Oxygen Carrier Aided Combustion (OCAC) of Wood Chips in a Semi-Commercial Circulating Fluidized Bed Boiler Using Manganese Ore as Bed Material

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Abstract: Oxygen Carrier Aided Combustion (OCAC) is realized by using an active oxygen-carrying bed material in fluidized bed boilers. The active material is reduced in fuel rich parts of the boiler and oxidized in air rich parts. Advantages could be achieved such as new mechanisms for oxygen transport in space and time. Here calcined manganese ore has been used as active bed material in a 12 MW$_{th}$ circulating fluidized bed boiler. The fuel was wood chips and the campaign lasted more than two weeks. From an operational point of view, manganese ore worked excellently. From the temperature profile of the boiler it can be concluded that fuel conversion was facilitated, especially in the dense bottom bed. The effect did not always translate to reduced emissions, which suggests that final combustion in the cyclone outlet was also influenced. Substituting 10% of the sand bed with manganese ore made it possible to reduce the air to fuel ratio without generating large amounts of CO. The use of 100% manganese ore resulted in higher emissions of CO than the sand reference, but, when combined sulphur feeding, dramatic reductions in CO emissions, up to 90% compared to sand reference, was achieved.

Keywords: Oxygen Carrier Aided Combustion; Chemical-Looping Combustion; fluidized bed combustion; biomass; bio energy; manganese ore

1. Introduction

Mixing of fuel and air is one of the most important aspects affecting the combustion performance in thermal power plants. Insufficient contact between fuel and air results in emissions of carbon monoxide, unburnt hydrocarbons and char particles in the flue gases. For combustion of solid fuels, good mixing is not easy to achieve due to the multi-phase nature of the process. Therefore, combustion facilities operate with an excess of air compared to what is needed for stoichiometric combustion. This is undesirable for several reasons:

- The excess air increases gas flows which increases the physical size of boiler, which in turn increases its capital costs and operational costs.
- The excess air increases gas velocity and the wear on heat transferring surfaces.
- The larger than necessary gas flow increases the heat loss associated with hot flue gas exiting the stack.
- It also increases the power consumption of support equipment such as fans.

In practice, excess air results in decreased thermal efficiency, increased fuel consumption, increased boiler footprint, increased environmental footprint and increased cost of generating heat and power.

Thus, it is highly desirable to reduce the amount of excess air required in thermal power plants, as long as emissions of unburnt do not increase above acceptable levels.

Fluidized bed (FB) boilers are attractive for combustion of solid fuels. In such boilers, the fuel is mixed with and burnt in a fluidized bed of solid particulate matter. For combustion of biomass and waste, the bed material usually is silica sand. The bed material is important: (i) to propagate heat transfer throughout the boiler; (ii) to equalize temperature in space and time; (iii) for the hydrodynamic performance of the boiler; and (iv) for absorption of certain elements present in fuel ash. For biomass combustion, these abilities are not necessarily connected to the chemical nature of the bed material. This suggests that switching from silica sand to a different bed material could be feasible. In this study, the use of chemically active bed materials capable of facilitating combustion and reducing the need for excess air is explored.

1.1. Background

The concept of oxidizing fuels with oxygen provided by solid oxygen carrier materials rather than with oxygen from air have several potential applications [1]. The one that has received the widest attention is Chemical-Looping Combustion (CLC) [2], which is a combustion technology that would enable carbon dioxide capture without significant costs for gas separation. In CLC, fuel is oxidized with oxygen from a solid oxygen carrier material in particle form, exemplified below by oxidation of methane with manganese (II,III) oxide, see Reaction (1).

$$CH_4(g) + 4Mn_3O_4(s) \rightarrow 12MnO(s) + CO_2(g) + 2H_2O(g) \quad \Delta H°_{298} = 125 \text{ kJ/mol}_{CH4} \tag{1}$$
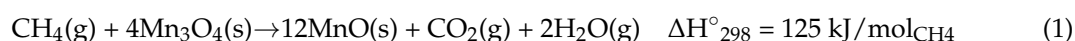
The products are carbon dioxide, steam and manganese (II) oxide, of which the latter is oxidized to its initial state with air in a separate reactor vessel, see Reaction (2).

$$2O_2(g) + 12MnO(s) \rightarrow 4Mn_3O_4(s) \quad \Delta H°_{298} = -927 \text{ kJ/mol}_{CH4} \tag{2}$$
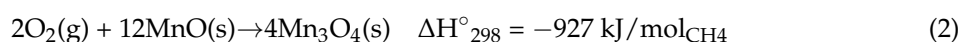
The oxidized material can then be returned to the first reactor vessel and oxidize more fuel. This way fuel and air is never mixed and the flue gas will be undiluted by N_2. The sum of Reactions (1) and (2) is Reaction (3), i.e., ordinary combustion of the fuel with oxygen.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta H°_{298} = -802 \text{ kJ/mol}_{CH4} \tag{3}$$

Some oxygen carriers such as for example manganese (III) oxide are capable of releasing gas phase oxygen directly into an atmosphere with low oxygen fugacity, see Reaction (4).

$$6Mn_2O_3(s) \rightarrow O_2(g) + 4Mn_3O_4(s) \quad \Delta H°_{298} = 195 \text{ kJ/mol}_{CH4} \tag{4}$$
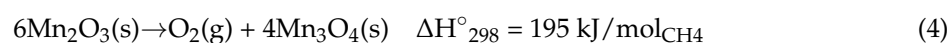
The mechanism described in Reaction (4) is referred to as Chemical-Looping with Oxygen Uncoupling (CLOU) [3]. Oxygen released can react directly with gaseous or solid fuel in accordance with Reaction (3). A chemical-looping process could very well involve fuel oxidation both via Reaction (1) and via Reactions (4) and (3).

1.2. Oxygen Carrier Aided Combustion

Oxygen Carrier Aided Combustion (OCAC) is a combustion concept related to CLC that can be implemented in existing fluidized bed boilers. It is realized by partial or complete substitution of the bed with an oxygen-carrying material, similar to the oxygen carrier used in CLC. The active bed material will be reduced in fuel rich parts of the combustion chamber, in accordance with Reaction (1). In oxygen rich parts it will be oxidized, in accordance with Reaction (2). Materials capable of releasing gas phase oxygen, such as described in Reaction (4), would actively release oxygen in parts of the combustion chamber where it is lacking, see Figure 1.
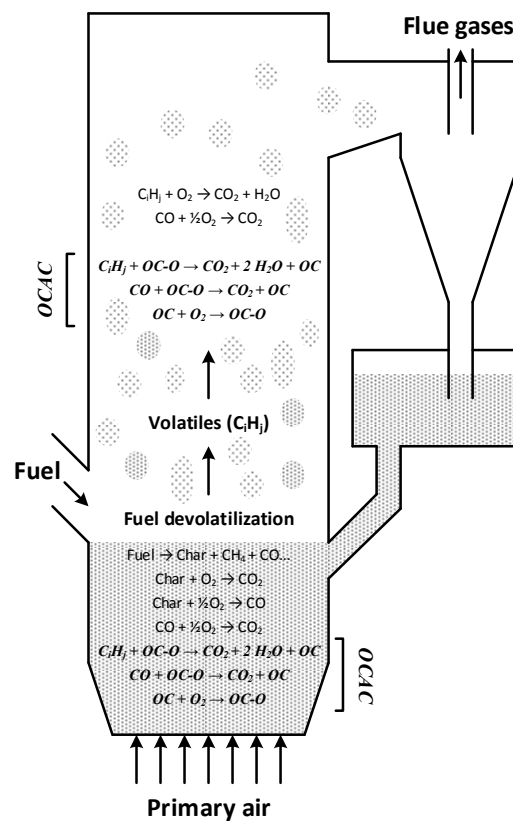
Figure 1. Schematic illustration of Oxygen Carrier Aided Combustion (OCAC) in Circulating Fluidized Bed (CFB) boiler. Simplified bulk reactions in dense bed and freeboard have been included, with new significant reaction pathways in italic. OC–O = oxidized oxygen carrier, OC = reduced oxygen carrier.

Several interesting effects could potentially be achieved:

- Gas phase components can now be oxidized not only by homogenous reactions with oxygen but also by heterogeneous reactions with the solid oxygen carrier, as described in Reaction (1).
- New ways for how oxygen is transported in the space dimension of the boiler will be introduced, thus minimizing the presence of reducing zones and reducing the emissions of CO and unburnt hydrocarbons, especially for combustion with low air-to-fuel-ratio.
- The oxygen retained in the bed will act as an oxygen buffer, thwarting negative effects of uneven fuel feeding and load changes.
- Enhanced fuel conversion in the bottom bed. In ordinary fluidized bed boilers, the more stable fuel components (such as for example CH_4) do not burn in the bottom bed to any larger extent. The moderate temperature ($\approx$800–870 $^\circ$C) and thermal inertia of the bed inhibits formation of sufficiently hot flames. However, it has been shown in CLC studies [2] that CH_4 is readily oxidized by oxygen carrying solids. The apparent reason would be that the heterogeneous reaction between CH_4 and oxygen carrier is not hampered by temperature to the same extent as the homogeneous reaction. Consequently, in OCAC the conversion of CH_4 should proceed rapidly also inside the dense bottom bed, which also has been demonstrated experimentally [4].
- OCAC may allow for innovative boiler designs. The temperature profile of the combustion chamber changes due to improved conversion in the bottom bed and a more evenly distributed oxygen fugacity throughout the boiler. This could reduce hot spots. New possibilities with respect to boiler design may arise such as for example heat extraction in the bottom bed for reduced boiler height, enhanced temperature control, cheaper designs by omitting secondary air, etc. Unlocking these opportunities will require rethinking fluidized bed boilers as we know them.

- OCAC may offer opportunities to reduce traditional problems in biomass combustion. This includes sintering, agglomeration, fouling and corrosion issues connected to combustion of biomass in fluidized beds [5].
- OCAC may allow for a reduction in NO_x emissions and dioxine emissions in waste incineration. Oxygen carriers typically have less oxidizing power compared to gaseous oxygen and there could also be heterogeneous effects.

OCAC was first demonstrated in a campaign in Chalmers 12 MW_{th} Circulating Fluidized Bed (CFB) Research Boiler in 2012 with promising results [6] (up to 80% reduction of CO emissions, up to 30% reduction of NO_x emissions and significantly altered temperature profile with 40 wt % substitution of silica sand with oxygen carrier). In the campaign the mineral ilmenite (titanium-iron ore) was used as bed material. An analysis of bed samples extracted during the campaign has also been published, showing interesting phenomena such as diffusion of potassium into the core of ilmenite particles [7]. Three different ilmenites have also been examined for the OCAC concept in laboratory experiments in a batch fluidized bed [8].

1.3. Manganese Ore as Oxygen Carrier

While synthetic particles sometimes are considered for CLC, it seems reasonable to believe that mineral based materials would be highly favored for OCAC of biomass. This is because ash components are expected to interact with the bed material. For example, in a previous OCAC campaign in Chalmers Research Boiler with ilmenite as oxygen carrier it was established that alkali metals diffuse into the particle core, which led to the formation of KTi_8O_{16} [7]. Therefore, in order to avoid enrichment of ash components in the boiler bed, material likely will need to be replaced in regular intervals. In conventional biomass combustion, typically one third of the sand bed is replaced ("regenerated") each day. For waste incineration, the whole bed can very well need to be replaced on daily basis. While it is not obvious that this will be the same for oxygen carrying materials, the use of synthetic particles nonetheless seems inconvenient. High-performing synthetic oxygen carriers are likely to be at least one order of magnitude more expensive compared to minerals.

Iron rich minerals such as hematite, magnetite and ilmenite are viable oxygen carriers [1,2]. However, iron based minerals have low reactivity with fuel gases compared to synthetic particles and are incapable of releasing significant amounts of gas phase O_2 via oxygen uncoupling [3].

Manganese ores represent an interesting alternative. The theoretical performance of oxide materials can relatively easy be determined by means of thermodynamic equilibrium calculations [9]. Manganese oxide has higher oxygen transfer capacity by weight (7–10 wt % depending on temperature of operation) compared to iron oxide (3.3 wt %). This is because complete conversion of fuel is possible both for reduction of $Mn_2O_3{\rightarrow}Mn_3O_4$ and for $Mn_3O_4{\rightarrow}MnO$, while iron is limited to the reaction $Fe_2O_3{\rightarrow}Fe_3O_4$.

Manganese (III) oxide also has the ability to release oxygen directly in gaseous form in inert atmosphere at temperatures around 800 °C [3]. For manganese ores, which are not pure but also contain elements such as iron and silicon, other more favourable mechanisms for oxygen release that work at higher temperatures could also be available [10,11].

From a practical and economic perspective manganese ores are rich ores which often contain more than 45 wt % manganese, in addition to other potential oxygen carrying components such as iron oxides. This means that the active metal content is similar to iron based ores, while oxygen capacity and reactivity should be better. The price for unprocessed manganese ore generally is below 200 €/ton (2015). This can be compared with the price of unprocessed ilmenite (≈150 €/ton in 2015), unprocessed iron ore (≈50 €/ton in 2015) and high grade silica sand used in CFB boilers (≈50 €/ton).

1.4. The Aim of the Study

The aims of the study were: (i) to study the use of manganese ore as bed material for OCAC in a circulating fluidized bed boiler with respect to operability and general behaviour; and (ii) to establish whether OCAC with manganese ore as bed material would provide benefits with respect to emissions compared to sand, especially at reduced air-to-fuel ratio.

2. Materials and Methods

2.1. Bed Material

The bed material was a pre-calcined industrial standard product provided by Sibelco, a global mining and trading corporation based in Antwerp, Belgium. The calcination conditions are not disclosed but since manganese is present mainly as Mn_2O_3 it can be assumed to have been taking place at 600–800 °C for >1 h in a rotary kiln. A calcined ore was used mainly to avoid rapid decomposition of MnO_2 to Mn_2O_3 and O_2, a reaction that otherwise could have been expected to take place immediately during feeding fresh material into the boiler.

One whole truckload of 25 metric tonnes was ordered. The ore was provided in the form of chunks, a few cm in diameter. The chunks were turned into bed material suitable for use in CFB boilers by UVR-FIA GmbH in Freiberg, Germany. The procedure consisted of pre-crushing followed by grinding, sieving and dedusting in several stages. The target size of the particles was 100–400 μm. The amount of particles received in the desired size range was 12.1 tonnes. The remaining 12.9 tonnes was rejected due to being obtained in too small particle size after the crushing and grinding process. A summary of the properties of the oxygen carrier material can be found in Table 1.

Table 1. Characteristics of the large batch of oxygen carrier.

| Material	Pre-Calcined Manganese Ore Provided by Sibelco
Chemical composition	46.2% Mn, 5.2% Fe, 3.7% Si, 3.4% Al, 1.9% Ca, 1.0% K, 0.3% Mg, 0.2% Ba, 0.2% Ti, 0.1% P, balance O
Provided as	Sintered lumps, a few cm in diameter
Treatment	Crushing, multi-step grinding, sieving, dedusting
Product sieved to size	100–400 μm
Mean particle size	200 μm
Bulk density	1840 kg/m^3
Batch size	12.1 tonnes
Yield in production process	≈50%

2.2. Fuel

The fuel was wood chips provided by a local company (Sjögårdens Energiflis AB, Laholm, Sweden). The product used is produced by chopping rather than crushing and therefore has a comparably uniform size distribution of 20–40 mm, lacking longer splinters. Since it is a commercial product, the precise quality varied slightly over the course of the campaign. However, the raw material was overwhelmingly softwood (pine, and spruce) from local sources in Sweden. The moisture content was measured each day and was 33.6–42.1 wt %.

During one day of operation at low temperature, the boiler was co-fired with minor amounts of white wood pellets for a short period of time. In addition, the gasification reactor connected to the boiler was fed with minor amounts of white wood pellets during two days of experiments. These activities have no bearing on the research presented in this paper though.

2.3. Description of Experimental Facility

Chalmers Research Boiler is a semi-commercial CFB-boiler/gasifier reactor system located at the main campus of Chalmers University of Technology (Gothenburg, Sweden). It is designed for a maximum load of 12 MW when using coal as fuel. When using wood chips the maximum load is 8 MW. Most often the boiler is operated at 5–6 MW, which corresponds to the heating demand of the campus on a cold day. A schematic description of the boiler can be found in Figure 2.
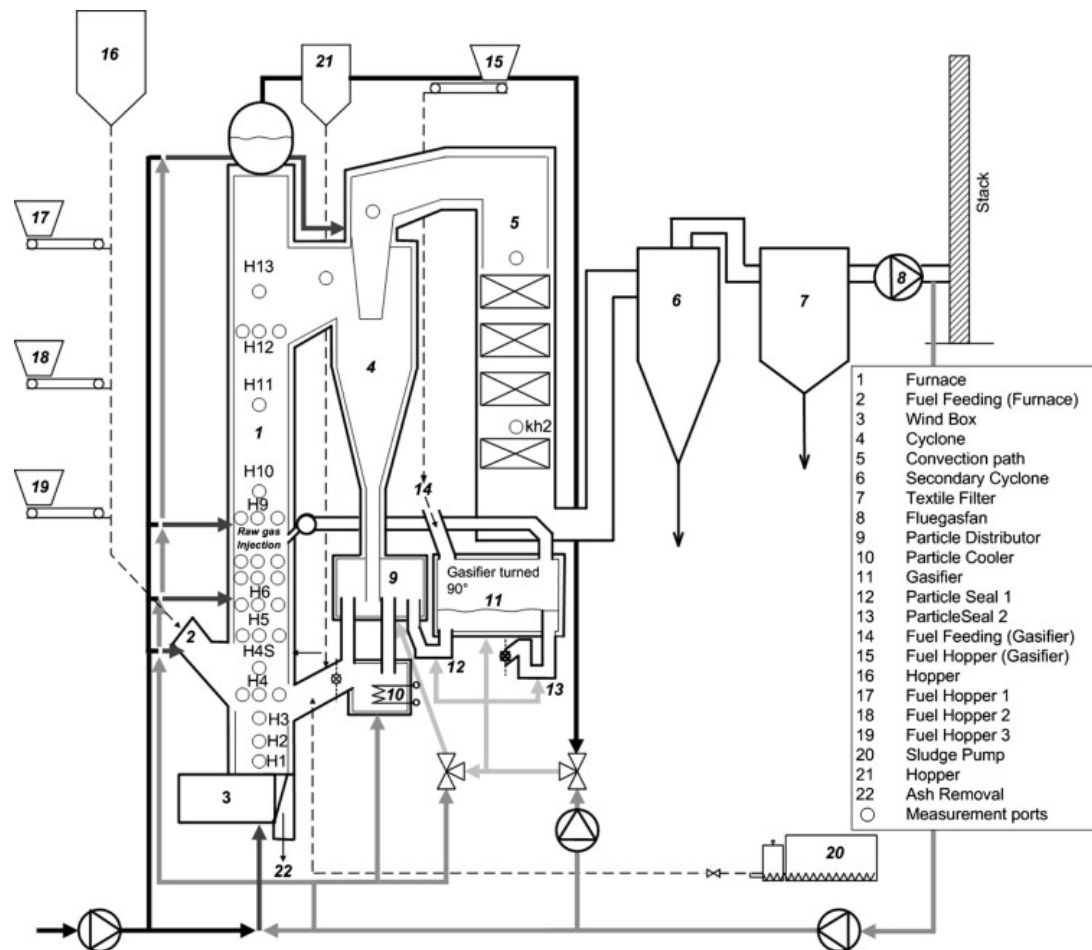
Figure 2. Schematic description of Chalmers Research Boiler/gasifier reactor system.

Regarding the main components of the boiler, as depicted in Figure 2, the furnace: (1) has a square cross-section of 2.25 m^2 and a height of 13.6 m; the fuel is fed at the top of the furnace bed via the fuel chute (2); the entrained bed material is separated from the flue gases in the water-cooled cyclone (4); and then transported to the particle distributer (9); through the particle distributer, it is possible to re-circulate the bed material back to the combustion furnace either via the gasifier (11) or the external particle cooler (10); the flue gases leave the furnace via the cyclone from which they enter the convection path (5), where the gases are cooled in heat exchangers using water which is subsequently used for district heating; the flue gases that exit the convection path are cleaned of ashes in a secondary cyclone (6) and thereafter in bag filters (7).

About 25% of the total fuel load to the system can be fed into the gasifier (11) instead of the boiler. The gasifier operates as a bubbling fluidized bed. About 70% of the fuel fed via the gasifier fuel chute (14–15) is converted into a raw gas. The remaining char follows the bed material to the boiler where it is combusted. A slip stream of the raw gas is extracted for analysis. The remaining raw gas is directed to the centre of the furnace freeboard where it is injected and combusted. Some

experiments with the gasifier was conducted during the campaign, but these experiments will not be further discussed in this article.

The combustion process can be followed in detail by monitoring a range of parameters throughout the boiler such as: (i) gas composition; (ii) temperature; (iii) pressure; and (iv) solids inventory calculated from pressure drops. Gas compositions are measured using three parallel gas analysis systems. All data in the article are based on measurements in the convection path at location kh2 in Figure 2. A summary of the types of instruments used can be found in Table 2.

Table 2. Overview of measured gas components and instrumentation. NDIR = Non-Dispersive Infrared Sensor, GC = Gas Chromatography, PMOD = paramagnetic oxygen detector, CL = Chemiluminescence, FID = Flame Ionization Detector.

Gas Component	Measuring Method
Methane (CH_4)	NDIR, GC
Carbon monoxide (CO)	NDIR, GC
Carbon dioxide (CO_2)	NDIR, GC
Oxygen (O_2)	PMOD, GC
Hydrogen (H_2)	GC
Nitrogen (N_2)	GC
Nitric oxide (NO)	CL
Nitric dioxide (NO_2)	CL
Dinitrogen oxide (N_2O)	GC
Total hydrocarbons (THC)	FID

2.4. Methodology

General operability and behaviour of the boiler when using manganese ore as bed material was studied by observations and measurements of process parameters over the course of the experimental campaign:

- Temperature at different key locations in the boiler. Shows whether manganese ore facilitates fuel conversion in the dense bed and if less combustion takes place in the cyclone, compared to when sand is used.
- Pressure drop over key components. Shows where the bed material is located in the system, whether the bed fluidizes as expected or if it has tendencies to agglomerate. It also provides an indication if there is excessive attrition of the bed material.
- Amount of elutriated ash and solids captured in the secondary cyclone and the textile filter. Samples were taken each day for the purpose of elemental analysis. This allowed for setting up a fundamental mass balance over the boiler.

Samples of bed material were also extracted from inside the boiler during operation. This was done using a special cooled collection probe. Extracted samples were subject to standard bed agglomeration tests at a research institute (SP Sveriges Tekniska Forskningsinstitut AB, (Borås, Sweden), in order to determine tendencies of the bed material to agglomerate at severe conditions. The methodology was as follows. A sample of 200 g was placed in a 140 cm long tube reactor with an inner diameter of 7 cm. The sample was located on a sintered metal plate allocated in the middle of the tube, which also acts as gas distributor. The sample was fluidized with 20 l_n/min air, which corresponds to a superficial gas velocity of about 0.5 m/s at 750 °C. The pressure drop over the bed is measured with a pressure transducer and the temperature is monitored with a K-type thermocouple. The test is initiated when the bed temperature is stabilized at 750 °C. From this point, the bed temperature is increased by 3.5 °C/min. The maximum temperature was 1100 °C. If the bed agglomerates, the pressure drop is reduced. Three temperatures were reported:

- T_{A1} (first tendency towards agglomeration): This is the lowest temperature when a disturbance in the pressure drop over the bed can be verified.

- T_{A2} (apparent agglomeration): The lowest temperature when agglomeration clearly is taking place. The bed is considered to be agglomerating when the pressure drop is reduced continuously with 5 Pa/min or more.
- T_{A3} (complete agglomeration): The temperature when the pressure drop is stabilized at its minimum value.

The effect on emissions and possibility to reduce air-to-fuel ratio was studied by performing lambda experiments. These experiments basically consisted of a step-wise reduction of air-to-fuel ratio during operation and measuring the emissions. Since the research boiler is an industrial production unit operated on commercial basis, the degrees of freedom to achieve this are limited. The control system of the boiler regulates the rate of fuel feeding based on the oxygen concentration in the flue gases. Any changes here affects bed temperature. However, it is possible to regulate temperature to some extent by changing the amount of flue gas recirculated to the boiler. The procedures during lambda experiments were as follows:

- The air flow was kept constant at 2.15 kg/s.
- The baseline fuel flow was 1800 kg/h, corresponding to roughly 5 MW_{th}. The flow was adjusted depending on current moisture content in order to achieve an outlet oxygen concentration of 3.5 vol %.
- The set point for the oxygen concentration was step-wise decreased. This resulted in the regulator system increasing the fuel flow.
- The boiler is normally operating with an outlet oxygen concentration of 3.5 vol %, which was decreased in 0.5 vol % steps down to 1.5 vol %. Each operating point was kept until the oxygen concentration had stabilized for at least 10 min.
- The target temperature was 870 °C in the dense bottom bed. Flue gas recirculation was increased only if necessary.

Using this methodology, the measured emissions could then be expressed as function of air-to-fuel-ratio, λ, which is defined in Equation (5).

$$\lambda = \frac{l_t}{l_{0t}} \qquad (5)$$

l_t = dry air volume added to the combustion chamber ($m_n^3/m_n^3{}_{,fuel}$)
l_{0t} = dry air volume needed for stoichiometric combustion of the fuel mix ($m_n^3/m_n^3{}_{,fuel}$)

In practice the air-to-fuel ratio was calculated from the flue gas concentration by the following expressions, which are derived from mass balances and fuel data:

$$\lambda = 1 + \frac{g_{0t}}{l_{0t}} \left[\frac{(CO_2)_{0t}}{(CO_2)_t} - 1 \right] \qquad (6)$$

$$\lambda = 1 + \frac{g_{0t}}{l_{0t}} * \frac{(O_2)_t}{0.2095 - (O_2)_t} \qquad (7)$$

where g_{0t} = specific dry flue gas flow for stoichiometric combustion (m_n^3/kg_{fuel}), l_{0t} = specific dry air flow for stoichiometric combustion (m_n^3/kg_{fuel}), $(CO_2)_{0t}$ = CO_2 concentration for stoichiometric combustion of the fuel (-), $(CO_2)_t$ = Measured CO_2 concentration (-), and $(O_2)_t$ = Measured O_2 concentration (-).

More than two weeks of operation of the research boiler was achieved, some of which used partial substitution of sand with manganese ore and some of which used 100% manganese ore. A summary of the experimental campaign can be found in Table 3.

Table 3. Overview of the experimental campaign in Chalmers Research Boiler.

Test	Day	Sand (wt %)	Mn Ore (wt %)	Comment
I	1	100	0	Reference experiment
II	2	90	10	
III	3	70	30	
	4	70	30	
IV	5	50	50	
Boiler stop during weekend (Days 6–7) to remove material contaminated with sand.				
	8		100	Start-up with 100% Mn ore
V–VI	9		100	Including operation at 800 °C
	10		100	
	11		100	
	12		100	
Operation with 100% manganese ore during weekend (Days 13–14) by the plant operator.				
VII	15		100	Experiments with sulphur feeding
VIII	16		100	Regenerated bed and sulphur feeding

Except for the planned stop Days 6–7 the plant was in continuous operation over the whole time period. In Table 3, the column "Test" indicates periods during which lambda tests were performed and which will be referred to below.

The experiments can be divided into four sub-campaigns. Day 1 is reference tests with sand, Days 2–5 the plant was operated with partial substitution of sand with manganese ore, Days 8–14 the plant was operated with 100% manganese ore and Days 15–16 it was operated with 100% manganese ore and sulphur feeding. Prior to Day 16, the bed was regenerated, with half of it being replaced with fresh manganese ore uncontaminated by ash.

The reason for doing experiments with sulphur feeding was that the results obtained with 100% manganese ore were disappointing. One hypothesis was that the poor burnout could be associated with the presence of gas phase alkali metals during burnout in the cyclone. Thus a small trickle of elemental sulphur (1 kg/h) was fed via a separate feeding system into the bed on Days 15–16 of operation, in order to propagate sulphation of potassium to solid K_2SO_4 [12], thus reducing the influence of gaseous alkali compounds on the combustion results. The effect of this will be further discussed below.

For experiments with sand and ore mixtures, care was taken to adjust the amount of manganese in the bed so that real values as close to the reported ones as possible were achieved. Each morning some bed material mix was removed via the ash screw located in the bottom of the plant and replaced with fresh manganese ore. The amounts removed and added were attuned to achieve the desired bed composition and a fixed pressure drop over the whole bed of 5.5 kPa. Two assumptions were required:

- It was assumed that the composition of the bed material removed is the same as it would be if the whole bed were perfectly mixed.
- It was assumed that there was no accumulation of ash or fuel in the bed.

Both assumptions are likely to be imperfect, hence the bed composition reported in Table 3 should be seen as approximate.

For the experiments with only manganese ore minor amounts of new material was added in the morning in order to obtain a pressure drop over the boiler of 5.5 kPa when necessary. However, in practice very little material was replaced during Days 8–15. A partial regeneration was done Day 16, during which 50% of the bed material was removed and replaced with fresh manganese ore. Aside from this, the bed was not regenerated over the course of the experimental campaign.

A basic mass balance over the boiler has also been carried out. It was based on the fuel and ash flows during each day of the period of operation. The amount of wood chips and wood pellets (the latter was used as supplementary fuel to a connected gasification reactor during a period of time

not covered in this article) added together with the fuel analysis were used in order to estimate the amount of ash added to the boiler:

$$\dot{m}_{ash,in} = \dot{m}_{wood\ chips}x_{ash,wood\ chips} + \dot{m}_{wood\ pellets}x_{ash,wood\ pellets} \tag{8}$$

where $\dot{m}_{ash,in}$ = mass flow of ash added to the boiler (kg/h), $\dot{m}_{wood\ chips}$ = mass flow of wood chips added to the boiler (kg/h), $x_{ash,wood\ chips}$ = approximate ash content wood chips (-), $\dot{m}_{woodpellets}$ = mass flow of wood pellets added to the boiler (kg/h), and $x_{ash,wood\ pellets}$ = approximate ash content wood pellets (-).

The amount of material elutriated from the boiler is accounted for at two collection points: the secondary cyclone (6) and the textile filter (7). The collection containers are each placed on a scale and their weight is logged during operation. The amount of material leaving the boiler was thus calculated as:

$$\dot{m}_{material,out} = \dot{m}_{sec.cyclone} + \dot{m}_{text.filter} \tag{9}$$

where $\dot{m}_{ash,imaterial,out}$ = mass flow material leaving the boiler (kg/h), $\dot{m}_{sec,cyclone}$ = material collected in secondary cyclone (kg/h), and $\dot{m}_{text,filter}$ = material collected in the textile filter (kg/h).

It was assumed that the difference between the amount of ash added with the fuel and the amount of material elutriated from the boiler consisted of bed material. This assumption neglects the amount of ash which is accumulated within the boiler. This implies that the rate of attrition calculated from this mass balance could be underestimated, since ash remaining in the boiler would mean that more bed material has been elutriated. The rate of attrition or attrition index (A_i) was calculated as:

$$A_i = \frac{\left(\dot{m}_{material,out} - \dot{m}_{ash,in}\right)}{m_{bed}t_{operation}} \tag{10}$$

where m_{bed} is the total bed mass (kg) and $t_{operation}$ (h) is the period of operation during each day. The period of operation was 24 h for all days which did not include start-up or shut-down of the boiler.

3. Results

3.1. Effect on Boiler Temperature Profile during Experiments

Detailed measuring of local temperatures in different parts of an industrial boiler is a complex issue. However, also a relatively simple analysis can provide quantitative insights. Figure 3 describes the temperature in four different measuring points when the boiler was operated at a low air-to-fuel ratio (1.07), while Figure 4 describes the same temperatures when operating the boiler at a higher air to fuel ratio (1.17). These temperatures were measured with conventional thermocouples of type-K.
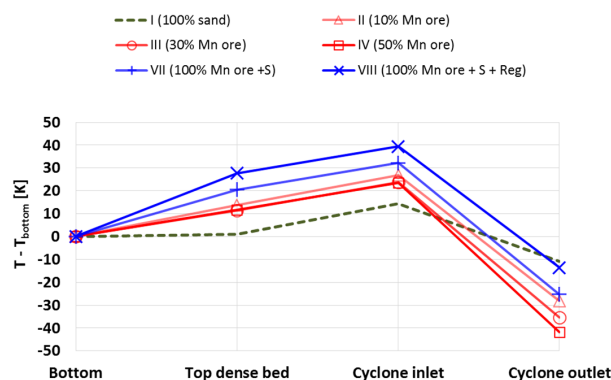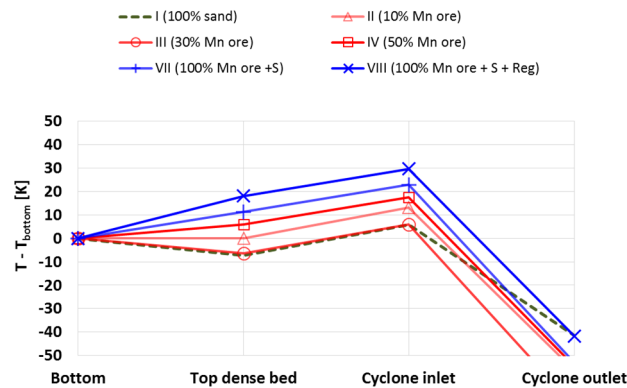

Figure 3. Temperature profile over the boiler when operated on lower air-to-fuel-ratio ($\approx$1.07). T_{bottom} was in the range 866–877 °C and have been used as reference.

Figure 4. Temperature profile over the boiler when operated on higher air-to-fuel-ratio ($\approx$1.17). Tbottom was in the range 855–875 °C and have been used as reference. For 50% Mn ore, data were for air-to-fuel ratio 1.13 since data for 1.17 are lacking.

In Figures 3 and 4, the following phenomena are evident:

- The cyclone is water-cooled, so there should always be and is a temperature drop here. However, it is much more pronounced for experiments involving manganese ore than when sand is used. This suggests that fewer combustibles enter the cyclone and are burnt here.
- From the temperature difference between the bottom of the boiler and the top of the dense bed it can be seen that more heat is generated in the dense bed when manganese ore is present. Especially with 100% manganese ore with sulphur addition, there is considerable temperature increase for both high and low air-to-fuel ratio, which should be compared to slight temperature decrease when sand is used. The cases with partial substitution is somewhere in between.
- The effect on the temperature profile of adding manganese ore is larger at the lower air-to-fuel ratio than at the higher.

Even though it should be acknowledged that the measured temperature data are only good for a qualitative analysis, Figures 3 and 4 are consistent with what could be expected. Addition of an oxygen carrying bed material is supposed to facilitate combustion in the dense part of the bed and to some extent also in the freeboard above it. This should result in a larger temperature increase in this part of the boiler compared to when sand is used. Another effect should be that fewer combustibles remain to be burned in the cyclone, leading to a sharper drop in temperature here. The effect should be more evident at lower air-to-fuel ratio than at higher.

Figures 3 and 4 indicate that 100% manganese ore has superior ability to facilitate combustion in the boiler compared to partial substitution. This is noteworthy since the effects on CO emissions are not as clear cut, as will be explained in Section 3.2 below. These results underlines that the ultimate level of emissions are dependent not only on what happens inside the boiler, but also on final burnout which normally takes place in the vortex finder, i.e., the exit tube from the cyclone.

3.2. Effect on CO Emissions during Reduced Air-to-Fuel Ratio

Switching from sand as bed material to manganese ore should facilitate fuel conversion via the mechanisms described in Section 1.2 above, thus allowing for a reduced air-to-fuel ratio without increasing the emissions of unburnt such as CO. Summaries of the measured CO emissions during lambda-experiments can be found in Figures 5 and 6.
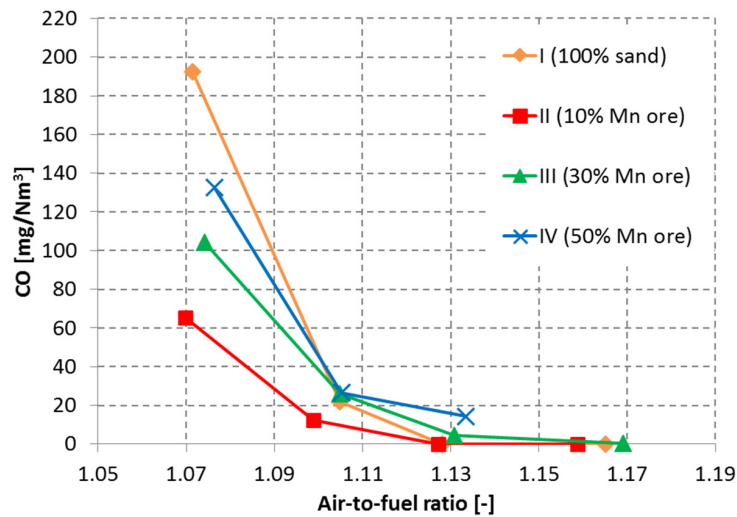
Figure 5. Measured concentrations of CO (mg/nm^3, at 6% O$_2$) at position kh2 in the convection path as a function of the air-to-fuel ratio for experiments with partial substitution of sand with manganese ore.
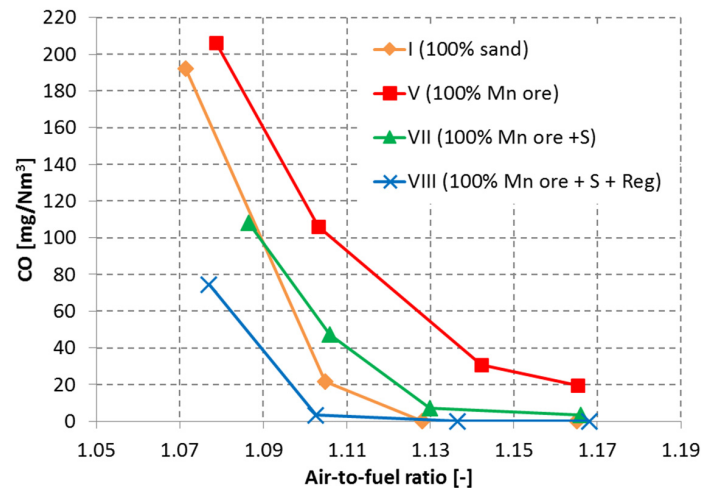
Figure 6. Measured concentrations of CO (mg/nm^3, at 6% O$_2$) at position kh2 in the convection path as a function of the air-to-fuel ratio for experiments with 100% substitution of sand with manganese ore.

As was explained above, the results in Figures 5 and 6 are not totally intuitive. Two things are apparent:

- By substituting sand with manganese ore, it was possible to achieve a substantial reduction in CO emissions compared to the sand reference. For low air to fuel ratios (>1.11), the measured effect on CO emissions varied from 70% reduction to 5% increase compared to a sand reference, depending on the degree of substitution with manganese ore. For higher air to fuel ratios the CO emissions were comparable or slightly higher. With 100% manganese ore as bed material, the emissions of CO and NO increased substantially, but in combination with secondary measure in form of sulphur feeding a reduction in CO-emissions of 60%–90% could be achieved for low air-to-fuel-ratios (>1.11).
- The positive effect is not a given. For experiments with partial substitution of sand, it can be seen that during the following days of operation (with 30% and 50% manganese ore) the CO emissions increased compared to the experiments with 10% manganese ore. For the experiments with 100% manganese ore, no positive effect is seen until active measures in form of sulphur feeding is taken. On the contrary, the CO emissions increases substantially compared to experiments with sand.

It is not straightforward to explain some of the phenomena from Figures 5 and 6. It is unexpected that CO emissions should decrease very considerably when adding 10% manganese ore, only for the effect to be smaller with 30%, negligible with 50% and greatly increase emissions with 100%.

One explanation model is that the results are connected to poor removal of ash components. During normal operation about 30% of the silica sand used as bed material is replaced each day. In practice, this means that alkali metals and other ash components absorbed by the bed material is continuously removed. This regeneration procedure was not implemented during the experiments campaign and may have resulted in accumulation of ash components in the boiler, which could have had a negative impact on the final combustion stage which determines emissions. The motivation for implementing sulphur feeding the last two days of the campaign was to add an alternate mechanism for removal of potassium and check if this would have any effect, which it obviously had. This possible explanation model will be further discussed in Section 5 below.

3.3. Effect on NO Emissions during Reduced Air-to-Fuel Ratio

NO emissions during operation at certain air-to-fuel ratios can be found in Figures 7 and 8.
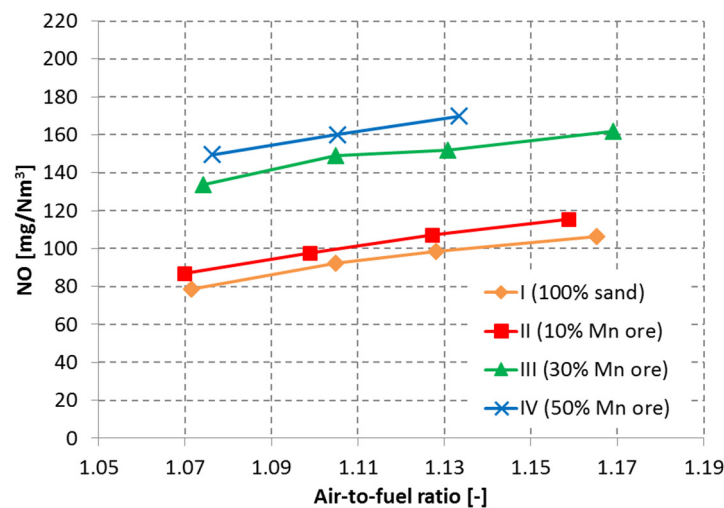

Figure 7. Measured concentrations of NO (mg/nm^3, at 6% O$_2$) at position kh2 in the convection path as a function of the air-to-fuel ratio for experiments with partial substitution of sand with manganese ore.
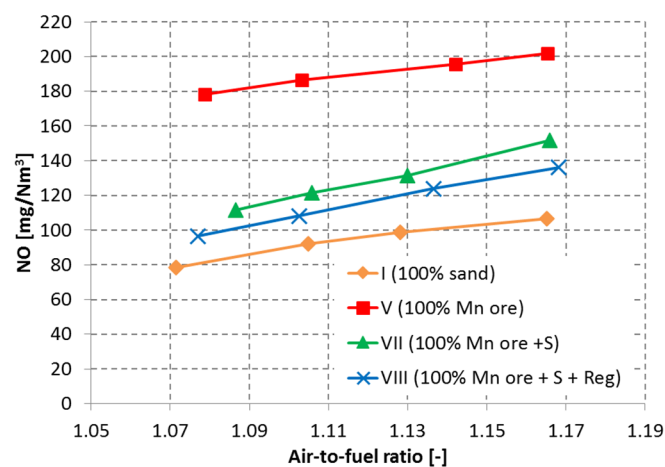

Figure 8. Measured concentrations of NO (mg/nm^3, at 6% O$_2$) at position kh2 in the convection path as a function of the air-to-fuel ratio for experiments with 100% manganese ore.

Based on the results presented in Figures 7 and 8, the following points can be made:

- High air factor results in higher NO emissions due to higher availability to oxygen. This is well-known within combustion chemistry and requires no further comment.
- The sand reference has the lowest NO emissions, meaning that no improvements could be verified by using manganese ore as bed material.
- Of the experiments where manganese ore is used, those which perform best with respect to CO emissions (10% manganese ore and 100% manganese ore with sulphur feeding) also perform decently with respect to NO emissions. A connection between the two seems very likely.

The positive effect of up to 30% reduction of NO shown during partial substitution of sand with ilmenite [6] could not be replicated with manganese ore. This will be further discussed in Section 5 below.

3.4. Observations with Respect to General Operability

Over the entire course of the experimental campaign no issues related to general operability was encountered. There were no tendencies to form agglomerations or other problems commonly occurring during operation of biomass boilers. This was despite the rather high temperature used with the target temperature in the bed being 870 °C, which is near the maximum temperature for biomass combustion in fluidized bed with silica sand as bed material. In fact, the absence of bed regeneration between Day 8 and Day 15 seems likely have resulted in problems related to sintering and bed agglomeration if sand would have been used as bed material rather than manganese ore.

It should also be mentioned that there was a accidental shutdown of the boiler at two occasions. None of the disruptions had anything to do with the performance of the boiler or the bed material. The first occasion was related to a failure in a fan and left the boiler without air for about a minute. The second was related to a disruption of power to the boiler, which shut the boiler down for about 30 min. At both occasions fluidization was suddenly disrupted which when it happens can result in agglomeration of the bed. The fact that no problems were experienced during these occasions suggests that manganese ore certainly is not worse than sand in this respect.

The results of the agglomeration tests can be found in Table 4 below.

Table 4. Results of agglomeration tests.

Sample	T_{A1} (°C)	T_{A2} (°C)	T_{A3} (°C)	Comments
Fresh manganese ore	-	-	-	Successfully reached 1100 °C without problems.
10% Manganese ore in sand (operated with biomass)	876	941	958	
100% manganese ore (operated with biomass)	959	959	998	Sample contained numerous mm-sized agglomerates.
100% manganese ore (operated with biomass and sulphur)	775 (1000)	820 (1000)	1025	Sample contained numerous mm-sized agglomerates.

The fresh ore performed excellently and showed no tendencies towards agglomeration. Ore that had been in operation with biomass eventually agglomerated, but still performed better than what could be expected from a corresponding sample of silica sand. The sand/ore mixture performed comparable to what could be expected for silica sand.

The sample of manganese ore which had been subject also to sulphur feeding showed peculiar behaviour. At 820 °C the pressure drop over the bed started to decrease (from 200 Pa to about 90 Pa). However, the pressure drop stabilized at this level and continued to show variance, suggesting that it fluidized well. Further tendencies towards decreased pressure drop was not seen until 1000 °C and complete agglomeration did not happen until 1025 °C. The higher numbers fit better with practical

experience from Chalmers Research Boiler, which was operated with this mixture at 870 °C without problems for several days.

To summarize, both practical operation of the boiler and dedicated agglomeration tests suggested that manganese ore is likely to have equal or less tendency towards defluidization and agglomeration than silica sand.

3.5. Material Balance and Attrition Behavior

The result from the mass balance and the rate of attrition are reported in Table 5 below.

**Table 5.** Mass balance and estimated rate of attrition.

Day	Ash Added with Fuel (kg)	Elutriated Material (kg)	In–out (kg)	Attrition (wt %/h)	Comment
1	105.2	124.5	−19.3	0.05	Ref. sand
2	141.4	117.6	23.8	−0.05	10% Mn ore
3	137.2	128.5	8.7	−0.02	30% Mn ore
4	128.3	119.1	9.2	−0.02	30% Mn ore
5	49.5	75.4	−25.9	0.16	50% Mn ore
8	93.6	178	−84.4	0.25	Start-up with 100% Mn ore
9	146.1	199.7	−53.6	0.11	Pellets added, also 800 °C
10	140.0	159.1	−19.1	0.04	Includes gasifier operation
11	139.2	174.8	−35.6	0.07	Includes gasifier operation
12	117.8	173.4	−55.6	0.12	
13	118.6	145.4	−26.8	0.06	
14	127.6	155.8	−28.2	0.06	
15	132.9	189.3	−56.4	0.12	Sulfur feeding
16	141.5	224.8	−83.3	0.17	Regenerated bed, sulfur

Because of the uncertainties pointed out in Section 4, one should be careful not to put too much weight into this very fundamental analysis. Nevertheless, the general pattern in Table 5 corresponds to what could be expected. The highest rate of attrition experienced was 0.25 wt %/h during the start-up with fresh manganese ore. In addition, for the other days when substantial amounts of fresh manganese ore were added (Day 5 and Day 16), the attrition rate was clearly above the baseline. Once the material had been in the boiler for a day or so, the attrition rate decreased. This could be expected as the attrition should be less severe after rough parts of the particles have been eroded and the smallest particles elutriated.

Solid samples from different locations were collected over the course of operation. Some were selected and examined in a high-resolution light microscope in order to examine morphological irregularities. Pictures of four such samples can be found in Figure 9.

It is evident that the manganese ore did undergo considerable changes over the course of the campaign. The fresh material is rough-edged, as could be expected from particles produced by crushing and grinding. Material that has been used during operation is smoother around the edges, albeit the general shapes are not substantially altered. This is consistent with the numbers in Table 5 and the general reasoning outlined above. There is also a noticeable change in colour, with fresh particles being almost black while used particles are dark brownish with rusty red also being present. The colour change is likely associated with an alteration of the chemical properties of the manganese ore, which will be subject to detailed analysis in future studies.

It can be concluded that over the course of the experimental campaign there has been no evidence of severe attrition and no indication that manganese ore should not have sufficient physical integrity for use in CFB boilers. Based on the material balance, the expected life time of the manganese ore is >1000 h. That is an order of magnitude higher than the time silica sand typically spends in a CFB boiler for biomass.
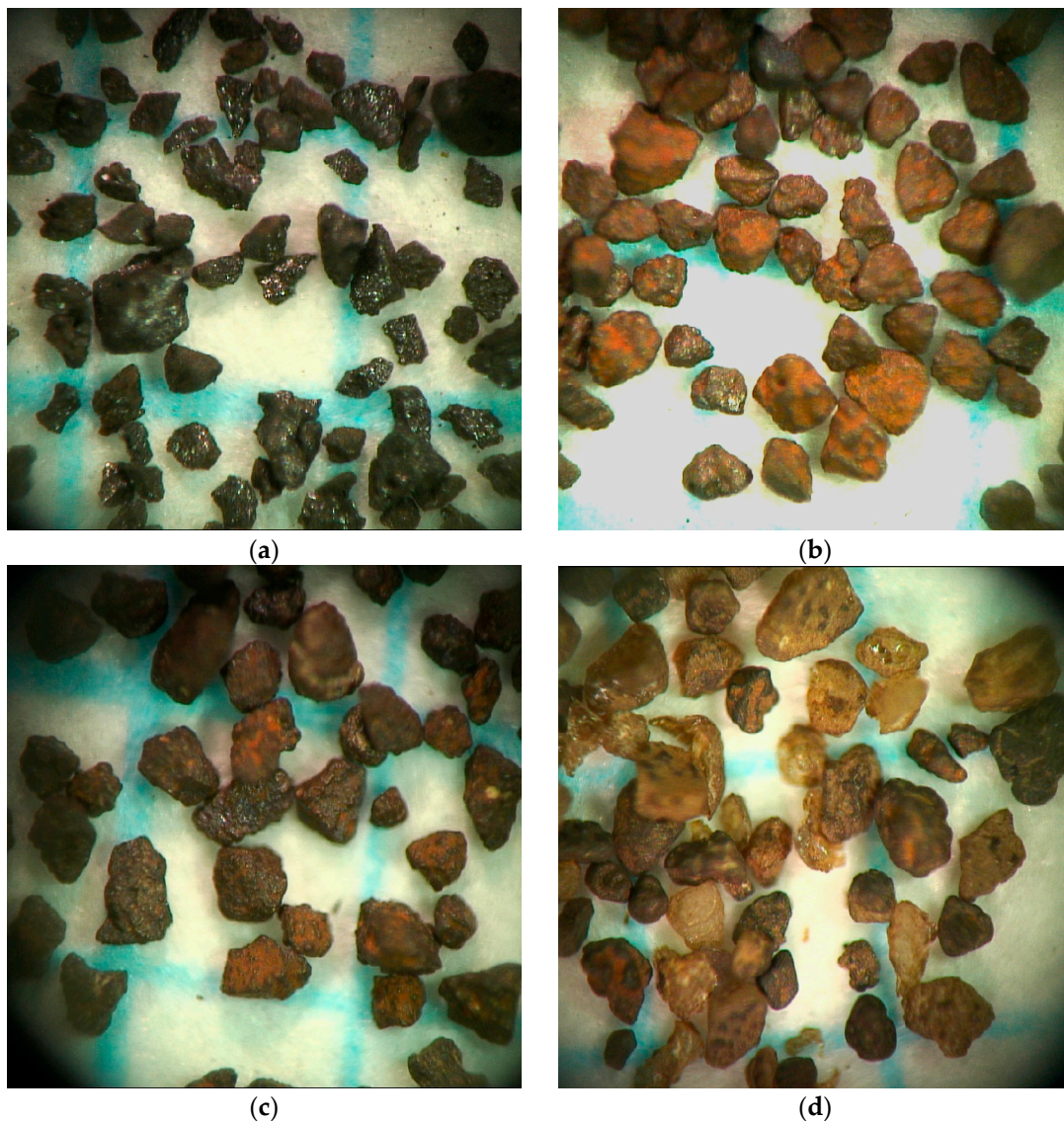
Figure 9. High-resolution light microscope pictures of fresh manganese ore and three bed samples extracted during operation. The blue squares has a side measuring 1 mm. Note that the particles in Figure 9d was extracted after the research campaign had been finished, during the replacement of ore with sand by plant personnel. (**a**) Fresh manganese ore; (**b**) 100% Mn ore after 20 h of operation; (**c**) 100% Mn ore after 172 h of operation; and (**d**) after >300 h of operation (mixed with sand).

4. Discussion

In ordinary fluidized bed combustion of biomass about one third of the silica sand used as bed material is replaced each day. In practice, regeneration means that alkali metals and other ash components absorbed by the bed material is continuously removed. The most critical ash component during combustion of softwood and many other biofuels is alkali metals (mostly potassium). Accumulation of alkali metals and other ash compounds in fluidized bed combustion is well-known to create a range of difficulties. This includes agglomerations and presence of KCl in the flue gas, which in turn may result in deposits on super-heater tubes [13]. In small-scale CFB boilers saturation of KCl and other ash components in the flue gas can also be associated with emissions. The precise mechanism is not universally accepted. One mechanism that has been suggested is that biomasses do not necessarily combust in accordance with the shrinking core model but rather via a shrinking sphere model, which could result in that the ash layer surrounding the fuel particle could make

the oxygen diffusion difficult [5]. Considering the reactive nature of alkali metals, heterogeneous effects could also be a possibility. Unfortunately, there is no way to show whether such effects could have contributed towards poor conditions for final combustion in the vortex finder of the cyclone in this study. This creates a number of difficulties with respect to interpretation of the results from the current study:

- The sand reference was performed at the start of the firing season in a clean boiler and with fresh sand. This resulted in reference data that correspond to "peak performance", rather than standard performance.
- From this point, there was no real bed regeneration. Experiments with partial substitution were done by adding manganese ore, while the used silica sand remained in the boiler.
- However, manganese ore contains alkali metals and other ash elements. The present ore had a potassium content of 1 wt % (see Table 1). Thus, replacing sand with manganese ore may not necessarily work as bed regeneration.
- It is in fact conceivable that the manganese ore was almost saturated with potassium and unable to adsorb much more.

Thus, there is an obvious risk that the mechanisms normally used to remove alkali and other ash components from the boiler may not have been present to adequate extent. This could be an explanation for the not straightforward effect on emissions for the experiments with partial substitution with manganese ore. With 10% substitution there is still 90% relatively fresh sand in the bed that can adsorb ash elements. With 30% and 50% manganese ore the amount of sand is reduced and becoming progressively more saturated with ash components. During experiments with 100% manganese ore, mechanisms to remove alkali from the boiler could in fact be completely absent.

The experiments with sulphur feeding were devised with the reasoning presented above in mind. Addition of elemental sulphur should result in sulphation of potassium, ultimately forming solid K_2SO_4 [12] and reducing the influence of gaseous alkali compounds on the combustion results. As can be seen in Figure 6, this resulted in improved performance already during Day 15. After replacing half of the bed with fresh manganese ore and applying sulphur feeding during Day 16, greatly improved combustion results were achieved.

Unfortunately, this does not prove the theory outlined above since sulphur feeding to biomass boilers have in fact occasionally been applied to reduce CO emission [14,15]. The mechanism for this improvement is not universally accepted either, but a heterogeneous mechanism have been suggested which involves formation of oxidative aerosols [16] of K_2SO_4. The reported effect is typically much smaller than the up to 90% reduction in CO emissions seen in Figure 6 though.

It is clear that further analysis of used bed material and experiments that takes ash removal more closely into account will be required in order to verify the poor performance with respect to emissions for when 100% manganese ore is used as bed material. The experiments with sulphur feeding show that the potential is there for dramatic improvements, but the mechanisms needs to be better understood.

With respect to NO emissions, it was explained above that earlier experiments with ilmenite have indicated that OCAC could reduce NO emissions [6]. Possible mechanisms for the reduction includes fewer hot spot, reduced reliance on flame combustion and catalytic activity of the bed material towards NO reduction. However, in the current campaign substitution of sand with manganese ore resulted in increased NO emissions. For experiments performing well with respect to CO emissions the increase was modest (10%–20%), but they did increase.

Based on the experimental campaign reported here it is not possible to draw any conclusions about mechanisms. However, it should be pointed out that the final NO emissions are equal to NO formation minus NO reduction. It is conceivable that the presence of manganese ore enhance NO formation by consuming reducing gas components such as H_2 and CO and forming oxidizing products

such as H_2O and CO_2, resulting in oxidizing conditions in parts of the boiler that normally would be reducing.

Despite these results, it is not inconceivable that the overall NO emissions could be reduced since NO is also a function of air-to-fuel-ratio. In addition, the impact of important factors such as air-staging was not examined. The understanding of this subject would likely benefit from further studies.

5. Conclusions

Based on the experiments presented in this paper, the following conclusions can be drawn:

- Oxygen Carrier Aided Combustion (OCAC) of biomass using manganese ore as bed material is a viable concept with some potential to improve performance of existing Circulating Fluidized Bed (CFB) boilers.

- From an operational point of view, manganese ore worked excellently as bed material. No problems were encountered related to factors such as attrition and agglomeration. In addition, the material was easy to handle, to fill into and remove from the boiler.

- From the temperature profile of the boiler it can be seen that the presence of the oxygen carrier facilitates fuel conversion inside the boiler, including in the dense bottom bed. The effect did not always translate to reduced emissions though which suggests that final combustion in the cyclone outlet was also influenced.

- Substitution 10% of the sand bed with manganese ore made it possible to reduce the air to fuel ratio considerably without generating large amounts of CO. This suggests that higher fuel flow could be feasible in existing facilities and that fan power and heat loss with flue gases could be reduced.

- The use of 100% manganese ore resulted in higher emissions of CO than the sand reference. However, when combined with sulphur feeding dramatic reductions in CO emissions with up to 90% was achieved.

- The method did not show great potential for reduction of NO emissions. For a given air-to-fuel ratio, NO emissions were always higher when manganese ore was included in the bed compared to when only sand was used.

Author Contributions: Magnus Rydén was project leader responsible for formulating the project, preparation and logistics of bed material, communication with funding agencies, participation in the experimental campaign and data evaluation. Fredrik Lind was responsible for planning of the campaign at the research boiler and communication with its personnel. Malin Hanning and Angelica Corcoran participated in the experimental campaign and contributed much to planning, methodology development, data gathering and data evaluation. Magnus Rydén wrote the article with input from the other three co-authors.

Conflicts of Interest: The authors declare no conflicts of interest.

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