



# Article Ash and Flue Gas from Oil Shale Oxy-Fuel Circulating Fluidized Bed Combustion

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Received: 13 April 2018; Accepted: 9 May 2018; Published: 10 May 2018



Abstract: Carbon dioxide emissions are considered a major environmental threat. To enable power production from carbon-containing fuels, carbon capture is required. Oxy-fuel combustion technology facilitates carbon capture by increasing the carbon dioxide concentration in flue gas. This study reports the results of calcium rich oil shale combustion in a 60 kW<sub>th</sub> circulating fluidized bed (CFB) combustor. The focus was on the composition of the formed flue gas and ash during air and oxy-fuel combustion. The fuel was typical Estonian oil shale characterized by high volatile and ash contents. No additional bed material was used in the CFB; the formed ash was enough for the purpose. Two modes of oxy-fuel combustion were investigated and compared with combustion in air. When  $N_2$ in the oxidizer was replaced with CO2, the CFB temperatures decreased by up to 100 °C. When oil shale was fired in the CFB with increased  $O_2$  content in  $CO_2$ , the temperatures in the furnace were similar to combustion in air. In air mode, the emissions of  $SO_2$  and  $NO_x$  were low (<14 and 141 mg/Nm<sup>3</sup> @ 6% O<sub>2</sub>, respectively). Pollutant concentrations in the flue gas during oxy-fuel operations remained low (for OXY30 SO<sub>2</sub> < 14 and NO<sub>x</sub> 130 mg/Nm<sup>3</sup> @ 6% O<sub>2</sub> and for OXY21 SO<sub>2</sub> 23 and NO<sub>x</sub> 156 mg/Nm<sup>3</sup> @ 6% O<sub>2</sub>). Analyses of the collected ash samples showed a decreased extent of carbonate minerals decomposition during both oxy-fuel experiments. This results in decreased carbon dioxide emissions. The outcomes show that oxy-fuel CFB combustion of the oil shale ensures sulfur binding and decreases CO<sub>2</sub> production.

**Keywords:** circulating fluidized bed combustion; carbon capture; storage and utilization; sulfur binding; nitrogen oxides; emissions; ash behavior; carbonate minerals

# 1. Introduction

Carbon dioxide emissions continue to be a major environmental concern of solid fuel combustion. Carbon capture and storage is required in order to meet future targets for greenhouse gas emissions. The typical technologies related to CO<sub>2</sub> capture are pre-combustion, post-combustion and oxy-fuel combustion [1]. Oxy-fuel combustion is considered as one of the most promising carbon dioxide capture approaches [2–4]. It involves combustion of fuel in a mixture of nearly pure oxygen and recycled flue gas to control the combustion temperature. There is a number of ongoing oxy-fuel combustion (PC) technology [5,6]. Circulating fluidized bed (CFB) combustion technology is proven and has advantages such as fuel flexibility and environmental performance. When applying oxy-fuel combustion with a CFB, the circulating solid matter offers another temperature control method. Due to this, less circulated flue gas is required for temperature control. Regardless of the exact solution, the main purpose of applying an oxy-fuel approach is to enable power production without carbon

dioxide emissions by producing an enriched carbon dioxide flow at the combustion unit's outlet to simplify its utilization or sequestration.

The fuel used in this study was typical Estonian oil shale. Oil shale is a low-grade fossil fuel that has extremely high ash and volatile contents. The worldwide oil shale reserves have enormous energy potential, but it is industrially used only in Estonia, Brazil and China [7]. Oil shale can be utilized for energy production via gasification, pyrolysis or combustion. Estonian oil shale based power production relies on PC and CFB combustion technologies [8,9]. Industrial experience has shown that, due to a high process efficiency, low emissions, and no requirements for SO<sub>x</sub> or NO<sub>x</sub> emission control systems, CFB combustion of oil shale is the best available technology [10–13]. Industrial trials [12,14] have shown that CFB combustion technology is suitable for oil shale co-firing with biomass, pyrolysis gas and peat, thereby enabling fuel flexibility.

Substituting N<sub>2</sub> with CO<sub>2</sub> has an influence on combustion, pollutant formation, mineral matter behavior and temperature in the combustor. Previous research has shown that, when the oxidizer contains a similar amount of O<sub>2</sub>, then, in CO<sub>2</sub>, the combustion is delayed [15–17]. Delayed combustion and increased specific heat of the gas mix leads to up to a 100 °C temperature decrease in the furnace [3,18]. To overcome this obstacle, O<sub>2</sub> concentration is increased. Generally, a mixture containing 30% O<sub>2</sub> and 70% CO<sub>2</sub> allows obtaining similar temperatures in furnace as in a regular air-fired CFB.

Sulfur oxides are one of the main pollutants from combustion, causing acid rains and disturbing  $CO_2$  compression when applying oxy-fuel combustion. The  $SO_2$  concentration in flue gas can be reduced by injecting sorbents, such as limestone or dolomite, into a CFB. Estonian oil shale has a high content of carbonate minerals (mostly calcite and dolomite). Due to this, no additional bed material is needed. The sulfur capture process depends on calcination, which depends on  $CO_2$  partial pressure and temperature. If the  $CO_2$  partial pressure is lower than the equilibrium pressure [19], limestone decomposes and forms CaO and  $CO_2$ ,

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g).$$
 (1)

The CaO then reacts with SO<sub>2</sub>,

$$CaO(s) + SO_2(g) + 0.5O_2 \leftrightarrow CaSO_4(s).$$
<sup>(2)</sup>

This process is called indirect sulfation. If the calcination process does not take place, then SO<sub>2</sub> may react directly with CaCO<sub>3</sub>,

$$CaCO_3(s) + SO_2(g) + 0.5O_2 \leftrightarrow CaSO_4(s) + CO_2(g).$$
(3)

In air-fired atmospheric units, sulfur capture occurs via relatively rapid calcination (Equation (1)) and much slower sulfation reactions (Equation (2)). In oxy-fuel CFB combustors, sulfation can occur directly without the calcination step (Equation (3)). Theoretical calculations [20–22] and a previous study in a lab-scale fluidized bed batch reactor [23] revealed that carbonate minerals do not fully decompose under oxy-fuel combustion environment and the sulfur binding rate decreases, similar to the experiments of Li et al. [24]. On the contrary, some other experiments [18,25,26] showed a decrease in sulfur emissions or increased sulfur capture efficiency when applying oxy-combustion. This means that, it is still unclear if sulfur binding rate is sufficient.

Other important pollutants from combustion are nitrogen oxides (NO<sub>x</sub>) [27,28]. Nitrogen content in the Estonian oil shale is low, below 0.1% in dry fuel. Due to this and the low temperatures in CFB combustors, no problems with excess nitrogen oxide formation were recorded from the utility boilers [10]. One advantage of oxy-fuel technology is its potentially lower NO<sub>x</sub> production. Results from different experimental facilities are rather diverse [18,29–33]. Overall, the results indicate that nitrogen behavior in the oxy-fuel mode is similar to combustion in air and no drastic changes are expected in fuel nitrogen conversion to oxides.

Changes in the gas composition in a combustor may alter the transformation of minerals and cause fouling or particles agglomeration in the bed. Estonian oil shale has a high ash and carbonates content. When PC was applied to Estonian oil shale combustion, major difficulties due to sediments formation on heating surfaces occurred [34]. Applying CFB technology resolved such problems, because it was possible to decrease temperatures in furnace below 850 °C [10]. From previous experience, we know that decreased decomposition of carbonate minerals results in up to 13% smaller carbon dioxide production [20]; at the same time, it increases total ash production from combustion.

Mapping waste is important for finding solutions to turn ash, or at least a part of it, into products [35,36]. Wang et al. [37] found no major differences in oxy-fuel residues when compared to regular ash. Our previous experiments at laboratory scale fluidized bed reactor showed a considerable decrease of carbonaceous minerals decomposition in oxy-fuel environment [23]. This means that  $CO_2$  emissions decrease, but the production of ash increases. [36]. More than 90% of oil shale ash is currently landfilled [38]. In landfills, it cements and binds approximately 8% of the total emitted carbon dioxide [39]. Experiments with oxy-fuel CFB ash showed that the ash can still fix a similar amount of  $CO_2$  [40]. The natural  $CO_2$  sequestration uses only a part of the ash's total potential, because only the surface of the particles is available for the reaction. The calcium rich ash could be employed for improved  $CO_2$  sequestration [41]. For example, Zevenhoven et al. [42] proposed precipitated calcium carbonate production from calcium-containing industrial wastes. The concept could be applied with oil shale ash; as a result, a large amount of  $CO_2$  would be fixed, and waste ash would be used and a valuable product would be produced.

Higher  $CO_2$  concentration in flue gas eases utilization or gas transportation to geological storage sites. The nearest option for  $CO_2$  storing from a possible oxy-fuel power plant in Estonia would be in the South Kandava sandstone in Latvia (500 km from the oil shale mines). The formation has been evaluated to be suitable for  $CO_2$  geological storage [43,44].

The experience shows that substituting nitrogen with carbon dioxide as diluent is not trivial and generates important differences. To investigate possible changes in the flue gas and produced ash when applying oxy-fuel combustion on Estonian oil shale, combustion experiments in a 60 kW<sub>th</sub> CFB combustor were performed using air and mixed gases to simulate possible oxy-fuel combustion environments. Flue gas and produced ash samples were collected and analyzed.

#### 2. Experimental Section

#### 2.1. The Oil Shale

The experiments were carried out with typical Estonian oil shale from the Ojamaa underground mine. The fuel was dried, crushed and sieved to under 3 mm. The ultimate and proximate analysis of the oil shale is listed in Table 1. The oil shale contained a considerable amount of sulfur, but had a low nitrogen content. The laboratory ash composition is shown in Table 2. The Ca/S molar ratio in the oil shale was 8.0. The values were typical for oil shale used in the Estonian oil shale industry. The only major difference was the fuel moisture content. The oil shale used in the experiments was room dry. Normally, the oil shale used in the industry has a moisture content slightly over 10% [11,45].

Net Heating Value, MJ/kg	Proximate Analysis, wt. <sub>as received</sub> %					Ultimate Analysis, wt. <sub>dry</sub> %				
	Moisture	Volatile Matter *	Fixed Carbon	Ash	C	Ν	S	Н	TOC **	(CO <sub>2</sub> ) <sub>mineral</sub>
8.56	0.50	47.5	1.3	50.7	27.4	0.07	1.6	2.7	21.8	20.6

Table 1. Proximate and ultimate analysis of the oil shale.

\* Volatile matter includes mineral CO<sub>2</sub> from decomposition of carbonate minerals; \*\* TOC—total organic carbon.

Constituent	CaO	SiO <sub>2</sub>	$Al_2O_3$	SO <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	C1	Na <sub>2</sub> O	Other
Content, wt %	43.9	27.5	8.6	5.5	4.9	4.8	3.3	0.4	0.1	1.0

Table 2. Chemical composition of the oil shale laboratory ash.

# 2.2. The Circulating Fluidized Bed Combustion Test Facility

The experiments were conducted using a 60 kW<sub>th</sub> CFB combustor, which was designed and constructed for fuels with high, up to 60 wt %, ash content. The main components of the test facility are shown in Figure 1. The height of the furnace was 4.90 m and its inner diameter was 0.12 m. The combustion chamber was isolated with ceramics and high temperature thermal isolation material. To minimize leaks, the combustor was enclosed in a stainless steel shell. The fuel was fed with a screw conveyer at the height of 0.49 m, and the recirculated solids were fed back at a height of 0.86 m with secondary air.



Figure 1. The 60 kW<sub>th</sub> circulating fluidized bed combustion test facility.

The solid particles were separated from flue gas in a cyclone (cut-point 10  $\mu$ m) and returned to the bottom bed through a return leg and an external heat exchanger (EHE) where solids were cooled in order to control the temperature of the bed. After the cyclone, the flue gas was cooled with a two-stage cooling system, consisting of two shell-and-tube heat exchangers in series. The heat transfer surfaces of these heat exchangers were composed of longitudinally-streamlined tubes. The fly ash was removed from flue gas with a fabric filter. The cleaned flue gas was led out of the system by means of an induced high pressure fan through the stack.

The combustion air was supplied with a compressor. The simulation of recycle flue gas was performed using bottled  $CO_2$  and  $O_2$ . All gas lines, for  $O_2$ ,  $CO_2$  and compressed air, were equipped with mass flow controllers for exact control of the mass flow rates and the ratio of  $O_2/CO_2$ . The combustion air tubes were equipped with electrical heaters to maintain the necessary gas temperature. Extra bed material was not needed since oil shale contains more than enough ash.

The test facility was equipped with two independent fuel/bed material feed silos and a gas burner. The control and data acquisition of the test facility was fully automated and operated by a LabVIEW system. The flue gas composition was simultaneously analyzed with a FTIR spectrometer and was presented as dry gases at 6% O<sub>2</sub>. Ash samples were collected from five points: bottom ash (BA), cyclone ash (CA), cooler 1 ash (C1), cooler 2 ash (C2) and fabric filter ash (FA). The collected samples were pulverized. The chemical composition of the produced ashes and the fuel were measured with Rigaku ZSX Primus II wavelength dispersive X-ray fluorescence spectrometer and elemental analyzer Vario

Macro CHNS Cube. Mineral  $CO_2$  amount was measured in the samples with the elemental analyzer using the total inorganic carbon module applying diluted HCl to decompose the carbonate minerals.

The combustor can operate both in a conventional air mode regime as well as in oxy-fuel regime. During the experiments the test facility was started in air-fired mode. After achieving the steady state regime, the gradual switch to oxy-fuel mode was started. The results presented in this paper were obtained at steady-state CFB combustion mode. The experiments were conducted using three different gas mixtures: air, OXY21 (21% oxygen and 79% carbon dioxide) and OXY30 (30% oxygen and 70% carbon dioxide). The air was used to create a base case scenario. In OXY21 mixture, nitrogen was replaced with CO<sub>2</sub>, thus showing the effect of replacing the carrier gas. Since previous experiments have shown temperature drops when using similar oxygen concertation in the oxy-fuel mode, OXY30 was chosen to try to obtain a similar temperature field in the furnace as in conventional CFB.

#### 2.3. Description of the Experiments

For the startup, a small amount (3 kg) of oil shale ash was inserted into the return leg. The typical startup began with preheating the riser, with electrically-heated air, up to 300 °C. Then the first small amount of oil shale was fed into the riser. The fuel ignited and the furnace was gradually warmed up to a working temperature.

CFB combustor main working parameters are shown in Table 3. During the experiments, the thermal load of the combustor was  $24 \pm 3$  kW. The OXY30 experiment was conducted at a lower thermal load due to fuel feeder problems. The primary and secondary air ratio was 4/6, because the fuel had a high volatile content. Although the thermal load varied due to fuel feeding problems, the data in Table 3 show that temperatures during all the experiments in the CFB combustor were similar.

	Air	OXY21	OXY30
Bed temperature, °C	749	676	773
Riser temperature, °C	752	692	743
Combustion air temperature, °C	284	250	242
Primary oxidizer flow, SLPM	394	279	198
Total oxidizer flow, SLPM	857	710	438
Thermal load, kW	25.3	23.8	14.1
Pressure drop in bed, kPa	2.4	3.6	1.4
Gas velocity in the bed, m/s	2.17	1.43	1.12

**Table 3.** Average working parameters of the circulating fluidized bed (CFB) during different experiments.

Temperature profiles in the riser during stable operation in air and oxy-fuel modes are shown in Figure 2. The temperatures in the riser during air operation were similar to the values used in oil shale industrial CFB boilers (800 °C) [10]. During OXY21 operation, the temperature in the riser dropped by up to 100 °C. Similar temperature drops in the furnace, when substituting N<sub>2</sub> with CO<sub>2</sub>, have been noticed before when oxy-firing coals [3,18]. At the same time, the temperature in the cyclone exit remained similar. Slight drop of primary air temperature from 284 to 250 °C was noticed. This might be the reason for decreased temperatures in the riser, together with decreased fuel reactivity and increased heat capacity of the CO<sub>2</sub> atmosphere [15]. During the experiment with an increased O<sub>2</sub> concentration (OXY30), the temperature distribution was similar to air mode. Specific heat and oxygen diffusivity were similar to air and most retrofit experiments suggest such a mixture for oxy-fuel operations [46].



**Figure 2.** (a) Temperature distribution along the circulating fluidized bed (CFB) combustor riser and in the cyclone; (b) temperatures in the CFB cyclone exit and furnace at different heights. The temperatures deviance, due to fuel feeder, was up to 5%.

## 3. Results and Discussion

#### 3.1. Sulfur Oxides Emissions

The average emission values during stable operation are shown in Table 4 and Figure 3. In spite of decreased temperatures in the riser during oxy-fuel operations (Figure 2), the SO<sub>2</sub> concentration in the flue gas remained similar. Higher CO<sub>2</sub> partial pressure and lower temperature in the system inhibited decomposition of CaCO<sub>3</sub>, but the Ca/S molar ratio in the oil shale was as high as 8.0. It means that there was a lot of excess calcium in the system and even if the sulfur binding rate was inhibited as noted in reference [23], it was still enough to bind more than 99% of the sulfur. The oxy-fuel ashes contained a considerable amount of carbonates ((CO<sub>2</sub>)<sub>mineral</sub>) (see Figure 4) indicating decreased decomposition of carbonate minerals. During oxy-fuel combustion, sulfation was likely direct (see Equation (3)); the calcite reacted directly with sulfur oxide. When the oil shale was fired in air, the sulfation likely occurred via indirect reaction, because low carbonate concentration in ash indicated free lime availability for indirect sulfation (Equation (2)). Our results suggest that the elevated CO<sub>2</sub> levels and the inhibited carbonate decomposition extent do not have a noticeable effect on the SO<sub>2</sub> binding (see Table 5).

Item	Unit	Air	OXY21	OXY30	
O <sub>2</sub>	%dry	$10.0\pm1.9$	$8.5\pm2.1$	$12.9\pm2.9$	
NO <sub>x</sub>	mg/Nm <sup>3</sup> @ 6%O <sub>2</sub>	$141\pm29$	$156\pm20$	$130\pm65$	
$SO_2$	mg/Nm <sup>3</sup> @ 6%O <sub>2</sub>	$<14\pm9$	$23\pm14$	$<14\pm4$	
CO	$mg/Nm^3 @ 6\%O_2$	$943\pm99$	$2361\pm953$	$337\pm466$	
Desulfurization efficiency	%	99	99	99	
$SO_2$ emission	mg/MJ	<8	9	<8	
NO <sub>x</sub> emission	mg/MJ	34	40	33	
Fuel nitrogen conversion ratio	%	20	24	20	

Table 4. Average emissions of oil shale firing in the CFB combustor.



Figure 3. Pollutant emissions during oil shale CFB and fluidized bed combustion.



Figure 4. Mineral CO<sub>2</sub> ((CO<sub>2</sub>)<sub>mineral</sub>) and unburnt carbon content in the CFB combustion ashes.

**Table 5.** Chemical composition of oil shale air and oxy-fuel firing carbon free ashes, wt %. Otherdenotes minor components with concentrations below 0.1% as F,  $P_2O_5$ , TiO<sub>2</sub>, MnO, SrO, ZrO<sub>2</sub>.

Ash Flow	Combustion Mode	CaO	SiO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Cl	Other
	Air	60.1	10.2	13.4	3.2	8.0	3.2	1.0	0.1	0.2	0.5
BA	OXY21	65.2	8.9	9.5	2.8	8.2	3.5	0.8	0.4	0.3	0.5
	OXY30	63.9	10.6	8.5	3.5	7.2	3.6	1.0	0.1	0.1	0.5
	Air	48.7	18.9	11.4	5.8	8.0	4.1	2.1	0.1	0.2	0.6
EHE	OXY21	51.8	18.3	9.1	5.6	8.4	3.8	1.7	0.2	0.2	0.8
	OXY30	50.3	20.2	8.7	6.2	7.2	4.3	2.2	0.1	0.1	0.8
	Air	30.9	35.8	5.6	10.7	5.8	4.9	4.6	0.2	0.4	1.0
CI	OXY21	33.9	32.7	6.7	10.1	6.5	4.7	3.9	0.3	0.3	0.9
	OXY30	28.3	38.0	5.5	11.1	5.8	5.0	4.7	0.2	0.3	1.0
	Air	31.1	35.7	5.6	10.6	5.8	4.9	4.6	0.2	0.5	1.0
CII	OXY21	28.6	36.2	5.7	11.6	6.4	4.9	4.8	0.2	0.5	1.2
	OXY30	30.9	35.8	5.5	10.5	6.1	5.1	4.2	0.2	0.5	1.3
	Air	29.3	36.0	5.2	11.8	5.8	4.9	5.2	0.2	0.6	1.0
FA	OXY21	27.7	37.0	5.1	12.1	6.1	5.1	5.2	0.2	0.5	1.1
	OXY30	28.6	37.7	5.1	11.2	5.9	5.2	4.6	0.2	0.5	1.0

To compare the influence of circulating solid matter, circulation was stopped (the airflow to EHE was stopped). The temperatures in the riser were unstable (see Figure 3). The combustion efficiency decreased (the CO level increased over the measuring range) and SO<sub>2</sub> concentration in flue gas increased notably (from 50 to 1500 mg/Nm<sup>3</sup>). The ash concentration in the furnace decreased and there was not enough material to bind all the sulfur. This implies that despite the high calcium concentration in the fuel, working in a bubbling bed mode, did not ensure sufficient sulfur binding. The CFB combustion mode ensured sufficient conditions for sulfur binding, even in oxy-fuel mode.

### 3.2. Nitrogen Oxides Emissions

NO<sub>x</sub> emissions remained below 200 mg/Nm<sup>3</sup> during all experiments (Table 4). Our experiments showed that switching to oxy-fuel combustion did not alter the NO<sub>x</sub> emissions. The nitrogen conversion ratio to NO<sub>x</sub> was up to 24%, similar to results from Jankowska et al. [32] with bituminous coal (20–25%). However, Pikkarainen et al. [33] measured higher nitrogen conversion ratios (28–50%). Oil shale nitrogen content remained below 0.1%. Accordingly, a high nitrogen conversion ratio to NO<sub>x</sub> was expected (>25%) [47]. The nitrogen conversion ratio to NO<sub>x</sub> was found to be 20–24% and the emissions were rather low.

# 3.3. Ashes

During the experiments, ash samples were collected from all ash flows (Figure 1). The results of chemical analysis of the ashes are displayed in Table 5. Typically for oil shale, the most abundant oxide was calcium, followed by silica, magnesium and alumina. Except for  $CO_2$  content, chemical compositions of the ashes formed during different experiments were almost identical.

The unburnt carbon content fly ashes (0.3–4.7%) was considerably higher than in hotter ash-flows from CFB (<0.7%) (Figure 4). Together with the high CO concentration in the flue gas, it indicated re-condensation of volatiles after the coolers. Since high content of unburnt carbon in the fly ash was noticed during all the experiments, this showed that the hot zone was too short for a complete combustion of volatiles.

Mineral CO<sub>2</sub> content of the oxy-fuel ashes was considerably higher than in the ashes obtained in air mode (Figure 4). The difference was especially large for BA and CA. The composition and share of ash flows is different in every boiler. For oil shale CFB combustion, the share of bottom and filter ash is the largest. The BA obtained contained the most calcium and thus the effect on total CO<sub>2</sub> emission was considerable. Of the total carbon in the fuel, 20% was inorganic (see Table 1). It is theoretically possible to reduce the extent of decomposition of carbonate minerals to 28% in an oxy-CFB combustor firing Estonian oil shale [20]. The minimum is defined by the dolomite and sulfur content in the fuel. Limited decomposition of the carbonate minerals decreases  $CO_2$  emissions from oil shale combustion, but increases ash production.

Oxy-fuel CFB combustion of fuels containing carbonate minerals [48–51] resulted in smaller CO<sub>2</sub> production due to decreased decomposition of carbonate minerals. The extent of carbonate decomposition was calculated based on the content of CaO, MgO and CO<sub>2</sub> in the ashes; the methodology is described more thoroughly by Arro et al. [52]. Based on the data obtained during experiments and expecting similar ash splits, such as in a utility CFB boiler [11], the average extent of carbonate minerals decomposition during regular air fired CFB experiments was 0.84, for OXY21 0.56 and OXY30 0.46. The value for utility CFB firing Estonian oil shale was 0.69 [53]. During operation in air mode, the ash calcination was more extensive than in the utility boiler, but with the oxy-fuel operation, the calcination was only partial. Figure 4 depicts that oxy-fuel ashes behaved similarly; both BA and CA contained large amounts of carbonates. The average extent of carbonate mineral decomposition of OXY30 was smaller than that of OXY21, likely because of the different thermal loads of the combustor. The measured values show that decomposition of carbonate minerals was partial, but the theoretical minimum value was not reached.

#### 3.4. Comparison with Utility Scale

A 60 kW<sub>th</sub> CFB is a relatively small device; the fuel flow rate is over 4000 times smaller than in the 250 MW<sub>th</sub> utility boilers used for power production in Estonia. Nevertheless, the produced ash and flue gas are rather similar to the values obtained from industrial devices [11,53]. Pollutant emissions during experiments were also comparable to the values recorded from utility boilers (see Table 6). Emissions of nitrogen oxides were slightly higher than in utility boilers, probably due to the non-optimized secondary air inlet location. During stable CFB combustion, the sulfur oxides level in the flue gas was low. When the ash circulation was stopped (see Figure 3), the sulfur concentration in the flue gas increased to a level above typical oil shale PC boilers [45].

**Table 6.** Pollutant emissions from oils shale combustion,  $mg/Nm^3$  at 6% O<sub>2</sub>.

	SO <sub>2</sub>	NO <sub>x</sub>	
CFB 250 MW <sub>th</sub> [11]	<14	120	
PC 300 MW <sub>th</sub> [45]	3000	220	
CFB 60 kW air	<14	141	
CFB 60 kW oxy20	23	156	
CFB 60 kW oxy30	<14	130	

## 4. Conclusions

Estonian oil shale was fired in a 60 kW<sub>th</sub> CFB combustor to investigate the formed flue gas and ash during air and oxy-fuel operations. The fuel was characterized by extremely high Ca-rich ash and volatiles contents. Experiments were conducted in the regular air fired CFB mode and in two different oxy-fuel modes:  $21/79 O_2/CO_2$  and  $30/70 O_2/CO_2$ . The average temperature in the riser was ~740 °C; however, the temperature was 50 °C lower during the OXY21 experiment. When oxygen concentration was increased to 30%, similar temperatures as in air fired CFB were acquired. The thermal load was around 20 kW.

Produced flue gas and ash were analyzed. In air mode, the flue gas emissions for SO<sub>2</sub> and NO<sub>x</sub> were <14 and 141 mg/Nm<sup>3</sup> @ 6% O<sub>2</sub>, respectively; during the oxy-fuel operations, the values remained at similar levels. The chemical compositions of the oxy-fuel ashes were similar to the ashes produced in the air mode. Analysis of the collected ashes showed a decreased extent of carbonate minerals decomposition in oxy-combustion ashes. Despite decreased calcination and an apparent change in the sulfation route, there were no problems with sulfur binding. The results show that firing oil shale in an oxy-fuel circulating fluidized bed boiler could decrease CO<sub>2</sub> production while pollutant concentrations in the flue gas remained at a similar level compared to conventional CFB combustion. This reduces the cost of flue gas compression and further transportation and storage/utilization.

**Author Contributions:** L.L. is the primary author of this manuscript; the other authors participated in the experimental work, discussion and development of the ideas, and to some extent in the writing and editing of the manuscript.

**Acknowledgments:** This work was supported by the EU Regional Development Fund grant AR12003. The oil shale was provided by AS Viru Keemia Grupp.

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

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