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Oxygen Carrier Aided Combustion (OCAC) of Wood Chips in a 12 MW_{th} Circulating Fluidized Bed Boiler Using Steel Converter Slag as Bed Material

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Abstract: The novel combustion concept Oxygen Carrier Aided Combustion (OCAC) is realized by addition of an active oxygen-carrying bed material to conventional fluidized bed boilers. The active bed material is meant to become reduced in fuel-rich parts of the boiler and oxidized in oxygen-rich parts, thus potentially providing advantages such as new mechanisms for oxygen transport in space and time. In this study, oxygen-carrier particles prepared from so called Linz-Donawitz (LD)-slag are examined as active bed material in a 12 MW_{th} Circulating Fluidized Bed (CFB) boiler. LD-slag is the second largest by-product in steel making and is generated in the basic LD oxygen converter process. The experimental campaign lasted for two full weeks. The fuel was wood chips. LD-slag worked well from an operational point of view and no problems related to handling, agglomeration or sintering were experienced, albeit the production of fly ash increased. The boiler temperature profile suggested that fuel conversion in the main boiler body was facilitated, but the effect did not readily translate into reduced emissions from the stack. Spraying an aqueous solution of ammonium sulphate directly into the cyclone outlet with the aim of rejecting alkali metals as alkali suphates was found to solve the problems related to carbon monoxide emissions, suggesting that the problems could be due to the poor ability of LD-slag to absorb certain ash components. Use of a mixed bed consisting of 10–50 wt% LD-slag, with the remaining part being silica sand for ash absorption, also worked well. It is concluded that LD-slag could be a very cheap and readily available oxygen-carrying bed material for use in fluidized bed applications.

Keywords: Oxygen Carrier Aided Combustion; fluidized bed combustion; Chemical Looping Combustion; oxygen carriers; Bio energy; LD-slag; slag utilization

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1. Introduction

1.1. Background

Fluidized bed (FB) boilers are commercially attractive as a technology used for combustion of solid fuels. For biomass and waste fuels, the fluidized bed usually consists of silica sand, in addition to char and ash, which are continuously added to the boiler via the fuel. The bed material is important for: (i) propagating heat transfer throughout the boiler; (ii) equalizing temperature in space and time; (iii) the hydrodynamic performance of the boiler; and (iv) absorption of certain ash elements that otherwise would affect performance with respect to emissions, corrosion and sintering. While silica sand is currently the bed material of choice for biomass combustion, switching to other types of bed material is feasible and could potentially also provide certain advantages. In this study, the use of a chemically active bed material is demonstrated in a large-scale combustion facility. The material used is Linz-Donawitz (LD)-slag, which is the second most abundant by-product in a typical integrated steel mill. LD-slag has properties which could potentially improve the performance of fluidized bed boilers. Notably, it contains significant fractions of iron and manganese oxides. Under conditions relevant to combustion, iron and manganese oxides can be expected to be subject to oxidation in oxygen-rich zones of the boiler and reduction in fuel-rich zones. Thus, LD-slag exhibits properties similar to the solid Oxygen Carrier (OC) materials used in Chemical Looping Combustion (CLC), a potential future technology for carbon capture. The concept of replacing silica sand with an oxygen carrier in fluidized bed combustion will here be referred to as Oxygen Carrier Aided Combustion (OCAC).

1.2. Chemical Looping Combustion and Oxygen Carriers

The concept of oxidizing fuels with oxygen provided by solid oxygen carrier materials, rather than with oxygen from air, has several possible applications [1,2]. Chemical Looping Combustion (CLC) [1–4] is a combustion technology that would enable carbon capture without significant costs for gas separation [5]. In CLC, fuel is oxidized with oxygen from a solid Oxygen Carrier (OC) in particle form, exemplified below by oxidation of methane with iron (III) oxide, see reaction (1).

$$\mathrm{CH_4(g) + 12Fe_2O_3(s) \rightarrow 8Fe_3O_4(s) + CO_2(g) + 2H_2O(g)} \tag{1}$$

The products are carbon dioxide, steam and iron (II, III) oxide, of which the latter is oxidized to its initial state with air in a separate air reactor, see reaction (2).

$$\mathrm{2O_2(g) + 8Fe_3O_4(s) \rightarrow 12Fe_2O_3(s)} \tag{2}$$

The oxidized material is then be returned to the first reactor vessel ready to oxidize more fuel. Since fuel and air are not mixed, the flue gas will be undiluted by N_2. The sum of reaction (1) and reaction (2) is reaction (3), that is, combustion of the fuel with oxygen.

$$\mathrm{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)} \tag{3}$$

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

$$\mathrm{6Mn_2O_3(s) \rightarrow O_2(g) + 4Mn_3O_4(s)} \tag{4}$$

The mechanism described in reaction (4) is typically referred to as Chemical Looping with Oxygen Uncoupling (CLOU) [6]. The oxygen that is released can react directly with fuels, in accordance with reaction (3). A chemical looping process could involve fuel oxidation both via reaction (1) and via reactions (4+3).

As of this moment, Chemical Looping Combustion is not a commercially available technology. Further, there is no clear consensus in the scientific community about reactor design and choice of oxygen carrier material. However, fluidized bed reactors with oxygen carrier as the bed material is currently the most examined design principle, and there are more than 10,000 h of operational experience with such pilot reactors [7]. A large majority of studies about solid fuel applications utilizes cheap and readily available oxygen carriers such as naturally occurring minerals or industrial by-products [4].

1.3. Oxygen Carrier Aided Combustion

Oxygen Carrier Aided Combustion (OCAC) is a concept strongly related to Chemical Looping Combustion which can be directly implemented in existing fluidized bed boilers. It is realized by partial or complete substitution of the standard semi-inert bed material with an active oxygen carrier material. The active bed material will be reduced in fuel rich parts of the combustion chamber in accordance with reactions such as reaction (1), as well as by reaction with other products of pyrolysis such as CO and H_2. 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 release oxygen in parts of the combustion chamber where it is lacking, see Figure 1.

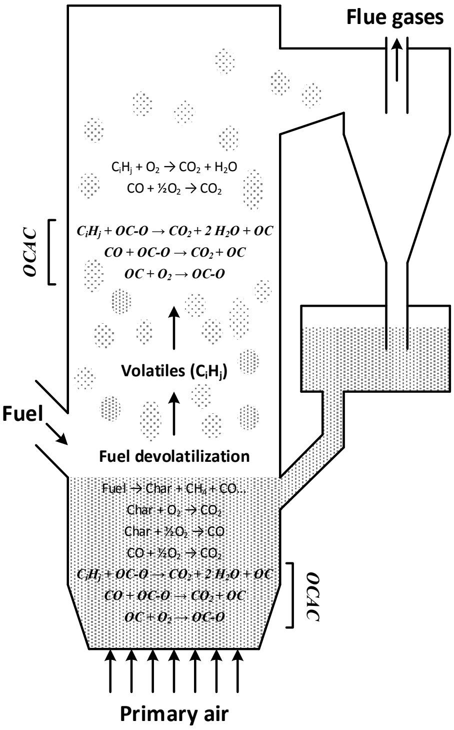

Figure 1. Schematic illustration of Oxygen Carrier Aided Combustion (OCAC) in Circulating Fluidized Bed (CFB) boiler. Simplified bulk reactions in dense bed and freeboard have been included, with new significant reaction pathways in italic. OC-O = oxidized oxygen carrier, OC = reduced oxygen carrier.

In OCAC several interesting effects could potentially be achieved:

- Gas phase fuel components can be oxidized not only by homogenous reactions with oxygen, but also by heterogeneous reactions with the oxygen carrier, as described in reaction (1).
- New mechanisms for oxygen transport in the boiler will be introduced, thus minimizing the presence of reducing zones and potentially reducing the emissions of CO, H_2 and unburnt hydrocarbons.
- The bed of oxygen carrier material will act as an oxygen buffer, possibly thwarting negative effects of uneven fuel feeding and load changes.
- Enhanced fuel conversion in the dense bottom bed. In ordinary fluidized bed boilers the more stable fuel components (such as for example CH_4) do not burn rapidly in the bottom bed since the moderate temperature (≈800–850 °C) and thermal inertia of the bed inhibits formation of hot flames. However, it has been shown in CLC studies [3] 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 more rapidly also inside the dense bottom bed, a phenomena that has also been demonstrated experimentally [8].
- 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 [9].
- OCAC may allow for the use of less excess air than what is needed in conventional boilers.

The last point is important. Mixing of oxygen and fuel is an important aspect affecting the performance of thermal power plants. Insufficient contact between fuel and oxygen results in emissions of carbon monoxide, unburnt hydrocarbons and char particles. For solid fuels, good mixing is sometimes difficult to achieve. In order to avoid poor fuel conversion and high emission levels, operation with a significant excess of air, compared to what is needed for stoichiometric combustion, is often necessary. This increase the total volumetric gas flow and results in: (i) increased boiler size, cost, and footprint; (ii) increased gas velocity and wear on heat transferring surfaces; (iii) increased heat losses associated with hot flue gas exiting the stack; and (iv) increased power consumption of support equipment, such as fans.

OCAC was first demonstrated in a campaign in Chalmers 12 MW_{th} Circulating Fluidized Bed (CFB) Research Boiler in 2012 with promising results [10] (up to 80% reduction of CO emissions and significantly altered temperature profile with 40 wt% substitution of silica sand with oxygen carrier). In that campaign the mineral ilmenite (titanium-iron ore) was used as the bed material. In the past few years OCAC with ilmenite has been subject to commercialization in Sweden by the company Improbed AB (a subsidy of the global corporation E.ON). As part of this effort, ilmenite has been used as a bed material in an undisclosed number of commercial fluidized bed boilers in Sweden burning biomass and waste fuels. An analysis of ilmenite bed samples extracted during operation show interesting phenomena, such as diffusion of ash components, such as potassium, into the core of ilmenite particles [11]. The oxygen buffering capability of ilmenite during rapid load change of large boilers has been verified [12]. The performance of sand and rock ilmenite has been compared [13]. An experimental campaign has also been conducted in Chalmers research boiler using a manganese-based bed material rather than ilmenite [14]. The OCAC concept has been examined also in small lab scale experiments [15].

1.4. LD-Slag as Oxygen Carrier

While it would be possible to produce synthetic oxygen carrier particles for OCAC, this would likely be a costly procedure. This is because ash elements present in biomass and waste fuels (K, Na, Ca, Si etc.) are expected to interact with the bed material in a potentially irreversible manner. For silica sand ash components are absorbed on the particle surface. For ilmenite it has been established that the ash component most central for operability during combustion of woody biomass, which is potassium, diffuses into the particle core resulting in formation of KTi_8O_{16} [11]. It is well established that alkali metals are central to several undesired phenomena such as sintering, agglomeration, corrosion and emissions [9].

Regardless of mechanism, perpetual enrichment of ash components in the bed material is not possible. Thus, the bed material will need to be replaced in regular intervals. In a biomass boiler it is common to replace one third of the sand bed each day, a procedure commonly referred to as regeneration. For waste incineration the whole sand inventory can very well need to be replaced on daily basis. An industrially accepted rule of thumb for the consumption of silica sand during biomass combustion is 3 kg/MWh_{th}. The corresponding number for waste incineration is 6 kg/MWh_{th}, but it can sometimes need to be considerably higher.

While it is not obvious that regeneration will have to be done in precisely the same way for oxygen carrying materials as for sand, it seems reasonable to believe that the use of synthetic particles will be inconvenient from a cost and resource perspective. High-performing synthetic oxygen carriers are likely to be at least one order of magnitude more expensive compared to virgin minerals, which in turn very well could be one order of magnitude more expensive per ton than silica sand. Silica sand already represents a significant cost for biomass fired boilers. For a fluidized bed boiler at the scale of 100 MWh_{th} (a common size in Swedish district heating system), the annual cost for silica sand is in the order of 1–5 MSEK annually, depending on fuel and annual hours of operation. Hence the use of considerably more expensive bed materials is not favored by plant operators, unless there are considerable practical gains. However, the use of bed materials with the potential to be even cheaper than silica sand and which also could provide certain technical advantages is met with considerable interest. Industrial by-products, for which there currently is limited demand, are likely the cheapest category of bed materials available.

The theoretical performance of oxide materials can quite easily be determined by means of thermodynamic equilibrium calculations [16]. Iron oxides are viable oxygen carriers [1–4,16]. However, iron oxides are incapable of releasing significant amounts of gas phase O_2 via oxygen uncoupling [6]. Manganese oxides have higher oxygen transfer capacity by weight (7–10 wt% depending on temperature of operation) compared to iron oxide (3.3 wt%) [16]. 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 oxides also have the ability to release oxygen directly in gaseous form in inert atmosphere at temperatures around 800 °C [6]. For mixed manganese oxides, which are not pure but also contain elements such as iron and silicon, other more favorable mechanisms for oxygen release which work at higher temperatures could also be available [17,18].

LD-slag is the second largest by-product in steelmaking. It is formed by reactions of slag formers (e.g., burned lime), silica, iron and other components during conversion of carbon-rich molten pig iron into steel in the basic oxygen-blown converter process (aka the Linz-Donawitz process). LD-slag and steel are generated during the converter process, the steel is then tapped from the converter and the slag remains in the converter vessel. The remaining molten slag is then poured into a slag pot which subsequently is discharged outside. Large slag lumps are then formed during cooling and solidification of the melt. The resulting lumps have high skeletal density (3500 kg/m^3), but its particulate bulk density in crushed form (1500–2000 kg/m^3) is not dissimilar to sand. A typical steel-mill may generate 100–200 kton/year. Depending on the level of impurities, parts of it can often be recirculated internally to replace limestone in the blast furnace. In Sweden the total production of LD-slag is >300 kton/year, of which only about half can be internally recirculated due to the size fractions in which the slag occurs. There is limited demand for the remaining part, however work is ongoing to find other usages for the material, for example through utilisation of the vanadium content in the slag as a raw material for vanadium production. To some extent, LD-slag is also used in low-value applications (e.g., construction, raw material in mineral-wool plants), but tens of thousands of tonnes is still being put into storage each year, in addition to the very large stock which is already available.

The chemical composition of LD-slag makes it highly interesting as oxygen carrier as it is rich in iron and manganese oxides. The precise composition will depend on the raw material fed to the steel converter. Guideline values are 22 wt% Fe_2O_3, 3 wt% MnO, 10 wt% SiO_2, 43 wt% CaO, 9 wt% MgO with oxides of aluminium, titanium and vanadium being the main impurities. It should be noted that combined Fe-Mn-Si oxides are among the more interesting combined oxide systems for oxygen carrying purposes [17,19].

1.5. The Aims of This Study

The aims of this study are: (i) to examine LD-slag as bed material during OCAC of biomass in a circulating fluidized bed boiler with respect to operability and general behaviour, (ii) to establish whether LD-slag could provide benefits with respect to emissions compared to silica sand, (iii) to form a preliminary opinion about whether LD-slag could be commercially or environmentally attractive as bed material in fluidized bed boilers.

2. Materials and Methods

2.1. Bed Material

The LD-slag was prepared by SSAB Merox AB at the integrated steel mill in Oxelösund, Sweden and provided to the research boiler by pressure discharge truck. The production procedure involved drying, crushing, grinding and sieving of roughly 180 metric tonnes of LD-slag taken from an open storage pile. The target size of the particles was 100–400 µm. The yield in the production process with respect to particles in the desired size interval was reportedly 20–25%. This number could likely be considerably higher in future efforts, since the production method used was rather ad-hoc and subject to some trial-and-error. Production of large batches of oxygen carriers from minerals have previously resulted in yields of about 50% [14]. The amount of LD-slag received was 38 metric tonnes. Neither sieving nor density measurements of random samples provided totally consistent results. This suggests that the LD-slag in the storage pile was not homogeneous. Further, as pointed out above, the production itself proceeded on a trial-and-error basis. Notably, a sieving pan was changed from 100 µm to 150 µm during the production process in an attempt to reduce the very time-consuming sieving effort. Nevertheless, the sieving was imperfect and analysis of small samples suggests that 10–15 wt% of the received batch consisted of particles smaller than 90 µm. During operation this had some minor consequences with respect to elutriation since smaller particles are more likely to be elutriated than larger ones, but this is not believed to have influenced the conclusions of the study. Sand was used as reference material and occasionally for mixing together with LD-slag. Standard silica sand provided by Sibelco Nordic AB (Baskarp B28) was used for this purpose. A summary of the properties of the bed material can be found in Table 1. Note that the composition, while based on elemental analysis, should be treated as approximate since the batch was inhomogeneous. For sand, the composition reported is the one provided by the supplier.

Table 1. Characteristics of bed material.

Material	LD-Slag	Baskarp B28
Composition (wt%)	31.7% Ca, 17.1% Fe, 5.9% Mg, 5.6% Si, 2.6% Mn, 1.5% V, 0.8% Al, 0.25% P, 0.10% S, 0.05% K, balance O	74% quartz, 22% feldspar, 2% biotite
Treatment	Crushing, drying, sieving	-
Size span	100–400 µm (nominal)	90–355 µm
Fraction below 90 µm	10–15%	-
Bulk density (aerated)	≈1600 kg/m^3	1500 kg/m^3
Bulk density (tapped)	≈1700 kg/m^3	-

2.2. Fuel

The fuel was wood chips of 20–40 mm provided by Sjögården Energiflis AB. Since it is a commercial product delivered in an open truck the quality and moisture content varied slightly over the course of the campaign. The raw material was always overwhelmingly softwood (pine, spruce) from local sources in Sweden. Two samples were sent for elemental analysis at the Research Institute of Sweden (RISE) (see Table 2). The moisture content was measured each day and was in the interval 36–42 wt%.

Table 2. Elemental analysis of two fuel samples. The measured data is for dry fuel and balance should be oxygen. The reported ash content was 0.5 wt% for both samples, including oxygen.

Component	Week 1	Week 2
Carbon (wt%)	50.4	50.1
Hydrogen (wt%)	6.0	6.0
Nitrogen (wt%)	0.1	0.1
Sulphur (wt%)	<0.02	<0.02
Chlorine (wt%)	<0.01	<0.01
Aluminium (wt%)	0.003	0.004
Silicon (wt%)	0.009	0.016
Iron (wt%)	0.003	0.003
Titanium (wt%)	<0.001	<0.001
Manganese (wt%)	0.008	0.008
Magnesium (wt%)	0.019	0.020
Calcium (wt%)	0.12	0.12
Barium (wt%)	0.001	0.001
Sodium (wt%)	0.004	0.005
Potassium (wt%)	0.061	0.071
Phosphorus (wt%)	0.007	0.009
Higher heating value (MJ/kg)	20.23	20.1
Lower heating value (MJ/kg)	18.93	18.78

2.3. Experimental Facility

Chalmers Research Boiler is located at the main campus of Chalmers University of Technology in Göteborg, Sweden. It is a commercial production facility owned and operated by Akademiska Hus AB, producing hot water for the local district heating network. It is designed for a maximum load of 12 MW_{th} when using coal as fuel. When using wood chips, the maximum load is 8 MW_{th}. Most often the boiler is operated at 5–6 MW_{th}, 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.

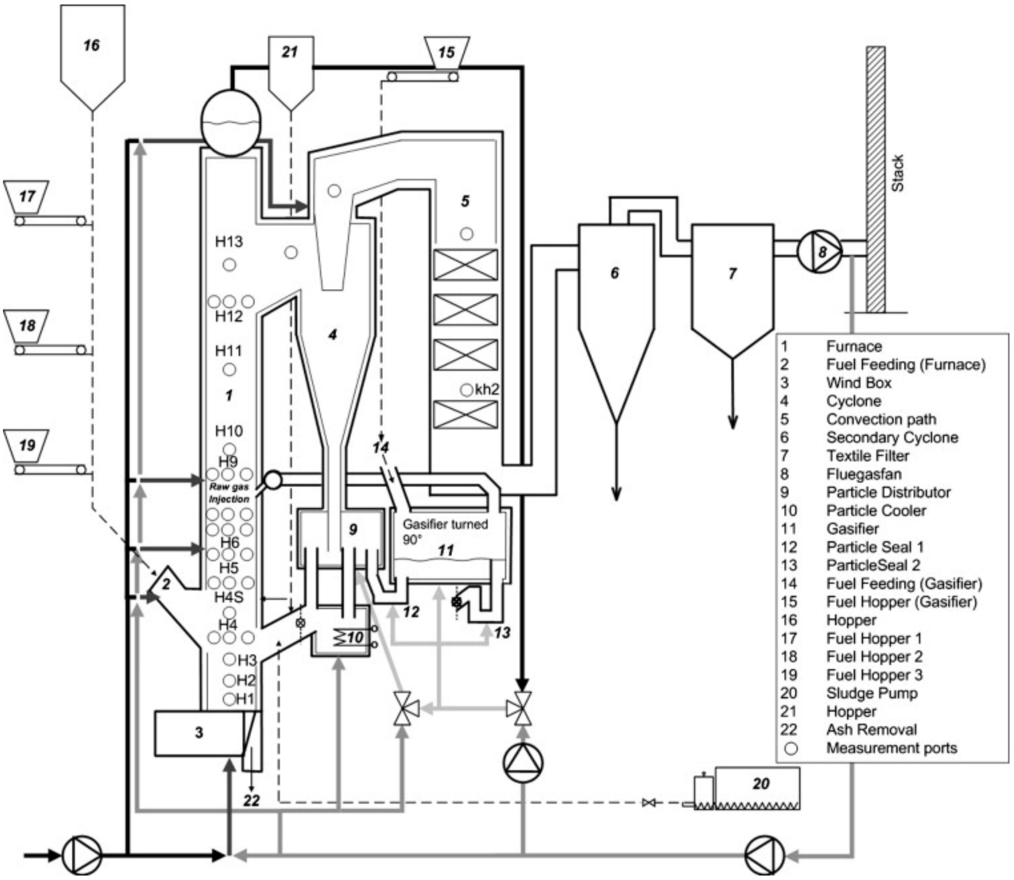

Figure 2. Schematic description of Chalmers research boiler/gasifier reactor system.

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 bubbling-fluidized bed gasifier (11) instead of the boiler, but during the campaign presented in this paper the gasifier was disconnected from the boiler.

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 is 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 3.

Table 3. 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

Operability and behaviour of the boiler when using LD-slag as the bed material was studied by observations and measurements of the following process parameters:

- Temperature at different key locations. Can potentially indicate whether LD-slag 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. Indicates where the bed material is located, whether the bed fluidizes, the materials tendencies to agglomerate and if there is excessive attrition.
- Amount of elutriated ash and solids captured in the secondary cyclone and the subsequent textile filter.
- Bed, ash and fuel samples were also taken each day for various analyses, some of which will be referred to below.

The effect on emissions was studied primarily by performing so called lambda experiments, which essentially consisted of a step-wise reduction of the air-to-fuel ratio during operation, and measuring of the resulting emissions. It should be pointed out that since the research boiler is an industrial production unit operated on commercial basis, the possibilities to perform truly comparative experiments are somewhat limited. For example, the control system of the boiler regulates the rate of fuel feeding based on the oxygen concentration in the flue gases and any changes here affect bed temperature. Also fuel quality and heat demand can vary over the course of a day or a campaign. The general procedures during lambda experiments were as follows:

- The baseline air flow was 2.15 kg/s.
- The baseline fuel flow was set to 1800 kg/h, which corresponds to roughly 5 MW_{th}. The flow was adjusted depending on moisture content in order to achieve an outlet oxygen concentration of 3.5 vol% on dry basis.
- The set point for the oxygen concentration was step-wise decreased, which results in the regulator system increasing the fuel flow.
- The outlet oxygen concentration was decreased in 0.5 vol% steps down to 1.5 vol%. Each operating point was kept until the oxygen concentration had stabilized, and remained stable for at least 10 min.
- The target temperature was 840–870 °C in the dense bottom bed. Temperature could be regulated by exchanging a fraction of the fuel for wood pellets with lower moisture content than wood

chips. Flue gas recirculation could also be altered for cooling the bed, but this was done only if necessary, since it can be expected to influence the fluid dynamics of the bed.

Using this methodology, the emissions measured could then be expressed as function of air-to-fuel-ratio (λ), which is defined in Equation (5). In practice the air-to-fuel ratio was rather calculated directly from the measured composition by expression (6), which is derived from mass balances and fuel data:

$$\lambda = \frac{\dot{v}_{air}}{\dot{v}_{air,0}} \tag{5}$$

$$\lambda \approx 1 + \frac{\dot{v}_{fg,0}}{\dot{v}_{air,0}} \left[\frac{(CO_2)_{d,0}}{(CO_2)_d} - 1 \right] \approx 1 + \frac{\dot{v}_{fg,0}}{\dot{v}_{air,0}} * \frac{(O_2)_d}{0.2095 - (O_2)_d} \tag{6}$$

$\dot{v}_{air}$ = dry air volume added to the combustion chamber ($m_n{}^3/m_n{}^3{}_{,fuel}$)
$\dot{v}_{air,0}$ = dry air volume needed for stoichiometric combustion of the fuel mix ($m_n{}^3/m_n{}^3{}_{,fuel}$)
$\dot{v}_{fg,0}$ = dry flue gas volume for stoichiometric combustion of the fuel mix ($m_n{}^3/m_n{}^3{}_{,fuel}$)
$(CO_2)_{d,0}$ = CO_2 fraction in dry flue gas for stoichiometric combustion of the fuel mix (-)
$(CO_2)_d$ = Measured CO_2 fraction in dry flue gas (-)
$(O_2)_d$ = Measured O_2 fraction in dry flue gas (-)

Samples of bed material were extracted from inside the boiler during operation. This was done using a special cooled collection probe. Some of these samples were subject to standardized bed agglomeration tests at the Research Institute of Sweden (RISE) in order to determine tendencies of the bed material to agglomerate at severe conditions. The methodology for agglomeration tests 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 lacated in the middle of the tube, which also acted as gas distributor. The sample was fluidized with 12 l_n/min air, which corresponds to a superficial gas velocity of about 0.3 m/s at 750 °C. The pressure drop over the bed was measured with a pressure transducer and the temperature was monitored with a K-type thermocouple. The test was initiated when the bed temperature was stabilized at 750 °C. From this point the bed temperature was increased by 3.5 °C/min. The maximum temperature was 1100 °C. A reduction in pressure drop across the fluidized bed was interpreted to indicate that agglomeration had occurred (elutriation is theoretically possible but should not occur at the conditions used). 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. The point was chosen where a continuous reduction in pressure drop of about 1 Pa/min could be seen.
- 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 research boiler was operated for two weeks, basically one week with practically 100% LD-slag and one week with partial substitution of silica sand. The boiler was stopped and emptied prior to the campaign, but since it is difficult to clean parts of the system, traces of sand (<1 wt%) could possibly be present also during the period of operation referred to as 100% LD-slag.

Further, experiments were performed with addition of ammonium sulphate to the vortex finder (i.e., primary cyclone outlet) and with sulphur granulates fed directly to the bed. Both measures will be discussed more in detail in Section 3 below. A summary of the experimental campaign can be found in Table 4.

Table 4. Overview of the experimental campaign with the Chalmers Research Boiler.

Day	Date	LD-Slag (wt%)	Si-Sand (wt%)	Comment
1	2017-11-13	≈100		Preparations for start-up.
2	2017-11-14	≈100		Start-up and operation with 100% LD-slag.
3	2017-11-15	≈100		100% LD-slag, ammonium sulphate experiments.
4	2017-11-16	≈100		100% LD-slag, ammonium sulphate experiments.
5	2017-11-17	≈100		100% LD-slag, experiments with sulphur granulates.
Boiler regeneration during weekend (days 6–7). This was done in order to replace all LD-slag with fresh silica sand. Boiler stop day 7 to get rid of as much remaining slag as possible.				
8	2017-11-20	≈1	≈99	Start-up and operation with mostly silica sand.
9	2017-11-21	≈10	≈90	Operation with ≈10% LD-slag. Lambda experiments.
10	2017-11-22	≈30	≈70	Operation with ≈30% LD-slag. Lambda experiments.
11	2017-11-23	≈50	≈50	Operation with ≈50% LD-slag. Lambda experiments.
12	2017-11-24	≈50	≈50	Conclusion, preparations for next campaign.

The experiments can be divided into a number of categories. Days 2–5 involved experiments with almost 100% LD-slag, with or without addition of ammonium sulphate or sulphur granulates. The reason for utilizing ammonium sulphate and sulphur was that the results obtained with 100% LD-slag during days 2–3 resulted in high emissions of CO. Our hypothesis is that this is associated with the presence of gas phase alkali metals during burnout in the cyclone, which is a topic that will be further discussed in Sections 3 and 4 below. To inhibit this unwanted effect, during days 3–5 an aqueous solution of ammonium sulphate was sprayed into the cyclone outlet. During day 5, experiments were also performed with addition of elemental sulphur directly into the bed. Addition of sulphur should propagate sulphation of potassium to solid K_2SO_4 [20], which is expected to reduce the influence of gaseous K on the combustion results.

In Table 4, the determination of the precise bed composition and average age of bed material is quite complex. Fly ash and fine bed material were continuously elutriated and captured after the secondary cyclone and in the subsequent textile filter. The filters are placed on scales, so it is possible to quantify how much is elutriated as function of time. Further, the bed material is removed from the furnace via the water cooled ash screw located in the bottom of the plant in irregular intervals and replaced with either fresh LD-slag or fresh silica sand. It is not possible to specifically remove ash, sand, LD-slag or particles of a certain age. While it is possible to make a reasonable species balance over the boiler, this involves an excessive effort with respect to analysis of bed and ash samples, which was beyond the scope of the study presented here. Nevertheless, for experiments with LD-slag and sand mixtures, care was taken to adjust the amount of slag in the bed so that real values were as close to the reported ones as possible. The following principles were used:

- The amounts of material removed and added were always attuned to achieve the desired bed composition and a fixed pressure drop over the whole bed of 5.5 kPa.
- It was assumed that the composition of the bed material removed was the same as it would be as if the whole bed was perfectly mixed.
- It was assumed that there was no accumulation of ash or fuel in the bed, that is, only LD-slag and sand counts.

It should also be mentioned that small amounts of LD-slag were automatically added during operation to maintain a pressure drop over the boiler of 5.5 kPa, thus increasing the fraction of LD-slag over the course of the day. This happens automatically to compensate for fine material elutriated from the bed due to imperfect separation of solids and gases in the cyclone. The amounts were not excessive and most likely associated with the relatively high content of fine material in the batch of LD-slag used, as was discussed in Section 2.1 above. As for start-up at day 8, the boiler was purged of as much LD-slag as practically possible during day 7. Nevertheless, it is estimated that there still was in the order of 1% LD-slag left in the inventory in locations which were impossible to reach. Considering all these factors, the bed composition reported in Table 4 should be seen as approximate.

3. Results

3.1. Operation with 100% LD-Slag

The experiments with LD-slag worked well on a practical level. It proved easy to pneumatically transport the LD-slag to the material silo via an ordinary pressure discharge truck. Feeding fresh bed material and removing bottom ash via ash screw worked flawlessly. The pressure drop over the bed and presumably also the fluidization behaviour were similar to operation with sand. There were no tendencies to form agglomerations or other problems commonly occurring during operation of biomass boilers. However, the measured emission levels of CO especially (but also NO) were not satisfactory:

- At startup with completely fresh LD-slag (day 2), the CO concentration was initially low. However, soon an increasing trend could be seen and after 7 h of operation the CO concentration was 100 ppm and still increasing. This is a considerably higher concentration than what would be expected for silica after a similar time of operation.
- In the next morning (day 3), the trend accelerated and the CO concentration soon exceeded 1200 ppm, which is outside the preferred measuring range of the instruments used. During operation with silica sand and wood fuel, such an increase in emissions would be expected to take place only after several days of operation without regeneration of bed material.

It was deemed likely that the high emission levels were related to poor absorption of ash components. Typically, alkali metals and especially potassium (K) are considered the most critical ash components during combustion of biomass. Accumulation of alkali in fluidized bed boilers is well-known to create a number of difficulties, including bed sintering and deposits on super-heater tubes [21]. In smaller CFB boilers, saturation of ash components in the flue gas can also be associated with emissions. The mechanism is debatable, but one mechanism that has been suggested is that biomass char would burn in accordance with the shrinking sphere model, in which case an ash layer surrounding the char particle would make oxygen diffusion difficult [9]. It has also been reported in a study comprising experimental work and chemical modeling that alkali metals can act as a strong inhibitor of CO oxidation at atmospheric pressure and in the temperature range of 773–1373 K [22]. Due to the reactive nature of alkali metals, heterogeneous effects could also be a possibility. Addition of fresh LD-slag to the boiler resulted in a minor temporary reduction in CO emissions, which seemingly supports the hypothesis that LD-slag absorbs ash components that influence the combustion result, but only at a low level. This topic will be further elaborated below.

Chalmers research boiler is a commercial production unit and sustained operation with CO emission levels above 1000 ppm were not acceptable to the plant operators (Akademiska Hus AB). Also, it seems reasonable to believe that the use of LD-slag as an alternative bed material in commercial boilers would not be favored if the emissions would increase in comparison to the use of silica sand. Therefore, it was decided to examine three potentially viable ways to achieve improved operational conditions with respect to emissions: (i) addition of elemental sulphur directly to the boiler; (ii) addition of aqueous ammonium sulphate to the cyclone outlet; or (iii) mixing LD-slag with silica sand.

3.2. Addition of Sulphur Granulates to the Boiler

Sulphur was added to the boiler in order to propagate sulphation of mainly potassium to solid K_2SO_4, which if the hypothesis presented above is correct, should reduce the influence of gaseous K on combustion performance. In an earlier OCAC campaign it was shown that a small trickle of elemental sulphur (1 kg/h) had a tremendous effect on emissions when used together with a manganese-based bed material [14]. Tests were performed on day 5, this time by adding three 500 g batches of Sulphur granulates directly to the bed. This did not work out particularly well and provided only minor and temporary relief. Two tests were done and each time the CO emissions dropped temporary from >1200 ppm to <600 ppm for a few minutes. This is far too small an effect to be of practical value. It seems likely that direct addition of sulphur to the bed is not a viable method to reduce emissions when

LD-slag is used as bed material. This was not unexpected, since LD-slag is rich in CaO, which could be expected to successfully compete with potassium in the bed forming $CaSO_4$. This also suggests that co-firing with Sulphur-rich fuels is not a viable method to decrease CO emissions when LD-slag is used as bed material.

3.3. Addition of Ammonium Sulphate to the Vortex Finder

During day 3 and day 4, experiments were performed in which a liquid solution of ammonium sulphate was sprayed directly into the cyclone outlet (i.e., vortex finder). This was done in order to actively convert gaseous potassium to solid K_2SO_4. Compared to direct addition of sulphur to the boiler this procedure has two advantages: (i) final combustion takes place in the cyclone outlet, so it is the conditions here determine the emissions exiting the stack; and (ii) there is no competition with CaO for the sulphur. The flow rate was 2.4–5.0 L/h aqueous solution with 20 wt% of ammonium sulphate. This worked excellently and reduced CO emissions to very low levels (0–30 ppm CO) at standard conditions (see Figure 3 for an example). The flow rate did not have any effect on emissions. Even at the lowest flow rate ammonium sulphate was seemingly supplied in significant excess.

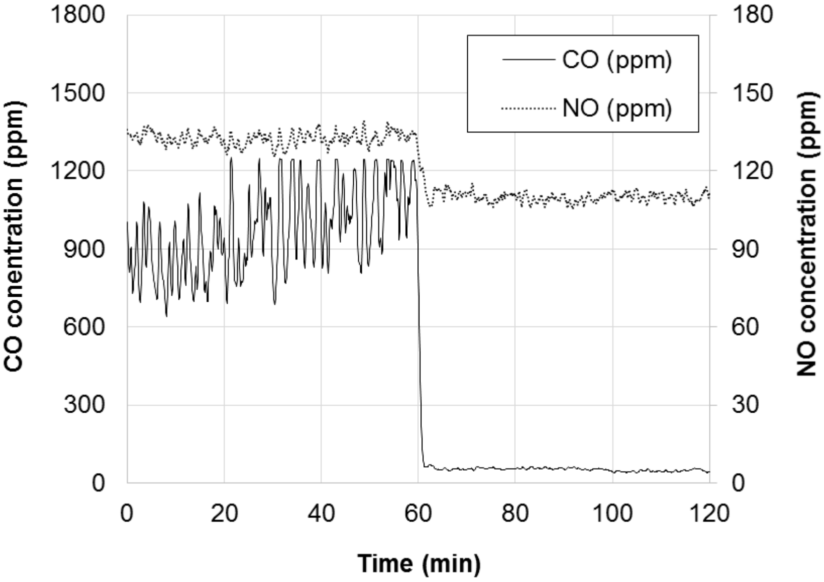

Figure 3. Effect on CO and NO emissions of injecting 4.0 L/h solution of 20 wt% of $(NH_4)_2SO_4$ in water into the cyclone outlet during operation with 100% LD-slag. Injections starts at t = 60 min.

A detailed analysis of bed and ash samples from the campaign described in this paper is provided elsewhere [23], where it is shown that the concentration of potassium and sulphur in fly ash samples increased greatly when ammonium sulphate was added to the vortex finder (K by a factor of 5–6 and S by a factor of 12–19). The increase in potassium should be due to formation of K_2SO_4. The even greater effect on sulphur is because it started at very low levels, due to the low sulphur content of the fuel.

Both the effect on CO emissions and on the potassium content in fly ash supports the general hypothesis, namely that LD-slag has a poor ability to absorb potassium and that the final combustion step, which takes place in the cyclone, is hampered by the presence of alkali metals. These experiments will be discussed further below.

3.4. Mixing of LD-Slag with Sand

By mixing LD-slag with a certain percentage of silica sand, it should be possible to utilize the well-documented ability of silica sand to bind ash components, while potentially still achieving benefits from the oxygen carrying properties of LD-slag. Mixing of oxygen carrier and silica sand in Chalmers research boiler has previously been successfully done with ilmenite [10] and manganese ore [14].

As shown in Table 4 above, experiments with up to 50% sand were performed. There was a radical decrease in CO emissions compared to the case when 100% LD-slag was used. The results will be elaborated in quantitative terms in Section 3.6 below. Further, mixing of the two materials did not result in any practical problems such as sintering.

3.5. Effect on Boiler Temperature Profile during Operation

The temperature profile of the boiler could be expected to reveal whether LD-slag promotes combustion in the bed. Figure 4 shows the temperature at four different measuring points when the boiler was operated at a low air-to-fuel ratio (1.07), while Figure 5 shows the same temperatures when operating the boiler at a higher air to fuel ratio (1.17). The temperatures were measured with conventional thermocouples of type-K.

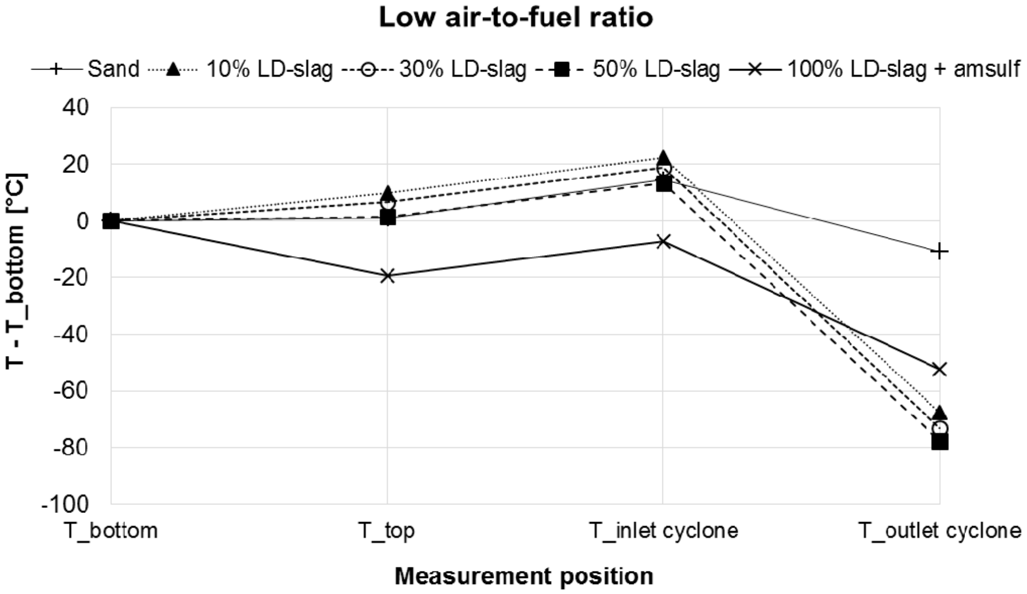

Figure 4. Temperature profile over the boiler when operated with low air-to-fuel-ratio.

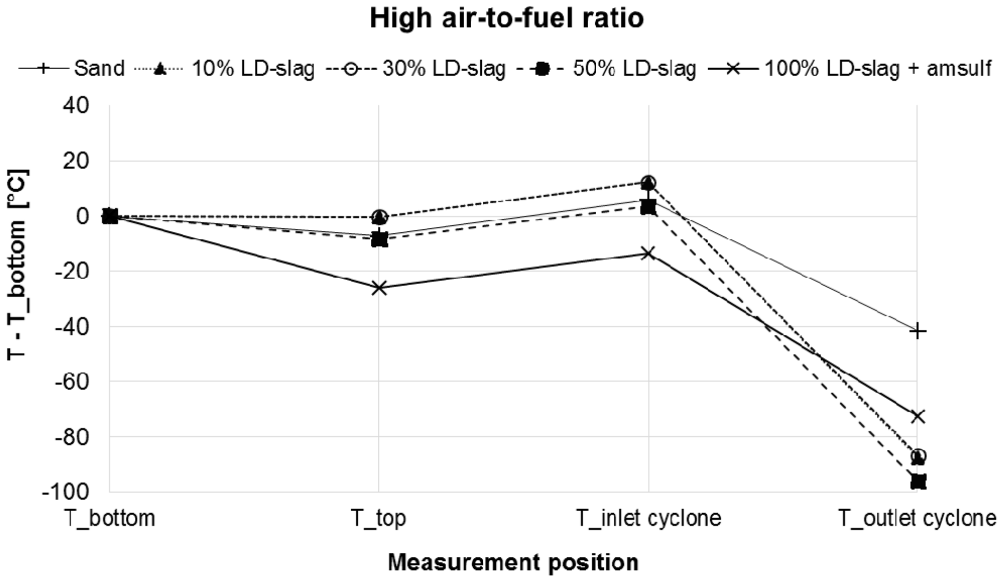

Figure 5. Temperature profile over the boiler when operated with high air-to-fuel-ratio. Note that the cases with 10% and 30% LD-slag overlaps so well that they are difficult to distinguish.

In Figures 4 and 5, T_{bottom} was 840–850 °C for experiments with LD-slag, and sand and 880 °C for experiments with LD-slag and ammonium sulphate. A reference curve for operation with sand has been included. The reference curve originates from operation with fresh silica sand with T_{bottom} at 870 °C in a clean boiler and thus represents a best-case scenario for conventional combustion with respect to emissions (over the course of the firing season base emission levels may increase as different parts of the boiler are subject to e.g., accumulation of ash). The fuel flow, boiler load and bed mass were comparable in all cases. The following phenomena can be observed:

- There is always a temperature drop over the cyclone, which is to be expected since it is water-cooled. The temperature drop is reduced by the fact that final combustion is also taking place here. It is clear that the temperature drop is much more pronounced for experiments involving LD-slag compared to when only sand is used. This suggests that, with LD-slag, significantly less combustibles enter the cyclone and burn there. Considering that the concentration of incombustibles (CO, H_2, CH_4, THC) in the stack are on ppm level, this suggests that more combustion must take place inside the actual boiler body when LD-slag is used, in comparison to the sand case.
- Also, 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 LD-slag is present for the 10% and 30% mixtures, than when only sand is used. This corroborates with the observation above.
- For the case with 100% LD-slag with addition of ammonium sulphate, the picture is somewhat unclear and can be interpreted in different ways. There are reaction enthalpies for dissolution of ammonium sulphate, oxidation of ammonia and sulphation of K, which can be expected to affect the temperature in the cyclone outlet. One should also consider the unit on the y-axis and the temperature in the bottom bed, which was significantly higher than in other experiments at 880 °C. So as of this time insufficient information is available to explain precisely what is taking place.

Even if we discard the experiments with ammonium sulphate from the analysis, it should be acknowledged that measured temperature data is good for qualitative analysis only. For example, sublime changes in boiler load could be expected to influence temperature profile. Nevertheless, Figures 4 and 5 are largely consistent with our hypotheses which is that the presence of an oxygen carrying bed material facilitates combustion in the dense part of the bed and to some extent also in the freeboard above it. The expected result would be a larger temperature increase here compared to when only sand is used. This in turn should result in less combustibles remaining to be burned in the cyclone, leading to a sharper drop in temperature here in comparison to when sand is used. The latter effect is extremely clear in Figures 4 and 5. For the same reason, the temperature drop in the cyclone should be higher for a high air-to-fuel-ratio, which was also observed. Finally, it should be pointed out that the temperature drop for experiments with partial substitution with LD-slag at low air-to-fuel-ratio is much larger than for silica sand even with the higher air-to-fuel-ratio. This suggests that the impact of LD-slag on fuel conversion in the boiler body is very significant, that is, more significant than increasing air-to-fuel-ratio from 1.07 to 1.17.

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

According to the theories presented in Section 1 above, switching from sand as bed material to LD-slag should facilitate fuel conversion and allow for reduced air-to-fuel ratio without increasing the emissions of unburnt, notably CO. The temperature profile of the boiler presented in Figures 4 and 5 supports this theory. As has already been explained above, the picture was less clear when it comes to emissions. Summaries of the measured CO emissions during lambda-experiments can be found in Figure 6.

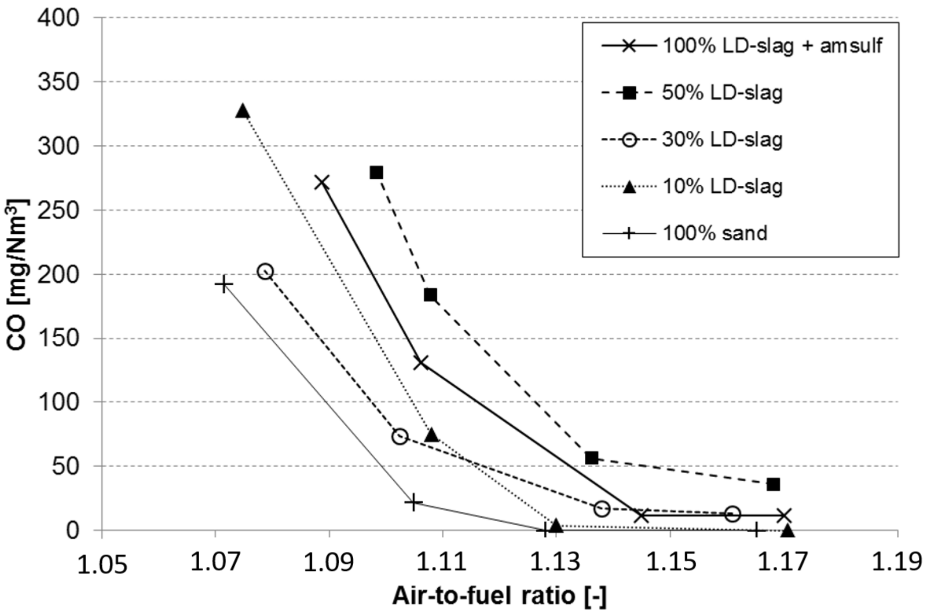

Figure 6. Measured concentrations of CO (mg/Nm^3, at 6% O_2) at position kh2 in the convection path as a function of the air-to-fuel ratio.

The results in Figure 6 are not necessarily intuitive:

- The reference experiments with silica sand provided the lowest emissions. Here it should be pointed out that the data for the reference case refers to experiments performed at slightly higher temperature (870 °C) and in a clean boiler directly at start-up of the firing season. Both factors are likely to contribute to slightly better than expected performance with respect to emissions.
- The results suggest that increased substitution of LD-slag increases CO emissions. The mix with 50% LD-slag clearly has higher emissions than the mix with 10% LD-slag. This is the opposite effect of what could be expected.
- For experiments with 100% LD-slag, the emissions were far above what is shown in the graph. However, as can be seen, addition of ammonium sulphate in the cyclone leg reduced the CO emissions to acceptable levels, as has been explained above.

In general, LD-slag did not result in very promising results with respect to CO emissions. Previous campaigns with ilmenite [10] and manganese ore [14] have both resulted in significant reduction of CO emission for a given air-to-fuel-ratio, also in comparison to the best-case scenario for sand used here. Such a reduction when using LD-slag was not observed. Our theories about why this is the case will be discussed in Section 4.1 below.

3.7. Effect on NO Emissions

NO emissions during operation at certain air-to-fuel ratios can be found in Figure 7.
The following points can be made:

- An increase in air-to-fuel ratio results in higher NO emissions. This is a well-known phenomenon within combustion chemistry.
- The sand reference has the lowest NO emissions, meaning that no improvements could be verified by using LD-slag as bed material.
- Of the experiments that involved LD-slag, those with lowest CO emissions also had the lowest NO emissions.

A positive effect of up to 30% reduction of NO have previously been reported in an OCAC campaign with partial substitution of sand with ilmenite [10]. However, similar effects have not been seen in subsequent campaigns with ilmenite and manganese ore [14]. Instead, the use of oxygen-carrying bed material typically has resulted in a modest increase in NO emissions, to a similar degree as is reported for LD-slag here. This is not unexpected, since the presence of an oxygen carrier should increase the availability of oxygen in the boiler, which in turn could be expected to result in higher NO emissions.

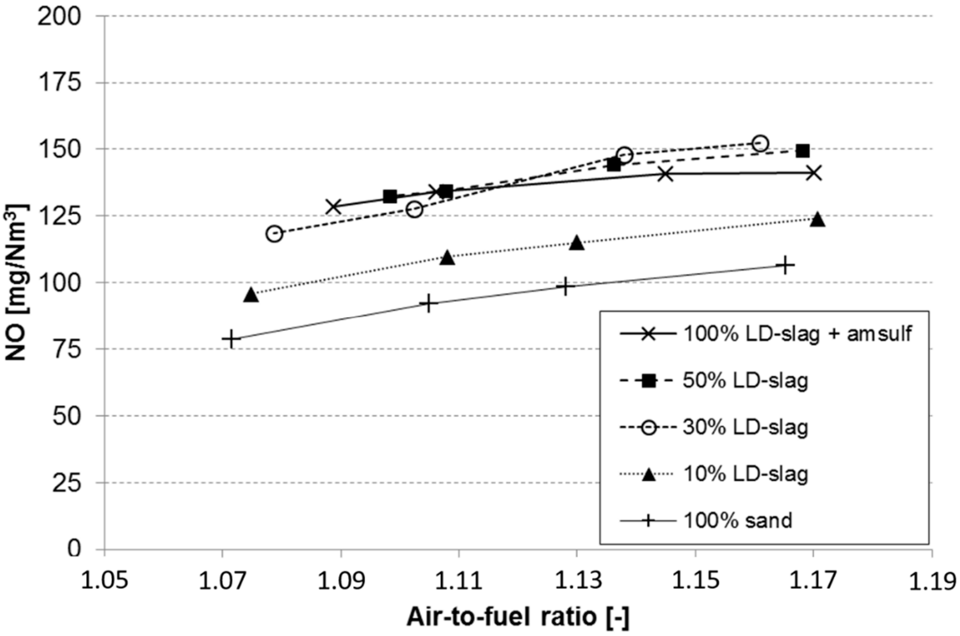

Figure 7. Measured concentrations of NO (mg/Nm^3, at 6% O_2) at position kh2 in the convection path as a function of the air-to-fuel ratio.

3.8. Observations with Respect to General Operability

Over the entire course of the experimental campaign, no issues related to general operability were encountered. All practical moments, such as handling by pressure discharge truck, pneumatic transport, filling up of the material silo and removal of bottom ash with ash screw worked flawlessly. There were no tendencies towards sintering and no agglomerations were found. This was despite the rather high temperature used, with the target temperature in the bed being 840–870 °C. This is near the maximum temperature for biomass combustion in a fluidized bed with silica sand as the bed material. The results of the dedicated agglomeration tests in lab reactor can be found in Table 5 below:

Table 5. Results of agglomeration tests.

Sample	T_{A1} (°C)	T_{A2} (°C)	T_{A3} (°C)	Comments
LD-slag (fresh)	-	-	-	Successfully reached maximum temperature without problems.
100% LD-slag (extracted 20171117)	-	-	-	Successfully reached maximum temperature without problems. Some micro-agglomerations noted during cleaning of reactor.
30/70% mixture LD-slag/sand (extracted 20171122)	1010	1060	1081	Agglomerates and increased bulk density noted during cleaning of reactor.

It can be concluded that both practical operation of the boiler and dedicated agglomeration tests suggest that LD-slag has lower tendency towards sintering than silica sand. The slag/sand mixture eventually agglomerated in dedicated tests, but nevertheless performed adequately well with no signs of problems below 1000 °C.

With respect to the generation of fly ash and bed material attrition, a simplistic but nonetheless illustrative comparison between LD-slag and silica sand have been performed. Basically, two representative 24 h periods with similar operational conditions, one for 100% LD-slag and one for 100% silica sand, were selected and compared to each other (see Table 6).

Table 6. Comparison of fly ash generation between LD-slag and silica sand.

Source of Ash	LD-Slag	Si-Sand
Secondary cyclone (kg/24 h)	360	132
Textile filter (kg/24 h)	43	11
Ash sweeping (kg/24 h)	155	50
Total (kg/24 h)	558	193

In Table 6 it can be seen that 365 kg more fine material was generated over the course of 24 h when LD-slag was used as bed material, compared to when sand was used. The increase was roughly a factor of three for all measured locations. There are three potential sources for fly ash: (i) fly ash generated from the fuel; (ii) fly ash generated by attrition of bed material; and (iii) the 10–15 wt% material below 90 µm present in the batch of LD-slag to begin with. Fly ash from fuel should not differ greatly between the two cases. Further, in the study covering the analysis of bed samples from the campaign [23], it is shown that fly ash samples contained the same elements as fresh LD-slag, albeit in somewhat reduced concentrations. The numbers reported in [23] support the premise that about the same amount of ash is generated from the fuel (source (i)) in both cases. Unfortunately, it is not possible to know whether the increase in fly ash generation came from attrition (source (ii)) or fine material already present in the batch due to imperfect sieving (source (iii)). A back-of-the-envelope calculation suggests that with a bed inventory of 2500 kg and a turnover of 800 kg/24h, there could be up 250–375 kg particles below 90 µm in the inventory to begin with, and that another 80–120 kg added over the reference period. These numbers should be compared with the 365 kg increase in fly ash production. This clearly is in the same order of magnitude as the increase in fly ash.

To summarize, operation with LD-slag did result in increased generation of fly ash. There are reasons to believe that this was largely due to the presence of fine material in the starting material, but as of this moment this cannot be proven. The increased production of fly ash did not have any practical consequences for the campaign. However, in a commercial power plant it could constitute a cost increase, if the deposition cost for fly ash is higher than for bottom ash (as is the case e.g., in Sweden).

4. Discussion

4.1. CO Emissions

As has been explained above, our current hypothesis is that the results with respect to CO emissions are connected to poor absorption of ash components, especially potassium, by LD-slag. During normal biomass combustion with silica sand as the bed material, critical ash components are absorbed on the surface of the sand particles. This limits the effect of ash on the final combustion step. Since about one third of the bed material is replaced each day during normal operation, alkali metals and other ash components are prevented from accumulating in the bed. Among other oxygen carriers, ilmenite [11] has shown excellent ability to absorb ash components, while the situation for manganese ore is more complex [24]. As reported in a separate study [23], LD-slag from this campaign that had been in the boiler for 65 h had a K-content of 1.4 wt%. This can be compared to ilmenite from a similar campaign that had been in the boiler 44 h, which had a K-content of >4 wt% [11]. The actual average age of the samples will be slightly different from 65 h and 44 h due to elutriation and make-up flow, but it can safely be concluded that LD-slag absorbs much less potassium than ilmenite.

If LD-slag has poor capability to absorb the critical ash components, this mechanism for their removal will not work. Ash components will eventually saturate the boiler and be present during the final combustion stage in the cyclone, which can be associated with increased emissions. As explained above, the mechanism is not known, but char combustion via the shrinking sphere model with an ash layer that hinders oxygen diffusion has been suggested [9]. Another possibility is that the improved fuel conversion in the boiler vessel results in little fuel being left to burn in the cooled cyclone, resulting in such big drop in temperature that final combustion is prevented. A significant temperature drop is indeed seen in Figures 4 and 5, but it is difficult to believe that the measured temperature of 770–800 °C would be insufficient for oxidation of CO with O_2. Considering the reactive nature of alkali metals, heterogeneous effects cannot be entirely discarded either.

The experiments presented here support the hypothesis that the effect on CO emissions in this case has to do with poor absorption of ash. With 10% substitution with LD-slag there is still 90% relatively fresh sand in the bed with proven capability to absorb ash. Consequently, the CO emissions are low. The increase to 30% and 50% LD-slag is achieved by removing bottom ash and adding fresh LD-slag, meaning that the amount of sand present in the bed is decreasing, while also becoming progressively more saturated with ash components as the hours of operation build up. Hence the ability of the bed to absorb ash should decrease greatly, and reduced performance with respect to CO emissions for the cases of 30% and 50% LD-slag seems reasonable. With 100% LD-slag, the mechanisms for removing alkali from the boiler could be expected to be poor, which should result in high emissions. Comparable CO emissions have previously been experienced with the Chalmers research boiler when bed materials for biomass gasification (e.g., olivine) have been tested, which by design should have poor ability to absorb alkali [25].

The experiments with ammonium sulphate added to the cyclone outlet were devised with the reasoning presented above in mind. Addition of sulphur to the vortex finder should result in sulphation of potassium, ultimately forming solid K_2SO_4 [20], thus reducing the influence of gaseous alkali compounds on the final combustion stage. This worked out as expected. However, this cannot be treated as an actual verification, since sulphur feeding to biomass boilers has occasionally been applied specifically to reduce CO emissions [26,27]. The reported effect, though, is an order of magnitude smaller than the drastic CO reduction showcased here. To summarize, CO emissions during biomass combustion and the connection to ash absorption is clearly a complex issue that merits further studies.

4.2. Commercial Outlook for LD-Slag as Bed Material

In order to be an immediately attractive replacement to silica sand in existing fluidized bed boilers, LD-slag should exhibit similar or improved performance with respect to technical factors such as emission levels, sintering behaviour, flowability and attrition. It should also have the potential to reduce total costs of operation, which includes not only purchase cost per ton but also costs for handling and disposal of ash, as well as cost for downtime and maintenance.

The campaign verified that LD-slag worked well as a bed material in a circulating fluidized bed boiler. At no occasion were there any problems related to material handling, agglomeration or sintering. The temperature profile of the boiler suggested that LD-slag did perform adequately as oxygen carrier, and it has been established in other studies that it has decent reactivity with fuel and air [23,28].

However, the effect on CO emissions is a significant concern. With secondary measures in the form of ammonium sulphate added to the cyclone outlet and mixing the LD-slag with silica sand, the performance with respect to emissions was, at best, comparable to operation with silica sand. It is not immediately obvious that this will be the case in larger CFB boilers or in Bubbling Fluidized Bed (BFB) boilers. But it is clear that issues such as absorption of ash elements and reaction mechanisms should be studied further.

The slight increase in NO emissions is probably not a big problem for commercial operators. In a modern utility boiler, NO emissions are typically controlled by addition of ammonia or urea, in order to reduce the final emissions so that they fulfil environmental criteria. As long as the amount saved on bed material is greater than the cost for NO reduction, the use of LD-slag will be attractive to plant operators from this perspective.

Whether the use of LD-slag can reduce the total cost of operation for a fluidized bed boiler is not immediately clear. Pricing of industrial by-products such as LD-slag is not transparent. Even though there is limited demand and large stockpiles are available, the companies involved are keen on getting as good a price as possible out of these products. The sales price for slag-based products in Sweden are mostly in the range of 5–30 €/ton (depending on the size fraction and quality). Most available products are based on blast furnace slag, but it seems reasonable to believe that LD-slag would be priced similarly. Onto this price the cost for transport as well as extra treatment such as crushing, drying, sieving and dedusting may need to be added. If elutriation is greater and more fly ash is generated, this would also add to the total costs. As comparison, the price for silica sand in Sweden is around 40–80 €/ton and the price for ilmenite can be expected to be 6–8 times that of silica sand. It can be concluded that while it is not obvious that the final price for prepared LD-slag will be lower, it certainly is conceivable that it will.

The use of LD-slag as a bed material in waste incineration in fluidized bed boilers is another option to consider. This is technically similar to biomass combustion but with significant differences in process economy. Waste incineration typically has very high consumption of bed material and very high air-to-fuel ratio. If LD-slag can be provided at a lower price than silica sand and provide improved combustion in the furnace, it could be attractive even if CO emissions have to be controlled with secondary measures such as ammonium sulphate injection. Also, the reduced tendency towards agglomeration of LD-slag could be a significant advantage for waste incineration.

Finally, the bed material in coal power plants is mostly coal ash and limestone. The latter is added to capture sulphur as $CaSO_4$. If added to a coal power plant, LD-slag could potentially propagate combustion in the furnace by the mechanisms described in Section 1 above, while at the same time replace limestone for sulphur capture. However, the price of limestone is very low and the volumes needed very big, so it is not obvious that this would be an attractive option.

4.3. Implications for the Viability of Chemical Looping Combustion

In a parallel study, LD-slag from the same source as used here has been examined as an oxygen carrier for chemical looping combustion in small pilot reactors for gaseous fuels and for biomass [28]. The results reported in the study were positive and suggested that LD-slag could be an attractive oxygen carrier for this process. The study presented here verifies that production of LD-slag particles of suitable size can be scaled up and constitutes a practically viable bed material for a CFB boiler of significant size, utilizing high gas velocities. Further, the bed samples extracted during the campaign presented in this paper have been analysed in a separate study [23], in which, among other things, it was shown that LD-slag was not deactivated by biomass ash during operation, but largely retained its reactivity with fuel gases. Together, these three studies suggest that LD-slag could indeed be a good choice for bed material in chemical looping combustion, especially for solid fuels such as biomass. Good availability and potentially very low cost are other attractive properties of LD-slag as an oxygen carrier for chemical looping combustion.

5. Conclusions

Based on the experimental campaign with LD-slag, the following conclusions can be drawn:

- From an operational point of view, LD-slag worked well as bed material in a CFB boiler. The material was easy to handle, to fill into and remove. No problems were encountered related to agglomeration.

- The production of fly ash was three times as high as for similar operation with silica sand, but this did not result in any operational problems. The high production of fly ash is likely at least partly a result of the 10–15 wt% fine particles below 90 µm present in the starting material.
- The temperature profile of the boiler suggests that the presence of LD-slag facilitates fuel conversion in the boiler, with the clearest sign being a much greater temperature drop in the cyclone in comparison to when only silica sand is used.
- The use of 100% LD-slag resulted in much higher emissions of CO than the sand reference. It is believed that this is connected to poor absorption of ash components, in particular potassium.
- During operation with 100% LD-slag, CO emissions could successfully be suppressed by addition of small amounts of ammonium sulphate to vortex finder of the primary cyclone.
- Operation with 10%, 30% and 50% LD-slag were feasible from a practical point of view and resulted in reasonably low CO emissions.
- Previous experiments with ilmenite [10] and manganese ore [14] in the same boiler both showed much better potential to achieve significantly reduced CO emissions at given air-to-fuel ratios. From this point of view LD-slag does not look promising.
- LD-slag did not show potential for reduction of NO emissions. For a given air-to-fuel ratio, NO emissions were always higher when LD-slag was included in the bed compared to the sand reference. This behavior was similar to previous experiments with ilmenite [10] and manganese ore [14] in the same boiler.
- In order to constitute a commercially attractive substitute for silica sand in fluidized bed combustion of biomass, the issue with CO emissions will need to be further examined and better understood. Also, the potential cost of LD-slag in the suitable size range and impact of changed ash properties needs to be carefully assessed.

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