Capture of CO$_2$ from Solid Fuels using Chemical-Looping Combustion and Chemical-Looping with Oxygen Uncoupling

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ABSTRACT

In order to meet the global demand of CO$_2$ neutral energy, chemical-looping combustion could play an important role. Oxygen can be transferred from the combustion air to the fuel by means of oxygen carrying metal oxide particles circulating between two reactors, an air- and a fuel reactor. This enables combustion of a fuel without mixing the products of combustion, CO$_2$ and H$_2$O with the nitrogen from the combustion air.

In this thesis two main strategies for using solid fuels with oxygen-carrier material have been investigated. The first is introduction of the coal directly to the fuel reactor where the gasification of the coal and subsequent reactions with the metal oxide will occur simultaneously. The second is to use an oxygen carrier which releases O$_2$ in the gas-phase in the fuel reactor. The solid fuel is oxidized through normal combustion. The last alternative is referred to as chemical-looping with oxygen uncoupling (CLOU). The results give proof of concept for both investigated options.

A small lab reactor designed for tests of solid fuels has been developed, and an experimental procedure for testing solid fuels established. The procedure involves the cyclic oxidation of oxygen carrier with oxygen containing gas and reduction with solid fuel. Also a larger screening was made of different ores and industrial materials identifying a number of possible low-cost oxygen carrying materials.

The gasification rate of the char was the rate limiting reaction, as the reaction of oxygen carrier with gasification products CO and H$_2$ was found to be quite rapid. The presence of an oxygen carrier enhances the gasification rates significantly, most likely because of removal of H$_2$ and CO. The conversion rate of the fuel was dependent on the fraction of steam and SO$_2$ in the fluidizing gas, as well as temperature and fraction of volatiles in the fuel. A preliminary estimation of the oxygen carrier inventory needed in a real CLC-system with solid fuel suggested that it would be between 200 and 2000 kg/MW$_{th}$ depending on which fuel and which oxygen carrier is used.

The rates of fuel conversion are much higher in CLOU compared to CLC and the rate increased significantly with increasing temperature. No CO was measured in the CLOU experiment with petroleum coke and oxidation of oxygen carriers could take place at low oxygen concentrations close to the equilibrium partial pressure.

Keywords: CO$_2$-capture; chemical looping combustion, CLC; chemical-looping with oxygen uncoupling, CLOU; oxygen carrier; gasification; fluidized bed; coal; petroleum coke; biofuels;
PREFACE
This thesis is primarily based on the work presented in the following appended papers:

**Paper I**
H. Leion, T. Mattisson, A. Lyngfelt;
“The use of ores and industrial products as an oxygen carrier in chemical-looping combustion”
*Submitted for publication*

**Paper II**
H. Leion, A. Lyngfelt, M Johansson, E. Jerndal, T. Mattisson;
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*Chemical Engineering Research and Design, 86, 1017-1026, 2008*

**Paper III**
H. Leion, T. Mattisson, A. Lyngfelt;
“The use of petroleum coke as fuel in chemical-looping combustion”
*Fuel, 86, 1947-1958, 2007*

**Paper IV**
H. Leion, T. Mattisson, A. Lyngfelt;
“Solid fuels in chemical-looping combustion”
*International Journal of Greenhouse Gas Control, 2, 180-193, 2008*

**Paper V**
H. Leion, A. Lyngfelt, T. Mattisson;
“Solid fuels in chemical-looping combustion using a NiO-based oxygen carrier”
*Submitted for publication*

**Paper VI**
H. Leion, T. Mattisson, A. Lyngfelt;
“CO₂ capture from direct combustion of solid fuels with Chemical-Looping Combustion”

**Paper VII**
“Solid fuels in chemical-looping combustion using unprocessed iron ore and oxide shells as oxygen carrier”
*Submitted for publication*

**Paper VIII**
T. Mattisson, A. Lyngfelt, H. Leion;
“Chemical-looping with oxygen uncoupling for combustion of solid fuels”
*Accepted for publication in International Journal of Greenhouse Gas Control, 2008*
Paper IX
T. Mattisson, H. Leion, A. Lyngfelt;
“Chemical-looping with oxygen uncoupling using CuO/ZrO$_2$ with petroleum coke”
*Accepted for publication in Fuel, 2008*

Paper X
H. Leion, T. Mattisson, A. Lyngfelt;
“Combustion of a German lignite using chemical-looping with oxygen uncoupling (CLOU)”
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**CONTRIBUTION REPORT**

**Paper I:** Responsible for most experimental work, evaluation of data and writing.

**Paper II:** Responsible for all evaluation of data and writing, and a large part of the experimental work.

**Paper III:** Responsible for all experimental work, evaluation of data and writing.

**Paper IV:** Responsible for all experimental work, evaluation of data and writing.

**Paper V:** Responsible for all experimental work, evaluation of data and writing.

**Paper VI:** Responsible for all experimental work, evaluation of data and writing.

**Paper VII:** Supervisor of experimental work, evaluation of data and writing of original Swedish version which was a student project work. Responsible for writing the final version in English.

**Paper VIII:** Responsible for a large part of the experimental work and evaluation of data, and a small part of the writing.

**Paper IX:** Responsible for all of the experimental work and evaluation of data, and a small part of the writing.

**Paper X:** Responsible for all of the experimental work and evaluation of data, and part of the writing.
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1 Introduction
Since Arrhenius, over 100 years ago, first discovered the connection between the amount of CO$_2$ in the atmosphere and the global average temperature [1] the concentration of CO$_2$ in the atmosphere has risen and is today approximately 30% higher than the pre-industrial level. The concentrations of other greenhouse gases, such as N$_2$O and CH$_4$, have also increased considerably. It is today believed that this increase in greenhouse gas concentrations has caused an increase in global temperature which in turn has caused changes in today’s climate [2]. Therefore a reduction in emissions of greenhouse gases, and in particular CO$_2$, is necessary. This could be achieved by improved efficiency of energy use as well as increasing the use of non-fossil energy sources. However, fossil fuels, and in particularly coals, are worldwide the dominant energy source and are likely to be used to a large extent in the future. This is especially true in fast growing economies, where coal is inexpensive and abundant, thus an attractive source for meeting the rapidly increasing energy demands. Therefore the use of carbon capture and storage from fossil fuels can serve as a bridge between a society highly dependent on fossil fuels and a future non-carbon based society and still reduce emissions of greenhouse gases from combustion of fossil fuels.

1.1 Capture and storage of CO$_2$
It is today possible to store CO$_2$ in depleted oil- and natural gas fields as well as in deep coal beds [3]. These types of storage sites may also be commercially interesting since injection of CO$_2$ opens the possibility to increase the amount of extracted oil or natural gas from these formations and thereby prolonging the lifetime of these energy sources.

Also storage in saline aquifers, which is a geologically sealed formation filled with salt water, provides a large potential for storage of CO$_2$. This is today practiced in the North Sea outside Norway at the Utsira Formation [3]. The natural gas from the nearby natural gas field Sleipner contains CO$_2$ which has to be removed before being sold to the customer. Due to the comparably high taxes for emitting CO$_2$ in Norway, it is more profitable to store the CO$_2$ than to emit it to the atmosphere. Other ongoing CO$_2$-storing projects are the Weyburn project for enhanced oil recovery in Saskatchewan,
Canada and the In Salah project in Algeria [3]. Altogether, the large global potential to store CO$_2$ can provide a significant help in preventing greenhouse gases from being emitted to the atmosphere. IPCC estimates that by 2050 20-40% of the CO$_2$ from all fossil sources could be geologically stored [3].

In order to store CO$_2$ from combustion, it first needs to be separated from the combustion gases. Compared to storing and transport of CO$_2$ to the storage site, capturing of CO$_2$ is rather energy consuming. This will add on to the production costs of electricity with 20-85% [4] and also lower energy efficiency by 7 -15%-units [5] as compared to a conventional power plant. The cost for capture is estimated to comprise about 75-80% of the total cost for CO$_2$ capture and storage [5].

There are several proposed processes for separating the carbon dioxide from the flue gases. The three main techniques are post-treatment, O$_2$/CO$_2$ firing (oxyfuel) and pre-treatment (CO-shift) [3]. In post-treatment, the CO$_2$ is separated from the nitrogen containing flue gases after a normal combustion step. This can for example be done with amine absorption, selective absorption or membrane separation. The advantage with post-treatment is that the CO$_2$ separation equipment can be added to an existing industrial plant.

In O$_2$/CO$_2$ firing, or oxyfuel, the combustion of the fuel takes place in a mixture of oxygen and recycled combustion gases, resulting in combustion gases consisting of mainly H$_2$O and CO$_2$, thus pure CO$_2$ can be obtained after condensation of the steam. This means that smaller amount of flue gases will have to be treated compared to post-treatment. Also formation of NO$_X$ is suppressed and a CO$_2$-capture efficiency of almost 100% is possible, compared to about 90% for post-treatment. However, pure oxygen has to be produced and the high CO$_2$ concentration in boilers and other equipment makes corrosion a larger problem in O$_2$/CO$_2$ firing compared to a normal air-fired boiler.

The third often mentioned technology is pre-treatment, or CO-shift. Here O$_2$ and/or H$_2$O are used to convert the fuel to a mixture of CO$_2$, CO, H$_2$O and H$_2$. This mixture is used in a shift reactor where it is converted to CO$_2$ and H$_2$ after which the CO$_2$ is separated. Hence, a stream of almost pure H$_2$ is obtained after separation that can be
burnt without the release of any carbon containing gases. A drawback is that the equipment for pre-treatment is rather complex and expensive. An advantage is that the produced hydrogen can be used in a wide range of applications, whereas post-treatment and O₂/CO₂ firing is limited to large stationary power plants.

These three techniques are all associated with large energy penalties and high costs for separation of gas. It would be favourable if the nitrogen in the air could be kept from being mixed with the fuel without the need for gas separation. This is achieved in unmixed combustion or Chemical-Looping Combustion (CLC).

### 1.2 Chemical Looping Combustion (CLC)

The ideas of CLC originate from a patent for CO₂ production by Lewis and Gilliland in 1954 [6]. An oxygen carrier is circulated between two fluidized bed reactors, an air and a fuel reactor, shown in Figure 1.

![Figure 1: Schematic picture of the CLC-process.](image)

The fuel is introduced to the fuel reactor where it reacts with an oxygen carrier to CO₂ and H₂O, reaction (1). The reduced oxygen carrier is transported to the air reactor where it is oxidized back to its original state by air, reaction (2). In this work, when oxidation and reduction is mentioned, it refers to oxidation and reduction of the oxygen carrier. With this arrangement the fuel never meets the air, resulting in one
stream of oxygen depleted air leaving the air reactor, and one stream of combustion gases, that mainly consist of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \), leaving the fuel reactor. The water is easily condensed and the \( \text{CO}_2 \) can, after compression, be transported for underground storage.

\[
C_yH_{2m} + (2n + m)\text{Me}_xO_y \leftrightarrow n\text{CO}_2 + m\text{H}_2\text{O} + (2n + m)\text{Me}_xO_{y-1} \quad (1)
\]

\[
\text{O}_2 + 2\text{Me}_xO_{y-1} \leftrightarrow 2\text{Me}_xO_y \quad (2)
\]

As a result, \( \text{CO}_2 \) can be inherently separated without any direct loss in efficiency, since the total amount of heat released in the air and the fuel reactor is equal to the heat released from normal combustion. This can also be seen if reaction (1) and reaction (2) are added, which gives the reaction for conventional combustion.

To produce hydrogen there is also the possibility to add less oxygen than is needed for complete combustion to the air reactor, resulting in flue gases with a high content of \( \text{H}_2 \) and \( \text{CO} \) that can be used in a shift reactor to produce \( \text{CO}_2 \) and more hydrogen [7].

Ishida et al. were the first to use the term CLC in 1987 [8]. Since then it has grown from a paper concept to one of the most promising techniques for \( \text{CO}_2 \)-capture [9]. A proposed design of a chemical-looping combustor for natural gas was given by Lyngfelt et al. [10] and is presented in Figure 2. In the air reactor the particles are oxidized by a high flow of air (1 in Figure 2). This flow is sufficiently high to entrain the particles. The particles are lead to a cyclone (2) from where they are separated from the oxygen depleted air. From the cyclone the particles fall down into the fuel-reactor (3) where they react with the added fuel. The fuel reactor is a bubbling fluidized bed and the particles are transported back to the air-reactor by gravity. The heat released from the process can be used in a conventional Clausius-Rankine process or, if the system is pressurized, the depleted air from the air reactor can be used in a gas turbine. The combustion products (\( \text{CO}_2 \) and \( \text{H}_2\text{O} \)) from the fuel reactor are separated in a condenser. Finally the \( \text{CO}_2 \) will be compressed to a liquid for further transportation. Between the reactors are particle locks to prevent any mixing of the gases, i.e. keep the two gas streams of the fuel and air reactor separate.
In 2003 a 10 kW prototype CLC-unit was built at Chalmers and successfully operated for more than 100 h using natural gas as fuel [11]. Since then the process has been demonstrated with gaseous fuel in reactor units ranging from 300 W to 120 kW [11-19]. Different aspects of the CLC-process have been investigated such as different oxygen carriers with different support materials and sintering temperatures [20-22], different manufacturing processes of oxygen carriers [23], fluidizing properties [24, 25], process simulations [26] and thermodynamic restrictions [27, 28]. The suggested references are only examples and a more complete overview of the present state of the CLC-technique with gaseous fuel is given by Lyngfelt et al. [29] or by Hossain and de Lasa [30].

1.2.1 CLC with solid fuel
Almost all of the work around chemical-looping combustion has focused on the use of gaseous fuels such as natural gas or methane. Since solid fuels, such as coal and petroleum coke, are considerably more abundant and less expensive than natural gas, it would be highly advantageous if the CLC-process could be adapted for solid fuels. One way of doing this is to introduce the coal directly to the fuel reactor where the gasification of the coal and subsequent reactions with the metal oxide particles will occur simultaneously. Another strategy is to use an oxygen carrier which releases O$_2$ in
the fuel reactor and thereby allowing the fuel to actually burn with gas-phase oxygen. This second alternative is referred to as chemical-looping with oxygen uncoupling (CLOU). There is also the possibility to use syngas from coal gasification in the fuel reactor which does not require much modification of the CLC-unit as compared to when natural gas or methane is used as fuel. However, this option requires the fuel to first be treated in a gasifier which is a rather expensive piece of equipment. Further, an air separation unit will be needed in order to produce pure oxygen for the gasification step, which will reduce the overall efficiency of such a process.

When the fuel is fed directly into the fuel reactor the solid-solid reaction between coal and a metal oxide is not very likely to occur at an appreciable rate. To gasify the fuel, from now on simplified as carbon (C), either steam or carbon dioxide can be used according to:

\[
C + H_2O \rightarrow CO + H_2 \quad (3)
\]

\[
C + CO_2 \rightarrow 2CO \quad (4)
\]

The oxygen can also be transferred within the gas phase by the CO-shift reaction.

\[
CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (5)
\]

The gasification products then react with the metal oxide according to:

\[
Me_xO_y + H_2 \rightarrow Me_xO_{y-1} + H_2O \quad (6)
\]

\[
Me_xO_y + CO \rightarrow Me_xO_{y-1} + CO_2 \quad (7)
\]

More or less all fuels contain volatiles consisting of CO, H_2, CH_4 or higher hydrocarbons. These volatiles will almost immediately be released as the fuel enters the hot environment of the fuel reactor and react with the oxygen carrier according to reaction (1), (6) or (7). It is important that the mixing between the oxygen carrier particles and the fuel is sufficient in the fuel reactor, so that the volatiles are not released without reacting. Studies of the reaction between the metal oxide particles and CO, H_2 or CH_4 have shown that these reactions are generally rapid at high
temperatures [31], thus the gasification of the char part of fuel in the fuel reactor can be expected to be the rate limiting step. An important advantage compared to normal gasification is that it will take place in a high concentration of CO$_2$ and H$_2$O which is highly beneficial for the gasification rate [32-34].

In CLOU an oxygen carrier is needed that releases O$_2$ in the fuel reactor according to:

\[
Me_xO_y \Rightarrow 2Me_xO_{y-1} + O_2 \tag{8}
\]

The fuel can then simply burn in the gas phase oxygen according to:

\[
C + O_2 \Rightarrow CO_2 \tag{9}
\]

In this way the slow gasification step in reaction (3) and (4) is avoided giving a much faster conversion of the fuel. However, the number of possible oxygen carriers in CLOU is limited, as discussed below. Also reaction (8) is governed by thermodynamics, resulting in restraints on the operational temperature for a CLOU-unit. Further, when it comes to oxidation of the oxygen carriers, according to reaction (2), the CLOU-process has additional thermodynamic limitations, whereas the oxidation in other CLC-applications is fast and seemingly limited only by the supply of oxygen. The concept of CLOU was proposed in 2005 by Lyngfelt and Mattisson in a patent application [35].

The reactor design for a CLC-system operating with solid fuels will be somewhat different compared to the design for a unit fired with gaseous fuels. For example there will be a need for separation of oxygen carrier particles from fuel and ash particles. The fuel particles have a lower density than the oxygen carrier and the fuel particles are gradually reduced in size due to chemical reactions as well as fragmentation and attrition which opens possibilities for separation. A carbon stripper after the outlet of the fuel reactor can be used to capture and recycle unconverted carbon to the fuel reactor. The separation of ash from the metal oxide particles can be accomplished by feeding small fuel particles to the system. During conversion of the fuel, the fuel particles will produce even smaller ash particles, small enough to be elutriated with the
fluidizing gas and separated in a cyclone. Nevertheless it can not be avoided that some of the oxygen carrying particles are lost with the ash, especially particles which, due to breakage and fragmentation, are so small that they have the same fluidizing properties as the ash. The oxygen carrying particles may also suffer from reactivity loss due to reaction with ash components.

It is also important to design the fuel reactor in such a way that volatiles and gasification products have good contact, and sufficient time to react, with the oxygen carriers. But since the metal oxides and fuel particles should be well mixed in the reactor there will be fuel particles at the top of the bed, and thus it is expected that there will be some gasification products, i.e. CO and H$_2$, from the outlet of a CLC fuel reactor even when the reactivity of the metal oxide particles is high. In the CLOU-process, the final oxidation of the fuel occurs in the gas phase which should make it possible to operate a CLOU-system without any unconverted flue gases.

### 1.2.2 Oxygen carriers in CLC

The oxygen-carrying particles are a cornerstone in the CLC-technique. The particles have to be able to convert the fuel to CO$_2$ and H$_2$O to the highest degree possible as well as have a high reactivity with oxygen in the air reactor. The conditions in a fluidizing bed demand sufficiently stable particles which are resistant towards fragmentation and attrition, as well as particles with good fluidization properties which do not agglomerate. For commercial use of the CLC-process the particles also need to be environmentally sound and have an overall reasonable price.

Most of the oxygen carrier development has been made using natural gas or methane as fuel. The main candidates for oxygen carrying materials are nickel, copper, manganese and iron oxides, but other systems have also been proposed [27]. Even if there are large differences between various particles the order of reactivity with methane is generally NiO > CuO > Mn$_3$O$_4$ > Fe$_2$O$_3$ [36]. The most reactive metal oxides are also generally the most expensive. With NiO there are also health aspects to be considered. Furthermore, NiO also differs from the other oxides by having a thermodynamic restriction, it cannot convert hydrocarbon fuels fully to CO$_2$ and H$_2$O
giving a maximum conversion of typically 99-99.5%, depending on fuel and temperature [27].

When methane is used as fuel, the reaction in the fuel reactor is endothermic for all the oxides except CuO [27]. This is clearly an advantage for CuO, since it reduces the particle circulation needed to maintain the temperature in the fuel reactor. On the other hand, Cu has the disadvantage of a comparably low melting temperature, 1085°C. However, for syngas the common oxides have an exothermic reaction in both fuel and air reactors.

CLC-particles can be made from any of these metal oxide or mixtures of two or more oxides. Also there are a vast number of different support materials which might add other properties to the particles. For instance Al₂O₃ and MgAl₂O₄ are well studied support materials for NiO and Fe₂O₃ [37-39]. Furthermore, the method used to produce the particles may also affect the particle properties. For an overview on oxygen carrier with methane see the work performed by Johansson [36].

Dealing with solid fuel puts some new demands on the oxygen carrier. Examples of factors which should be considered are:

- The possibility that the fuel ash may react with the particles, causing deactivation and decreased reactivity of the particle.

- Ash has to be separated from the oxygen carriers which may result in losses of some of the oxygen carrying material during separation.

- Highly reactive materials in chemical-looping combustion are often understood to be materials with high reactivity towards methane. For solid fuels, however, reactivity towards methane is less important and the reactivity towards CO and H₂, reaction (6) and (7), should be high. Some low-cost materials have been found to have quite high reaction rate with CO and H₂ [31].
The gasification reactions in the fuel reactor are in most cases slower than the reactions of the metal oxide with the intermediate syngas, resulting in a long residence time and a large solids inventory in the fuel reactor, thus high reactivity of oxygen-carriers could be of less importance.

Thus, it is clear that materials of higher reactivity, and thereby higher cost, are not necessarily needed for solid fuels because particle life-time may be restricted by presence of ash, whereas low-cost materials having sufficient reactivity towards H₂ and CO on the other hand may prove quite useful. However, a large number of solid fuels contain considerable fractions of volatiles. If these volatiles are released as methane or high hydrocarbons the oxygen carrier also need to have a high reactivity towards these gases.

1.2.3 Oxygen carriers in CLOU

The oxygen carrier for CLOU needs to have special characteristics and needs to react reversibly with gas-phase oxygen at high temperature. As mention before, this places special thermodynamic and kinetic demands on the oxygen carrier in the CLOU-application. Here the particles must have the ability to react both with oxygen in the air reactor and also to release this oxygen sufficiently fast in the fuel reactor. Thus, CLOU utilizes the fact that some metal oxides have a suitable equilibrium partial pressure of gas phase oxygen at temperatures of interest for combustion, i.e. 800-1200°C. Certain oxides based on copper, manganese and cobalt have this property [27] and Figure 3 presents the partial pressure of gas phase O₂ over the metal oxide as a function of temperature for these metal oxide systems.

From Figure 3 it is seen that CuO releases oxygen in air at temperatures above 1028°C, Mn₂O₃ at temperatures above 899°C and Co₃O₄ at temperatures above 889°C. However, in the air reactor, the reduced metal oxide must be able to react with air to the oxidized form and hence lower the oxygen concentration to a reasonable level, given by the excess air. For instance, if the maximum outlet partial pressure of O₂ from the air reactor should be 5%, then it can be seen from Figure 3 that Cu₂O should be able to stay below this level at a temperature below 955°C.
Figure 3: The partial pressure of gas phase $O_2$ over the metal oxide systems at the pressure of one bar as a function of temperature CuO/Cu$_2$O(—), Mn$_2$O$_3$/Mn$_3$O$_4$(-----) and Co$_3$O$_4$/CoO (——).  

When oxidized particles are transferred to the fuel reactor where the partial pressure of $O_2$ is low, they will release gaseous $O_2$. The maximum concentration of oxygen is given by the temperature in the fuel reactor, which is determined by the temperature of the incoming particles, the circulation rate, as well as the heat of reaction in the fuel reactor. Apart from this, all aspects concerning ash and particle separation discussed in section 1.2.2 must also be taken into account, which of course puts high demands on the design of a CLOU-unit.

1.2.4 Literature on CLC with solid fuels

The idea to produce pure carbon dioxide using a “solid oxygen carrier” and “any oxidizable carbonaceous material, such as charcoal, coal, coke and natural gas in two interconnected fluidized beds”, was patented by Lewis and Gilliland already in 1954 [6]. But since then there have been only a few publications investigating CLC with solid fuel, even if the number today is increasing very fast.

The first time solid fuels were used in CLC was when Lyon et al. [40] showed that SO$_2$ improves the conversion of coal with Fe$_2$O$_3$ as oxygen carrier in a small fluidized bed reactor. Pan and co-workers [41] proposed a design for a CLC-unit with solid fuel. Cao et al. [42] have made TGA experiments showing that it is possible to reduce an oxygen
carrier consisting of CuO using coal as fuel. Moreover, Dennis and co-workers [43, 44] demonstrated that lignite char could be oxidized using \( \text{Fe}_2\text{O}_3 \) as oxygen carrier in a small reactor fluidized with steam and \( \text{CO}_2 \). Gao et al. [45] used a Ni-based oxygen carrier with coal also in a fluidized bed batch reactor. Alstom has a development programme for solid fuel CLC with major focus on hydrogen production [46] with the \( \text{CaSO}_4/\text{CaS} \) system as oxygen carrier. Finally Berguerand and Lyngfelt [47, 48] have operated a 10 kW CLC-unit designed for solid fuels with South African coal and petroleum coke as fuel and the mineral ilmenite as oxygen carrier.

Since it is the gasification products of the solid fuel, mainly CO and \( \text{H}_2 \), which reacts with the oxygen carrier, the following publications [14, 31, 49, 50] using syngas in CLC are also of relevance. Here all investigated materials showed high reactivity with syngas. Moreover, Gupta et al. [51] have performed TGA experiments where \( \text{Fe}_2\text{O}_3 \) supported with \( \text{TiO}_2 \) is used to produce syngas from coal and Fan et al. [52] proposed three strategies for coal gasification with CLC.

Regarding CLOU, the only existing publications except for the original patent application [35], are Paper VIII to X included in this thesis.

From the limited literature investigations it is clear that there is a need for more systematic investigations of possible oxygen carriers for solid fuel application, as well as investigations of parameters which may be important for chemical-looping with solid fuels.

1.3 **Objective**

The main objective of this work is to investigate if the CLC-process can be adapted to solid fuels. Paper I to VII explores different aspects of CLC with solid fuels, with investigation of a number of different oxygen carriers and solid fuels. With respect to oxygen carriers, different naturally occurring materials and industrial products have been investigated in addition to synthetically produced particles. Here, both solid and gaseous fuels have been used. Further, several different types of solid fuels have also been investigated, i.e. coal, petroleum coke and bio fuel. Finally, Paper VIII to X focuses on Chemical-looping with oxygen uncoupling (CLOU).
The work in this thesis was mainly experimental, using a batch fluidized bed reactor for the majority of the experiments. Here, the oxygen carriers are exposed to alternating oxidizing and reducing conditions. An important part of the work has been to establish a well-working procedure for investigating the interaction between different solid fuels and oxygen carrier materials under relevant conditions. Apart from the different oxygen carriers, important parameters, such as temperature and steam concentrations, have been varied in order to establish preliminary design criteria of a CLC-system.
2 Experimental

2.1 Experimental setup

The experiments in this thesis were performed with two similar reactor systems. Both systems had the same general layout as presented in Figure 4. The first system (system 1) had for many years been used for CLC experiments with gaseous fuel [36, 53] but could with small modifications be used also for solid fuels. The second system (system 2) was built with additional features making it more suitable for CLC with solid fuels, e.g. a sweeping gas to help feed the fuel and additional filters. This system could also be used for gaseous fuels. The two systems gave close to identical results with gaseous fuel but when it comes to solid fuels, and especially high volatile solid fuels, there was a small difference between the results from the two systems. Paper VI, VII and X mainly include results from system 2 whereas the experiments in the other papers primarily are made on system 1.

![Diagram of laboratory setup, System 2](image)

Figure 4: Schematic layout of the laboratory setup, System 2.

The solid fuel experiments in this work were conducted with a fluidized-bed reactor of quartz presented in Figure 5. In order to achieve good solid mixing in the bed, the reactor was conically shaped just above the distributor plate. The reactor had a total length of 870 mm with a porous quartz plate placed 370 mm from the bottom of the reactor. Below the porous plate the reactor had an inner diameter of 10 mm. Above the distributor plate, the inner diameter of the reactor increased to 30 mm over a height of 20 mm. The diameter was then constant for 250 mm, after which the diameter was
increased to 45 mm for a length of 100 mm. This disengaging section was added in order to avoid smaller fuel and metal oxide particles from leaving the reactor.

Figure 5: Fluidized-bed reactor of quartz.

For the experiments with syngas (50% H\textsubscript{2}, 50% CO) and methane in Paper I, II and VII as well as for the CLOU experiment in Paper VIII and IX a straight reactor was used. This reactor had the same length and a porous quartz plate placed at the same height as the conical reactor, and the inner diameter was 22 mm throughout the reactor.

A sample of oxygen carrier particles was placed on the porous plate and was then initially heated to the reaction temperature. The bed was then alternatingly exposed to an oxidation flow of O\textsubscript{2} in N\textsubscript{2} and the fuel, thus simulating the cyclic conditions of a CLC-system with alternating oxidizing and reducing conditions. Nitrogen gas was also introduced during an inert period of 180 s after each oxidizing and reducing period. For CLOU experiments this inert period was shortened since the oxygen carriers release oxygen in the absence of O\textsubscript{2} and a three minute inert period would have meant that too much oxygen would have been lost during this inert period.

During the reducing period of the solid fuel experiments, the fluidizing gas was normally a mixture of steam and nitrogen, which was introduced from the bottom of
the reactor. At the same time as the fluidizing gas of the reducing cycle entered the bottom of the reactor, solid fuel was inserted through a valve in the top of the reactor, falling down into the fluidized bed. When the fuel was a gas, the fuel itself was used as fluidizing medium. Also, in System 2 a small flow of nitrogen was added at the top of the reactor, partly to help sweep the fuel down into the reactor and partly to serve as additional carrier gas after the steam had been removed in the downstream electric cooler.

The gas from the cooler was then led to a gas analyzer (Rosemount NGA-2000) where the concentrations of CO$_2$, CO, CH$_4$, and O$_2$ were measured in addition to the gas flow. The analyzer in system 2 also had a channel to measure SO$_2$ which System 1 lacked. However, due to interference on the CH$_4$ channel on system 1, SO$_2$ could also be measured on this channel but it was then not possible to obtain accurate measurements when both these compounds were present, i.e. to separate the response of SO$_2$ from that of CH$_4$. System 2 had no such interference.

For some experiments, gas from the outlet of the reactor was collected in bags and analysed with a gas chromatograph (Varian Micro-GC with Molsieve and Poraplot columns). With this gas chromatograph the concentrations of H$_2$ could be measured. The concentrations of CO$_2$, CO, O$_2$ and CH$_4$ were also measured with the gas chromatograph to confirm the accuracy of the regular gas analysis.

In system 1 steam was generated by letting the inlet gas pass a steam bath before entering the reactor. This gave an even flow of steam but limited the steam concentration to a maximum of 50% in the fluidizing gas. In the other setup (system 2) the steam was generated by a steam generator (Cellkraft, Precision Evaporator E-1000). This method of generating steam resulted in some fluctuations in the steam flow, but allowed system 2 to operate with steam concentrations up to 92%.

The temperature was measured 5 mm under and 10 mm above the porous quartz plate. In system 1 this was done with 10% Pt/Rh thermocouples and in system 2 with Pentronic CrAl/NiAl thermocouples enclosed inconel-600. In both setups the thermocouples were enclosed in quartz shells. In system 1 the temperature measurement below the bed was also used for temperature control, referred to as the
set-point temperature in Paper III and IV. The reason for using the lower thermocouple was that it was much less affected by the temperature changes in the bed due to the heat of reaction, compared to the upper thermocouples. System 2 had a built-in regulator in the furnace. Thus both thermocouples in the reactor could be used for direct measurement without having any regulating function. The measurement above the porous plate is most likely a better measure of the actual bed temperature, even if it is less stable. Normally, the measurement above the porous plate was about 20°C higher than the one under the bed. The temperatures measurement had an accuracy of +/- 5°C. In this thesis, and in most of the included papers, all temperatures refer to the upper measurement in the bed of particles. However, it is important to keep in mind that results presented in Paper III and IV uses data from the lower thermocouple located just under the porous quartz plate.

The exothermic nature of the oxidation reaction means that there will be release of heat and therefore a subsequent temperature rise in the bed. Since there was no possibility to cool the reactor in the present setup this temperature increase was limited by, in most cases, using a gas mixture with 5% O₂ in N₂ instead of air.

Most solid fuel experiments were conducted with a gas flow of 600 ml/min (at 1 bar, 0°C), both for the reducing and oxidizing periods. For the experiments with gaseous fuel a flow of 450 ml/min was use during the reduction and 1000 ml/min during oxidation. Depending on the chosen experimental settings this gave gas velocities 5 to 20 times the minimum fluidization velocity. The velocities never exceeded half of the terminal velocity, as calculated from the equations given by Kunii and Levenspiel [54]. With these flows the fuel and oxygen carrier particles should be well mixed in the reactor, which was confirmed in cold-flow experiments. However, reference experiments also indicate that small fuel particles still elutriated from the reactor, which is not surprising since fuel particles become smaller as gradually converted. Also some fuel was lost in the feeding device. These losses are excluded from the calculations, which are based on the carbon containing gases leaving the reactor. From high frequency measurements of the pressure drop over the reactor it was possible to determine whether the bed was fluidized or not [24]. For more information regarding fluidization see section 3.1.4.
Usually a sample of 15-40 g of oxygen carrier particles of size 90-125 μm or 125-180 μm was placed in the reactor on the porous plate. The larger particle size was primarily used for experiments with gaseous fuel as well as for CLOU experiments. The bed height was approximately 20-30 mm when the bed was not fluidized. The diameter of the fuel particles was most often 125-180 μm, i.e. somewhat larger than the oxide particles during solid fuel experiments, in order to promote better mixing when the fuel was fed into the reactor. It was later discovered that different sizes of the oxygen carrier and fuel particles had no or very little effect on the overall reactivity.

The larger bed mass of 40 g was used in the CLC experiments testing different coal types, and was used in order to avoid a high degree of reduction of the oxygen carrier particles. Iron-based particles can be hard to fluidize if reduced to FeO [24] and therefore concerns were raised that ilmenite and the other oxygen carriers used in this work may behave the same way. It was later discovered that this change in bed mass had no or very little effect on the overall reactivity.

2.2 Data evaluation

The gas yield ($\gamma$) is used to quantify the conversion of gas in the gaseous fuel experiments. $\gamma$ is the fraction of CO₂ in the outgoing gas divided with the sum of the fractions of carbon containing gases in the outgoing gas. Hence, a $\gamma$ of 1 corresponds to total conversion of the fuel to CO₂. With CH₄ or CO as reducing gas this gives:

$$
\gamma = \frac{x_{CO_2}}{x_{CO_2} + x_{CO} + x_{CH_4}}
$$
(10)

$x_i$ is the fraction of component $i$ in the outgoing gases after water has been removed. When syngas (CO/H₂) was used as fuel the gas yield was defined with respect to CO, and calculated as in equation (10), but with $x_{CH_4} = 0$. It is also possible to define a gas yield with respect to H₂ as the fraction of H₂O in the outgoing gas divided with the sum of the fractions of hydrogen containing gases in the outgoing gas. But since neither H₂ nor H₂O were directly measured in the experiments in this thesis, no gas yield was defined with respect to H₂. H₂ was, however included when calculating conversion of the particles, see below.
In CLC literature the degree of conversion $X$ of the oxygen carrier is often used to quantify the conversion of the oxygen carrier and is defined as the fraction of the difference between the mass of the oxygen carrier ($m$) and the mass of the oxygen carrier in its most reduced state ($m_{\text{red}}$), and the difference between the mass of the oxygen carrier in its most oxidized state ($m_{\text{ox}}$) and in its most reduced state:

$$X = \frac{m - m_{\text{red}}}{m_{\text{ox}} - m_{\text{red}}}$$  \hspace{1cm} (11)

In some cases the degree of mass-based conversion $\omega$ is used as a measure of the oxygen carrier conversion, as it is convenient for comparisons of different materials of different oxygen carrying capacity. Here $\omega$ is defined as the mass of the oxygen carrier divided with the mass of the oxygen carrier in its most oxidized state:

$$\omega = \frac{m}{m_{\text{ox}}}$$  \hspace{1cm} (12)

With CH$_4$ as fuel $\omega$ can be calculated as the time integral of exhaust gas concentrations through:

$$\omega_i = \omega_{i-1} - \int_{t_i}^{t_{i-1}} \frac{n_{M_o}}{m_{\text{ox}}} (4x_{CO_2} + 3x_{CO} - x_{H_2}) dt$$  \hspace{1cm} (13)

and when syngas is used as fuel:

$$\omega_i = \omega_{i-1} - \int_{t_i}^{t_{i-1}} \frac{n_{M_o}}{m_{\text{ox}}} (2x_{CO_2} + x_{CO} - x_{H_2}) dt$$  \hspace{1cm} (14)

where $n$ is the molar flux of the outgoing dry gas and $M_o$ is the molar mass of oxygen.
$X$ can easily be converted to $\omega$ via:

$$\omega = 1 + R_0(X - 1) \quad (15)$$

where $R_0$ is the oxygen transfer capacity, i.e. the fraction of available oxygen in the oxygen carrier.

$$R_0 = \frac{m_{ox} - m_{red}}{m_{ox}} \quad (16)$$

Since $H_2$ could not be measured it was assumed to be related to the measured faction of CO and CO$_2$ through an empirical relation used in earlier work [55]. This calculated fraction of $H_2$ agreed reasonably well with the fraction calculated from the difference $1 - x_{CO_2} - x_{CO} - x_{CH_4}$ in the part of the reduction period where there is little or no back-mixing. The rate of conversion of the solid fuel is given as an average rate, calculated from:

$$r_{Ave} = \frac{1}{m_{tot}} \frac{m_i}{t} \quad (17)$$

where $t$ is the time elapsed since the start of the cycle, $m_{tot}$ is the total mass of carbon converted during the entire reducing period and $m_i$ is the mass of carbon converted up until time $t$.

The total amount of carbon in the CLC solid fuel experiments were determined from the integration of the outgoing flow times the CO and CO$_2$ concentrations, whereas for the CLOU-experiments the CH$_4$ concentrations were also included. The CH$_4$ measurement on the analyser on system 1 interfered with SO$_2$ and was therefore excluded in the evaluation of the CLC-experiments. Unless specified, the rate used in this work, is the average rate of mass conversion during the time period needed to reach 95% fuel conversion. Also, in order to obtain more reliable results, all rates and conversion times which refer to solid fuel experiments are averages values over several cycles.
2.3 Material preparation
All oxygen in an oxygen carrier is not necessarily available for reaction. This has already been mentioned in section 1.2.3 regarding CLOU particles where in copper particles only CuO releases O\textsubscript{2} in an inert atmosphere. But there are also similar limitations in CLC-applications. It would for example not be useful to reduce iron oxide to lower forms than Fe\textsubscript{3}O\textsubscript{4}, i.e. FeO and Fe, since thermodynamic restraints otherwise would prevent full conversion of the fuel [27]. Table 1 presents the expected phases of the oxygen carriers used in this thesis together with the $R_0$ for these systems. The $R_0$ assumes only active metal oxide in the particles without any inert material. The data in Table 1 is from Jerndal et al. [27] except for the ilmenite (FeTiO\textsubscript{3}/Fe\textsubscript{2}TiO\textsubscript{5} + TiO\textsubscript{2}) which originates from Paper II.

Table 1: The oxidized and reduced phases of different oxygen carrier system and the resulting $R_0$ for these systems assuming pure metal oxide without any inert material.

<table>
<thead>
<tr>
<th>Oxidized form</th>
<th>Reduced form</th>
<th>$R_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>Ni</td>
<td>0.214</td>
</tr>
<tr>
<td>CuO</td>
<td>Cu\textsubscript{2}O</td>
<td>0.089</td>
</tr>
<tr>
<td>Mn\textsubscript{3}O\textsubscript{4}</td>
<td>MnO</td>
<td>0.07</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>Fe\textsubscript{3}O\textsubscript{4}</td>
<td>0.033</td>
</tr>
<tr>
<td>Fe\textsubscript{2}TiO\textsubscript{3} + TiO\textsubscript{2}</td>
<td>FeTiO\textsubscript{3}</td>
<td>0.05</td>
</tr>
</tbody>
</table>

2.3.1 Oxygen carriers in CLC with gaseous fuel
In Paper I a large screening of ores and industrial products was performed in order to identify suitable low cost materials which could be used as oxygen carriers. The iron materials, mainly ores and residual materials from the steel industry, are summarized in Table 2 and the manganese materials are presented in Table 3.

All materials were sieved before being used in order to obtain a suitable particle size. Ores also had to be crushed before being sieved. Glödskal A and B as well as Colormax P, R and S were heat treated in 950°C for 24 h before they were sieved and Glödskal A and B were also crushed after heat treatment. In the case of the Glödskal particles the heat treatment was done in order to remove impurities such as oil. In the case of the Colormax particles heat treatment was a way to harden the particles since
the raw particles were very soft. The materials SSAB Brun and SSAB Röd were obtained as a very fine powder with a particle size too small for the fluidized bed experiments. Therefore particles of suitable size were produced by freeze granulation from these materials before being heat treated and sieved.

<table>
<thead>
<tr>
<th>Name</th>
<th>Type of material</th>
<th>Origin of Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ilmenite</td>
<td>Ilmenite mineral</td>
<td>Norway, Titania A/S</td>
</tr>
<tr>
<td>Carajas</td>
<td>Iron ore</td>
<td>Brazil via Studiengesellschaft für Eisenerzaufbereitung</td>
</tr>
<tr>
<td>Malmberget</td>
<td>Iron ore</td>
<td>Sweden, LKAB</td>
</tr>
<tr>
<td>Mt Wright</td>
<td>Iron ore</td>
<td>Australia via Studiengesellschaft für Eisenerzaufbereitung</td>
</tr>
<tr>
<td>Pea Ridge</td>
<td>Iron ore</td>
<td>USA via Studiengesellschaft für Eisenerzaufbereitung</td>
</tr>
<tr>
<td>QCM</td>
<td>Iron ore</td>
<td>Canada via Studiengesellschaft für Eisenerzaufbereitung</td>
</tr>
<tr>
<td>Glödskal B</td>
<td>Residue product from rolling of steel sheets</td>
<td>Sweden, SSAB</td>
</tr>
<tr>
<td>Glödskal A</td>
<td>Residue product from rolling of steel sheets</td>
<td>Sweden, SSAB</td>
</tr>
<tr>
<td>SSAB Röd</td>
<td>Residue product from steel sheet production</td>
<td>Sweden, SSAB</td>
</tr>
<tr>
<td>SSAB Brun</td>
<td>Residue product from surface refinement of steel sheeting</td>
<td>Sweden, SSAB</td>
</tr>
<tr>
<td>Höganäs</td>
<td>Dye powder</td>
<td>Sweden, Höganäs</td>
</tr>
<tr>
<td>Fe$_2$O$_3$/MgAl$_2$O$_4$</td>
<td>Synthetic particles</td>
<td>Sweden, Chalmers</td>
</tr>
</tbody>
</table>

Table 3: Manganese based materials used as oxygen carrier.

<table>
<thead>
<tr>
<th>Name</th>
<th>Type of material</th>
<th>Origin of Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colormax EF</td>
<td>Up-concentration of Mn from minerals</td>
<td>Norway, Elkem AS via SINTEF</td>
</tr>
<tr>
<td>Colormax P</td>
<td>Up-concentration of Mn from minerals</td>
<td>Norway, Elkem AS via SINTEF</td>
</tr>
<tr>
<td>Colormax R</td>
<td>Up-concentration of Mn from minerals</td>
<td>Norway, Elkem AS via SINTEF</td>
</tr>
<tr>
<td>Colormax S</td>
<td>Up-concentration of Mn from minerals</td>
<td>Norway, Elkem AS via SINTEF</td>
</tr>
<tr>
<td>Tinfoss</td>
<td>Manganese ore</td>
<td>Norway, Tinfoss</td>
</tr>
<tr>
<td>Elkem</td>
<td>Manganese ore</td>
<td>Norway, Elkem AS via SINTEF</td>
</tr>
<tr>
<td>Eramet</td>
<td>Manganese ore</td>
<td>Gabon, Eramet AS via Alstom</td>
</tr>
</tbody>
</table>

A synthetically produced iron based particle that previously had been used successfully in experiments with gaseous fuel [38, 56] and contained 60 wt-percent active material of Fe$_2$O$_3$ and 40 wt-percent MgAl$_2$O$_4$ was included as reference. These particles were produced by freeze granulation and were sintered at 1100°C for 6 h.
using a heating rate of 10°C/min. The details of the freeze granulation procedure and particle characteristics can be found in earlier work [53].

The ilmenite mineral was concentrated from a naturally occurring ore containing 40 wt-percent ilmenite. The iron to titanium content has a mass ratio of 45:55, giving a molar ratio close to 1:1. Ilmenite is the only oxygen carrier that so far has been used in an actual circulating fluidized bed CLC-unit with solid fuel [47, 48]. Ilmenite also has interesting thermodynamic properties and Paper II explores this oxygen carrier in more detail.

A SEM image of fresh ilmenite is presented in Figure 6. Since ilmenite is an unprocessed mineral the particles look like small rocks, which was the typical appearance for most unprocessed ores used in Paper I. Particles like this are much rougher and less spherical than the usual synthetic particles previously used in CLC-experiments with gaseous fuel [36].

![SEM images of fresh ilmenite](image_url)

**Figure 6:** SEM images of fresh ilmenite.
2.3.2 Oxygen carriers in CLC with solid fuel

Ilmenite, Glödskal A, Mt Wright ore and the synthetic Fe$_2$O$_3$/MgAl$_2$O$_4$ were selected for solid fuel experiments in Paper III, IV, VI and VII. To make sure that the oxygen carrier particles were in their most oxidized state before solid fuel experiments started the ilmenite, Glödskal A and Mt Wright ore particles were heat treated in air for 24 h at 950°C before they were again crushed and sieved to the proper particle size. It has previously been noted that in many oxygen carrier materials the reactivity increases during the first cycles before stabilizing [57]. In order to avoid this increase in reactivity of the oxygen carrier in the solid fuel experiments, the particles were, after the heat treatment, exposed to an alternating flow of either 5% O$_2$ in nitrogen or syngas (50 % CO, 50% H$_2$) in a cyclic manner at 950°C for roughly 10 cycles, before the testing with solid fuels started.

A Ni-particle with 60 wt-percent NiO and 40 wt-percent NiAl$_2$O$_4$, that previously had been used in CLC with methane [18], was used in the solid fuel experiments presented in Paper V. These particles were supplied by IFP (Institut Francais du Pétrole) and were prepared by spin flash drying.

In most CLC experiments with solid fuel, 0.2 g of fuel was added to the bed for every cycle. In the experiments using 20 g of oxygen carrier the mass reduction of the bed with the most reducing fuel, petroleum coke, was 2%. This is assuming complete reaction between the oxygen carrier and all added fuel. However, all added fuel did not reach the bed since a small fraction of the fuel was lost in the feeding valve. In addition a small part of the fuel was likely elutriated with the fluidizing gas.

The synthetic iron oxide particles contain 40 wt-percent inert material, reducing the $R_0$ of these particles from the theoretical 0.033 to 0.02 for full conversion of these particles from Fe$_2$O$_3$ to Fe$_3$O$_4$. Mt Wright ore and Glödskal A are similar to the synthetic iron particles with the exception that they contain very little inert material giving them a $R_0$ of close to the theoretical 3.3 wt-percent. However, in the solid fuel experiments the concentration of oxidizing gases, such as H$_2$O, in the fluidizing gas should be high enough to prevent the further reaction from Fe$_3$O$_4$ to FeO under conditions with high conversion of the fuel [27].
The reduction of ilmenite is somewhat more complicated and is discussed more in detail in Paper II. The reduced level is ilmenite, FeTiO$_3$, corresponding to FeO+TiO$_2$, and the most oxidized level is Fe$_2$TiO$_5$ + TiO$_2$, corresponding to Fe$_2$O$_3$ + 2 TiO$_2$ [58]. Since the used ilmenite particles contain over 90 wt-percent ilmenite the $R_0$ of these particles is close to 0.05.

The Ni-particles with 60 wt-percent NiO have an $R_0$ of 0.13 and with the experimental setup used in Paper V only a fraction of the available oxygen is used.

2.3.3 Oxygen carriers in CLOU

For the CLOU-experiments in Paper VIII to X a previously tested Cu-based oxygen carrier particle was used [59]. These particles were prepared by freeze granulation and composed of 40 wt-percent active material of CuO and 60 wt-percent ZrO$_2$.

Due to the inert fraction in the Cu particles used in the CLOU-experiments the $R_0$ for the conversion between CuO and Cu$_2$O is 0.04. However, in these experiments not only the added fuel has to be considered since CuO releases O$_2$ during both the reduction and the inert phases as it decomposed to Cu$_2$O. On the other hand this also means that as long as there is O$_2$ in the outgoing gas there is still CuO left in the bed. Since this was the case in more or less all CLOU-experiments it can be concluded that the reactions of the oxygen carriers in the experiments performed involve the phases CuO and Cu$_2$O, although formation of some Cu can not be entirely excluded.

2.3.4 Solid fuels

The fuels used in this work are presented in Table 4. All fuels were crushed and sieved to obtain particles in the size range 125-180 μm. As can be seen from Table 4 the volatile content varied in a wide range from 8.8% in the coal from China to 45.3% in the Indonesian coal. The ash content varies from 0.5% in petroleum coke to 21.8 % in the coal from southern France. Also note the high sulphur content of 6% in the petroleum coke.
<table>
<thead>
<tr>
<th>Fuel</th>
<th>H_i (MJ/kg)</th>
<th>Proximate analysis (wt% as received)</th>
<th>Ultimate analysis (wt% as received)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Volatiles</td>
<td>Moisture</td>
</tr>
<tr>
<td>Mexican Petroleum coke</td>
<td>31.7</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>South Africa coal</td>
<td>29.9</td>
<td>21.6</td>
<td>8.3</td>
</tr>
<tr>
<td>Chinese coal</td>
<td>26.6</td>
<td>8.8</td>
<td>21</td>
</tr>
<tr>
<td>Indonesian coal</td>
<td>26.4</td>
<td>45.3</td>
<td>8.5</td>
</tr>
<tr>
<td>Taiwanese coal</td>
<td>27.9</td>
<td>31.5</td>
<td>2.5</td>
</tr>
<tr>
<td>South France coal (raw)</td>
<td>24.9</td>
<td>25</td>
<td>1.5</td>
</tr>
<tr>
<td>South France coal (sieved)</td>
<td>24.9</td>
<td>25</td>
<td>1.5</td>
</tr>
<tr>
<td>Colombian coal</td>
<td>29.1</td>
<td>37</td>
<td>3.3</td>
</tr>
<tr>
<td>German lignite</td>
<td>20.9</td>
<td>50.5</td>
<td>10</td>
</tr>
<tr>
<td>Swedish wood char</td>
<td>-</td>
<td>11</td>
<td>3</td>
</tr>
</tbody>
</table>
3 Results

3.1 Gaseous fuel experiments
Solid fuel applications in CLC put slightly different demands on the oxygen carrier particles compared to natural gas application. As previously mentioned the reactivity of the oxygen carrier with \( \text{H}_2 \) and \( \text{CO} \) becomes more important since the solid fuel is gasified to syngas before reacting with the oxygen carriers. However, the particles also need to be able to react with volatiles from the fuel. These volatiles often consist of methane and higher hydrocarbons and therefore the materials investigated in this work were not only tested with syngas but also with methane.

3.1.1 Syngas
In Figure 7 the outlet gas concentrations after condensation of water is shown for a reducing period with ilmenite as oxygen carrier when syngas was used as fuel.

![Figure 7: Concentration profile for the reduction period of ilmenite with syngas as reducing gas.](image)

After a period of 20 to 25 seconds into the cycle the \( \text{CO}_2 \) rapidly increases. The delay is due to gas residence time in the system. Almost all incoming \( \text{CO} \) is converted to \( \text{CO}_2 \) but some small amounts of unreacted \( \text{CO} \) are detected some 20 seconds after the initial \( \text{CO}_2 \) increase, after this the \( \text{CO} \) increases throughout the rest of the cycle. This
means that the gas yield to CO\(_2\) in the beginning of the cycle is close to 100%.
However, CO\(_2\) does not reach 100% in this initial phase due to back-mixing of
nitrogen from the previous inert period. Most investigated materials had a similar,
almost complete, gas yield to CO\(_2\) with syngas.

In Figure 8 the gas yield, \(\gamma\), for syngas is presented as a function of \(\omega\) for some of the
investigated materials. Since the reactivity increased somewhat with every cycle, the
cycle where the difference in gas conversions between two cycles is less than 2% is
presented. The reactivity towards syngas is generally high for all particles with
manganese based materials, such as Colormax R, being the most reactive and iron ores
the least. But except for the Höganäs dye powder and the QCM iron ore all materials
have, at least initially, a gas yield of over 90%. Worth noting is that a lot of the iron-
based industrial materials have higher reactivity than the synthetically produced iron
oxide particle Fe\(_2\)O\(_3\)/MgAl\(_2\)O\(_4\).

Figure 8: Gas yield, \(\gamma\), as a function of \(\omega\) for some of the investigated materials when
syngas is used as fuel.
3.1.2 Methane

Figure 9 shows the outlet gas concentrations after condensation of water as a function of time for ilmenite when methane was used as fuel. Figure 10 shows the corresponding concentrations for Colormax R.

Figure 9: Concentration profile for the reduction period of ilmenite with methane as reducing gas.

Figure 10: Concentration profile for the reduction period of Colormax R with methane as reducing gas.
In both Figure 9 and 10 the methane is turned on at time 0 but the response appears after 20 to 25 seconds, again this is due to the delay in the system. CO₂ and CH₄ increase rapidly and CO increases slowly throughout the whole cycle. The concentrations presented in these figures are typical for iron and manganese based particles with generally higher reactivity for manganese based particles compared to iron. Common for all materials investigated in this work is that some CH₄ passed through the system without reacting with the oxygen carrier.

![Graph showing gas yield, \( \gamma \), as a function of \( \omega \) for some of the investigated materials when methane is used as fuel.](image)

Figure 11: Gas yield, \( \gamma \), as a function of \( \omega \) for some of the investigated materials when methane is used as fuel.

Figure 11 shows the gas yield for methane as a function of \( \omega \) for some of investigated materials. Again, since most particles showed increased reactivity with every cycle, and these increases in-between cycles were larger than in the experiments with syngas. Figure 11 presents the cycle where the difference in gas conversions between two cycles is less than 4%. The synthetically produced iron particle Fe₂O₃/MgAl₂O₄ together with some of the manganese based materials, such as Colormax R, had the highest reactivity. The synthetic Fe₂O₃/MgAl₂O₄ converts about twice as much methane as most of the other iron based materials which is no surprise since it is one of the better iron based oxygen carriers designed for methane conversion [60].
3.1.3 Oxidation
The oxidation of particles was usually a rather boring event with little or no differences between cycles independent of what particles that were used. An oxidation period with normal fluidization is shown in Figure 12. During the first part of the oxidation all incoming oxygen reacts with the reduced oxygen carrier resulting in only inert nitrogen in the outgoing flow, at least as long as the bed is fluidized. Thus the reaction is limited by the access to oxygen. When the particles are more or less fully oxidized, there is a rapid increase in oxygen concentration that reaches the inlet O₂ content of 5%. When gaseous fuel was used during the reduction no CO₂ or other carbon containing gases were detected during the following oxidation. This means that no carbon was formed on the oxygen carrier in the reduction period, something that has been detected on other oxygen carriers [31, 61].

![Figure 12: Concentration profile for one oxidation period with fluidization (normal) and one oxidation period with defluidization with 5% O₂ in nitrogen. The oxygen carrier was in both cases ilmenite.](image)

3.1.4 Fluidization behaviour
As mentioned, the oxidation looked very much the same, independent of the previous reduction, as long as the bed fluidizes. But if the bed stopped fluidizing it resulted in initially higher O₂ concentration and longer oxidation periods, as seen in Figure 12. Defluidization leads to channelling and to bypass of the gas stream and makes the
contact between gas and particles less efficient, which explains the higher \( \text{O}_2 \) concentration and the longer oxidation period.

Defluidization usually occurred at the end of a reduction period, when the particles were in the most reduced state or in the beginning of an oxidation when the temperature increased due to the highly exothermic reaction of the oxidation. In some cases defluidizations occurred due to problems in gas supply and in Paper III a number of experiments were made where the bed was deliberately defluidized by shutting off the gas flow. This did not seem to have any effect on the particles since the bed immediately started to fluidize again once the flow was switched back to normal. This is a good sign since it means that particle beds can be defluidized for several minutes even in presence of fuel without agglomerating. Defluidization also occurred in the beginning of some of experiments when fresh ilmenite was oxidized for the first time. However, after this first oxidation defluidization was no longer a problem for ilmenite, as long as it was not very strongly reduced.

The causes and mechanisms of these defluidisations are not fully understood. Similar defluidisations have previously been seen for iron oxide particles [24] in a similar CLC system for gaseous fuel. It should be pointed out that the gas flow during all experiments were over the minimum fluidization velocity, with typical gas velocities of 0.1 m/s, but nevertheless the velocities are generally low compared to large-scale fluidised applications. Also the same kind of ilmenite particles as tested in this work have been used in a 10 kW CLC-unit for long periods without difficulties of defluidization under normal operation [47, 48].

### 3.1.5 Stability of tested oxygen-carrier materials

It is not only the reactivity of particles that is important in a real CLC reactor system, mechanical and fluidization properties of the particles are also important. In the fluidized bed experiments, the particles were exposed to oxidizing and reducing conditions for several cycles. From pressure drop measurements it was possible to see if the bed was fluidized or not. The crushing strength was measured on all the tested particles and is given for iron particles in Table 5 and for the manganese particles in Table 6. Crushing strength is the average force (N) it takes to crush one particle in the
size range of 180-250 μm. Some particles were so soft that the force to crush them could not be measured, hence n.n..

Table 5: Crushing strength and fluidizing properties of iron materials.

<table>
<thead>
<tr>
<th>Name</th>
<th>Crushing Strength (N)</th>
<th>Fluidizing Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ilmenite</td>
<td>3.7</td>
<td>+</td>
</tr>
<tr>
<td>Carajas</td>
<td>n.n.</td>
<td>-</td>
</tr>
<tr>
<td>Malmberget</td>
<td>11.5</td>
<td>-</td>
</tr>
<tr>
<td>Mt Wright</td>
<td>12</td>
<td>+</td>
</tr>
<tr>
<td>Pea Ridge</td>
<td>n.n.</td>
<td>-</td>
</tr>
<tr>
<td>QCM</td>
<td>11.7</td>
<td>+</td>
</tr>
<tr>
<td>Glödskal B</td>
<td>7.8</td>
<td>+</td>
</tr>
<tr>
<td>Glödskal A</td>
<td>8.3</td>
<td>+</td>
</tr>
<tr>
<td>SSAB Röd</td>
<td>2</td>
<td>+</td>
</tr>
<tr>
<td>SSAB Brun</td>
<td>0.6</td>
<td>+</td>
</tr>
<tr>
<td>Höganäs</td>
<td>4.6</td>
<td>+</td>
</tr>
<tr>
<td>Fe$_2$O$_3$/MgAl$_2$O$_4$</td>
<td>1.5</td>
<td>+</td>
</tr>
</tbody>
</table>

Table 6: Crushing strength and fluidizing properties of manganese materials.

<table>
<thead>
<tr>
<th>Name</th>
<th>Crushing Strength (N)</th>
<th>Fluidizing Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colormax EF</td>
<td>1.5</td>
<td>+</td>
</tr>
<tr>
<td>Colormax P</td>
<td>n.n.</td>
<td>-</td>
</tr>
<tr>
<td>Colormax R</td>
<td>0.4</td>
<td>+</td>
</tr>
<tr>
<td>Colormax S</td>
<td>n.n.</td>
<td>-</td>
</tr>
<tr>
<td>Tinforss</td>
<td>4.5</td>
<td>-</td>
</tr>
<tr>
<td>Elkem</td>
<td>n.n.</td>
<td>-</td>
</tr>
<tr>
<td>Eramet</td>
<td>n.n.</td>
<td>-</td>
</tr>
</tbody>
</table>

Also given in Table 5 and 6 is a grading of the fluidizing properties of the particles. A minus sign in the column for fluidizing property means that the particle defluidized or even agglomerated. A plus sign in the same column means that the particles fluidized more or less without any problems throughout the whole experiment.

Most of the iron based particles showed good fluidization properties and were unaffected by the mechanical strain in the bed. However, the Malmberget ore did not fluidize at all, whereas for the Carajas and Pea Ridge ores the particles were ground down to a fine dust, of which a substantial fraction left the reactor with the fluidizing
gas. For the manganese particles only Colormax EF and R fluidized in a controlled manner, all other were too soft and were therefore ground down to a fine dust which was also elutriated from the reactor.

![Graph showing the reactivity of Carajas iron ore with methane as fuel](image)

**Figure 13:** \( \omega \) as a function of time for the seven first cycles for Carajas iron ore with methane as fuel.

For most particles the reactivity increased with the number of cycles. An example of this is the Carajas ore shown in Figure 13. Neither the Colormax particles nor the synthetic iron showed this behaviour but all other materials did. The difference in reactivity decreased as a function of cycle and in most cases the reactivity was more or less constant after five to seven cycles. However, some ores, as well as Glödskal B, showed a small increase in reactivity for every cycle without stabilizing, and in the case of Glödskal B an extra day of experiment was performed, Paper I, giving a total of 25 cycles, but the reactivity still did not stabilize fully.

Increased reactivity probably means that the particles are getting more porous and if this continues too far it can lead to breaking and fragmentation of particles. However, reaching stable condition may only be a question of time. Therefore long-term experiments were made on ilmenite in Paper II and on Glödskal A and the Mt Wright ore in Paper VII to investigate the effect on the particles after many cycles. Around 40 cycles were performed during 3 days, with approximately 25 h at a temperature of 950°C. During night-time the furnace was turned off and so was the flow when the
sample had cooled down to room temperature. In these long-term experiments the reactivity stabilized for all three oxygen carriers. It also indicates that these materials can withstand fluidized bed condition under several cycles of reduction and oxidation, thus making them promising candidates as oxygen carriers in a real system.

### 3.1.6 Analysis of oxygen carriers

Elementary analyses were performed on all fresh oxygen carriers, except for the Fe$_2$O$_3$/MgAl$_2$O$_4$ particle. All iron based materials had an iron content corresponding to at least 90 wt-percent of Fe$_2$O$_3$ except for ilmenite that consisted mainly of FeTiO$_3$ and the Malmberget ore that had only 50 wt-percent Fe$_2$O$_3$, the rest being mainly SiO$_2$. The Colormax particles had a manganese content corresponding to between 78 wt-percent and 84 wt-percent of Mn$_3$O$_4$ whereas the manganese ores had between 33 wt-percent and 68 wt-percent of Mn$_3$O$_4$. All manganese based materials also contained some percentage of Fe, Si and Al. For more information of the elementary analyses see Paper I.

<table>
<thead>
<tr>
<th></th>
<th>Fresh particles</th>
<th>Used particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ilmenite</td>
<td>FeTiO$_3$, Fe$_2$O$_3$</td>
<td>Fe$_3$TiO$_5$, Fe$_2$O$_3$, TiO$_2$</td>
</tr>
<tr>
<td>Carajas</td>
<td>Fe$_3$O$_3$</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Malmberget</td>
<td>Fe$_2$O$_3$, Fe$_3$O$_4$, SiO$_2$</td>
<td>Fe$_2$O$_3$, SiO$_2$</td>
</tr>
<tr>
<td>Mt Wright</td>
<td>Fe$_2$O$_3$, Fe$_3$O$_4$, SiO$_2$</td>
<td>Fe$_2$O$_3$, SiO$_2$</td>
</tr>
<tr>
<td>Pea Ridge</td>
<td>Fe$_2$O$_3$</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>QCM</td>
<td>Fe$_2$O$_3$, SiO$_2$</td>
<td>Fe$_2$O$_3$, SiO$_2$</td>
</tr>
<tr>
<td>Glödskal B</td>
<td>Fe$_2$O$_3$, Fe$_3$O$_4$</td>
<td>Fe$_2$O$_3$, Fe$_3$O$_4$</td>
</tr>
<tr>
<td>Glödskal A</td>
<td>Fe$_2$O$_3$</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>SSAB Röd</td>
<td>Fe$_2$O$_3$</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>SSAB Brun</td>
<td>Fe$_2$O$_3$</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Höganäs</td>
<td>Fe$_2$O$_3$, Fe$_3$O$_4$</td>
<td>Fe$_2$O$_3$, Fe$_3$O$_4$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$/MgAl$_2$O$_4$</td>
<td>Fe$_2$O$_3$, MgAl$_2$O$_4$</td>
<td>Fe$_2$O$_3$, MgAl$_2$O$_4$, MgFeAlO$_4$</td>
</tr>
</tbody>
</table>

All fresh and used materials were examined with powder X-ray diffraction (XRD) and the identified phases are presented in Table 7 and 8. However, some of the XRD patterns were rather difficult to interpret. The ilmenite mineral and all the manganese ores also had unidentified peaks. But overall the XRD results were more or less the expected.
Table 8: Phases identified with XRD in the manganese based materials.

<table>
<thead>
<tr>
<th></th>
<th>Fresh particles</th>
<th>Used particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colormax EF</td>
<td>Mn$_3$O$_4$</td>
<td>Mn$_3$O$_4$</td>
</tr>
<tr>
<td>Colormax P</td>
<td>Mn$_3$O$_4$</td>
<td>Mn$_3$O$_4$</td>
</tr>
<tr>
<td>Colormax R</td>
<td>Mn$_3$O$_4$</td>
<td>Mn$_3$O$_4$</td>
</tr>
<tr>
<td>Colormax S</td>
<td>Mn$_3$O$_4$, Fe$_2$O$_3$</td>
<td>Mn$_3$O$_4$, Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Tinforss</td>
<td>Mn$_3$O$_4$, SiO$_2$, MnO$_2$, Fe$_2$O$_3$, MnAl$_2$O$_4$</td>
<td>Mn$_3$O$_4$, Mn$_2$O$_3$, Fe$_2$O$_3$, SiO$_2$</td>
</tr>
<tr>
<td>Elkem</td>
<td>Mn$_3$O$_4$, SiO$_2$, MnO$_2$, Fe$_2$O$_3$, FeO</td>
<td>Mn$_3$O$_4$, SiO$_2$, Mn$_2$O$_3$, Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Eramet</td>
<td>Mn$_3$O$_4$, SiO$_2$, MnO, Fe$_2$O$_3$, Al$_2$O$_3$, FeO</td>
<td>Mn$_3$O$_4$, SiO$_2$, Mn$_2$O$_3$, Fe$_2$O$_3$, Al$_2$O$_3$</td>
</tr>
</tbody>
</table>

### 3.2 CLC with solid fuels

As mentioned previously, two different experimental systems were used for performing experiments. These systems gave close to identical results with gaseous fuels but when it comes to solid fuels, and especially high volatile solid fuels, the two systems showed some discrepancy with respect to the measured reactivity. However, for a low volatile fuel, such as petroleum coke which was used in all CLC solid fuel papers in this thesis, the choice of system does not significantly affect the conversion of the fuel.

#### 3.2.1 Fuel reactivity

Figure 14 shows the outlet gas concentrations after condensation of water as a function of time for a reducing period where 0.2 g of petroleum coke was used as fuel and 40 g of Fe$_2$O$_3$/MgAl$_2$O$_4$ was used as oxygen carrier. The experiment in Figure 14 was performed using system 1 with a temperature of 970°C in the bed. The same experiments are presented in Paper IV but then using the temperature under the bed as reference. Hydrogen concentrations obtained from bag samples analyzed with gas chromatography are also shown in Figure 14. The initial peak of CH$_4$ is mainly from devolatilization of the petroleum coke. The initial peaks of CO and CO$_2$ are also due to the release of volatiles and reaction of volatiles with the iron oxide. After this devolatilization phase, the remaining char reacts with the added steam to syngas, i.e. CO and H$_2$, which reacts further with the metal oxide to CO$_2$ and H$_2$O. The CO$_2$ concentration starts to decrease after approximately 10 minutes into the cycle and after about 20 minutes all of the added petroleum coke has reacted.
Figure 14: Gas concentrations from System 1 during the reduction period with 40 g Fe$_2$O$_3$/MgAl$_2$O$_4$ and 0.2 g of petroleum coke. The inlet concentration of H$_2$O was 50% in N$_2$ and the temperature in the bed was 970°C.

Some CO was found in all experiments, and can be related to the gas-solids mixing. Assuming that the metal oxides and fuel particles are well mixed in the reactor, there will be fuel particles all the way up to the top of the bed, thus there will always be a fraction of the gasification products, i.e. CO and H$_2$, which will not have sufficient contact with the oxygen carrier even if the reactivity of the metal oxide particles is high. It can not be excluded that there also is some segregation, increasing the fraction of lighter fuel particles in the top of the bed.

Figure 15 shows the concentration profile for the same condition as in Figure 14 but with South African coal as fuel and ilmenite as oxygen carrier. South African coal has a higher content of volatiles in comparison to petroleum coke, and therefore a higher fraction of the solid fuel is reacting during the devolatilization stage. This is seen by higher initial peaks of CO$_2$ and CO. For South African coal, as well as for the other investigated solid fuels, possibly with exception of petroleum coke, it is not possible to separate the char reaction from the reaction of the volatiles, giving a gradual decrease of CO$_2$ and CO from the initial peaks.
Figure 15: Gas concentrations from System 1 during the reduction period with 40 g ilmenite and 0.2 g of South African coal. The inlet concentration of H$_2$O was 50% in N$_2$ and the temperature in the bed was 970°C.

The reduction periods were independent of if a fuel size of if 125-180 or 180-250 μm was used. The conversion time of the fuel did not change if 0.05 g of fuel was added instead of 0.2 g. Also variation in the velocity of the fluidizing gas did not seem to have any effect.

Table 9 show the average rate of fuel conversion for all oxygen carriers used in solid fuel experiments in this thesis. Keep in mind that data from the two different systems can not be directly compared.

Table 9: Conversion rates (%/min), in the interval 0-95%, for the fuel in the used oxygen carriers.

<table>
<thead>
<tr>
<th>Oxygen carrier</th>
<th>System</th>
<th>Steam content</th>
<th>Mexican petroleum coke</th>
<th>South African coal</th>
<th>Indonesian coal</th>
<th>German lignite</th>
<th>Swedish wood char</th>
<th>Colombian coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO/NiAl$_2$O$_4$</td>
<td>1</td>
<td>50%</td>
<td>4.0</td>
<td>6.4</td>
<td>26.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe$_2$O$_3$/MgAl$_2$O$_4$</td>
<td>1</td>
<td>50%</td>
<td>6.3</td>
<td>9.6</td>
<td>18.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>1</td>
<td>50%</td>
<td>6.7</td>
<td>8.8</td>
<td>22.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>2</td>
<td>50%</td>
<td>6.5</td>
<td>6.9</td>
<td>17.9</td>
<td>79.2</td>
<td>7.2</td>
<td>5.1</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>2</td>
<td>92%</td>
<td>8.8</td>
<td>9.3</td>
<td>20.2</td>
<td>67.9</td>
<td>15.1</td>
<td>9.4</td>
</tr>
<tr>
<td>Mt Wright</td>
<td>2</td>
<td>92%</td>
<td>7.4</td>
<td>-</td>
<td>16.6</td>
<td>61.3</td>
<td>12.7</td>
<td>9.4</td>
</tr>
<tr>
<td>Glödskal A</td>
<td>2</td>
<td>92%</td>
<td>8.2</td>
<td>-</td>
<td>22.7</td>
<td>67.9</td>
<td>16.8</td>
<td>13.1</td>
</tr>
</tbody>
</table>
Generally fuels with higher content of volatiles are more rapidly converted. Volatiles are, due to the high temperature, rapidly released when the coal particles are introduced into the reactor and can therefore react directly with the metal oxide. The solid char in the fuel takes longer time to convert since it first has to be gasified, reaction (3) and (4), before reacting with the metal oxide. High volatile coals usually have a poorer reproducibility from one cycle to another. Therefore at least three cycles were made with the same experimental parameters in order to get a more reliable average. Still, rates for fast reacting coal, such as lignite or Indonesian coals, have a higher uncertainty.

The fuel conversion rates for Fe$\text{}_2\text{O}_3$/MgAl$_2$O$_4$ are similar to the conversion rates of ilmenite when 50% steam is used. The two oxygen carriers are considerably different with respect to appearance, density, crushing strength and BET-surface area. The similarity is nevertheless expected since the gasification reactions should be limiting the overall rate of conversion. Also, ilmenite and Mt Wright have similar rates. Glödskal A has higher reactivity especially if all of the experiments in Paper VII are considered. This is a surprise and is probably related to Glödskal A having better conversion of inhibiting gases such as CO and H$_2$. This will be addressed further in section 3.2.5.

The fuel conversion with the Ni-based oxygen carrier was substantially different compared to when the other oxygen carriers were used. The nickel particles react faster with methane compared to ilmenite and Fe$\text{}_2\text{O}_3$/MgAl$_2$O$_4$, whereas the reactivity with syngas is roughly the same, Paper I and V. This is consistent with the higher gas conversion and the faster fuel conversion seen for nickel oxide with Indonesian coal. The much slower conversion of petroleum coke in nickel oxide as compared to when ilmenite or Fe$\text{}_2\text{O}_3$/MgAl$_2$O$_4$ is used as oxygen carrier, clearly suggests a loss of reactivity for the Ni particles. This is not surprising in view of the very high sulphur content of petroleum coke, since sulphur is known to deactivate Ni, due to formation of nickel sulphides [62]. South African coal, which also had a lower conversion rate for nickel compared to ilmenite or Fe$\text{}_2\text{O}_3$/MgAl$_2$O$_4$, has a sulphur content one order of magnitude lower than petroleum coke, but still very much higher than Indonesian coal, Table 4.
3.2.2 Effect of temperature
Figure 16 shows the average rate of conversion for 0.2 g of fuel in four different oxygen carriers. It is an evident trend that the conversion rate is increasing with temperature independent of fuel, oxygen carrier, steam content or which laboratory system was used.

![Figure 16: Average rate of conversion, in the interval 0-95%, as a function of temperature as measured in the bed of oxygen carriers.](image)

The results with Fe$_2$O$_3$/MgAl$_2$O$_4$ and ilmenite from Paper III and Paper IV are in these two papers presented as a function of the set-point temperature under the bed. Here they are given as a function of the temperature in the bed, thus making them more comparable with the results of the other two oxygen carriers from Paper VII. At the highest temperature, over 1000°C, some temporary defluidization was noted for Fe$_2$O$_3$/MgAl$_2$O$_4$ and ilmenite, but no agglomeration occurred.

3.2.3 Effect of sulphur dioxide
As shown in Figure 17, an SO$_2$ content of 5% in the fluidizing gas almost doubles the rate of conversion compared to experiments without SO$_2$. This is in agreement with the results of Lyon et al. who found that the rate of coal conversion in a bed of iron-based oxygen carriers can be improved by SO$_2$ [40].
Figure 17: Average rate of conversion, in the interval 0-95%, of the petroleum coke as a function of the inlet concentration of sulphur dioxide at a temperature of 970°C.

It is believed that SO$_2$ oxidizes carbon, forming CO$_2$ or CO and elementary sulphur. The sulphur then reacts with the iron oxide, again forming SO$_2$. Thermodynamic analysis indicates that neither elemental sulphur nor iron sulphides are likely to be stable when iron oxide is used as oxygen carrier [27]. However, in the current experiments condensed sulphur was noted downstream of the reactor. Since the bed is small and well-mixed with respect to particles, some of the sulphur formed does not have sufficient residence time in the bed to react with the oxygen carrier particles, and instead follows the flue gases out of the reactor.

3.2.4 Effect of steam content

Figure 18 shows the average rate of conversion as a function of different steam content in the fluidizing stream. As expected there is a clear trend of increased reactivity with increased steam content. When no steam is added to the inlet it takes 50 minutes to convert 95% of the petroleum coke, while at 50% steam the same degree of conversion is reached in 8 minutes. However, these petroleum coke experiments were made with 5% SO$_2$ in the fluidizing gas which contributes strongly to the conversion of the fuel, meaning that the difference can be even larger. As expected reference experiment made with petroleum coke and pure nitrogen in the fluidizing gas resulted in very long conversion time, see section 3.2.5 for more details.
Figure 18: Average rate of conversion, in the interval 0-95%, as a function of the inlet concentration of steam. The temperature was 970°C and in the case of petroleum coke the fluidizing gas contained 5% SO₂.

Table 10 shows the average rate of conversion needed to reach 95% conversion for different fuels with a steam content of 50% and 92% in the fluidizing gas. As seen previously, fuels with larger fractions of volatiles are generally converted faster. The release of the volatiles is always fast independent of which fluidizing gas that is used, whereas the conversion of the char part of the fuel is strongly influenced by the fluidizing atmosphere. This makes the overall conversion of high-volatile fuels less affected by different steam fractions. In the case of the German lignite, the conversion is even faster for the lower fraction of steam. However, the variation in conversion rate for different cycles with German lignite was very large.

Table 10: Average rate of conversion (%/min), in the interval 0-95%, for the used fuels with a steam content of 50% and 92% in the fluidizing stream.

<table>
<thead>
<tr>
<th>Steam content</th>
<th>Mexican petroleum coke</th>
<th>South African coal</th>
<th>Indonesian coal</th>
<th>Colombian coal</th>
<th>German lignite</th>
<th>Swedish wood char</th>
</tr>
</thead>
<tbody>
<tr>
<td>50%</td>
<td>6.5</td>
<td>6.9</td>
<td>17.9</td>
<td>5.1</td>
<td>79.2</td>
<td>15.1</td>
</tr>
<tr>
<td>92%</td>
<td>8.8</td>
<td>9.3</td>
<td>20.2</td>
<td>9.4</td>
<td>67.9</td>
<td>15.1</td>
</tr>
</tbody>
</table>
3.2.5 Hydrogen inhibition and fuel gasification

The reactions in the bed under reducing conditions involve both gasification of the solid fuel and the reactions of mainly CO and H$_2$ with the oxygen carrier. These reactions were investigated separately. In the case of the reaction between the gasification products, CO and H$_2$, and the oxygen carrier the reactivity of all investigated materials was high as presented in section 3.1.1. To investigate only gasification of the solid fuel, the oxygen carrying particles were replaced by quartz sand of the same size, but leaving all other parameters unchanged. In these experiments the char slowly reacts with the steam, forming primarily CO and H$_2$, reaction (3) and (4). Some of this CO reacts further with the steam forming CO$_2$ and more H$_2$, reaction (5), resulting in a CO/CO$_2$ ratio of roughly 2:1.

![Graph showing the average time to reach 95% conversion for different fuels in sand as a function of the average time to reach 95% conversion for the same fuels with different oxygen carriers. The dashed line corresponds to a factor two faster conversion with oxygen carrier compared to sand. The temperature was 970°C.]

The time needed to convert 95% of an investigated fuel with an oxygen carrier is about half of the time to convert the same fuel in sand, Figure 19. One major difference between CLC and coal gasification is the concentrations of H$_2$ and CO in the reactor. These are lower in a CLC reactor since the oxygen carrier reacts fast with CO and H$_2$,
thereby removing these gases. Thus, it is likely that the slower gasification in sand can be explained by hydrogen inhibition.

Table 11 presents the fraction of CO in the flue gases for the solid fuel experiments with Glödskal A, Mt Wright ore and ilmenite together with the fraction of H₂ for Glödskal A and the Mt Wright ore. These experiments were performed with 92% steam in the fluidizing gas and at 970°C if not stated otherwise. As seen, Glödskal A has a lower fraction of CO compared to the other two oxygen carriers, and in most cases also a lower fraction of H₂ compared to the Mt Wright ore.

Table 11: Fraction of CO and H₂ in the flue gases. Values in parenthesis are average values over at least 3 cycles whereas the other values are from the last cycle.

<table>
<thead>
<tr>
<th></th>
<th>Mt Wright</th>
<th>Glödskal A</th>
<th>Ilmenite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂/(CO+CO₂)</td>
<td>CO/(CO+CO₂)</td>
<td>H₂/(CO+CO₂)</td>
</tr>
<tr>
<td>German lignite</td>
<td>0.23</td>
<td>0.50 (0.49)</td>
<td>0.18</td>
</tr>
<tr>
<td>Colombian coal</td>
<td>0.34</td>
<td>0.23 (0.25)</td>
<td>0.41</td>
</tr>
<tr>
<td>Indonesian coal</td>
<td>0.31</td>
<td>0.32 (0.33)</td>
<td>0.30</td>
</tr>
<tr>
<td>Mexican petroleum coke</td>
<td>0.08</td>
<td>0.10 (0.10)</td>
<td>0.02</td>
</tr>
<tr>
<td>Swedish wood chips</td>
<td>n.n</td>
<td>n.n</td>
<td>0.01</td>
</tr>
<tr>
<td>Swedish wood char 900°C</td>
<td>0.26</td>
<td>0.21 (0.14)</td>
<td>0.05</td>
</tr>
<tr>
<td>Swedish wood char 950°C</td>
<td>0.20</td>
<td>0.20 (0.19)</td>
<td>n.n</td>
</tr>
<tr>
<td>Swedish wood char 970°C</td>
<td>0.17</td>
<td>0.21 (0.22)</td>
<td>0.11</td>
</tr>
<tr>
<td>Swedish wood char 1000°C</td>
<td>0.18</td>
<td>0.25 (0.24)</td>
<td>0.05</td>
</tr>
</tbody>
</table>

As can be seen in Figure 16 and Table 9 Glödskal A has a slightly higher conversion rate compared to the Mt Wright ore and ilmenite. This is somewhat of a surprise since Glödskal A and ilmenite have similar reactivity with CH₄, as seen in Figure 11, as well as with syngas, as seen in Figure 8. It is therefore possible that Glödskal A enhances the gasification of the solid fuel by better converting the hydrogen in the reactor and thereby limiting the effect of hydrogen inhibition, thus making Glödskal A a better oxygen carrier. The lower fraction of hydrogen for Glödskal A in Table 11 strengthens this argument. It is also interesting to note that high conversion of gas seems to be correlated to faster fuel conversion, this is quite evident in Paper VII where Glödskal A and the Mt Wright ore are compared.
3.2.6 Oxidation of particles
Figure 20 shows the oxidation of ilmenite that followed a reducing period with petroleum coke. The inlet O\textsubscript{2} content was 5%. During the first minutes all incoming oxygen reacts with the reduced metal oxide particles resulting in only inert nitrogen in the outgoing flow. After one and a half minutes the oxygen concentration increases rapidly. After this rapid, increase the concentration slowly approaches the inlet concentration.

![Concentration profile during oxidation with ilmenite as oxygen carrier. The inlet concentration of O\textsubscript{2} is 5% and the temperature is 970°C.]

Figure 20: Concentration profile during oxidation with ilmenite as oxygen carrier. The inlet concentration of O\textsubscript{2} is 5% and the temperature is 970°C.

Since there is no CO\textsubscript{2} produced during the very first part of the oxidation, i.e. the period when all oxygen is consumed, this indicates that there is no carbon left in the bed. To confirm this, a few reference experiments were performed where 0.1 g of petroleum coke was added at the very beginning of the oxidation to a reduced bed. In these cases the added fuel was immediately converted to CO\textsubscript{2}, showing that if there are char residues in a reduced bed these will react immediately with the O\textsubscript{2} in the very beginning of the oxidation. The CO\textsubscript{2} and CO peaks that appear when the O\textsubscript{2} concentration increases are most likely due to unburned carbon which elutriated and stuck to the walls in the top section of the reactor, or fuel particles which never reached the bed during the solids feeding. The oxidation looked very much the same in all cases, independent of fuel, oxygen carrier or other parameters in the previous reduction period.
3.2.7 Stability of tested particles
In the solid fuel experiments performed, the particles were exposed to oxidizing and reducing conditions, in one case for over 100 h. From pressure drop measurements it was possible to see if the bed was fluidized or not. The particles were heated up to 970˚C and cooled to room temperature again several times since the oven had to be turned off at night. Furthermore, they were exposed to ash and combustion gases from the fuel. Except for the possible sulphur deactivation of the nickel particles, there were no losses in reactivity for any of the other oxygen carriers used in solid fuel experiments. Also, all oxygen carriers always showed good fluidization properties, except on two occasions when the temperature exceeded 1000˚C in the bed. But in these cases the bed started to fluidize again when the temperature was lowered.

![SEM image of ilmenite](image)

Figure 21: SEM images of ilmenite used in over 50 cycles of solid fuel experiments

The surface of both fresh and used oxygen-carriers used in the experiments were analysed in a scanning electron microscope, SEM. In Figure 21 a SEM image is shown for ilmenite used in the solid fuel experiments in Paper IV. It is clear that the used particles have much smoother edges and rougher surfaces than the fresh ilmenite particles presented in Figure 6. The Mt Wright ore and Glödskal A showed similar
changes after the solid fuel experiments, whereas no visible change was seen on the Fe$_2$O$_3$/MgAl$_2$O$_4$ or the NiO/NiAl$_2$O$_4$ particles.

All used and fresh oxygen carriers in the solid fuel experiments have been investigated with X-ray diffraction but no major phase change of the particles could be observed.

The BET-surface area of the used and fresh particles was determined by a Micromeritics Gemini 2362 for the ilmenite and Fe$_2$O$_3$/MgAl$_2$O$_4$ particles used in Paper IV. The Fe$_2$O$_3$/MgAl$_2$O$_4$ particles showed a drastic decrease in BET-area from 8.58 m$^2$/g for the fresh particles to only 0.76 m$^2$/g for the ones used in solid fuel experiments. It is possible that the interior structure of these particles sinter during testing. As this effect has been noticed earlier during batch experiments with gaseous fuels, it is likely not due to the solid fuel ash [38]. Interestingly, the particles maintained a high reactivity even after the particle restructuring. The BET-area of the used ilmenite increased from 0.11 to 0.58 m$^2$/g after solid fuel experiments. Hence, the relative change in surface area after cycling is quite large, and it indicates that the particles are gaining porosity during the experiments. This increase in porosity is confirmed by the rougher structure on the particles surface, seen in Figure 21, as compared to the fresh particles in Figure 6.

Usually the same batches of oxygen carrying particles were used throughout the tests with different coals. Some small ash particles were visible in the bed at the end of these experiments. However, analysis with SEM and XRD did not show any ash fouling on the particle surface, and the ash did not seem to affect the reactivity or fluidizing properties of the oxygen carrier particles.

### 3.3 CLOU with solid fuels

Since the oxygen carriers in CLOU need to have very different properties compared to normal CLC-particles the results from the CLOU-experiments will be given some extra consideration. Since the particles in CLOU releases O$_2$ in an inert atmosphere the inert period between oxidation and reduction was shortened in order to avoid too much oxygen being lost from the particles during this time. The very high temperature dependency of the O$_2$ concentration also introduces uncertainties since small changes
in the temperature significantly affect the O$_2$ concentration. These factors together with the much faster solid fuel conversion in CLOU compared to CLC make the results from CLOU-experiments somewhat harder to interpret.

### 3.3.1 Fuel reactivity

Figure 22 shows the outlet gas concentrations as a function of time for a reducing period with petroleum coke and an oxygen carrier consisting of 40 wt-percent active material of CuO and 60 wt-percent of inert ZrO$_2$. The temperature is 985°C just prior to the introduction of the fuel to the bed. The concentration of oxygen at the start of the reduction is near the equilibrium partial pressure for CuO. As the fuel is added a small peak of CH$_4$ is seen in the beginning of the reduction period, which is due to the devolatilization of the fuel. At the same time the combustion of the fuel starts and the CO$_2$ concentration increases rapidly. In these experiments with petroleum coke the oxygen concentration never drops to zero during the reduction, meaning that more oxygen is released from CuO than is needed for the combustion of the fuel. Thus the release of oxygen from the oxygen carrier is quite rapid making it possible to burn all added coke completely to CO$_2$ since no CO is detected. As the fuel is consumed the O$_2$ concentration again reaches the equilibrium partial pressure.

![Figure 22: Concentration profile during the conversion of 0.1 g of petroleum coke in 15 g CuO/ZrO$_2$. The temperature was 985°C and the fluidizing gas was pure nitrogen.](image-url)
Figure 23 shows the outlet gas concentrations as a function of time for a reducing period for the same settings as in Figure 22 but with lignite as fuel. The behaviour is in many ways similar except for that here the concentration of oxygen drops to zero during a part of the reduction, and for that a large part of the fuel is only converted to CO. The oxygen concentration increases again as the fuel burns out. Hence, the conversion of the lignite fuel is faster in comparison to the release of oxygen from the particles. Also at the very end of the cycle the oxygen again drops to zero. This is due to the lack of CuO in the bed. So much oxygen has been released that the particles in the bed now completely consists of Cu$_2$O which does not release any oxygen to the gas-phase.

![Figure 23: Concentration profile during the conversion of 0.1 g of lignite in 15 g CuO/ZrO$_2$. The temperature was 985°C and the fluidizing gas was pure nitrogen.](image)

### 3.3.2 Effect of temperature

Figure 24 shows the average rate of conversion for 0.1 g of fuel in CuO on ZrO$_2$. It is clear that the conversion rate is increasing with temperature for all fuels. Also observe that that conversion rate is given in %/second instead of %/minute as in the CLC-experiments. The rates shown in Figure 24 are considerably faster in comparison to the rates obtained with regular CLC presented in Figure 16. The difference is due to the difference in reaction mechanisms between CLC and CLOU, i.e. for the latter the fuel is burnt with gas-phase oxygen while for CLC the char of the solid fuel needs to be
gasified to a reactive intermediate syngas, before reacting with the oxygen carrier particles.

Figure 24: The average rate of conversion, in the interval 0-95%, of lignite and petroleum coke as a function of bed temperature in 15 g CuO/ZrO$_2$. The fluidizing gas was pure nitrogen.

3.3.3 Oxidation in CLOU

The oxidation of the oxygen carrier in CLOU is of central importance since there will always be oxygen released from the outlet of the air reactor, i.e. the minimum concentration of oxygen at the outlet of the air reactor is associated with the thermodynamic partial pressure of the CuO/Cu$_2$O system at any given temperature. In CLC there is no such thermodynamic limitation. Figure 25 shows the partial pressure of the O$_2$ as a function of the cumulative fraction of oxygen absorbed by the oxygen carrier at different temperatures. Included is also the equilibrium concentration of oxygen calculated from the measured temperature in the bed.

Clearly, a substantial part of the reaction occurs fairly close to the equilibrium concentration. In fact, for the higher temperatures the outlet concentration is actually below equilibrium. A possible explanation for this difference could be that the measured temperature deviates somewhat from the actual temperature of the particles in the bed. As the reaction rate slows down, the O$_2$ concentration increases and approaches the inlet concentration.
Figure 25: The partial pressure of O\(_2\) in the gas from the reactor during oxidation of particles of 40 wt-percent CuO on 60 wt-percent ZrO\(_2\) as a function of the cumulative fraction of oxygen reacted for different temperatures. The inlet gas has an O\(_2\) concentration of 10%. Included is also the equilibrium partial pressure (+) as determined from temperature measurements in the bed.

These experiments clearly indicate that oxidation of the particles should be possible in the CLOU-process, meaning that the oxygen partial pressure from the air reactor can be chosen reasonably close to the equilibrium partial pressure. Thus there is nothing to indicate that the CLOU process would need to be operated at air ratios that significantly diverge from what is normal used in conventional circulating fluidized bed (CFB) boilers with solid fuels.
4 Design considerations in solid fuel application

When a full-scale CLC-unit is built many components and a lot of experience can be adapted from conventional CFB boilers. These have, just as a CLC-boiler will have, a large internal circulation of solids. However, the solids in a CFB are primarily used to transport heat. In a CLC-unit both heat and oxygen will be transported with the solids and this will affect design parameters such as solids inventories and residence times in different parts of the system.

It is necessary to point out that the average residence time in the fuel reactor for the oxygen carrier particles and the fuel is not necessarily the same. In addition the residence time distribution is also important. Therefore, the needed residence time in an actual CLC system depends on several factors, for example the reactor arrangement. A well-stirred tank reactor system, with respect to the solids, would require a greater inventory compared to a tubular flow reactor, or several well-stirred tank reactors in series. It should be possible to arrange the fluidization of the fuel reactor system so as to avoid a well-stirred tank case.

There will also be the issue of separation of solids, both separation of ash and of unconverted fuel from oxygen carriers. Here it is assumed that the fresh fuel particles are of the same size as, or smaller than, the oxygen carrier particles. The fuel particles have a lower density than the oxygen carrier and they are gradually reduced in size due to chemical reactions as well as fragmentation and attrition. This opens possibilities for separation since the terminal velocity of the fuel and ash particles will be lower compare to the terminal velocity of the oxygen carrier particles. Firstly a carbon stripper after the outlet of the oxygen carrier flow from the fuel reactor can be used to capture and recycle carbon to the fuel reactor. Secondly it might also be possible to arrange internal separation of carbon in the fuel reactor in a way that reduces the amount of carbon in the exiting stream.
4.1 CLC design considerations
The slow overall conversion rate of solid fuel with oxygen carrier particles has implications for the amount of oxygen carrying material needed in a CLC fuel reactor. A heat and mass balance of the system was performed to evaluate the potential recirculation rate of oxygen carrier particles and the solid inventory needed. Also the choice of oxygen carrier affects how much heat is needed in the fuel reactor. For all CLC-particles investigated in this thesis the overall reaction in the fuel reactor is endothermic. However, with Cu-particles in CLOU there is an overall exothermic reaction in the fuel reactor and the implications for that case are further dealt with in section 4.2.

In Table 12 the ratios of the reaction enthalpy for the oxidation to that of conventional combustion are listed for the oxygen carriers in this thesis. Normal combustion is in this case combustion of CH$_4$ but the values do not differ greatly from those of common solid fuels, when the values are given per kg of oxygen consumed. In fact dry solid fuels like bituminous coal, anthracite and peat normally have heating values which only deviate a few percents from that of CH$_4$, 12.5 MJ per kg of oxygen. The values for ilmenite are from Paper II whereas the others are calculated by Jerndal et al. [27].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H/\Delta H_{\text{dir comb CH}_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$ + 1/2CH$_4$ → 1/2CO$_2$ + H$_2$O</td>
<td>1</td>
</tr>
<tr>
<td>O$_2$ + 2Ni → 2NiO</td>
<td>1.17</td>
</tr>
<tr>
<td>O$_2$ + 6MnO → 2Mn$_2$O$_4$</td>
<td>1.12</td>
</tr>
<tr>
<td>O$_2$ + 4Fe$_3$O$_4$ → 6Fe$_2$O$_3$</td>
<td>1.19</td>
</tr>
<tr>
<td>O$_2$ + 4FeTiO$_3$ → 2Fe$_2$TiO$_5$ + 2TiO$_2$</td>
<td>1.11</td>
</tr>
</tbody>
</table>

The values in Table 12 should be used as follow: If the thermal power of the entire system is 1 MW, then the heat of reaction produced in the air reactor from the reaction between oxygen and metal oxide is 1.19 MW if iron oxide is used as oxygen carrier and 1.11 MW if ilmenite is used. The heat loss in the fuel reactor due to reaction between fuel and metal oxide is 0.19 and 0.11 MW for iron oxide and ilmenite respectively. Furthermore, in the heat and mass balance calculations, it is assumed that the fuel reactor is fluidized by a flow of steam as large as the CO$_2$ produced in the
reaction, and that this flow is heated by the particles in the fuel reactor with a temperature difference of 800°C. The heat needed for this, in a 1 MW case, is 0.068 MW. Thus when iron is used as oxygen carrier there is a total heat loss in the fuel reactor of 0.258 MW that has to be supplied by the recycled oxygen carriers. The same assumptions require a heat supply of 0.178 MW with ilmenite as oxygen carrier.

For a thermal power of 1 MW, and assuming that the fuel reactor is adiabatic and the temperature difference between the two reactors should not be more than 50°C, this gives a needed recirculation flow of 360 kg/min for an iron oxygen carrier. The less endothermic reaction in the fuel reactor for ilmenite gives a recirculation flow of 240 kg/min. With the same assumptions Ni-based materials would have values close to iron oxide and Mn$_3$O$_4$ close to ilmenite.

The second important parameter is the solids inventory in the reactor system. The solids inventory in the fuel reactor is related to the needed residence time of the fuel in the fuel reactor for complete conversion of the fuel. In this thesis several parameters have been investigated that affect the conversion rates of the fuel but for simplification the calculations will be performed using results from experiments where 95% conversion was reached with 92% steam, at 970°C and without any SO$_2$. Conversion times for three different fuels with ilmenite, Mt Wright ore and Glödskal A for such experiments are given in Table 13.

Table 13: Time, in minutes, for 95% conversion for three fuels with different oxygen carriers using 92% steam at 970°C.

<table>
<thead>
<tr>
<th>Oxygen carrier</th>
<th>Mexican petroleum coke</th>
<th>Indonesian coal</th>
<th>German lignite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ilmenite</td>
<td>10.8</td>
<td>4.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Mt Wright</td>
<td>12.9</td>
<td>5.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Glödskal A</td>
<td>11.6</td>
<td>4.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

It is assumed that a significant part of the unreacted char can be separated from the flow going to the air reactor and by recycling this unconverted fuel it should be possible to further decrease the needed residence time in the fuel reactor. Therefore, as a preliminary assumption the residence time of the oxygen carrier particles could possibly be reduced to half for petroleum coke whereas a conversion time under 1
minute should be possible for the high volatile German lignite. In the case of ilmenite this would give a solids inventory of 1300 kg/MWth for the slow reacting petroleum coke and below 250 kg/MWth for lignite. In the cases of the Mt Wright iron ore and petroleum coke this would give a solids inventory of 2000 kg/MWth and with lignite a solids inventory of below 350 kg/MWth. Glödskal A has a somewhat shorter conversion time and would therefore be expected to need a slightly lower solid inventory than the Mt Wright iron ore.

The design of a CLC-unit must aim at good contact between oxygen carrier particles and gases released during gasification. But as discussed in 3.2.1 it is not expected that it would be possible to reach complete conversion of gases from the fuel reactor. Full fuel conversion can be realized, for instance, with a small oxygen addition step immediately after the fuel reactor outlet, which would result in oxidation of these gases. However, this oxygen has to be supplied somehow, and the less oxygen needed, the lower the additional oxygen production cost. This favours reactive oxygen carriers like Glödskal A that have a lower fraction of unconverted gases such as CO and H2 in the outgoing flow.

The conversion rates of the solid fuels are dependent on the type of fuel which is used, e.g. Table 9. Although the presence of an oxygen carrier doubles the conversion rate, Figure 19, the fuel gasification is still the time limiting step. The gasification products, i.e. mostly H2 and CO, react rapidly with all investigated oxygen carriers, Figure 8. However, a higher reaction temperature or a higher fraction of steam or SO2 in the fluidizing gas, Figure 16 to 18, will increase the rate of conversion and thereby lower the needed solid inventory.

### 4.2 CLOU design considerations

From Figure 3 it is seen that CuO releases oxygen in air at temperatures above 1028°C. However, in the air reactor, the reduced metal oxide must be able to react with air to the oxidized form and hence lower the oxygen concentration to a reasonable level, given by the excess air ratio. For instance, if the maximum outlet partial pressure of O2 from the air reactor should be 5%, then it can be seen from Figure 3 that the temperatures in the air reactor should be below 955°C.
When these oxidized particles are transferred to the fuel reactor, where the partial pressure of O$_2$ is low, they will release gaseous O$_2$. The maximum concentration of oxygen released is given by the temperature in the fuel reactor, which is determined by the temperature of the incoming particles and the circulation rate as well as by the heat of reaction in the fuel reactor. For CuO the reactions in the fuel reactor are exothermic, and thus it is possible to have a temperature increase in the fuel reactor, which in turn makes it possible to achieve a higher partial pressure of O$_2$ in the fuel reactor compared to the outlet partial pressure of O$_2$ from the air reactor. A high equilibrium partial pressure of oxygen together with the fast kinetics, i.e. rapid release of oxygen from the CuO particles, will promote the overall conversion rate of the solid fuel. Also assuming that the kinetics of the fuel conversion and thereby the consumption of oxygen is fast a CLOU-system will be operated with a partial pressure of O$_2$ in the fuel reactor that is well below the equilibrium partial pressure. This will create a driving force for the oxygen carriers to release O$_2$ rapidly.

In the case of conventional CLC the solids inventory is not governed by the circulation rate and the temperature difference between the reactors. Since the overall reactions in a fuel reactor in a CLOU-system with Cu-particles are exothermic there is no need to transport heat from the air to the fuel reactor. Instead the degree of conversion of the particles will be directly proportional to the chosen recirculation rate between the reactors. Further, it is also possible to use the temperature increase in the fuel reactor to choose a lower temperature in the air reactor if that for some reason favours the overall economics of the system.

In earlier work for regular CLC, there have been agglomeration problems when using Cu-based oxygen carriers [53]. This has been attributed to the low melting temperature of metallic Cu, which has a melting temperature of 1085°C. In CLOU the oxygen carrier is not reduced to Cu, and both CuO and Cu$_2$O have higher melting temperatures, 1446°C and 1235°C, compared to metallic Cu. Also, the work of de Diego et al.[63] concerning Cu-based oxygen carriers suggests that it is possible to manufacture Cu-based oxygen carriers which do not suffer from agglomeration.
5 Discussion

The dominating environmental issue today is the increased amount of greenhouse gases in the atmosphere, especially CO$_2$, and the climate change that this will result in. Fossil fuel power plants and similar large point sources are large emitters of CO$_2$, and suitable for CO$_2$-capture. In the introduction of this thesis, three different technologies for CO$_2$-capture are mentioned, i.e. post-combustion, pre-combustion and oxyfuel. These are all associated with large investment costs and substantial efficiency losses as compared to conventional power production without CO$_2$-capture. In contrast, chemical-looping offers the possibility to produce power with more effective CO$_2$ capture and with no losses in efficiency for the CO$_2$-separation.

Prior to the work presented in this thesis, almost all development concerning CLC was performed using gaseous fuels and oxygen carriers which were produced from pure and often expensive materials. This thesis demonstrates that chemical-looping should be feasible for solid fuels, such as different coals, petroleum coke and bio fuel, and that it is possible to use cheap materials, such as ores or industrial waste products as oxygen carriers. This of course makes chemical-looping more cost effective, hence an even more competitive technology for CO$_2$-capture.

A CLC-system can be built up with known technology and conventional equipment as shown in the demonstrations of the process with gaseous fuels in 300 W to 120 kW [11-19] units, and in the 10 kW unit for solid fuel at Chalmers [47, 48]. Important experience can be gained from conventional CFB-boilers which to a large part are built in similar ways as a chemical-looping unit, with large solid inventory and effective particle separation.

The most important difference in chemical-looping for solid fuel applications, compared to gaseous fuel, is the need to design an optimal fuel reactor system. Such a system should provide good contact between oxygen carrier and gases coming from the fuel, in order to achieve good gas conversion. Moreover, the system should minimize loss of char both to the air reactor and with the exiting gas stream.
The two options for solid fuel combustion proposed in the thesis, i.e., direct combustion of solid fuels with CLC and CLOU, have different advantages and disadvantages. In CLOU it is possible to reach full conversion of the fuel whereas CLC always will have a small fraction of not fully converted volatiles or gasification products in the outlet gas coming from fuel reactor. CLC also has the drawback of the slow conversion rates of char and the need for heat transport between the air and fuel reactor, which will result in a large solids inventory. In CLOU, on the other hand, there is a higher cost for the Cu-based oxygen carriers, even if considerably less material is needed compared to CLC. The higher cost means that longer lifetime of CLOU-particles would be desired. These particles should therefore preferably be more resistant towards ash fouling. Also a CLOU-unit needs to be operated at temperatures where the equilibrium pressure of oxygen over the oxygen carrying particles is favourable, whereas in CLC the possible operation temperature is not as restricted, although high temperatures will be aimed at in order to increase the conversion rate.

The CLOU conversion rates for petroleum coke and lignite were more or less the same at temperatures around 950°C, whereas the CLC conversion rates for the same fuels at 970°C differed with a factor of 10, with lignite being converted more rapidly. This would suggest that the choice between CLOU and CLC could be fuel dependent, but there are more aspects to consider and it is still too early to judge which of the two processes is the better, and for which fuels.

As shown in this thesis, similar rates of conversion were seen for the same type of solid fuel for the investigated CLC oxygen carriers. From this point of view it would make more sense to use the most inexpensive materials in a real CLC boiler. This makes Ni an unlikely candidate since the price of Ni is very much higher and the reactivity is more or less the same compared to the investigated iron-based particles. Ni also has health aspects that make it less attractive and since NiO is susceptible to deactivation by sulphur, it is likely not a good option with high sulphur fuels. Also synthetically produced particles, such as Fe₂O₃/MgAl₂O₄, are not very likely to be chosen since they have a significantly higher production cost and seemingly the same reactivity as the more or less unprocessed ilmenite or Mt Wright ore.
Glödskal A may be better choice compared to the Mt Wright ore since it has faster conversion rates for most solid fuels and less unconverted fuel such as CO and H₂. However, the choice between ilmenite and Glödskal A is not as straightforward. Again, Glödskal A has faster conversion rates and less unconverted flue gases from the outlet, but ilmenite has more favourable thermodynamics, thus reducing the needed amount of solid inventory. Although the titanium containing ilmenite is cheap, the cost of Glödskal A can be expected to be even lower as it is a kind of oxide scale which is usually deposited in landfills. This means that the industry may have a cost to get rid of the material. This is, however, not the case for all types of oxide scales but scales going to landfill are still available in large quantities from the steel industry.

The investigations in this thesis have been carried out for a limited number of cycles in a small reactor at relatively low velocities. To fully evaluate the performance of the oxygen carriers, it is necessary to conduct longer tests, preferably in continuous operation. So far this has only been done for ilmenite [47, 48], with promising results.

Adapting the chemical-looping process to solid fuel and using inexpensive oxygen carriers opens a new field of research within chemical-looping. The purpose of this technology is that it should be used to lower the CO₂ emission. It is urgent that more effort is spent on developing chemical-looping, especially up-scaling and process design is of importance, so efficient CO₂ free power production can be realized within a near future.
6 Conclusions

A small lab reactor designed for investigation of the reactivity of solid fuels in chemical-looping combustion has been developed, and an experimental procedure for testing solid fuels in this system was established. The procedure involves the cyclic oxidation of oxygen carrier particles with oxygen-containing gas and reduction with solid fuel. The results give proof of concept for both investigated options, CLC and CLOU, for a number of different solid fuels. Also a number of inexpensive materials, such as different ores and industrial products, were identified as possible oxygen-carriers for CLC solid fuel application.

For CLC the following main conclusions of the work are:

- All oxygen-carriers tested, except an iron based dye powder, react fast with gasification products such as CO and H₂.

- A number of different solid fuels with different properties were used. High volatile fuels generally resulted in much faster conversion rates than low volatile fuels.

- The conversion rate of solid fuel in CLC increased significantly with increasing temperature. An increase of 50°C typically doubled the conversion rate.

- The conversion rate of petroleum coke in CLC increased significantly with increased fraction of SO₂ in the fluidizing gas. An SO₂ content of 5% in the fluidizing gas almost doubles the rate of conversion compared to experiments without SO₂.

- The conversion rate of solid fuels in CLC increased significantly with increased fraction of steam in the fluidizing gas. For a low volatile fuel a doubling of the steam content could result in give a doubling of the fuel conversion rate.
The gasification reaction of the fuel is slow compared to the reaction of the metal oxide with the gasification products, i.e. mainly $\text{H}_2$ and $\text{CO}$. Thus gasification is the rate limiting step and will determine the needed solids inventory of the fuel reactor for CLC with solid fuels.

The gasification of the fuel is about two times faster when conducted in the presence of oxygen-carrying particles compared to sand. This is believed to be explained by efficient removal of gases that inhibits gasification, e.g. $\text{H}_2$. Moreover the fuel conversion was faster with oxygen carriers that showed high conversion of gas, e.g. Glödskal A.

Almost all investigated oxygen carriers that were used in solid fuel experiments showed good fluidization properties without any agglomeration. The exception was in experiments at temperatures above 1000°C.

The amount of oxygen carrying particles needed in an optimized fuel reactor system of a CLC-system was estimated to be between 2000 and 250 kg/MW$_{th}$ depending on which fuel and which oxygen carrier is used.

The following conclusions can be made for the work around CLOU:

- CLOU gives significantly higher conversion rates than CLC with solid fuels, in some cases up to two orders of magnitude greater.

- The conversion rate in CLOU increased significantly with increasing temperature. For petroleum coke the conversion rate increased with a factor 3 as the temperature increased from 900 to 950°C.

- No CO was measured in the CLOU experiment with petroleum coke.

- In CLOU the oxidation of oxygen carriers can take place at low oxygen concentrations close to the equilibrium partial pressure. Thus it should be possible to achieve oxygen concentrations in the air reactor corresponding to air ratios typical of normal combustion.
7 Acknowledgement

Here last in this thesis there is to be found
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8 References


