

CO₂ capture from coal combustion using chemical-looping combustion – Reactivity investigation of Fe, Ni and Mn based oxygen carriers using syngas

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ABSTRACT

Chemical-looping combustion (CLC) is a combustion technology where an oxygen carrier is used to transfer oxygen from the combustion air to the fuel, thus avoiding direct contact between air and fuel. The system is composed of two reactors, a fuel and an air reactor, where the flue gas from the fuel reactor contains CO₂ and H₂O and the flue gas from the air reactor contains only N₂ and some unreacted O₂. Thus, CO₂ and H₂O are inherently separated from the rest of the flue gases, and no major energy is expended for this separation. This paper investigates the use of three promising oxygen carriers based on the metals Mn, Fe and Ni together with syngas from coal gasification. Reactivity investigations in a laboratory fluidized bed reactor under alternating oxidizing and reducing conditions, using 50% H₂ and 50% CO for the reducing period, and 5% O₂ for the oxidation period, found that the reactivity of all three was high at 950°C. For the Mn and Ni based oxygen carriers, there was full conversion of the fuel gas using bed masses of 46 and 173 kg oxygen carrier per MW of syngas. The Fe based carrier had a somewhat lower reactivity, but the gas yield to CO₂ was still high. The effect of temperature was investigated, and manganese oxide showed high reactivity and conversion interval in the temperature range 650-950°C. For Ni and Fe based carriers the degree of conversion decreased as a function of temperature, although the initial reactivity was high. At lower temperatures there was formation of both carbon and methane for some of the oxygen carriers. This was associated with low degrees of gas yields, and is not expected in a real system. For comparison methane was also used as fuel. The nickel based carrier showed a much higher reactivity in comparison to manganese- and iron oxide at 950°C. Thus one implication of the results in this paper are that when using syngas as fuel, the cheaper and more environmentally sound Mn or Fe-based particles may be better candidates compared to Ni. On the other hand, when using natural gas, which has a high content of methane, Ni based particles would be the preferred oxygen carrier.

INTRODUCTION

CO₂ is the primary greenhouse gas and it is very likely that CO₂ formed by combustion of fossil fuels contribute to an increased global average temperature. [1] One way to achieve combustion without CO₂ emissions and still use fossil fuels is separation and sequestration of CO₂.

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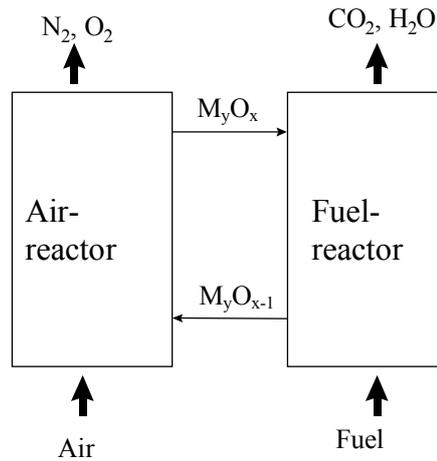
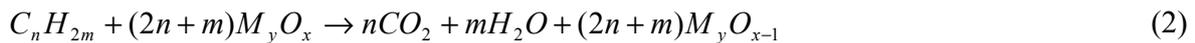


Figure 1. Chemical-looping combustion

Separation can be made by a number of different techniques, but most of them have the disadvantage of requiring a large amount of energy. [2] Chemical-looping combustion has emerged as an attractive option for carbon dioxide capture because CO_2 is inherently separated from the other flue gas components, i.e. N_2 and unused O_2 and thus no energy is expended for the separation. Although the concept of CLC was proposed already in the 1980's, [3, 4] most of the experimental work has been performed in the last decade by research teams around the world.

Chemical-looping combustion. The chemical-looping combustion system consists of two reactors, a fuel and an air reactor, as seen in Figure 1. An oxygen carrier, usually a metal oxide, transports oxygen from the air reactor to the fuel reactor. The oxygen carrier is circulating between the reactors and is oxidized in the air reactor, according to the overall reaction (1), and reduced back to its initial state by the fuel, according to the overall reaction (2).



The total amount of heat evolved from reaction (1) and (2) is equal to the heat released from conventional combustion, where the oxygen is in direct contact with the fuel. However, the actual heat load of the reactions in the fuel and air reactor is dependent on the fuel as well as the metal oxide system. The process has been successfully demonstrated using gaseous fuel in several prototype units based on interconnected fluidized beds, for instance in a 10-kW unit at Chalmers University of Technology, using oxygen carriers based on both Ni and Fe. [5] Although considerable work has been carried out in the last decade around CLC most of the investigations have focused on natural gas as fuel, see [6] for a recent review of the CLC literature. As coal is a much more abundant fossil fuel in comparison to natural gas, it would be highly advantageous if CLC could be adapted for coal combustion. Two possibilities for achieving this are: i) introduction of the coal directly to the fuel reactor where the gasification of the coal and subsequent reactions with the metal oxide particles will occur simultaneously in the same reactor or ii) using syngas from coal gasification in the fuel reactor. Here, an energy intensive air separation unit would be needed for the gasification step, but only a small part of the total oxygen for complete combustion would be required. This paper will focus on the second route, i.e. combustion of syngas. However, as it is important that the oxygen carrier has a high

reactivity with the products of coal gasification also when the reactions are occurring in the same reactor, the results presented here have important implications also for the direct combustion route. [7]

Thermal considerations. It is paramount to the success of the process that the oxygen carrier can fully convert the fuel gas, i.e. CO and H₂ to CO₂ and H₂O. In a theoretical study, Jerndal et al. showed that the equilibrium degree of gas yield, γ , of the fuels CO, H₂ and CH₄ was high for several metal oxide systems. [8] For the systems investigated here, i.e. Fe₂O₃/Fe₃O₄, Mn₃O₄/MnO and NiO/Ni, the equilibrium yield of the fuel gases were high in the temperature range 800 to 1000°C. For the Fe and Mn systems the conversion of the fuel to CO₂ and H₂O was complete, while NiO had small amounts of H₂ and CO from the outlet of the reactor. When using a syngas of CO and H₂, the reaction in the fuel reactor, reaction (2), is exothermic for these metal oxide systems. This is an important consideration since this means that there will not be a temperature drop in the fuel reactor when burning syngas directly in the fuel reactor, which may be the case for natural gas and methane, where the reactions in the fuel reactor often are endothermic. [9]

In a recent study, approximately 50 different types of oxygen carriers were investigated with respect to parameters which are important for chemical-looping combustion using methane. [10] From this study, three of the better oxygen carriers based on the metals Mn, Fe and Ni were chosen to be investigated with syngas as fuel. These showed a combination of high reactivity both under reducing conditions with methane and oxidizing conditions, high mechanical strength, limited or no attrition and no deactivation.

EXPERIMENTAL

Particle production. The oxygen carriers were produced by freeze granulation. Here the particles are formed by atomizing a slurry of fine particles of the starting material. The drops are sprayed into liquid nitrogen where the water based drops freeze. The water is then removed by sublimation at low pressure and finally the particles are heat treated for 6 h. The particles were sieved to obtain particles of 0.180-0.250 mm. The chemical and physical characteristics of the particles are given in Table 1. The shape and surface structure of the Mn-based oxygen carrier can be seen in Figure 2. The particles are spherical and with a granular structure.

Fluidized bed experiments. The experiments were conducted in a laboratory fluidised-bed reactor of quartz. The reactor had a length of 820 mm with a porous quartz plate of 22 mm in diameter placed 400 mm from the bottom. The inner diameters of the bottom and top sections were 10 and 22 mm. The temperature was measured under and above the porous quartz plate, using 10% Pt/Rh thermocouples enclosed in quartz shells. A sample of 4 or 15 grams of oxygen carrier particles was initially heated in an inert atmosphere to the reaction temperature. For the experiments with 4 g oxygen carrier also 11 g quartz was added to the bed and thus the total solids inventory was 15 g for all experiments. The particles were exposed alternatively to 5% O₂ and a simulated syngas of 50% H₂/50% CO for between 13 and 17 cycles, thus simulating the cyclic conditions of a CLC system. The reactant gas mixtures were led from mass flow

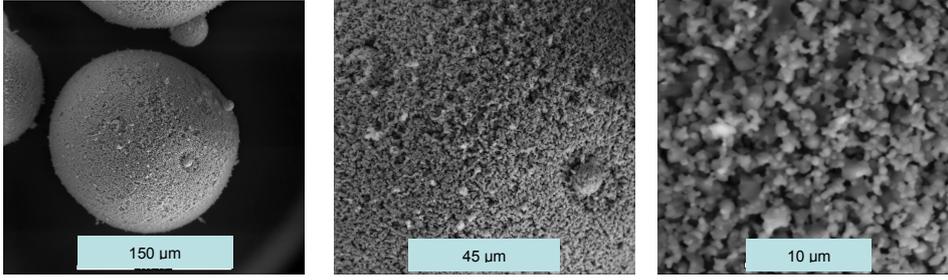


Figure 2. Images of the oxygen carrier composed of 40% Mn_3O_4 on 60% $Mg-ZrO_2$.

controllers to the bottom of the fluidized bed at a flow rate of 450 ml/min for syngas and 1000 ml/min using oxygen (at 0°C and 1 bar). Depending upon the oxygen carrier and the temperature the flows during reduction correspond to $1.2 - 2.8u_{mf}$ and to $3.9 - 8.9u_{mf}$ during oxidation. To avoid air and syngas mixing during the shifts between reduction and oxidation, nitrogen gas was introduced during 180 s after each period. For comparison, fluidized bed tests conducted with 100% CH_4 using a flow of 450 ml/min are also presented.

Data evaluation. The degree of solid conversion is defined as,

$$X = \frac{m - m_{red}}{m_{ox} - m_{red}} \quad (3)$$

which can be calculated as a function of time for the reducing period using syngas with 50% CO and 50% H_2 :

$$X_i = X_{i-1} - \int_{t_0}^{t_1} \frac{1}{M_o P_{tot}} \dot{n}_{out} (2p_{CO_2,out} + p_{CO,out} - p_{H_2,out} - 2p_{CH_4,out}) dt \quad (4)$$

For the reduction periods the outlet flow was too low to be measured accurately, and thus it was calculated from the inlet molar flow rate as well as a mass balance. The partial pressure of H_2 was not measured for all experiments, but calculated from the difference $1 - p_{CO_2,out} - p_{CO,out} - p_{CH_4,out}$ in the part of the reduction period where there is little or no back-mixing. Further, the H_2 was measured for some cycles using a gas chromatograph. In general the agreement between the measured and calculated concentrations was very good. The conversion as a function of time when using methane can be calculated in a similar way, see [11] for details. For the oxidation period the conversion was calculated from:

$$X_i = X_{i-1} + \int_{t_0}^{t_1} \frac{2}{M_o P_{tot}} (\dot{n}_{in} p_{O_2,in} - \dot{n}_{out} p_{O_2,out}) dt \quad (5)$$

As is apparent from Table 1, the investigated particles have considerably different oxygen ratios, R_o , i.e. the particles can transfer different masses of oxygen per total mass of circulating carrier. Thus, in order to facilitate a comparison between the different oxygen carriers which contain varying amounts of oxygen, a mass-based conversion was defined as:

$$\omega = \frac{m}{m_{ox}} = 1 + R_o(X - 1) \quad \text{where } R_o = (m_{ox} - m_{red}) / m_{ox} \quad (6)$$

In addition to the solids reactivity, the gas yields were calculated, and defined as the ratio of the H₂ and CO added which reacted to H₂O and CO₂ respectively and were calculated for syngas from:

$$\gamma_{CO} = \frac{p_{CO_2,out}}{p_{CO,out} + p_{CO_2,out} + p_{CH_4,out}} ; \quad \gamma_{H_2} = \frac{p_{H_2O}}{p_{H_2O} + p_{H_2} + 2p_{CH_4}} = 1 - \frac{p_{H_2,out} + 2p_{CH_4,out}}{p_{CO_2,out} + p_{CO,out} + p_{CH_4,out}} \quad (7)$$

The gas yield for methane combustion, γ_{CH_4} , is defined as the gas yield for CO, i.e. eq. (7). A gas yield was defined for the oxidation period as:

$$\gamma_{ox} = \frac{P_{O_2,in} - P_{O_2,out}}{P_{O_2,in}} \quad (7b)$$

Table 1. Properties of the tested oxygen carriers

Active material (wt-%)	NiO (60%)	Fe ₂ O ₃ (60%)	Mn ₃ O ₄ (40%)
Support material (wt-%)	MgAl ₂ O ₄ (40%)	Al ₂ O ₃ (40%)	Mg-ZrO ₂ (60%)
Sintering temperature (°C)	1400	1100	1150
Oxygen ratio (R _o)	0.129	0.020	0.028
Crushing strength (N) ^a	2.2	1.4	0.7
Porosity (-) ^b	0.42	0.56	0.58
Apparent density (kg/m ³) ^b	3002	2047	2264
BET surface area (m ² /g)	1.24	Not measured	Not measured

^ameasured on particles of 180-250µm ^bCalculated from packed bed volume and mass using a packing factor of 0.63

RESULTS AND DISCUSSION

Reduction and oxidation behaviour. Figure 3a-b shows the outlet gas concentrations from one reduction period for the experiment with the nickel and iron based oxygen carriers at 950°C. The relatively low concentrations of outlet gases initially is due to some dispersion in the reactor system. It is evident that the nickel based oxygen carrier is more reactive, and almost full yield of the CO and H₂ is achieved for the experiments with both 4 g and 15 g bed masses. There are some small amounts of unconverted CO and H₂ throughout the period, which are likely explained by the thermodynamic limitations discussed above. For iron oxide, there are also high gas yields initially although CO starts increasing early in the reduction period. Interestingly no H₂ was released throughout the period when using a 15g bed, although the CO concentration was high. For the experiment with the lower oxygen carrier mass, the concentrations of CO and H₂ were similar. Figure 4a shows a similar figure, but using the manganese oxygen carrier. Here the particles react completely with the CO and H₂ initially, but as the time of the reduction period increases, the CO and H₂ increase. The last measurement of H₂ for the 15 g sample is likely a measurement error. Figure 4b shows the following oxidation period for the experiment with the manganese based oxygen carrier. The inlet oxygen reacts completely with the carrier in the beginning, and after reaching breakthrough, returns rapidly to the inlet concentration. A similar

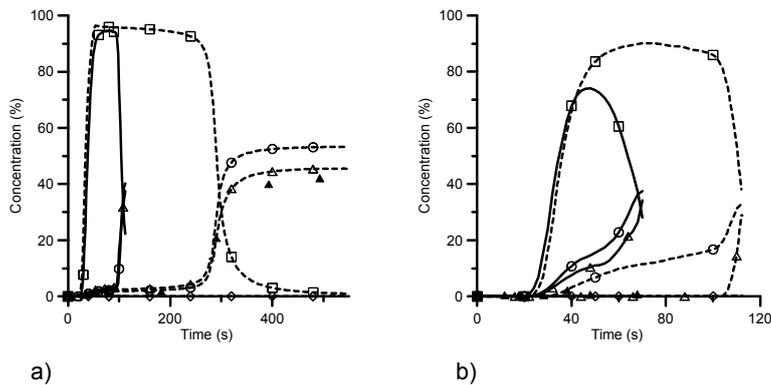


Figure 3. Outlet gas concentrations after condensation of water for one reduction period at 950°C for a) NiO/MgAl₂O₄ and b) Fe₂O₃/Al₂O₃. Solid lines indicate experiment with 4 g bed material (in quartz) and dashed lines is the experiment with 15 g oxygen carrier. Concentrations: CO₂ (□), CO (○), CH₄ (◇), H₂, calculated (△), H₂, measured (▲).

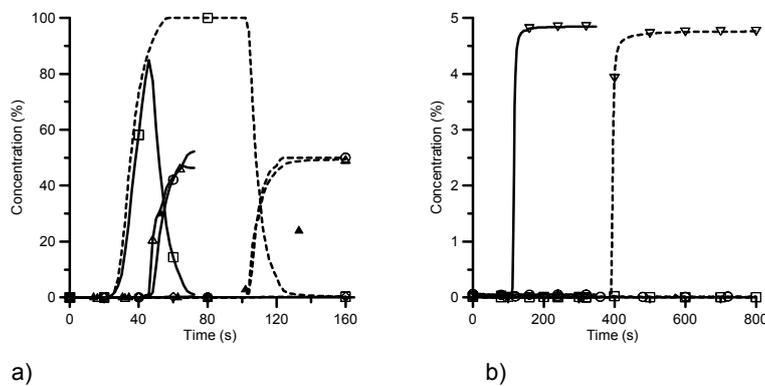


Figure 4. Outlet gas concentrations for the a) a reduction period and b) following oxidation period at 950°C for Mn₃O₄/Mg-ZrO₂. Solid lines indicate experiment with 4 g bed material (in quartz) and dashed lines is the experiment with 15 g oxygen carrier. Concentrations: CO₂ (□), CO (○), CH₄ (◇), H₂, calculated (△), H₂, measured (▲), O₂ (▽).

oxidation behaviour was found for the nickel and iron based particles. In Figure 4b the CO and CO₂ concentrations are zero throughout the oxidizing period indicating that there was no carbon formation during the reduction period in these experiments. The gas yields of H₂ and CO are shown as a function of the mass-based conversion in Figure 5. Again, the Mn and Ni based particles performs very well at this temperature, although the latter is able to maintain a high gas yield for a longer period of mass based conversion, explained by the high oxygen ratio for this particle, see Table 1. For comparison Figure 5c shows the gas yield for experiments conducted with methane at 950°C using 15 g bed material. Clearly, there is considerable difference with respect to the syngas reactivity, and only the nickel based particle has a nearly full yield to carbon dioxide. As metallic Ni is a good catalyst for both methane decomposition and steam reforming, the methane is most likely reformed to CO and H₂ on the external and internal pore structure of the particle where Ni sites are present. The CO and H₂ then react at a high rate with the NiO. On the other hand, Fe₃O₄ and MnO do not catalyze pyrolysis and reforming reactions to such a high extent, which means that the overall reaction will proceed at a slower rate.

Effect of cycle number. It is important that the oxygen carriers can be used for a substantial amount of reduction and oxidation cycles in a real CLC process. In these batch tests each experiment was performed for 13-17 cycles. For the Mn and Ni based oxygen carriers, no effect in

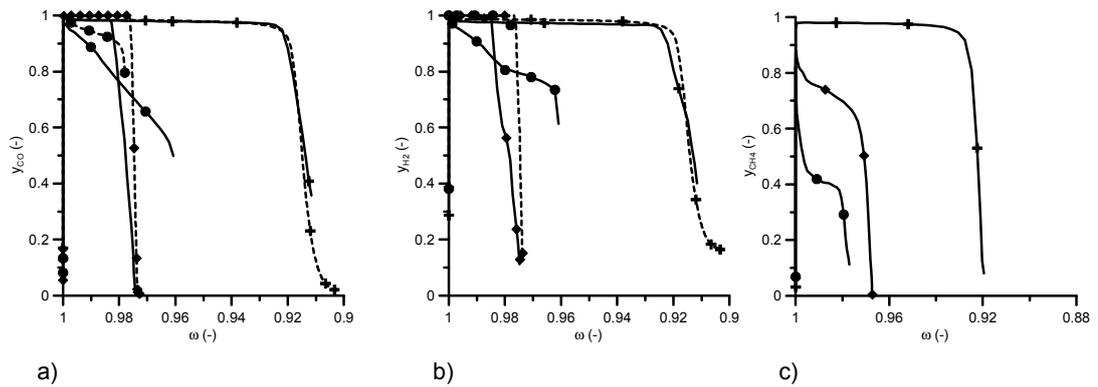


Figure 5. The gas yield for a) CO, γ_{CO} , and b) H₂, γ_{H_2} , as a function of ω for the second reduction period using Ni (+), Mn (◆) and Fe (●) at a temperature of 950°C. Solid lines indicate experiments with 4 g bed material (in quartz) and dashed lines experiments with 15 g oxygen carrier. For comparison Figure 5c shows the gas yield of methane to carbon dioxide, γ_{CH_4} , for experiments conducted with 100% CH₄ using 15 g bed material.

the reactivity as a function of cycle was seen, but for the Fe based oxygen carrier a clear increase in the reactivity was noted. It is believed that this may be due to the formation of the non-stoichiometric phase Fe_xO in the sample, as earlier investigations of this particle using short periods of reduction showed no increase in reactivity. Further, the particle has successfully been used in a 300 W continuous operating CLC reactor. [12]

Effect of temperature. The reactivity with syngas was investigated for different temperatures in the range 650-950°C. Fig. 6 shows the mass-based conversion as a function of time for the three metal oxides using 4 g oxygen carrier. The reactivity and extent of reaction for the nickel based carrier decreases rapidly as a function of temperature. Some small decrease in the extent of conversion was seen for the iron based sample, but no difference in rate of reaction and conversion level was seen for the manganese oxygen carrier, see Fig. 6c. The gas yield of CO to CO₂, γ_{CO} , for the oxygen carriers is shown in Figure 7. The manganese based carrier showed little difference in gas yield as a function of temperature, for the iron based small differences were found, but still a high gas yield was achieved for all temperatures. Although the extent of the reaction decreased as a function of temperature for the Ni based particles, the initial reaction was quite high, and almost full yield of the CO was achieved. The difference in final solid conversion for the experiments with different bed masses seen for 650 and 750°C is likely explained by the difference in time under reducing conditions.

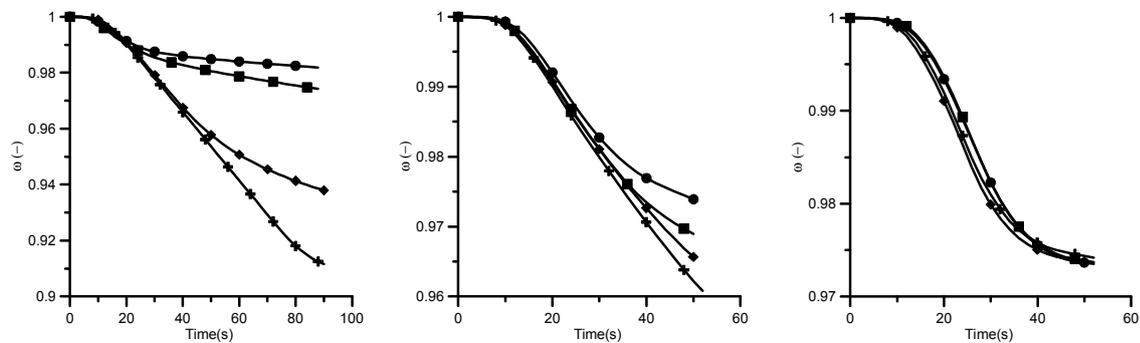


Figure 6. The mass-based conversion, ω , as a function of time for a) Ni, b) Fe and c) Mn for different reaction temperatures: 950°C (+), 850°C (◆), 750°C (■) and 650°C (●). The mass of oxygen carrier was 4 g in quartz.

Formation of methane. At lower levels of temperature there was formation of methane for the tested oxygen carriers, see Figure 8. The extent of methane formation was highest for the nickel based carrier and lowest for the iron based carrier. For the nickel particles the methane formation starts at rather high degrees of solid oxidation, and thus there is considerable amounts of active oxygen present in the sample. For the systems NiO/Ni, Mn₃O₄/MnO and Fe₂O₃/Fe₃O₄ there should not be any methane at equilibrium in the temperature range 650-950°C, as seen in Mattisson and Lyngfelt. [13] It is likely that the methane is formed through the reaction:



Figure 9a shows the equilibrium fraction of methane for a syngas with 50% H₂ and 50% CO as a function of temperature. Clearly, the formation is favored at low temperatures. The equilibrium concentrations are higher than those found in the current experiments.

Carbon deposition. At 950°C there was no carbon formation detected for any of the oxygen carriers. However at lower temperatures there was carbon formation, which was detected by outlet carbon dioxide and carbon monoxide during the oxidation cycle. For manganese and nickel based carriers there was carbon formation for the experiments in the temperature range 650 to 850°C and for the iron based carrier some small amounts of carbon was formed at 650 and 750°C for the experiments conducted with 4 g material. For all oxygen carriers the degree of carbon formation decreased as the temperature increased. Although it is likely that the carbon is formed via the Bourdourad mechanism, reaction (9), the fact that carbon formation was always accompanied by methane formation, suggests that methane decomposition can not be ruled out.



Jerndal et al. analyzed the formation of carbon in CLC using CH₄ and CO as fuel, using minimization of Gibbs free energy. [8] The carbon deposition was found to be a function of both temperature and amount of oxygen introduced to the system via the metal oxide. Figure 9b shows the critical oxygen ratio, ζ, as a function of temperatures for pure CO as well as syngas composed of 50% CO and 50% H₂. Here ζ, is defined as the fraction of oxygen added with the metal oxide to the amount needed for complete conversion to CO₂ and H₂O,

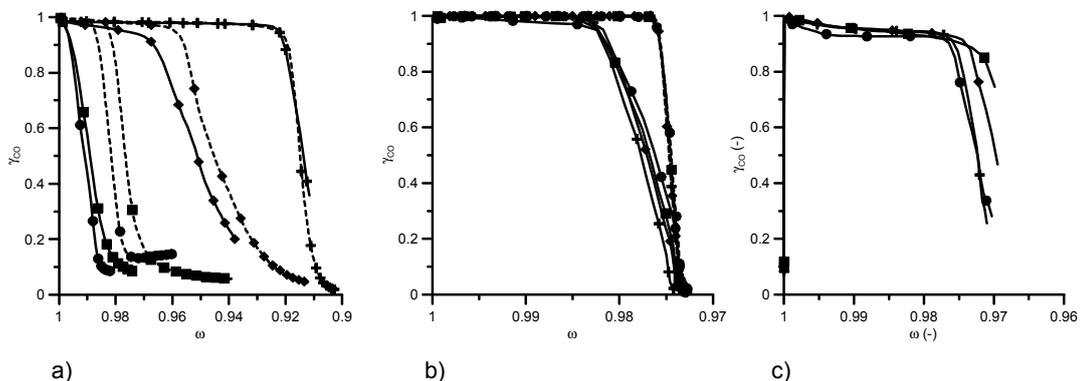


Figure 7. The gas yield, γ_{CO} , for a) Ni, b) Mn and c) Fe as a function of ω for different temperatures: 950°C (+), 850°C (◆), 750°C (■) and 650°C (●). Solid lines indicate experiment with 4 g oxygen carrier (in quartz) and dashed lines are experiments with 15 g oxygen carrier.

$$\zeta = \frac{n_{O_2,added}}{n_{O_2,stoich}} \quad (10)$$

and the critical oxygen ratio is the ratio below which formation of carbon occurs at thermodynamic equilibrium. At temperatures above 950°C carbon is not expected for syngas. Furthermore, at lower temperatures carbon is not expected as long as there is high yields of the fuel gas to carbon dioxide and water. Less oxygen is needed to avoid carbon deposition if the hydrogen content in the fuel gas is increased. In the batch experiments the period of reduction is long enough so that the gas yield is quite low at the end of the experiments, see Figure 7, and thus carbon formation is possible. In a real system with high gas yields, this is not expected.

The carbon formed during the experiments oxidized to a mixture of CO₂ and CO during the oxidation period. However, the mechanism of oxidation was different for the investigated particles. The carbon deposited on the nickel and iron based oxygen carriers was immediately oxidized as the oxygen was introduced into the reactor. For manganese a two step oxidation was observed, see Figure 10. Here, a small peak of CO and CO₂ is also observed directly as the O₂ is introduced, but most of the carbon is oxidized immediately before the O₂ breakthrough is obtained and γ_{ox} starts to decrease. A similar observation was made by Johansson et al. [14]

Implications for design. Two important aspects which need to be considered in a design of a CLC are i) the recirculation rate of particles between the reactors and ii) the solids inventory. With syngas the recirculation rate of particles is not restricted by the heat balance since the reactions in both the air and fuel reactor are exothermic and a large temperature drop is not expected. Thus the recirculation rate needs only to be sufficient to transfer enough oxygen from the air to the fuel. In certain cases there may be a small temperature drop although the reactions are exothermic, if the incoming fuel is at a low temperature. The solids inventory is related to the reaction rate of the oxygen carrier, and a high rate of reaction with fuel and oxygen will mean less bed material in the reactors. [15, 16] The solids inventory in test with syngas and 4 g in Fig. 5 corresponds to 46 kg/MW_{th} whereas those with methane and 15 g corresponds to 57 kg/MW_{th}.

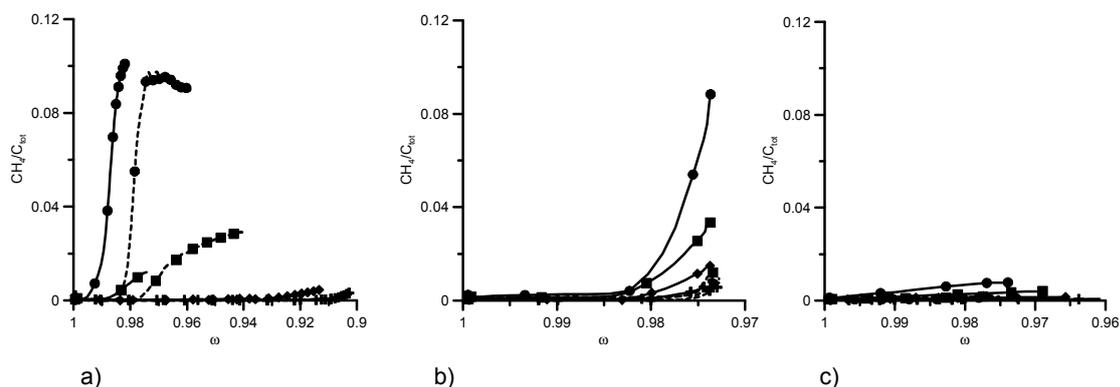


Figure 8. The fraction of outlet methane concentration to total outlet carbon containing gaseous compounds as a function of mass-based conversion for a) Ni, b) Mn and c) Fe for different temperatures: 950°C (+), 850°C (◆), 750°C (■) and 650°C (●). Solid lines indicated experiment with 4 g bed material (in quartz) and dashed lines is the experiment with 15 g oxygen carrier.

For the current experiments with syngas, a full yield of the Mn and Ni was seen at 950°C using 46 kg/MW_{th}, see Fig. 5. Although not complete, also a high yield was seen for iron. In comparison, for methane a complete gas yield was seen only for Ni at this temperature using 57 kg/MW_{th}, see Fig 5c. And for manganese and iron the syngas shows a much higher yield with 46 kg/MW_{th} in comparison to methane. As these two metals are cheaper and more environmentally acceptable than Ni, they are likely a much better choice of particles when using syngas, and also when burning solid fuels directly in the fuel reactor. [7] The oxygen carriers have only been tested for 13-17 cycles in the batch tests. No agglomeration or structural damage was observed for these experiments. As the production price of particles is important for the economic feasibility of the process, it is important that the particles can survive for thousands of cycles in a real process. As all three of these particles have been tested successfully with combustion for between 30-70 h in a continuous CLC system without major attrition, agglomeration or deactivation, all three carriers could be considered as potential oxygen carriers for a commercial CLC system. [12, 17, 18]

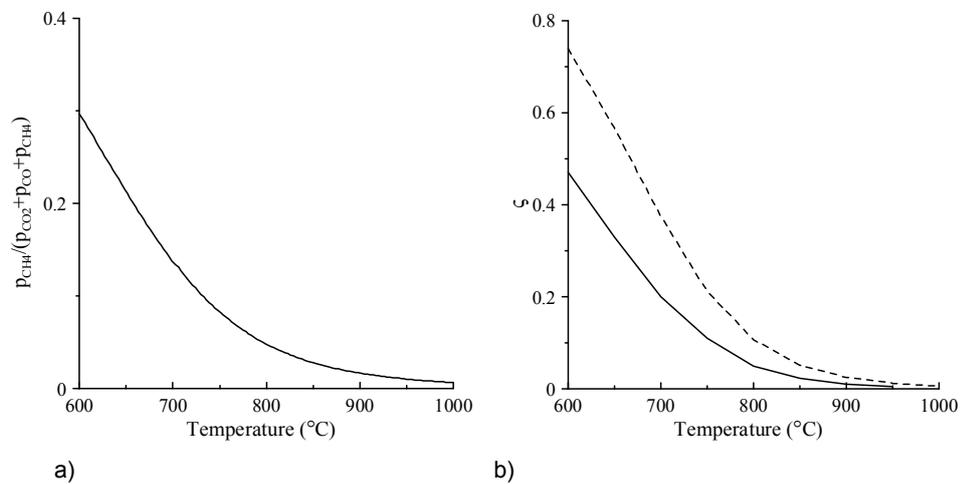


Figure 9. a) Equilibrium fraction of methane as a function of temperature for a 50/50 mixture of H₂ and CO and b) critical oxygen ratio, ζ , as a function of temperature for CO (dashed line) and 50%/50% H₂/CO (solid line).

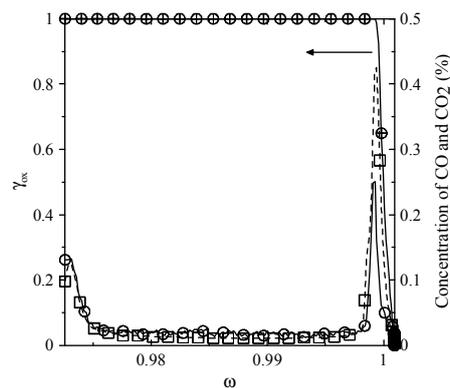


Figure 10. Gas yield, $\gamma_{ox_i}(\oplus)$ and concentrations of CO₂ (□) and CO (○) as a function of mass based-conversion.

CONCLUSIONS

The reactivity with of three types of oxygen carriers syngas was investigated for different temperatures in the range 650-950°C. For the Mn and Ni based oxygen carriers, there was full yield of the fuel gas to CO₂ and H₂O using bed masses of 46 and 173 kg oxygen carrier per MW of syngas at 950°C. The Fe based carrier did not have the same high reactivity. Manganese oxide showed high reactivity and conversion interval at temperatures as low as 650°C. For Ni- and Fe the degree of conversion decreased as a function of temperature, although the initial reactivity was high. No methanisation or carbon deposition was seen at 950°C for any oxygen carriers. However, methane and carbon was formed at lower temperatures. The methane and carbon is likely associated with low degrees of gas yield to CO₂ and H₂O, which is not expected in a continuous system. A comparison was also made of these carriers using methane as the fuel. Here, the nickel based carrier showed a much higher reactivity in comparison to manganese- and iron oxide at 950°C. Thus one implication of the results in this paper are that when using syngas as fuel, the cheaper and more environmentally sound Mn or Fe based particles may be better candidates compared to Ni. On the other hand, when using natural gas, which has a high content of methane, Ni seems to be the preferred oxygen carrier.

ACKNOWLEDGMENT

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NOTATION

m = actual mass of oxygen carriers (kg)

m_{ox} = mass of oxygen carriers in oxidized form (kg)

m_{red} = mass of oxygen carriers in reduced form (kg)

M_o = moles of active oxygen in fully oxidized sample (mole)

$n_{O,added}$ = actual amount of O added with the oxygen carrier (mole)

$n_{O,stoich}$ = stoichiometric amount of oxygen needed for full conversion of the fuel (mole)

\dot{n}_{in} = molar flow of the gas to the reactor (mole/s)

\dot{n}_{out} = molar flow of the gas exiting the reactor after the water has been removed (mole/s)

P_{tot} = total pressure (Pa)

$p_{i,in}$ = inlet partial pressure of component i (Pa)

$p_{i,out}$ = partial pressure of component i after condensation of steam (Pa)

R_o = oxygen ratio (-)

t = time (s)

u_{mf} = minimum fluidization velocity (m/s)

X = solid conversion (-)

greek letters

γ_i = gas yield of component i (-)

γ_{ox} = gas yield during oxidation (-)

ς = oxygen ratio (-)

ω = mass conversion of oxygen carrier (-)

REFERENCES

- [1] Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC). Climate Change 2001: The Scientific Basis, ed. J.T. Houghton, et al. 2001: Cambridge University Press, UK.
- [2] Carbon dioxide Capture and Storage. Intergovernmental Panel on Climate Change, ed. B. Metz, et al. 2005, New York: Cambridge University Press.
- [3] Ishida, M., Zheng, D., and Akehata, T. Evaluation of a chemical-looping-combustion power-generation system by graphic exergy analysis. *Energy - the International Journal* 1987; 12: 147-54.
- [4] Richter, H. and Knocke, K. Reversibility of combustion processes. *ACS Symp. Series* 1983; 235: 71-86.
- [5] Lyngfelt, A. and Thunman, H., *Construction and 100 h of operational experience of a 10-kW chemical-looping combustor*, in *Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO₂ Capture Project, Volume 1 - Capture and Separation of Carbon Dioxide From Combustion Sources*. 2005, Elsevier Science: London. p. 625-45.
- [6] Johansson, M. Selection of Oxygen-Carriers for Chemical-Looping Combustion Using Methane as Fuel, Lic.Eng. Thesis. 2005, Göteborg, Sweden: Department of Chemical and Biological Engineering, Environmental Inorganic Chemistry, Chalmers University of Technology.
- [7] Leion, H., Mattisson, T., and Lyngfelt, A. The use of petroleum coke as fuel in chemical-looping combustion. Submitted for publication 2006.
- [8] Jerndal, E., Mattisson, T., and Lyngfelt, A. Thermal analysis of chemical-looping combustion. *Chemical Engineering Research and Design* (in press) 2006.
- [9] Lyngfelt, A., Leckner, B., and Mattisson, T. A fluidized-bed combustion process with inherent CO₂ separation; application of chemical-looping combustion. *Chem. Eng. Sci* 2001; 56: 3101-13.
- [10] Johansson, M., Mattisson, T., and Lyngfelt, A. Comparison of oxygen carriers for chemical-looping combustion. *Thermal Science* (in press) 2006.
- [11] Mattisson, T., Johansson, M., and Lyngfelt, A. Multi-cycle reduction and oxidation of different types of iron oxide particles - Application to chemical-looping combustion. *Energy and Fuels* 2004; 18: 628-37.
- [12] Abad, A., Mattisson, T., Lyngfelt, A., and Johansson, M. Iron-based oxygen carrier for chemical-looping combustion-Use in a 300 W continuously operating reactor system. Submitted for publication 2006.
- [13] Mattisson, T. and Lyngfelt, A. Capture of CO₂ using chemical-looping combustion. in *Scandinavian-Nordic Section of Combustion Institute*. 2001. Göteborg, 163-8
- [14] Johansson, M., Mattisson, T., and Lyngfelt, A. Investigation of Mn₃O₄ with stabilized ZrO₂ for chemical-looping combustion. *Chemical Engineering Research and Design* (in press) 2006.
- [15] Abad, A., Adanez, J., Garcia-Labiano, F., De Diego, L.F., Gayan, P., and Celaya, J. Mapping of the range of operational conditions for Cu-, Fe-, and Ni-based oxygen carriers in chemical-looping combustion. *Chem. Eng. Sci* (in press) 2006.
- [16] Garcia-Labiano, F., de Diego, L., Adanez, J., Abad, A., and Gayan, P. Reduction and oxidation kinetics of a copper-based oxygen carrier prepared by impregnation for chemical-looping combustion. *Ind. Eng. Chem. Res* 2004; 43: 8168-77.
- [17] Abad, A., Mattisson, T., Lyngfelt, A., and Rydén, M. Chemical-looping combustion in a 300 W continuously operating reactor system using a manganese-based oxygen carrier. *Fuel* 2006; 85: 1174-85.
- [18] Johansson, E., Mattisson, T., Lyngfelt, A., and Thunman, H. Combustion of syngas and natural gas in a 300 W chemical-looping combustor. *Chemical Engineering Research and Design* (in press) 2006.