

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Chemical-Looping Combustion with Liquid Fuel — Operation in a 300 W Chemical-Looping Combustor

Patrick Moldenhauer



CHALMERS

Division of Energy Technology
Department of Energy and Environment
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2011

Chemical-Looping Combustion with Liquid Fuel — Operation in a 300 W Chemical-Looping Combustor

Patrick Moldenhauer

© Patrick Moldenhauer, 2011

Division of Energy Technology
Department of Energy and Environment

Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone +46 (0)31-772 1000

Cover:

The cover image shows a schematic of how kerosene is injected into the 300 W chemical-looping combustor.

Printed in Sweden
Chalmers Reproservice
Gothenburg, Sweden 2011

Abstract

Chemical-looping combustion (CLC) is a promising technology for future energy conversion based on combustion of fossil fuel with inherent CO₂ separation. In comparison to other carbon capture technologies there is no need for energy demanding gas separation using CLC in order to obtain pure CO₂. In the past, CLC research has mainly focussed on the use of gaseous and solid fuels. This study is a first step towards the use of liquid fuels in chemical-looping combustion.

Experiments were conducted in a laboratory scale chemical-looping reactor system with continuous circulation of oxygen carrier particles. An injection system for liquid fuel was designed and tested. The fuel used was a sulphur-free kerosene. Four different oxygen carrier materials were investigated, of which three were synthesized and one was a mineral. The synthesized materials were based on nickel, manganese and copper. The natural material was ilmenite, which is an iron titanium oxide.

The highest fuel conversion to CO₂ was achieved with the copper- and manganese-based oxygen carriers. The temperature necessary to achieve high fuel conversion however, was considerably lower for copper-based oxygen carrier than for manganese-based oxygen carrier. Of these two materials, the copper-based oxygen carrier showed clear oxygen release properties, meaning that it is likely that a substantial part of the fuel was converted by direct reaction with gaseous oxygen. This is called chemical-looping combustion with oxygen uncoupling (CLOU). Fuel conversion to CO₂ and H₂O with nickel-based oxygen carrier was high but somewhat lower than with copper- and manganese-based oxygen carrier, which can be explained by thermodynamic limitations. Ilmenite showed the lowest reactivity of all tested oxygen carriers.

All the particles were analyzed before and after the experiments using XRD, SEM, BET surface area and particle size distribution. Whereas copper-based and ilmenite oxygen carrier particles showed a high degree of stability, nickel- and manganese-based oxygen carrier particles were subject to particle disintegration and nearly the entire particle batch was destroyed after the experiments.

Acknowledgements

I would very much like to thank my supervisors Tobias Mattisson and Magnus Rydén and my examiner Anders Lyngfelt. You introduced me to the field of chemical-looping, listened patiently to my questions and always have open doors and ears for discussion. Thank you for this!

A big thanks to the chemical-looping crowd for the good group spirit, fruitful discussions and shared agony in the lab. Thank you Peter, Calle, Pontus, Erik, Henrik, Golnar, Mehdi, Dazheng and Martin. A special thanks to Ulf, the backbone of the lab, for uncounted help and the exchange of Swedish and German sayings. We had quite a few guests from other universities, who breathed some fresh air and ideas into our group. Thank you Azad, Ana and Georg.

Not all of the help I received came from within the chemical-looping group. Helping hands and ideas came from all around: Martin Seemann, Fredrik Lind, Anton Larsson, Nicolas Berguerand, Sven-Ingvar Andersson, David Pallarès, Filip Johnsson, Sven Andersson and Lars-Erik Åmand. Tack, tack, tack!

One big collective thank you to the rest of my co-workers at the division of Energy Technology for the nice working atmosphere!

Last but not least I want to thank Jean-Pierre Ballaguet, Bandar Fadhel and Wajdi Sadat from Saudi Aramco for the friendly cooperation. This work is part of the project "Chemical-looping with liquid hydrocarbon fuels", which is financed by Saudi Aramco.

Patrick Moldenhauer
Göteborg, November 2011

List of Publications

This thesis is based on the following publications:

- I. P. Moldenhauer, M. Rydén, and A. Lyngfelt. Testing of minerals and industrial by-products as oxygen carriers for chemical-looping combustion in a circulating fluidized-bed 300 W laboratory reactor. accepted for publication in *Fuel*,
- II. P. Moldenhauer, M. Rydén, T. Mattisson, and A. Lyngfelt. Chemical-looping combustion and chemical-looping reforming of kerosene in a circulating fluidized-bed 300 W laboratory reactor. submitted for publication,
- III. P. Moldenhauer, M. Rydén, T. Mattisson, and A. Lyngfelt. Chemical-looping combustion and chemical-looping with oxygen uncoupling of kerosene with Mn- and Cu-based oxygen carriers in a circulating fluidized-bed 300 W laboratory reactor. submitted for publication,

Patrick Moldenhauer is the principal author of papers I – III. Magnus Rydén assisted the work in paper I, contributed the part about chemical-looping reforming experiments to paper II and helped with all papers by means of editing and discussion. Erik Jerndal contributed to paper I with a reactivity analysis to compare fresh and used ilmenite oxygen carrier particles. Tobias Mattisson is the principal academic supervisor and contributed to papers II and III with discussion and editing. Anders Lyngfelt is the examiner and contributed to paper I – III with discussion and editing.

Contents

1	Introduction	1
1.1	Chemical-Looping Combustion	1
1.2	Aim and Scope	3
1.3	Content of the Thesis	3
2	Experimental Details	5
2.1	300 W Laboratory Reactor	5
2.2	Fuel	7
2.3	Injection Principle of Liquid Fuel	7
2.4	Measurements	8
2.5	Oxygen Carriers Investigated	9
2.5.1	Syngas Experiments	9
2.5.2	Liquid Fuel Experiments	10
2.5.3	Particle Preparation	11
3	Results	13
3.1	Syngas Experiments	13
3.2	Liquid Fuel Experiments	13
4	Conclusions	21
	Nomenclature	23
	Bibliography	25

1 Introduction

The concentrations of greenhouse gases in the atmosphere are rising unhampered towards levels where serious consequences for the world's climate are expected [4–7]. Attempts to regulate and reduce greenhouse gas emissions seem to fall far short of expectations. The industrialized countries as a whole, which are defined as Annex I countries in the Kyoto Protocol, may meet their greenhouse gas emission obligations during the first commitment period, 2008-2012, of the Kyoto Protocol [7, 8]. The global CO₂ emissions however, are increasing and were about 45 % higher in 2010 as compared to emissions in 1990 [7].

One possibility to reduce CO₂ emissions for the combustion of carbon-based fuels is through carbon capture and storage (CCS). In CCS CO₂ is captured, transported and stored in underground storage locations [9]. One approach is to capture CO₂ at the combustion site, *e.g.* from fossil fuel power plants, via post-combustion CO₂ capture or oxyfuel combustion. Alternatively, carbon-based fuel is reformed into a carbon-free fuel, *i.e.* hydrogen, and CO₂ is captured before the actual fuel is used. This is commonly referred to as pre-combustion capture.

1.1 Chemical-Looping Combustion

Chemical-looping combustion (CLC) is a combustion technology with inherent separation of CO₂. CO₂ and N₂ in the flue gases are obtained in different gas streams. Thus, a direct energy penalty for the separation of gases, which many other alternative CCS techniques suffer from, is avoided.

In the most commonly proposed CLC approach, oxygen carrier particles are circulated between two interconnected reactors, the air reactor and the fuel reactor, with no gas leakage between the reactors. In the air reactor (AR) the particles are oxidized with air and in the fuel reactor (FR) reduced by fuel, before the cycle begins anew. As the oxygen carrier is circulated between air reactor and fuel reactor, it transports oxygen from air to fuel. Thus, air and fuel are never mixed, and after condensing the water, the stream of flue gases consists of nearly pure CO₂. Figure 1.1 illustrates the working principle of chemical-looping combustion. High CO₂-capture efficiency, high CO₂-capture rate and the possibility of using different kinds of fuels suggest that CLC could be economically feasible and thus competitive [10, 11].

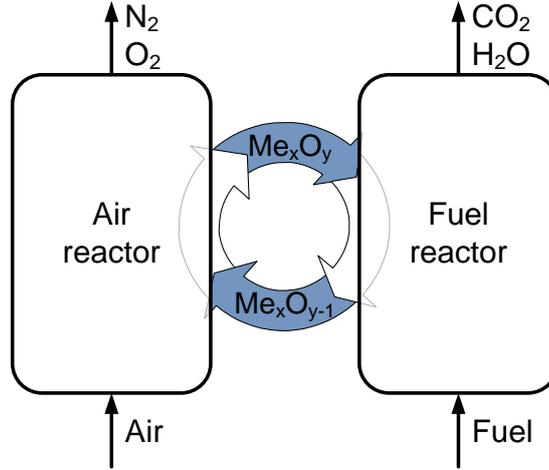
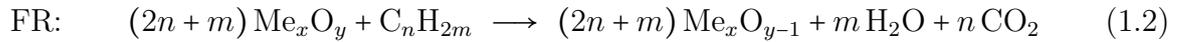
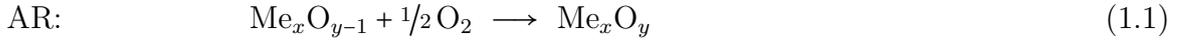


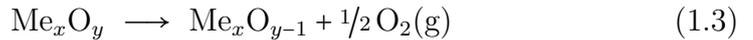
Figure 1.1: Schematic illustration of the chemical-looping combustion process

Figure 1.1 shows the basic design of a CLC system and illustrates the working principle. The reactions in air reactor and fuel reactor are expressed by reactions (1.1) and (1.2).



Here Me_xO_y denotes a metal oxide. The oxidation of particles in the air reactor, see reaction (1.1), is exothermic. The reducing reaction in the fuel reactor, see reaction (1.2), can be either exothermic or endothermic, depending on oxygen carrier material and fuel used.

Chemical-looping combustion with oxygen uncoupling (CLOU) is a variant of chemical-looping combustion. After oxidation of oxygen carrier in the air reactor according to reaction (1.1), the oxidized oxygen carrier is transported into the fuel reactor, where it releases oxygen in gaseous form, see reaction (1.3). Reactions between solid fuel and gas-phase oxygen, see reaction (1.4), could be much faster than the corresponding CLC reaction, see reaction (1.2), where fuel reacts with oxygen that is bound to the solid oxygen carrier.



The typical mechanism for oxygen release is a phase change of the oxygen carrier between air reactor and fuel reactor. The phase change in turn is triggered by a change in oxygen concentration and/or temperature. Whether or not a CLC process is also a CLOU process is determined by the properties of the oxygen carrier, *i.e.* its ability to undergo phase changes under prevailing conditions.

Reactions between two solids, as in CLC with solid fuels, are potentially slow. The use of an oxygen carrier with CLOU properties in combination with solid fuel is thus beneficial. But even for liquid fuel the use of a CLOU material is expected to show a clear improvement in fuel conversion. Deposition of char, which is expected when higher oil fractions are used, could become less problematic as carbon would be burned off by gaseous oxygen.

Review articles about developments in the field of chemical-looping have been written by Lyngfelt *et al.* (2008) [12], Hossain and De Lasa (2008) [13], Fang *et al.* [14] and Lyngfelt (2011) [15, 16]. Results have been published from twelve operational continuous chemical-looping combustors with thermal capacities ranging from 300 W to 140 kW and a total operational experience of more than 4000 h. The majority these experiments were performed with gaseous fuel, methane, natural gas or syngas, followed by solid fuels. Liquid fuels have been examined in laboratory batch experiments [17–22] and in continuous operation [2, 3] (paper I & II in this work).

1.2 Aim and Scope

The main focus of this thesis is the investigation of different oxygen carrier materials in the 300 W chemical-looping reactor with liquid fuel. The liquid fuel used was a sulphur-free kerosene, which was fed continuously into the 300 W chemical-looping reactor. The use of kerosene is a first step towards using heavy oil residues, which may be more applicable from an economic point of view. From the work in this thesis some promising oxygen carrier materials are selected for subsequent long-term testing in a larger chemical-looping combustor with heavier oil fractions as fuel.

1.3 Content of the Thesis

This thesis has essentially the same structure as papers I – III. Chapter 1 gives an introduction to the topic and describes the aim of the research. Chapter 2 describes the experimental setup, which includes the chemical-looping reactor, the measurement system, fuel and oxygen carriers used and the experiments conducted. The results are summarized in chapter 3 and chapter 4 provides the main conclusions of the work.

This thesis is based on experimental work, which was performed at Chalmers University of Technology in a circulating fluidized-bed laboratory reactor. The focus lies on the use of liquid fuel in chemical-looping combustion.

In paper I a mineral, ilmenite, and an industrial by-product, iron oxide scale, are investigated with syngas as fuel. Both oxygen carriers are cheap and potentially abundant. Syngas, which consisted of 50 vol% H₂ and 50 vol% CO, is an intermediate combustion product of liquid and solid fuels. Especially the ilmenite oxygen carrier worked well over long operating periods and showed promising results, which made further investigation with liquid fuel reasonable.

Paper II is a proof-of-concept paper on the use of liquid fuel in a continuous chemical-looping reactor. A nickel-based oxygen carrier was used due to its good conversion properties for gaseous fuels. Both chemical-looping combustion and chemical-looping reforming (CLR) experiments were performed with kerosene as fuel. The oxygen carrier was analyzed before and after the experiments with XRD, SEM, BET surface area measurements and particle size distribution. For CLC, nearly complete fuel conversion was achieved with virtually no hydrocarbons left in the flue gases. For CLR a synthesis gas was produced with a hydrocarbon content as low as 0.01 %. Unfortunately nickel-based oxygen carriers also involve disadvantages. Besides health issues and the high price, nickel oxide comes with thermodynamic limitations, which never allow a 100 % conversion of any hydrogen- and/or carbon-based fuels into CO_2 and H_2O . Nickel oxide is also known to suffer from poisoning/deactivation if it gets in contact with sulphur species. The process is reversible, but only if the oxygen carrier is treated in a high temperature, sulphur-free atmosphere [23, 24]. Hence, nickel-based oxygen carriers do not seem to be a realistic option for future applications with sulphur-containing liquid fuels.

Paper III continues the work of paper II by investigating the conversion properties of kerosene with two more oxygen carriers, a manganese-based material and a copper-based material. At typical CLC conditions copper-based oxygen carriers release gas-phase oxygen in the fuel reactor, which allows potentially higher fuel conversion compared to a regular oxygen carrier material. Both oxygen carriers showed good results, though clearly higher fuel conversion to CO_2 and H_2O was achieved with the copper-based material.

Additional to the results published in paper I – III, results are presented from experiments with ilmenite oxygen carrier and liquid fuel.

2 Experimental Details

2.1 300 W Laboratory Reactor

The working principle of the chemical-looping reactors, which were used for the experiments in papers I – III, are shown in Figure 2.1. Both reactors have a similar design. Version 3 of the reactor, see Figure 2.1b, was designed and constructed as part of this work.

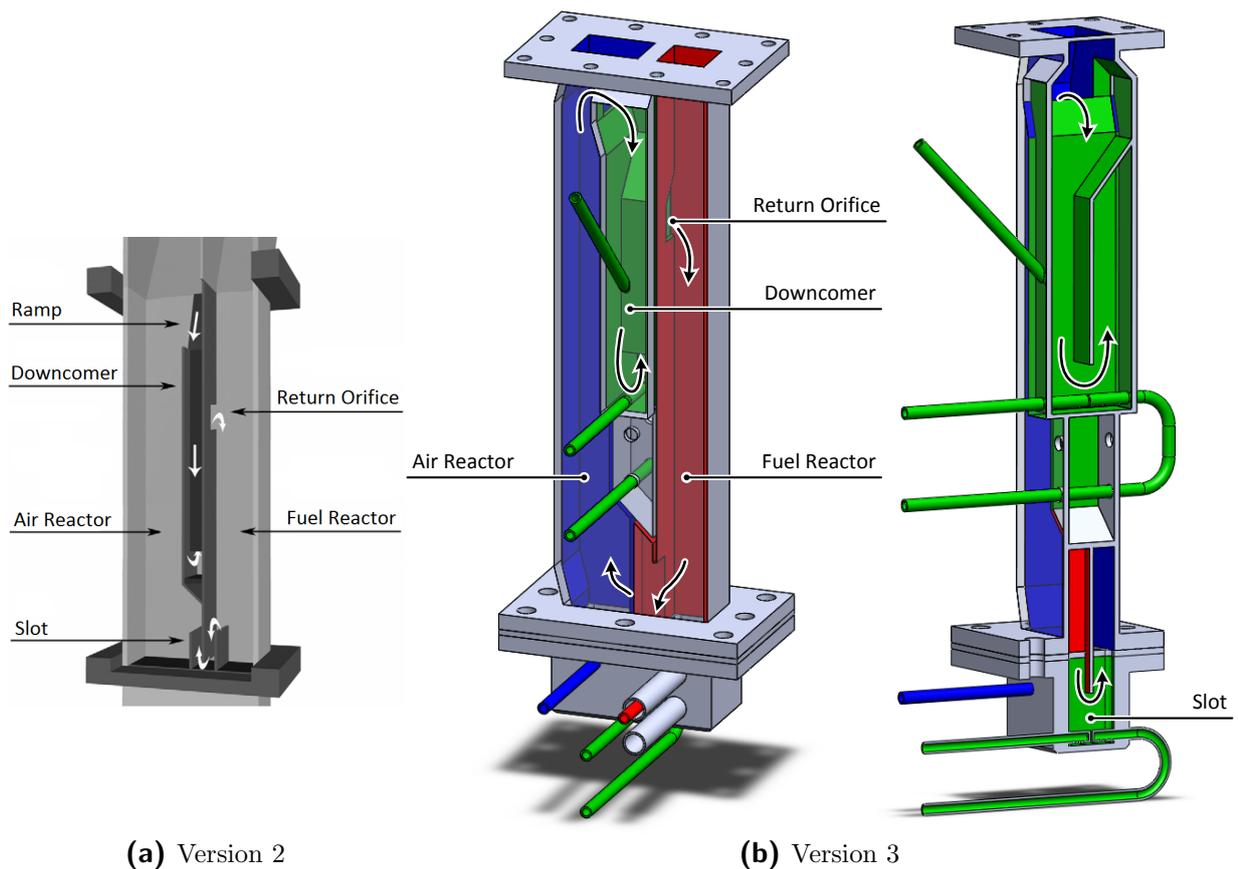


Figure 2.1: True-to-scale representation of the two versions of the 300 W chemical-looping reactor

Fuel and air enter the system through separate windboxes, located in the bottom of each reactor. Porous quartz plates act as gas distributors. In the air reactor, the gas velocity is

sufficiently high to create a circulating fluidized bed and oxygen carrier particles are thrown upwards. The particle-gas mixture is then separated: oxygen depleted air is returned to the atmosphere, whereas a fraction of particles falls into the standpipe of the downcomer, which is the inlet of a J-type loop-seal. From the loop-seal, particles overflow into the fuel reactor via the return orifice. The fuel reactor is a bubbling bed counterflow reactor, *i.e.* particles move downwards while gas moves upwards. From the bottom of the fuel reactor, particles flow into the underflow standpipe of the slot, which is essentially a J-type loop-seal, and return to the air reactor, where the whole cycle starts over again.

Metal oxide particles in the air reactor are fluidized with air, and reduced particles ($\text{Me}_x\text{O}_{y-1}$) are oxidized according to reaction (1.1). In the fuel reactor the metal particles are fluidized by gas-phase fuel or, in case of kerosene, a gaseous steam-fuel mixture. Particle reduction occurs either directly by fuel, according to reaction (1.2), or, if a CLOU oxygen carrier is used, indirectly through oxygen released. In this reactor, both loop-seals are fluidized with argon.

Version 3 of the reactor is a further development of version 2 with the following improvements:

- Increased height of air reactor and fuel reactor in order to gain more flexibility regarding solids inventory
- Improved slot design in order to reduce gas leakage and enhance circulation
- Improved downcomer design in order to enhance circulation

Version 2 of the reactor, see Figure 2.1a, was used for the experiments with ilmenite oxygen carrier with syngas as fuel and nickel-based oxygen carrier with liquid fuel. Version 3, see Figure 2.1b, was used for all other materials with liquid fuel. The main dimensions of both reactor versions are summarized in Table 2.1.

Table 2.1: Main dimensions of reactor versions 2 and 3

Reactor part	Version 2	Version 3
Reactor height	212	300
Fuel reactor area	25×25	25×25
Air reactor bottom area	45×25	42×25
Air reactor riser area	25×25	25×25
Downcomer height	75	83
Downcomer area	16×11.5	21×21
Slot height	18	48
Slot area	7.5×25	10×11.5

all dimensions are in mm

Due to the small thermal output, the heat of reaction is not enough to generate a sufficiently high temperature, typically 750°C to 950°C. The reactor is therefore encased in an electric furnace.

2.2 Fuel

The fuel used in paper I was syngas, which consisted of 50 vol% H₂ and 50 vol% CO.

The liquid fuel used in papers II and III was kerosene, which was provided by courtesy of Preem AB in Gothenburg, Sweden. By definition kerosene consists of different hydrocarbons with evaporation temperatures between 150 °C and 320 °C. An elemental analysis showed a composition of 86.2 wt% carbon and 13.5 wt% hydrogen, which corresponds to a molar hydrogen-to-carbon ratio H/C of 1.88. The lower heating value was determined to be 43.34 MJ/kg. It is likely that the fuel not only contains linear alkanes but also branched iso-alkanes and possibly even cyclic alkanes. The elemental analysis suggests the presence of arenes. Alkenes and alkynes are rather unlikely in mineral oil.

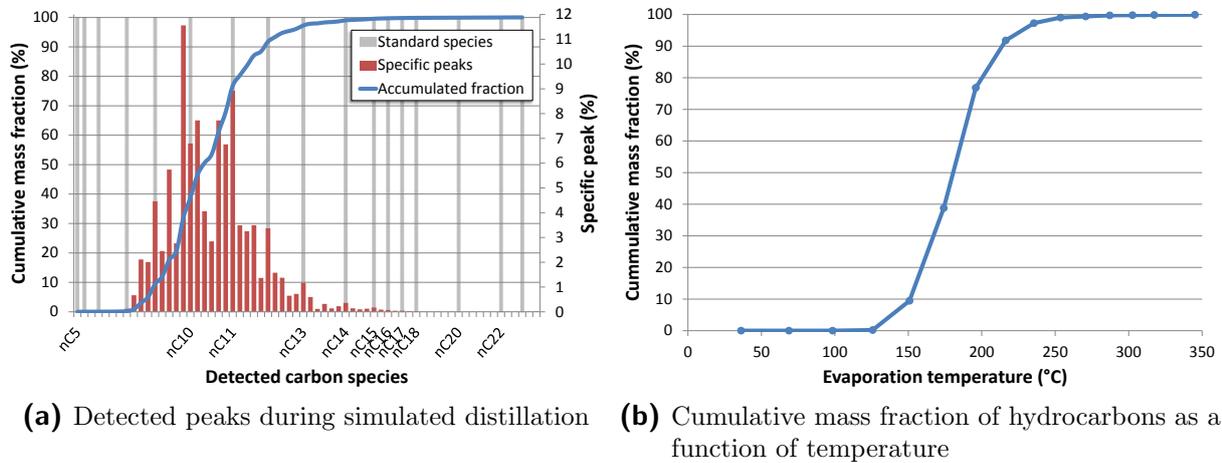


Figure 2.2: Fuel analysis with simulated distillation according to ASTM standard D-2887-08

The fuel was also analyzed in a gas chromatograph (GC) with the simulated distillation method according to ASTM standard D-2887-08, see Figure 2.2a, which is a standard test method for boiling range distribution of petroleum fractions. It was found that 99 wt% of the fuel content has an evaporation point below 250 °C and 80 wt% below 200 °C, see Figure 2.2b. Some of the peaks in the analysis coincided with those of linear alkanes. The most prominent ones were n-C10, *i.e.* C₁₀H₂₂, (H/C = 2.20; $T_{\text{boil}} = 174$ °C) and n-C11 (H/C = 2.18; $T_{\text{boil}} = 196$ °C).

2.3 Injection Principle of Liquid Fuel

An injection system for liquid fuel was constructed and tested using the 300 W chemical-looping reactor, see Figure 2.1. The basic principle behind the injection system is to evaporate the liquid fuel using superheated steam as heat source and to inject the resulting steam-fuel gas mixture into the fuel reactor. This is most convenient, because it causes the least changes to the reactor system, which is designed for gaseous fuels.

When the fuel molecules are converted the gas volume will increase. Hence, the volume flow of the gaseous steam-fuel mixture is a function of the extent of hydrocarbon converted. The steam fulfils the secondary function of ensuring that enough gas is available to fluidize the particles in the fuel reactor. Poorly fluidized particles increase the risk of agglomeration, which may destroy the oxygen carrier batch, depending upon the type of material used.

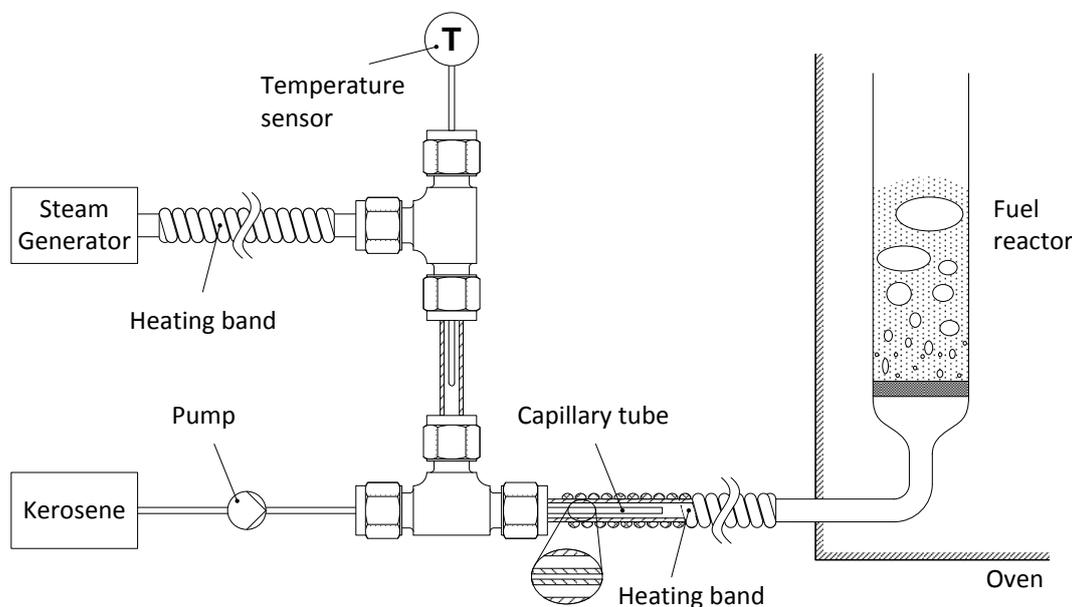


Figure 2.3: Schematic illustration of the injection principle for kerosene injection

Figure 2.3 shows how evaporation, mixing and injection are realized. Steam is generated continuously by a steam generator. A heating band is used to superheat the steam to the desired temperature, which is measured by a thermocouple temperature sensor. A continuous fuel flow is provided by a diaphragm metering pump. The fuel is fed through a capillary tube, which is concentrically arranged within the steam pipe. The heat necessary for evaporation of the fuel is thereby transported from steam to fuel.

2.4 Measurements

Figure 2.4 shows a schematic of the downstream gas measurements. The top part of the 300 W reactor is connected to a gravitational solid/gas separator, one for the air reactor and one for the fuel reactor. Part of the hot flue gases of the fuel reactor are diverted and led through a heated line, at 155°C, to a flame ionization detector (FID). The FID measures the content of organic carbon as a CH₄ equivalent, without giving information about aromaticity or hydrogen content. The flue gases of both air reactor and fuel reactor are separately filtered and cooled down to 5°C, before they pass through gas analyzers. The dry-gas content of CH₄, CO and CO₂ is measured continuously by an IR analyzer and the content of O₂ by a paramagnetic sensor. Additionally, the dry fuel reactor gas is intermittently analyzed in a gas chromatograph (GC), which measures, besides the previously

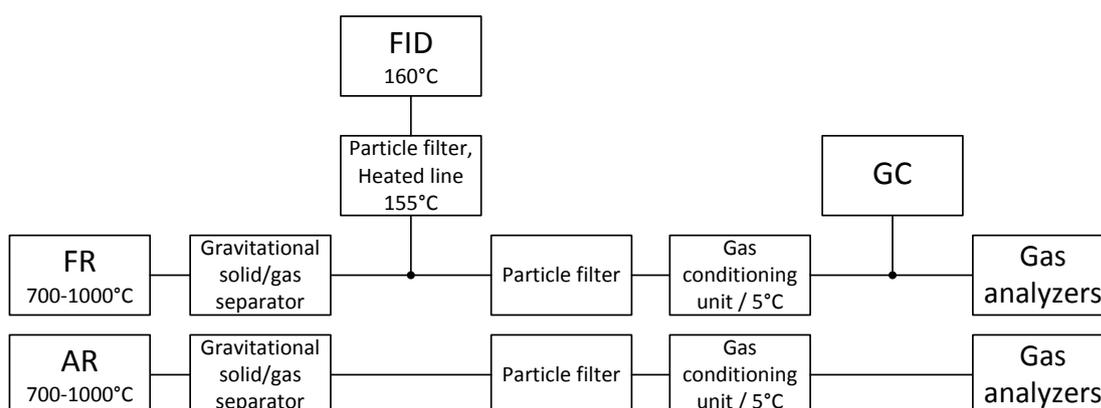


Figure 2.4: Schematic measurement layout

mentioned gases, H_2 , N_2 , and hydrocarbons up to C_3H_8 . The GC used is equipped with two columns, Molsieve MS5Å 10 m × 0.32 mm (ID) and PoraPLOT Q 10 m × 0.15 mm (ID), in which the gas sample is injected in parallel.

In addition to the analysis of in situ data, XRD measurements, density measurements and measurements of the BET surface area (through gas adsorption) were performed with particles before and after the experiments.

2.5 Oxygen Carriers Investigated

2.5.1 Syngas Experiments

Experiments with syngas as fuel, see paper I [1], were conducted with two low-cost oxygen carrier materials, ilmenite and iron oxide scale.

Ilmenite is a mineral iron titanium oxide with the chemical formula $FeTiO_3$. Mined ilmenite is in a reduced state and usually contains some Fe_2O_3 (hematite). When first heated, ilmenite is oxidized to Fe_2TiO_5 (pseudobrookite) and TiO_2 (rutile). The particles were heated treated before the experiments outside the reactor, because ilmenite is known to form hard agglomerations during the first heating period. Ilmenite is not toxic, radioactive or hazardous in any known way. Apart from grinding and physical beneficiation, ilmenite is unprocessed. Ilmenite has earlier been tested successfully for use with both gaseous and solid fuels, *e.g.* [25–29].

Iron oxide scale (IOS) is a waste product from the steel industry, which is produced during the rolling of steel sheets, and basically consists of Fe_2O_3 [30]. This material is available in large amounts and is cheap. Iron oxide scale is delivered as small scales in undefined size ranges. The material is fully oxidized to Fe_2O_3 but contaminated with oil. The first step to making this material usable as oxygen carrier is heat treatment to get rid of the oil. The downside to this procedure is that the particles partially agglomerate. In order to

obtain particles in a suitable size range, it is necessary to grind the particles and then sieve them. IOS particles have been investigated thoroughly in a batch fluidized-bed reactor with methane and syngas as fuels by Leion *et al.* [30]. During those experiments IOS particles proved to have good conversion rates for both fuel types but failed to reach stable reactivity.

2.5.2 Liquid Fuel Experiments

Experiments with liquid fuel were commenced with a nickel-based material (N4MZ-1400), which was used as oxygen carrier, see paper II [2]. Due to the prevailing disadvantages of nickel-based oxygen carriers, their use in industrial sized plants may not be feasible for sulphur-containing fuels. However, in view of its high reactivity and the significant previous experience with such materials, a nickel-based oxygen carrier was considered as suitable to establish a proof-of-concept for liquid fuel. After that, the main focus is on finding a suitable oxygen carrier that is immune to sulphur, has good fuel conversion properties, has good mechanical and chemical stability, is environmentally benign and preferably cheap. These characteristics would make an oxygen carrier suitable for industrial scale application. Hence, a series of materials based on Fe, Mn and Cu, which should resist deactivation by sulphur [31], were identified as interesting from previous works, see Table 2.2.

Table 2.2: Oxygen carriers investigated with liquid fuel

Short name	Oxygen carrier composition	Calcination temperature	Reactor version	Experiments conducted	Reference
N4MZ-1400	40 % NiO, 60 % Mg-ZrO ₂	1400 °C	2	CLC & CLR w/ kerosene	Paper II [2]
M4MZ-1200	40 % Mn ₃ O ₄ , 60 % Mg-ZrO ₂	1200 °C	3	CLC w/ kerosene	Paper III [3]
C2Z-1050	20 % CuO, 80 % ZrO ₂	1050 °C	3	CLC (CLOU) w/ kerosene	Paper III [3]
Ilmenite	Fe ₂ TiO ₅ , TiO ₂ , Fe ₂ O ₃ [†]	900 °C	3	CLC w/ syngas and kerosene	–

[†] composition after physical beneficiation and initial calcination

The nickel-based oxygen carrier N4MZ-1400 was produced by freeze-granulation, *cf.* Section 2.5.3, and has been investigated previously in the 300 W combustor using natural gas as fuel [32]. It has a very high reactivity, is an active catalyst for certain reactions in the fuel reactor and has very good fluidization properties. Experiments with liquid fuel were conducted for about 41 h.

M4MZ-1200 was produced by spray-drying, *cf.* Section 2.5.3. A similar freeze-granulated material has been investigated previously in both batch reactor [33] and 300 W combustor [34] using syngas and natural gas as fuel. In those experiments the particles had high fuel

conversion properties, although not quite as good as those of nickel based oxygen carriers. No issues regarding agglomeration and fluidization were noted. Experiments under addition of liquid fuel were conducted for about 17 h.

Copper-based oxygen carriers have been investigated by different research groups [35–38]. Chalmers work includes experiments with petroleum coke and lignite coal and varied amounts of copper on inert material [39–41]. The results were generally very promising. Copper-based oxygen carriers are known to have good conversion capabilities for solid fuels, which can be attributed by the so called CLOU effect, *i.e.* the release of gas-phase oxygen in the fuel reactor. Due to the rather low melting point of metallic copper, which can be formed during reduction, high temperatures sometimes cause agglomeration of the oxygen carrier particles. The particles investigated here were produced by spray-drying, *cf.* Section 2.5.3. The total operation time under fuel addition was about 45 h.

Experiments with ilmenite oxygen carrier, *cf.* Section 2.5.1, and liquid fuel were conducted for about 41 h.

2.5.3 Particle Preparation

The particle preparation method has a great impact on both the structural properties and the price of the particles produced. The two methods that were used to manufacture the oxygen carrier particles used in this work are summarized in the following sections.

Freeze-Granulation

A water-based slurry is prepared out of the milled raw materials. An organic binder is added to the slurry to bind the mixed raw materials together during later stages in the production process, *i.e.* freeze-drying and calcination. The slurry is dispersed in an atomizer nozzle, which produces spherical drops, and sprayed into liquid nitrogen where the drops freeze instantaneously. The frozen water in the resulting particles is then removed by sublimation in a freeze-dryer. After drying, the particles are calcined to remove the binder and finally sieved to obtain particles in the desired size fraction. Typical calcination temperatures are 950 °C to 1400 °C.

Freeze-granulation is a small scale production method. Typically batches of a few hundred grams are produced. The removal of water through freezing and sublimation produces regular spherical particles in a narrow size distribution.

Spray-Drying

A water-based slurry is prepared out of the powdered raw materials and organic binder additives and further homogenized by milling in a planetary ball mill. The water-based suspension is pumped through a spray-dry nozzle, which produces spherical droplets, into a stream of drying gas, where water is removed through evaporation. After spray-drying,

the particles are sieved to a desired size fraction and calcined to remove the binder, typically at temperatures between 950°C and 1400°C.

Spray-drying is an established large scale production method. Fixed cost degression is valid, *i.e.* the larger the batch sized produced the lower the specific costs. Spray-drying produces spherical particles, which are, however, prone to defects like hollow or perforated (doughnut shaped) particles.

3 Results

3.1 Syngas Experiments

Full conversion of syngas to CO_2 and H_2O was achieved with a fuel flow corresponding to about $190 W_{\text{th}}$ at 900°C . A clear change in the particle structure was observed together with an improvement in fuel conversion during the first hours of fuel addition. Fuel conversion did not change considerably over the course of 85 h of fuel operation and the particles were mostly stable.

The fuel conversion achieved with iron oxide scale oxygen-carrier was below the fuel conversion achieved with ilmenite oxygen carrier. Full conversion of syngas to CO_2 and H_2O could not be achieved even when the fuel flow was reduced to $100 W_{\text{th}}$. The variation in fuel conversion was high and circulation collapsed during a number of occasions. Iron oxide scale oxygen-carrier particles were subject to attrition and agglomeration. Experiment with fuel addition were conducted for about 37 h.

More detailed results and discussion can be found in paper I [1].

3.2 Liquid Fuel Experiments

The evaluation of the combustion process with liquid fuel is based on the fate of carbon. A carbon balance is performed around the whole reactor system, *i.e.* air reactor and fuel reactor, where the exiting carbon species are compared to the amount of carbon added by the fuel. The carbon species are listed in Table 3.1. A more detailed description of the evaluation can be found in [2, 3] (paper II & III).

A more compact way of evaluating the combustion process is the use of the CO_2 yield, which is a single valued measure of how much carbon in the fuel reactor is fully converted into CO_2 , without differentiating between intermediate conversion products. It is calculated by dividing the molar amount of CO_2 leaving the fuel reactor by the sum of all carbon that leaves the fuel reactor. The CO_2 yield, expressed through γ_{CO_2} , does not take gas leakage or transport of solid carbon from fuel reactor to air reactor into account. This is

Table 3.1: Carbon fate categories

C-Species ¹	Explanation
CO ₂ in FR	Reaction product in case of complete conversion
CO in FR	Intermediate reaction product; hydrocarbons are fully cracked but only partially converted
CH ₄ in FR	Intermediate reaction product; hydrocarbons are mostly cracked but not fully converted
>CH ₄ [†] in FR	Intermediate reaction product; hydrocarbons are not or partially cracked
CO ₂ in AR	All carbon that gets into the air reactor is expected to be fully converted into CO ₂ . Carbon can either get into the air reactor in the form of gas, <i>i.e.</i> by gas leakage from fuel reactor to air reactor, or as solid carbon from coke formation, which is transported into the air reactor by the global particle circulation. However, it is only possible to observe the sum of both effects.

[†] >CH₄ denotes hydrocarbons higher than CH₄

reasonable since two different versions of the 300 W reactor were used, which have different gas leakage characteristics.

Both carbon fate and CO₂ yield are shown in Figure 3.1 for each oxygen carrier at varied temperature and a fuel flow corresponding to 144 W_{th}.

A clear difference in fuel conversion can be observed for the different oxygen carriers. Fuel conversion with N4MZ-1400 was very good and nearly complete. The CO₂ yield was above 95% at all times. The unconverted gases were mainly CO and H₂, which is not shown here. The high but incomplete conversion of fuel can be ascribed to thermodynamic limitations of nickel-based oxygen carriers. No noteworthy concentrations of CH₄ or any higher hydrocarbon were observed. For a more detailed discussion see [2] (paper II).

Fuel conversion with M4MZ-1200 clearly increased with higher temperatures. The amount of CO is low for all temperatures, whereas methane and other hydrocarbons were detected at temperatures below 950 °C. Fuel conversion was nearly complete at 950 °C. More detailed results are displayed in [3] (paper III).

CLC experiments with C2Z-1050 were run at lower temperatures than the experiments with other oxygen carriers. The fuel conversion achieved was higher than for the other oxygen carriers in this study, including the nickel-based N4MZ-1400. The CO₂ yield was above 85% at all times and higher than 95% at temperatures above 750 °C. The amount of higher hydrocarbon clearly decreases with higher temperature and the dry-gas concentrations of CO and CH₄ were below 1% at all times. The dry-gas H₂ concentration was as high as 4% at the lowest tested temperature. This comparatively high value can be attributed to the water-gas shift equation, which favours a shift from CO + H₂O to CO₂ + H₂ at temperatures below 800 °C. C2Z-1050 not only reached the highest CO₂ yield but also the

¹ *cf.* Figure 3.1

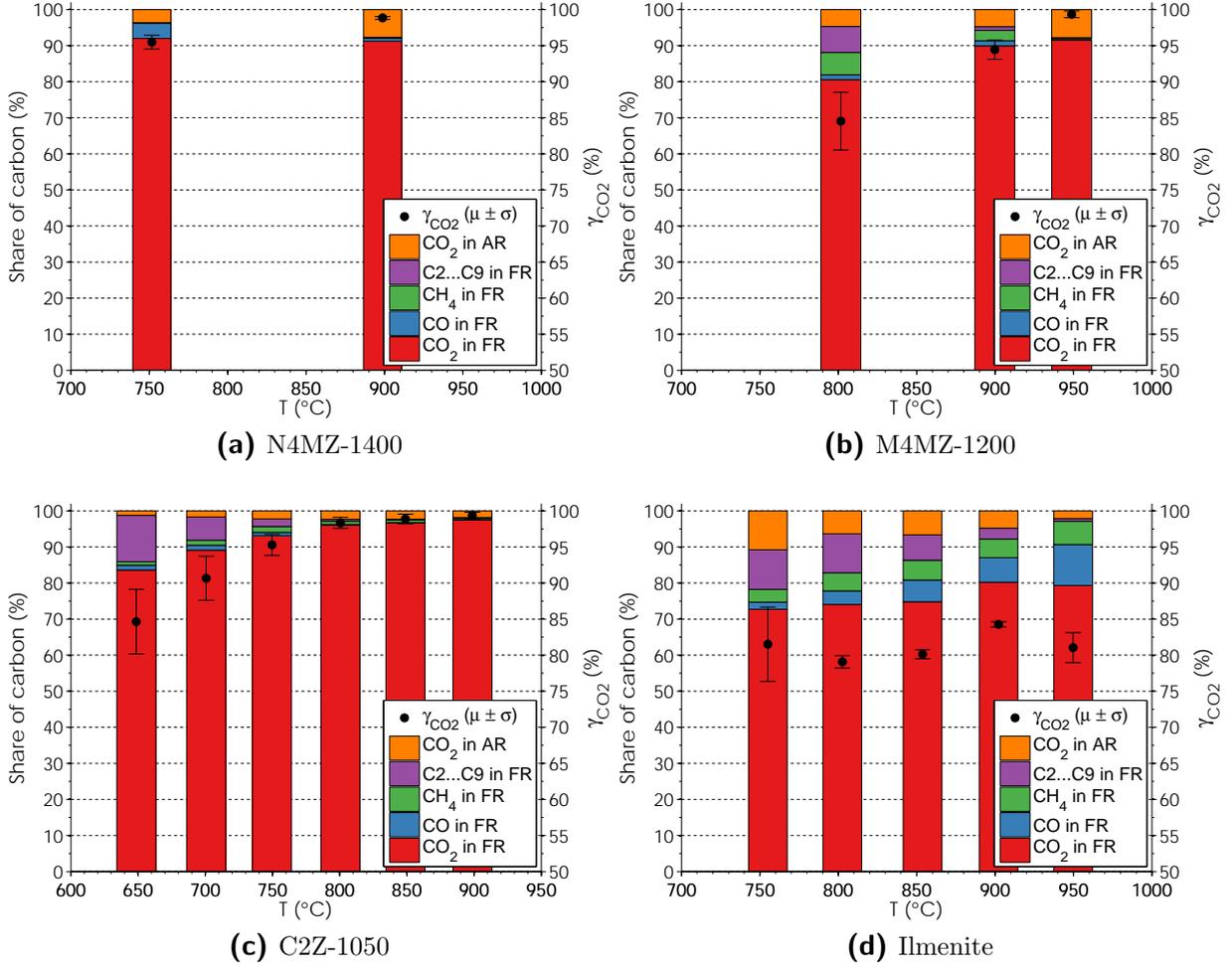


Figure 3.1: Carbon fate² and CO₂ yield for CLC experiments with oxygen carriers tested at varied temperatures using a fuel flow of 0.25 ml/min (144 W_{th})

highest amount of CO₂ in the fuel reactor. The reason for this was that only very little carbon leaked into the air reactor. More details can be found in [3] (paper II).

Fuel conversion with the natural ilmenite oxygen carrier differs from fuel conversion with the other oxygen carriers tested. Fuel conversion is clearly lower, *i.e.* the amounts unconverted H₂, CO, CH₄ and hydrocarbons are higher, and the CO₂ yield does not seem to increase with higher temperatures. The following observations were made with respect to these experiments:

- The amount of carbon, which ends up in the air reactor decreases with higher temperatures.
- The amount of carbon in the form of higher hydrocarbon decreases with higher temperatures.

²*cf.* Table 3.1

- The amount of carbon in the form of CH_4 seems to be rather constant.
- The amount of carbon as CO increases with higher temperatures respectively as more higher hydrocarbons are broken down.

It is generally difficult to draw clear conclusions about carbon leakage to the air reactor. This is because the carbon leakage observed is the sum of carbon transport and gas leakage. Gas leakage might be influenced by an oxygen carrier's fluidization properties, whereas coke formation and transport are affected by chemical properties. Furthermore, carbon leakage seems to be connected to the use of liquid fuel, but also to the design and size of the 300 W combustor as it has not been observed in larger ones, see discussion in [2, 3] (papers II & III).

Figure 3.2 shows a comparison of the CO_2 yield of the oxygen carriers tested with varied temperature and a fuel equivalent, which corresponds to $144 \text{ W}_{\text{th}}$ ($0.25 \text{ ml}_{\text{liq}}/\text{min}$). Hence, fuel conversion properties of the oxygen carriers can be compared without considering carbon leakage into the air reactor.

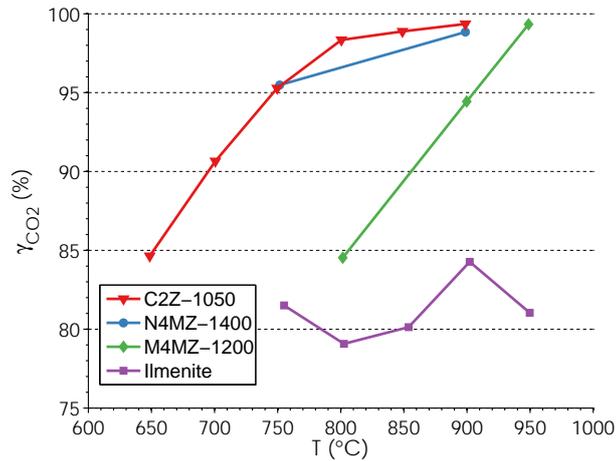


Figure 3.2: Comparison of CO_2 yield for CLC experiments with oxygen carriers tested

The highest gas yield was clearly reached with the copper-based C2Z-1050 and nickel-based N4MZ-1400. Although it was possible to achieve almost full conversion with manganese-based M4MZ-1200, a higher temperature than for the afore mentioned oxygen carriers was required. The CO_2 yield for the ilmenite oxygen carrier does not seem to change much when the temperature was varied.

Figure 3.3 shows scanning electron microscope (SEM) images of the oxygen carriers tested in different magnifications, before and after the experiments with kerosene. A clear difference can be seen between the synthesized oxygen carrier particles, N4MZ-1400, M4MZ-1200 and C2Z-1050, and ilmenite. Whereas synthesized particles are mostly uniformly spherical, ilmenite particles have a rather bulky edgey shape. But even the synthesized particles show differences. The amount of so called defects, *e.g.* holes or satellites of small attached particles, clearly differs. The copper-based oxygen carrier C2Z-1050, Figure 3.3e, shows much more defect than the manganese-based one, Figure 3.3c. SEM images can offer valuable

clues about the mechanical stability of an oxygen carrier. The estimated average attrition rate, which is based on the amount of fines produced during an experiment and the operational time, was about one order of magnitude lower for C2Z-1050 than for M4MZ-1200 even though SEM images of the respective fresh particles would have suggested otherwise. The images of fresh nickel-based oxygen carrier N4MZ-1400 is of a somewhat larger size fraction than was used in the actual experiments. It is assumed that fresh particles of the size fraction used have a much more regular shape and fewer defects.

Ilmenite oxygen carrier particles undergo drastic changes during the first hours of fuel operation: reactivity increases, particles swell, and iron phases migrate to the surface of the particle [1, 29]. The SEM images show light spots on the surface of used ilmenite. Adánez *et al.* found that iron oxide can form a solid shell around the particle depending on the intensity of the reductions and the number of redox cycles [29]. In order to achieve a better understanding for the phase migration, an EDX analysis was performed. Figure 3.4 shows a summary of a multitude of EDX spot analysis of the spots on the surface of the particle and on the area between spots. It was found that the spots on the surface consist mainly of an iron oxide, possibly Fe_2O_3 , whereas the particle core shows increased levels of titanium. This matches earlier results with the difference that iron did not form an enclosing shell around the particle, but only formed patches on the surface. It is not clear whether those patches are just an intermediate step, which would eventually lead to an enclosing iron shell if the experiments had been continued longer.

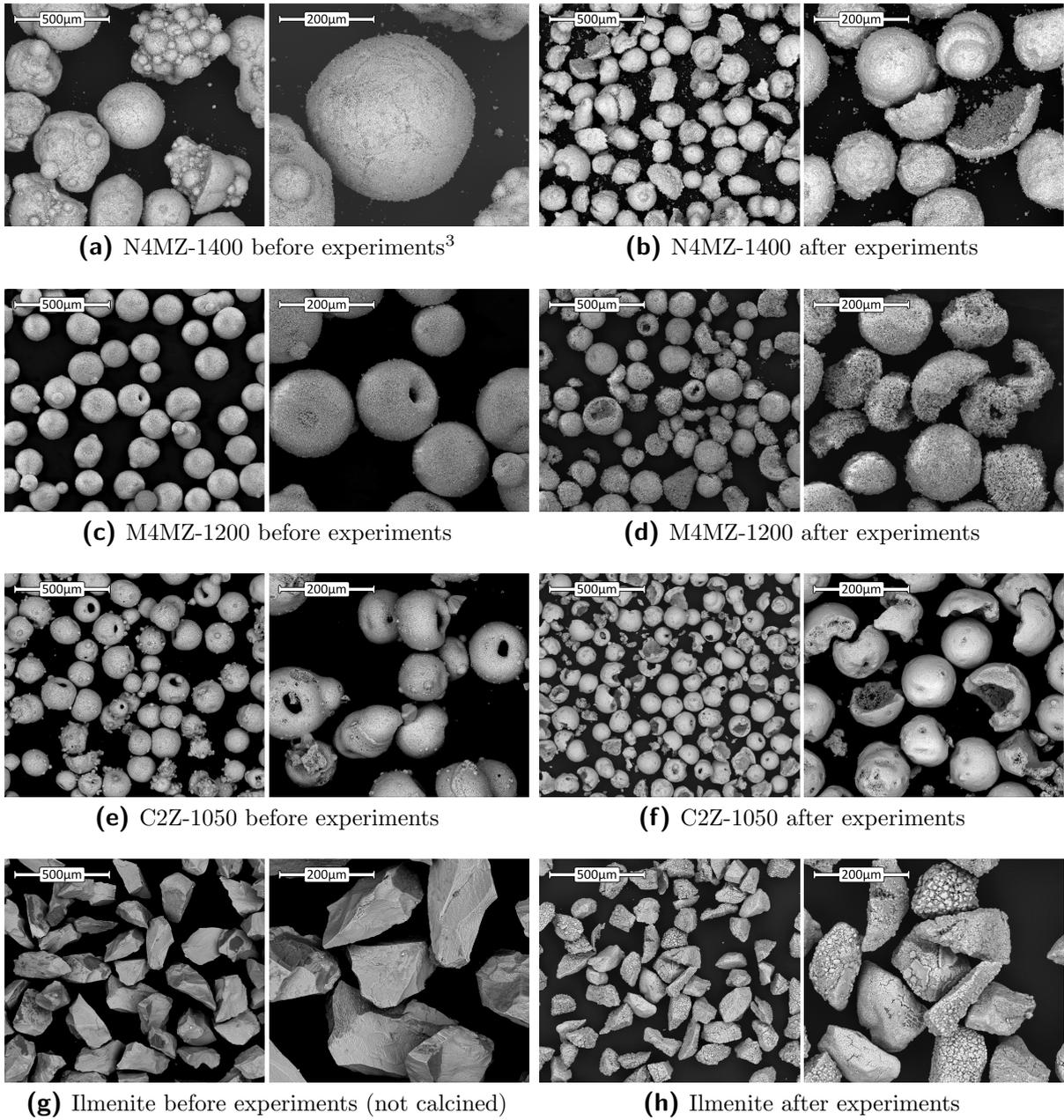


Figure 3.3: SEM images of oxygen carrier tested before and after CLC experiments with liquid fuel

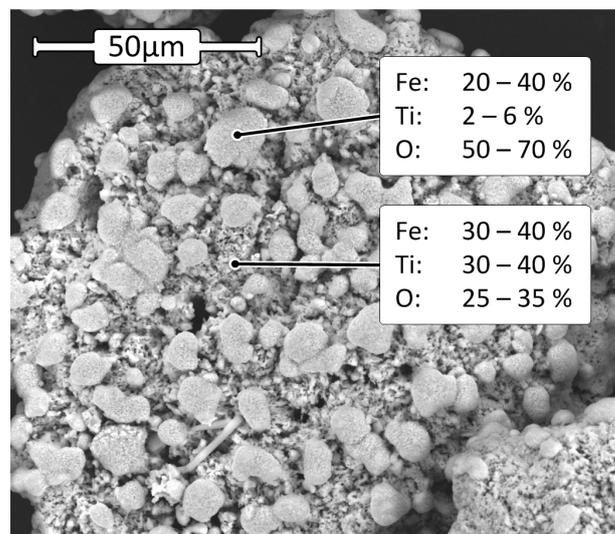


Figure 3.4: Surface EDX of an ilmenite oxygen-carrier particle after experiments with liquid fuel⁴

³Pictures show particles from a larger size fraction (212 μm – 250 μm) than the ones actually used for the chemical-looping experiments in the 300 W reactor (90 μm – 212 μm).

⁴Results are shown in atomic percent.

4 Conclusions

This study showed that chemical-looping combustion with liquid fuel is possible, and also that different oxygen carriers can be used, although they have very different properties, such as fuel conversion, coke formation, lifetime and the tendency to agglomerate. Generally, CLC with liquid fuels does not differ that much from CLC with gaseous fuels. Exceptions are the fuel injection and the measurement techniques. Coke formation also seems to be a somewhat bigger issue when liquid fuel is used in comparison to gas, although it will likely not be a problem in a well-designed industrial reactor. However, an industrial process will likely not utilize kerosene in a CLC unit, but rather heavier oil residues containing higher hydrocarbons and more impurities, such as sulphur. This means that it is also important to study the oxygen carriers using these types of fuels.

The summary in Table 4.1 is an attempt to condense the findings of this study into one simple comparison. The symbols are to be interpreted as follows:

- + favourable property
- unfavourable property

Table 4.1: Comparison of crucial properties of the oxygen carriers tested with liquid fuel

Oxygen carrier	Fuel conversion	Lifetime	Agglomeration tendency	Estimated costs
N4MZ-1400	++	-	+	--
M4MZ-1200	+	--	+	-
C2Z-1050	++	+	-	-
Ilmenite	-	++	+/-	++

As can be seen in Table 4.1, there is no oxygen carrier that only has advantages or disadvantages. A compromise has to be made. From experience gained during about 120 h of experiments, oxygen carrier materials C2Z-1050 and ilmenite seem to have certain advantages over the other oxygen carriers and are therefore recommended for further testing.

Both oxygen carriers, ilmenite and C2Z-1050, have good lifetime expectations. C2Z-1050 stands out due to its excellent fuel conversion properties, but may agglomerate if reduced too far. Ilmenite is a material, which has been investigated at considerable lengths earlier. It is reliable, but has in the case of liquid fuel a rather low fuel conversion.

4 CONCLUSIONS

Nickel-based oxygen carriers N4MZ-1400 and M4MZ-1200 have good conversion properties. However, in the case of N4MZ-1400 complete gas conversion of the fuel is impossible due to thermodynamic restrictions. The attrition rate of both oxygen carriers was high. This might be improved through slight changes in the particle preparation method or raw materials.

Nomenclature

Latin symbols

H/C	[-]	hydrogen-to-carbon ratio
T_{boil}	[°C]	boiling temperature

Greek symbols

γ_{CO_2}	[%]	CO ₂ gas yield
μ	varies	mean value
σ	[-]	standard deviation

Acronyms

AR	air reactor
C2Z-1050	20 wt% CuO / 80 wt% ZrO ₂ calcined at 1050 °C
CLC	chemical-looping combustion
CLOU	chemical-looping combustion with oxygen uncoupling
CLR	chemical-looping reforming
EDX	energy-dispersive X-ray spectroscopy
FR	fuel reactor
GC	gas chromatograph
M4MZ-1200	40 wt% Mn ₃ O ₄ / 60 wt% MgO-ZrO ₂ calcined at 1200 °C
N4MZ-1400	40 wt% NiO / 60 wt% MgO-ZrO ₂ calcined at 1400 °C
OC	oxygen carrier
SEM	scanning electron microscopy
XRD	X-ray powder diffraction

Bibliography

- [1] P. Moldenhauer, M. Rydén, and A. Lyngfelt. Testing of minerals and industrial by-products as oxygen carriers for chemical-looping combustion in a circulating fluidized-bed 300 W laboratory reactor. accepted for publication in *Fuel*,
- [2] P. Moldenhauer, M. Rydén, T. Mattisson, and A. Lyngfelt. Chemical-looping combustion and chemical-looping reforming of kerosene in a circulating fluidized-bed 300 W laboratory reactor. submitted for publication,
- [3] P. Moldenhauer, M. Rydén, T. Mattisson, and A. Lyngfelt. Chemical-looping combustion and chemical-looping with oxygen uncoupling of kerosene with Mn- and Cu-based oxygen carriers in a circulating fluidized-bed 300 W laboratory reactor. submitted for publication,
- [4] IPCC. *Climate Change 2007 - The Physical Science Basis: Working Group I Contribution to the Fourth Assessment Report of the IPCC*. Cambridge University Press, Cambridge, UK and New York, NY, USA, 2007.
- [5] IPCC. *Climate Change 2007 - Impacts, Adaptation and Vulnerability: Working Group II contribution to the Fourth Assessment Report of the IPCC*. Cambridge University Press, Cambridge, UK and New York, NY, USA, 2007.
- [6] P. Friedlingstein, R. A. Houghton, G. Marland, J. Hackler, T. A. Boden, T. J. Conway, J. G. Canadell, M. R. Raupach, P. Ciais, and C. Le Quéré. Update on CO₂ emissions. *Nature Geoscience*, 3(12):811–812, 2010.
- [7] J. G. Olivier, G. Janssens-Maenhout, J. A. Peters, and J. Wilson. Long-Term Trend in Global CO₂ Emissions. 2011 report. Technical Report 500253004, PBL Netherlands Environmental Assessment Agency Institute for Environment and Sustainability (IES) of the European Commission’s Joint Research Centre (JRC), 2011.
- [8] UNFCCC. *Kyoto Protocol*. United Nations Framework Convention on Climate Change, 1998.
- [9] IPCC. *IPCC Special Report on Carbon Dioxide Capture and Storage*. Cambridge University Press, Cambridge, UK and New York, NY, USA, 2005.
- [10] M. Ishida and H. Jin. A new advanced power-generation system using chemical-looping combustion. *Energy*, 19(4):415–422, 1994.

- [11] A. Lyngfelt, B. Leckner, and T. Mattisson. A fluidized-bed combustion process with inherent CO₂ separation; application of chemical-looping combustion. *Chemical Engineering Science*, 56:3101–3113, 2001.
- [12] A. Lyngfelt, M. Johansson, and T. Mattisson. Chemical-Looping Combustion – Status of Development. In *9th International Conference on Circulating Fluidized Beds (CFB-9)*, Hamburg, Germany, 2008.
- [13] M. M. Hossain and H. I. de Lasa. Chemical-looping combustion (CLC) for inherent CO₂ separations—a review. *Chemical Engineering Science*, 63(18):4433–4451, 2008.
- [14] H. Fang, L. Haibin, and Z. Zengli. Advancements in Development of Chemical-Looping Combustion: A Review. *International Journal of Chemical Engineering*, 2009:16, 2009.
- [15] A. Lyngfelt. Oxygen carriers for chemical-looping combustion – 4000 h of operational experience. *Oil & Gas Science and Technology*, 66(2):161–172, 2011.
- [16] A. Lyngfelt and T. Mattisson. Chemical Looping Materials for CO₂ Separation. In D. Stolten and V. Scherer, editors, *Efficient Carbon Capture for Coal Power Plants*, chapter 17, pages 475–504. Wiley-VCH Verlag, Weinheim, first edition, 2011.
- [17] P. Pimenidou, G. Rickett, V. Dupont, and M. Twigg. Chemical looping reforming of waste cooking oil in packed bed reactor. *Bioresource Technology*, 101(16):6389–6397, 2010.
- [18] P. Pimenidou, G. Rickett, V. Dupont, and M. Twigg. High purity H₂ by sorption-enhanced chemical looping reforming of waste cooking oil in a packed bed reactor. *Bioresource Technology*, 101(23):9279–9286, 2010.
- [19] Y. Cao, B. Lia, H.-Y. Zhao, C.-W. Lin, S. P. Sit, and W.-P. Pan. Investigation of Asphalt (Bitumen)-fuelled Chemical Looping Combustion using Durable Copper-based Oxygen Carrier. *Energy Procedia*, 4:457–464, 2011.
- [20] A. Forret, A. Hoteit, and T. Gauthier. Chemical Looping Combustion Process applied to liquid fuels. In *British – French Flame Days*, pages 37–37, Lille, France, 2009.
- [21] A. Hoteit, A. Forret, W. Pelletant, J. Roesler, and T. Gauthier. Chemical Looping Combustion with Different Types of Liquid Fuels. *Oil & Gas Science and Technology – Reb IFP Energies nouvelles*, 66(2):193–199, 2011.
- [22] T. Mendiara, J. M. Johansen, R. Utrilla, P. Geraldo, A. D. Jensen, and P. Glarborg. Evaluation of different oxygen carriers for biomass tar reforming (I): Carbon deposition in experiments with toluene. *Fuel*, 90(3):1049–1060, 2011.
- [23] F. García-Labiano, L. F. de Diego, P. Gayán, J. Adánez, A. Abad, and C. Dueso. Effect of Fuel Gas Composition in Chemical-Looping Combustion with Ni-Based Oxygen Carriers. 1. Fate of Sulfur. *Industrial & Engineering Chemistry Research*, 48(5):2499–2508, 2009.
- [24] T. Mattisson, M. Johansson, and A. Lyngfelt. The use of NiO as an oxygen carrier in chemical-looping combustion. *Fuel*, 85(5-6):736–747, 2006.

-
- [25] N. Berguerand and A. Lyngfelt. Design and operation of a 10 kW_{th} chemical-looping combustor for solid fuels – Testing with South African coal. *Fuel*, 87:2713–2726, 2008.
- [26] N. Berguerand and A. Lyngfelt. Operation in a 10 kW_{th} chemical-looping combustor for solid fuel — Testing with a Mexican petroleum coke. *Energy Procedia*, 1(1):407–414, 2009.
- [27] T. Pröll, K. Mayer, J. Bolhàr-Nordenkamp, P. Kolbitsch, T. Mattisson, A. Lyngfelt, and H. Hofbauer. Natural minerals as oxygen carriers for chemical looping combustion in a dual circulating fluidized bed system. *Energy Procedia*, 1:27–34, 2009.
- [28] M. Rydén, M. Johansson, E. Cleverstam, A. Lyngfelt, and T. Mattisson. Ilmenite with addition of NiO as oxygen carrier for chemical-looping combustion. *Fuel*, 89(11):3523–3533, 2010.
- [29] J. Adánez, A. Cuadrat, A. Abad, P. Gayán, L. de Diego, and F. García-Labiano. Ilmenite activation during consecutive redox cycles in chemical-looping combustion. *Energy & Fuels*, 24(2):1402–1413, 2010.
- [30] H. Leion, T. Mattisson, and A. Lyngfelt. Use of Ores and Industrial Products As Oxygen Carriers in Chemical-Looping Combustion. *Energy & Fuels*, 23:2307–2315, 2009.
- [31] E. Jerndal, T. Mattisson, and A. Lyngfelt. Thermal analysis of chemical-looping combustion. *Chemical Engineering Research and Design*, 84(9):795–806, 2006.
- [32] M. Rydén, M. Johansson, A. Lyngfelt, and T. Mattisson. NiO supported on Mg-ZrO₂ as oxygen carrier for chemical-looping combustion and chemical-looping reforming. *Energy and Environmental Science*, 2 (9):970–981, 2009.
- [33] M. Johansson, T. Mattisson, and A. Lyngfelt. Investigation of Mn₃O₄ with stabilized ZrO₂ for chemical-looping combustion. *Chemical Engineering Research and Design*, 84(9 A):807–818, 2006.
- [34] A. Abad, T. Mattisson, A. Lyngfelt, and M. Rydén. Chemical-looping combustion in a 300 W continuously operating reactor system using a manganese-based oxygen carrier. *Fuel*, 85(9):1174–1185, 2006.
- [35] L. F. de Diego, F. García-Labiano, P. Gayán, J. Celaya, J. M. Palacios, and J. Adánez. Operation of a 10 kW_{th} chemical-looping combustor during 200 h with a CuO–Al₂O₃ oxygen carrier. *Fuel*, 86(7-8):1036–1045, 2007.
- [36] C. Saha and S. Bhattacharya. Comparison of CuO and NiO as oxygen carrier in chemical looping combustion of a Victorian brown coal. *International Journal of Hydrogen Energy*, 36(18):12048–12057, 2011.
- [37] C. Forero, P. Gayán, F. García-Labiano, L. de Diego, A. Abad, and J. Adánez. High temperature behaviour of a CuO/γAl₂O₃ oxygen carrier for chemical-looping combustion. *International Journal of Greenhouse Gas Control*, 5(4):659–667, 2011.

- [38] I. Adánez-Rubio, P. Gayán, F. García-Labiano, L. F. de Diego, J. Adánez, and A. Abad. Development of CuO-based oxygen-carrier materials suitable for Chemical-Looping with Oxygen Uncoupling (CLOU) process. *Energy Procedia*, 4:417–424, 2011.
- [39] T. Mattisson, H. Leion, and A. Lyngfelt. Chemical-looping with oxygen uncoupling using CuO/ZrO₂ with petroleum coke. *Fuel*, 88(4):683–690, 2009.
- [40] H. Leion, T. Mattisson, and A. Lyngfelt. Combustion of a German lignite using chemical-looping with oxygen uncoupling (CLOU). In *The Proceedings of 33rd International Technical Conference on Coal Utilization & Fuel Systems*, 2008.
- [41] T. Mattisson, A. Lyngfelt, and H. Leion. Chemical-looping with oxygen uncoupling for combustion of solid fuels. *International Journal of Greenhouse Gas Control*, 3(1): 11–19, 2009.