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Chemical Looping Combustion of Sulphurous Solid Fuels using Spray-Dried Calcium Manganate Particles as Oxygen Carrier

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Abstract

A perovskite material, $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$, has been investigated as oxygen carrier in a 10 kW chemical looping pilot using sulphurous fuels. Operation with inert gas in the fuel reactor showed that the material released significant amounts of gas-phase oxygen, indicating CLOU properties. Stable operation with fuel was performed during 29 hours with performance superior to previously tested oxygen carriers like ilmenite. A slight deterioration of the conversion was detected during the experiments, which can be attributed to the accumulation of sulphur in the oxygen carrier. However, a regeneration test with non-sulphurous fuel showed that this process is reversible and that the oxygen carrier can be regenerated after being subjected to sulphurous fuels.

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Keywords: Chemical looping combustion; CLOU; carbon capture; perovskite; oxygen carrier

1. Introduction

The emissions of anthropogenic CO_2 are widely considered an important contributor to global warming. One possible mitigation strategy is the large-scale implementation of carbon capture and storage (CCS), in which CO_2 from point sources is separated from the flue gas, compressed and stored in deep geological formations. In effect, CO_2 emissions to the atmosphere can be minimized while still using fossil fuels for heat and power generation.

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If the gas separation is carried out in a conventional way, for example by the use of cryogenic distillation, adsorption or membrane separation, this step is associated with a considerable loss of plant efficiency.

Chemical looping combustion (CLC) aims at minimizing that loss of efficiency by capturing CO₂ without gas separation. This is possible because fuel and combustion air are not mixed. Instead, the oxygen is transferred to the fuel by means of an oxygen carrier, which typically consists of metal oxide particles. 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.

If a reaction between oxygen carrier and a solid fuel is to be achieved at the desired rate, solid-solid contact between the reactants is not sufficient. In conventional CLC, the solid fuel therefore has to be gasified prior to reacting with the oxygen carrier. The gasification reaction is comparably slow, which can lead to a loss of char to the air reactor or the fuel reactor exhaust.

Chemical looping with oxygen uncoupling (CLOU) is a way to avoid the gasification step. As opposed to conventional CLC, the oxygen carriers used in CLOU are not only transporting chemically bound oxygen which can be used for the oxidation of gaseous compounds, but are able to release gas-phase oxygen under relevant conditions. The oxygen released can oxidize the solid fuel particles directly, thus eliminating the need for a gasification step, which could facilitate the system design, improve the performance and reduce cost.

Thermodynamics limit the range of possible CLOU oxygen carrier materials, which both have to take up oxygen in the air reactor and release it in the fuel reactor. The structure of perovskites materials, which can be written ABO_{3-δ}, makes those materials suited as CLOU oxygen carriers [1]. In the structural formula, A is a larger and B a smaller cation. δ describes the degree of oxygen deficiency, which among others depends on temperature and pressure and thus provides the above-mentioned CLOU properties. Above that, the same requirements as for conventional CLC oxygen carriers have to be met: the particles should be sufficiently reactive, environmentally benign, non-toxic, mechanically durable and easily fluidized. Especially in the combustion of solid fuels, cost plays an important role because oxygen carrier will be continuously lost in ash separation.

Of all known CLC oxygen carriers, ilmenite has been tested most extensively, which can be attributed to its low cost, high durability and non-toxicity [2, 3, 4, 5, 6, 7]. When used with solid fuels, however, ilmenite could not perform full gas conversion. The need for gasification also slows down the solid fuel conversion, which leads to carbon slip to the air reactor.

In the attempt to improve the overall process performance, the search for new oxygen carriers plays an important role. Experiments with solid biomass fuels and a copper-based CLOU oxygen carrier have been carried out by Adánez-Rubio et.al. [8]. Calcium manganate and variations of that material have been tested in both batch reactors [9, 10] and continuous units with gaseous fuels and solid biomass fuels [11, 12, 13, 14] with promising results concerning fuel conversion and durability. Moreover, the mechanical properties of the material have been investigated in jet-cup attrition tests [15].

The oxygen carrier tested contains large amounts of calcium, which is known to bond with sulphur. As sulphur is present in most solid fossil fuels, the sulphur tolerance of oxygen carriers for CLC/CLOU of these fuels is a crucial point. If the oxygen carrier is irreversibly deactivated by sulphur addition during operation, it might have to be replaced at a higher rate, leading to costs that render the oxygen carrier unsuitable.

Sundqvist [16] and Arjmand [17] have examined the sulphur tolerance of calcium manganates in a batch reactor and found a decrease in reactivity, which is likely to be caused by the formation of CaSO₄.

The purpose of this study is the investigation of both the overall performance of calcium manganate in conjunction with sulphurous fuels when used in a continuous chemical looping unit and in particular the effect of sulphur on the oxygen carrier.

2. Experimental

2.1. 10 kW reactor system

The pilot, which was the world's first chemical-looping combustor for solid fuels, 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, most of the fuel is oxidized to CO_2 and H_2O . The char remaining after devolatilization is either gasified followed by oxidation of the gasification products by the oxygen carrier (CLC operation) or burnt with released oxygen (CLOU operation). Either way, this section is usually fluidized with steam. The particles are forced to pass under a vertical wall in the fuel reactor (s. Fig. 1) to remain in the bed long enough, thus ensuring sufficient gas-solids contact. To separate char and oxygen carrier particles, a carbon stripper, which is fluidized by nitrogen, is integrated into the fuel reactor. The less dense char particles entrained in the carbon stripper are reintroduced to the low velocity section via a cyclone and a small loop seal, whereas the reduced particles enter the air reactor again.

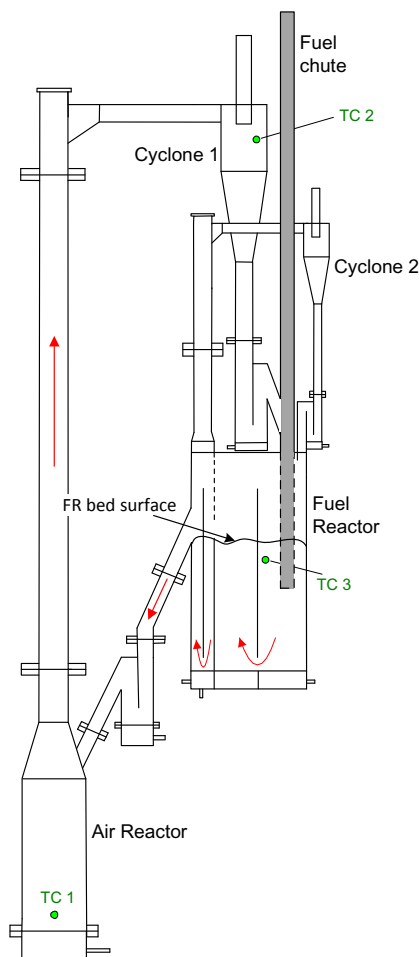


Fig. 1 10 kW solid fuel chemical looping combustor. TC 1-3 mark thermocouple positions

Fuel is introduced into the fuel-reactor via a coal screw and a fuel chute which extends into the fluidized bed. The operating temperature is measured by three thermocouples located in the air reactor, fuel reactor and air reactor cyclone. Fluidization behaviour, solids circulation and inventory can be estimated from a number of 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 both used to collect condensate from fuel conversion and steam fluidization and to impose a hydrostatic pressure on the fuel reactor exhaust, thus creating the desired pressure difference between the outlets of the fuel and air reactor.

A part of the exhaust gas streams is led through gas conditioning systems and then analysed by IR- (CO , CO_2 and CH_4) or paramagnetic analysers (O_2). Apart from that, gas samples can be withdrawn and analysed in detector tubes.

As the heat losses are higher than the thermal power generated by fuel addition, the unit is enclosed in an electrically heated furnace, which also is used to heat up the unit initially. Further description of the unit can be found elsewhere [18, 19].

Previous operational experience in this unit has been achieved using different natural minerals as oxygen carrier – mainly ilmenite and manganese ores.

2.2. Oxygen carrier

The oxygen carrier particles had previously been used in combustion experiments with biomass fuel containing very little sulphur. In those experiments, fuel was added during 37 hours while hot fluidization duration was 73 hours, after which the particles were still in a good state [14]. The particles were produced by spray-drying and calcination for four hours at 1300°C . The volume-weighted mean diameter was determined to $154\ \mu\text{m}$; crushing strength was $1.6\ \text{N}$ and the bulk density $1.97\ \text{g/cm}^3$. A particle size distribution is displayed in Fig. 2

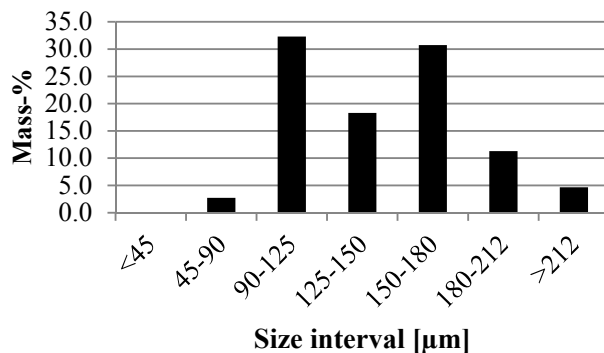


Fig. 2 Particle size distribution of fresh oxygen carrier particles

2.3. Fuels

In this study, two different fuels were used: Mexican petroleum coke and a mix of 80 mass-% Swedish wood char and 20 mass-% petroleum coke corresponding to a sulphur content usually found in hard coal. A proximate and ultimate fuel analysis is displayed in Table 1.

Table 1 Proximate and ultimate fuel analysis

[Mass-%]	Pet coke	Wood char
Fixed carbon	83.3	73.9
Volatiles	11.6	16.7
Moisture	1.1	3.9
Ash	3.9	5.5
C	84.2	78.7
H	3.2	2.9
O	0.2	8.6
N	1.84	0.4
S	6.6	0.03
LHV [MJ/kg]	33.078	29.84

The wood char was milled and mixed with the pet coke before being fed to the reactor by means of a screw feeder.

2.4. Key performance indicators

In general terms, the performance evaluation of a chemical looping unit is based on the analysis and quantification of the fuel components which are not converted to their highest stable oxidation state. Instead of being gasified and burned in a reaction with the oxygen carrier, the fuel particles can evade a conversion to the desired combustion products using different routes. Having these possible reasons for decreased performance in mind, the reactor system can be evaluated by calculation of some key indicators:

- a) The volatiles and the gasification products, respectively, might react incompletely, mainly resulting in emissions of CO, CH₄ and H₂. This can be addressed by calculation of the *oxygen demand*, describing the amount of oxygen which is lacking to fully oxidize the main species present in the gasified fuel:

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

in which Φ_0 expresses how many moles of oxygen are needed to fully oxidize the fuel in proportion to moles of carbon in the fuel. This means that Φ_0 is 1 for pure carbon and increases for higher contents of non-carbon combustibles in the fuel. As an alternative measure, the *gas conversion*, defined as $\eta_{Gas} = 1 - \Omega_{OD}$, can be used. In practice, the calculated percentage of lacking oxygen would have to be supplied by an air separation unit in a subsequent oxygen polishing step.

- b) As the global circulation forces both fuel and oxygen carrier particles to pass from the fuel reactor into the air reactor, some particles – mainly containing devolatilized char – will enter the air reactor and thus be oxidized by air. The *oxide oxygen efficiency* is defined as the amount of oxygen which is used to oxidize the oxygen carrier divided by the total amount of oxygen consumed in the air reactor and can be calculated to:

$$\eta_{OO} = \frac{0.21 - x_{O_2,AR} - x_{CO_2,AR}}{0.21 - x_{O_2,AR} - 0.21x_{CO_2,AR}}$$

Following that definition, η_{OO} is solely dependent on gas concentrations, which facilitates an accurate calculation. Following the explanation made in [5], η_{OO} will be referred to as *carbon capture efficiency*.

- c) Loss of fuel in the form of elutriated char particles may occur via 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 in the fuel.

$$\eta_{SF} = \frac{F_{C,FR} + F_{C,AR}}{F_{C,FUEL}}$$

The present reactor system is neither equipped with gas flow measurements on the exhaust side or fuel feed flow measurements. Consequently, this study does not focus on the evaluation of η_{SF} .

2.5. Operating parameters

With respect to the oxygen carrier's density and the theoretical considerations found in [18], around 5.8 kg of particles should be found in the fuel reactor during operation. The unit's fuel power was calculated as an average of

each test session and varied between 3.5 and 7.5 kW_{th}, corresponding to a solids inventory in the fuel reactor of 0.77 to 1.66 t/MW_{th}.

Char and oxygen carrier may leave the system both via the fuel reactor and the air reactor. Particles collected in the air reactor outlet filters are dry and contain a negligible amount of char, which is why they were reintroduced into the system. In the fuel reactor outlet, however, both oxygen carrier and fuel particles are mixed with condensate from steam fluidization and would therefore have to be dried before recycling, which is impractical during operation.

Thus, fresh particles were added to keep the solids inventory stable. During 29 hours of fuel operation, 3 kg of fresh particles were added, which corresponds to a make-up stream of about 0.103 kg/h. The system had to be electrically heated for 2-2.5 hours to reach the desired temperature of 950-970°C. During that time, the whole system was fluidized with air. Before fuel operation started, the fluidization gas of the fuel reactor, carbon stripper and loop seals was switched to nitrogen for some minutes after which the fuel reactor fluidization was changed to steam. Fuel addition was started as soon as all gas concentrations had normalized.

3. Results and discussion

In the case of CaMn_{0.9}Mg_{0.1}O_{3-δ}, the calcium cation might bond with SO₂ from the combustion process to form CaSO₄, thus inactivating the oxygen carrier. Sulphur poisoning of perovskite materials has been reported [20, 21, 22] and is explained by sulphate formation.

The diagram depicted in Fig. 3 shows the stable regions of CaSO₄, CaS and CaO as a function of O₂ and SO₂ partial pressures.

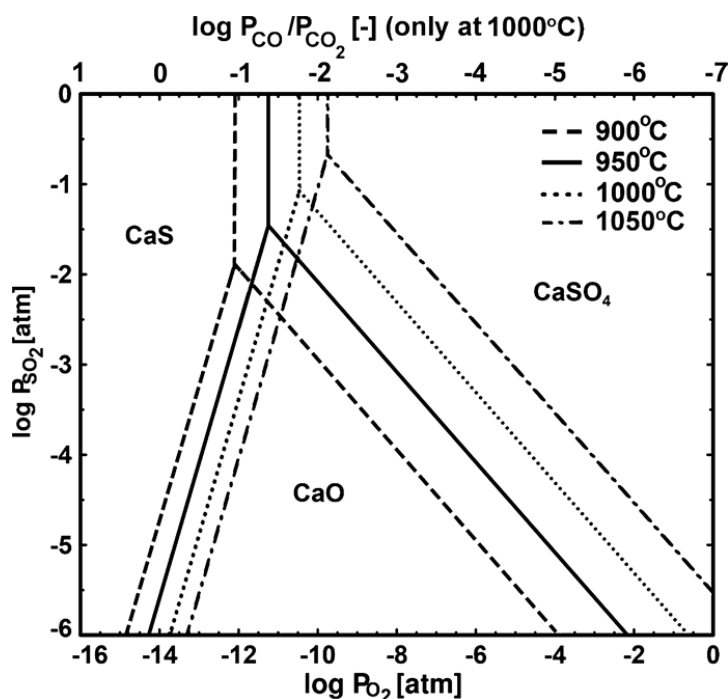


Fig. 3 Predominance diagram for the system Ca-O-S [17]

Higher temperatures favour the formation of CaO at certain SO₂ and O₂ partial pressures. Considering that CaMn_{0.9}Mg_{0.1}O_{3-δ} should behave similarly as CaO [17], it can be assumed that operation at higher temperatures and mildly reducing conditions, i.e., $P_{CO}/P_{CO_2} \approx 0.01$ should allow for combustion of sulphurous fuels without

poisoning and deactivating the oxygen carrier. Above that, CaSO_4 already formed should decompose again according to Fig. 3, making a regeneration of poisoned oxygen carrier particles possible.

To investigate the sulphur tolerance of $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$, 29 hours of experiments with fuels containing sulphur in different concentrations were conducted. An additional test with low-sulphur biomass as fuel was carried out after those experiments to investigate the possibility of regenerating a poisoned oxygen carrier. Assuming that sulphur exiting the system in the regeneration experiment would have to originate from decomposing solid sulphur species in the oxygen carrier, the SO_2 and H_2S contents of the exhaust gases were monitored by online gas measurements and detector tubes.

3.1. Continuous operation with sulphurous fuels

Fig. 4 shows the oxygen demand and carbon capture in a representative experiment with a mixture of 20 mass-% pet coke and 80 mass-% wood char, resulting in a sulphur content of about 1.3 mass-%. The corresponding gas concentrations are shown in Fig. 5

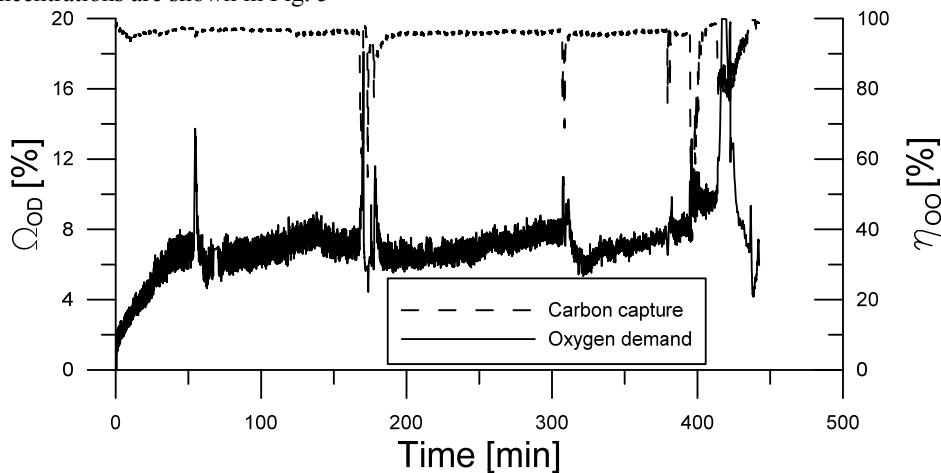


Fig. 4 Oxygen demand and carbon capture during experiment with sulphurous fuel (tests 36-38)

The only parameter changed during that experiment was the fuel feeding speed, which can be seen clearly as sudden variations in CO_2 -concentration in Fig. 5. Table 2 shows all tests which were included in the evaluation, i.e., in which stable operation was reached.

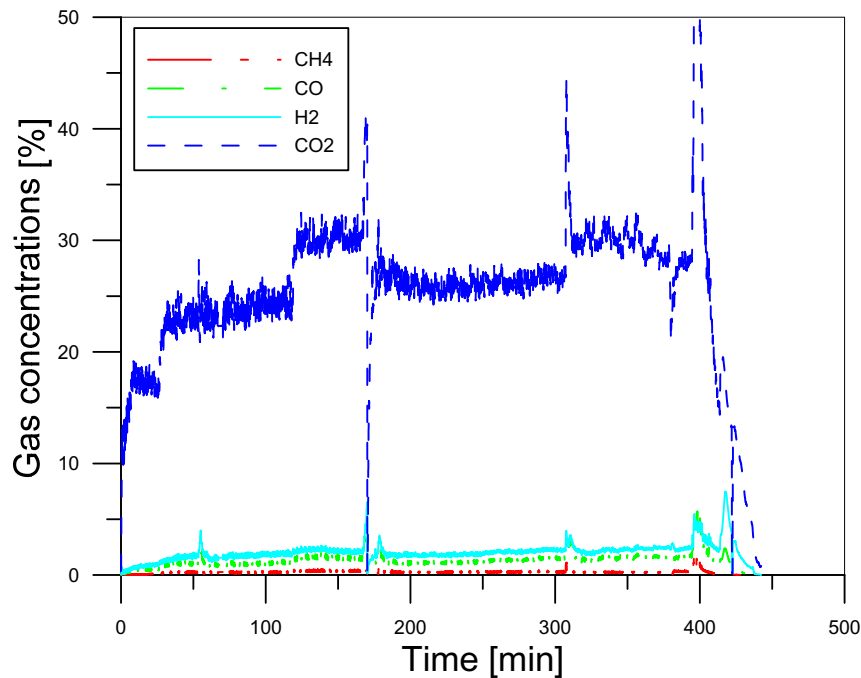


Fig. 5 Gas concentrations during experiment with sulphurous fuel (tests 36-38)

Table 2 Compilation of tests with sulphurous fuels

Test #	Fuel	T_FR [°C]	Ω_{OD} [%]	η_{oo} [%]	Duration [min]
33	80/20	972	5.13	97.39	32
34	80/20	962	5.19	98.06	32
35	80/20	969	6.88	96.11	58
36	80/20	964	6.60	96.71	86
37	80/20	962	7.35	94.83	51
38	80/20	966	7.02	95.36	212
39	80/20	948	6.48	95.19	24
40	80/20	954	6.37	89.25	59
41	Pet coke	961	8.46	88.45	133
42	Pet coke	957	7.71	83.49	202
43	Pet coke	958	7.82	75.84	41
44	Pet coke	955	9.05	78.55	107
45	Pet coke	933	10.13	75.26	75
46	Pet coke	961	9.64	82.09	14
47	Pet coke	951	11.17	83.48	54
54	80/20	1031	4.54	98.86	40
55	80/20	973	6.25	51.43	28

When using the manufactured mix of 80 mass-% wood char and 20 mass-% petroleum coke, an oxygen demand of little more than 5% could be reached at best, leaving high temperature tests aside. The lowest oxygen demand

when using pure pet coke was around 7.7%. Those results can be compared to previous experiments with the same oxygen carrier and pure wood char in this unit, which yielded an oxygen demand of around 2%. Previous operation with ilmenite in a 100-kW unit [23], showed a significantly better conversion with wood char as compared to pet coke. The reactivity of ilmenite is not believed to be affected by sulphur and therefore the difference is likely explained by other differences between the fuels. Thus, the poorer conversion found in the present tests with sulphurous fuel, i.e. pet coke, is expected and likely not explained by the sulphur content but by other fuel properties. When using ilmenite as oxygen carrier and the same pet coke as fuel [2, 24] in the 10 kW unit, the system's performance was considerably lower, with a minimum oxygen demand of 23.6%.

The results of all experiments which were conducted with sulphur containing fuels, for better comparability excluding high and low temperature tests, are depicted in Fig. 6.

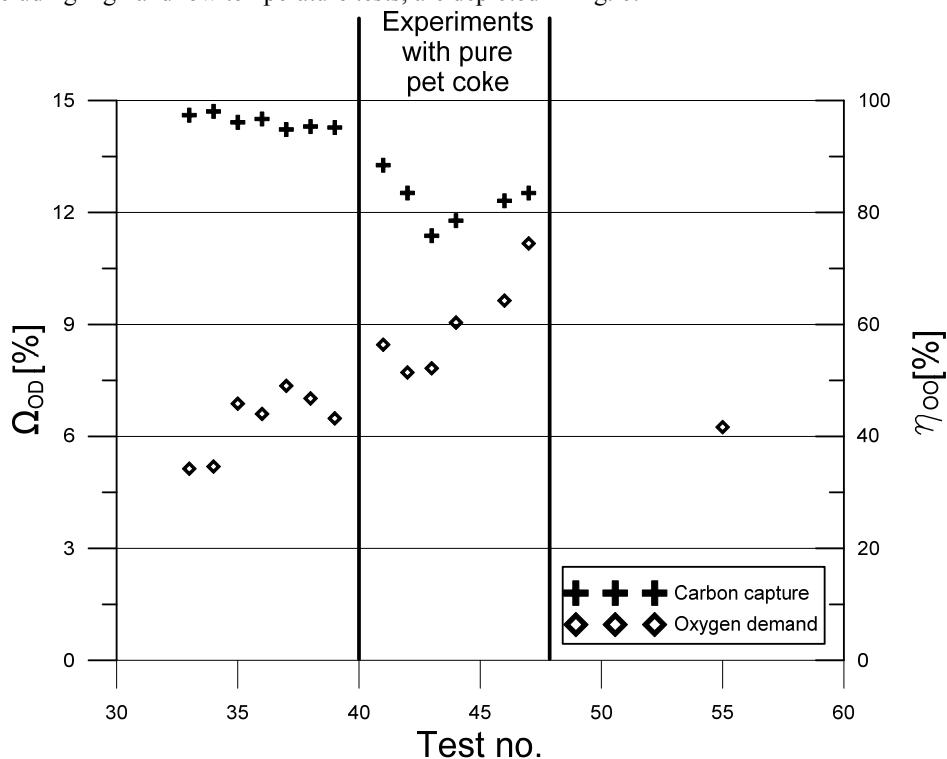


Fig. 6 Average values for oxygen demand and carbon capture for all sulphur experiments ($T_{FR} \approx 950-970^\circ\text{C}$)

All experiments shown were made in a narrow enough fuel reactor temperature interval to exclude a considerable temperature dependency. Other parameters known to have an influence on the system's performance like solids circulation or fuel reactor pressure drop were kept as stable as possible. Starting at very favourable initial values for Ω_{OD} and η_{OD} , a weak trend towards worse system performance can be observed with time. It is, however, unclear if this decline can be attributed to the amount of sulphur aggregating in the oxygen carrier or to normal fluctuations in other operating parameters such as temperature or solids circulation. The general difference in performance between tests with 80/20-mix and pet coke was expected. Detector tube measurements showed only low levels of sulphurous gas species in the fuel reactor exhaust gases. This supports the theory of sulphur accumulation and poisoning of the oxygen carrier. In the last experiment (test no. 55), which was conducted after the sulphur regeneration test, the oxygen demand had dropped approximately to the base level. In this test, carbon capture efficiency could not be calculated due to a gas leakage.

3.2. Regeneration experiment with wood char

According to the theory presented above, a regeneration test, partially at high temperature ($T_{FR} \approx 1030^\circ\text{C}$), with low-sulphur biomass as fuel was made to investigate the possibility of oxygen carrier regeneration. Fig. 7 shows the oxygen demand and carbon capture during that test, both of which were in the same range as in previous biomass tests.

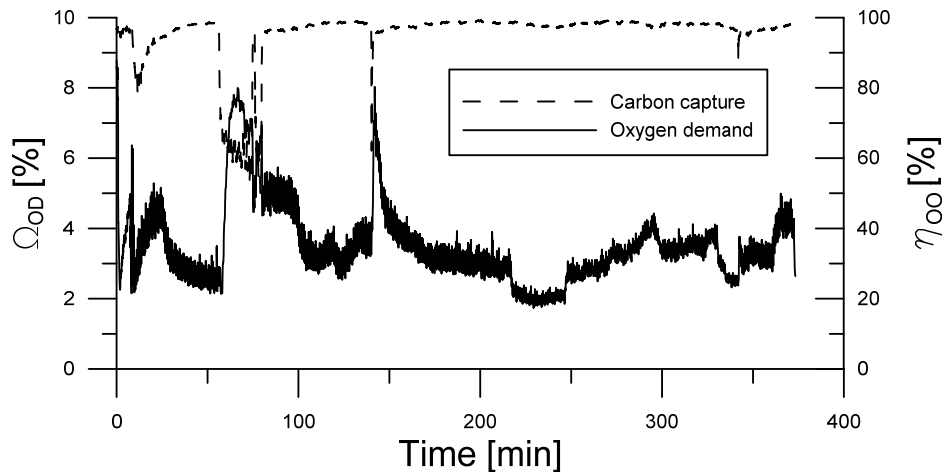


Fig. 7 Oxygen demand and carbon capture during regeneration test (tests 48-53); increased air reactor flow between 220 and 245 minutes

The high temperature of 1030°C was maintained between approximately 180 and 280 minutes in the graph shown above. At two occasions ($t \approx 60$ and 145 min), operational problems in the form of gas leakage to the air reactor were experienced. A distinct and permanent change in the performance of the system could not be detected. Both oxygen demand and carbon capture efficiency remained in the same range as in the beginning of the regeneration test. Similar results had also been obtained in previous tests with wood char in the same unit [14]. During the experiment, the sulphur content in the exhaust gases was measured every fifth minute, s. Fig. 8.

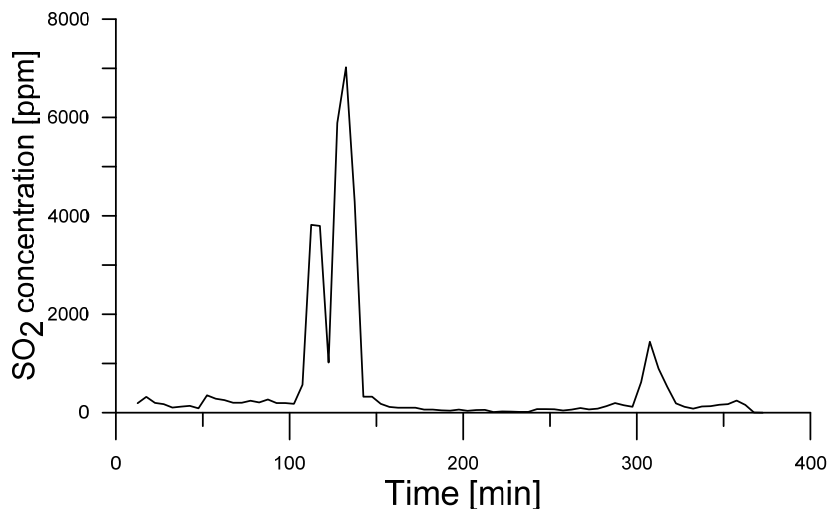


Fig. 8 SO_2 concentration during regeneration experiment (tests 48-53). Measurements were made every fifth minute

After around 100 minutes, in which the SO₂ levels ranged from 100 to 350 ppm, values of over 7000 ppm were measured although the fuel did not contain any significant amounts of sulphur. The highest levels were reached before the fuel reactor temperature was increased to 1030°C, which could mean that the use of a biomass fuel rather than the elevated temperature caused the sulphur release.

To further investigate whether sulphur was accumulated in the oxygen carrier while burning sulphurous fuels before being released in the regeneration experiment, four particle samples elutriated from the air reactor during different operational periods were analysed: Sample 1 was taken after previous experiments with biomass, sample 2 after around 3.5 hours of experiments with the 80/20-mixture, sample 3 after the last experiment with pure pet coke and sample 4 after the regeneration test at high temperature. As can be seen in Table 3, the sulphur content increased when sulphurous fuels were used, and decreased during the regeneration test. This is consistent with the gas measurements indicating low concentrations of sulphur compounds when burning sulphurous fuels as well as the release of SO₂ when burning wood char.

Table 3 Ultimate analysis (C,H,N and S) of particles elutriated from the air reactor at different tests

[Mass-%]	Sample 1	Sample 2	Sample 3	Sample 4
C	<0.1	0.2	5	0.5
H	<0.1	<0.1	<0.1	<0.1
N	<0.1	<0.1	0.1	<0.1
S	0.216	0.294	2.261	1.636

3.3. CLOU operation

Most of the experiments were conducted with steam fluidization in the fuel reactor. However, in one experiment, the ability of the oxygen carrier to oxidize the fuel relying on the release of gaseous oxygen was tested as well by fluidizing the fuel reactor with nitrogen and thus essentially stopping fuel gasification. The 80/20-mix was used as fuel in this test.

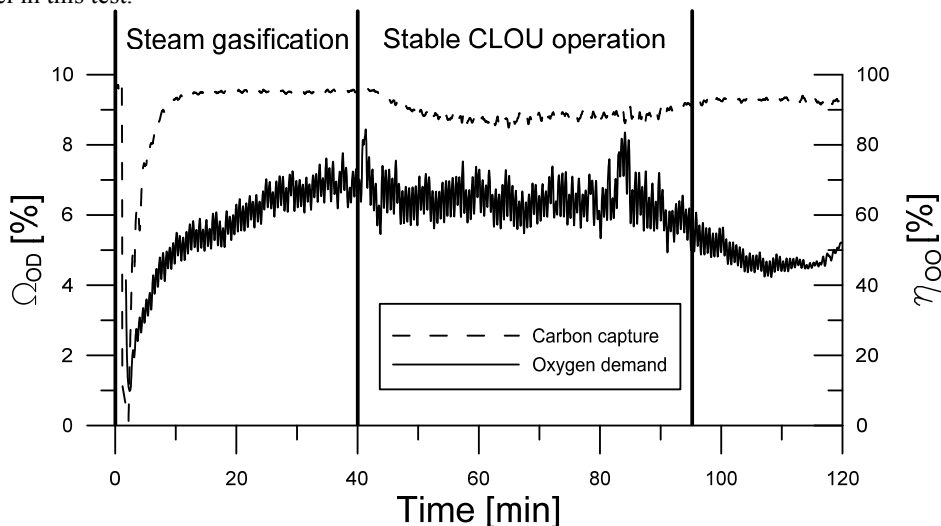


Fig. 9 Oxygen demand and carbon capture during tests 39-40. Nitrogen fluidization between $t=40$ and 120 minutes

Stable operation was reached between $t=40$ -95 minutes, before the fuel tank started emptying, which in this unit is characterized by a steady decline rather than a sudden stop of the fuel flow. While the oxygen demand averaged at 6.4% during that period and thereby was in the same range as for steam fluidization of the fuel reactor, the carbon capture fell to 89% as compared to around 95% in the previous experiments. Also, the volume flow of carbon

containing gases in the fuel reactor exhaust gas decreased with about 20.6%, meaning that less solid fuel was converted to gas in the fuel reactor during CLOU operation. Both results indicate that fuel conversion without steam fluidization was slower and thus that the release of oxygen in the fuel reactor was not sufficiently fast to reach the same levels of fuel conversion in pure CLOU operation as with steam fluidization. This is in line with previous findings for calcium manganate [10], which indicated that the release of oxygen for that material is slower than for copper-based oxygen carriers. On the other hand, the test clearly shows that a substantial fraction of the fuel was converted via the CLOU mechanism. The solid fuel conversion based on both air reactor and fuel reactor exhaust gases as defined in chapter 2 only decreased by 9.7%. This suggests that CO₂ instead of steam might be used to fluidize the fuel reactor, which would be an advantage with respect to energy efficiency and costs.

Apart from that experiment, the material's CLOU properties were also examined by measurements of the oxygen release in an inert atmosphere, i.e., when fluidizing the fuel reactor with nitrogen and without adding fuel. The oxygen concentration ranged from 2.5 to 3.8% at temperatures of 950-970°C and was not dependent on whether the oxygen carrier had been subjected to sulphur or not.

4. Conclusions

CaMn_{0.9}Mg_{0.1}O_{3-δ} has been investigated with respect to its suitability as oxygen carrier in chemical looping combustion. The system performance was considerably higher as compared to previously tested oxygen carriers like ilmenite, both in the beginning and in the end of the experimental series. An oxygen demand as low as 5% could be reached under stable operating conditions, whereas the carbon capture efficiency peaked at around 98%.

The oxygen carrier was susceptible to sulphur poisoning. The extent to which the accumulation of sulphur in the oxygen carrier worsened its performance remained unclear: while a certain trend towards higher oxygen demands and lower carbon capture could be detected, the reactivity towards biomass remained essentially unchanged during and after a regeneration experiment with biomass as fuel. The uptake and release of sulphur could be verified both by gas measurements and by analysis of the oxygen carrier particles.

Operation purely based on the CLOU effect, i.e., the direct combustion of solid fuel particles with gaseous oxygen, was possible. Due to an insufficient oxygen release rate, this led to slightly decreased carbon capture and solid fuel conversion. It can be concluded that the tested oxygen carrier could be used to enhance the performance of conventional CLC with steam gasification but also for genuine CLOU operation, e.g. with CO₂ fluidization in the fuel reactor. The decision which solution to choose would then result from balancing the effect of lower carbon capture efficiency and solid fuel conversion with the cost for steam generation.

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