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Operation with combined oxides of manganese and silica as oxygen carriers in a 300 W_{th} chemical-looping combustion unit

Malin Källén*, Magnus Rydén, Tobias Mattisson, Anders Lyngfelt

Department of Energy and Environment, Chalmers University of Technology, Gothenburg, Sweden

Abstract

Chemical-looping combustion is a carbon capture technology which has received increased attention during the last years. The technology is based on fuel oxidation with oxygen provided by solid oxygen carrier particles. In this study two such oxygen carrier materials have been examined in a continuously circulating chemical-looping reactor system designed for a thermal power of 300 W. The two materials consisted of manganese and silica oxides, with an addition of titania in one of them. The oxygen carrier particles were produced by spray drying, followed by calcination and sintering. Both materials released gas phase oxygen in inert atmosphere at 800-950°C, with the highest concentration at 1.8% observed at 850°C. The oxygen carrier consisting of only manganese and silica gave the highest fuel conversion for both syngas and natural gas. Full fuel conversion was achieved at 950°C for syngas and at 900°C for natural gas with this oxygen carrier material. The fuel conversion increased with temperature for both materials. The material consisting of only manganese and silica suffered from severe attrition and could only be operated for seven hours with fuel. The addition of titania increased the mechanical stability of the particles considerably, and this material was operated for 24 h with fuel. No large production of fines was observed with this material. Combined oxides of manganese and silica are shown to be promising as oxygen carriers for chemical-looping. The mechanical stability can be increased by adding titanium to the MnSi material. The composition would however need to be further examined to optimize the performance of the oxygen carrier.

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Keywords: chemical-looping combustion; chemical-looping with oxygen uncoupling; manganese oxide; silica; titania

* Corresponding author. Tel.: +46 31 772 14 38; fax: +0-000-000-0000 .
E-mail address: malin.kallen@chalmers.se

1. Introduction

Chemical-looping combustion has emerged as a promising carbon capture technology during the past decade. The technology is based on the cyclical reduction and oxidation of a metal oxide, referred to as oxygen carrier, which is alternately exposed to fuel and air. This combustion scheme eliminates the need for energy intensive gas separation to obtain a pure carbon dioxide stream. The technology is most often realized as two interconnected fluidized beds with the oxygen carrier particles circulating between them. See recent review articles by Lyngfelt [1] and Adanez et.al. [2] for an overview of the development of the technology.

A major part of the research in this area has focused on finding viable oxygen carrier materials. The oxygen carrier has to be capable of being oxidized and reduced at sufficient rates at the desired temperature level. It also has to have sufficient oxygen transfer capacity, i.e. the amount of oxygen which the oxygen carrier can deliver to the fuel per cycle must be reasonably high. If the oxygen carrier is able to release gaseous oxygen, the rate of oxygen release is also an important parameter. The oxygen carrier material also needs to be mechanically and chemically stable to keep attrition and elutriation of fines at low levels. The particles should also be inert towards fuel impurities in order to avoid deactivation and loss of reactivity. Furthermore, the cost and the environmental impact of the material should be reasonable.

The range of investigated oxygen carrier materials has recently been extended to include combined oxides, i.e. oxides with two or more cations. Many of these materials have the ability to release gas phase oxygen in reducing conditions, a process referred to as chemical-looping with oxygen uncoupling [3]. Manganese has been identified as one of the metals whose oxides can release gas phase oxygen under suitable conditions. However, the relevant equilibrium concentrations for oxygen release occur at relatively low temperatures (below 800°C). It is possible to alter the thermodynamics by combining manganese with other metal oxides [4]. One of the investigated systems with suitable thermodynamics is the combination of manganese and silica oxides. This material would be advantageous since the raw materials are cheap, widely available and not harmful for humans or the environment. Furthermore, it could also be suitable to use for combustion of coal since none of the components are expected to react with sulfur.

There is presently not much work done on combined oxides of manganese and silica. Two studies on manganese-silica oxides examined in batch experiments which show promising results are reported in the literature [5, 6]. Batch experiments are a good method to evaluate the reactivity, the fluidization behavior and the chemical integrity of oxygen carrier particles. However, to get more comprehensive information of the material's performance as oxygen carrier, experiments in a continuously circulating unit are needed. The objective of this study is to provide such information.

Nomenclature

γ_{CO_2}	CO ₂ yield
x_i	gas concentration, $i = \text{CO}, \text{CO}_2, \text{CH}_4$

2. Experimentally

2.1. Oxygen carrier materials

Two oxygen carrier materials have been examined; one consisting of only manganese and silica oxides (MnSi) and one consisting of manganese and silica oxides and titania (MnSiTi). The materials were produced by VITO in Belgium by spray drying followed by calcination and sintering for four hours. The properties of the fresh materials and the sintering temperature are summarized in Table 1. MnSiTi was sintered at a slightly lower temperature due to an observed tendency to melt during sintering.

Table 1. Properties of the fresh materials and sintering temperature.

Material	MnSi	MnSiTi
Synthesis composition (wt%)	75% Mn ₃ O ₄ , 25% SiO ₂	66.7% Mn ₃ O ₄ , 22.2% SiO ₂ , 11.0% TiO ₂
Sintering temperature (°C)	1150	1140
Bulk density (g/cm ³)	1.0	1.7
Mean particle size (µm)	136	126
Crushing strength (N)	0.5	2.1
Attrition index (wt%/h)	17.35	0.49

The reported bulk density was measured as the mass poured into a known volume. The reported attrition index was calculated from measurements using a customized jet cup; see the article by Rydén et. al. for a description of the jet cup and methodology [7]. The results from these tests which were conducted with fresh particles are used as a comparison to the experimental attrition behavior in the hot unit.

2.2. Experimental setup

The experiments were carried out in a continuously circulating fluidized bed reactor designed for a thermal power of 300 W. The reactor consists of three compartments: the air reactor, the fuel reactor and the downcomer functioning as a loop seal. The reactor is depicted in Fig. 1 with the air reactor colored blue, the fuel reactor colored red and the downcomer colored green.

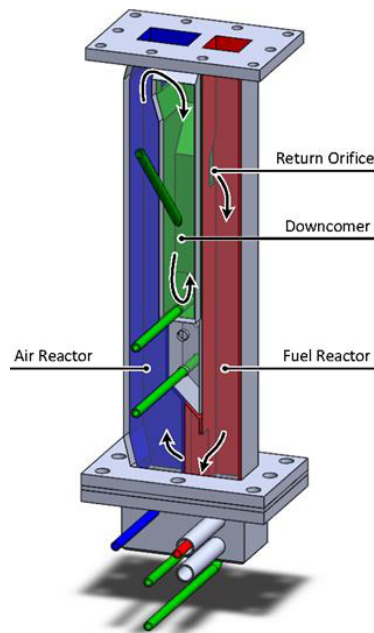


Fig. 1. Schematic illustration of the circulating fluidized bed reactor.

The air reactor is divided into two parts with a lower bed section in which the cross section is larger than in the riser section above the bed. The precondition for achieving solids circulation is a gas velocity in the air reactor high enough to carry the particles up from the bed surface. When the gas with the suspended particles exits the air reactor it enters a separation box (not shown in Fig. 1) where the gas velocity decreases due to an increased cross sectional area. This low-velocity section results in a separation of gas and particles, and the latter will fall down towards the air reactor. However, a certain fraction of particles enter the downcomer between the air and fuel reactor. The

downcomer works as a J-type loop seal with an overflow exit into the fuel reactor. After being in the air reactor the particles eventually return to the air reactor through the lower loop seal located in the bottom of the system between the wind box of the air reactor and the wind box of the fuel reactor.

The air reactor is fluidized with air and the fuel reactor is fluidized with natural gas or syngas during fuel operation and with carbon dioxide during oxygen release experiments. Porous quartz plates are used as gas distributors in both the air reactor and the fuel reactor. The downcomer and the lower loop seal are fluidized with argon which is added through small holes in the pipes which can be seen in Fig. 1. Since the reactor system has a high area to volume ratio, there will be significant heat losses through the walls. Therefore the reactor system is enclosed in an electric furnace in order to keep the desired temperature.

The temperature is measured with one thermocouple in the air reactor and one in the fuel reactor. The thermocouples are located approximately 1 cm above the distributor plate in each reactor. The pressure drops in the reactor system are measured by pressure transducers in the air reactor, fuel reactor and in the downcomer. The pressure drops are measured in order to be able to assess the fluidization behavior and the solids inventory in the different parts of the reactor system.

The outlet of the fuel reactor is connected to a water seal with a 1-2 cm column of water giving a slightly higher pressure in the fuel reactor than in the air reactor. A part of each outlet stream is lead through a particle filter and a gas conditioning unit before entering the gas analyzers. Methane, carbon monoxide and carbon dioxide are measured with IR-sensors while oxygen is measured with a paramagnetic sensor. The outlet from the fuel reactor is also analyzed with a gas chromatograph which measures hydrogen and nitrogen, as well as the previously mentioned gases. The entire reactor setup has been thoroughly described in previous publications [8, 9]. Syngas (50% CO and 50% H₂) and natural gas were used as fuels. The composition of the natural gas is shown in Table 2.

Table 2. Annual average composition for 2013 of the natural gas as reported by the gas supplier.

Species	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀ +	N ₂	CO ₂
Mol%	89.82	5.65	2.00	1.02	0.55	0.96

2.3. Methodology

The amount of solids added to the reactor system was determined by the bulk density of the particles. The bed surface in the air reactor should be above the height where the cross section area is reduced. The amount of material was chosen to achieve a fluidized bed height in the air reactor slightly above the height where the cross section is decreased. This will give a bed height of around 10 cm. As a result the experiments with MnSi required a total bed mass of 200 g, while the experiments with MnSiTi required 300 g. The reactor system was heated from room temperature at the beginning of each day of experiments and cooled down again at the end of the day. The electric furnace was heating the system during all experiments in order to control the temperature.

The materials were first examined in inert atmosphere to evaluate their ability to release gas phase oxygen. During these experiments the air reactor was fluidized with air, the fuel reactor was fluidized with carbon dioxide and the loop seals were fluidized with argon.

The materials were then subjected to fuel operation. The combustion of syngas and natural gas was carried out in continuous operation. The fuel reactor temperature and the fuel flow were varied during these experiments. The air reactor was fluidized with air during all fuel experiments.

All gas concentrations were measured on dry basis. From the measurements the CO₂ yield was calculated to evaluate the combustion performance. The CO₂ yield is defined as the volume fraction of carbon dioxide formed divided by the total volume fraction of carbon species in the outlet flow according to:

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

3. Results

The measured oxygen concentration when the fuel reactor was fluidized with carbon dioxide can be seen in Fig. 2. Each line shows the oxygen concentration as a function of time during a period with constant fuel reactor temperature. MnSiTi clearly released higher concentrations of oxygen than MnSi did for all temperatures investigated. It should however be noted that a higher solids inventory was used for MnSiTi. The highest concentrations were observed at 850°C for both materials. The oxygen concentration initially peaked and then continued to decrease during some of the periods with constant temperature. This behaviour was most distinct for MnSiTi and this is believed to be a result of the high density of this material. The oxygen release experiments were carried out with a lower air flow than the fuel operation and this has likely resulted in too low circulation for the heavier material. This was confirmed during later operation when the oxygen release was studied during a higher air flow, which gave a more constant released oxygen concentration. The peaks occurring at 800°C for MnSiTi were likely caused by irregularities in the circulation.

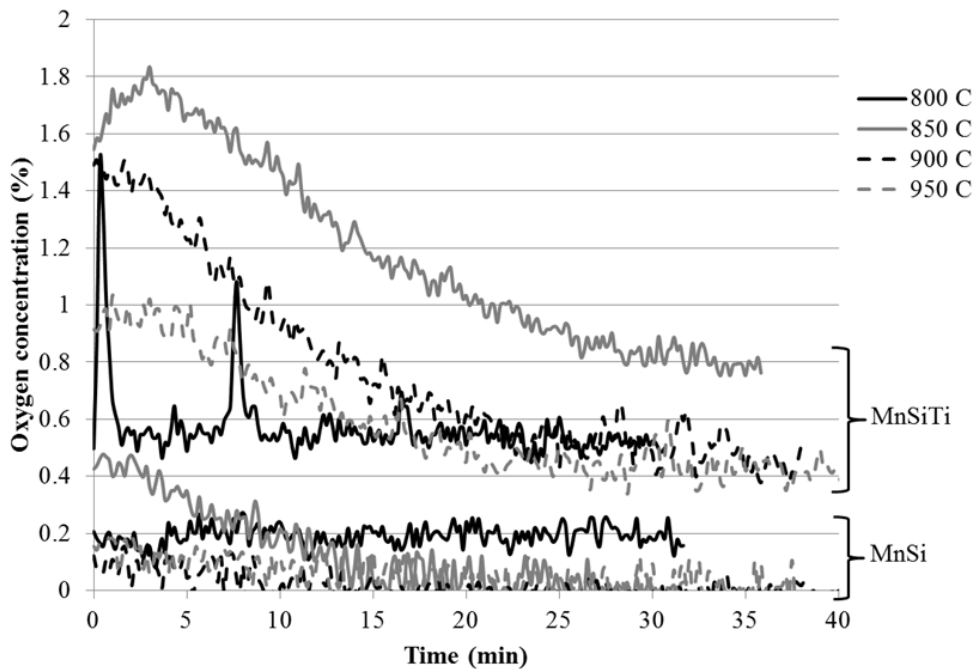


Fig. 2. Released oxygen concentration for both oxygen carrier materials during periods with constant temperature.

The fuel conversion calculated as CO₂ yield during operation with syngas is shown in Fig. 3. The CO₂ yield will underestimate the total fuel conversion as the measured hydrogen concentration was lower than the concentration of carbon monoxide at all temperatures studied. The syngas conversion was much higher with MnSi than with MnSiTi even though the fuel reactor solids inventory was larger for MnSiTi. The fuel conversion increased with temperature for both materials. MnSi gave complete fuel conversion at a fuel reactor temperature of 950°C and a fuel power of 330 W.

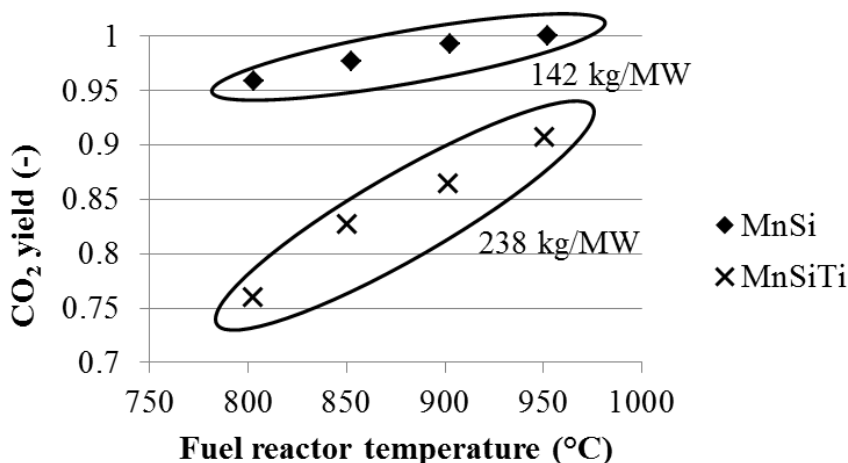


Fig. 3. CO₂ yield as function of fuel reactor temperature during combustion of syngas. Each data point represents an average value during a period with constant temperature. The solids inventory over thermal power is based on the bed mass in the fuel reactor.

Fig. 4 shows the outlet volume fractions from the fuel reactor as well as the fuel reactor temperature during natural gas operation with MnSi. The sudden change in concentrations at 22 min was caused by switching from syngas to natural gas. In this case the conversion of syngas was complete at 800°C as the fuel flow was much lower than during continuous syngas operation. The fuel reactor temperature was later increased first from 800°C to 850°C and then to 900°C. Increasing the temperature gave improved fuel conversion and the fuel conversion was complete at 900°C. The flow of natural gas corresponded to a thermal power of 220 W during this operation.

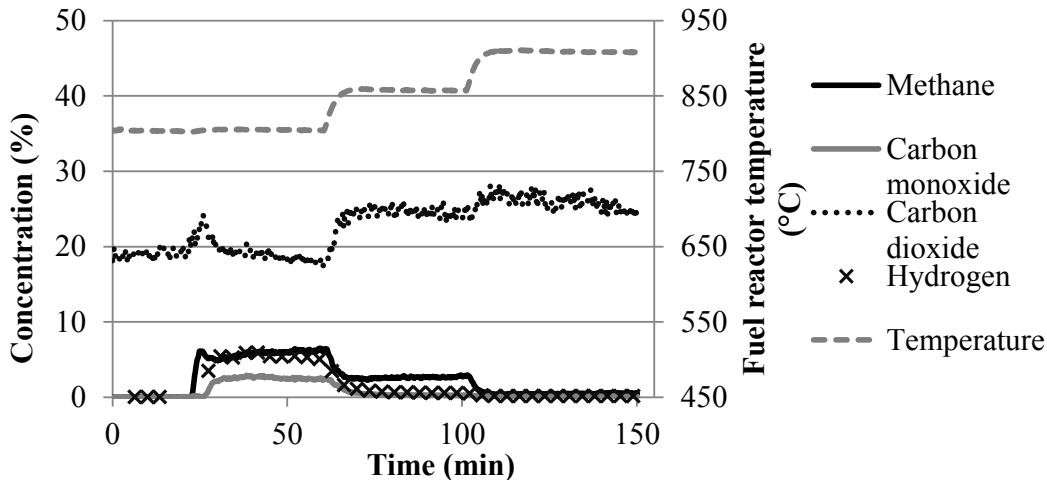


Fig. 4. Outlet concentrations from the fuel reactor and fuel reactor temperature during natural gas operation with MnSi as oxygen carrier. The concentrations do not add up to 100% since argon is used to fluidize the loop seals.

A stepwise temperature increase was also performed with MnSiTi as oxygen carrier with the same fuel flow. In this case the temperature was increased up to 950°C. A summary of the CO₂ yield during these temperature increases can be seen in Fig. 5. It is clear that MnSiTi is much less reactive with fuel than MnSi is. Each data point represents ten seconds and since the temperature was kept constant during longer periods at certain temperatures, there are many data points at these temperatures.

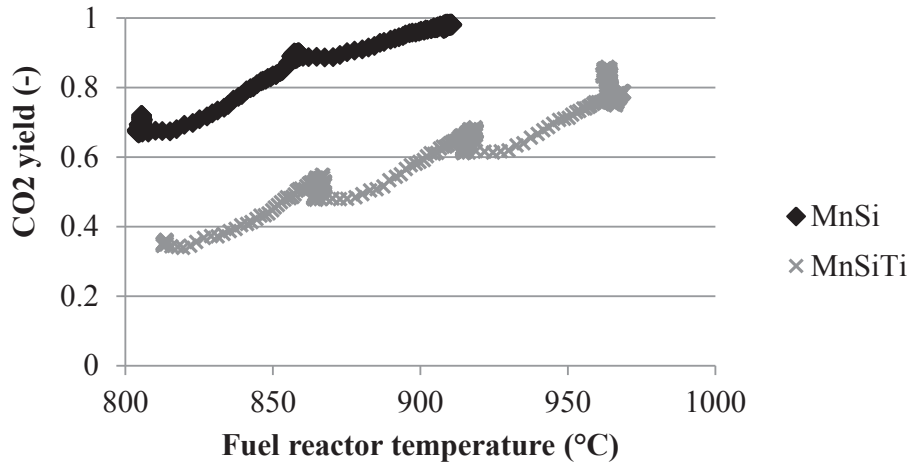


Fig. 5. CO₂ yield as function of fuel reactor temperature during a stepwise increase in temperature.

The difference in reactivity is even clearer when the solids inventory is taken into account. Fig. 6 shows the CO₂ yield as a function of fuel reactor inventory per thermal power. There is only one data point for MnSiTi as the fuel flow was never increased for this material due to the poor conversion. Each data point represents an average value during a period with constant fuel at 960°C.

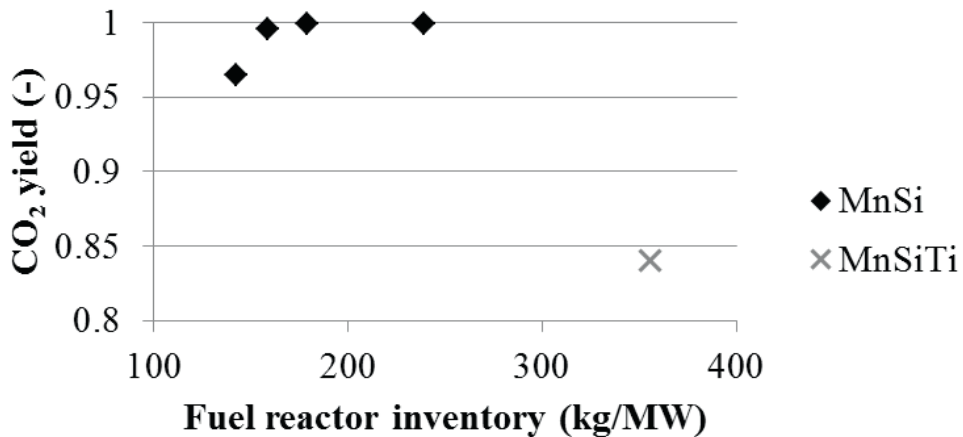


Fig. 6. CO₂ yield as function of fuel reactor solid inventory per added fuel power during operation with natural gas.

The bulk densities of these materials were very different and that would likely affect the circulation rate. Heavier materials would be carried up from the air reactor bed to a lesser extent. This behavior is illustrated in Fig. 7. During the first period in the figure the air reactor is fluidized with air and the fuel conversion is stable. The gas flow in the air reactor is then increased by adding 1 L_N/min of nitrogen. This will result in a dilution of the oxygen concentration, but also a higher velocity in the air reactor. This may affect the performance in several ways. The rate of oxidation may decrease due to the lower oxygen partial pressure, resulting in particles of lower oxidation degree reaching the fuel reactor. However, the high velocity will likely result in a higher degree of circulation, and it is likely that more oxidized particles reach the fuel reactor due to this effect. In this case a distinct difference in the

behavior of the oxygen carrier materials is observed. The fuel conversion decreased by adding nitrogen to the air reactor for MnSi and the fuel conversion increased by the addition for MnSiTi. This indicated that the gas velocity in the air reactor was too low for MnSiTi so that the circulation was a limiting factor for the fuel conversion. This seems not to be the case for MnSi as the increase in gas velocity actually decreased the fuel conversion.

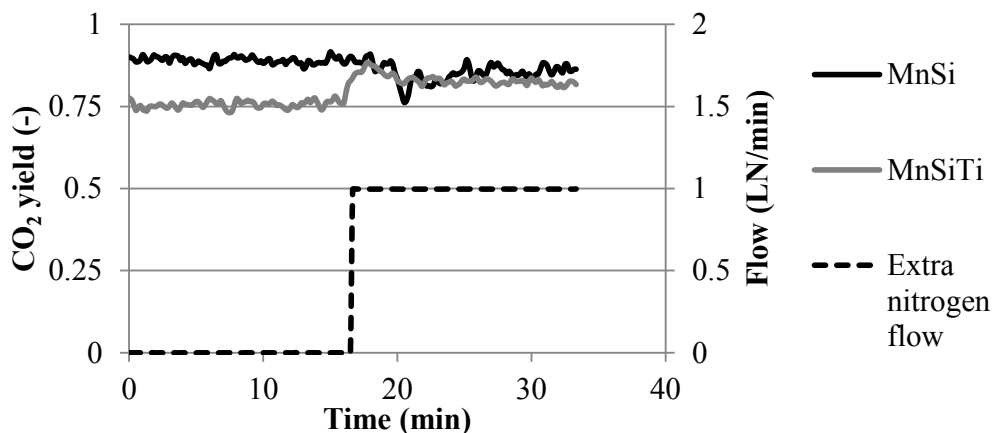


Fig. 7. CO₂ yield as function of time when the air flow in the air reactor was diluted with an extra nitrogen flow.

The operation with MnSi had very high fuel conversion, but the experiments had to be aborted after only seven hours with fuel addition. The reason was a high attrition rate which resulted in a disruption of the solids circulation because of a too high fraction of very fine particles. Most of the fines were elutriated from the system and ended up in the filters, but also the material left in the reactor system was difficult to fluidize due to a high fraction of fines.

MnSiTi was possible to operate for 24 h with fuel addition before the circulation was disrupted. It is not clear why the operation encountered problems at this time. When the reactor system was opened, still almost 90% of the added mass remained in the system and did not contain any significant amount of fines. From this observation it is clear that the attrition rate was much lower than for MnSi. These observations correspond well with the measured attrition indices of the fresh materials.

4. Conclusions

Two oxygen carrier materials have been examined in a continuously circulating chemical-looping reactor system designed for a thermal power of 300 W. The two materials consisted of manganese and silica oxides with an addition of titania in one of the materials. The oxygen carriers have been investigated in oxygen release experiments as well as during fuel operation with both syngas and natural gas as fuels. The following conclusions have been drawn:

- Both materials released gaseous oxygen in inert atmosphere above 800°C. MnSiTi released higher concentrations than MnSi did.
- Both materials were able to convert syngas and natural gas and the fuel conversion increased with fuel reactor temperature.
- MnSi gave much higher fuel conversion than MnSiTi did, even though the solids inventory over thermal power was almost twice as high for MnSiTi.
- It is likely that the circulation rate was a limiting factor during operation with MnSiTi because of the much higher density of this material.
- The rate of attrition was high for MnSi and the material could only be operated for seven hours with fuel addition. MnSiTi was much more resistant to attrition and could be operated for 24 h without any large production of fines.

- Materials consisting of manganese and silica oxides have been shown to work well as oxygen carrier for chemical-looping. Titania was a promising addition which gave an increased mechanical stability of the particles.
- Further work would include optimizing possible additives to the manganese-silica system to maximize both fuel conversion and mechanical stability.

Acknowledgements

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