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Chemical-looping combustion of solid fuels in a 10 kW reactor system using natural minerals as oxygen carrier

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Abstract

Chemical-looping combustion (CLC) is an unmixed combustion concept where fuel and combustion air are kept separate by means of an oxygen carrier, and the CO_2 capture is inherently achieved. This work presents findings from a continuously operated 10 kW pilot for solid fuels. Using petcoke as fuel, the following oxygen carriers are compared: (a) ilmenite, (b) ilmenite + lime, (c) manganese ore, and (d) manganese ore + lime. Compared to ilmenite, the use of manganese ore as oxygen carrier greatly enhanced the rate of gasification. By adding lime particles to the Mn ore, performance improved further. The addition of lime to ilmenite had a small beneficial effect on gas conversion and char gasification rate.

Keywords: Carbon Capture, Chemical-Looping Combustion (CLC), Oxygen Carrier, Fluidized Bed, Manganese Ore, Ilmenite, lime

1. Introduction

Chemical-looping combustion (CLC) is a 2nd generation capture technology with potential for very low cost of carbon capture. The separation of CO_2 from other flue gases is actually inherent to the CLC process, whereas other options for carbon capture require energy intensive steps of gas separation, which is reflected on the overall economy of these processes. Therefore, CLC should be considered as a prime contender for carbon capture. Nevertheless, given the urgency with which CCS need be implemented in order to mitigate climate change, other capture technologies also have important roles to play, since they may be more mature and more suitable for retrofitting existing power producing facilities. The overall aim of research on carbon capture must be to provide industrial players and policy makers with a portfolio of feasible capture technologies.

The CLC reactor system used in this study is based on circulating fluidized-bed (CFB) technology. A growing share of the power generation from fossil fuels takes place in power stations based on CFB

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combustion. CFB has been considered a “niche” technology, but is emerging as a competitive alternative to more conventional alternatives for power generation by combustion, *e.g.* pulverized coal (PC) boilers. In comparison to PC plants, the low combustion temperature (~850°C) of the CFB minimizes NO_x and permits optimum sulfur capture by the simple addition of limestone [1]. Hence, extra equipment (“add-ons”) that conventional coal plants need to capture SO_2 and NO_x is reduced or entirely eliminated in CFB combustion. Another advantage of the CFB boiler is the ability to handle difficult fuels such as discarded tires, pet coke and sewage sludge. The currently largest commercial CFB boiler, put into operation in 2009, is the 460 MW_e Łagisza plant in Poland [2], built by Foster Wheeler, with a net efficiency of 43%.

1.1 Chemical-looping combustion

In chemical-looping combustion, metal-oxide particles, referred to as oxygen carrier, are used to transfer oxygen from combustion air to fuel. The CLC reactor system consists of two principal reaction chambers: the air reactor (AR) and the fuel reactor (FR). Fuel is oxidized by the oxygen carrier in the FR, after which the reduced metal oxide particles are returned to the AR, where they are regenerated to an oxidized state. After condensing the water, pure CO_2 is obtained from the exhaust gas of the fuel reactor, which means that the CO_2 separation is inherent to the process.

CLC with gaseous fuels, *e.g.* natural gas, has been widely investigated [3,4,5] and it has been shown that high gas conversion can be obtained while maintaining particle integrity [6]. Since fossil carbon is usually occurring as solids rather than gases or liquids, it is desirable to adapt the CLC process to solid fuels. Design and operation of chemical-looping combustors for solid fuels have been reported by several researchers, *e.g.* [7,8,9,10,11,12,13,14,15,16,17,18,19], many of which are quite recent contributions. These systems normally operate under atmospheric conditions, but there is one study that concerns pressurized CLC at 50 kW and up to 5 bar using coal as fuel [20].

When solid fuels are used in CLC applications, fuel conversion to gas occurs sequentially: (a) drying, (b) devolatilization, and (c) gasification, reaction (1). Gas produced by devolatilization and gasification can be oxidized by the oxygen carrier according to reactions (2-3). For fuel particle sizes normally used in CLC (< 250 μm), drying is a very rapid, devolatilization is essentially complete in 1 s, whereas gasification may take several minutes at 970°C.

$$C + H_2O/CO_2 \rightarrow CO + H_2/CO \tag{1}$$

$$CH_4 + 4\ Me_xO_y \rightarrow CO_2 + 2\ H_2O + 4\ Me_xO_{y-1} \tag{2}$$

$$H_2/CO + Me_xO_y \rightarrow H_2O/CO_2 + Me_xO_{y-1} \tag{3}$$

The net chemical reaction in CLC is identical to normal combustion which means that the net heat release also is the same. The distribution of heat release varies depending on metal oxide and the fuel. For Ni-, Fe- and Mn-based materials, the reaction in the FR is normally endothermic, which makes the reaction taking place in the AR strongly exothermic.

1.2 Scope of study

Combustion of solid fuels inevitably involves the formation of ash, which means that a large mass flow of ash has to be continuously discharged. In CLC with solid fuels, this discharge is expected to limit the lifetime of the oxygen carrier, since exiting ashes will – to some extent – be mixed with oxygen carrier, and the separation of the two may be difficult. Furthermore, ash fouling may also affect reactivity and lifetime of the oxygen carrier material. Hence, oxygen carriers of low cost are the primary choice for CLC with solid fuels. Natural minerals provide a low-cost option for oxygen carriers. Here, we present results using Mn ore as well as Mn ore + lime (CaO) as oxygen carriers. Mn ore has shown great potential to increase gasification rate in previous studies [14,21]. The results are then compared to previous findings using ilmenite and ilmenite + lime as oxygen carriers in the same reactor system. Lime promotes sulfur up-take from the fuel, catalyzes the water-gas shift reaction, and could possibly provide increased stability to the Mn ore particles.

The mechanical strength of the Mn ore particles is low. It is possible that Ca from lime particles could migrate to the surface of the ore and form $CaMnO_3$, which is believed to increase the particle stability. This is based on results from the Chalmers 300 W unit with manganese ore [22] and $CaMn_{0.875}Ti_{0.125}O_3$ [23] as oxygen carriers, where the latter showed less tendency to form fines.

In summary, the purpose of the study is to investigate if lime addition to ilmenite and manganese ore can improve general performance and/or structural integrity. Furthermore, by using the same batch of Mn ore particles as in a previous study, it was possible to investigate whether the mechanical stability would change as an effect of operation time.

2. Theory and experimental

2.1 The 10 kW chemical-looping combustor

The reactor system (Fig. 1) consists of a fuel reactor (FR), where the fuel is gasified by steam and gasification products are oxidized by the oxygen carrier, an air reactor (AR), where the particles are oxidized, and a riser, which brings particles back to the fuel reactor via the cyclone – a gas/solids separator – and the upper loop seal (ULS). The gas velocity in the AR and riser provides the driving force for particle circulation. The upper and lower loop seals are present in the reactor system in order to eliminate gas leakages between AR and FR.

The FR is divided into two main sections; a low-velocity section (LOVEL) which is operated as a bubbling bed, and a carbon stripper which is operated between the terminal velocities of the oxygen carrier and the char, hence enabling separation of the two types of particles. The FR is also equipped with a recirculation loop, the function of which is to return elutriated char particles to LOVEL. All reactions occur in the LOVEL, which is fluidized with steam.

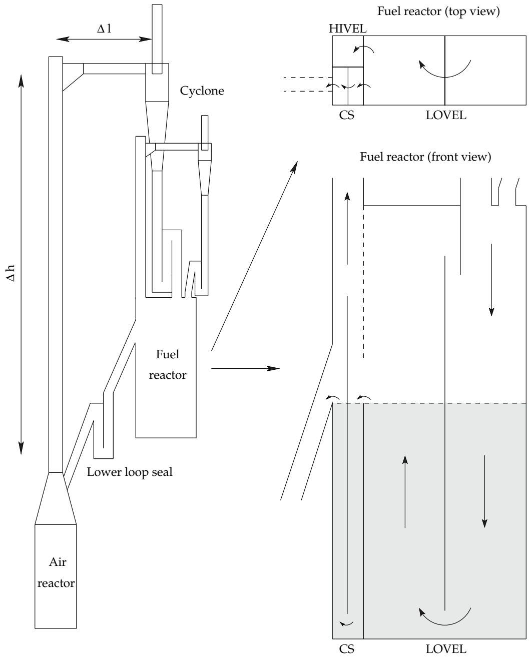

Figure 1. Principal layout of reactor system with fuel-reactor close-up. The height of the riser, Δh, is approximately 1.5 m.

A detailed description of the 10 kW unit is given in [7,14]. Exhaust gas from AR is analysed for O_2 and CO_2, whereas the FR exhaust gas analyzers measure concentrations of CO_2, CO, CH_4, O_2, H_2, and SO_2.

The solids inventory in the FR is approximately 6 kg. The total inventory in the reactor system is around 15 kg when lime is not used, and around 18-20 kg when lime is added to ilmenite or Mn ore. The mass fraction of lime was approximately 20%.

Table 1 describes the conditions and parameter variations during the experiments. u_{AR}, u_{riser} and u_{LOVEL} are superficial velocities. u_{AR} and u_{riser} change with the air flow, whereas velocity interval for u_{LOVEL} (Table 1) is due to different steam flows in the two LOVEL chambers. The steam flow in the first chamber, where the fuel enters, is lower to avoid excessive velocity around the fuel chute. The total flow of nitrogen is 23 L_n/min. Half of the flow from the loop seals is assumed to exit via the AR and riser and the other half through the FR, which means that the total flow of N_2 exiting the FR chimney is 19 L_n/min. This flow dilutes the gas originating from fuel conversion. HIVEL is a small chamber within the FR which has no purpose in the present tests, but it still needs to be fluidized.

Table 1. Operating conditions in the 10 kW unit.

P_{fuel} (kW)	T_{FR} (°C)	T_{AR} (°C)	u_{AR} (m/s)	u_{riser} (m/s)	u_{LOVEL} (m/s)	F_{air} (L_n/min)	F_{steam} (L_n/min)	F_{N2} (L_n/min)					
						AR	LOVEL	CS	ULS	LLS	HIVEL	FRLS	S.g.
4.4-9	950-1000	800-950	0.5-0.9	2.9-4.9	0.10-0.18	125-210	29	6	4	4	2	2	5

S.g.: sweep gas

F_{air} (Table 1) is directly linked to the global mass flow of oxygen carrier, $\dot{m}_{OC}$, which has a determining influence on the residence time of the char in the LOVEL. $\dot{m}_{OC}$ was 0.25-2.5 kg/min during the experiments, according to correlations below. The overall air-to-fuel ratio was well above unity in all experiments. The residence time for fluidization gas in LOVEL is approximately 2 s, which means that the residence time of volatiles and syngas from char gasification is < 2 s.

1.2 Oxygen carriers

Natural minerals offer a low-cost alternative for oxygen carriers, which, as mentioned above, is a desirable characteristic in CLC with solid fuels.

Ilmenite has been widely investigated due to low cost, good fluidizability, high melting point and low production of fines. Although no comprehensive study has been made about the long-term structural integrity of ilmenite in fluidized beds, there are indications that the lifetime of ilmenite as oxygen carrier could be thousands of hours [8,24].

Table 2. Characteristics of the oxygen carriers ilmenite and manganese ore.

Property	Units	Ilmenite	Mn ore
$\overline{d}_p$	µm	171	165
ρ_{bulk}*	kg/m^3	2050	1750
$\rho_{particle}$*	kg/m^3	3700	3200
Crushing strength	N	3.85	1.25
u_{mf}^1	m/s	0.025	0.017
u_t^2	m/s	0.85	0.62

^{1}H_2O, 970°C; ^{2}air, 900°C. *for used material

Manganese ore has high reactivity with syngas [25], and can promote the rate of gasification [14,26]. The batch of manganese ore used in the present experiments originates from Brazil. The ore has a complex mineralogy, including oxides, hydroxides, carbonates and silicates, with a predominance of cryptomelane, lithiophorite and amorphous manganese bioxides (MnO_2). The ratio Mn/(Mn+Fe) is 0.93. The original batch contained mostly MnO_2, which was reduced to Mn_3O_4 during the initial heat-up of the reactor system. It should be mentioned that the ore contains smaller amounts of potassium and barium. Table 2 shows some characteristics of the oxygen carriers.

The lime (CaO) was produced by calcination of Mexican limestone which has a density of 1900 kg/m^3, and particle size 90-200 µm.

2.3 Fuel

A Mexican pet coke was used as fuel in the experiments. Pet coke is produced by coking of feedstocks from the residue of oil refinery processes. Although not as reactive as *e.g.* bituminous coals, it has the advantage of low volatile content, which has been identified as a crucial parameter when it comes to feeding the fuel successfully into the fuel reactor in the present reactor system. Table 3 shows general characteristics of the petcoke used in the study.

Table 3. Fuel specification: proximate and ultimate analyses.

Fuel	Proximate analysis (wt-% as received)				Ultimate analysis (wt-% maf)					LHV (MJ/kg)	Φ_O	ρ_{bulk} (kg/m^3)
	C-fix	V	M	A	C	H	O	N	S			
Pet coke	83.3	11.6	1.1	3.9	87.7	3.2	0.2	1.9	6.9	33.1	1.14	780

C-fix: fixed carbon; V: volatile matter; M: moisture; A: ash. Maf: moisture and ash free. LHV: lower heating value. $\Phi_{O,}$ oxygen-to-fuel ratio, described below.

A large share of the fuel consists of fine material, *i.e.* 25 wt-% is smaller than 45 μm. The average particle diameter is 80 μm.

2.2 Performance indicators for fuel conversion

Fuel that enters the FR can follow one of three routes: (a) conversion to gas in the FR, which is the desired case, (b) conversion in the AR – some char will inevitably follow the flow of oxygen carrier to the AR where it burns to CO_2, or (c) exit the FR via the chimney as unconverted char. The fuel fraction that is converted to gas in the entire system, *i.e.* in both FR and AR, can be written as

$$\eta_{SF} = \frac{F_{CO2,AR} + F_{CO2,FR} + F_{CO,FR} + F_{CH4,FR}}{\dot{m}_{C,fuel}} \frac{M_C}{V_n} \tag{4}$$

where $\dot{m}_{C,fuel}$ (g/min) is the mass flow of carbon in the fuel to the FR, M_C (g/mole) is the molar mass of carbon and V_n is the molar volume of an ideal gas normalized at 0.1 MPa and 0°C, 22.7 L_n/mole.

Gaseous species produced in the FR are either volatile compounds or products of char gasification. Volatiles include mainly CH_4, H_2, CO and CO_2. Higher hydrocarbons are also present to smaller extent, but these are not measured. The oxygen demand,

$$\Omega_{OD} = \frac{0.5x_{CO} + 2x_{CH_4} + 0.5x_{H_2}}{\Phi_O(x_{CO_2} + x_{CO} + x_{CH_4})}, \tag{5}$$

describes the fraction of oxygen lacking to achieve complete combustion of the gas produced in the FR, where x_i is the volume fraction of gas i, Φ_0 is the molar ratio [n_{O2} required for combustion/kg fuel] / [n_C /kg fuel]. Pet coke is rich in sulfur, but in this work the fate of sulfur will not be further discussed. Ω_{OD} is related to the gas conversion efficiency in the FR, which can be defined simply as

$$\eta_{conv,FR} = 1 - \Omega_{OD}. \tag{6}$$

The CO_2 capture efficiency can be based on gas measurements of AR flue gas. The oxide-oxygen efficiency, η_{OO}, is defined as the amount of oxygen used to re-oxidize the oxygen carrier in the AR divided by the total amount of oxygen consumed in the AR,

$$\eta_{OO} = \frac{F_{air}\cdot 0.21 - F_{AR}\left(x_{CO_2,AR} + x_{O_2,AR}\right)}{F_{air}\cdot 0.21 - F_{AR}\cdot x_{O_2,AR}}, \tag{7}$$

where F_{air} is the air flow introduced in the AR and F_{AR} is the exit gas flow from the riser and cyclone. The oxygen needed for char combustion in the AR yields an O_2/C ratio of one. The oxygen needed for oxidation of the fuel yields a somewhat higher ratio (Φ_0). However, because of the incomplete oxidation in the FR, the O_2/C ratio is close to unity. Thus, the numerator in Eq. (7) represents the carbon released as gas in the FR, whereas the denominator represents the total carbon released. η_{OO} is referred to as "CO_2 capture efficiency" in the text.

3. Results and discussion

Most previous experience with the 10 kW pilot has been accomplished using ilmenite as oxygen carrier. Compared to ilmenite, fuel conversion using Mn ore as oxygen carrier is excellent. This has been seen in previous testing [14].

In this study, experiments were performed for 15.2 h. First, 9.2 h were carried out using only Mn ore as oxygen carrier, and subsequently, 6 h were accomplished using the Mn ore with lime particles as additive. In general, performance using Mn ore was similar to what was observed in the previous study. Furthermore, performance improved by addition of lime. Fig. 2 shows dry gas concentrations (top)

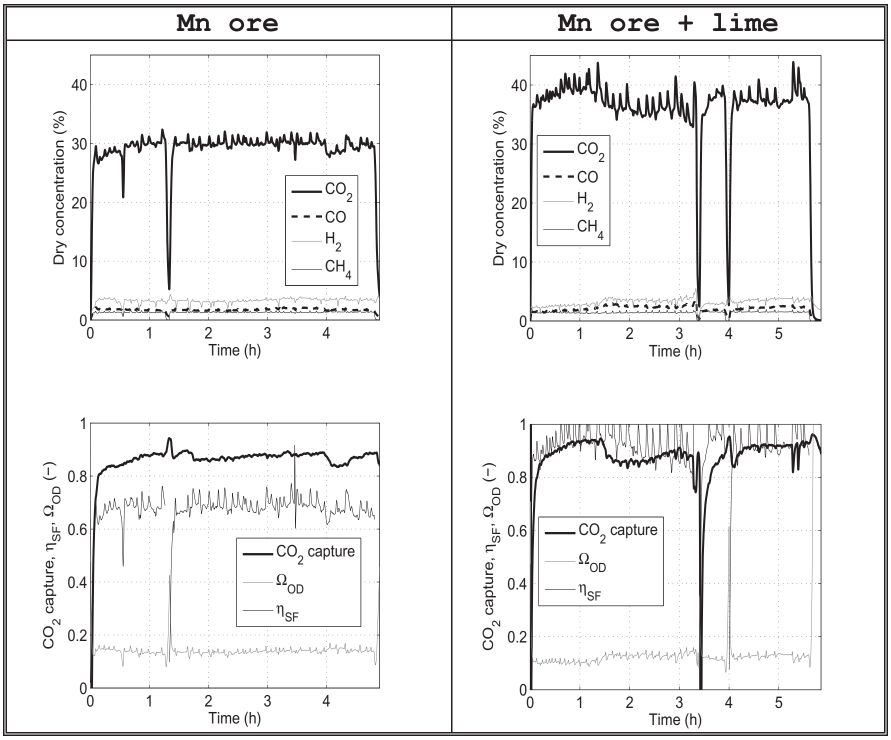

Figure 2. Gas concentrations and performance indicators using Mn ore and Mn ore + lime as oxygen carrier.

and key performance numbers (bottom) for Mn ore (left), and Mn ore + lime (right). Operating conditions are kept as stable as possible, in order to be able to compare results obtained with/without lime. The fuel flow was 645 g/h, corresponding to a fuel power of 5.9 kW. The operation temperature in the fuel reactor was approximately 960°C, except for one hour at 930°C. Gas concentrations are time averaged over 3 min in order to improve clarity.

As can be observed in Fig. 2, high CO_2 capture and improved gas conversion – *i.e.* lower oxygen demand – was achieved using Mn ore + lime. Furthermore, solid fuel conversion is very high. The concentration of CO_2 is higher so it seems as though gasification is improved, and since most operating conditions are constant, this should imply higher rate of gasification. This could be an effect of the lime. The added lime breaks into very fine particles inside the reactor system. It is possible that these particles could catalyze gasification. It should be mentioned that the lime is calcined prior to being added to the batch of oxygen carriers, and it is unlikely that CO_2 produced during the experiments originate from the lime.

The fuel flow was intentionally stopped for a few minutes and then resumed, using both Mn and Mn ore + lime. When this is done, there are no volatiles released in the fuel reactor, and hence, gases produced in the FR directly after fuel stop originate from the char. Consequently, this period provides valuable information about the oxygen demand of the char. Since the contact between syngas from char gasification and the oxygen carrier is better than contact between volatiles and oxygen carrier, the oxygen demand is much lower, as is illustrated in Fig. 3. Here, gas measurements are time averaged over 20 s. The minimum oxygen demand is 6.2% for the Mn ore case and 5.0% for Mn + lime case. These values represent the oxygen demand for syngas from char gasification, without the interference of volatiles, and they are similar to the minimum oxygen demand found for ilmenite and petcoke in [27].

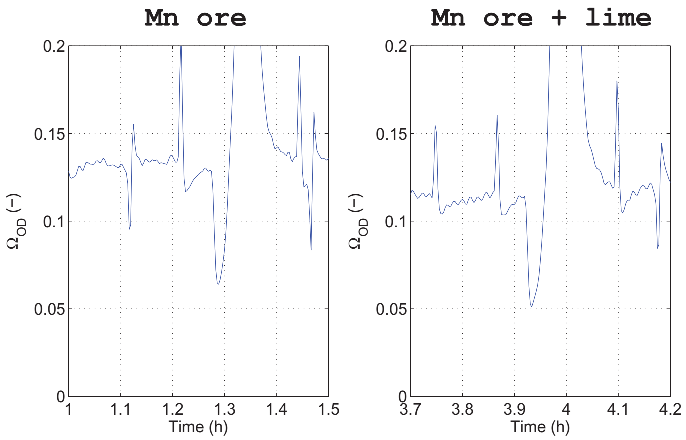

Figure 3. Minimum oxygen demand. Mn ore (left) and Mn ore + lime (right). The fuel flow is stopped between 1.26 h < t < 1.29 h (left) and 3.91 h < t < 3.93 h (right).

Table 4 compares the results obtained in this study to previous findings. Each line represents a test with duration of 20 min or more. The first five columns describes the operational settings, and the following three (shaded) reflect operational performance. It should be noted that two modes of fuel feed have been employed; above-bed and in-bed feed. The latter improves gas-solid contact and hence volatile conversion (*cf.* [14]). The global solids circulation controls the residence time of the oxygen carrier (τ_{OC}), which in turn is strongly correlated with the residence time of the char. Increasing the residence time means that there is more time for the char to gasify, and therefore, the CO_2 capture efficiency (η_{OO}) should increase.

Table 4. Comparison of oxygen carriers. Each line represents a test with duration of 20 min or more.

Fuel feed	OC	T_{FR} (°C)	P_{fuel} (kW)	τ_{OC} (min)	Ω_{OD} (-)	η_{OO} (-)	η_{SF} (-)	Source
Above -bed	Ilm	950	4.4	3.0	0.32	0.59	0.57	[14]
		950	4.4	6.2	0.29	0.67	0.54	
		950	4.4	11.1	0.28	0.72	0.51	
		1000	4.4	3.0	0.32	0.63	0.63	
	Ilm + lime	950	4.4	10.7	0.24	0.70	-	[13]
		1000	4.4	10.8	0.28	0.81	-	
In-bed	Ilm	970	5.7	5.3	0.20	0.76	0.49	[14]
		970	5.7	7.2	0.19	0.67	0.48	
		970	5.7	17.7	0.18	0.83	0.45	
		970	9.0	3.2	0.21	0.61	0.55	
		970	9.0	4.2	0.20	0.66	0.49	
		970	9.0	7.3	0.19	0.72	0.53	
		970	9.0	7.7	0.18	0.72	0.49	
	Mn	960	5.9	2.6	0.16	0.90	0.71	*This study*
		960	5.9	3.1	0.15	0.92	0.76	
		960	5.9	4.1	0.16	0.94	0.68	
		960	5.9	4.8	0.15	0.94	0.68	
	Mn + lime	960	5.9	3.4	0.13	0.88	0.90	
		960	5.9	3.7	0.13	0.92	0.93	
		960	5.9	4.7	0.10	0.93	0.97	

τ_{OC}: residence time of oxygen carrier (see Markström et al. [28]). Ilm: ilmenite: Mn: manganese ore.

Comparing Mn ore to ilmenite, it is clear that substantial improvements are seen in gas conversion, CO_2 capture, and solid fuel conversion. The most notable improvement is that of the CO_2 capture, which is increased from around 70% to around 94%. This reflects a much higher gasification rate for Mn ore, which could be explained by the presence of alkali metals – gasification catalysts – in the ore [26]. The oxygen demand observed using Mn ore in this study is somewhat higher than reported in [14]. The reason for this is higher methane concentrations in the present study compared to the previous one, which is likely due to two different gas analyzers having been used in the two studies.

Effect of lime addition. Generally, performance improves with the addition of lime; the gas conversion improves, and the solid fuel conversion increases. The trend is less clear for ilmenite. The improvement seen in gas conversion using ilmenite + lime compared to only ilmenite was explained by the catalytic effect of lime on the water-gas shift reaction [13]. Ilmenite reacts faster with H_2 than CO. Consequently, when CO is shifted to H_2, overall gas conversion improves. Furthermore, Cuadrat et al. found that the rate of gasification increases as an effect of lime addition, although the mechanism behind this is not fully understood [13].

3.1 Structural integrity of the carrier and the effect of lime addition

The structural integrity of manganese ore as oxygen carrier in CLC is poor, as has been observed in a previous work [14]. In order to investigate if fines production was subject to change with time of operation, it was decided to use the same batch of particles as in the previous work. Some fresh particles needed to be added to compensate for the particles lost as fines. However, during the 9.2 h of operation with only Mn ore as oxygen carrier, the loss of fines continued to be substantial, and no time-dependent decay could be established. Furthermore, the subsequent addition of lime to the batch of Mn ore was made to increase mechanical stability and attrition resistance, which should decrease the loss of fines, but no such decrease was seen. However, the time of operation, 6 h, may have been insufficient. During the course of the operation described here, several kilograms of oxygen carrier material were lost as fines, most of which came from the fuel reactor.

No significant difference in crushing strength was observed for Mn ore particles before and after lime addition (Table 5). If anything, crushing strength seemed to decrease.

Table 5. Crushing strength of Mn ore particles.

Oxygen carrier	Crush. strength (N)
Mn, fresh	1.2
Mn, used, before lime addition	1.1
Mn, used, after lime addition	0.9

A sample of used Mn ore and lime was investigated by X-ray photoelectron spectroscopy (XPS). First, Mn ore and lime particles were separated, hence enabling analysis of only Mn ore particles. The analyses were carried out with an ESCAPlus OMICROM system equipped with a hemispherical electron energy analyser. Although the content of calcium in the sample was high, it was mainly in the form of aluminate ($CaAl_2O_4$ and $CaAl_4O_7$ cannot be distinguished). A pattern with these two aluminates was prepared. There were no energy deviations for the sample with respect to the pattern. Manganese was in the form of a mixed-oxide MnO-Mn_2O_3. There was also $MnAl_2O_4$, although it was minority. In summary, there seems to be no interaction between calcium and manganese.

4. Conclusions

- The use of a manganese ore as oxygen carrier greatly enhanced the rate of gasification, which occurred approximately four times faster than with ilmenite. This is illustrated by the loss of char to the AR ($1-\eta_{OO}$), which is reduced from around 30% to 6%.
- Gas conversion also improved significantly using manganese ore, which is reflected in low oxygen demand: around 15%.
- By adding lime particles to the Mn ore, performance improved further. The oxygen demand decreased down to as low as 10%.
- The addition of lime to Mn ore also had a beneficial effect on the solid fuel conversion.
- Mechanical stability of the Mn ore was inferior to ilmenite, judged by the production of fines.
- The mechanical stability of the Mn particles seemed unaffected by the addition of lime particles.
- Compared to a base case with only ilmenite, the use of lime as additive to ilmenite was found to improve gas conversion as well as increase the rate of char gasification, although the extent of the improvements were marginal.

Acknowledgements

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References

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[1] Leckner B. Fluidized bed combustion: Mixing and pollutant limitation. *Prog. in Energy and Comb. Sci.* 1998; **24**: 31-61.

[2] Hotta A. Foster Wheeler's Solutions for Large Scale CFB Boiler Technology: Features and Operational Performance of Łagisza 460 MWe CFB Boiler. *Proceedings of the 20th International Conference on Fluidized Bed Combustion* 2010, Part 1, 59-70.

[3] Hossain M, de Lasa H. Chemical-looping combustion (CLC) for inherent CO2 separations – a review. *Chemical Engineering Science 63 (2008) 4433 – 4451.*

[4] Lyngfelt A, and Mattisson T. Materials for chemical-looping combustion, Chapter 17 in *Efficient Carbon Capture for Coal Power Plants, Ed. Stolten, D., and Scherer, V., WILEY-VCH Verlag GmbH & Co.. KGaA, Weinheim 2011, pages 475-504.*

[5] Adanez J, Abad A, Garcia-Labiano F, Gayan P, Diego LF. Progress in Chemical-Looping Combustion and Reforming technologies. *Progress in Energy and Combustion Science*, *Volume 38, Issue 2*, *April 2012*, *Pages 215-282.*

[6] Linderholm C, Mattisson T, and Lyngfelt A. Long-term integrity testing of spray-dried particles in a 10 kW chemical-looping combustor using natural gas as fuel. *Fuel* 88 (2009) 2083-2096.

[7] Berguerand N, Lyngfelt A. Design and operation of a 10 kWth chemical-looping combustor for solid fuels – Testing with South African coal. *Fuel 2008; 87:2713-2726.*

[8] Berguerand N, Lyngfelt A. The use of Petroleum coke in a 10 kWth Chemical-Looping Combustor. *International Journal of Greenhouse Gas Control 2008; 2(2):169-179.*

[9] Shen L, Wu J, Xiao J. Experiments on Chemical-looping Combustion of Coal with a NiO based Oxygen Carrier. *Combustion and Flame 2009; 156(3): 721-728.*

[10] Shen L, Wu J, Xiao J, Song Q, and Xiao R. Chemical looping combustion of biomass in a 10 kWth reactor with iron oxide as an oxygen carrier. *Energy Fuels* (2009) 23:2498-2505.

[11] Wu J, Shen L, Xiao J, Wang L, and Hao J. Chemical looping combustion of sawdust in a 10 kWth interconnected fluidized bed. *Huagong Xuebao/CIESC Journal* (2009) 60:8, 2080-2088.

[12] Cuadrat A, Abad A, García-Labiano F, Gayán P, de Diego L-F, Adánez J. Effect of operating conditions in Chemical-Looping Combustion of Coal in a 500 Wth unit. *Int. J. Greenhouse Gas Control* (2012), 6(4), 153-163.

[13] Cuadrat A, Linderholm C, Abad A, Lyngfelt A, Adánez J. Influence of limestone addition in a 10 kWth Chemical-Looping Combustion unit operated with pet coke. *Energy & Fuels* 25:10 (2011) 4818–4828

[14] Linderholm C, Lyngfelt A, Cuadrat A, Jerndal E. Chemical-looping combustion of solid fuels – operation in 10 kW unit with two fuels, above-bed and in-bed fuel feed and two oxygen carriers, manganese ore and ilmenite. *Fuel* 2012; 102: 808-822.

[15] Markström P, Lyngfelt A, and Linderholm C, Chemical-Looping Combustion in a 100 kW unit for Solid Fuels. *21st International Conference on Fluidized Bed Combustion,* Naples, June 3-6, 2012.

[16] Sozinho T, Pelletant W, Gauthier T, Stainton H. Main results of the 10 kW coal pilot plant operation. *Int. Conf. on Chemical Looping,* 26-28 Sept., 2012, Darmstadt.

[17] Orth M, Ströhle J, Epple B. Design and operation of a coal-fired 1 MWth chemical looping pilot plant. *Int. Conf. on Chemical Looping,* 26-28 Sept., 2012, Darmstadt.

[18] Thon A, Kramp M, Hartge EU, Heinrich S, Werther J. Operational experience with a coupled fluidized bed system for chemical looping combustion of solid fuels. *Int. Conf. on Chemical Looping,* 26-28 Sept., 2012, Darmstadt.

[19] Mayer F, Bidwe A, Schopf A, Taheri K, Zieba M, Scheffknecht G. Adaptation of a 10 kWth DFB system for CLC to solid fuels and comparison of a new micaceaous iron oxide and ilmenite with respect to syngas conversion. *Int. Conf. on Chemical Looping,* 26-28 Sept., 2012, Darmstadt.

[20] Xiao R, Chen L, Saha C, Zhang S, Bhattacharya S, Pressurized chemical-looping combustion of coal using an iron ore as oxygen carrier in a pilot-scale unit. *Int. Journal of Greenhouse Gas Control*, Volume 10, September 2012, Pages 363-373.

[21] Arjmand M, Leion H, Lyngfelt A, and Mattisson T, Use of Manganese Ore in Chemical-looping Combustion (CLC) – Effect on Steam Gasification. *Int. Journal of Greenhouse Gas Control,* 8 (2012) 56-60.

[22] Rydén M, Lyngfelt A, Mattisson T. Combined manganese/iron oxides as oxygen carrier for chemical-looping combustion with oxygen uncoupling (CLOU) in a circulating fluidized bed reactor system. *Energy Procedia* 4 (2011) 341–348.

[23] Rydén M, Lyngfelt A, and Mattisson T. $CaMn_{0.875}Ti_{0.125}O_3$ as oxygen carrier for chemical-looping combustion with oxygen uncoupling (CLOU) – experiments in continuously operating fluidized bed reactor system. *International Journal of Greenhouse Gas Control* 5 (2011) 356-366.

[24] Cuadrat A, Abad A, Adánez A, de Diego LF, García-Labiano F, Gayán P, Behavior of ilmenite as oxygen carrier in chemical-looping combustion. *Fuel Processing Technology*, Volume 94, Issue 1, February 2012, Pages 101–112.

[25] Leion H, Mattisson T, and Lyngfelt A. The use of ores and industrial products as oxygen carriers in chemical-looping combustion. *Energy & Fuels 23 (2009) 2307-2315.*

[26] Arjmand M, Leion H, Mattisson T, and Lyngfelt A. Evaluation of different manganese ores in chemical-looping combustion (CLC) for solid fuels. *2nd International Conference on Chemical Looping*, 26-28 September 2012, Darmstadt.

[27] Linderholm C, Cuadrat A, and Lyngfelt A. Chemical-looping combustion of solid fuels in a 10 kW_{th} pilot – batch tests with five fuels. *Energy Procedia* 4 (2011) 385-392.

[28] Markström P, Berguerand N, and Lyngfelt A. The Application of a Multistage-Bed Model for Residence-Time Analysis in Chemical-Looping Combustion of Solid Fuel. *Chem.Eng.Sci. 65 (2010) 5055-5066.*