 kg of alumina (6.49 liters) considering the back pressure of the air reactor rotameter.

AR flow rate [SLPM]	396.44	453.07	509.70	566.34	622.97	679.60
Average CR [kg/min]	0.31	1.83	3.81	4.97	5.01	4.01
Standard deviation [kg/min]	0.15	0.88	1.83	2.39	2.41	1.93
Pressure AR [kPa]	2.12	3.24	3.61	4.36	6.23	6.35
Pressure Riser [kPa]	0.62	1.62	1.99	2.74	2.87	3.49
Pressure top riser [kPa]	0.44	1.06	1.37	1.99	1.74	1.87
Pressure bottom cyclone [kPa]	0.37	0.87	1.12	1.74	1.74	1.99
Pressure upper LS [kPa]	6.48	7.23	7.48	8.35	8.22	8.47
Pressure lower LS [kPa]	4.86	6.35	6.60	7.97	8.10	8.72

Table A.8: Results from testing with the CLC system with 14 kg of alumina (6.73 liters) considering the back pressure of the air reactor rotameter.

AR flow rate [SLPM]	396.44	453.07	509.70	566.34	622.97	679.60
Average CR [kg/min]	0.64	2.02	3.77	5.66	5.31	4.34
Standard deviation [kg/min]	0.31	0.97	1.81	2.72	2.55	2.09
Pressure AR [kPa]	2.43	3.74	4.73	5.23	5.98	7.23
Pressure Riser [kPa]	0.87	1.25	1.87	2.37	2.87	3.24
Pressure top riser [kPa]	0.37	0.69	1.00	1.37	1.50	1.87
Pressure bottom cyclone [kPa]	0.50	0.56	1.06	1.37	1.62	2.12
Pressure upper LS [kPa]	6.85	7.10	7.72	7.85	9.34	9.47
Pressure lower LS [kPa]	5.36	6.10	6.98	7.85	8.47	9.22

A.1.3 Experimental results - Silicon carbide

Table A.9: Results from testing with the CLC system with 9.1 kg of silicon carbide (6.01 liters) considering the back pressure of the air reactor rotameter.

AR flow rate [SLPM]	396.44	453.07	509.70	566.34	622.97	679.60
Average CR [kg/min]	0.02	0.12	0.22	0.90	0.81	1.53
Standard deviation [kg/min]	0.00	0.03	0.05	0.14	0.09	0.10
Pressure AR [kPa]	1.50	2.49	2.99	3.99	4.49	5.48
Pressure Riser [kPa]	0.62	1.12	1.50	2.24	2.12	2.99
Pressure top riser [kPa]	0.31	0.56	0.81	1.12	1.12	1.62
Pressure bottom cyclone [kPa]	0.44	0.87	1.12	1.62	1.56	2.12
Pressure upper LS [kPa]	4.36	4.73	4.98	5.23	5.23	5.73
Pressure lower LS [kPa]	3.24	3.99	4.61	5.61	5.98	7.23

Table A.10: Results from testing with the CLC system with 9.49 kg of silicon carbide (6.25 liters) considering the back pressure of the air reactor rotameter.

AR flow rate [SLPM]	396.44	453.07	509.70	566.34	622.97	679.60
Average CR [kg/min]	0.04	0.23	0.57	1.02	1.27	1.99
Standard deviation [kg/min]	0.01	0.04	0.22	0.20	0.17	0.37
Pressure AR [kPa]	1.99	2.49	2.99	3.99	4.24	5.73
Pressure Riser [kPa]	0.50	0.75	1.00	1.50	1.50	2.12
Pressure top riser [kPa]	0.37	0.62	0.75	1.06	1.25	1.62
Pressure bottom cyclone [kPa]	0.44	0.87	1.00	1.37	1.50	2.12
Pressure upper LS [kPa]	4.61	4.86	5.23	5.48	5.61	5.86
Pressure lower LS [kPa]	3.49	4.11	4.73	5.73	6.23	7.72

Table A.11: Results from testing with the CLC system with 9.85 kg of silicon carbide (6.49 liters) considering the back pressure of the air reactor rotameter.

AR flow rate [SLPM]	396.44	453.07	509.70	566.34	622.97	679.60
Average CR [kg/min]	0.09	0.53	0.72	1.53	2.29	2.28
Standard deviation [kg/min]	0.01	0.18	0.14	0.51	0.28	0.27
Pressure AR [kPa]	1.99	2.74	3.49	4.24	4.73	5.98
Pressure Riser [kPa]	0.37	0.62	1.00	1.37	1.50	2.24
Pressure top riser [kPa]	0.31	0.69	0.87	1.25	1.37	1.74
Pressure bottom cyclone [kPa]	0.37	0.87	0.93	1.50	1.62	1.99
Pressure upper LS [kPa]	4.98	5.11	5.36	5.73	5.86	6.10
Pressure lower LS [kPa]	3.61	4.49	4.98	6.23	6.48	7.72

Table A.12: Results from testing with the CLC system with 10.2 kg of silicon carbide (6.73 liters) considering the back pressure of the air reactor rotameter.

AR flow rate [SLPM]	396.44	453.07	509.70	566.34	622.97	679.60
Average CR [kg/min]	0.22	0.64	1.47	2.77	2.11	2.24
Standard deviation [kg/min]	0.05	0.12	0.13	0.31	0.45	0.28
Pressure AR [kPa]	2.24	2.99	3.49	4.73	5.23	5.98
Pressure Riser [kPa]	0.37	0.62	1.00	1.50	1.68	1.99
Pressure top riser [kPa]	0.37	0.56	0.75	1.25	1.37	1.99
Pressure bottom cyclone [kPa]	0.50	0.69	0.87	1.37	1.62	2.12
Pressure upper LS [kPa]	4.98	5.36	5.61	6.48	6.23	6.73
Pressure lower LS [kPa]	3.99	4.49	5.36	5.98	6.98	7.72

A.2 Bubbling fluidized bed

A.2.1 Minimum Fluidization calculations

Table A.13: Additional parameters used for the calculation of the theoretical value of the minimum fluidization velocity.

Temperature [K]	293.15
Dynamic viscosity of the gas [kg/m·s]	$1.81 \cdot 10^{-5}$
Density of the gas [kg/m ³]	1.206
C_1	27.2
C_2	0.0408
Density particle [kg/m ³]	2500
Gravitational acceleration [m/s ²]	9.8

Table A.14: Differential pressure (dP) over the fluidized bed for varying air flows (notified with the superficial velocity u_0 and with the chosen estimation of the minimum fluidization velocity in bold for each bed material.

Small particles (120-180 μm)		Medium particles (250-350 μm)		Large particles (500-710 μm)	
dP [kPa]	u_0	dP [kPa]	u_0	dP [kPa]	u_0
0	0	0	0	0	0
1.121	0.007	0.997	0.018	0.623	0.035
1.370	0.009	1.495	0.026	0.872	0.053
1.744	0.011	1.993	0.035	1.121	0.070
2.118	0.012	2.616	0.044	1.370	0.088
2.492	0.014	3.364	0.053	1.620	0.105
2.741	0.016	3.862	0.061	1.993	0.123
2.990	0.018	4.236	0.070	2.243	0.140
3.364	0.019	4.361	0.074	2.616	0.158
3.613	0.021	4.361	0.075	2.866	0.175
3.987	0.023	4.485	0.081	3.115	0.193
4.361	0.025	4.734	0.088	3.364	0.210
4.485	0.026	4.734	0.096	3.738	0.228
4.485	0.028	4.734	0.105	4.111	0.245
4.485	0.030	4.734	0.123	4.236	0.254
4.485	0.032	4.734	0.140	4.361	0.263
4.485	0.035	4.734	0.151	4.485	0.272
4.485	0.037	4.734	0.158	4.485	0.280
4.485	0.039	4.734	0.175	4.610	0.289
4.485	0.042	4.734	0.193	4.734	0.298
4.485	0.046	4.734	0.210	4.921	0.307
4.485	0.049	4.734	0.228	4.921	0.315
4.485	0.053	4.734	0.245	4.921	0.324
4.485	0.061	4.734	0.263	4.921	0.333
4.485	0.070	4.734	0.280	4.921	0.350
				4.921	0.368
				4.921	0.385
				4.921	0.403
				4.921	0.421

A.2.2 Experimental work with small particles (120-180 μm)

A.2.2.1 Graphs for varying air flows

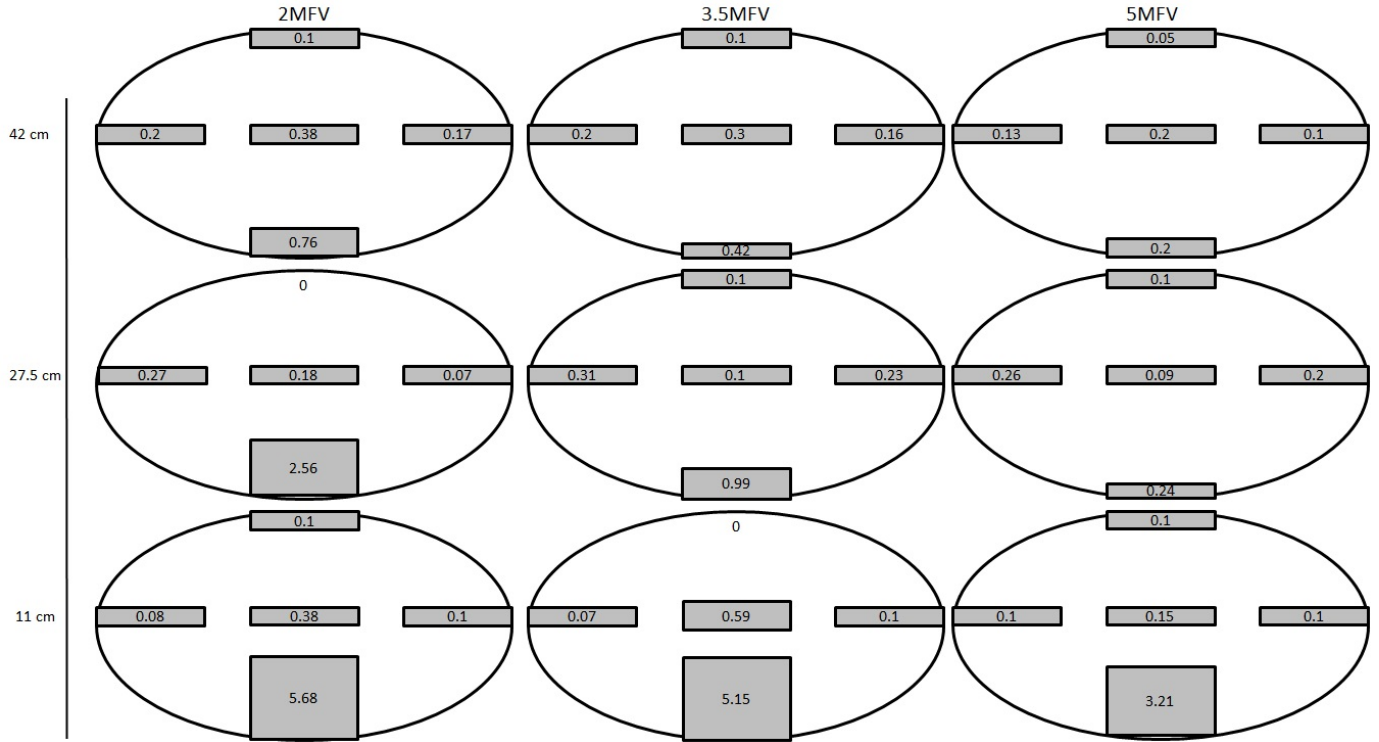


Figure A.1: Visualization of the concentration of CO₂ in volume-% at different points in the bed for the three air flows used when injecting at 4.56 SLPM for the smallest particle size (120-180 μm).

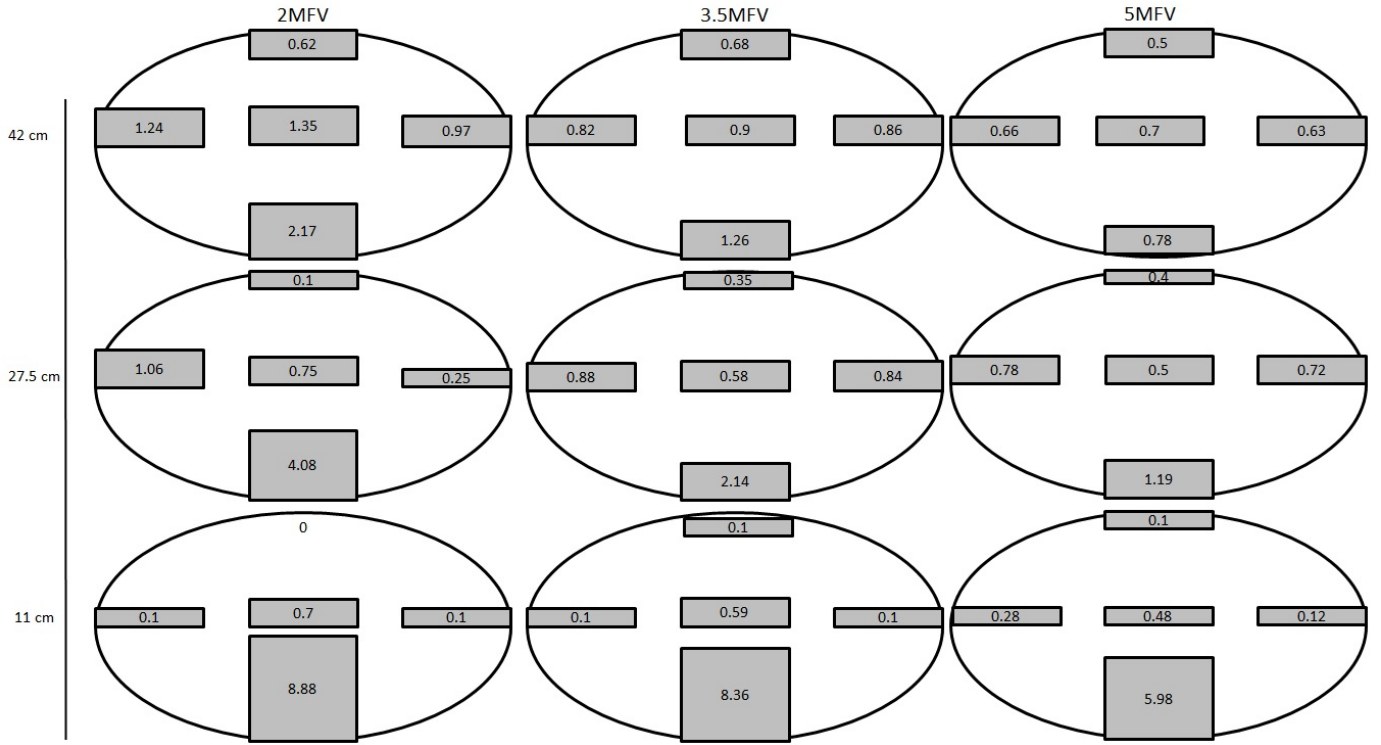


Figure A.2: Visualization of the concentration of CO₂ in volume-% at different points in the bed for the three air flows used when injecting at 13.66 SLPM for the smallest particle size (120-180 μm).

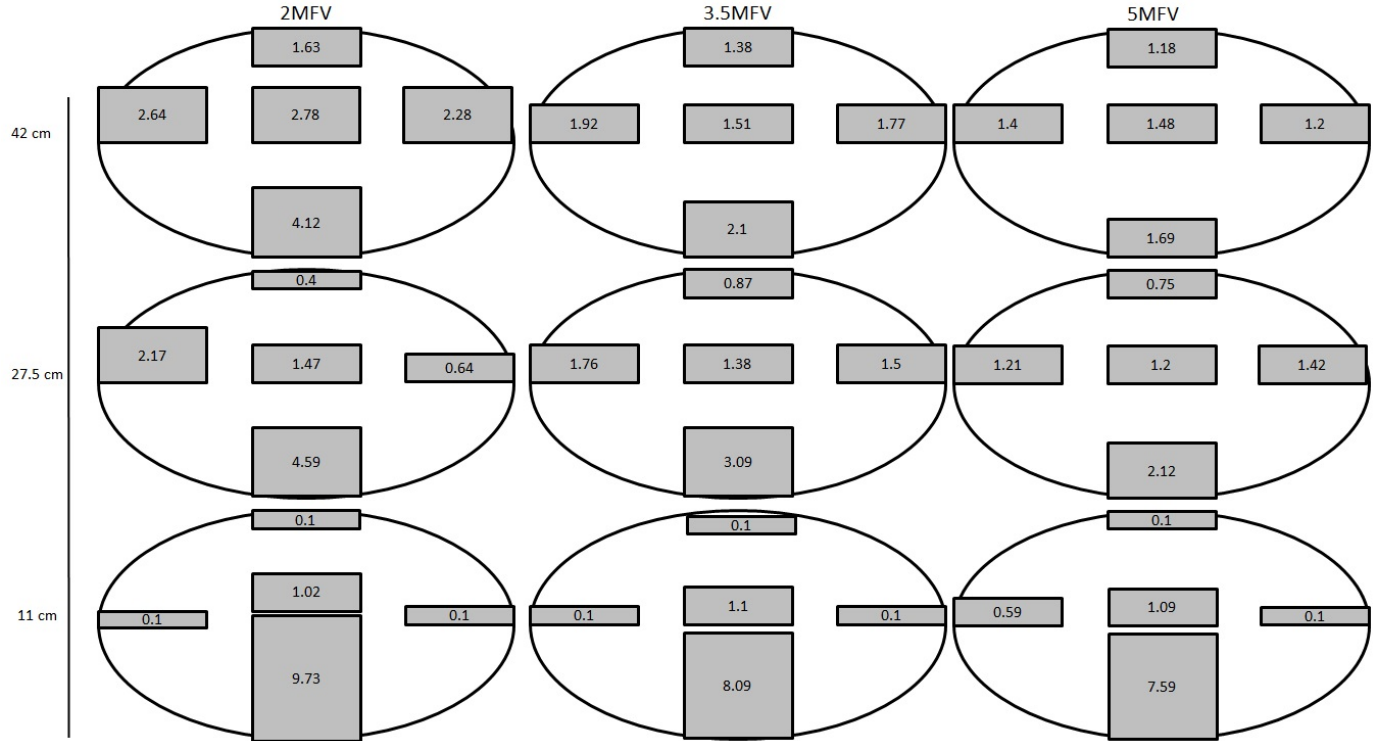


Figure A.3: Visualization of the concentration of CO₂ in volume-% at different points in the bed for the three air flows used when injecting at 22.77 SLPM for the smallest particle size (120-180 μm).

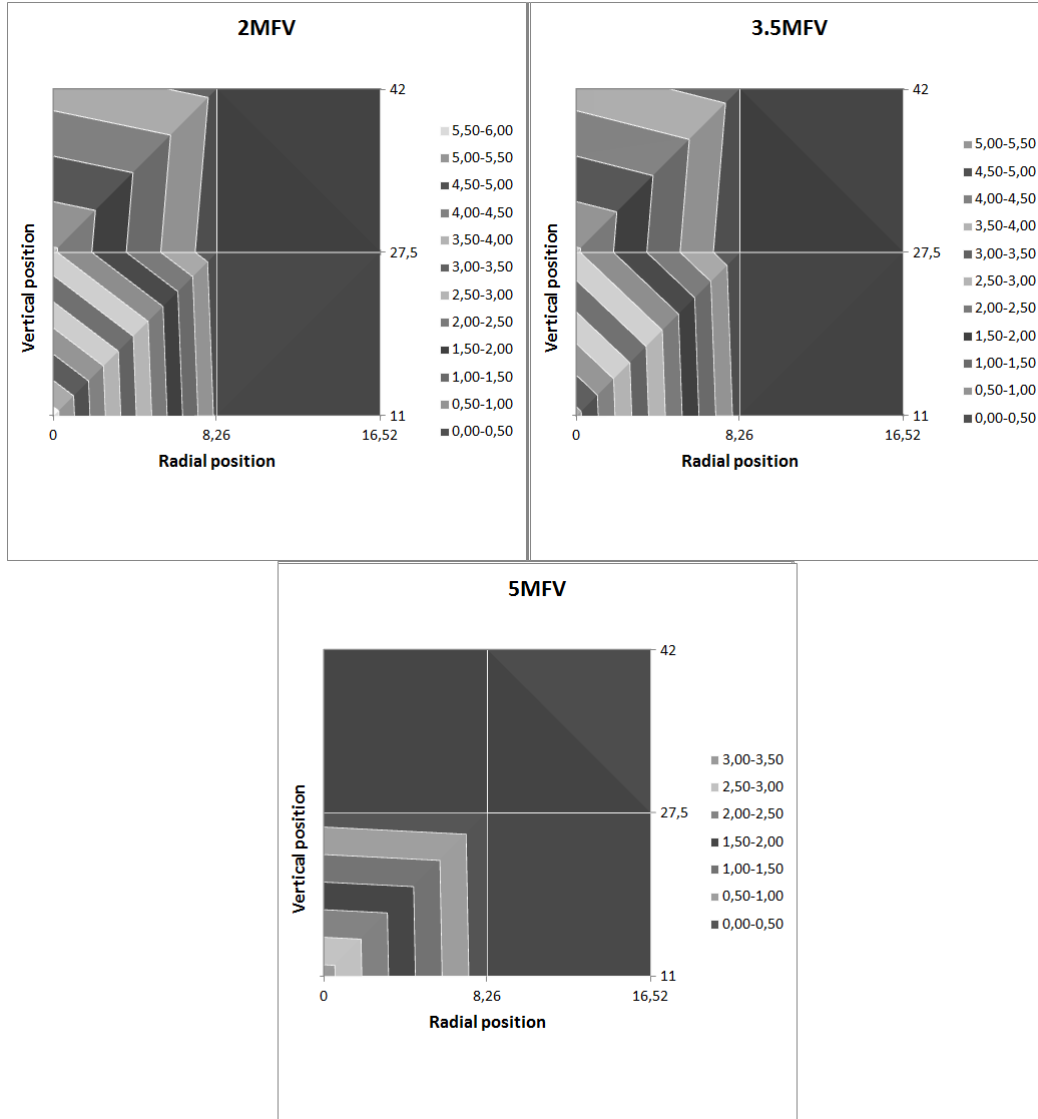


Figure A.4: Contour plots of the concentration of CO₂ in volume-% across the cross section in the direction of the injection port for CO₂-injection of 4.56 SLPM for the medium-sized particles (120-180 μm) for air flows in the range of 2MFV to 5MFV.

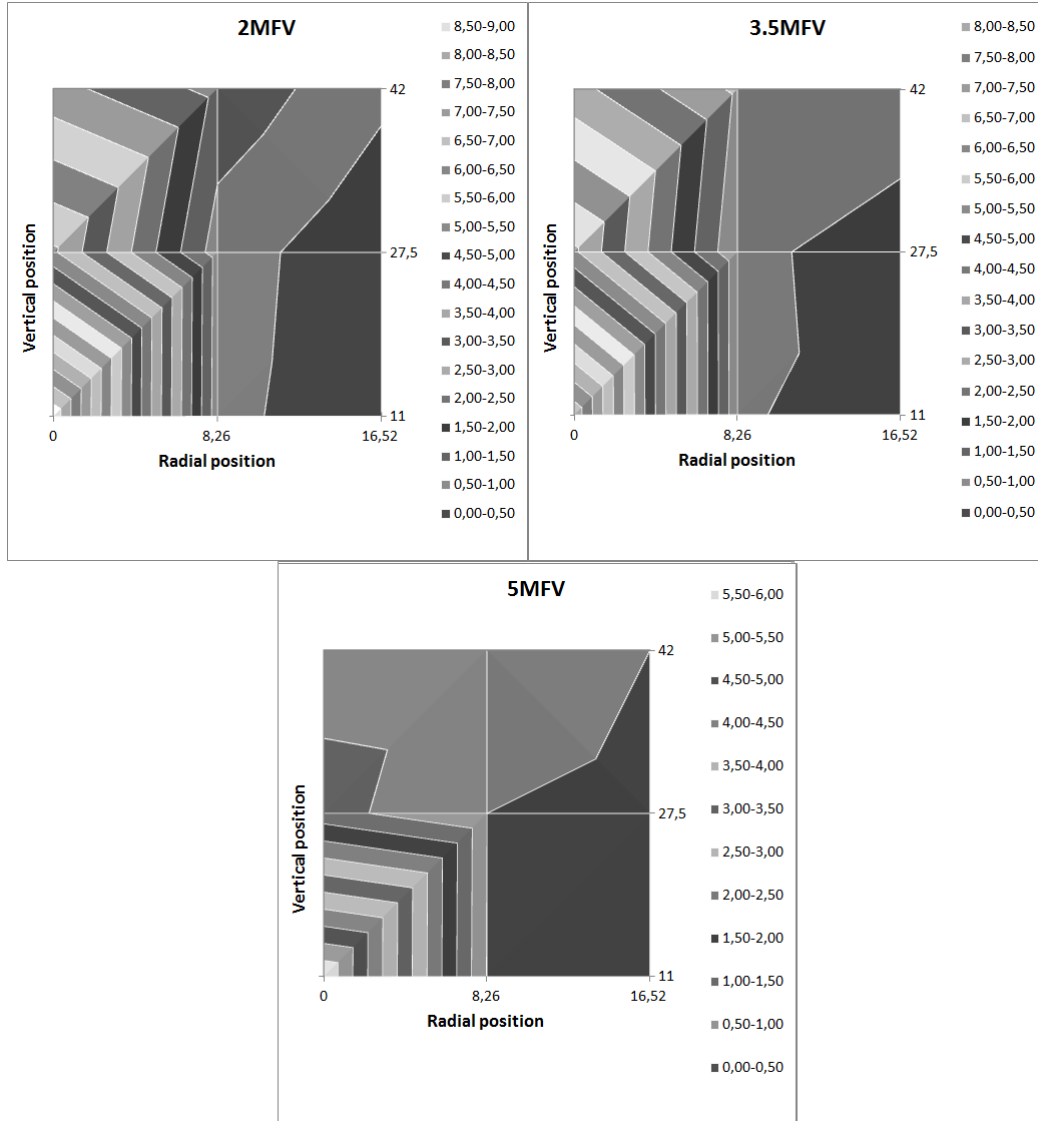


Figure A.5: Contour plots of the concentration of CO₂ in volume-% across the cross section in the direction of the injection port for CO₂-injection of 13.66 SLPM for the medium-sized particles (120-180 μm) for air flows in the range of 2MFV to 5MFV.

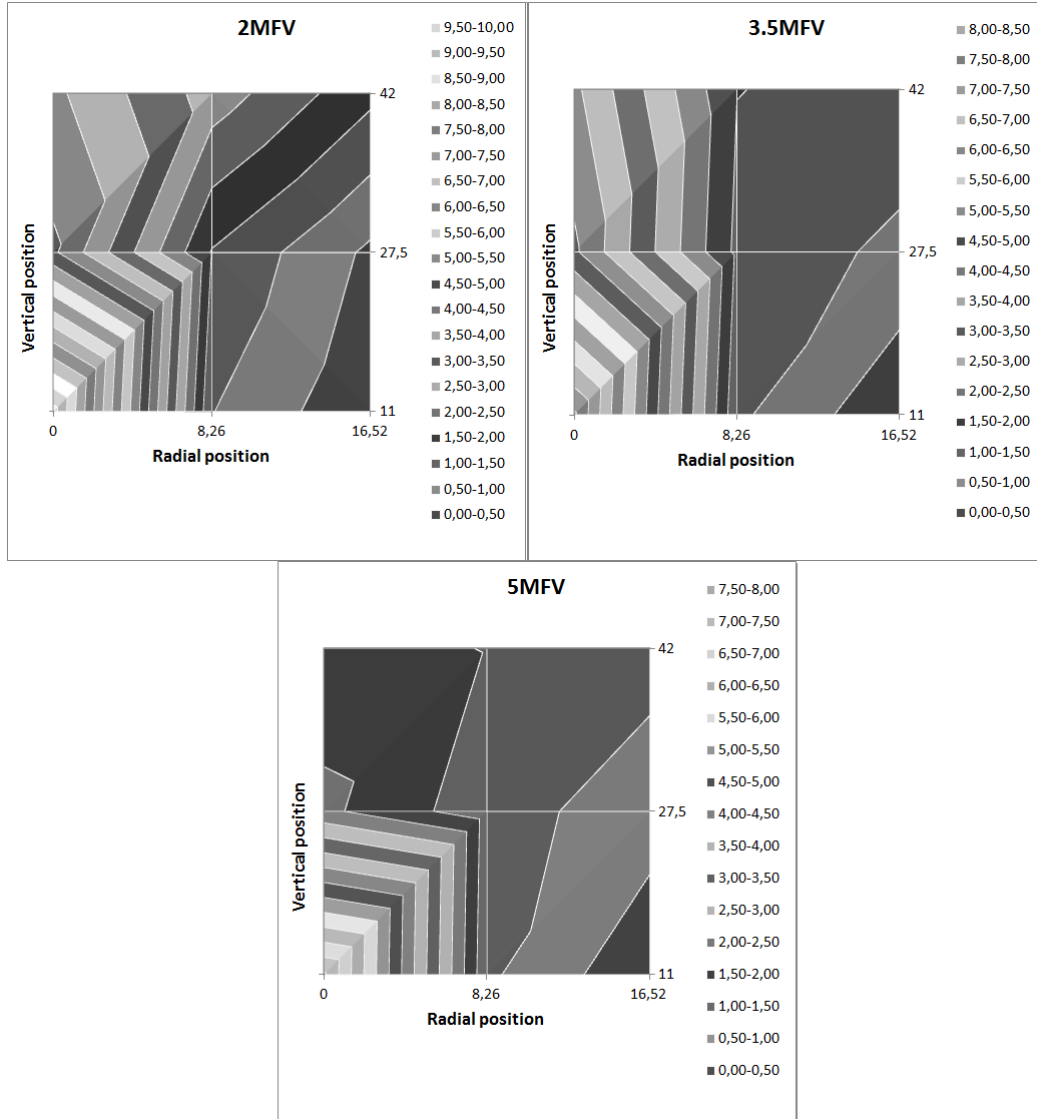


Figure A.6: Contour plots of the concentration of CO₂ in volume-% across the cross section in the direction of the injection port for CO₂-injection of 22.77 SLPM for the medium-sized particles (120-180 μm) for air flows in the range of 2MFV to 5MFV.

A.2.2.2 Collection of all experimental data and aggregated sums of measured CO₂

Here follows a summary of the scaled individual values as well as the sum of the scaled values for each air flow, CO₂-flow and measurement layer. Note that all measured values are scaled towards air flow of 2MFV and injection of 4.56 SLPM of CO₂.

Table A.15: Scaled measurement values in volume-% of CO₂ for injection with 4.56 SLPM of CO₂ and for varying flows of air as well as aggregated amounts of CO₂ considering the dilution effects for the small particles (120-180 μm).

CO₂ Injection at 4.56 SLPM	2 MFV	3.5 MFV	5 MFV	
Vertical 11 - Wall 0	5.68	9.01	8.02	
Vertical 11 - Wall 90	0.10	0.18	0.25	
Vertical 11 - Wall 180	0.10	0.00	0.25	
Vertical 11 - Wall 270	0.08	0.12	0.25	
Vertical 11 - Centre	0.38	0.48	0.38	
Vertical 27.5 - Wall 0	2.56	1.74	0.60	
Vertical 27.5 - Wall 90	0.07	0.39	0.50	
Vertical 27.5 - Wall 180	0.00	0.18	0.25	
Vertical 27.5 - Wall 270	0.27	0.54	0.65	
Vertical 27.5 - Centre	0.18	0.18	0.23	
Vertical 42 - Wall 0	0.76	0.73	0.50	
Vertical 42 - Wall 90	0.17	0.28	0.25	
Vertical 42 - Wall 180	0.10	0.18	0.13	
Vertical 42 - Wall 270	0.20	0.35	0.31	
Vertical 42 - Centre	0.38	0.53	0.5	
	Scaled sum	Scaled sum	Scaled sum	Sum each layer
Scaled sum Vertical 11 cm	6.34	9.79	9.15	25.27
Scaled sum Vertical 27.5 cm	3.08	3.02	2.23	8.32
Scaled sum Vertical 42 cm	1.61	2.06	1.69	5.35
Sum for each air flow	11.03	14.86	13.06	$\Sigma = 38.95$

Table A.16: Scaled measurement values in volume-% of CO₂ for injection with 13.66 SLPM of CO₂ and for varying flows of air as well as aggregated amounts of CO₂ considering the dilution effects for the small particles (120-180 μm).

CO₂ Injection at 13.66 SLPM	2 MFV	3.5 MFV	5 MFV	
Vertical 11 - Wall 0	2.96	4.88	4.98	
Vertical 11 - Wall 90	0.03	0.06	0.10	
Vertical 11 - Wall 180	0.00	0.06	0.08	
Vertical 11 - Wall 270	0.23	0.06	0.24	
Vertical 11 - Centre	1.36	0.35	0.40	
Vertical 27.5 - Wall 0	1.36	1.25	0.99	
Vertical 27.5 - Wall 90	0.08	0.49	0.60	
Vertical 27.5 - Wall 180	0.03	0.20	0.33	
Vertical 27.5 - Wall 270	0.35	0.51	0.65	
Vertical 27.5 - Centre	0.25	0.34	0.42	
Vertical 42 - Wall 0	0.72	0.73	0.65	
Vertical 42 - Wall 90	0.32	0.50	0.53	
Vertical 42 - Wall 180	0.21	0.40	0.42	
Vertical 42 - Wall 270	0.41	0.48	0.55	
Vertical 42 - Centre	0.45	0.53	0.58	
	Scaled sum	Scaled sum	Scaled sum	Sum each layer
Scaled sum Vertical 11 cm	3.26	5.40	5.79	14.45
Scaled sum Vertical 27.5 cm	2.08	2.79	2.99	7.86
Scaled sum Vertical 42 cm	2.11	2.63	2.72	7.47
Sum for each air flow	7.45	10.82	11.50	$\Sigma = 29.77$

Table A.17: Scaled measurement values in volume-% of CO₂ for injection with 22.77 SLPM of CO₂ and for varying flows of air as well as aggregated amounts of CO₂ considering the dilution effects for the small particles (120-180 μm).

CO₂ Injection at 22.77 SLPM	2 MFV	3.5 MFV	5 MFV	
Vertical 11 - Wall 0	1.95	2.83	3.80	
Vertical 11 - Wall 90	0.02	0.04	0.05	
Vertical 11 - Wall 180	0.02	0.04	0.05	
Vertical 11 - Wall 270	0.02	0.04	0.30	
Vertical 11 - Centre	1.20	0.39	0.55	
Vertical 27.5 - Wall 0	0.92	1.08	1.06	
Vertical 27.5 - Wall 90	0.13	0.53	0.71	
Vertical 27.5 - Wall 180	0.08	0.30	0.38	
Vertical 27.5 - Wall 270	0.43	0.62	0.60	
Vertical 27.5 - Centre	0.43	0.48	0.60	
Vertical 42 - Wall 0	0.82	0.74	0.85	
Vertical 42 - Wall 90	0.46	0.62	0.60	
Vertical 42 - Wall 180	0.33	0.48	0.59	
Vertical 42 - Wall 270	0.53	0.67	0.70	
Vertical 42 - Centre	0.56	0.53	0.74	
	Scaled sum	Scaled sum	Scaled sum	Sum each layer
Scaled sum Vertical 11 cm	2.21	3.32	4.74	10.27
Scaled sum Vertical 27.5 cm	1.85	3.01	3.35	8.21
Scaled sum Vertical 42 cm	2.69	3.03	3.48	9.20
Sum for each air flow	6.75	9.37	11.56	$\Sigma = 27.68$

A.2.3 Experimental work with medium-sized particles (250-350 μm)

A.2.3.1 Graphs for varying air flows

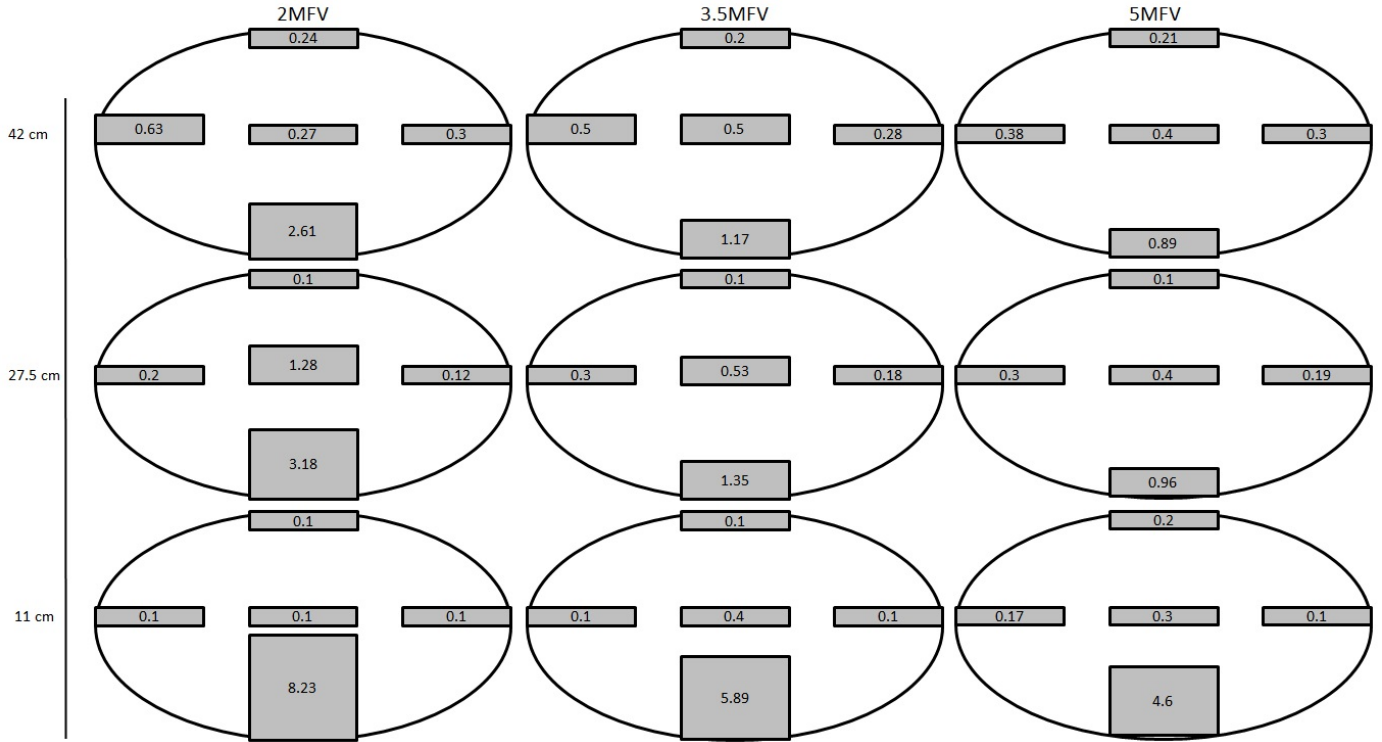


Figure A.7: Visualization of the concentration of CO₂ in volume-% at different points in the bed for the three air flows used when injecting at 14.2 SLPM for the medium-sized bed particles (250-350 μm).

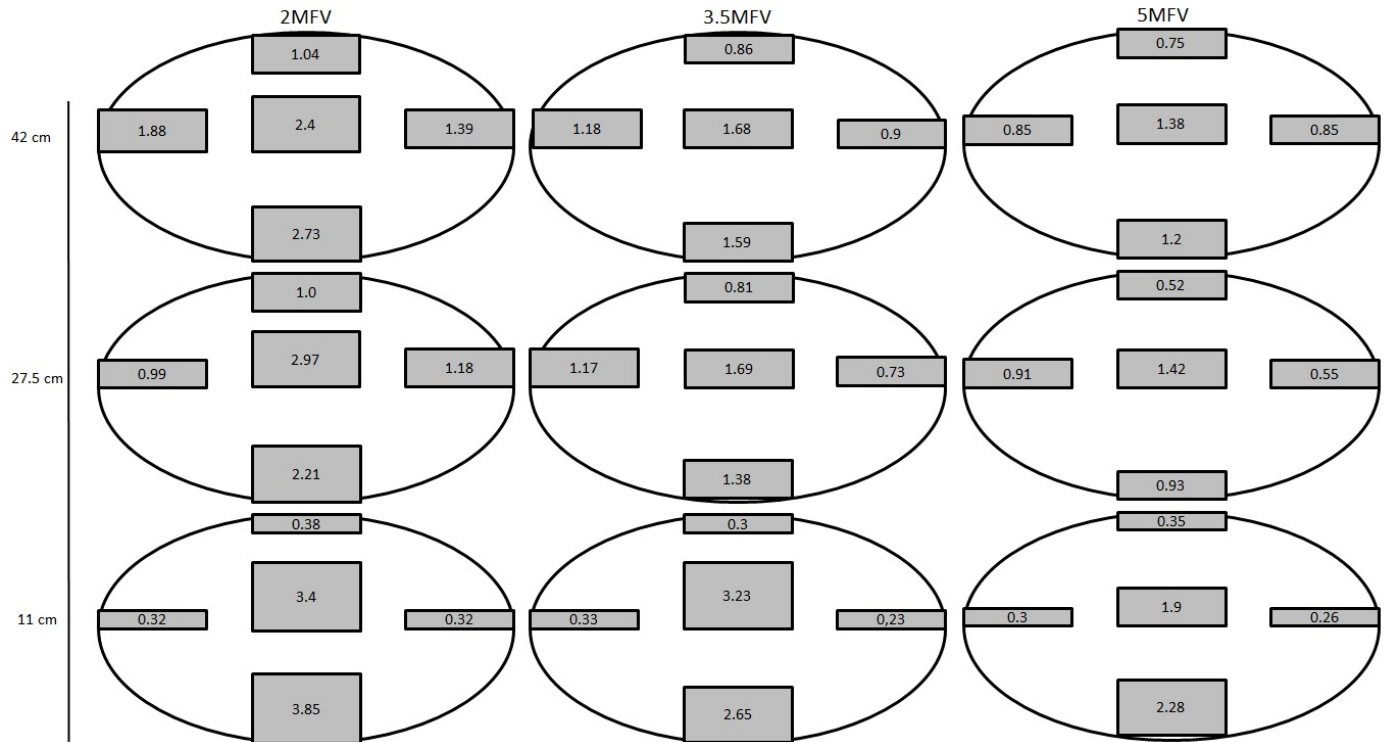


Figure A.8: Visualization of the concentration of CO₂ in volume-% at different points in the bed for the three air flows used when injecting at 42.5 SLPM for the medium-sized bed particles (250-350 μm).

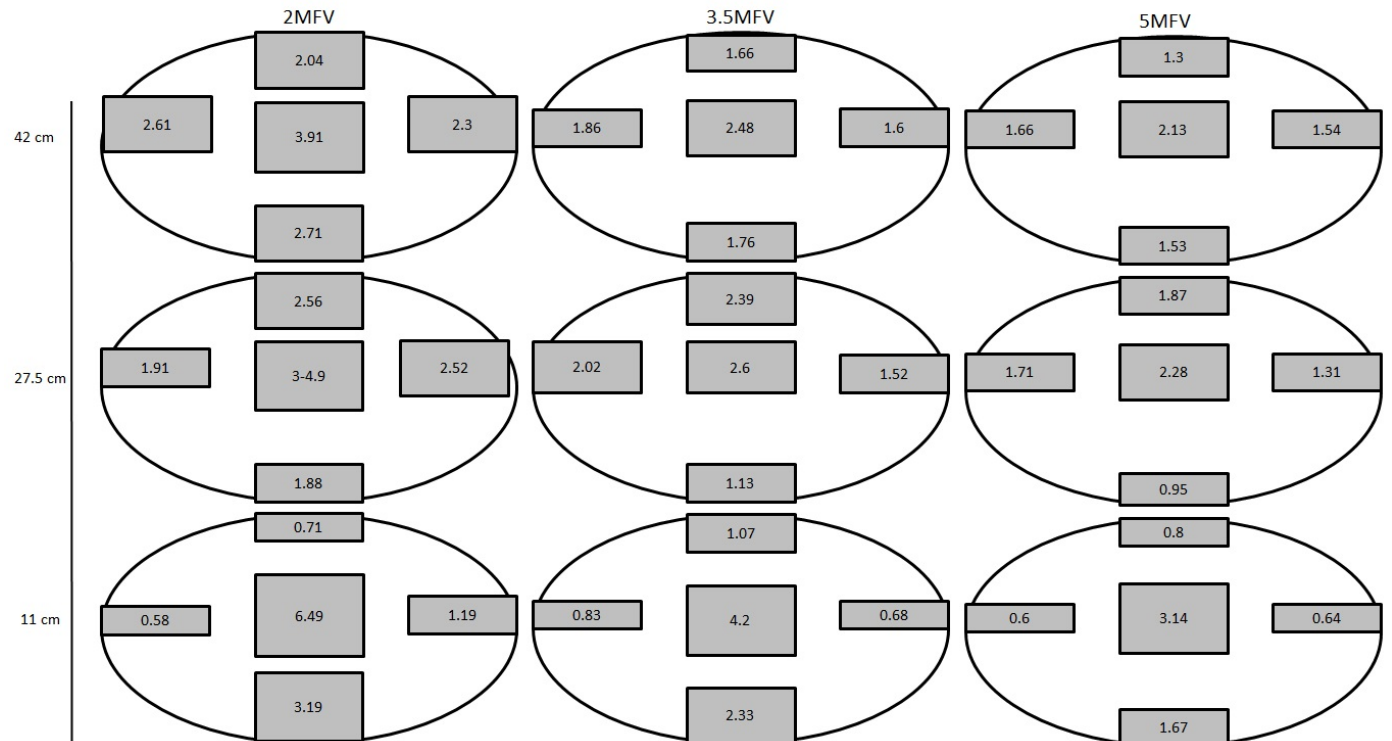


Figure A.9: Visualization of the concentration of CO₂ in volume-% at different points in the bed for the three air flows used when injecting 70.8 SLPM for the medium-sized bed particles (250-350 μm).

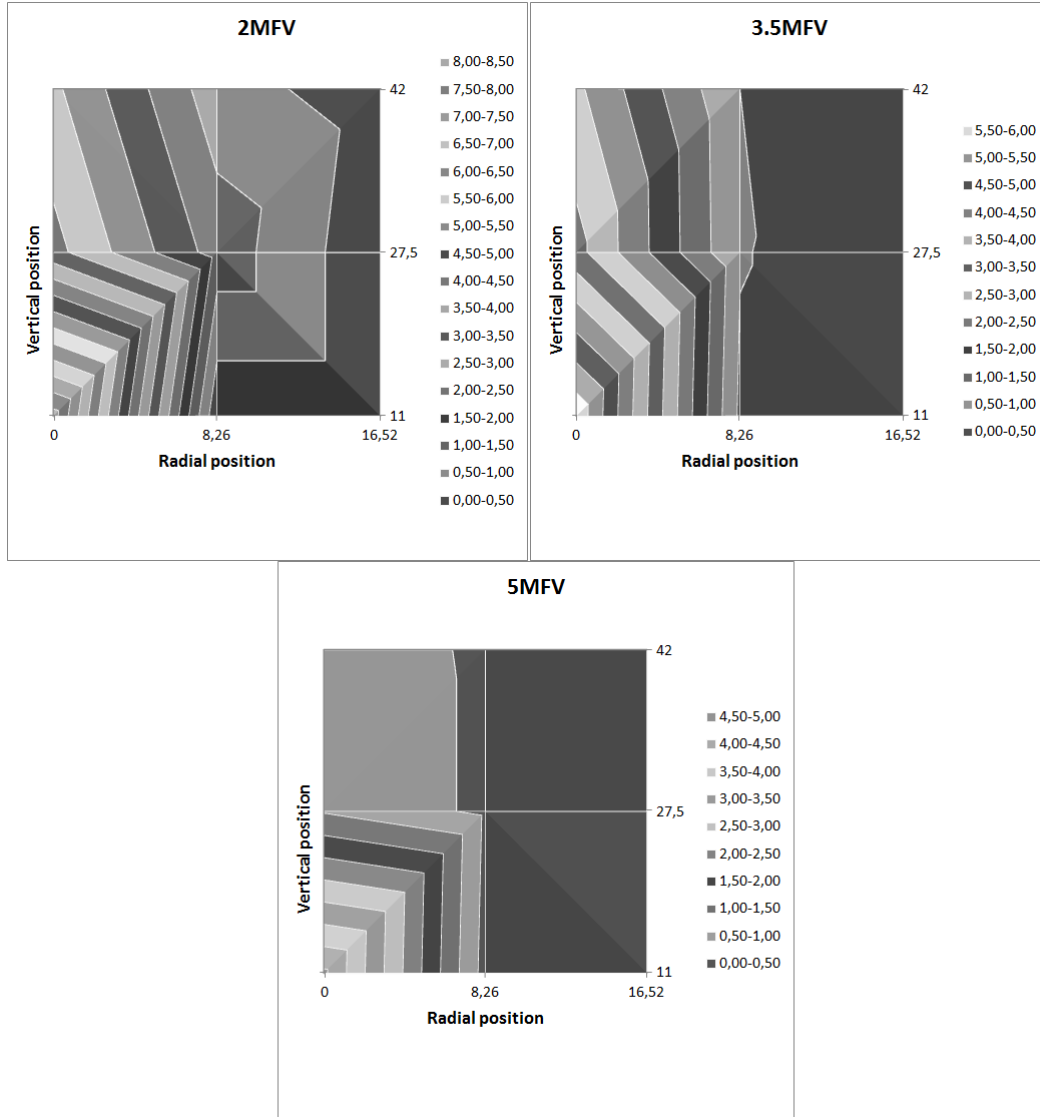


Figure A.10: Contour plots of the concentration of CO₂ in volume-% across the cross section in the direction of the injection port for CO₂-injection of 14.2 SLPM for the medium-sized particles (250-350 μm) for air flows in the range of 2MFV to 5MFV.

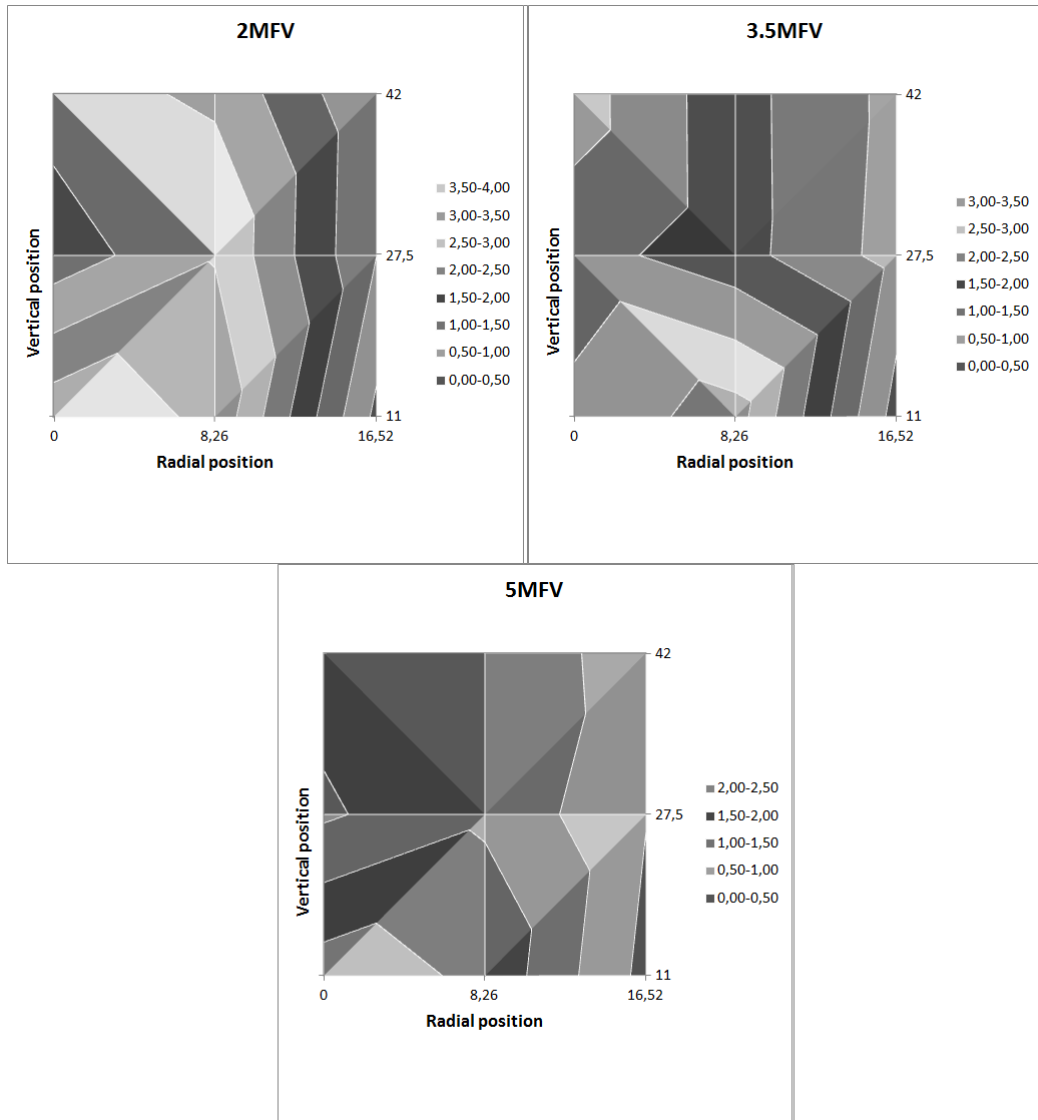


Figure A.11: Contour plots of the concentration of CO₂ in volume-% across the cross section in the direction of the injection port for CO₂-injection of 42.5 SLPM for the medium-sized particles (250-350 μm) for air flows in the range of 2MFV to 5MFV.

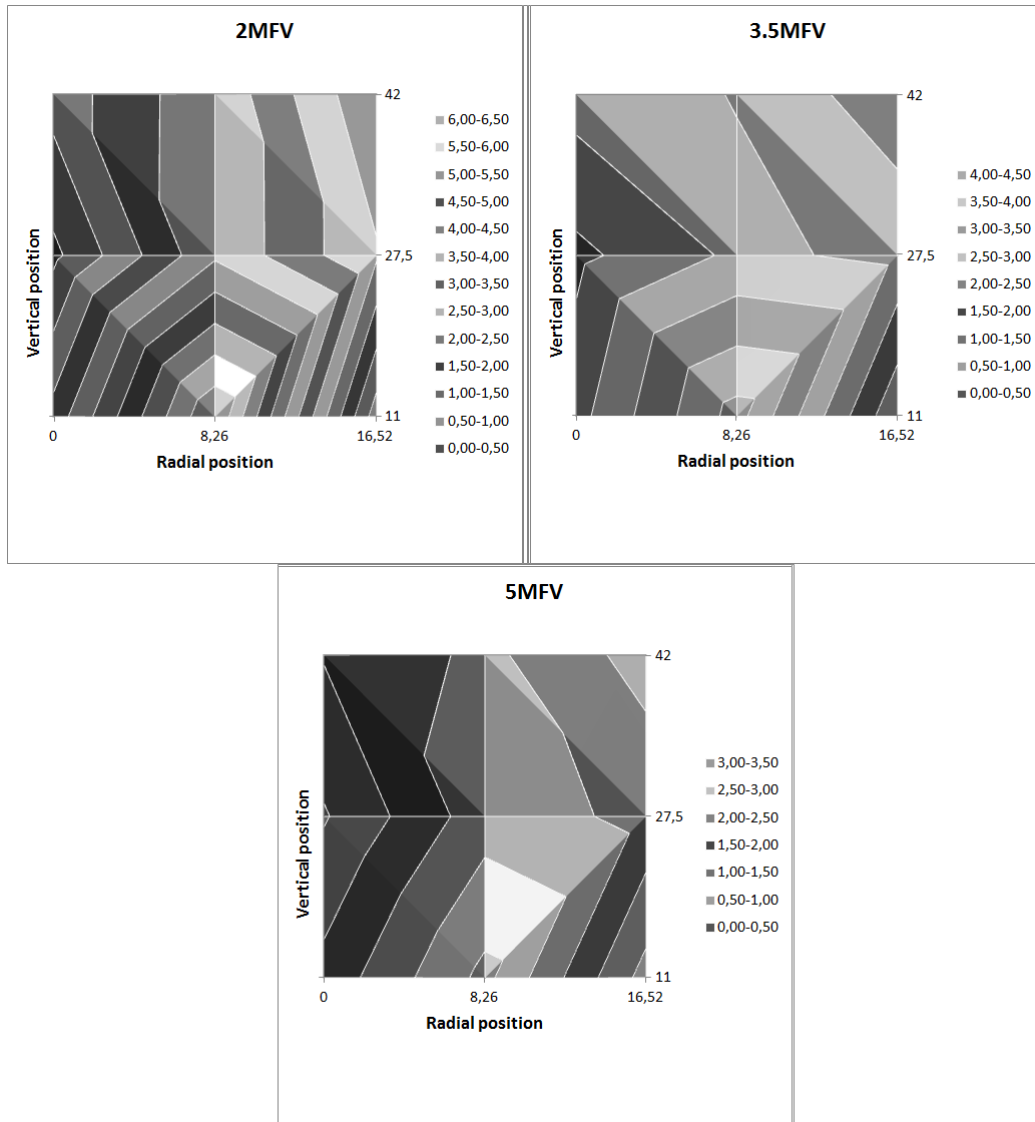


Figure A.12: Contour plots of the concentration of CO₂ in volume-% across the cross section in the direction of the injection port for CO₂-injection of 70.8 SLPM for the medium-sized particles (250-350 μm) for air flows in the range of 2MFV to 5MFV.

A.2.3.2 Collection of all experimental data and aggregated sums of measured CO₂

Here follows a summary of the scaled individual values as well as the sum of the scaled values for each air flow, CO₂-flow and measurement layer. Note that all measured values are scaled towards air flow of 2MFV and injection of 14.2 SLPM of CO₂.

Table A.18: Scaled measurement values in volume-% of CO₂ for injection with 14.2 SLPM of CO₂ and for varying flows of air as well as aggregated amounts of CO₂ considering the dilution effects for the medium-sized particles (250-350 μm).

CO₂ Injection at 14.2 SLPM	2 MFV	3.5 MFV	5 MFV	
Vertical 11 - Wall 0	8.23	10.31	11.50	
Vertical 11 - Wall 90	0.10	0.18	0.25	
Vertical 11 - Wall 180	0.10	0.18	0.50	
Vertical 11 - Wall 270	0.10	0.18	0.42	
Vertical 11 - Centre	0.10	0.7	0.75	
Vertical 27.5 - Wall 0	3.18	2.36	2.40	
Vertical 27.5- Wall 90	0.12	0.32	0.48	
Vertical 27.5 - Wall 180	0.10	0.18	0.25	
Vertical 27.5 - Wall 270	0.20	0.53	0.75	
Vertical 27.5 - Centre	1.28	0.93	1.00	
Vertical 42 - Wall 0	2.61	2.04	2.23	
Vertical 42 - Wall 90	0.30	0.50	0.75	
Vertical 42 - Wall 180	0.24	0.35	0.52	
Vertical 42 - Wall 270	0.63	0.88	0.94	
Vertical 42 - Centre	0.70	0.88	1.00	
	Scaled sum	Scaled sum	Scaled sum	Sum each layer
Scaled sum Vertical 11 cm	8.63	11.54	13.42	33.59
Scaled sum Vertical 27.5 cm	4.88	4.32	4.88	14.07
Scaled sum Vertical 42 cm	4.48	4.64	5.44	14.56
Sum for each air flow	17.99	20.49	23.73	$\Sigma = 62.21$

Table A.19: Scaled measurement values in volume-% of CO₂ for injection with 42.5 SLPM of CO₂ and for varying flows of air as well as aggregated amounts of CO₂ considering the dilution effects for the medium-sized particles (250-350 μm).

CO₂-injection at 42.5 SLPM	2 MFV	3.5 MFV	5 MFV	
Vertical 11 - Wall 0	1.28	1.55	1.90	
Vertical 11 - Wall 90	0.11	0.13	0.22	
Vertical 11 - Wall 180	0.13	0.18	0.29	
Vertical 11 - Wall 270	0.11	0.19	0.25	
Vertical 11 - Centre	1.13	1.89	1.58	
Vertical 27.5 - Wall 0	0.74	0.81	0.77	
Vertical 27.5 - Wall 90	0.39	0.43	0.46	
Vertical 27.5 - Wall 180	0.33	0.47	0.43	
Vertical 27.5 - Wall 270	0.33	0.68	0.76	
Vertical 27.5 - Centre	0.99	0.99	1.18	
Vertical 42 - Wall 0	0.91	0.93	1.00	
Vertical 42 - Wall 90	0.46	0.53	0.71	
Vertical 42 - Wall 180	0.35	0.50	0.63	
Vertical 42 - Wall 270	0.63	0.69	0.71	
Vertical 42 - Centre	0.80	0.98	1.15	
	Scaled sum	Scaled sum	Scaled sum	Sum each layer
Scaled sum Vertical 11 cm	2.75	3.93	4.24	10.92
Scaled sum Vertical 27.5 cm	2.78	3.37	3.60	9.75
Scaled sum Vertical 42 cm	3.15	3.62	4.19	10.96
Sum for each air flow	8.68	10.92	12.03	$\Sigma = 31.63$

Table A.20: Scaled measurement values in volume-% of CO₂ for injection with 70.8 SLPM of CO₂ and for varying flows of air as well as aggregated amounts of CO₂ considering the dilution effects for the medium-sized particles (250-350 μm).

CO₂ Injection at 70.8 SLPM	2 MFV	3.5 MFV	5 MFV	
Vertical 11 - Wall 0	0.64	0.81	0.83	
Vertical 11 - Wall 90	0.24	0.24	0.32	
Vertical 11 - Wall 180	0.14	0.37	0.40	
Vertical 11 - Wall 270	0.12	0.29	0.30	
Vertical 11 - Centre	1.30	1.47	1.57	
Vertical 27.5 - Wall 0	0.38	0.40	0.48	
Vertical 27.5 - Wall 90	0.50	0.53	0.65	
Vertical 27.5 - Wall 180	0.51	0.84	0.93	
Vertical 27.5 - Wall 270	0.38	0.71	0.85	
Vertical 27.5 - Centre	0.78	0.91	1.14	
Vertical 42 - Wall 0	0.54	0.62	0.77	
Vertical 42 - Wall 90	0.46	0.56	0.77	
Vertical 42 - Wall 180	0.41	0.58	0.65	
Vertical 42 - Wall 270	0.52	0.65	0.83	
Vertical 42 - Centre	0.78	0.87	1.06	
	Scaled sum	Scaled sum	Scaled sum	Sum each layer
Scaled sum Vertical 11 cm	2.43	3.18	3.43	9.04
Scaled sum Vertical 27.5 cm	2.56	3.38	4.06	9.99
Scaled sum Vertical 42 cm	2.72	3.28	4.08	10.07
Sum for each air flow	7.70	9.84	11.57	$\Sigma = 29.10$