CaMnO3-δ Made from Low Cost Material Examined as Oxygen Carrier in Chemical-looping Combustion

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$CaMnO_{3-\delta}$ made from low cost material examined as oxygen carrier in Chemical-Looping Combustion

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Abstract

Carbon Capture and Storage is a promising method to limit the increasing amount of greenhouse gases in the atmosphere. In this method high purity carbon dioxide is captured at large emission sources, e. g. fossil fuelled power plants. The carbon dioxide can then be transported to a long term storage site, rather than being emitted to the atmosphere. Among the different alternatives for obtaining high purity carbon dioxide during combustion of fossil fuels, Chemical-looping Combustion (CLC) is one of the most promising. Here, the oxygen needed to oxidize a fuel is provided by a solid oxygen carrier. The oxygen carrier is subsequently circulated to another reactor where it is reoxidized with air. By separating these two operations mixing of the combustion products and the nitrogen in the air is avoided. An energy demanding gas separation is thus not necessary.

The most crucial part of Chemical-looping Combustion is the solid oxygen carrier. The oxygen carrier should have high reactivity with fuel and oxygen, sufficient oxygen carrying capacity and preferably also low cost. Furthermore it is important that it is able to withstand the tough conditions it is exposed to in a hot fluidizing environment, both with respect to physical attrition and chemical degradation. The most commonly suggested setup of Chemical-looping Combustion is a dual fluidized bed system where gas velocities and mechanical abrasion can be high. When the technology was first demonstrated, nickel oxide based oxygen carriers were typically used. But as nickel is quite costly as well as potentially harmful, alternatives have been sought after.

In 2009 Leion et al. [1] investigated an oxygen carrier based on calcium manganite of perovskite structure $CaMnO_{3-}$

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$_{\delta}$ for chemical looping combustion. The results were very promising and similar materials have since then been successfully tested in pilot rigs up to 120 kWth, including extended operation in continuously operating 10 kWth reactor with very positive results, see Källén et al. [2]. A key feature of these materials is that they are able to release gas phase oxygen at relevant conditions, so called Chemical-looping with Oxygen Uncoupling, see Rydén et al. [3]. Having gas phase oxygen available for fuel oxidation makes gas-solid mixing less critical and thus makes it easier to reach complete fuel conversion.2

Most studies in which $CaMnO_{3-\delta}$ based oxygen carriers have been examined have been using particles manufactured from high quality chemicals. While that is reasonable in the early stages of development, cheaper raw materials would be favourable for industrial applications. Promising oxygen carriers based on manganese ores have been manufactured and characterized by Fossdal et al. [4] and Mohammad Pour et al. [5].

This study aims to further examine $CaMnO_{3-\delta}$ based oxygen carriers made from low cost, commercial raw materials available in large quantities such as manganese ore. The materials are examined during continuous Chemical-looping Combustion and Oxygen Uncoupling in an experimental reactor with the nominal fuel power 300 W_{th}. The reactor has previously been used in numerous studies which make comparisons with materials made from high purity chemicals straightforward. During operation several gas concentrations as well as temperatures and pressure drops are measured which allows monitoring of the chemical reactions and fluidization behaviour in the reactor. Fines (particles <45 μm) are collected from exiting gas streams which gives an indication of the degree of attrition of the particles. Attrition was also studied in separate jet cup attrition test.

The study show that it is possible to manufacture $CaMnO_{3-\delta}$ based oxygen carrier with appropriate properties for continuous operation from low-cost materials. The ability to release gas phase oxygen to an inert atmosphere and high conversion of natural gas is demonstrated. The results indicate that this approach should be feasible also for large-scale applications.

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Keywords: CLC; perovskite; CLOU; CaMnO3

1. Introduction

Our planet is warming faster than ever due to anthropogenic increase in atmospheric CO_2. One way to limit further increase would be to capture and store CO_2 from large emission sources [6].One method for separation CO_2 from combustion of carbonaceous fuels is Chemical-Looping Combustion (CLC). In CLC the fuel is oxidized by a solid oxygen carrier in a reaction that produces only CO_2 and H_2O. H_2O is easily condensed and voilà: pure CO_2! CLC was invented in the 50's [7] but was not demonstrated until 2003 by Lyngfelt et al. [8]. Since then the process the process have been demonstrated multiple times and the most commonly proposed setup is a dual fluidized bed [9]. In this setup the fuel is oxidized in one reactor by the oxygen carrier that is circulating and is reoxidized in the other reactor.

The oxygen carrier is vital in CLC and much of the research effort has been devoted to it [9]. The requirements of the oxygen carrier include high reactivity towards the fuel, high life time, low cost, harmlessness, temperature tolerance etc. Fuel specificity is another requirement as different fuels pose different demands. When natural gas is used no ash formation and low sulfur content is expected and thus less fouling of the oxygen carrier compared to when coal is used and a relatively expensive oxygen carrier can be used. For years a synthetic Ni-based oxygen carrier was state of the art in CLC with natural gas. With extreme durability as well as being very reactive towards methane no competitor was in sight. But a replacement was needed due to a few crucial shortcomings of the Ni-

based particle. Although catalytic the methane conversion is thermodynamically limited to ca. 99.5 % and in addition to that Nickel is carcinogenic and has a very high cost.

In 2009 Leion et al made a study on a $CaMnO_{3-\delta}$-based oxygen carrier with very promising results [1]. The oxygen carrier exhibited ability to release gas phase oxygen, so called Chemical-Looping with Oxygen Uncoupling (CLOU). CLOU can potentially have a positive effect on fuel reactivity as mixing with the fuel is increased. $CaMnO_{3-\delta}$ has a perovskite structure and differentiates itself from other metal oxides in that there is no distinct phase change when it is reduced (unless reduced too far). Instead it is δ, the oxygen deficiency, which varies. In an air reactor (AR), where the partial pressure of O_2 is high, δ would be small while the opposite would be true for the fuel reactor (FR) and $\delta_{FR} - \delta_{AR}$ would be the amount of oxygen available for fuel oxidation. In the perovskite structure it is possible to change ions to other with similar charge and size and for this particular material some of the Mn is replaced with Ti.

Similar materials as used in this study have previously been tested successfully in other studies [1, 2, 10] Those materials were produced using hi purity raw materials and efforts were put into finding suitable low-cost raw materials that is available in large quantity. The manganese material used to manufacture the oxygen carriers in this study is a pigment with hi Mn_3O_4 content.

2. Method and material

Based on measured density of 1290 kg m^{-3} 310 g was used as the total inventory in the continuous testing to fill up the desired volume of the reactor.

2.1 Attrition test

The structural integrity of particles was examined in a jet cup attrition testing rig. The apparatus consists of a conical cup with 13 to 25 mm ID and an air inlet with 1.5 mm ID mounted at the bottom of a 634 mm high gravitational separator. At the top of the separator a filter (Parker P31FA12CGMN) with a pore size of 0.01 µm (Parker P31KA00ESC) were mounted to collect the fines produced. The rate of fine formation 30 – 60 min into the test was used to compare materials.

2.2 Chemical-looping reactor

A small scale pilot for continuous testing was used to examine particle behavior during hot fluidization. The reactor consists of a fuel reactor (FR), 25*25 mm wide. Particles exit the FR through a loop-seal at the bottom and continue to an air reactor (AR). The AR is 25*42 mm and thins out to 25*25 mm in the riser section. Above the riser is a wider settling zone where gas velocity decrease and particles fall down and some of them enter the downcomer loop seal from where they return to the FR through an overflow exit. The gas velocity in the AR is responsible for the global circulation of particles. In AR and FR gas enters through porous quartz plates whereas in the loop seal gas enters through pipes with holes drilled in the bottom. A water seal on the FR gas exits provide a small over pressure in the FR to prevent leakage of air into it. Slip streams of gas is taken from both AR and FR gas exits and concentrations of CO, O_2, CO_2, CH_4 are continuously measured with a Emerson Rosemount NGA2000. Other species from FR, such as H_2 and N_2, are measured periodically by gas chromatography. Temperatures in the AR and FR are measured with thermocouples approximately 1 cm above the quartz plate. Pressure is measured a multiple locations in the reactor to monitor the fluidization behavior.

2.3 CLOU testing

Tests were performed to measure oxygen release. During these tests air was used to fluidize AR, CO_2 in FR and Ar in the loop seals. By using CO_2 in FR it is possible that leakage (from AR) could be quantified by measuring the N_2. The oxygen released to the inert atmosphere in FR was measured at multiple temperatures.

2.4 Fuel testing

Natural gas was used to fluidize FR, air AR and Ar in the loop seals. Temperature and gas flows of air and fuel were varied to find settings that produced full, or almost full, fuel conversion. As a simple measure of fuel conversion CO_2-yield, γ, is used.

$$\gamma = \frac{x_{CO_2}}{x_{CO_2}+x_{CO}+x_{CH_4}} \quad (1)$$

x_i is the gas fraction of specie *i*.

3. Results

Particles showed great oxygen release ability and almost 11 % O_2 was measured in gas from FR at 950 °C. That can be compared to 7 % release from $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ that was tested at identical parameters by Hallberg et al. in another study [10]. Figure 1 shows the oxygen concentration from FR at different temperatures, the data points are the average values over 10 min.

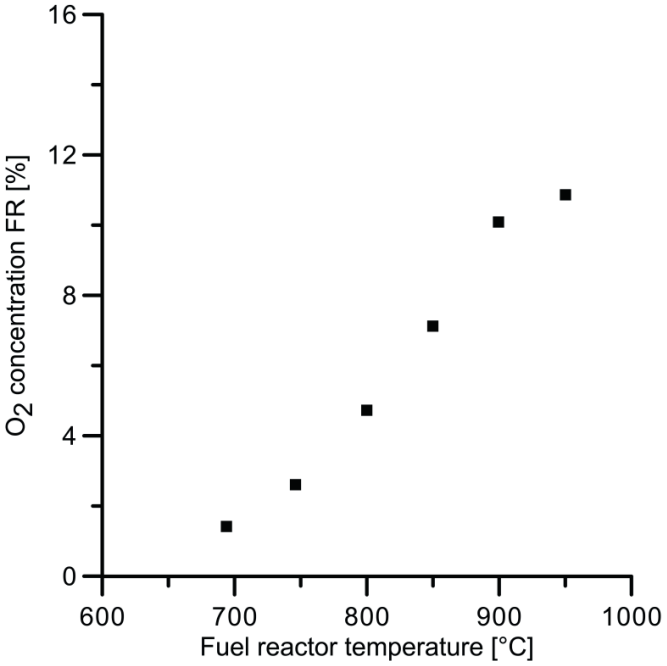

Figure 1 Effect of fuel reactor temperature on oxygen uncoupling.

A total of 35 hours of operation with fuel was done. The parameters AR-flow, fuel flow and temperature were adjusted to stay at conditions with complete or almost complete fuel conversion.

The CO_2-yield together with varied parameters AR-flow, fuel power and FR-temperature, are shown for the total time of fuel operation in figure 2. As can be seen in the figure 950 °C was the temperature mainly used. The fourth day 900 °C was briefly tested with the result that the CO_2-yield was drastically decreased. Two attempts were made to increase temperature to 1000 °C. Initially it seemed promising and it was even possible to complete fuel conversion with as little as 2.1 % oxygen leaving the air reactor. That is a stoichiometric air to fuel ratio of 1.08 and fuel reactor particles load per fuel power of 238 kg/MW (FR inventory is estimated to 30 % of total particle inventory from post experiment inspection of reactor) . Unfortunately it was not possible to maintain this for long as fluidization problem occurred after 20 minutes of operation at 1000 °C at both attempts. Data from the second attempt is shown in figure 3.

During the experiments 10.4 g of fines were collected in filters. That corresponds to 0.1 %/hour of fuel operation or a life time of 1000 hours.

The rate of fine formation measured in the jet cup attrition rig was 8.2 %/h which is higher than most well performing oxygen carriers [11].

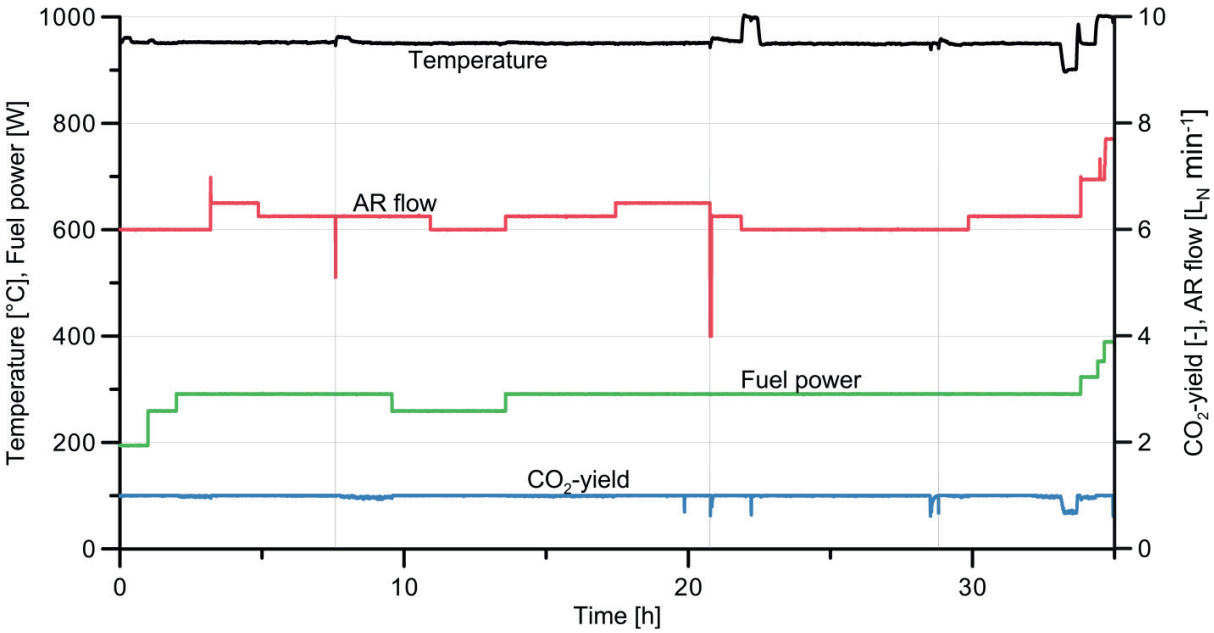

Figure 2 How temperature, AR-flow, fuel power and CO_2-yield varied over total time of fuel operation. Vertical lines indicate change of day.

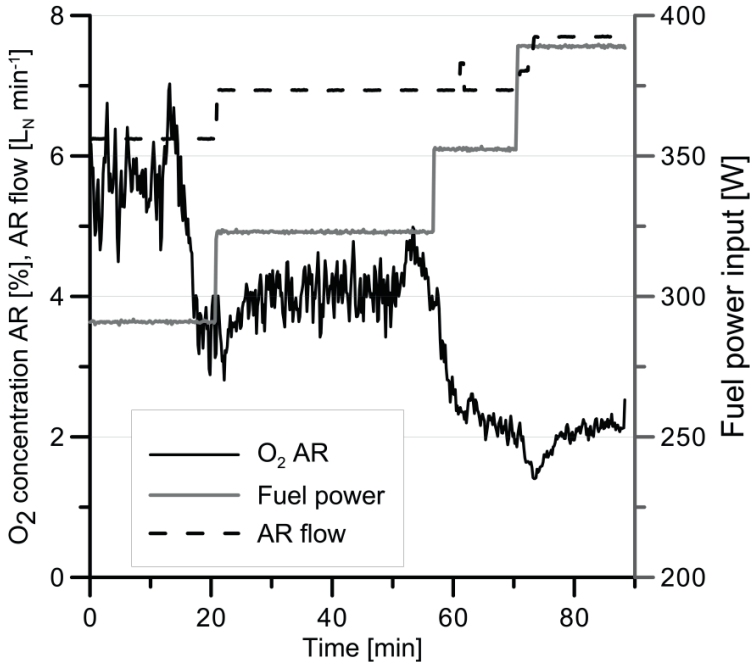

Figure 3 The response in O_2 concentration in AR gas outlet when fuel power input and AR flow was increased.

4. Conclusions

- The material showed very high oxygen release to inert atmosphere compared to similar material previously tested.

- The material showed high fuel reactivity. At 1000 °C fuel was completely converted at a low air-to-fuel ratio and a low fuel reactor particle loading per fuel power.
- Fluidization problems occurred at 1000 °C after approximately 20 minutes of operation at that temperature.
- The attrition behavior of the material was not good and the estimated particle life time based on fine production during continuous operation was 1000 h.

Acknowledgements

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