Modeling Aspects of Chemical-Looping Combustion for Solid Fuels

Pontus Markström

Energy and Environment
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2011
Modeling Aspects of Chemical-Looping Combustion for Solid Fuels
Pontus Markström

©Pontus Markström, 2011.

Department of Energy and Environment
Chalmers University of Technology
SE-412 96 Göteborg, Sweden
Telephone +46-(0)31-772 1000

Chalmers Reproservice
Göteborg, Sweden 2011
Modeling Aspects of Chemical-Looping Combustion for Solid Fuels

Pontus Markström
Department of Energy and Environment
Chalmers University of Technology
SE-412 96 Göteborg, Sweden

Abstract
Chemical-looping combustion is a novel technology for combustion of fossil fuel. By using a circulating bed material to transfer oxygen to the fuel, a pure stream of carbon dioxide can be obtained from the flue gas, undiluted by nitrogen. The main advantage of this capture technology is that there is no direct efficiency loss in obtaining the CO$_2$ in a separate stream.

The work presented in this thesis is divided into two parts. The first part deals with the behaviour of a 10 kW chemical-looping combustor for solid fuels. This combustor is normally operated in continuous mode but has here been studied with addition of fuel batches. From analysis of gas leaving the air reactor, it was possible to determine the residence-time and residence-time distribution of particles in the fuel reactor. Knowing the solids inventory in the fuel reactor, the circulation mass flow could be directly correlated to measured operational data, i.e. pressure drop, temperature and gas flow in air reactor riser. Using results for carbon-capture efficiency and residence-time distribution, a model was developed which could determine a mass-based reaction-rate constant for char conversion. This reaction-rate constant could also be determined independently from the conversion rates of char during the batch tests. The results showed a good agreement between the two approaches, indicating that the model well describes the behaviour of the unit.

The second part of this work presents the design and experimental evaluation of a cold-flow model system, built to simulate a 100 kW chemical-looping combustor for solid fuels. A theoretical background with details on design and calculations on the dynamic similarity is provided. The system has been operated for about 10 hours and shows no indication of imbalances in the bed inventories. Both the internal circulation in the fuel reactor and the circulation between air and fuel reactor could be varied in a large range with only minor impact on the solids inventories. Studies were made on the mass flows, mass fluxes and residence-times in the air and fuel reactors using air as fluidization medium.
Publications

This thesis consists of an introductory text and the following two appended research papers, henceforth referred to as Paper I–II:


Contribution

I. Corresponding author, responsible for data evaluation and writing.

II. Corresponding author, responsible for experimental work, data evaluation and writing.

Related Publications not Included in the Thesis

Acknowledgements

First and foremost, I would like to thank my supervisor, Prof. Anders Lyngfelt. Being completely new to this area of science, I am grateful for the perfect mix of patience, guidance and responsibility you have given me. I am also grateful to my co-supervisor, Ass. Prof. Tobias Mattisson, for all the support.

Also, a big thank you to all the employees at the division of Energy Conversion for providing a great working atmosphere, especially the chemical-looping gang: Carl Linderholm, Patrick Moldenhauer, Magnus Rydén, Peter Hallberg, DaZheng Jing, Golnar Azimi, Mehdi Arjmand, Erik Jerndal and Henrik Leion.

A special thanks goes to Nicolas Berguerand for the great collaboration in Paper I and to Ulf Stenman for providing such a good working company.

Finally, I would like to thank my financers, the Research Fund for Coal and Steel of the European Community, Carl Trygger’s Foundation for Scientific Research, J. Gust. Richert Memorial Fund and Ångpanneföreningen’s Foundation for Research and Development.
# Contents

## Outline

1 **Introduction**  
   1.1 Global Warming .............................. 3  
   1.2 Carbon Capture and Storage  
      1.2.1 Capturing the CO$_2$ ......................... 6  
      1.2.2 Storing the CO$_2$  

2 **Chemical-Looping Combustion**  
   2.1 Concept................................... 9  
   2.2 Origin.................................... 10  
   2.3 CLC with Gaseous Fuels ...................... 10  
   2.4 CLC with Solid Fuels ....................... 11  
   2.5 Oxygen Carriers  
      2.5.1 Ilmenite............................... 12  
   2.6 Measurements of Circulation in a Riser ......... 14

3 **Modeling**  
   3.1 Residence-Time Analysis of a 10 kW Unit (Paper I)  
      3.1.1 Unit Description  
      3.1.2 The Multistage-Bed Model ................. 17  
      3.1.3 Correlation to Measured Data .............. 18  
      3.1.4 The Riser Mass Flow ..................... 20  
      3.1.5 The Mass-Based Reaction-Rate Constant ..... 20  
   3.2 Cold-Flow Model of a 100 kW Unit (Paper II) .... 24  
      3.2.1 System Labels  
      3.2.2 The Scaling Laws ....................... 25  
      3.2.3 Slugging Analysis in the Circulation Riser 27  
      3.2.4 Bed Inventory Stability .................. 28  
      3.2.5 The Riser Mass Flow .................... 29  
      3.2.6 Residence-Time ......................... 30  
      3.2.7 Pressure Profile  

vii
Outline

This thesis is based on two papers in the field of chemical-looping combustion. As the two papers present research that are quite different in both the experimental and analysis part, a brief overview of the chapters in this thesis are given below. In **Chapter 1**, an introduction as to why research in this field is important. Here, the problem of global warming due to greenhouse gas emissions is discussed, as well as a background to Carbon Capture and Storage. **Chapter 2** provides a summary to the field of research, including an introduction to chemical-looping combustion. It describes the origin of the technology and a discussion on fuels and oxygen carriers. It also presents the basic chemical reactions that take place in the reactor system. **Chapter 3** describes how different aspects of chemical-looping combustion for solid fuels can be modeled. It will focus on two sizes of reactor systems. One 10 kW and one 100 kW unit. The modeling of the 10 kW unit describes how the residence-time can be obtained from data of the oxygen concentration in the air reactor. Some implications, such as the calculation of the reaction-rate constant of the fuel, are also investigated. This includes a verification of the validity of the model by comparison to results obtained in other experiments with different solid fuels. The 100 kW unit is analysed in terms of a cold-flow model. The design outline and initial results using air as fluidization medium are presented. Finally, in **Chapter 4** the results are summarized and an outlook for further work is provided.
1

Introduction

1.1 Global Warming

In recent years, the greenhouse effect has gained a lot of attention due to alarming reports of global warming. Instrumental recordings over the past 157 years show that temperatures at the surface have risen globally in two main phases [1]. In the first phase, from the 1910s to the 1940s, the average temperature rose $0.35^\circ C$ and in the second phase, from the 1970s to the 2000s, the average temperature rose $0.55^\circ C$, see Fig. 1.1. In addition, 11 of the 12 warmest years on record have occurred in the past 12 years.

![Global Mean Temperature](image)

**Fig. 1.1:** Annual global mean observed temperatures, from [1].
1.1. Global Warming

In addition to the increase in global average surface temperature, many indications of global warming exist. The increase in global average sea level and the decrease in the northern hemisphere snow cover are such indications. If the global mean temperature continues to increase, it will lead to serious changes in the climate that may be irreversible. A major part of the scientific community today agrees that the cause of global warming is an anthropogenic greenhouse effect, rather than a natural process. As combustion of fossil fuels results in large emissions, it was natural to envisage a correlation between increased temperatures and an increased production of greenhouse gases.

The greenhouse effect has been named from the process occurring in a greenhouse with glass walls, where the airflow is reduced and the temperature of the air inside is increased. The effect occurring on Earth is analogous in the sense that it is the surface of the planet that becomes warmer. The process on Earth can be described in the following way. From the sun, radiation in all wavelengths is emitted continuously. Approximately 1/3 of the radiation that reaches the Earth is reflected in the atmosphere back to space, 1/6 is absorbed in the atmosphere and about 1/2 is absorbed by the Earth’s surface and makes it warmer [2]. As the surface gets warmer, it radiates more and more heat through infrared radiation.

Greenhouse gases in the atmosphere, predominantly water vapor (H$_2$O) and carbon dioxide (CO$_2$), absorbs and re-emits most of this radiation in all directions, including back to Earth. This effect creates a situation where trapped infrared radiation, or heat, continuously warms the Earth’s surface and the lower atmosphere. Other gases present in the atmosphere, e.g. methane (CH$_4$), nitrous oxide (N$_2$O) and ozone (O$_3$), also contribute to the greenhouse effect. The three most important greenhouse gases that not only originate from natural processes, but also from human activities, e.g. industrial emissions, are CO$_2$, CH$_4$ and N$_2$O. More than 60 other greenhouse gases, in groupings of hydrofluorocarbons, perfluorinated compounds, fluorinated ethers and other hydrocarbons are present in the atmosphere, but only in minute concentrations [3].

One means of comparing these emissions to some reference is by using a metric called GWP, Global Warming Potential, which is based on radiative forcing. Radiative forcing is defined as “the change in net irradiance at the top of the troposphere after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at the unperturbed values” [3]. The GWP is based on the time-integrated global mean radiative forcing of a pulse emission of 1 kg of some compound relative to that of 1 kg of a reference gas. It is a number, providing a measure of the contribution to climate change from emissions of various components over time. The reference gas was chosen to be CO$_2$ and has a GWP equal to 1.

This metric was developed by IPCC in 1990 and was adopted for use in e.g. the Kyoto Protocol. It can be calculated for different time horizons, but most often it is the 100 year horizon that is stated. For example, the 100-yr GWP of CH$_4$ and N$_2$O are 25 and 298, respectively [3]. This means that both CH$_4$ and N$_2$O are much more effective as greenhouse gases compared to CO$_2$. However, as the concentration of CO$_2$ in the atmosphere is in the order of 1000 times higher than the other two (ppm instead of ppb) and because it is completely dominant in the flue gases from
fossil fuel combustion, it has become the center of attention when discussing greenhouse gas emissions. The historical concentration of these three greenhouse gases in the atmosphere can be measured indirectly by analyzing trapped gas pockets in the polar ice caps, dating back thousands of years. Combining averages from such analysis with modern measurements reveals a drastic change, caused by emissions from anthropogenic processes, see Fig. 1.2. Post-industrial development across the world continues to increase the amount of greenhouse gas emissions, which in turn may lead to increased temperatures at the surface of the Earth. This in turn leads to increased evaporation of water from the oceans, and thus increased concentration of water vapor in the atmosphere. As water vapor is a powerful greenhouse gas, the greenhouse effect becomes self-reinforced. It is believed that this water vapor feedback may in fact double the increase in the greenhouse effect due to the added CO$_2$ [2].

According to the Copenhagen Accord [4], the increase in global temperature should be kept below 2°C in order to prevent dangerous anthropogenic interference with the climate system. To meet this target, countries need to drastically cut their emissions of greenhouse gases. Due to the continuously increasing demands of energy around the world, it is in practice extremely difficult to remove the usage of fossil fuels today and solely replace it with renewable energy sources like wind and solar power. Consequently, the CO$_2$ resulting from combustion processes would need to be removed. A possible solution is to use Carbon Capture and Storage (CCS). This concept can be used as a bridge to a more long-term solution, in which renewable energy sources can take over. This thesis studies a capture technology, called chemical-looping combustion (CLC). Chemical-looping combustion is a novel combustion process for fossil
1.2 Carbon Capture and Storage

Technologies that enable the possibility for combustion without nitrogen-diluted exhaust gases have in recent years received more and more attention. Due to global warming, the effects of releasing fossil-fuel produced CO$_2$ to the atmosphere is a debated issue and several methods to capture and store the CO$_2$ are investigated. The concept has been applied in various locations around the world and is now considered to be an important option for decelerating the increase of atmospheric CO$_2$. Most information in Section 1.2 is adapted from [5] unless otherwise stated.

1.2.1 Capturing the CO$_2$

The stationary sources that are mostly responsible for anthropogenic CO$_2$ emissions are power plants, cement production and steel production plants. For example, in 1995, more than 1400 Mt CO$_2$ were released in steel production associated emissions. Other processes like natural gas sweetening, which is a separation method for CO$_2$ contaminated natural gas, also produces large amounts of CO$_2$. There are ways to capture the CO$_2$, many of which are directed towards e.g. combustion systems. Below, a brief summary of the main CO$_2$ capture technologies is provided. For these examples, the CO$_2$ is generated in large-scale combustion processes using fossil fuels.

- Post-combustion: Here, the CO$_2$ rich flue gas is treated downstream of the combustion process. Examples of post-combustion capture processes are absorption processes, adsorption processes, membranes and solid sorbents. The most common ones are the absorption processes, which use the reversibility of chemical reactions to capture and then release the CO$_2$. By letting a solvent be brought in contact with the flue gas, CO$_2$ will be absorbed. The solvent is then regenerated and CO$_2$ is released in a stripper at 100–140°C. This leads to a drop in efficiency as this temperature needs to be maintained. Using the absorption process, typically 80-95% of the CO$_2$ is recovered. Usually an amine is used, but recently, chilled ammonia has received a lot of attention. The chilled ammonia process uses an aqueous ammonium solution at 0–10°C to capture CO$_2$ by forming ammonium bicarbonate [6]. Membranes work in a slightly different way. They could be used in natural gas sweetening (as mentioned above) when the CO$_2$ concentration and pressure is high. For flue gas CO$_2$ recovery, an option is the hybrid membrane absorbent system where the membrane forms a gas permeable barrier between a liquid and a gaseous phase. Membranes can either be porous or non-porous. In porous membranes, the CO$_2$ is allowed to diffuse through the pores and be absorbed by the liquid. In non-porous membranes, the CO$_2$ is first dissolved and then diffused through the membrane itself.

- Oxy-fuel combustion: By separating the oxygen from air and use it directly in a combustion process, it is possible to produce flue gases free from nitrogen contamination. After subsequent steps of steam condensation and cleaning of
impurities, such as NO\textsubscript{x} and SO\textsubscript{x}, a pure stream of CO\textsubscript{2} can be obtained and captured. Methods of air separation techniques include e.g. cryogenic distillation, adsorption using multi-bed pressure swing units, and polymeric membranes. To keep the temperature down in the combustion chamber, the oxygen is diluted on purpose with recycled CO\textsubscript{2} rich flue gas. This process has an efficiency drop due to the air separation process, but captures close to 100\% of all CO\textsubscript{2}.

- Pre-combustion: This process is essentially a method of producing hydrogen from a hydrocarbon or carbonaceous fuel with the help of steam. As the by-product in this production is CO\textsubscript{2}, pre-combustion is a very convenient alternative for CO\textsubscript{2} capture. By letting the hydrocarbon react with either steam or oxygen in substoichiometric amounts, syngas (H\textsubscript{2} and CO) are produced. The first method is called steam reforming and the latter is called partial oxidation or gasification, depending on if the fuel is gaseous/liquid or solid, respectively. Finally, by adding more steam, the water-gas shift reaction,

\[
CO + H_2O \leftrightarrow CO_2 + H_2, \quad (1.1)
\]

can be used to push the CO to CO\textsubscript{2}. This CO\textsubscript{2} can then be captured after a subsequent separation step. The separation step may use e.g. pressure swing adsorption or an absorbing amine solvent. Hence, this capture technology shares the efficiency drop with the post-combustion and oxy-fuel combustion processes. Pre-combustion may also involve a chemical-looping technology (see below), in a process called chemical-looping reforming \cite{7, 8}.

- Chemical-looping combustion: Just like oxy-fuel combustion, this process provides a nitrogen-free alternative to burn fossil fuels or biomass. More information on the background of this novel technology is provided in Chapter 2.

### 1.2.2 Storing the CO\textsubscript{2}

Just as for the capture process, there are several alternatives to store the CO\textsubscript{2} captured from the technologies previously mentioned. Three examples of storage technologies are on and off-shore geological storage, ocean storage and mineral carbonation.

The one that shows most promise is geological storage. This is due to research showing that is very likely that over 99\% will be retained over 100 years and likely that over 99\% will be retained over 1000 years. In geological storage, the CO\textsubscript{2}, compressed to its supercritical state, is injected into geological formations under ground. Geological storage locations could be e.g. oil fields for enhanced oil recovery, unmineable coal seams in which the injected CO\textsubscript{2} attaches to the surface of coal, or porous rocks such as sandstone reservoirs.

The most prominent example for enhanced oil recovery is the Weyburn CO\textsubscript{2}–EOR project, which started in late 2000. Here, CO\textsubscript{2} at a rate between 1.1–1.8 Mt/yr is injected into a 180 km\textsuperscript{2} fractured carbonate oil reservoir, expected to store 20 Mt in total.

Sandstone reservoirs are in use in several commercial scale projects across the world today. Their use as geological storage for CO\textsubscript{2} is often connected to a gas field,
where natural gas is taken from large production wells. As the gas will contain an amount of unwanted CO$_2$, it will undergo a separation process that captures the CO$_2$. This CO$_2$ is then injected into a sandstone reservoir, either beneath, above, or into the original gas field. Two successful projects with sandstone reservoirs are listed below.

- The first storage site began operation in 1996. It was when Statoil started the off-shore Sleipner CO$_2$ storage project in the North-Sea, 250 km off the coast of Norway. The Sleipner project is located in the south of the Utsira formation, a saline aquifer, and is a 5 km$^2$ large injection well, 800–1000 m below the sea floor. CO$_2$ is injected into the sandstone reservoir, located above a natural gas field, from an ocean platform at a rate of approximately 1 Mt/yr until 20 Mt is reached.

- Another example is BP’s In Salah gas project in the central Saharan region of Algeria. Here, the CO$_2$ is injected into the same sandstone reservoir as the natural gas is produced from. However, the production wells and the injection wells are separated in such a way that a migration of CO$_2$ to the gas field will happen long after depletion of the gas zone. 17 Mt of CO$_2$ will be stored here at a rate of up to 1.2 Mt/yr. Operation started in 2004 and the CO$_2$ is injected to a depth of 1800 m.

In ocean storage, there are several proposals available. One proposal is to inject the CO$_2$ below 3 km depth, where CO$_2$ is denser than sea water. This leads to the formation of CO$_2$ lakes at the bottom of the seafloor. A second proposal is to inject the CO$_2$ somewhere between 1–3 km depth. Then the CO$_2$ will form an upward plume, dissolving into the seawater on its way up. Here, research shows that 65-100% will be retained after 100 years and that 30-85% will be retained after 500 years, depending on if the depth of injection was closer to 1000 m or 3000 m.

Mineral carbonation involves converting CO$_2$ to solid inorganic carbonates, which are geologically stable. This may be accomplished from chemical reactions between CO$_2$ and silicate minerals containing magnesium and calcium. Mineral carbonation is at an early stage of development and the feasibility of such a process is uncertain, but it has the advantage of highly irreversible CO$_2$ retainment.
2

Chemical-Looping Combustion

2.1 Concept

As discussed in Section 1.2, regular combustion uses air to burn the fuel, where the CO$_2$ produced is contaminated by nitrogen. Technologies that use different forms of gas separation are being studied, but will inevitably lead to a drop in efficiency. In this aspect, chemical-looping combustion is relevant. As a carbon-capture technology with inherent separation of CO$_2$, chemical-looping combustion is both feasible and fully compatible with the new storage technologies.

The principle of chemical-looping combustion is the circulation of an oxygen carrier particle between two main reactors. In one of these main reactors, air is introduced from below. Here, the particles become oxidized in exothermal reactions as they are fluidized. Hence, this reactor is normally called the air reactor. The particles are then transported through a loop seal, entering the other main reactor. As this reactor is where the fuel is inserted, it is called the fuel reactor. Depending on the kind of fuel used, this reactor could be fluidized with either steam, CO$_2$ or the fuel itself. The fuel then reacts with oxygen available in the particles, which become reduced. Loop seals prevent gases between the air and fuel reactor to mix, and hence the net effect of the process is a transport of oxygen to the fuel reactor with no nitrogen contamination and without any direct efficiency loss. After subsequent steps of steam condensation and gas cleaning from e.g. sulphur compounds, a pure stream of CO$_2$ is obtained. This CO$_2$ can then be transported to a suitable location for long-time storage.

More than 900 materials have been investigated as possible oxygen carrier materials for this process, mostly including active oxides of iron, nickel, copper and manganese [9]. Actual operation for more than 4000 h has been accomplished in 12 units of 0.3–140 kW [10], although mostly for gaseous fuels. In recent years, both lab investigations [11,18] as well as studies in continuous operation [19,21] have been made with solid fuels.
2.2 Origin

Already in the fifties, Lewis and Gilliland [22] patented the concept for use in the production of high purity CO\textsubscript{2} from fossil fuels. However, the process was not commercialized and was not called chemical-looping combustion. The name “chemical-looping” was given by Ishida et al. [23] in 1987. According to Masaru Ishida, the name was a reference, or homage, to the human cardiovascular system as both are circulating and both confine chemical reactions. It was not until the mid-nineties that the concept was recognized as a possibility to capture CO\textsubscript{2} from fossil fuels in order to reduce climate impact [24]. More recently, the first tentative chemical-looping combustion design based on the circulating fluidized bed principle was presented by Lyngfelt et al. [25].

2.3 CLC with Gaseous Fuels

The concept of chemical-looping combustion, as described in Section 2.1, is depicted in Fig. 2.1. It shows the oxygen carrier as a metal oxide, labeled Me\textsubscript{x}O\textsubscript{y} in oxidized form and Me\textsubscript{x}O\textsubscript{y−1} the reduced form. Combusting e.g. natural gas or syngas, the fuel itself is used as the fluidization medium in the fuel reactor. For gaseous fuels in the form of various hydrocarbons, the resulting chemical reactions (2.1) and (2.2) describe the processes in the fuel and air reactor, respectively.

\[
\begin{align*}
C_nH_{2m} + (2n + m)Me_xO_y & \rightarrow nCO_2 + mH_2O + (2n + m)Me_xO_{y−1} \quad (2.1) \\
O_2 + 2Me_xO_{y−1} & \rightarrow 2Me_xO_y \quad (2.2)
\end{align*}
\]

A fuel like natural gas often consists of more than 90% methane (CH\textsubscript{4}). In addition, it also contains ethane, propane, butane, CO\textsubscript{2}, nitrogen, and sometimes sulphuric
compounds that may lead to SO\(_x\) emissions. However, as the combustion does not involve high temperature flames, there will not be any thermal NO\(_x\) production. The reactions above show that the only products of sulphur-free hydrocarbon combustion should be steam and CO\(_2\).

### 2.4 CLC with Solid Fuels

The method of feeding solid fuels into a chemical-looping combustor is a bit different compared to using gaseous fuels. Clearly, the fuel cannot be fed in the same fashion as indicated in Fig. 2.1. Instead, two other options are available [21]. The fuel can either be fed from above in the fuel reactor, or it can feed into the bed directly. Releasing the fuel above the bed has a major drawback in that the release of volatiles may occur before they have had the time to react with the oxygen carriers. If these volatiles leave the system with the flue gases un-reacted, they need to be burnt in an oxy-fuel process further downstream, which in turn leads to increased costs. Therefore, in-bed feeding is preferred. For solid fuels with in-bed feeding, the volatile content will react according to (2.1), but the char has to be gasified first since no direct solid-solid reaction between the fuel and oxygen carrier is expected. In this step, the char must first react with steam (2.3) or carbon dioxide (2.4) to form syngas,

\[
\begin{align*}
C + H_2O &\rightarrow CO + H_2 \\
C + CO_2 &\rightarrow 2CO.
\end{align*}
\tag{2.3, 2.4}
\]

The resulting \(H_2\) and CO react according to

\[
H_2/CO + Me_x O_y \rightarrow H_2O/CO_2 + Me_x O_{y-1},
\tag{2.5}
\]

i.e. yielding steam and CO\(_2\) as end products. However, there will also be sulphuric emissions, mostly in the form of SO\(_x\) and H\(_2\)S. The levels depend on the kind of solid fuels used, i.e. on the amounts of elemental sulphur present in the fuel. For some fuels like South African coal, it can be relatively moderate levels (< 1 wt%), while for others like Mexican petroleum coke, the sulphur content can be over 6 wt% [26]. Another difference compared to gaseous fuels is that solid fuels always contain a certain amount of ashes, which need to be managed. These differences, together with the problem of fuel feeding, makes chemical-looping combustion with solid fuels more complicated than with gaseous fuels. As for gaseous fuels, there will be no thermal NO\(_x\) production with solid fuels but fuel-NO\(_x\) formation is possible.
2.5 Oxygen Carriers

A substantial part of the research in chemical-looping combustion is focused on testing new oxygen carriers. This is understandable, considering the major role it plays in the chemical-looping process. There are many important factors to consider when choosing an oxygen carrier, such as oxygen-transfer capacity, reactivity with the fuel and oxygen, cost, health and environmental impacts, thermodynamic properties and melting point. The oxygen carriers are often manufactured, using either freeze-granulation, spray-drying, impregnation, co-precipitation or spin-flash drying. Manufactured oxygen carriers are normally metal oxides, with or without a support material to increase mechanical stability. However, they could also be natural ores or industrial by-products. Using thermodynamic analysis, Jerndal et al. [27] has shown that the metal oxides Fe$_2$O$_3$/Fe$_3$O$_4$, Cu$_2$O/Cu, Mn$_3$O$_4$/MnO and NiO/Ni appear to be the most suitable ones for natural gas. Durability of oxygen carriers with natural gas has also been tested extensively, e.g. in [28], where Ni/NiO oxygen carriers were subject to operation for more than 1000 hours. The oxygen carrier in Paper I-II is a 94.3% pure iron-titanium oxide, Fe$_2$TiO$_5$+TiO$_2$/FeTiO$_3$, called ilmenite.

2.5.1 Ilmenite

For Paper I-II, it was necessary to make a detailed analysis of some of the available literature concerning the structure and density of ilmenite. When fresh ilmenite particles are used, they need several cycles before they show stable oxidation-reduction behaviour. In addition, as the particles circulate in the system, as indicated in Fig. 2.1 and oxidizes/reduces in each cycle, their density will decrease. This initial process is called activation and may be due to a chemical migration of the elements in ilmenite [29]. As the particles are oxidized and subsequently reduced in each cycle, the internal structure may be altered and new compounds may be formed. This may explain the formation of a more porous structure and thus lower density.

With no migration, reduced ilmenite reacts in the air reactor to its most oxidized form according to

\[
4\text{FeTiO}_3 + \text{O}_2 \rightarrow 2\text{Fe}_2\text{TiO}_5 + 2\text{TiO}_2.
\]

(2.6)

However, at the surface of activated ilmenite, an external shell enriched with hematite (Fe$_2$O$_3$) has been found that would significantly change the thermodynamic properties of ilmenite [29]. If the oxidized ilmenite reorganizes to a hematite shell and rutile (TiO$_2$) core structure during activation according to

\[
\text{Fe}_2\text{TiO}_5 + \text{TiO}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2\text{TiO}_2,
\]

(2.7)

then, if the rutile core is inert, the subsequent reduction may instead produce surface magnetite (Fe$_3$O$_4$). For the remaining cycles, oxidation would then follow

\[
4\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow 6\text{Fe}_2\text{O}_3
\]

(2.8)

instead of (2.6). The heat balance in the fuel reactor will depend on whether it is reaction (2.6) or (2.8) that occurs in the air reactor. This is due to the different enthalpies of reaction, $-444.82$ kJ/mol $\text{O}_2$ or $-480.42$ kJ/mol $\text{O}_2$ at $950^\circ\text{C}$, respectively.
What is also affected is the oxygen transfer capacity,

\[ R_0 = \frac{m_{0,ox} - m_{0,red}}{m_{0,ox}}, \quad (2.9) \]

where \( m_{0,ox} \) and \( m_{0,red} \) are the masses of a fully oxidized and a fully reduced oxygen carrier, respectively. With reaction (2.6), \( R_0 = 0.0501 \) kg O\(_2\)/kg oxidized ilmenite, while with reaction (2.8), \( R_0 = 0.0334 \) kg O\(_2\)/kg hematite. As the molar weight of Fe\(_2\)O\(_3\) is almost exactly the same as for 2TiO\(_2\), reaction (2.7) yields that there is 0.5 kg hematite/kg oxidized ilmenite. Hence, it is likely that \( 1.7 \leq R_0 \leq 5.0 \) wt\% for activated ilmenite. This uncertainty range in \( R_0 \) is considered in Paper I and is supported by Adánez et al. [30], who have shown that \( R_0 \) for ilmenite is initially 4% but decreases down to 2.1% after 100 redox cycles with hydrogen as fuel gas.

Ilmenite’s true density has been measured to 4580 kg/m\(^3\) for fresh particles [30] using helium pycnometry. As helium penetrates even the finest pores, this method also considers the internal structure of the particles, i.e. it excludes the pores. With that in mind, “particle density” will from now on be referred to as the density of the particle including the pores. Eqs. (2.10)–(2.11) show the relations between particle density, true density and bulk density.

\[ \rho_p = (1 - \varphi)\rho_t \quad (2.10) \]
\[ \rho_b = (1 - \epsilon)\rho_p. \quad (2.11) \]

Here, the variables \( \varphi \) and \( \epsilon \) denote the porosity of the particle and the voidage of the bed, respectively. For fresh ilmenite, \( \varphi = 0 \) [30], i.e. \( \rho_p = \rho_t \), while \( \rho_b = 2370 \pm 120 \) kg/m\(^3\) depending on if the bed is loosely packed or more densely packed. From this, \( \epsilon \approx 0.48 \) for a normally packed bed of fresh ilmenite. After a a number of cycles, when the particles have become activated, there is a significant decrease in the particle density as compared to the fresh case.

The question now comes to the activated ilmenite’s particle density. During activation, the sphericity of the particles is increased due to rounding effects. Thus, it is likely that the voidage decreases when going from fresh to activated particles and ends up between the fresh case and the ideal case of uniformly sized spherical particles, i.e. \( 0.37 \leq \epsilon \leq 0.48 \). Using a measuring jug and a scale, the bulk density of activated ilmenite has been found to lie in the range of 1170–2050 kg/m\(^3\) [21, 31, 32]. Assuming \( \epsilon = 0.43 \), Eq. (2.11) yields instead a range in the activated particle density as \( 2050 \leq \rho_p \leq 3600 \) kg/m\(^3\), averaging at 2825 kg/m\(^3\). Using instead He pycnometry and Hg intrusion techniques, Adánez et al. [30] measured the true density to 4250 kg/m\(^3\) and porosity to 0.35 for activated ilmenite. Eq. (2.10) can then be used to calculate \( \rho_p = 2760 \) kg/m\(^3\). This value of the activated ilmenite’s particle density is the one used in Paper II. Table 2.1 summarizes the findings using these methods and their respective sources. It is observed that there is a significant variation in the particle density from particles activated under different conditions. Density decrease seems to be higher using gaseous fuels.
### Table 2.1: Different methods in determining the particle density of activated ilmenite.

<table>
<thead>
<tr>
<th>$\rho_b$ (kg/m$^3$)</th>
<th>$\rho_t$ (kg/m$^3$)</th>
<th>$\epsilon$ (-)</th>
<th>$\varphi$ (-)</th>
<th>$\rho_p$ (kg/m$^3$)</th>
<th>Fuel</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1170–1750</td>
<td>n/a</td>
<td>0.43</td>
<td>n/a</td>
<td>2050–3070</td>
<td>Natural gas</td>
<td>[31]</td>
</tr>
<tr>
<td>2050</td>
<td>n/a</td>
<td>0.43</td>
<td>n/a</td>
<td>3600</td>
<td>Bit. coal</td>
<td>[21]</td>
</tr>
<tr>
<td>1200–1600</td>
<td>n/a</td>
<td>0.43</td>
<td>n/a</td>
<td>2100–2810</td>
<td>Syngas</td>
<td>[32]</td>
</tr>
<tr>
<td>n/a</td>
<td>4250</td>
<td>n/a</td>
<td>0.35</td>
<td>2760</td>
<td>CH$_4$/H$_2$/CO</td>
<td>[30]</td>
</tr>
</tbody>
</table>

### 2.6 Measurements of Circulation in a Riser

The upward mass flux of particles in a riser can be estimated from Eq. (2.12) \[ G_s = \frac{1}{g} \frac{\Delta P_{\Delta h}}{\Delta h} (u_0 - u_t), \] (2.12)

where $g$ is the gravitational acceleration, $\Delta h$ a small distance at the top of the riser over which a pressure $\Delta P_{\Delta h}$ is measured, $u_0$ the superficial velocity and $u_t$ the terminal velocity of a particle. This estimate is used in both Paper I and Paper II when analyzing the upward mass flux of particles in a riser. The mass flow derived from Eq. (2.12) is $A \cdot G_s$, where $A$ is the cross-section area of the riser. In Paper I, it is called $\dot{m}_{G_s}$, while in Paper II it is called $\dot{m}_{\text{riser}}$. This mass flow is different from the mass flow that actually passes through to the cyclone. This is due to the fact that some upward moving particles will hit the ceiling of the riser and fall down again along the walls. Hence, the (estimated) riser mass flow overestimates the (actual) circulation mass flow, $\dot{m}$. The ratio $\dot{m}_r/\dot{m}_{G_s}$ or $\dot{m}/\dot{m}_{\text{riser}}$ will from here on be referred to as the flow-through ratio.

Inspired by Eq. (2.12), another measure of the circulation was used by Berguerand and Lyngfelt [19]. This measure is called the circulation index, $CI$, where

$$CI = \Delta P_{\Delta h + \Delta l} \cdot F_{AR, out}.$$

(2.13)

Here, $\Delta P_{\Delta h + \Delta l}$ is the pressure drop measured between pressure taps located at the riser bottom and at the cyclone inlet, directly after the riser exit, cf. Fig. 3.1, and $F_{AR, out}$ is the volume flow of gas in the air reactor at the current temperature. This relation is used in Paper I as a measure of the circulation rate in the 10 kW unit.
3

Modeling

3.1 Residence-Time Analysis of a 10 kW Unit (Paper I)

The aim here is to investigate the residence-time distribution of circulating bed material in a 10 kW chemical-looping combustor for solid fuels. The residence-time is a basic variable in any study of a combustion unit with a circulating fluidized bed.

For example, assume that the mass flow of particles cannot be measured directly. Then the mass flow needs to be determined by some other means. If the residence-time and bed mass are known, then the mass flow could be calculated from the definition of the residence-time as

\[ \dot{m} = \frac{m}{\tau}. \]  

(3.1)

3.1.1 Unit Description

The chemical-looping combustor used in this study consists of an air reactor, connected to a loop seal on the inlet and outlet side, a fuel reactor and a smaller fuel reactor loop. It has two cyclones, one after the air reactor, where oxygen depleted air leaves the system, and one in the fuel reactor loop, where unreacted combustibles, combustion products and fluidization gases leave the system.

A sketch of the unit is shown in Fig. 3.1.
The fuel reactor is divided into the following sections:

- **LOVEL** is the largest section and contains the majority of the bed material. For batch feeding, the fuel is fed through an external valve above the upper loop seal (not indicated in Fig. 3.1). Each batch, typically around 25 g, then drops down on top of the right-hand bed in LOVEL in a small clingfilm package. LOVEL is fluidized with steam.

- **HIVEL** is a small section below the riser, serving as outlet for the gases from the fuel reactor. This section is fluidized with inert nitrogen.

- **CS** is the carbon stripper, whose purpose is to elutriate unreacted char from the particle flow prior to its entrance into the air reactor. CS is also fluidized with nitrogen.

If the section is fluidized with nitrogen, reaction (2.3) can not occur. In those sections, only residual reactions and mixing takes place. With the lower loop seal also fluidized with nitrogen, LOVEL is the section with almost all syngas production.
3.1.2 The Multistage-Bed Model

Inspired by [34], the derivation of the multistage-bed model is sketched below. First, assume that there is a fluid passing through a series of \(N\) continuously stirred tank reactors (CSTRs). Let \(V_k\) denote the volume of the \(k\):th CSTR (m\(^3\)) and \(Q\) the overall volume flow (m\(^3\)/s). After the \(k\):th CSTR, let \(n_k\) denote the molar flow (mol/s) and \(C_k\) the concentration (mol/m\(^3\)) of a substance in the fluid. The aim of this analysis is to find the time dependent concentration of the batch after the last CSTR. A molar balance over the \(k\):th CSTR can be written

\[
\dot{n}_k = \dot{n}_{k-1} - d\dot{n}_k. \tag{3.2}
\]

If the molar content is \(dn_k = V_k dC_k\) and \(\dot{n}_k = QC_k\), Eq. (3.2) can be written

\[
QC_k = QC_{k-1} - V_k \frac{dC_k}{dt}. \tag{3.3}
\]

Dividing with \(Q\) on both sides and recognizing that \(\tau_k = V_k/Q\) then yields

\[
C_k(t) = C_{k-1}(t) - \tau_k \frac{d}{dt}C_k(t). \tag{3.4}
\]

This differential equation can be solved using Laplace transforms. A Laplace transform of Eq. (3.4) would effectively change \(d/dt \to s\) and \(C_k(t) \to \tilde{C}_k(s)\). Treating the time derivative as a parameter \(s\), Eq. (3.4) can be transformed to

\[
\frac{\tilde{C}_k(s)}{\tilde{C}_{k-1}(s)} = \frac{1}{1 + \tau_k s}. \tag{3.5}
\]

Assuming that the volume of each reactor is equally large, i.e. \(\tau_k = \tau/N\), where \(\tau\) is the total residence-time, means that Eq. (3.5) is the same for all CSTRs. Hence

\[
\frac{\tilde{C}_N}{\tilde{C}_1} = \frac{\tilde{C}_N}{\tilde{C}_{N-1}} \cdot \frac{\tilde{C}_{N-1}}{\tilde{C}_{N-2}} \cdot \ldots \cdot \frac{\tilde{C}_2}{\tilde{C}_1} = \left(\frac{1}{1 + \tau s/N}\right)^N. \tag{3.6}
\]

Defining the last expression as \(\tilde{H}(s)\) yields \(\tilde{C}_N(s) = \tilde{H}(s)\tilde{C}_1(s)\). The inverse Laplace transform of a product becomes an integral, hence

\[
C_N(t) = \int_{t'}^t H(t')C_1(t-t')dt', \tag{3.7}
\]

where \(H(t)\) and \(C_1(t)\) are the individual inverse transforms of \(\tilde{H}(s)\) and \(\tilde{C}_1(s)\), respectively. If the the substance is released at time \(t = 0\), then \(C_1(t) = C_1 \delta(t)\), where \(C_1\) is a constant. Eq. (3.7) then simplifies to

\[
C_N(t) = H(t), \tag{3.8}
\]

where \(H(t)\) is found in standard mathematical tables to be

\[
H(t) = \frac{1}{(N-1)!} \left(\frac{N}{\tau}\right) t^{N-1} e^{-t/(\tau/N)}. \tag{3.9}
\]

The time dependence of the concentration after the \(N\):th CSTR is thus

\[
C_N(t) \sim t^{N-1} e^{-t/(\tau/N)}. \tag{3.10}
\]
3.1.3 Correlation to Measured Data

When feeding the fuel reactor with a batch of fuel, the char content will gasify and reduce the ilmenite. This will effectively create a batch of reduced ilmenite that eventually will enter the air reactor. This batch can be viewed as a batch of oxygen with negative concentration. With the bed material acting as the fluid and the batch of oxygen with negative concentration acting as the added substance, Eq. (3.10) can be correlated to measured concentrations in the 10 kW unit. It is assumed that the fuel reactor and lower loop seal can be modeled as a series of \( N \) equally sized CSTR reactors. When the batch of reduced ilmenite reaches the air reactor, the oxygen concentration will decrease. If the model is successful, then the oxygen concentration should be possible to fit

\[
(O_2)_{AR}(0) - (O_2)_{AR}(t) \sim t^{N-1}e^{-t/(\tau/N)}. \tag{3.11}
\]

The experimental data used in the model is obtained with Mexican petroleum coke, fed in batches for different circulations at 950°C and 970°C. By varying the circulation index while measuring the oxygen concentration in the air reactor, it is possible to correlate the variables in Eq. (3.11) to the measured data. With \( N \) as input, the residence-time is found using a least squares fit. See Fig. 3.2 for the correlation at \( CI = 141 \text{ kPa-L/min} \). This plot also shows how \( N \) is chosen. For this example, three alternatives for \( N \) are studied: 2.5, 3 and 3.5. \( N = 2.5 \) produces a curve with too low amplitude, while \( N = 3.5 \) drops off too steep. Hence, the middle alternative \( N = 3 \) was chosen. The results for all \( CI \) are shown in Table 3.1.

![Fig. 3.2:](image)

Fig. 3.2: \( CI = 141 \). The three lines here correspond to \( N = 2.5, N = 3 \) and \( N = 3.5 \), where \( \tau = 8.2 \text{ min} \) is found for \( N = 3 \). The fuel-reactor temperature was 950°C.
Table 3.1: Results of the residence-time analysis.

<table>
<thead>
<tr>
<th>CI [kPa·L/min]</th>
<th>34</th>
<th>78</th>
<th>102</th>
<th>121</th>
<th>141</th>
<th>256</th>
</tr>
</thead>
<tbody>
<tr>
<td>N [-]</td>
<td>1.8</td>
<td>2.0</td>
<td>2.5</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>τ [min]</td>
<td>35.5</td>
<td>14.3</td>
<td>11.0</td>
<td>9.6</td>
<td>8.2</td>
<td>5.7</td>
</tr>
</tbody>
</table>

As this analysis was done for several different CI, it was possible to correlate the residence-time to the circulation index. The correlation found was

$$\tau = \frac{1178 \pm 58}{CI},$$  

(3.12)

with a 95% confidence bound, see Fig. 3.3. Eqs. (3.1) and (3.12) then yield a relation to the mass flow as

$$\dot{m} = \frac{m_\tau}{1178} \cdot CI.$$  

(3.13)

Fig. 3.3: Measured data and least-squares fit of the residence-time versus circulation index for 950°C and 970°C. The data points are accompanied by error bars corresponding to the lower and upper limits (dashed and dotted, respectively) for the different choices of N.
3.1.4 The Riser Mass Flow

As discussed in Section 2.6, the circulation mass flow is smaller than the riser mass flow. Exactly how much smaller is partly dependent on e.g. the shape of the cyclone entrance and the fluidization velocity. Using \( \dot{m} \) as the label for the circulation mass flow, as calculated from the residence-time model results, and \( \dot{m}_{G_s} \) as the riser mass flow from Eq. (2.12), a plot as in Fig. 3.4 can be produced. It shows that the circulation mass flow from the air reactor is approximately 22% of the riser mass flow, for the lower circulation indices. Here, the last point has been excluded from the fit, hence for \( \dot{m} > 1 \text{ kg/min} \) it is likely that the flow-through ratio, \( \dot{m}/\dot{m}_{G_s} \), is less than 22%.

![Fig. 3.4: The circulation mass flow \( \dot{m} \), determined from the residence-time, versus \( \dot{m}_{G_s} \), determined from the mass flux of Eq. (2.12).](image)

3.1.5 The Mass-Based Reaction-Rate Constant

Assuming a first order reaction for \( N \) equally sized CSTRs in series \[35\], the relation involving the mass-based reaction-rate constant \( k \) is

\[
\frac{m_{\text{loss}}}{m_{\text{in}}} = \left( \frac{1}{k\tau/N + 1} \right)^N.
\]  

The multistage-bed analysis of the reaction-rate of the fuel assumes 100% steam in all the CSTRs. It is the steam that enables the char to gasify, hence \( k = 0 \text{ %/min} \).
when fluidized with nitrogen. This means that as only LOVEL is fluidized with stem, it is necessary to make an assumption which will modify Eq. (3.14) to better fit the situation in the 10 kW unit. It is observed that the LOVEL contains 75% of the combined bed mass in LOVEL, HIVE, CS and the lower loop seal. This means the residence-time in LOVEL is 75% of the total residence-time. Hence, if $\tau^*$ is the residence-time in LOVEL, then $\tau^* = 0.75 \tau$.

As the fuel is fed to the fuel reactor, different components will take different paths. The fate of the carbon content can be studied with a mass balance in the fuel reactor. In Fig. 3.5 an illustration showing the fate of the carbon is presented. Here, $m_{C,\text{fuel}}$ is the total batch mass of carbon, $m_{C,\text{vol}}$ is the carbon mass of the volatiles, $m_{C,\text{conv}}$ is the carbon mass of gasified char (excluding volatiles), $m_{C,\text{AR}}$ is the carbon mass reaching the air reactor and $m_{C,\text{ws}}$ is the carbon loss to the water seal. Thus, $m_{\text{in}}$ is the mass of char that is not elutriated, i.e. the char that is either converted or lost to the air reactor. The mass balance can be written

$$m_{C,\text{fuel}} = m_{C,\text{ws}} + m_{C,\text{AR}} + m_{C,\text{FR}} = m_{C,\text{ws}} + m_{\text{loss}} + m_{C,\text{conv}} + m_{C,\text{vol}}. \quad (3.15)$$

![Mass balance of carbon in the fuel reactor.](image)

**Fig. 3.5:** Mass balance of carbon in the fuel reactor.
3.1. Residence-Time Analysis of a 10 kW Unit (Paper I)

Following the previous discussion, it is now assumed that Eq. (3.14) can be applied to the 10 kW unit if $\tau \to \tau^*$, yielding

$$\frac{m_{loss}}{m_{in}} = \left( \frac{1}{k\tau^*/N + 1} \right)^N. \quad (3.16)$$

Berguerand and Lyngfelt \[26\] defines two useful efficiencies, the carbon-capture and solid-fuel conversion efficiency:

$$\eta_{CC} = \frac{m_{C,FR}}{m_{C,AR} + m_{C,FR}}, \quad (3.17)$$

$$\eta_{SF} = \frac{m_{C,AR} + m_{C,FR}}{m_{C,fuel}}. \quad (3.18)$$

From a mass balance, as illustrated in Fig. 3.5 it is possible to relate the reaction-rate constant to $\eta_{CC}$ and $\eta_{SF}$. After some simplification of Eq. (3.14), with $f_{vol} \equiv m_{C,vol}/m_{C,fuel}$, it can be shown that

$$k = \frac{N}{\tau^*} \left[ \left( \frac{1 - f_{vol}/\eta_{SF}}{1 - \eta_{CC}} \right)^{1/N} - 1 \right]. \quad (3.19)$$

The reaction-rate constant is calculated by first relating the residence-time to the circulation index using Eq. (3.12) and then inserting measured values on $\eta_{CC}$, $\eta_{SF}$ and $f_{vol}$ into Eq. (3.19).

In order to test the model, Eq. (3.19) can be applied to data from the batch-fed Mexican pet coke of Paper I and continuously fed coal from the Republic of South Africa (RSA coal) \[19\]. The results are then interesting to compare to reaction-rate constants, previously calculated for these fuels at different temperatures. Such data are available in \[19, 26\], but without circulation.

The results, shown in Fig. 3.6 seem to agree fairly well with previously calculated reaction-rate constants. Here, the symbols ◦, ⋄ and □ are the results from applying Eq. (3.19) to pet coke experiments (Paper I) and RSA coal (\[19\]). Also appended in Fig. 3.6 are △, ◁, ▽, ⊳ and ⋆, which are from batch experiments in \[26\] for different temperatures. The results from the model yield an average rates for the pet coke of $k_{950 ºC} = 18.2$ wt%/min and $k_{970 ºC} = 28.8$ wt%/min, while the average rate for the South African coal was found to be $k_{950 ºC} = 26.1$ wt%/min.
Fig. 3.6: The reaction-rate constant versus circulation index.
The aim of this analysis is to investigate the hydrodynamics of a 100 kW chemical looping combustor, fluidized by steam and air for use with solid fossil fuel. The modeling tool is an experimental cold-flow model made in transparent acrylic glass. A cold-flow model will have the benefits of working at room temperature and enabling a clear view of the fluidization and mixing behaviour. A 2D sketch of the 100 kW system is shown in Fig. 3.7.

**Fig. 3.7:** A 2D sketch (in scale) of the 100 kW unit.
3.2.1 System Labels

The system includes two interconnected circulating fluidized beds, i.e. the air and the fuel reactor, as well as a carbon stripper. Starting in the fuel reactor, the circulation path in the 100 kW unit is outlined below. All sections are fluidized by steam, except for LS2 and AR, which are fluidized by nitrogen and air, respectively.

- The fuel reactor, FR: Here, gas and particles are transferred to CY2.
- Cyclone CY2: Particles from FR may enter here and fall down the connected downcomer to LS2.
- Loop seal LS2: Fuel is added in this part using in-bed feeding with a coal screw. From this point, bed material enters FR again.
- The circulation riser, CR: This riser transfers particles to CY3.
- Cyclone CY3: Here, particles will fall down the downcomer to CS, while gases and lighter particles are transported back to FR.
- The carbon stripper, CS: This section has four chambers separated by weirs. The purpose of CS is to gasify or separate the residual char in the particle flow. Gases, entrained fines and entrained residual char fragments are returned to FR.
- Loop seal LS4: The particles in CS are passed on to this loop seal, leading to AR.
- The air reactor, AR: This part will re-oxidize the oxygen carriers before they are transported back to FR.
- Cyclone CY1: Here, particles from AR are separated and fall down the connected downcomer to LS1.
- Loop seal LS1: The final loop seal before the particles begin a new cycle in FR.

3.2.2 The Scaling Laws

The key in designing a scale model is to identify the set of dimensionless parameters that successfully describe the physical processes of the full-scale system. This can be done by using Buckingham’s $\pi$-theorem as a scheme for non-dimensionalization of the governing equations \[36\]. For fluidized beds, a full and a simplified set of scaling laws have been derived, each consisting of a special set of so-called $\pi$-groups. The $\pi$-groups, or scaling laws, are dimensionless combinations of the dimensionfull parameters that describe the physical process. A detailed description on how these groups can be derived is provided by Glicksman et al. \[36\]. The simplified set of scaling laws is a good option if an arbitrary scale-size is to be chosen. On the downside, some assumptions have been made regarding the flow regimes that might make it less accurate compared
to the full set of scaling laws. However, the full set of scaling laws is not as flexible as the simplified set. In fact, the scale of the model will be determined by Eq. \((3.20)\) as

\[
f_{\text{scale}} = \frac{D_{\text{cold}}}{D_{\text{hot}}} = \left(\frac{(\mu_f/\rho_f)_{\text{cold}}}{(\mu_f/\rho_f)_{\text{hot}}}ight)^{2/3}.
\]

(3.20)

Hence, the scale of the model using the full set is determined by the dynamic viscosity and density of the fluidization medium in the two systems. The full set of scaling laws can be written on the following form

\[
Fr, \frac{\rho_p}{\rho_f}, Re_{d_p}, Re_D, \frac{G_s}{\rho_p u_0}, \frac{L}{D}, \phi, \text{PSD},
\]

(3.21)

where \(Fr\) is the Froude number, \(Re_{d_p}\) is the Reynolds number based on particle diameter, \(Re_D\) is the Reynolds number based on bed diameter, \(u_0\) is the superficial velocity, \(D\) is the bed diameter, \(\rho_p\) is the particle density, \(\rho_f\) is the fluidization gas density, \(G_s\) is the particle flux, \(L\) is a bed related length (e.g. height), \(\phi\) is the particle sphericity and PSD is the particle size distribution. Choosing to use the same density particles in the hot and cold-flow model, i.e. \((\rho_p)_{\text{cold}} = (\rho_p)_{\text{hot}}\), the cold-flow model fluidization gas must have the same density at ambient temperature \((20^\circ\text{C})\) as steam at \(950^\circ\text{C}\). The only gas that would be possible for this task is helium. Thus, using helium in room temperature, i.e. \((\rho_f)_{\text{cold}} = (\rho_f)_{\text{hot}}\), then \(f_{\text{scale}} = 0.5766 \approx 58\%\). This is an acceptable size, hence the construction of the cold-flow model was determined to follow the full set of scaling laws. A summary of the requirements for dynamic similarity between the systems is provided in Table 3.2 and the model itself, with supporting scaffold, is shown in Fig. 3.8.

### Table 3.2: Atmospheric chemical-looping combustor (CLC unit) with corresponding ideal cold-flow model (Ideal CFM).

<table>
<thead>
<tr>
<th>Given</th>
<th>CLC unit</th>
<th>Ideal CFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>950</td>
<td>20</td>
</tr>
<tr>
<td>Gas viscosity (μPas)</td>
<td>45.03</td>
<td>19.72</td>
</tr>
<tr>
<td>Part. density (g/cm³)</td>
<td>(\sim 2.76)</td>
<td>(\sim 2.76)</td>
</tr>
<tr>
<td>From scaling laws</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas density</td>
<td>((\rho_f)_{\text{hot}})</td>
<td>((\rho_f)_{\text{hot}})</td>
</tr>
<tr>
<td>Diameters or lengths</td>
<td>(D_{\text{hot}})</td>
<td>0.577(D_{\text{hot}})</td>
</tr>
<tr>
<td>Particle diameter</td>
<td>((d_p)_{\text{hot}})</td>
<td>0.577((d_p)_{\text{hot}})</td>
</tr>
<tr>
<td>Superficial velocity</td>
<td>((u_0)_{\text{hot}})</td>
<td>0.759((u_0)_{\text{hot}})</td>
</tr>
<tr>
<td>Volumetric part. flux</td>
<td>((G_s/\rho_p)_{\text{hot}})</td>
<td>0.759((G_s/\rho_p)_{\text{hot}})</td>
</tr>
<tr>
<td>Time</td>
<td>(t_{\text{hot}})</td>
<td>0.759(t_{\text{hot}})</td>
</tr>
</tbody>
</table>

26
3.2.3 Slugging Analysis in the Circulation Riser

Slugging is common in tall, narrow beds of solids. The most critical part concerning slugging in the cold-flow model is the circulation riser. Observations during operation in a default fluidization setting confirm that there indeed is slugging in this section. The bed material chosen is a fine silica sand, consisting of 98.8% SiO$_2$. These particles, having average particle diameter $d_p = 92$ and particle density $\rho_p = 2.65$ g/cm$^3$, are Geldart B solids, hence the slugs formed are a mixture of axial slugs and wall slugs $[37]$. Fluidization in the circulation riser was investigated for four different fluidization velocities, varying from 0.21 – 0.57 m/s, see Fig. 3.9. It shows the pressure drop between two points in the upper part of the riser, above the bed. This figure also includes information on the mean value $\mu$, the standard deviation $\sigma$, and the current bed height in the fuel reactor $h_{FR}$. As can be observed, the peaks are cut at roughly 6 kPa. This is a limitation in the pressure transmitter installed between these two
points. However, despite this it is possible to see a trend with more fluctuations for the lower velocities and less fluctuations for the higher velocities. This has to do with the terminal velocity of the sand particles. It was calculated that $u_t \approx 0.41 \text{ m/s}$, hence, when passing this limit, the transfer of particles will not only occur with slugs, but will be diluted with a small continuous flow. This decreases the pressure fluctuations. On the other hand, the bed height in the fuel reactor falls considerably when $u_{0,CR} > u_t$. The desired bed height in FR is around 59–60 cm, i.e. the height to the exit to LS3, hence $u_{0,CR} = 0.33 \text{ m/s}$ was chosen as default velocity in the circulation riser.

![Graph showing pressure differences with varying velocities](image)

**Fig. 3.9:** Pressure difference between two points in the top of the circulation riser.

### 3.2.4 Bed Inventory Stability

If no changes are made to the flow in the circulation riser, i.e. $u_{0,CR} = 0.33 \text{ m/s}$, then an increase in either the air or the fuel reactor flow may rearrange the bed inventories by transferring particles from the fuel reactor to the air reactor or vice versa. Evidence of this is shown in Fig. 3.10. For example, increasing the fluidization velocity in the air reactor will increase the circulation mass flow, but it will only decrease its bed mass slightly. At the same time, the bed mass in the fuel reactor will increase slightly. Experiments show that this rearrangement of bed inventories is small. After a change, a new steady state will appear. This means that if the outgoing mass flow is increased by a certain amount, the incoming mass flow will also increase with the same amount. It is evident from Fig. 3.10 that the circulation, both in the fuel reactor loop and between the air and fuel reactor, can be varied in a large range with only minor changes in solids inventory. Thus, the system is very stable.
Chapter 3. Modeling

3.2.5 The Riser Mass Flow

Similar to the analysis in Section 3.1.4, the flow-through ratio for both the fuel reactor, $\dot{m}_{FR}/\dot{m}_{\text{riser}}$, and air reactor, $\dot{m}_{AR}/\dot{m}_{\text{riser}}$, in the cold-flow model is measured. The riser mass flow, $\dot{m}_{\text{riser}}$, is calculated from Eq. (2.12), while the circulation mass flow, $\dot{m}$, is measured with the aid of valves implemented in the downcomer after each cyclone. The results are shown in Fig. 3.11. The circulation mass flow was found to be about 45% of the riser mass flow for the fuel reactor and 29% for the air reactor.

Fig. 3.11: The circulation mass flow entering the cyclone versus the riser mass flow.
3.2.6 Residence-Time

With knowledge of the bed mass in different parts of the system, the residence-time can be calculated from Eq. (3.1). The mass flow is calculated as described in Section 3.2.5. This is done for both the air and fuel reactor. However, for the fuel reactor, it is more interesting to also include the loop seal LS2. The results are shown in Fig. 3.12. The bed material of the fuel reactor is part of two different loops, i.e. the major AR–FR loop and the internal FR loop via CY2. Here, the turnover of particles in the FR loop is neglected. Thus, $\tau_{AR}$ is an average residence-time of a particle in the air reactor, while $\tau_{FR+LS2}$ is a measure of the residence-time in the fuel reactor and loop seal LS2 with respect to the overall mass flow from the air reactor.

\[
\begin{align*}
\text{(a) For FR and LS2: } & \tau_{FR+LS2} = \frac{m_{FR+LS2}}{m_{AR}}. \\
\text{(b) For the air reactor: } & \tau_{AR} = \frac{m_{AR}}{m_{AR}}.
\end{align*}
\]

Fig. 3.12: The residence-time versus the superficial velocity in the (narrow part of the) air reactor riser.

3.2.7 Pressure Profile

Height vs pressure profiles can be used to illustrate the characteristics of interconnected fluidized beds. One such image is given in Fig. 3.13. The sketch enclosed is Fig. 3.7 appended with numbers that indicate a flow path. This path begins at the bottom of loop seal LS2 and follows the numbers in a complete cycle. Thus, each number in the sketch corresponds to a point in the pressure profile as compared with the atmospheric pressure.
Fig. 3.13: Pressure profile from fluidizing the system with air.
3.2. Cold-Flow Model of a 100 kW Unit (Paper II)
Discussion and Conclusions

4.1 Remarks

In both the 10 kW unit and the cold-flow model, correlations between the circulation mass flow and the riser mass flow were derived. The circulation mass flow is the mass flow of particles that can be measured after the connected cyclone, while the riser mass flow is calculated from pressure drops in the riser. The two should not be the same, as a fraction of the particles entrained is separated at the riser top and falls back along the walls.

For the air reactor of the 10 kW unit, the ratio between the circulation and the riser mass flows was found to be approximately 22%, while for the fuel and air reactor of the cold-flow model 45% and 29% were found. One difference between these two units is the cyclone inlet. The cyclone inlet has a constant cross-section in the 10 kW unit, while it has a varying cross-section, going from large to small, in the 100 kW unit. A varying cross-section, as described above, may increase the transfer of particles.

The two big cyclones, CY1 and CY2, in the cold-flow model are identical in size and geometry. The difference in flow-through ratio is most likely explained by the difference in Δh, i.e. the distance between the pressure tap in the top of the riser to the closest pressure tap below. The smaller the distance, the more adequate estimate Eq. (2.12) will yield for the riser mass flow in the top part of the riser. As ΔPΔh/Δh increases with increasing Δh, and as Δh_{AR} > Δh_{FR}, cf. Fig. 3.13, the riser mass flow in the AR–FR loop is over-estimated in comparison with the riser mass flow in the FR loop.
4.2 Conclusions

This thesis summarizes many important findings from Paper I and II. Paper I contains a study of a multistage-bed model, applied to a residence-time analysis in a 10 kW chemical-looping combustor. Conclusions from the study of the 10 kW unit include:

- From experiments, where fuel was added batch-wise to the 10 kW unit, and using analysis of gas concentrations exiting the air reactor, it was possible to determine the residence-time and residence-time distribution of particles in the fuel reactor for a number of operational cases with different particle circulation. Knowing the solids inventory in the fuel reactor, the circulation mass flow could also be determined.

- The circulation mass flow could be directly correlated to the riser mass flow, determined from pressure drop measurements in the riser. This correlation could be used to determine the circulation mass flows in previous operation with continuous fuel addition.

- Using results for carbon-capture efficiency and residence-time distribution, a model was developed which could determine a mass-based reaction-rate constant for char conversion. The reaction-rate constant of a Mexican petroleum coke at both 950°C and 970°C was calculated to 18.2 wt%/min and 28.8 wt%/min, respectively. The reaction-rate constant of a South African coal at 950°C was calculated to 26.1 wt%/min. This mass-based reaction-rate constant could also be determined independently from the conversion rates of char obtained in batch tests. There was reasonable agreement between these two ways of assessing the reaction-rate constant, indicating that the model well describes the behaviour of the unit.

Paper II provides design and first operation experience of a cold-flow model for a 100 kW chemical-looping combustor. Conclusions from the study of the cold-flow model include:

- The solids inventories in the fuel and air reactors of the cold-flow model are stable to changes in the fluidization velocity, i.e. the system is self-stabilizing in a large range of circulation mass flows.

- The cold-flow model residence-time in the fuel and air reactor sections were found to lie between 2–11 minutes and 3–21 minutes, respectively, for the investigated fluidization velocities of the air reactor. This showed that it was possible to vary the residence-times in a large range.

- The circulation mass flows in the fuel reactor loop and air reactor were approximately linear in the riser mass flow, as determined by pressure drops. The relations found should be useful when estimating the circulation flows in the 100 kW unit.
4.3 Outlook

Future research will focus on the 100 kW hot unit for solid fuels. Results from the cold-flow model may not be directly transferred to the 100 kW unit, as all experiments so far have been conducted with air fluidization. In order to satisfy the conditions for dynamical similarity, fluidization with helium is a requirement. In fact, a helium recirculation system has already been designed and implemented in the cold-flow model. Results from coming experiments involving this system, together with the lessons learned from Paper II with air fluidization, will likely be of great value in the study of the 100 kW unit.

Initial operation of the 100 kW unit has recently commenced using ilmenite oxygen carriers and Colombian coal. Preliminary results in fuel operation yield a very similar pressure profile as that in Fig. 3.13. The multistage-bed model from Paper I may be implemented into the 100 kW study. However, it is not yet known how the complicated nature of the flow path and the (even greater) dissimilarities to the analogy of equal-sized CSTRs in series will effect the results. A residence-time analysis of the 100 kW unit will most likely be based on a combination of cold-flow model comparisons and a study of time-differentials in the gas concentration measurements.
4.3. Outlook
Nomenclature

\( \bar{d}_p \)  Average particle diameter (\( \mu \text{m} \))

\( \Delta h \)  Distance between two pressure taps in the riser (m)

\( \Delta P_{\Delta h} \)  Pressure drop over \( \Delta h \) (kPa)

\( \dot{m} \)  (Actual) circulation mass flow (kg/min)

\( \dot{m}_{AR} \)  (Actual) circulation mass flow in the AR–FR loop (kg/min)

\( \dot{m}_{FR} \)  (Actual) circulation mass flow in the FR loop (kg/min)

\( \dot{m}_{G_s, \ riser} \)  (Estimated) riser mass flow, i.e. the upward mass flow of particles in the riser (kg/min)

\( \dot{n}_k \)  Molar flow of particles after the \( k \):th CSTR (mol/s)

\( \epsilon \)  Bed voidage (-)

\( \eta_{CC} \)  Carbon-capture efficiency (wt%)

\( \eta_{SF} \)  Solid fuel conversion efficiency (wt%)

\( \text{Fr} \)  The Froude number (-)

\( \text{Re}_D \)  The Reynolds number based on bed diameter (-)

\( \text{Re}_{d_p} \)  The Reynolds number based on particle diameter (-)

\( \mu_f \)  Dynamic viscosity of the fluidization gas (\( \mu \text{Pas} \))

\( \phi \)  Particle sphericity (-)

\( \rho_b \)  Bulk density (kg/m\(^3\))

\( \rho_f \)  Fluidization gas density (kg/m\(^3\))

\( \rho_p \)  Particle density (kg/m\(^3\))

\( \rho_t \)  True density (kg/m\(^3\))

\( \tau \)  Total residence-time (min)

\( \tau_k \)  Residence-time in the \( k \):th CSTR (min)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varphi$</td>
<td>Particle porosity (-)</td>
</tr>
<tr>
<td>$A$</td>
<td>Cross-section area of the riser (m$^2$)</td>
</tr>
<tr>
<td>$C_k$</td>
<td>Concentration of particles after the $k$:th CSTR (mol/s)</td>
</tr>
<tr>
<td>$CI$</td>
<td>Circulation index (kPa·L/min)</td>
</tr>
<tr>
<td>$D$</td>
<td>Bed diameter (m)</td>
</tr>
<tr>
<td>$F_{AR,out}$</td>
<td>Volumetric flow of gas in the air reactor (L/min)</td>
</tr>
<tr>
<td>$f_{scale}$</td>
<td>The scale factor determined by the full set of scaling laws (-)</td>
</tr>
<tr>
<td>$f_{vol}$</td>
<td>Ratio of the carbon mass in the volatiles to the total carbon mass in the fuel (wt%)</td>
</tr>
<tr>
<td>$g$</td>
<td>The gravitational acceleration on Earth (m/s$^2$)</td>
</tr>
<tr>
<td>$G_s$</td>
<td>Particle mass flux (kg/(m$^2$·s))</td>
</tr>
<tr>
<td>$k$</td>
<td>Reaction-rate constant (%/min)</td>
</tr>
<tr>
<td>$L$</td>
<td>Characteristic bed length, e.g. height (m)</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass (kg)</td>
</tr>
<tr>
<td>$m_\tau$</td>
<td>Total bed mass in the four sections that the bed particle “passes” from the fuel reactor to the air reactor (kg)</td>
</tr>
<tr>
<td>$m_{0,ox}/m_{0,red}$</td>
<td>Mass of a fully oxidized/reduced oxygen carrier particle (kg)</td>
</tr>
<tr>
<td>$m_{C,FR}/m_{C,conv}$</td>
<td>Carbon mass of gasified char (including/-excluding volatiles) (g)</td>
</tr>
<tr>
<td>$m_{C,fuel}$</td>
<td>Total batch mass of carbon (g)</td>
</tr>
<tr>
<td>$m_{C,vol}$</td>
<td>Carbon mass of the volatiles (g)</td>
</tr>
<tr>
<td>$m_{C,ws}$</td>
<td>Carbon loss to the water seal (g)</td>
</tr>
<tr>
<td>$m_{in}$</td>
<td>Carbon mass reaching the air reactor plus the total carbon mass of gasified char (g)</td>
</tr>
<tr>
<td>$m_{loss, m_{C,AR}}$</td>
<td>Carbon mass reaching the air reactor (g)</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure (kPa)</td>
</tr>
<tr>
<td>$Q$</td>
<td>Overall volume flow (m$^3$/s)</td>
</tr>
<tr>
<td>$R_0$</td>
<td>Oxygen-transfer capacity of the oxygen carrier (wt%)</td>
</tr>
<tr>
<td>$u_0$</td>
<td>Superficial gas velocity (m/s)</td>
</tr>
<tr>
<td>$u_t$</td>
<td>Terminal velocity of the oxygen carrier particles (m/s)</td>
</tr>
<tr>
<td>$V_k$</td>
<td>Volume of the $k$:th CSTR (m$^3$)</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle size distribution (-)</td>
</tr>
</tbody>
</table>
Bibliography


Paper II