

Improved Performance in Fluidised Bed Combustion by the Use of Manganese Ore as Active Bed Material

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Abstract

Insufficient mixing between fuel and air during combustion results in carbon monoxide and unburnt hydrocarbons in the flue gases. In order to minimize these emissions commercial combustion plants are operated with an excess of air added to the furnace. This increases the heat loss associated with the flue gas and thus decreases the overall efficiency of the plant. If combustion is carried out in a fluidised bed, the mixing between fuel and oxygen could be facilitated by using an active bed material with the ability to absorb and release chemically bonded oxygen, depending on the local oxygen concentration. Such active oxygen carriers would also facilitate conversion of relatively stable fuel components such as methane inside the bed, where ignition may be hampered by thermal inertia. This technology, Oxygen Carrier Aided Combustion (OCAC), which is a spin-off technology from Chemical-Looping Combustion (CLC), has recently been proposed.

In this study, the potential of using manganese ores as active bed material has been investigated. Combustion of methane in a fluidised bed was carried out with two mixtures of manganese ore and silica sand (50/50 wt.%) in a laboratory circulating fluidised bed combustor. The performance of the manganese ores as active bed materials was compared with the performance of only silica sand in the same experimental unit.

The main conclusion drawn from these experiments is that it was possible to significantly reduce the exhaust concentration of carbon monoxide by replacing 50 wt.% of the bed inventory of silica sand with manganese ore. Both ores released gaseous oxygen in inert atmosphere and oxygen was present in the exhaust gas at all times during combustion. The use of the active bed materials thus increased the fuel conversion for a given air-to-fuel ratio.

Keywords: Oxygen Carrier Aided Combustion (OCAC), manganese ore, air-to-fuel ratio, Chemical-Looping Combustion (CLC)

1. Introduction

Fuel mixing is a key aspect affecting the combustion performance in fluidised bed boilers. Insufficient mixing between fuel and oxygen during combustion results in emissions of carbon monoxide and unburnt hydrocarbons in the flue gases. In order to minimize these emissions, commercial combustion plants are operated with an excess of air added to the furnace. This implies that the physical size of the combustion plants must be oversized to meet a particular fuel load. The air excess also increases the heat loss associated with the flue gas and thus decreases the overall efficiency of the plant. Common measures to avoid poor mixing are optimisation of the air staging and of the fuel feeding. Combustion in fluidised beds offers an opportunity to use an additional measure to facilitate the mixing: the choice of bed material.

The fundamental idea behind the current study is to replace the inert bed material commonly used in fluidised bed combustion with an active bed material with the ability to absorb and release chemically bonded oxygen, depending on the local oxygen potential. The bed material will be oxidised in parts of the combustion chamber where oxygen is available in excess, while it will be reduced in parts where fuel is available in excess. Thus the availability of a given amount of oxygen can be more evenly distributed throughout the combustion chamber. The active bed material will also work as an oxygen buffer preventing spikes in emissions during uneven fuel feeding and would facilitate conversion of relatively stable fuel components such as methane by direct solid-gas reactions inside the bed, where ignition otherwise may be hampered by thermal inertia.

The technology has been named Oxygen Carrier Aided Combustion (OCAC) and has only recently been proposed. The required type of active bed material, commonly referred to as oxygen carriers, have been extensively studied during the past years for the carbon capture technology Chemical-Looping Combustion (CLC). [1-3] Various oxygen carrying materials have been operated in pilot chemical-looping combustion reactors (0.3-140 kW) with similar design as fluidised bed boilers during the last ten years. [4]

A previous study concerning oxygen carrier aided combustion conducted in the 12 MW_{th} circulating fluidised bed research boiler at Chalmers University has shown very promising results. [5] By substituting 40 wt.% of the inert sand bed with the oxygen carrying mineral ilmenite (consisting of iron and titanium oxides), an 80% decrease of carbon monoxide in the flue gases could be achieved. A 30% decrease in nitric oxide could also be observed. This suggests that a more even distribution of oxygen in the bed and less reliance on flame combustion could even out the temperature and help avoiding hot spots. It is also possible that the addition of oxygen carrier material to the bed may have a catalytic effect on nitric oxide reduction, as it is established that some metal oxides can have this effect. [6] Ilmenites of three different origins have also been examined for oxygen carrier aided combustion of solid fuel in a batch fluidised bed. [7]

In this study oxygen carrier aided combustion was further investigated by examining the use of manganese ores as active bed materials. Manganese ores reacts faster with fuels than ilmenite. [8] Manganese oxides also have the ability to release oxygen directly in gaseous form, which in chemical-looping contexts is referred to as Chemical-Looping with Oxygen Uncoupling (CLOU) [9]. This implies that manganese ores would not only even out the amount of available oxygen in the bed, but also provide the available oxygen in gas phase. Manganese ores are rich ores that often has more than 45 wt.% manganese, in addition to other potential oxygen carrying components such as iron oxides. In chemical-looping combustion research manganese based combined oxides have been identified as one of the most promising concepts for oxygen carriers, and oxygen carrier particles based on manganese ores can be provided in very large quantities at low cost. [10]

The experiments were carried out in a small laboratory circulating fluidised bed in order to be able to examine a number of bed materials. The performance of the active bed materials was evaluated in comparison with an inert bed material used in the same unit and with a varied air-to-fuel ratio. This

study is the first step in finding a manganese ore suitable for experiments in the Chalmers circulating fluidised bed boiler, for verification of the concept in semi-industrial scale.

2. Experimental

Two manganese ores have been examined for oxygen carrier aided combustion and compared with operation with silica sand which does not have any oxygen carrying properties. One ore was supplied by UMK and one ore was supplied by Sibelco. The ores were crushed, sieved to the size interval 90-212 μm and heat treated at 950°C for 24 h. The elemental compositions of the manganese ores are reported in Table 1. The elemental analysis was carried out after heat treatment during which MnO_2 decomposes and the manganese is reduced to lower oxidation states. Thus the metal fraction of the ores increases as oxygen is released from the solid in gas phase, compared to raw ore taken directly from the mine. The remaining fraction not included in the table mainly consists of oxygen. The mean particle size and the bulk density of the materials are reported in Table 2. The bulk densities reported were measured as the mass poured into a known volume.

Table 1. Elemental composition of the examined manganese ores reported in weight%. Elements present in concentrations lower than 0.1 wt% are not included in the table. Balance is oxygen.

Material	Mn	Fe	Al	Si	K	Ba	Ca	Mg	P	Ti
SIB	66.4	3.0	3.1	1.4	0.7	0.3	0.1	0.1	0.1	0.1
UMK	62.0	3.8	2.0	0.9	0.6	1.8	0.2	0.3	0.1	0.1

Table 2. Mean particle size and bulk density of the examined materials.

Material	Mean particle size (μm)	Bulk density (kg/m^3)
Sand	152	1550
UMK	139	1370
SIB	142	1880

The experiments were carried out in a continuously circulating fluidised bed combustor designed for a thermal power of 300 W. The combustor consists of three compartments: a combustion chamber, a secondary bubbling bed and a downcomer functioning as a loop seal. The reactor is depicted in Figure 1 with the combustion chamber coloured blue, the secondary bed coloured red and the downcomer coloured green. This experimental setup was initially designed for small-scale operation of chemical-looping combustion and therefore the design differs from conventional circulating fluidised bed boilers.

The combustion chamber is divided into two parts with a lower bed section in which the cross section (40 x 25 mm) is larger than in the riser section above the bed (25 x 25 mm). The precondition for achieving solids circulation is a gas velocity in the combustion chamber high enough to carry the particles up from the bed surface. When the gas with the suspended particles exits the combustion chamber it enters a separation box 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 combustion chamber. However, a certain fraction of particles enter the downcomer between the combustion chamber and the secondary bed. The downcomer works as a J-type loop seal (25 x 25 mm) with an overflow exit into the secondary bed. After fluidising in the secondary bed the particles eventually return to the combustion chamber through a lower loop seal located in the bottom of the system between the wind box of the combustion chamber and the wind box of the secondary bed.

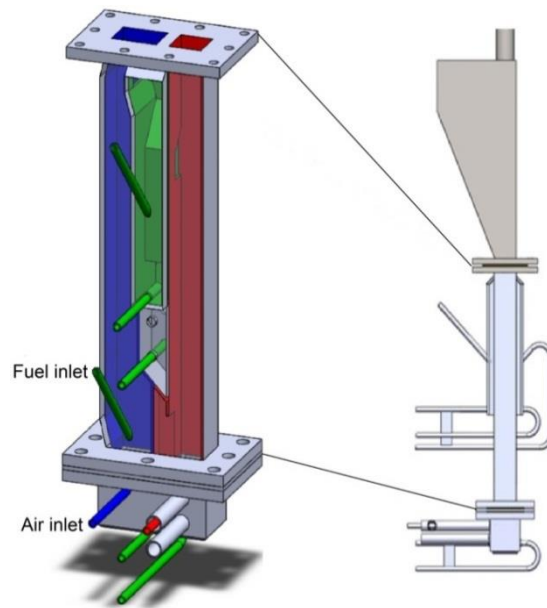


Figure 1. Schematic illustration of the smaller fluidised bed reactor: open front view to the left and side view including the particle separation box to the right.

The combustion chamber is fluidised with air and the fuel is added through a pipe entering approximately 1 cm above the bottom plate. Methane was used as fuel in all experiments. The target application is combustion of solid fuels such as biomass, but the use of solid fuel was not possible with the current reactor setup. Porous quartz plates are used as gas distributors in both the combustion chamber and the secondary bed. The secondary bed, the downcomer and the lower loop seal are fluidised with argon. In the loop seals, the fluidising gas is added through small holes in the pipes which can be seen in Figure 1. Since the combustor has a high area to volume ratio, there will be significant heat losses through the walls. Therefore it is enclosed in an electric furnace in order to keep the desired temperature.

The temperature is measured with one thermocouple in the combustion chamber and one in the secondary bed. The thermocouples are located approximately 1 cm above the distributor plate in each compartment. The pressure drops in the system are measured by pressure transducers which are connected to the combustion chamber, secondary bed and the downcomer via pressure legs. The pressure drops are measured in order to be able to assess the fluidisation behaviour and the solids inventory in the different parts of the system.

A part of each outlet stream is lead through a particle filter and a gas conditioning unit before entering the gas analysers (SICK MAIHAK). Methane, carbon monoxide and carbon dioxide are sampled online and analysed using IR-sensors while oxygen is sampled online and analysed using a paramagnetic sensor. The outlet from the combustion chamber is also analysed with a gas chromatograph (Varian micro-GC) which measures hydrogen and nitrogen, as well as the previously mentioned gases. The gas chromatograph samples gas every three minutes.

Prior to operation with the manganese ores, reference experiments were carried out with silica sand, which is a commonly used bed material for circulating fluidised bed boilers. The operation with the manganese ores was carried out with 50 wt.% of the bed inventory consisting of manganese ore and 50 wt.% consisting of silica sand. The mass of bed materials added to the system was adjusted to get the same bed height (13 cm) in the combustion chamber for all materials. This implies that the added mass was determined by the bulk density of the mix of ore and sand. The amounts of bed material added to the system correspond to a bed mass in the combustion chamber of approximately 140-170 g.

The experiments with varying air-to-fuel ratio were operated with a fixed air flow and the fuel flow was increased step-wise. Each set of gas flows was kept for 20 minutes to get stable operating conditions. The temperature was kept constant at 850°C for all experiment except one experiment with only silica sand as bed material when the temperature was set to 800°C to investigate the temperature dependence of the results. The attrition rate of the bed materials were evaluated by the increased weight of the particle filters at the gas exhaust. The laboratory circulating fluidised bed combustor was first operated with only silica sand as bed material. These experiments were used as reference points for the results from the operation with partially substitution of the bed material with manganese ores.

3. Results

The measured concentrations of carbon monoxide and oxygen in the gas exhaust during the operation with silica sand at 800°C and 850°C are shown in Figure 2. The concentrations are reported as functions of air-to-fuel ratio. The concentration of carbon monoxide remained at a few hundred ppm until the air-to-fuel ratio was decreased below 1.05. At an air-to-fuel ratio of one, the concentration of carbon monoxide reached several thousand ppm. The concentration of oxygen decreased from 18000 ppm to zero as the air-to-fuel ratio was decreased from 1.23 to 1. The concentration levels were very similar at the two investigated temperatures, but the carbon monoxide concentration was slightly higher at 800°C than at 850°C. As the oxygen concentration approached zero (an air-to-fuel ratio of one), the concentration of carbon monoxide increased significantly. However, the change in combustion temperature seemed to have low influence on the carbon monoxide concentration.

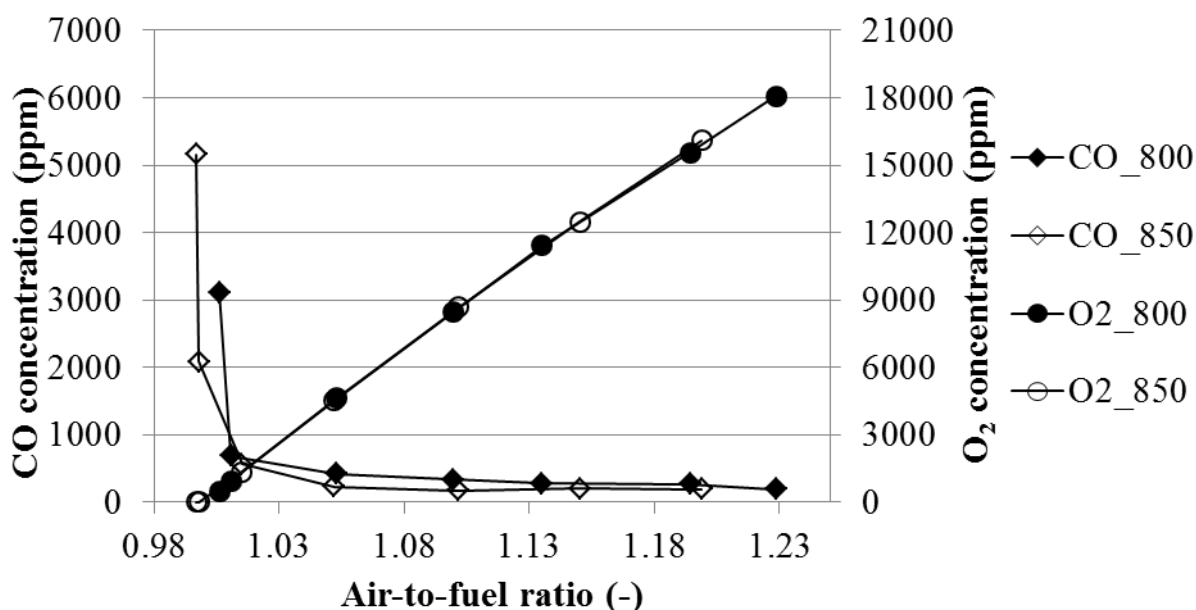


Figure 2. Measured outlet concentration of carbon monoxide as a function of air-to-fuel ratio during operation with sand as bed material.

The same procedure was repeated for the two manganese ores mixed with 50 wt.% silica sand. The temperature was kept at 850°C. The measured concentrations of carbon monoxide in the gas exhaust during the operation with the two ores are shown in Figure 3. The silica sand reference points for 850°C are also included in the figure.

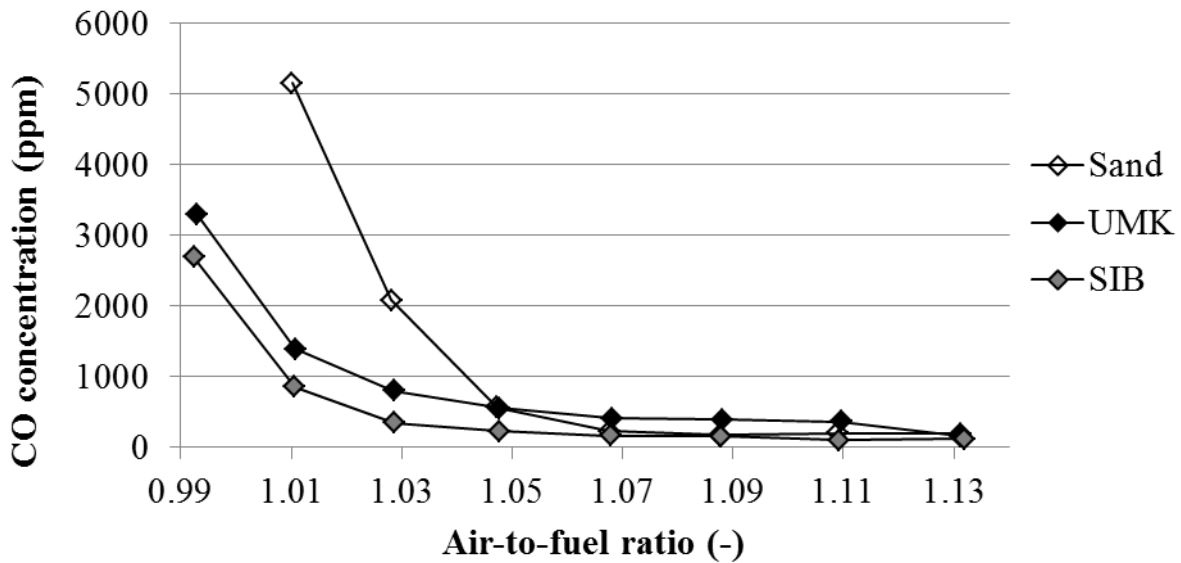


Figure 3. Measured outlet concentration of carbon monoxide as a function of air-to-fuel ratio during operation with 100 wt.% sand, 50 wt.% UMK ore in sand and 50 wt.% SIB ore in sand.

The carbon monoxide concentration remained at a rather low level until the air-to-fuel ratio was decreased below 1.05. When the air-to-fuel ratio approached 1, the carbon monoxide concentration increased to 5000 ppm for the case with 100 wt.% sand and to around 1000 ppm for the cases with 50 wt.% manganese ore in the sand. The air-to-fuel ratio was even lowered to below 1 for the manganese ores, which resulted in around 3000 ppm carbon monoxide in the gas exhaust. The carbon monoxide concentration was significantly reduced at the lower air-to-fuel ratios when the active bed materials were used.

At several of the higher air-to-fuel ratios, the concentration of carbon monoxide is higher for UMK ore than for sand. The reason for this is currently not fully understood. It could however be caused by fluidisation aspects such as slugging in the combustion chamber or stops in one of the loop seals. It was noticed during handling and operation that the flow and fluidisation behaviour of crushed manganese ore differed quite significantly from that of silica sand.

The measured concentrations of oxygen in the gas exhaust during the operation with the two ores and the silica sand are shown in Figure 4. Both mixtures of manganese ore with the sand provided higher concentrations of oxygen in the exhaust gas. These results show the effect of the oxygen release ability of the manganese ores during fuel addition. Both manganese ores release gaseous oxygen in inert atmosphere at 850°C. When all part of the combustor was fluidised with argon, the measured outlet concentration stabilised at 3000-5000 ppm. It can also be seen in the figure for the lowest air-to-fuel ratios that steady state was not achieved. When an air-to-fuel ratio at one or below one was implemented, the oxygen concentration should be zero at steady state. The presence of oxygen in the exhaust shows that the bed material is in average continuously slowly reduced.

The presence of oxygen in the exhaust gas could enable even lower concentrations of carbon monoxide than reported here. The residence time in the outlet pipe kept at temperatures high enough for gas conversion is a few seconds for this combustor. A longer residence time at high temperature and a facilitated gas mixing could potentially drive the reaction further.

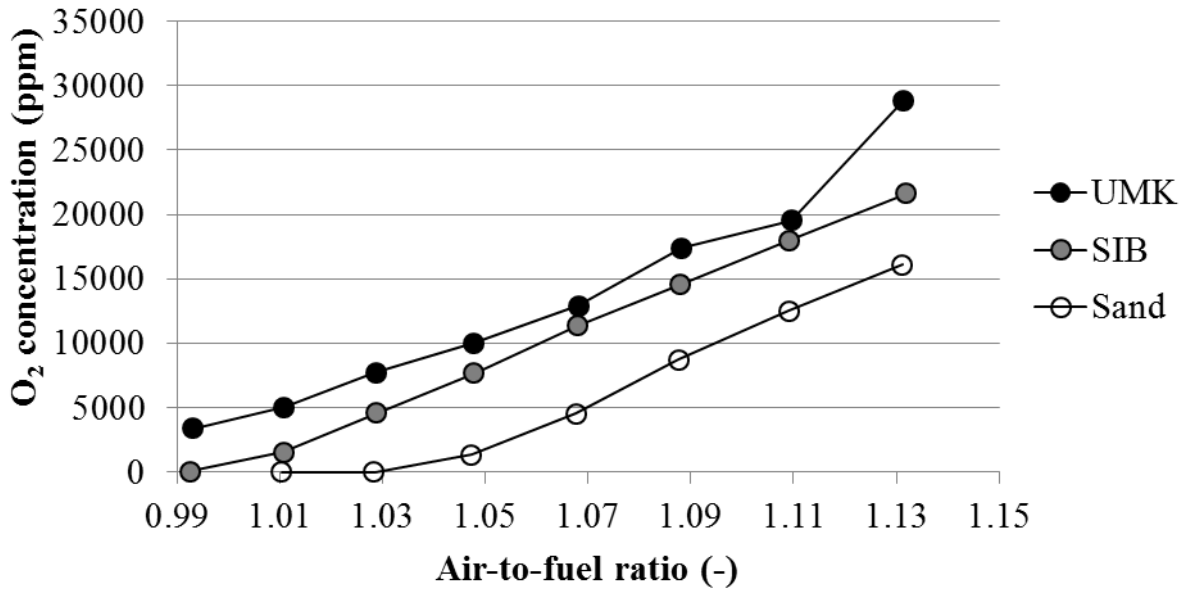


Figure 4. Measured outlet concentration of oxygen as a function of air-to-fuel ratio during operation with 100 wt.% sand, 50 wt.% UMK ore in sand and 50 wt.% SIB ore in sand.

Since all data points included in the figures above only represent 20 min of operation each, longer operational time with fixed parameters was carried out for the two manganese ores. This was done in order to confirm that the results reported above would be valid also during long-term operation. Six hours of stable operation at an air-to-fuel ratio of 1.05 with 50 wt.% SIB ore in sand is shown in Figure 5. The oxygen concentration remained at around 7000 ppm the entire day. The concentration of carbon monoxide slowly decreased from 300 ppm to 200 ppm during the day, which could indicate that the results presented above do not overestimate the fuel conversion. However, this decrease occurred very slowly and the operation could be regarded as stable.

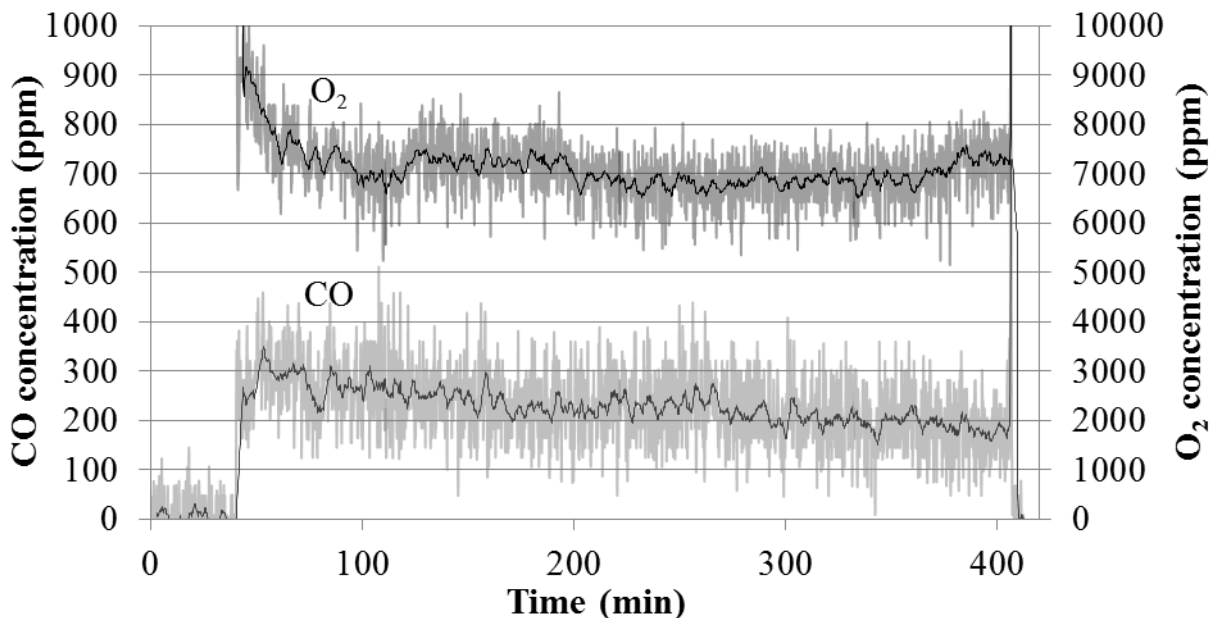


Figure 5. Measured outlet concentrations of carbon monoxide and oxygen during operation with 50 wt.% SIB ore in sand at a constant air-to-fuel ratio of 1.05.

The fines produced during operation, i.e. particles with a diameter below 45 μm , were collected in the filters at the gas exhaust. After the operation with SIB ore, 0.34 wt.% of the solids inventory was found in the filters and after the operation with UMK ore, 0.52 wt.% of the solids inventory was found in the

filters. No measurable amount of fines was found in the filters during the operation of 100 wt.% silica sand.

The particle filters were weighed before and after the six hours of operation shown in Figure 5. The amount of fines produced during this day was assumed to consist only of manganese ore. The loss of manganese ore would then be 0.027 wt.%/h which would correspond to a particle lifetime of 3 700 h for the SIB ore. This is much longer than the typical turnover time in circulating fluidised beds and suggests that attrition may not necessarily be a big concern for practical applications. However, it shall be noticed that the reactor used for these experiments lacks cyclone and use rather low gas velocities (below 1 m/s).

4. Conclusions

Combustion of methane in a fluidised bed has been carried out with two mixtures of manganese ore and silica sand (50/50 wt.%) in a laboratory circulating fluidised bed combustor. The performance of the manganese ores as active bed materials was compared with the performance of only silica sand in the same experimental unit. The main performance indicator studied was the exhaust concentration of carbon monoxide and how it was affected by a varied air-to-fuel ratio.

The main conclusion to draw from these experiments is that it was possible to significantly reduce the exhaust concentration of carbon monoxide by replacing 50 wt.% of the bed inventory of silica sand with manganese ore. The SIB ore performed slightly better than the UMK ore at all investigated air-to-fuel ratios. Both ores could be operated without excess air with a carbon monoxide concentration of around 3000 ppm.

Both ores released gaseous oxygen in inert atmosphere and oxygen was present in the exhaust gas at all times during combustion. The use of the active bed materials thus increased the fuel conversion as well as increased the concentration of oxygen in the exhaust which could facilitate fuel conversion in the freeboard.

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