THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Manganese Materials in Solid Fuel Chemical Looping Combustion

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Gothenburg, Sweden 2016

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Reproservice
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Abstract

Against the background of rising anthropogenic greenhouse gas emissions, carbon capture and storage (CCS) has been proposed as a means of mitigating climate change by storing CO_2 captured from large point sources in underground geological formations such as aquifers or depleted oil- and gas fields. While first generation CCS technologies rely on active gas separation with an associated energy penalty, chemical looping combustion (CLC) can avoid that step by utilizing solid metal oxide particles to transfer oxygen from combustion air to fuel, making CO_2 capture inherent to the process. The concept can be realized using two interconnected fluidized bed reactors, the air and the fuel reactor, to ensure that the two reactions incorporating the oxygen carrier, i.e. oxidation with combustion air and reduction with fuel, are unmixed.

A key research issue is to find oxygen carriers which perform satisfactorily with respect to fuel conversion and lifetime. Manganese materials are promising candidates from a thermodynamic point of view, potentially cheap and environmentally benign.

In this study, the performance of four different oxygen carrier materials was investigated in a 10 kW pilot using both biochar and petroleum coke as fuel. Performance - with respect to fuel conversion - of all oxygen carriers was higher than that of the state-of-the-art material, i.e. ilmenite. $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$, a manufactured perovskite material, showed the best results of all materials but was susceptible to sulphur poisoning, which was proven to be at least in parts reversible. The three other materials, all of them natural manganese ores, showed high gas conversion as well and offer the advantage of low oxygen carrier cost. The lifetime of the most durable manganese ore reached 284 hours, which is deemed sufficient in the context.

The results suggest that manganese materials, both manufactured and of natural origin, can be a feasible, efficient and cost-effective alternative as oxygen carrier in chemical looping combustion.

Keywords: carbon capture, chemical-looping, CLOU, manganese ores

List of Publications

This thesis is based on the following publications:

Paper I	Schmitz M, Linderholm C, “Performance of Calcium Manganate as Oxygen Carrier in Chemical Looping Combustion of Biochar in a 10 kW pilot”, *Applied Energy* **169**, 2016, 729–737
Paper II	Schmitz M, Linderholm C, Lyngfelt A, “Chemical Looping Combustion of Sulphurous Solid Fuels Using Spray-dried Calcium Manganate Particles as Oxygen Carrier”, *Energy Procedia* **63**, 2014, 140–152
Paper III	Schmitz M, Linderholm C, Hallberg P, Sundqvist S, Lyngfelt A, “Chemical-looping combustion of solid fuels using manganese ores as oxygen carriers”, *Energy and Fuels* **30**, 2016, 1204–1216

Contribution report:

Paper I and II:	principal author, responsible for the experimental work and data evaluation.
Paper III:	principal author, responsible for parts of the experimental work and data evaluation.

Related publications not included in this thesis:

- Linderholm C, Schmitz M, Knutsson P, Källén M, Lyngfelt A, "Use of low-volatile solid fuels in a 100 kW chemical-looping combustor", *Energy and Fuels* **28**, 2014, 5942–52.

- Linderholm C, Schmitz M, "Chemical-looping combustion of solid fuels in a 100kW dual circulating fluidized bed system using iron ore as oxygen carrier", *Journal of Environmental Chemical Engineering*, **4**, 2016, 1029–1039

- Linderholm C, Schmitz M, Knutsson P, Lyngfelt A, "Chemical-looping combustion in a 100-kW unit using a mixture of ilmenite and manganese ore as oxygen carrier", *Fuel* **166**, 2016, 533–542

- Linderholm C, Knutsson P, Schmitz M, Markström P, Lyngfelt A, "Material balances of carbon, sulfur, nitrogen and ilmenite in a 100 kW CLC reactor", *International Journal of Greenhouse Gas Control* **27**, 2014, 188–202

Acknowledgement

My sincere thanks go to my supervisors Anders Lyngfelt and Calle Linderholm. Anders, thank you for introducing me into an exciting field. How you always find the time to share your knowledge while being in charge of all that administration amazes me every day. Calle, I am truly grateful for all your support and motivation during the last years, especially when the going got tough. I owe you big time.

The European Research Council and the European Union's Research Fund for Coal and Steel are acknowledged for funding this work.

Big thanks also to the chemical looping group, both past and present, for being such nice and helpful colleagues: Malin, Jesper, Peter, Patrick, Viktor, Max, Tobias, Magnus and Pontus at Energy Technology and Henrik, Dazheng, Sebastian, Martin, Pavleta, Volkmar, Dongmei, Nasim, Georg and Golnar at Inorganic Chemistry. Ulf, our lab wizard, thank you for saving our experiments on countless occasions. My great office mate Dima has earned extra thanks for enduring the particle-container-and-research-paper chaos I constantly produce in our room.

I also would like to thank the rest of the Energy Technology Division for creating a pleasant working atmosphere. Special thanks to the football gang! Katarina and Marie, our administrators: without you, we all would be about as helpless as two-year olds.

Speaking of which: I want to thank my son Johannes for putting a smile on my face every day. My family and friends, thank you for everything.

And finally, Linnea, my fantastic wife. I don't even know where to start. Du är bäst. Ich liebe dich.

Table of Contents

1. Introduction

Since the 1950s, the earth's climate has been subject to changes which are unprecedented over time scales ranging from decades to millennia [1]. While the atmosphere and the oceans have grown ever warmer, the anthropogenic emission of greenhouse gases has reached new heights every year, with CO_2 responsible for the bulk of the greenhouse effect, s. Fig. 1.

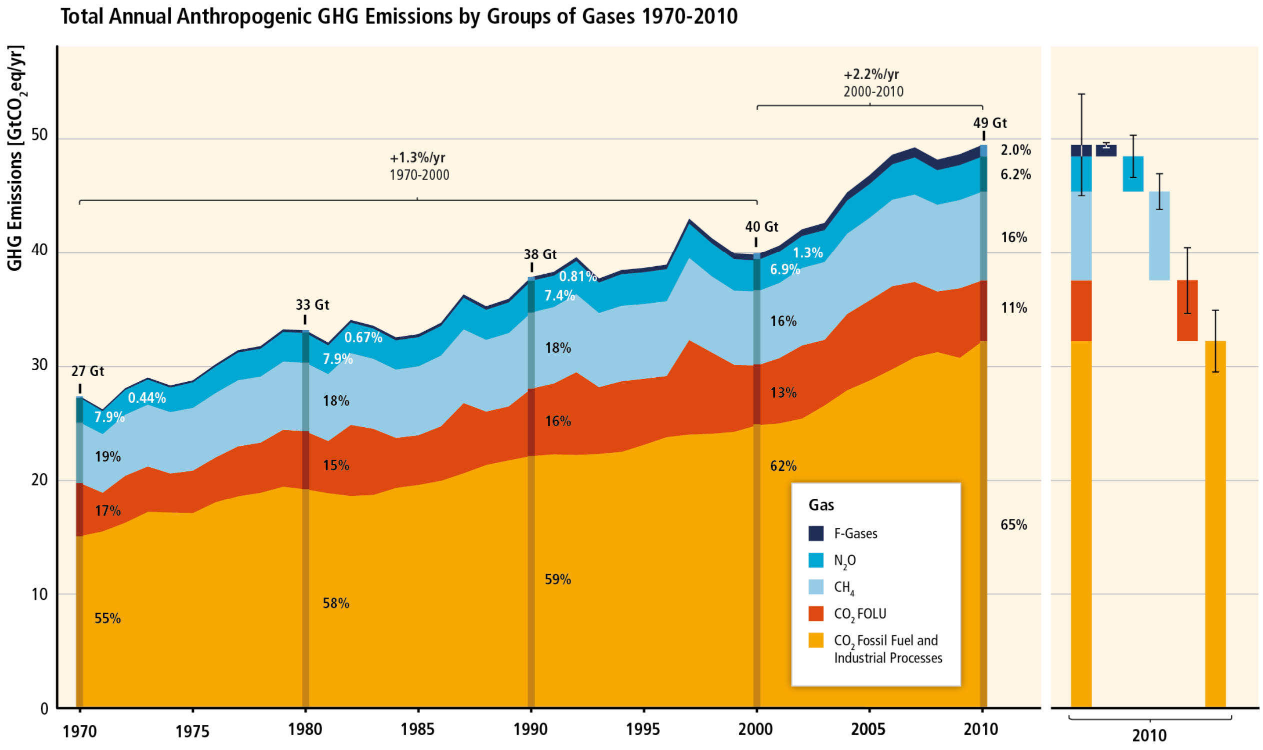

Fig. 1. Total annual greenhouse gas emissions 1970-2010 [2]

The concentration of CO_2 in the atmosphere is to date above 400 ppm, the highest value for at least 800 000 years. Data retrieved from ice core drillings in Antarctica suggest that the CO_2 concentration in the atmosphere correlates well with global temperature fluctuations [3].

Anthropogenic emissions of CO_2 and other greenhouse gases are thus widely considered to be the major cause of global warming, with 97% of climate scientists agreeing on that paradigm [4]. The basic physical connection between CO_2 concentration in the atmosphere and temperature on the ground has been known for 120 years [5].

Globally, 2015 was the warmest year ever recorded with a surface temperature of 0.90°C above the 20th century average, s. Fig. 2. On a larger time scale, the 16 warmest years since temperature recordings started in 1880 have occurred since 1998 [6].

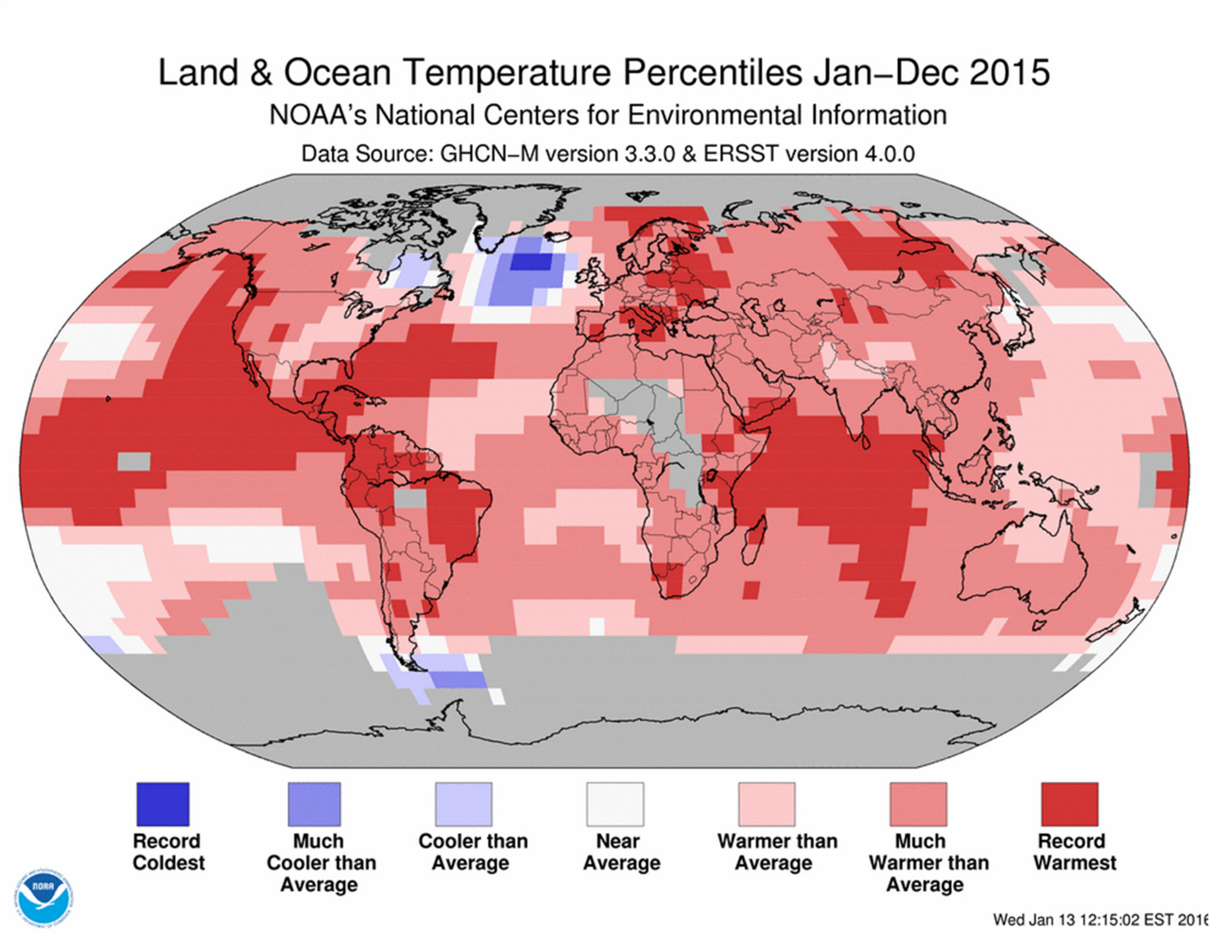

Fig. 2. Global temperature deviations for 2015 [6]

If no measures for a reduction of greenhouse gas emissions are taken, the consequences for all humankind may be catastrophic. In December 2015, the United Nations Climate Change Conference (COP 21) in Paris thus resulted in 195 countries agreeing to limit the increase in the global average temperature "to well below 2°C above pre-industrial levels and to pursue efforts to limit the temperature increase to 1.5°C above pre-industrial levels" [7].

1.1 Climate Mitigation Strategies

Possible ways of decreasing CO_2 emissions are to reduce overall energy consumption or to replace fossil fuels with renewable energy sources. However, instead of decreasing, both primary energy use and the use of fossil fuels are expected to go on growing until 2040 according to the International Energy Agency's World Energy Outlook 2015 [8], with only 18% of the worldwide primary energy demand in that year being covered by renewables. However, to meet the climate goals recently decided in Paris, it is necessary to reduce the emissions significantly.

A solution which has been proposed to deal with the expected increase of CO_2 emissions is Carbon Capture and Storage (CCS), in which CO_2 is captured from combustion- or industrial processes and permanently stored in deep geological formations. If a biomass fuel is used (BECCS, Bioenergy Carbon Capture and Storage), the net CO_2 balance of the process is negative. The Intergovernmental Panel on Climate Change (IPCC) anticipates that the aim of limiting global warming to an average of 2°C, which corresponds to a CO_2 concentration of less than 450 ppm, can only be reached by wide-spread deployment of carbon capture and storage (CCS) [9]. In addition, most scenarios simulated by the IPCC assume negative emission technologies such as BECCS to be deployed in the second half of the century. The climate mitigation cost in scenarios prohibiting the use of CCS is 138% higher than in the base case [2].

As the CO_2 stream to be stored in CCS has to be rather pure, the technologies used for CO_2 capture typically use a gas separation step: in oxyfuel processes, O_2 is extracted from air. In a subsequent step, the fuel is burnt with a mixture of O_2 and recirculated CO_2 to form exhaust gas ideally consisting of mainly CO_2 and water. In post- and pre-combustion processes, CO_2 is separated from the exhaust gas or the product gas of a preceding gasification process, respectively. As gas separation is inevitably associated with an energy penalty, all three technologies suffer from considerable losses in overall process efficiency.

1.2 Chemical Looping Combustion

Within CCS, chemical looping combustion (CLC) represents a capture technology aimed at avoiding the above-mentioned energy penalty in the combustion of gaseous, liquid or solid fuels. In chemical looping, fuel and air are never mixed. Instead, oxygen is transferred to the fuel by a solid oxygen carrier, typically a metal oxide. The concept can be realized using two interconnected fluidized bed reactors to ensure good heat and mass transfer. In the air reactor, the oxygen carrier particles are oxidized, after which they are transported to the fuel reactor, reduced by the fuel and transported back to the air reactor. Figure 3 shows a schematic drawing of the process.

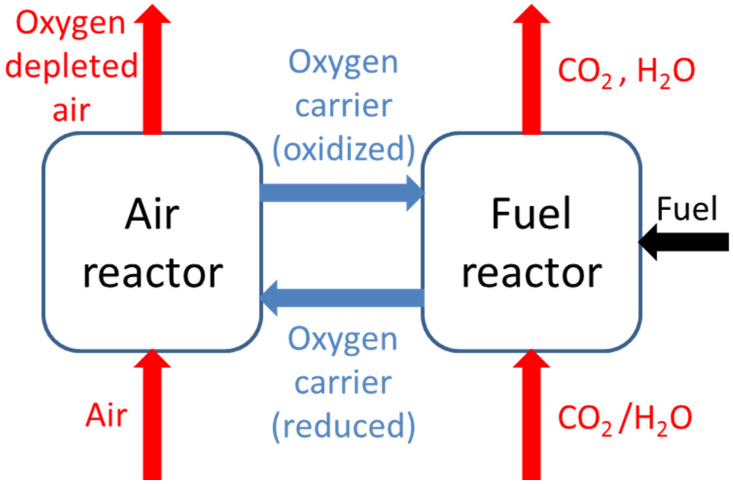

Figure 3. Schematic of the CLC process for solid fuels

The first prototype reactors built were operated with gaseous fuels. However, focus has shifted towards solid fuels in the recent years.

Solid-fuel CLC was first studied by Lewis et al. [10]. Fifty years later, new studies emerged [11-13]. Leion et al. investigated the process in a bench-scale reactor, e.g. [14-16]. Lyngfelt recently presented a review on chemical-looping combustion with solid fuels [17].

While gaseous fuels can be used in the CLC process right away, solid fuels have to be gasified by steam or CO_2 first. Fuel devolatilization and gasification are carried out in the same reactor as the reaction of these gases with the oxygen carrier. The gaseous volatiles and gasification products react with the oxygen carrier to form CO_2, H_2O and, if a sulphurous fuel is burnt, SO_2. It has been shown that the presence of an oxygen carrier can increase the velocity of gasification [16]. Equations (1) - (6) describe the principle of solid fuel gasification and subsequent chemical looping combustion:

$$\text{Solid fuel} \rightarrow \text{char (C)} + \text{tar} + \text{gas } (H_2, CO, CO_2, CH_4, C_xH_y) \qquad \textbf{(1)}$$

$$C + H_2O \rightarrow CO + H_2 \qquad \textbf{(2)}$$

$$C + CO_2 \rightarrow 2\,CO \qquad \textbf{(3)}$$

Reaction of volatiles and gasification products with oxygen carrier particles:

$$Me_xO_y + H_2 \rightarrow Me_xO_{y-1} + H_2O, \qquad \textbf{(4)}$$

$$Me_xO_y + CO \rightarrow Me_xO_{y-1} + CO_2, \qquad \textbf{(5)}$$

$$4\,Me_xO_y + CH_4 \rightarrow 4\,Me_xO_{y-1} + CO_2 + 2\,H_2O, \qquad \textbf{(6)}$$

where methane represents all hydrocarbons released during devolatilization.

Gasification is a comparably slow reaction, which can lead to losses of unconverted char to the air reactor or fuel reactor exhaust. A possible solution for that problem is chemical looping with oxygen uncoupling (CLOU). In that concept, the oxygen carrier releases gaseous oxygen in the fuel reactor rather than merely transporting it in a chemically bound form [18]. In this case, a part of the solid fuel can react with gaseous oxygen without the need of gasification, which might facilitate the conversion of solid fuel especially in conditions with poor gas-solids mixing.

1.3 The Role of Oxygen Carriers

The choice of the oxygen carrier material is crucial to the process performance. Potential materials have to meet a series of requirements:

- Sufficient oxidation and reduction rates, which are decisive for the needed amount of oxygen material and reactor size
- Environmental benignity and non-toxicity
- Mechanical and chemical durability to minimize the need for material make-up
- Inert behaviour towards possible fuel impurities
- Good fluidizability
- Low cost

The last point is especially important in chemical looping combustion of solid fuels, in which oxygen carrier material will be continuously lost in ash separation.

In general, two major pathways can be followed in the choice of oxygen carrier materials:

1) Use of manufactured particles
2) Use of natural materials, e.g. ores or waste materials

While manufactured particles offer the possibility to be tailored to the specific use intended, which can result in better process performance, natural materials are cheaper. The gain in performance would thus have to be weighed against extra oxygen carrier cost in utility-size chemical looping units.

Besides the choice between natural or manufactured materials, the chemical composition of the oxygen carrier is also important. According to thermodynamic analyses [19], oxides of nickel, iron, copper and manganese are feasible base materials for oxygen carriers. Most solid fuel chemical looping operation has been carried out with ilmenite, a naturally occurring iron-titanium material, as oxygen carrier. Ilmenite was chosen due to its comparably low cost, mechanical durability and non-toxicity [20-25] and has become the state-of-the-art oxygen carrier material [26]. When used with solid fuels, full gas conversion could not be reached with ilmenite, however. The material does not have considerable CLOU properties, either, which makes a slow gasification step necessary. Other iron oxides have been tested as well with varying results [27-29].

The limitations of known oxygen carriers have spurred the search for alternatives. Copper oxides possess CLOU properties and show good reactivity [30]. Experiments with solid biomass fuels and an oxygen carrier based on copper have been conducted by Adánez-Rubio et.al. [31]. However, copper is an expensive raw material and the mechanical stability of copper-based oxygen carriers is uncertain [32]. Manganese oxide can release gaseous oxygen as well, but the use of pure manganese oxide is limited by slow re-oxidation and a low equilibrium temperature [18]. On the other hand, the combination of manganese with other metals can change those properties [33]. Combined oxides of manganese with iron, nickel, calcium, silicon, copper and magnesium have been tested previously, e.g. [34-37]. In combination with calcium, manganese can form a perovskite structure with the unit cell formula $ABO_{3-\delta}$, in which A is a larger and B a smaller cation.

δ describes the degree of oxygen deficiency, which is zero for a perfect perovskite and depends on temperature, pressure and oxygen concentration in the surroundings. The possibility to change the oxygen content in the material by changing these parameters provides oxygen release properties and makes perovskites well suited as oxygen carriers.

Manufactured calcium manganate perovskites have proven to be resistant to mechanical wear in jet-cup attrition tests [38]. Taking up the promising work which has been done with these oxygen carriers in combination with gaseous fuels previously [39, 40], papers I and II investigate their performance when used with solid fuels. In addition, paper II analyses the sulphur tolerance of the oxygen carrier.

As mentioned above, ores can be used as a potentially cost-effective alternative to manufactured particles. Manganese ores typically have a high manganese content and are both cheap and abundant. The possibility of using manganese ores as oxygen carriers has been documented before: Sundqvist et al. [41] found that the rate of gas conversion could be increased by a factor 2.7 to 6 compared to ilmenite. Linderholm et al. [42] essentially halved the amount of unconverted gases leaving the fuel reactor by using a mixture of ilmenite and manganese ore in a 100 kW chemical looping combustor. On the other hand, some manganese materials have proven to be more prone to attrition than ilmenite [43]. In paper III, three manganese materials are investigated with respect to their performance and durability, especially in comparison with ilmenite.

1.4 Aim of Study

The objective of this work is to investigate the feasibility of using manganese-based oxygen carriers in continuous solid-fuel chemical looping combustion, both by testing new materials and materials that have shown promising results in bench-scale reactors or with gaseous fuels previously. The experiments are carried out in a 10 kW chemical looping reactor as described in section 2, with a focus on process performance and particle integrity. Both manufactured (papers I and II) and natural materials (paper III) are investigated and a comparison as to the cost and benefits of either material category is conducted. Establishing several working alternatives for oxygen carrier materials could greatly improve the robustness of the technology with respect to material price changes and availability issues, the long-term objective is to find a range of different materials which can be used in utility-scale operation.

2. Experimental Setup

All experiments in papers I-III were conducted in a 10 kW dual fluidized bed unit, which will be described in the following section. The description is largely adopted from paper III.

2.1 10 kW unit

The reactor is based on interconnected fluidized-bed technology. In the riser, which constitutes the upper part of the air reactor, high gas flows in combination with a small cross-section area ensure high gas velocities which provide the driving force for the circulation. The entrained oxygen carrier particles enter a cyclone, where they are separated from the air flow and fall into the fuel reactor via a loop seal to avoid gas mixing. The fuel reactor is designed as a bubbling bed and consists of several parts: in the main section, fuel is oxidized to CO_2 and H_2O. The char remaining after devolatilization is gasified followed by oxidation of the gasification products by the oxygen carrier. The main section is usually fluidized with steam. The particles are forced to pass under a vertical wall, see Figure 4. The left section of the fuel reactor is fluidized by nitrogen. By increasing the fluidization velocity, char and oxygen carrier particles are separated due to their different densities. The lighter char particles are entrained and returned to the fuel reactor via a small loop seal, whereas the heavier reduced oxygen carrier particles continue to the air reactor.

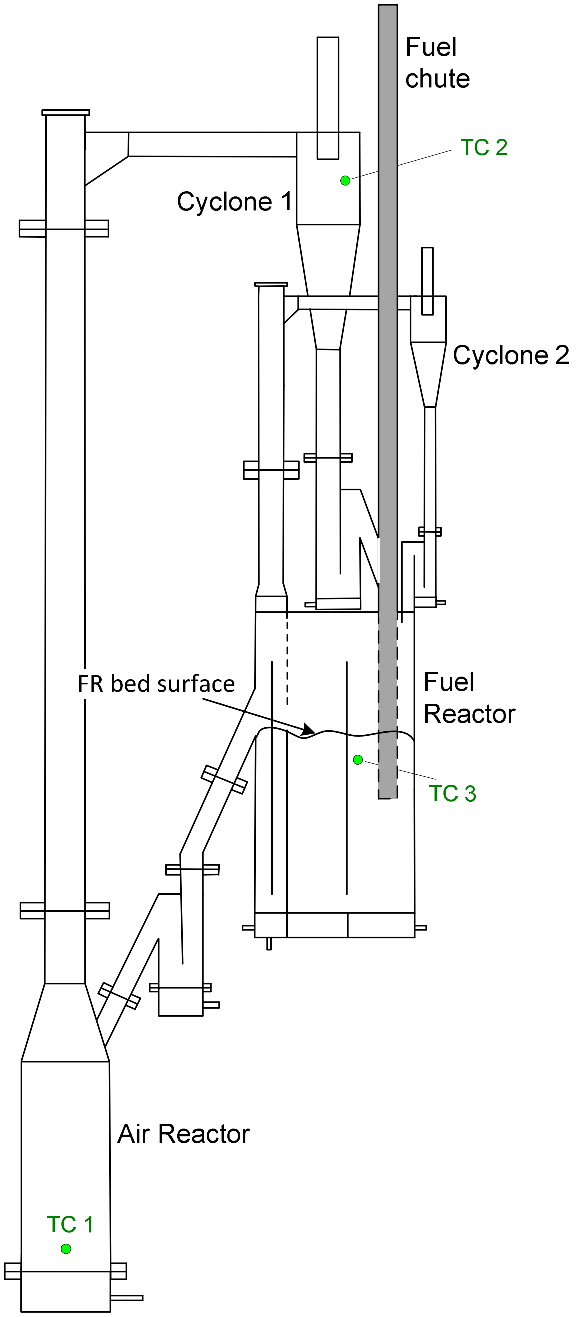

Figure 4. 10 kW solid fuel chemical looping combustor. TC 1-3 mark thermocouple positions

Fuel is introduced into the fuel-reactor bed via a coal screw and a fuel chute. The operating temperature is measured via three thermocouples located in the air reactor, fuel reactor and air reactor cyclone. Fluidization behaviour, solids circulation and inventory can be estimated from numerous pressure measurements. The exhaust gas streams from both air and fuel reactor are passively cooled before entering filter bags (air reactor exhaust) or a water seal (fuel reactor exhaust). The water seal is used both to collect condensate from fuel conversion and steam fluidization and to impose a hydrostatic pressure on the fuel reactor exhaust, thus creating a pressure difference between the outlets of the fuel reactor and air reactor. This is necessary to avoid inadequate pressure differences over the loop seals connecting the reactors.

A part of the exhaust gas streams is cooled, filtered for removal of fines, led through gas conditioning systems to condense remaining steam and then analysed by infrared- (CO, CO_2 and CH_4), thermal conductivity- (H_2) or paramagnetic analysers (O_2). Apart from that, gas samples can be withdrawn and analysed in detector tubes.

Before heat-up and operation with fuel, the 10 kW unit is filled with 15-20 kg of oxygen carrier particles. To maintain operating temperature, the unit is enclosed in an electrically heated furnace, which also is used to heat up the unit initially. During heat-up, all parts of the unit are fluidized by air before switching to steam-/nitrogen fluidization of the fuel reactor, the loop seals and the carbon stripper.

Previous operational experience in this unit has been achieved using ilmenite and manganese ore [20, 22, 43-47].

2.2 Oxygen Carriers

Four different oxygen carriers were investigated in the experiments, one manufactured material and three ores, one of which consisted of sintered ore fines. The mean particle size was in the range of 150-200 µm.

The manufactured material used in papers I and II ($CaMn_{0.9}Mg_{0.1}O_{3-\delta}$) has CLOU properties and was produced by spray-drying a mixture of 46.8% Mn_3O_4, 50.5% $Ca(OH)_2$ and 2.7% MgO followed by a four-hour calcination period at 1300°C. The natural materials (“Mangagran”, “Mesa” and “Sinfin”) used in paper III were chosen with respect to chemical composition and mechanical properties such as crushing strength to cover a wide range of potential oxygen carrier materials. The manganese content was between 40 and 66%. All three materials were crushed and calcined at 950˚C for 24 hours.

2.3 Fuels

Wood char, petcoke and a mixture of both were used as fuels. The mixture was meant to simulate a sulphur content typically found in hard coal. The wood char is produced by subjecting wood chips of both hard- and softwood to 450°C for 8 h in the absence of oxygen. The as-received wood char has a size of approximately 5 mm, which is reduced to 200-1000 µm when the fuel is passed through the feeding screw. The petcoke has a mass-weighted mean diameter of 79 µm.

Table 1 shows composition and heating value of the fuels.

Table 1. Composition of the fuel: proximate and ultimate analyses.

Component	Wood char (%)	Petcoke (%)	Comment
Fixed carbon	73.9	81.5	as received
Volatiles	16.7	10.0	as received
Moisture	3.9	8.0	as received
Ash	5.5	0.5	as received
C	86.9	88.8	maf
H	3.2	3.1	maf
O	9.5	0.5	maf
N	0.4	1.0	maf
S	0.03	6.6	maf
LHV (MJ/kg)	29.8	31.8	as received

maf: moisture and ash free

2.4 Data Evaluation

The performance of the materials is judged based upon two main characteristics: chemical and mechanical performance. While the chemical performance is measured by the conversion of fuel to combustible gases and finally to fully oxidized combustion products, the mechanical properties determine the average time an oxygen carrier particle can be used in the system without breaking down.

Oftentimes, the choice of oxygen carrier material is a trade-off between mechanical and chemical properties; materials offering high mechanical strength can be less reactive, e.g. due to lower internal particle surface, and vice versa. For manufactured materials, the properties can be fine-tuned by the adaption of sintering temperature and duration.

2.4.1 Conversion performance

Unconverted fuel species can escape the fuel reactor in three different ways: as unconverted gas, as char particles to the air reactor or as elutriated char.

The unconverted gas species in the fuel reactor exhaust are made up of both volatile fuel compounds and gasification products. The *oxygen demand,*

$$\Omega_{OD} = \frac{0.5x_{CO,FR} + 2x_{CH_4,FR} + 0.5x_{H_2,FR}}{\Phi_0\left(x_{CO_2,FR} + x_{CO,FR} + x_{CH_4,FR}\right)} \qquad \textbf{(7)}$$

describes the fraction of oxygen which after conversion in the fuel reactor is lacking to achieve full conversion and would have to be added in an oxygen polishing step. In this definition, Φ_0 is the molar ratio of oxygen needed to oxidize the fuel to moles of carbon contained in the fuel [20].

Both oxygen carrier and unconverted fuel particles move in a continuous flow from the fuel reactor to the air reactor. Some char particles will therefore escape the fuel reactor before they can be fully gasified. These particles will eventually be oxidized by air in the air reactor and thus evade the carbon capture process. The *oxide oxygen efficiency* is the ratio of oxygen used for reoxidation of the oxygen carrier to the total oxygen consumption in the air reactor:

$$\eta_{OO} = \frac{0.21 - x_{O_2,AR} - x_{CO_2,AR}}{0.21 - x_{O_2,AR} - 0.21x_{CO_2,AR}} \qquad \textbf{(8)}$$

A precise calculation of that performance indicator is possible because it only depends on gas concentrations. Because the oxygen not used for oxidizing the oxygen carrier is used for oxidizing the char, η_{OO} provides a good estimation of the carbon capture efficiency. This is further explained in [23]. Therefore, η_{OO} will be referred to as *carbon capture efficiency* in the following.

A certain portion of the fuel will be lost as char particles elutriated to the fuel reactor chimney. This loss of unconverted fuel can be described by the *solid fuel conversion,* defined as the sum of all carbon in the form of gaseous compounds leaving the fuel and air reactor divided by the total carbon added with the fuel.

$$\eta_{SF} = \frac{F_{C,FR}+F_{C,AR}}{F_{C,FUEL}} \qquad \textbf{(9)}$$

$F_{c,FR}$ and $F_{c,AR}$ denote the molar flows of carbon from the fuel reactor and air reactor, and $F_{c,FR}$ the flow of carbon to the reactor system with the added fuel. The 10 kW reactor is mainly designed to evaluate gas conversion and carbon capture efficiency. The cyclone efficiency is poor and the low fuel reactor height in the 10 kW unit results in considerably shorter residence times for fuel (char) particles entrained from the bed than in industrial size units. Findings on solid fuel conversion were therefore not considered in the performance evaluation of oxygen carriers in this reactor, but experiments in a 100 kW solid fuel unit have shown carbon elutriation rates of up to 35% with ilmenite as oxygen carrier [48]. For industrial size units, Lyngfelt and Leckner [49] assume the char conversion to be 97% in the fuel reactor of a 1000 MW unit, with the remainder reacting in the post-oxidation chamber.

2.4.2 Lifetime of the oxygen carrier

During operation, some of the oxygen carrier particles break into smaller pieces. Repeated oxidation and reduction processes with the associated phase changes in combination with high-velocity collisions with the bottom plate and cyclone walls demand a high attrition resistance of the oxygen carrier particles. In paper III, all particles elutriated from the air reactor and caught in the downstream filters were wet-sieved and dried in an oven. Particles smaller than 45 µm are called *fines.* These were not returned into the reactor system. The mass of elutriated particles was determined before and after the sieving and drying process with the balance being the production of fines, Δm_{fines} during a certain period of time, Δt. Based on that, the production of fines L_f can be calculated to

$$L_f = \frac{\Delta m_{fines}}{\Delta t} \cdot \frac{1}{m_I} \qquad \textbf{(10)}$$

with m_I being the total solids inventory. The corresponding oxygen carrier lifetime can be expressed as:

$$t_{life} = \frac{1}{L_f} \qquad \textbf{(11)}$$

It should be noted that the oxygen carrier in solid fuel chemical looping combustion is also exposed to ash fouling which may cause loss in reactivity and ultimately particle deactivation. The rate of ash fouling is not known, but should depend on the fuel used. It cannot be ruled out that fouling leading to significant loss of reactivity occurs well before $1/L_f$ is reached, in which case the lifetime of the carrier is governed not by the attrition rate but by the rate of fouling.

3. Results and Discussion

The most important results from papers I-III with a focus on conversion performance and particle lifetime will be presented in this chapter.

3.1 Experiments with calcium manganate and biofuel (paper I)

$CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ was operated for 37 hours with a fuel power of 3.5-7.5 kW_{th}, yielding a solids inventory of 0.77 to 1.66 t/MW_{th}. The standard fuel reactor operating temperature was set to about 970°C, with low temperature tests being performed as parameter studies. Stable operation throughout a long period of time was reached in most cases.

Fig. 5 shows a compilation of the average values of Ω_{OD} and η_{OO} for all tests done at T_{FR}≈970°C.

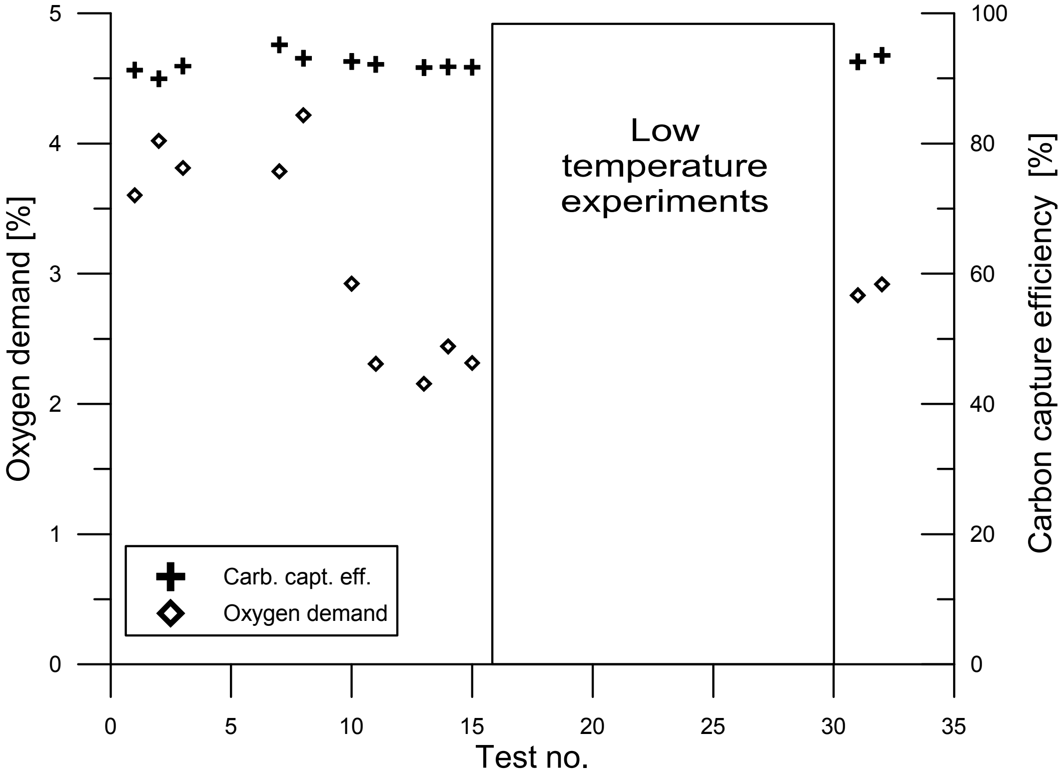

Fig. 5. Average values for Ω_{OD} and η_{OO} for all experiments done at T_{FR}≈970°C

An oxygen demand between 2.1 and 4.3% was reached while the carbon capture efficiency was in the range of 90-95.2%. Ilmenite has not been tested with the same fuel in the same unit. However, Linderholm et al. [50] used the same fuel and ilmenite as an oxygen carrier in a 100 kW chemical looping combustor, which gave an oxygen demand of 4.7-10% and a carbon capture efficiency of 93-97%. The same authors also found that the performance of the 100 kW unit is generally superior to that of the 10 kW unit. Combined, these findings indicate that $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ offers conversion performance superior to that of ilmenite.

In theory, the oxygen carrier should release more oxygen at higher temperatures [51], resulting in higher conversion. Fig. 6 shows the system performance as a function of temperature.

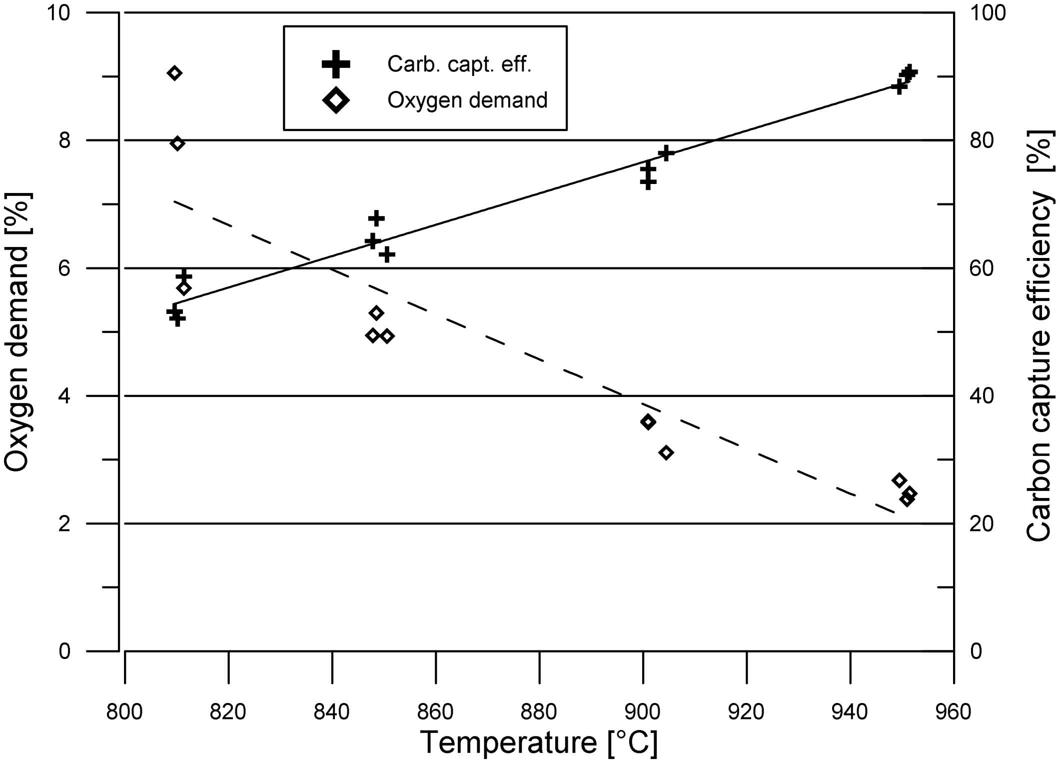

Fig. 6. Average values for Ω_{OD} and η_{OO} at low temperatures (T<970°C)

Different fuel feeding rates were examined as well and shown to have a considerable effect only at low temperatures. Overall, higher fuel reactor temperatures proved to be beneficial for process performance, both with regard to oxygen demand and carbon capture efficiency.

The air reactor gas flow is one of the main drivers for solids circulation in the system as stated in [44]. Fig. 7 shows the results of an experiment in which the air reactor flow was varied to determine the influence of solids circulation on the system performance. The fuel reactor temperature ranged from 917 to 928°C.

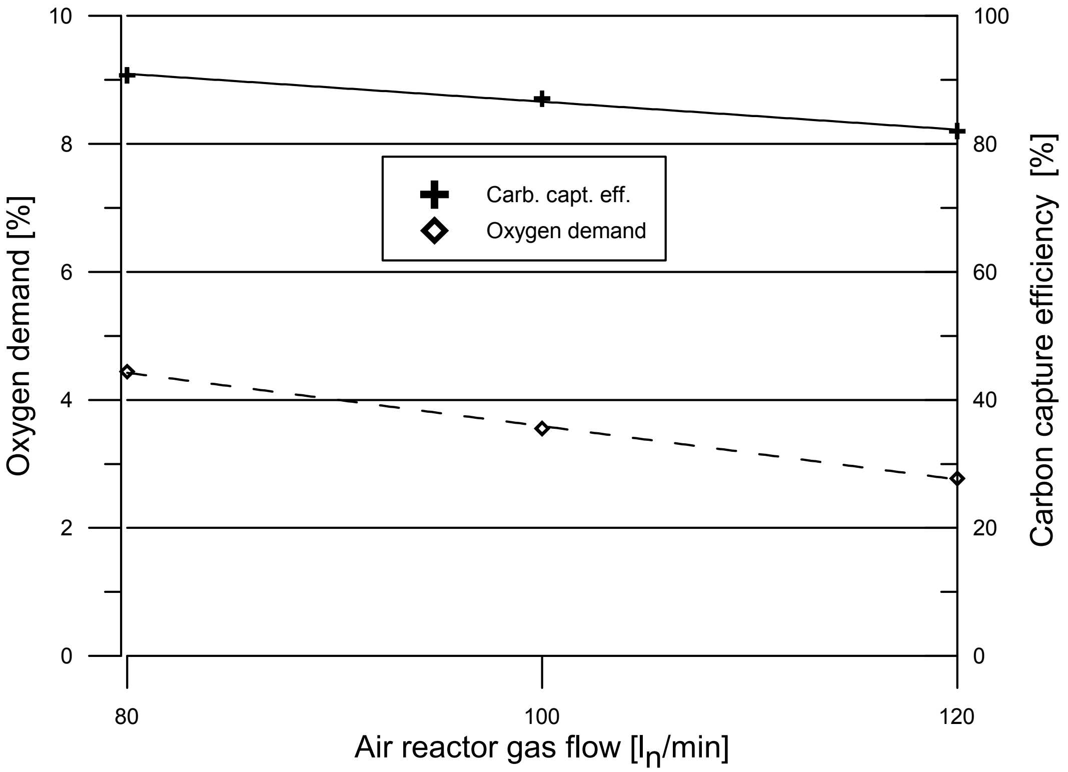

Fig. 7. Average values for Ω_{OD} *and* η_{OO} *while varying the air reactor gas flow*

Both oxygen demand and carbon capture efficiency decreased, an outcome which was expected: while a higher solids circulation leads to a thermodynamically favourable situation with more oxygen available, it also results in shorter solids residence time in the fuel reactor, giving the fuel particles less time to gasify before re-entering the air reactor.

The oxygen releasing properties of the material could be investigated prior to each experimental campaign. Once the operating temperature had been reached, fluidization of the fuel reactor and loop seals was switched to nitrogen. An average oxygen concentration of 2.5-3.8% was measured for fuel reactor temperatures of 950-970°C, which confirms previous experiments with the same type of oxygen carrier [39, 52]. Also, one experiment with fuel addition and nitrogen fluidization in the fuel reactor was conducted to investigate whether operation without steam gasification was possible, see Fig. 8. When fluidizing with nitrogen, i.e. in the absence of steam gasification, pure CLOU operation was possible. In these conditions, the carbon capture efficiency decreased due to slower char conversion. On the other hand, this resulted in a decrease of the total amount of combustible gases present in the fuel reactor while the available amount of oxygen remained constant, which in turn effectively increased the oxygen-carrier-to-fuel ratio and gave a lower oxygen demand.

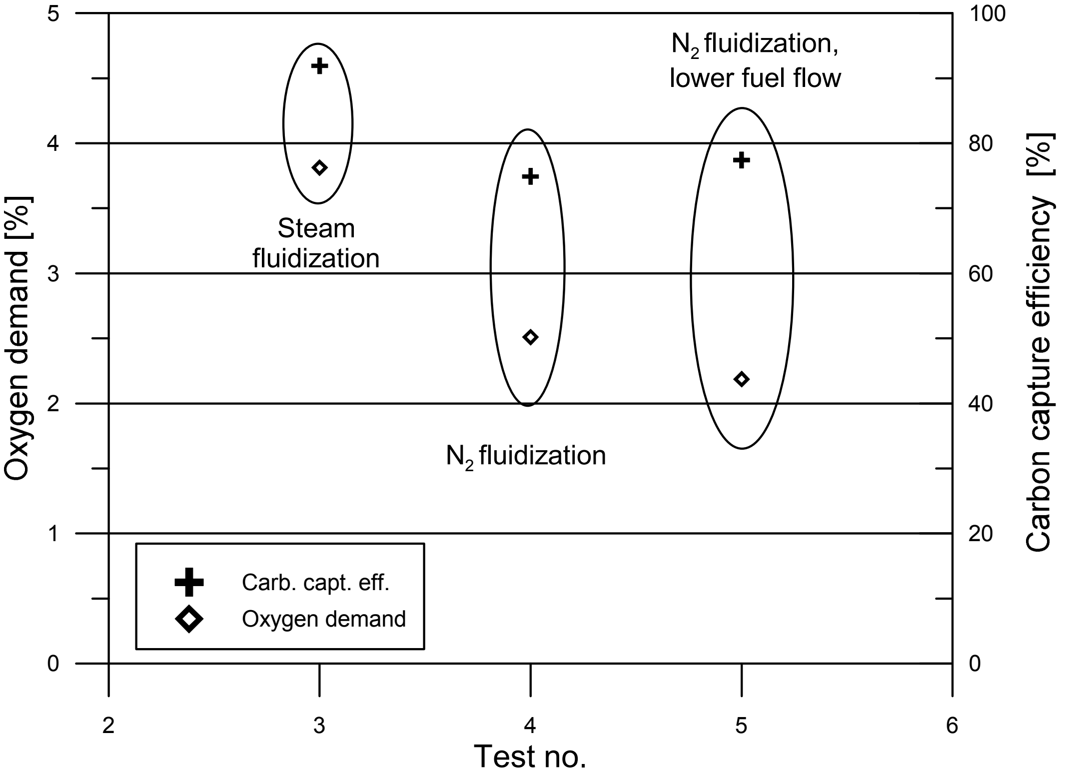

Fig. 8. Ω_{OD} *and* η_{OO} *as a function of fuel reactor fluidization gas and fuel feeding speed*

The oxygen carrier was easily fluidized and did not form hard agglomerations. The estimation of particle lifetime was complicated by the fact that the exact amount of ash and char in the elutriated particles was unknown and could only be determined in post-operation sample analysis. The results suggested that particle fines production more or less stopped toward the end of the experimental series. This indicates a high potential oxygen carrier lifetime, which is in line with earlier findings from a similar unit using gaseous fuels [39].

3.2 Experiments with calcium manganate and sulphurous fuels (paper II)

When using $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ with sulphurous fuels, the calcium cation might bond with SO_2 from the combustion process to form $CaSO_4$, which could inactivate the oxygen carrier [53-56]. Higher temperatures favour the formation of CaO at certain SO_2 and O_2 partial pressures. Assuming a similar behaviour for $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ as for CaO [52], high temperatures should allow for combustion of sulphurous fuels without $CaSO_4$ formation and the regeneration of $CaSO_4$ already formed.

29 hours of experiments with sulphur-containing fuels were conducted followed by a test with low-sulphur biochar to investigate the possibility of oxygen carrier regeneration.

When using a mix of 80 mass-% wood char and 20 mass-% petroleum coke, an oxygen demand of little more than 5% could be reached at standard conditions. The lowest oxygen demand with pure pet coke was around 7.7%, which can be compared to an oxygen demand of around 2% for pure biochar as described in paper I. The difference in gas conversion is believed to originate from the reactivity of the char, not the sulphur content: wood char has previously been shown to be more reactive than pet coke char [50]. Also, char gasification products are converted to a higher extent than volatiles due to better gas-solids mixing. Consequently, a fuel with low volatile content and high char reactivity such as wood char is expected to show good gas conversion. Fig. 9 shows oxygen demand and carbon capture efficiency for all tests at standard conditions.

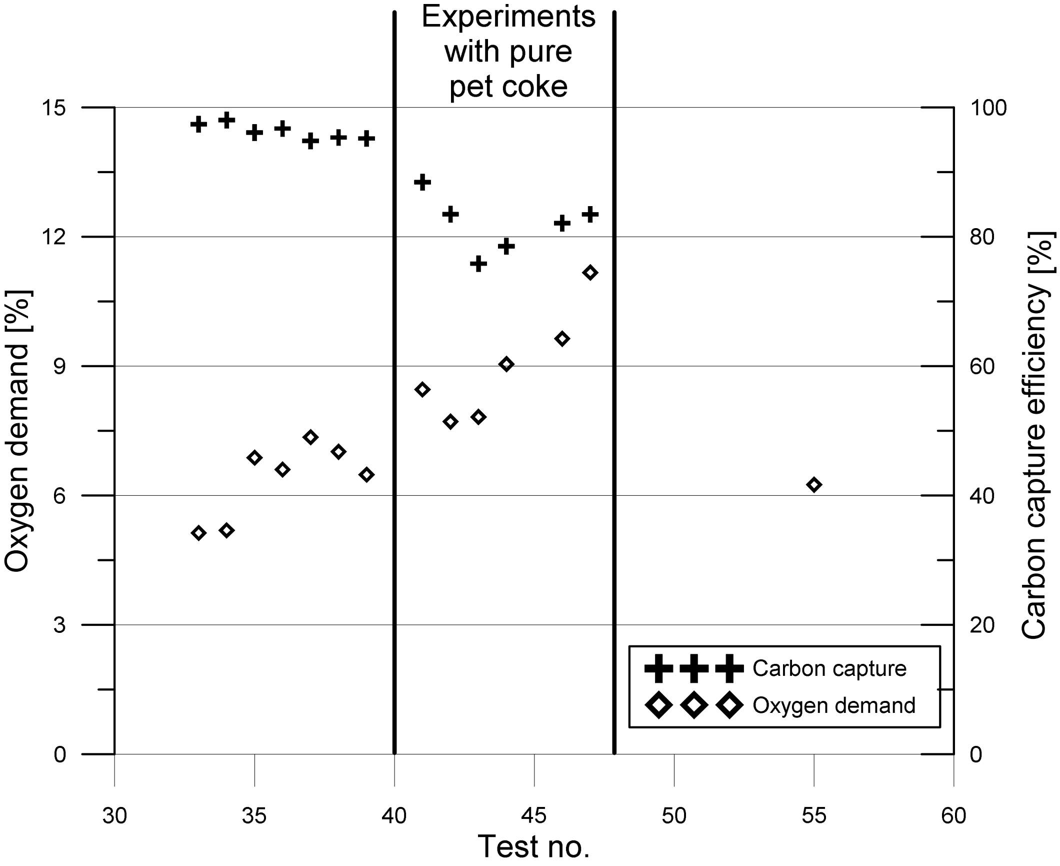

Fig. 9. Average values for Ω_{OD} and η_{OO} at standard conditions

During the experiments with pet coke, system performance worsened with time. The observed levels of sulphurous gas species in the fuel reactor exhaust gases were low, which indicated sulphur accumulation and poisoning of the oxygen carrier. After oxygen carrier regeneration (test no. 55), the oxygen demand decreased approximately to the base level. In this test, carbon capture efficiency could not be calculated due to a gas leakage.

The regeneration test was conducted at fuel reactor temperatures of 970-1030°C using low-sulphur biochar. During the experiment, the sulphur content in the exhaust gases was measured every five minutes, see Fig. 10.

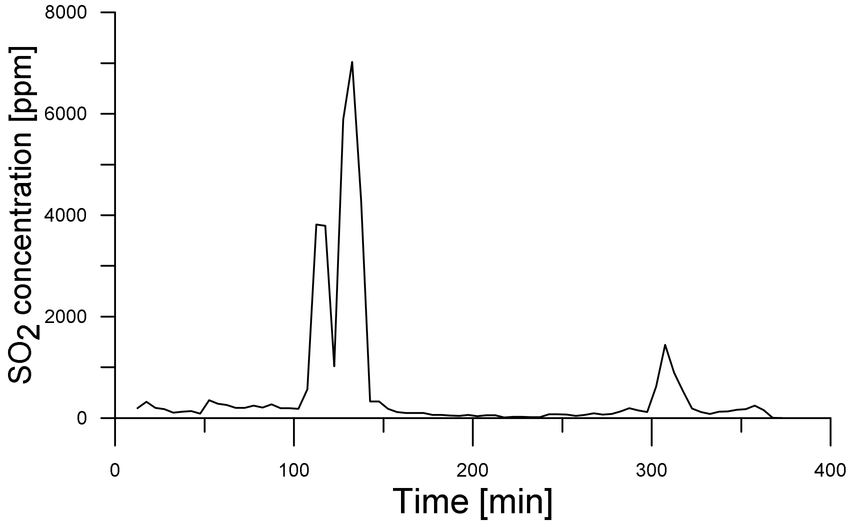

Fig. 10 SO_2 concentration during regeneration experiment (tests 48-53). Measurements were made every five minutes

After around 100 minutes, SO_2 levels increased to more than 7000 ppm although the fuel used contained almost no sulphur. The highest levels were reached before the fuel reactor temperature was increased to 1030°C at t=180 min, which could mean that the absence of sulphur in the fuel rather than the high temperature caused the sulphur release. Analyses of particle samples taken throughout all experiments confirmed that sulphur was first accumulated in the oxygen carrier during the experiments with sulphurous fuel, and then released during the regeneration test.

Although regeneration of the oxygen carrier is possible according to these results, it can be discussed if and to which extent the need for regular regeneration cycles, i.e. changes in operating temperature and fuel type, would impede the use of the material in larger scale.

3.3 Experiments with manganese ores (paper III)

Three materials (“Sinfin”, “Mangagran” and “Mesa”) were tested for 14.6 h, 16 h and 11.5 h, respectively. Besides wood char, petcoke was used as fuel in the Sinfin tests to compare the oxygen carrier’s performance with ilmenite, which had been tested with the same fuel in the same unit [22, 43, 57].

Fig. 11 shows average values for oxygen demand and carbon capture efficiency for all test periods with Sinfin.

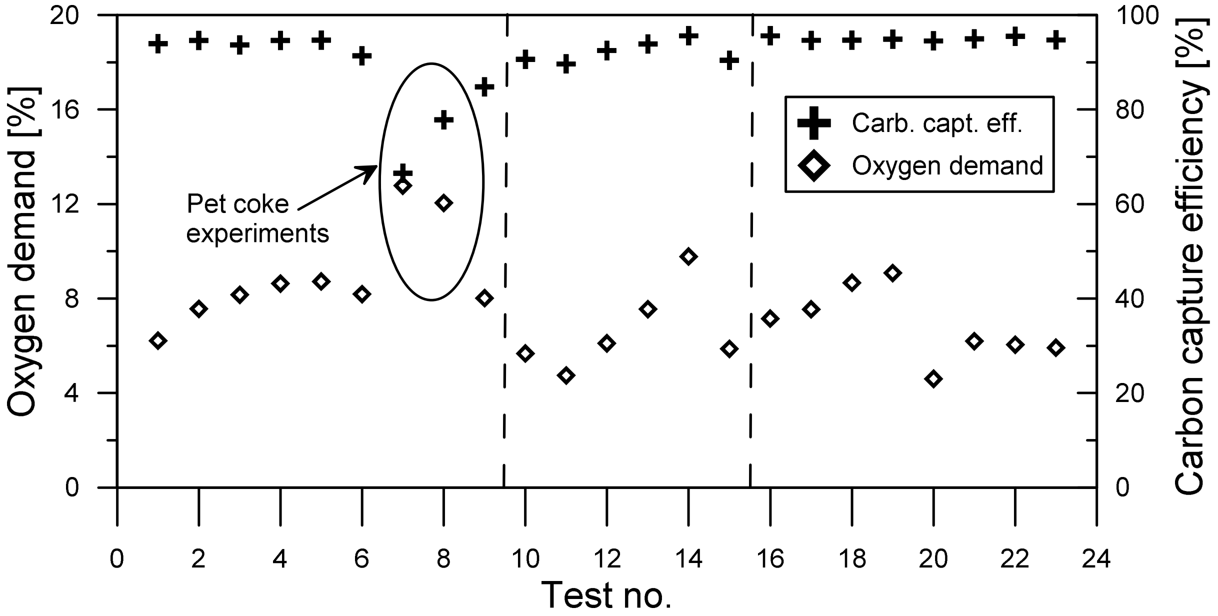

Fig. 11. Average values for oxygen demand and carbon capture for all Sinfin test periods.

In tests 7 and 8, petcoke was used as fuel. Experiments took place on three days, separated by vertical dashed lines in the diagram. After the first two test days and prior to test 17, fresh oxygen carrier material was added to the reactor to compensate for attrition losses. A clear correlation between higher solids inventory and better gas conversion, i.e. lower oxygen demand was observed, most likely caused by the increase in solids circulation associated with a higher solids inventory. Fig. 12 shows average values of oxygen demand and carbon capture efficiency in all test periods with Mangagran. Fig. 13 shows all tests with Mesa.

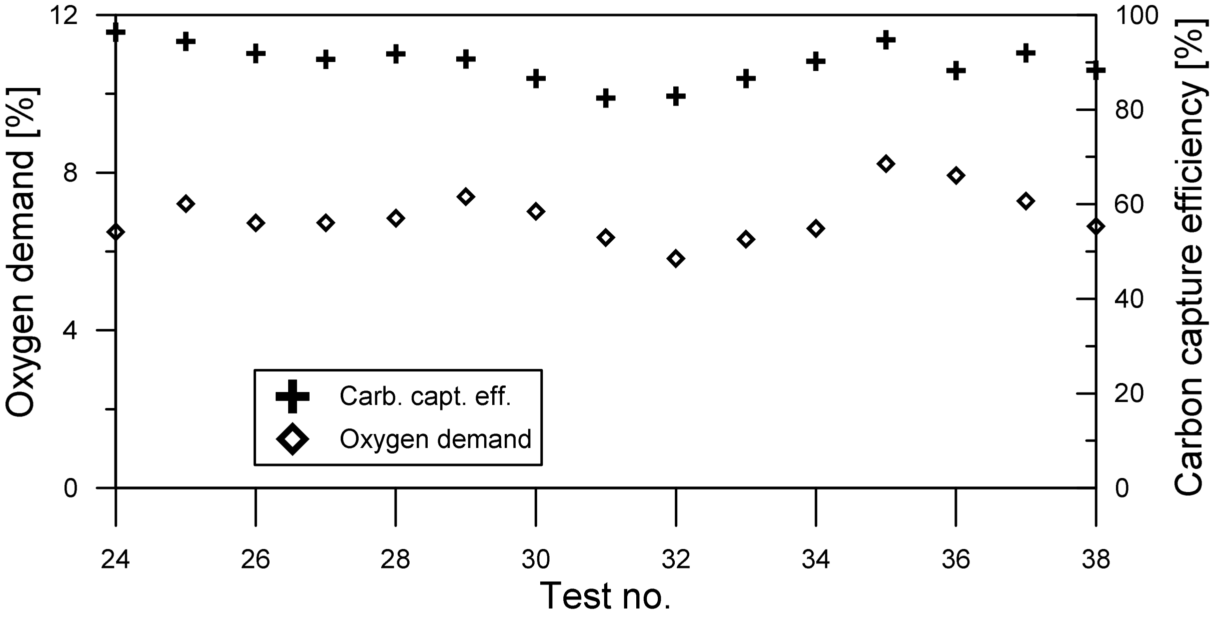

Fig. 12. Average values for oxygen demand and carbon capture for all Mangagran test periods.

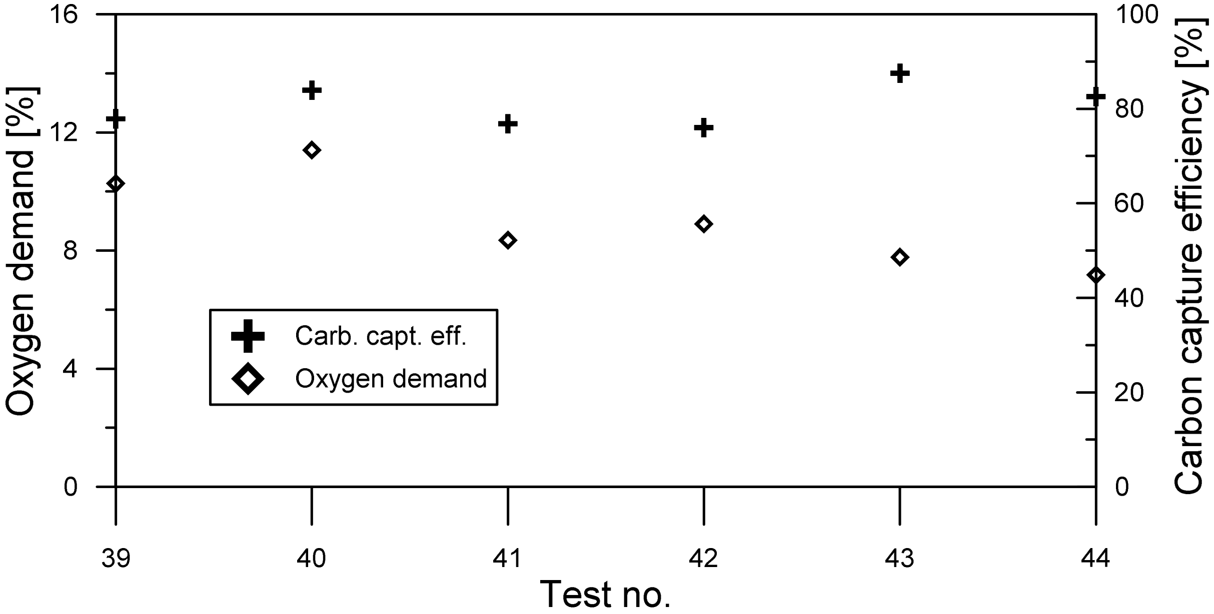

Fig. 13. Average values for oxygen demand and carbon capture for all Mesa experiments.

The Mesa tests had to be run at a lower temperature to avoid agglomeration, which had occurred in an earlier experiment with the same material. Poorer performance was therefore expected. When trying to increase the temperature over 925°C, the experiment had to be aborted due to agglomeration build-up. Upon opening of the reactor, it was found that the particles had formed both microagglomerates, s. Fig. 14, and a major macroagglomerate blocking about half the cross-section of the fuel reactor.

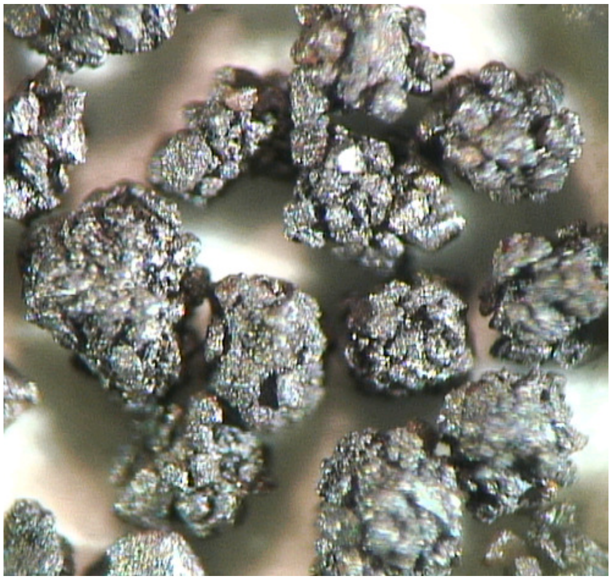

Fig. 14. Microagglomerates >500 µm formed after operation with Mesa.

The lifetime of the particles was calculated according to equations (10) and (11) based on fines production. While Mangagran and Mesa reached 109 and 99 h, respectively, Sinfin outperformed both with an estimated lifetime of 284 h. With Mangagran and Sinfin, no operational problems were encountered, although an increase in average particle size was observed for Mangagran.

For Sinfin, a few soft agglomerates were found when opening the reactor. Those fell apart when not handled carefully and are thus not seen as problematic.

3.4 Performance comparison

Table 2 compares the performance indicators of all tested materials with two reference materials as mentioned earlier. The main differences between the tested manganese ores lie in their mechanical properties and durability rather than in their performance. It should be noted that the results for Mesa were obtained at lower temperatures.

Table 2. Performance comparison of all tested materials with two reference materials (average values). τ_{OC} describes the residence time of the oxygen carrier in the fuel reactor, see [58]

	Calcium manganate (paper I and II)	Mangagran (paper III)	Sinfin (paper III)	Mesa (paper III)	Ilmenite [43]	Buritirama [57]
Oxygen demand (wood char/ petcoke) [%]	3.5/8.6	7.0/-	7.2/12.4	7.4/-	-/20	-/15
Carbon capture (wood char/ petcoke) [%]	92.6/88.18	90.5/-	93.1/72.5	84.7/-	-/66	-/94
Temperature [°C]	970	970	970	925	970	960
Fuel power (wood char/pet coke) [kW]	3.9/7.1	3.6/-	4.9/17.2	3.9/-	-/5.9	-/5.9
τ_{OC} (wood char/pet coke) [min]	3.2/3.6	1.6/-	1.9/1.2	1.8/-	-/4.2	-/4.8

Of the materials tested in this study, calcium manganate offers the lowest oxygen demand and highest carbon capture, which is assumed to be a result of the CLOU effect. In the tests using biochar and ores, the lowest oxygen demand was achieved for operation with Mangagran, the highest carbon capture with Sinfin. With petcoke, the performance of Sinfin was clearly better than that of ilmenite. With ilmenite as oxygen carrier using the same fuel in the same 10 kW unit, an oxygen demand of 20% and a carbon capture efficiency of 66% were reached [43]. As Sinfin performs better than ilmenite when using petcoke and shows similar performance as Mesa and Mangagran when using biochar, it can be concluded that all four tested manganese materials are significantly more reactive than ilmenite, with calcium manganate outperforming the three manganese ores. Another manganese ore ("Buritirama") also performed better than ilmenite with 15% oxygen demand and 94% carbon capture in a previous study [57], although at the price of lower lifetime, which was estimated to 48 h based on fines production. The high value for carbon capture efficiency can in part be explained by the high potassium and sodium contents in Buritirama, which are known to catalyse gasification reactions [59]. Other reasons are the lower fuel power and solids circulation as compared to the current study.

When burning biochar, oxygen demand could be more than halved as compared to the most promising material from paper III, Sinfin, by using the manufactured calcium manganate. In an industrial size unit, this would mean considerable savings in the oxygen polishing step. For petcoke, the same trend can be observed. Both Sinfin and calcium manganate performed better compared to the reference materials ilmenite and Buritirama as far as gas conversion was concerned.

The raw materials for calcium manganates are potentially cheap but the additional cost related to spray-drying is hard to estimate. Previous publications assumed 1 €/kg of oxygen carrier for spray-drying, calcination and sieving [60].

The lifetime of the oxygen carrier would be decisive for the use in an industrial size unit and has been found to be an issue for manganese ores in a previous study [57]. The lifetime of ilmenite has been investigated in a 100 kW unit and was found to be around 700 hours based on fines production [47], more than twice as high as for Sinfin, the most durable manganese material tested in paper III, which reached 284 hours. However, the actual lifetime might be determined by ash removal and fouling of the oxygen carrier by the ash rather than oxygen carrier attrition. Because of that, Lyngfelt and Leckner [49] conservatively estimate the lifetimes of manganese materials to 100 hours and for ilmenite to 200 hours for a 1000 MW chemical looping plant. At utility scale, the decreased cost for oxygen polishing and potential longer lifetime would then have to be weighed against the additional cost of a manufactured oxygen carrier.

Concerning the cost of manganese ores as compared to ilmenite, Lyngfelt and Leckner assumed an ilmenite price of 175 €/ton and a manganese ore price of 225 €/ton, leading to a cost of 2 and 5 €/ton captured CO_2. This can be compared to an approximate CO_2 compression cost of 10 €/ ton CO_2. Assuming a similar lifetime of for instance 100 h for both materials would reduce the difference in cost from 3 to 1 €/ton CO_2.

In a utility-scale unit, a reduction in oxygen demand by 5%-units would save around 2.5 €/ton CO_2 Thus, it is clear that manganese ores have a potential for reducing costs, provided that their price does not differ too much from ilmenite. An option might be to mix these materials, as previously done by Linderholm et al. [41], who showed that the oxygen demand could almost be halved using a mixture of ilmenite and manganese ore.

4. Conclusions

Although manganese materials have been known to possess characteristics relevant for chemical looping combustion, experimental experience with solid fuels and manganese materials was limited prior to this study. While it was known that higher gas conversion and carbon capture than with the state-of-the-art oxygen carrier ilmenite were possible, the lifetime issues related to manganese materials had not been addressed sufficiently.

In this study, four different oxygen carriers have been tested towards their reactivity and long-term integrity in a 10 kW chemical looping combustor. The main findings are:

- The calcium manganate material $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ (papers I and II) performed better than ilmenite with respect to gas conversion and carbon capture efficiency. The material released gaseous oxygen via the CLOU mechanism at all tested conditions and mechanical stability was good.
- When used with sulphurous fuels, the oxygen carrier accumulated sulphur, which eventually might lead to worse performance. However, regeneration of the material by using low-sulphur fuel and a high fuel reactor temperature was possible. It can be concluded that $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ is suitable for chemical looping combustion of low-sulphur fuels, where it offers the potential of considerable cost reductions in utility scale. The suitability for use with sulphurous fuels depends on whether regeneration cycles are acceptable during operation or not.
- Two out of three manganese ores performed well in the process while one material formed agglomerations (paper III). All materials had higher gas conversion and carbon capture efficiency than ilmenite. The most durable material ("Sinfin") reached a lifetime of 284 hours based on fines production, which is almost six times longer than a previously tested manganese ore. This indicates that manganese ores can combine high gas conversion with reasonable lifetime.
- Comparing $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ to the best-performing manganese ores, the oxygen demand was halved when using biochar. Whether a more expensive manufactured calcium manganate or a naturally occurring manganese ore would be used in large scale will be a trade-off between oxygen carrier cost and the cost of oxygen polishing.

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