

Emissions from Co-firing Lignite and Biomass in an Oxy-fired CFBC

Murat Varol^{a,b}, Robert Symonds^c, E.J. Anthony^{c,d,*}, Dennis Lu^c, Lufei Jia^c, Yewen Tan^c

^aDepartment of Environmental Engineering, Middle East Technical University, Ankara, 06800, Turkey

^bDepartment of Environmental Engineering, Akdeniz University, Antalya, 07058, Turkey (present address)

^cNatural Resources Canada, CanmetENERGY, 1 Haanel Drive, Ottawa, ON K1A 1M1, Canada

^dCranfield University, Cranfield, Bedfordshire MK43 0AL, United Kingdom

*Corresponding author. Tel.: 44(0)1234111 x2823; Fax: 44(0)7853 167530+.

E-mail address: b.j.anthony@cranfield.ac.uk,

Abstract:

The co-combustion of a high-sulphur lignite and biomass blend (up to 50% by weight) has been studied in a small oxy-fired circulating fluidized bed combustion (CFBC) pilot plant. Here the goal is to examine the effect of biomass share on NO_x, SO₂ and CO emissions. In these tests, a series of runs has looked at the effect of increasing biomass share under air firing, followed by tests in oxy-firing mode. The results show that the emissions are remarkably insensitive to the biomass share, and are comparable to other results for coal combustion, and likely to be well below any current emission guidelines. Overall, there appear to be no direct challenges to oxy-fuel co-firing in terms of gaseous emissions, although the simple lack of studies means that significantly more data are required on CFBC oxy-firing using a much wider range of biomass and coal types. K doping was also examined and did not result in significant formation of K phases on deposit probes.

Keywords: oxy-firing, circulating fluidized bed combustion, emissions, co-firing

Highlights:

- CO emissions are less than 400 ppm in all tests and are lower in the case of co-firing and comparable to or better than levels seen for air-fired CFB work.
- NO_x levels were consistently between 100-200 ppm and co-firing did not appear to significantly affect them up to a biomass share of 50%.
- Changing from air- to oxygen-firing decreased the efficiency of SO₂ capture.
- K doping did not produce significant K containing deposits on deposit probes.
- Hydrocarbon emissions for oxy-firing were generally extremely low.

1 Introduction

Oxy-fuel combustion is one of the most promising routes for using fossil fuels in a CO₂-neutral manner. When combined with biomass firing it may also offer net reductions of CO₂ emissions, the so-called Bio-Energy with Carbon Storage (BECS) option [Toftegaard et al., 2010; Cormos, 2016]. Here fluidized bed combustion is arguably the best available co-firing technology [Leckner, 2007], and it has recently been demonstrated in its oxy-combustion form at the 30 MW_{th} scale at Ciuden, in Spain [Anthony and Hack, 2013; Lupion et al., 2013]. However, despite rapid advances in the technology, there are remarkably few studies on the co-firing of biomass and coal in an oxy-fuel circulating fluidized bed combustion (CFBC) environment [Tan et al., 2013; Varol et al., 2014a,b; Duan et al., 2015] and, for that matter, relatively few papers on the operation of oxy-fuel CFBC [Jia et al., 2007, 2010; Romeo et al., 2011; Tan et al., 2013; Singh and Kumar, 2016] in general. Moreover, the necessity for recycling flue gas, in order to control the temperature in the primary reaction loop, means higher emission levels in the flue gases with the potential for fouling, corrosion and other problems [Jia et al., 2012; Tan et al., 2012]. Given the interest in the potential for achieving negative CO₂ emissions [Bui et al., 2017], and the very successful oxy-fuel CFBC trials carried out by Foster Wheeler at Ciuden, in Spain, there is a need to accelerate such developments. To do this we must explore a wide range of coals and biomass products in order to investigate the behavior of oxy-fuel CFBC technology with a range of feedstocks beyond the three co-firing studies currently available, which were carried out on a 0.4 m dia. CFBC [Tan et al., 2013], and a 0.1 m dia. CFBC [Varol et al., 2014a,b], respectively. In this work, a Spanish lignite was used and K doping was adopted for the oxy-fuel trials, to simulate the co-combustion of Turkish lignite and olive cake which typically contains high levels of K. It was anticipated that emissions would be similarly low compared with our previous studies, and that K doping would not influence those emissions. Less certain was whether the K doping would lead to measurable fouling or the production of agglomerates.

2 Materials and Methods

2.1 Characteristics of Fuels and Limestone

A Spanish lignite and wood pellets (obtained from a commercial supplier (Valfei) in Canada) were used in this study. The proximate and ultimate analyses of these fuels are given in Table 1. In all combustion tests, the lignite particle size was less than 4.76 mm and the wood pellets were approximately 20 mm in length and 5 mm in diameter.

Havelock limestone from Canada, which is a high-purity limestone (>98% CaCO₃), was also used to examine SO₂ emissions under co-firing conditions. Havelock has been used extensively in other FBC work at CanmetENERGY and elsewhere [Lu et al., 2009; Al-Jeboori et al., 2013].

Table 1. Proximate and ultimate analyses of Spanish lignite and wood pellets

	Spanish lignite	Wood pellets
Proximate analysis, % by wt. (as fired)		
FC	29.26	15.40
VM	29.36	80.17
Ash	28.40	0.4
Moisture	12.98	4.03

Ultimate analysis, % by wt. (dry basis)

C	44.4	49.6
H	2.92	5.92
N	0.52	0.13
S_{total}	5.72	
O	13.83	43.93
Ash	32.64	0.42
HHV, kJ/kg (as fired)	14,600	18,900

FC: Fixed Carbon, VM: Volatile Matter, HHV: Higher Heating Value

2.2 Experimental

Combustion tests were carried out in a lab-scale circulating fluidized bed combustor located at Natural Resources Canada – CanmetENERGY in Ottawa, Canada. The schematic diagram of the experimental setup is shown in Figure 1. The experimental setup consists of a combustor, a cyclone, a return leg, a bag filter and a feeding system. The feeding system is comprised of two fuel hoppers for lignite and wood pellets. Limestone was added to the system by mixing it with lignite. The combustor is constructed of SS310 steel and has an internal diameter of 0.1 m, and height of 5.1 m. It is fitted with electric heaters capable of operating at temperatures up to 1100 °C. This facility has been described in detail elsewhere [Jia et al., 2007, 2010; Symonds et al., 2016].

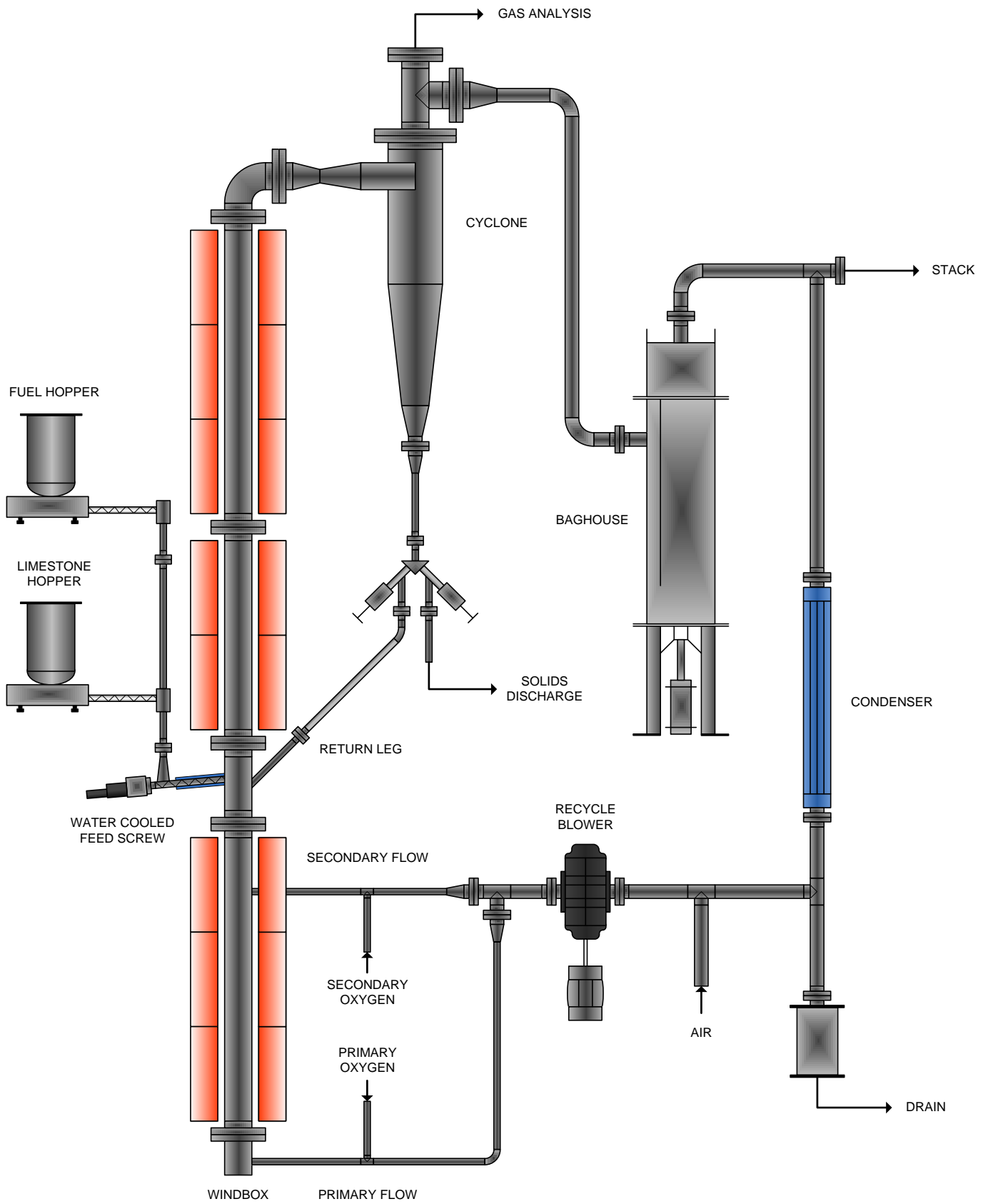


Figure 1. Schematic of Natural Resources Canada – CanmetENERGY Mini Bed CFBC

In all, eight tests of several hours duration were carried out in order to determine the effect of biomass share, O₂ percentage in the combustion gas and dense phase bed temperature on flue gas emissions. Five of these tests were air-fired and the remaining tests were oxy-fuel-fired. The experimental matrix consists of three different experimental sets which are described in Table 2. All but one of these tests were done at 850°C, with a final test carried out at 915°C to determine the effect of temperature. Both the percentage of biomass and the oxygen in the recirculated flue gas were varied, and the three distinct campaigns are as shown in Table 2. Here, no attempt was made to keep the heat input constant; instead the mass fraction of biomass was changed (10, 30 and 50% weight) by changing the coal feed rate accordingly. Secondary air was not used, and all emission figures in the tables and figures have been re-calculated to 6% O₂.

Table 2. Experimental Matrix

Test #	Run designation	Ca:S molar ratio	Biomass Share of Fuel Mixture (% by wt.)	Nominal O ₂ (vol.%)	Bed Temperature T _{dense phase} (°C)
1-1	C-1	2	0	air-fired	850
1-2	CB-1	2	10	air-fired	850
1-3	CB-2	2	30	air-fired	850
1-4	CB-3	2	50	air-fired	850
2-1	CB-4	2	50	air-fired	850
2-2	CB-5	2	50	25	850
2-3	CB-6	3	50	30	850
3-1	CB-7*	-	50	30	850
3-2	CB-8*	3	50	30	850
3-3	CB-9*	3	50	30	915

* With K doping.

The first campaign was carried out in an air-fired mode to determine the effect of biomass share on flue gas emissions. In these tests both temperature in the dense bed (T_{dense phase}) and superficial velocity in the combustor were kept effectively constant, at about 850 °C and between 2.5 and 3 m/s, respectively, as far as possible. The experiments involved combustion of Spanish lignite, and co-combustion of Spanish lignite and wood pellet fuel mixtures containing 0, 10, 30, and 50% by weight of wood pellets (Tests no. 1-1 to 1-4).

In the second campaign the tests were designed to determine the effect of O₂ percentage in the combustion gas on emission levels in the flue gas. The experiments included co-combustion of Spanish lignite and wood pellets (1:1 weight ratio) for two different oxygen levels fed to the combustor (25% and 30% O₂) (Tests no. 2-2 and 2-3) and these results are compared along with those for air firing (Test no. 2-1).

In the last campaign, three experiments were conducted to investigate the effect of biomass and limestone interaction and bed temperature on ash composition and deposit formation under oxy-firing conditions (30% O₂). Three tests (3-1, 3-2 and 3-3) were carried out with K doping bringing the K₂O content in the “biomass

ash” to an overall 34-39%. This is roughly equivalent to levels associated with Turkish olive cake, which is a potentially important fuel in Turkey since it produces about 8% of the world’s olives [Demirbas, 2009]. All three tests were carried out for a nominal 24 h period. To simulate the K effect, K_2CO_3 solution was sprayed onto the wood pellets, which were then air dried prior to feeding. The amount of K_2CO_3 added was based on the ash content of the wood pellets and the K content typical of olive cake ash.

Spanish lignite/wood pellets (1:1 weight ratio) mixture was oxy-fired (30% O_2) at $850^\circ C$ in Test no. 3-1. Test no. 3-2 was the same test with limestone addition (0-2 mm particle size). Tests no. 3-1 and 3-2 were used to see the effect of limestone addition to the fuel mixture on ash composition. The third test (Test no. 3-3) in this campaign was a repeat of test 3-2 with the operating temperature raised to $915^\circ C$ to see the effect of dense phase temperature on ash composition.

In order to carry out this work, a special “deposit sampling probe” was designed and manufactured to simulate a heat exchanger tube in the combustor (Figure 2). The surface of the deposit sampling probe is cooled internally down to $550^\circ C$ with air in order to represent the surface temperature of the superheaters. The deposit sampling probe was used in order to collect fly ash samples during the combustion process. The particles accumulated on the probe’s surface were collected at the end of the test. After the probe was removed from the combustor, the particles collected on the probe were very slowly scraped from the surface into a sampling pot. The deposit sampling probe itself was located at a level of 4.5 m above the distributor plate. The probe was made from a stainless steel tube with a 26.7 mm outer diameter (OD) and its length was 230 mm. The deposit samples themselves accumulated on the surface of the probe on the detachable ring which has a length of 60 mm, and a 26.7 mm OD. The probe temperature at this level was around $790-830^\circ C$ for the tests where dense phase temperature was kept at a nominal $850^\circ C$ (C-1, CB-1 to CB-8), and a temperature of $845^\circ C$ for the test where dense phase temperature was kept at $915^\circ C$ (CB-9).

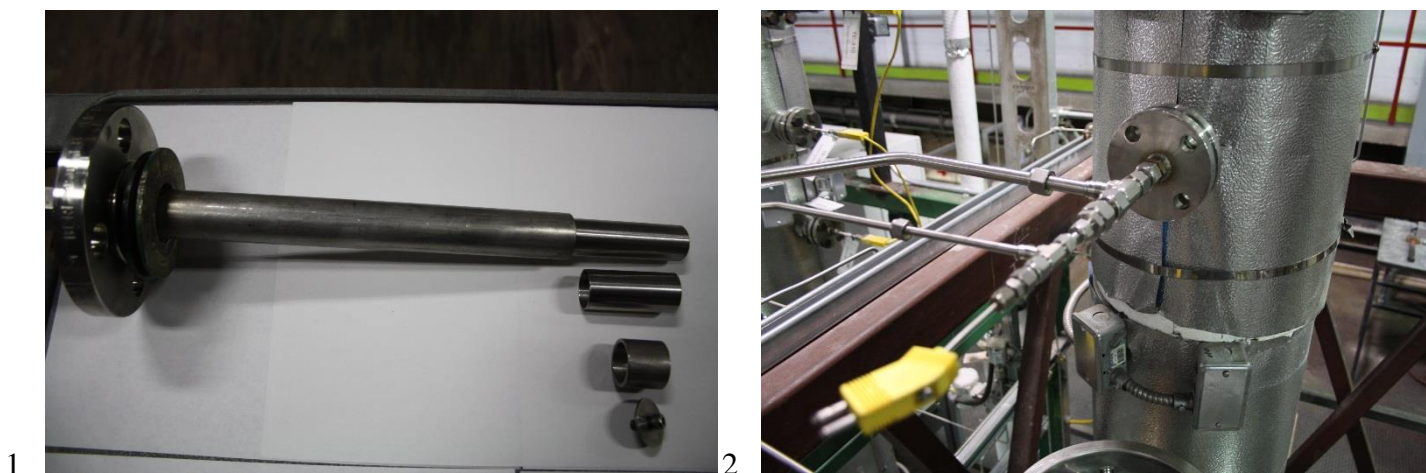


Figure 2. Air cooled deposit sampling probe with a detachable ring

The deposit characteristic X-ray diffraction (XRD) data were collected on a Rigaku Ultima IV XRD spectrometer over the angular range 7 to 80° (2-theta) in 0.02° steps at 1 degree/min. The XRD system operates in the theta:theta geometry, uses $Cu(K\alpha)$ radiation, 0.154 nm. The generator voltage and current settings were 40 kV and 44 mA, respectively. At the end of the co-combustion tests (Tests no 3-1 to 3-3), bed ash from the combustor and fly ash from the bag filter were collected. X-ray fluorescence (XRF) and XRD analyses of ash samples were carried out.

The diffraction spectra were processed using the JADE version 9.0 XRD processing software. Identification of the chemical or mineral compounds was performed using the search/match option in JADE. Accurate integrated intensities of diffraction peaks were derived through “peak deconvolution” or more commonly called “line profile fitting”, another software tool in JADE. These data were used for quantitative analysis. Quantitative analysis of the samples was done using a variety of different internal spiking standards. This technique is known as the reference intensity ratio (RIR) method. For quantitative XRD, each sample was mixed with a spiking agent. The resulting mixture was thoroughly ground using a mortar and pestle to ensure homogeneity of the phases. The resulting powdered mixture was loaded into a holder. The holder was transferred to the XRD instrument and data were collected. Integrated intensities for strong diffracting peaks of each phase were obtained using JADE. Concentrations of the chemicals identified in each sample were calculated using the method mentioned above. The amorphous content was estimated by difference.

For this work EPA Method 0031 was used for volatile organic compounds (VOC) sampling. The VOC sampling train consists of a heated glass-lined probe, two sorbent tubes containing Tenax®-GC (1.6 ± 0.1 g each), a third sorbent tube containing Anasorb®-747 (5.0 g ± 0.1 g), flow measurement and other related devices. Once steady state operation of the oxy-fuel mini-CFB was achieved, flue gas samples were pumped through the VOC sampling train. As the flue gas passed through the sorbent tubes, VOCs were absorbed onto the Tenax and the Anasorb sorbents. At the end of the VOC sampling period, the sorbent cartridges were analyzed to determine the amount of each volatile organic compound absorbed. Together with the volume of flue gas sample passing through the VOC sampling train, concentrations of VOCs were determined.

3 Results and Discussion

3.1 Effect of Biomass Share on Emissions

Four tests were conducted in order to determine the effect of wood pellets on major pollutants in flue gas (CO₂, CO, NO_x, and SO₂). Here the percentage of biomass by weight was varied (0%, 10%, 30%, and 50%) and CO₂ levels were typically around 15-16%. Limestone was used in all combustion tests at a Ca/S ratio of 2.

The effect of the proportion of wood pellets in the fuel mixture on CO₂, CO, SO₂, and NO_x emissions is shown in Table 3, 4 and 5 and Figure 3. Here λ is excess air.

Table 3. Emissions for Air-Fired Coal/Biomass Mixtures (all emissions expressed to 6% O₂)

Run	Coal feed rate (kg/h)	Biomass feed rate (kg/h)	Air flow rate (kg/h)	λ	CO ₂ (vol.%)	CO (ppm)	NO _x (ppm)	% N conversion	SO ₂ (ppm)	% S capture
C-1	6	0	15.8	1.49	15.5±0.8	86±12	131±13	3.7	977±130	89%
CB-1	4.2	0.47	18.0	1.50	15.5±0.8	59±5	144±13	6.4	806±72	85%
CB-2	3.22	1.38	18.8	1.37	15.3±0.7	30±7	120±7	6.7	410±87	89%
CB-3	2.02	2.02	22.1	1.50	15.4±1.2	56±15	120±19	11.0	303±83	85%

Table 4. Emissions for Air-Fired Coal/Biomass Mixtures (all emissions expressed to 6% O₂)

Run	Coal feed rate	Biomass feed rate	Air flow rate	λ	CO ₂ (vol.%)	CO (ppm)	NO _x (ppm)	SO ₂ (ppm)
-----	----------------	-------------------	---------------	-----------	-------------------------	----------	-----------------------	-----------------------

	(kg/h)	(kg/h)	(kg/h)					
CB-4	2.02	2.02	22.1	1.50	15.4±1.2	56±15	120±19	303±83
CB-5	2.27	2.27	17.2	1.22	83.0±7.1	316±261	116±18	2354±387
CB-6	2.29	2.27	11.4	1.15	81.1±5.5	410±289	121±25	779±288

*CB-4 and CB-3 are the same test.

Table 5. Emissions for Air-Fired Coal/Biomass Mixtures (all emissions expressed to 6% O₂)

Run	Coal feed rate (kg/h)	Biomass feed rate (kg/h)	Air flow rate (kg/h)	λ	CO ₂ (vol.%)	CO (ppm)	NO _x (ppm)	SO ₂ (ppm)
CB-8	2.29	2.27	11.4	1.15	81.1±5.5	410±289	121±25	779±288
CB-9	2.52	2.52	12.9	1.12	85.3±3.8	436±288	110±20	1416±425

*CB-8 and CB-6 are the same test.

Average CO emission was about 86 ppm for lignite (only) combustion. However, CO emissions decreased with an increasing share of wood pellets in the fuel mixture and reached a minimum value of less than 50 ppm for a fuel mixture containing 30% wood pellets. Interestingly, a further increase in the share of wood pellets increased CO emissions to above 50 ppm, but still below the 86 ppm value seen for lignite combustion alone. However, these results do not seem out of line with those for a well-run air-fired CFBC plant.

Due to the relative S contents of the two fuels, SO₂ emissions decreased with an increase in the share of wood pellets in the fuel mixture from values above 1000 ppm for 100% lignite combustion to 300 ppm for fuel mixtures containing 50% wood pellets and here limestone performance was remarkably consistent. More surprisingly, in the case of NO_x emissions, the wood pellets appeared to have a fairly small effect on the emissions in terms of ppm, but a much larger effect on the overall nitrogen conversions. NO_x emissions were consistently between 100 ppm and 150 ppm for all cases despite the fact that the fuel nitrogen in the biomass is only a quarter of that for the lignite. A possible explanation is that, as the coal fraction drops significantly, so does the char carbon and, despite the fall-off in fuel nitrogen, the bed's ability to reduce NO_x starts to decline. This phenomenon was previously observed by Leckner and Karlsson [1993] in co-firing coal and biomass tests in a 12 MW_{th} CFBC.

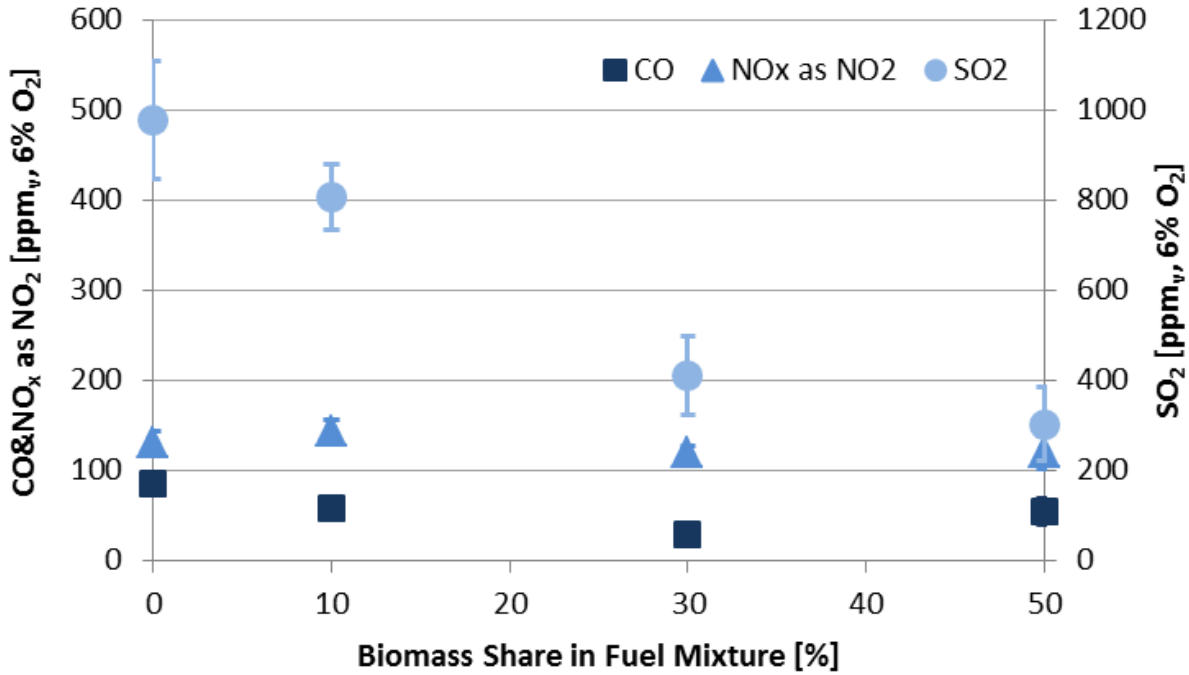


Figure 3. Effect of biomass share in fuel mixture on CO₂, CO, SO₂, and NO_x emissions under air-firing combustion conditions

3.2 Effect of O₂ Concentration on Emissions

The effect of the O₂ percentage in the combustion gas on CO₂, CO, SO₂, and NO_x emissions for the co-combustion of wood pellets (50% by wt.) and Spanish lignite is shown in Figure 3. Three co-combustion tests with 21% (by vol.), 25% (by vol.) and 30% (by vol.) of O₂ were conducted. For the oxy-firing tests CO₂ rose from 15% for the air-fired case to around 82% for the 30% O₂ case.

In the case of air-firing (21% O₂) with 50% biomass, SO₂ emissions were about 300 ppm due to indirect sulphation (Eqn. 1). However, they increased dramatically to 2300 ppm with 25% O₂ because of flue gas recirculation and presumably the fact that sulphation then occurred *via* the direct route (Eqn. 2). The average temperature of the dense phase region was 844°C, 850°C, and 853°C for 21%, 25% and 30% O₂, respectively. Simple equilibrium calculations suggest that, for 82% CO₂ in the flue gas, sulphation should be *via* the direct route since the partial pressure of CO₂ should be approximately 50 kPa, while at 915°C the partial pressure of CO₂ over CaCO₃ is 137 kPa, so sulphation must be by the indirect route [Stanmore, 2005] and qualitative XRD (QXRD) measurements on the bed ash also confirmed that the bulk of the Ca component was in the form of CaO.



It seems reasonably well established at this point that SO₂ emissions are likely to be higher for direct sulphation than for indirect sulphation [Jia et al., 2007, 2010; García-Labiano et al., 2011; Lupiáñez et al., 2013; Tan et al., 2012].

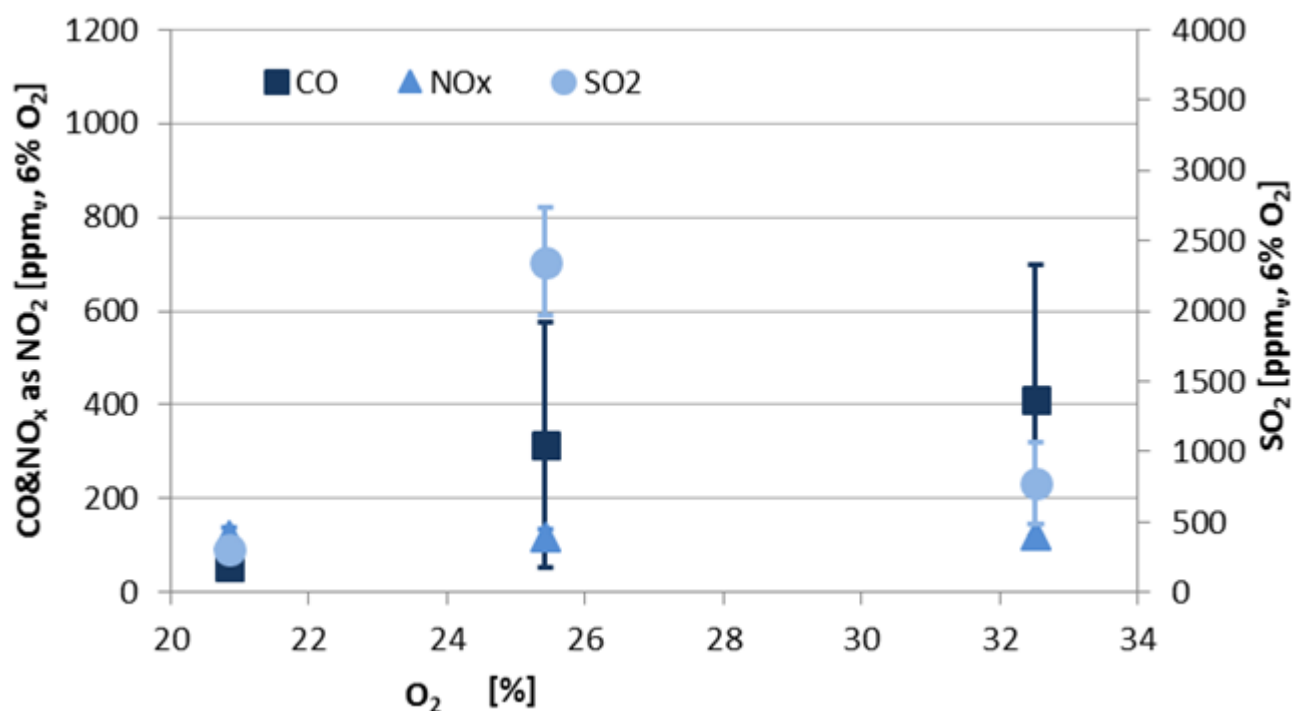


Figure 4. Effect of O₂ percentage on CO, SO₂, and NO_x emissions for the co-combustion of wood pellets (50% by wt.) and Spanish lignite (Ca:S molar ratio was 3 for 32% O₂ result)

In the case of a nominal 30% O₂, SO₂ emission was measured as 780 ppm which was lower than that for 25% O₂ (2300 ppm). This is partially due to the increased Ca:S molar ratio from 2 to 3, but the change is still rather high. After the SO₂ emission results obtained from the experiment with 25% O₂, it was decided to increase the Ca/S ratio because the maximum range of the gas analyzer for SO₂ was 3000 ppm. The summary of these tests is shown in Figure 4.

Interestingly, NO_x emissions were between 100 ppm and 150 ppm for all cases and it is clear that the percentage of O₂ in the primary gas supplied to the base of the combustor had no effect on NO_x emission. However, the CO levels rose considerably above those from the air-fired case, reaching values around 400 ppm. These values are about double those seen in the work of Tan et al. [2013] and this is probably due to the smaller scale of the oxy-fuel combustor used in this work, and possible differences in cyclone design, as earlier work on this oxy-fuel combustor indicated that CO emissions are very sensitive to cyclone operation [Jia et al., 2010]. However, it is worth noting that all the CO results are comparable to those of Varol et al. [2014a] when firing a high-sulphur Turkish lignite and wood pellets in a 0.1 m dia. oxy-CFB unit, whose values were between 165-530 ppm.

3.3 Effect of Temperature on Emissions

The effect of operating temperature on CO₂, CO, SO₂, and NO_x emissions for the co-combustion of wood pellets (50% by wt.) and Spanish lignite was examined by increasing the bed temperature (Figure 5). Tests were conducted at 850°C and 915°C. The oxygen percentage in the gas was about 30% and the Ca/S ratio was 3 for both runs. While operating with an increase in temperature from 850°C to 915°C is associated with only a slight increase in CO₂ levels (82% vs. 85%), it has a large effect on SO₂ emissions which increased from about 780 ppm to around 1410 ppm, which is reasonable if one assumes that despite the fact that

indirect sulphation is expected to be better than direct sulphation, the temperature is beyond the peak for optimum sulphur capture in the indirect mode [Anthony and Granatstein, 2001]. By contrast, the higher temperature levels do not appear to influence the CO and NO_x emissions.

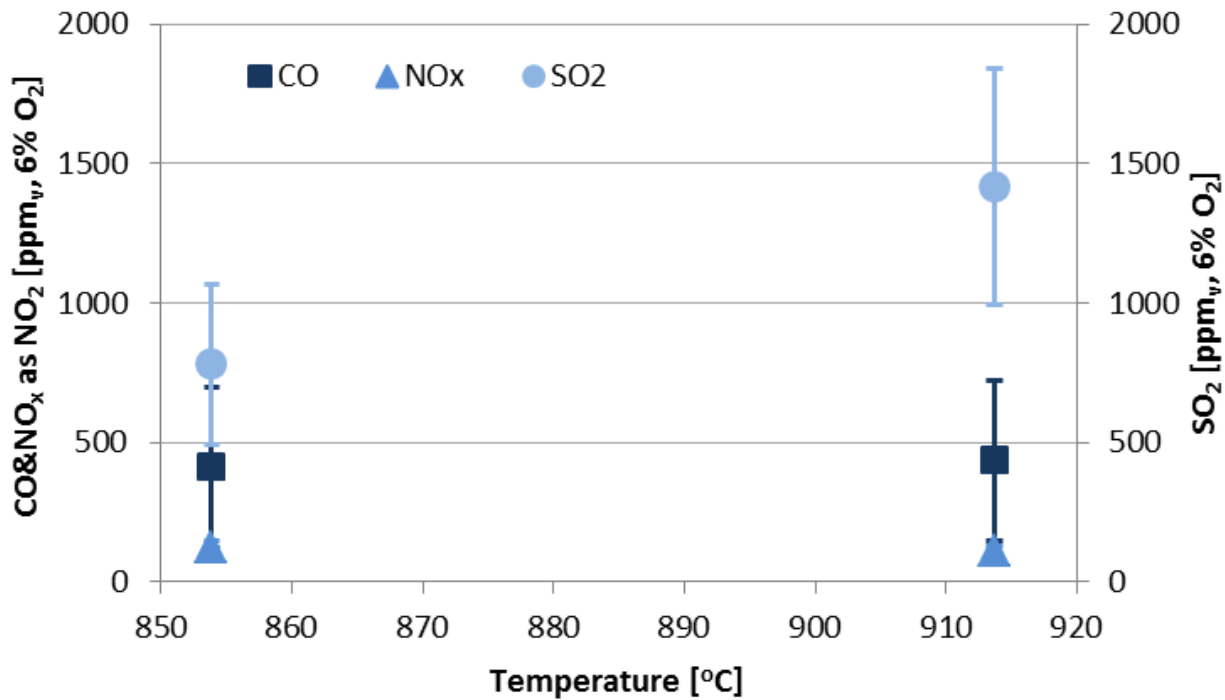


Figure 5. Effect of O₂ percentage in gas on CO, SO₂, and NO_x emissions for the co-combustion of wood pellets (50% by wt.) and Spanish lignite

What is interesting in these results is the clear demonstration that co-firing biomass even up to the extent of 50% by weight does not significantly affect emissions, other than SO₂. In this respect, this study is in agreement with earlier findings for a 0.8 MW_{th} pilot-scale oxy-fuel CFBC [Tan et al., 2013].

As in the case of previous work [Tan et al., 2013], the volatile organic compound (VOC) emissions were also low and mostly well below current EU standards as shown in Table 6 below. (All runs in Table are co-combustion of lignite and wood pellets including 50% wood pellets). The exception is one result for CS₂, and benzene emissions. Comparing the VOCs emissions of our oxy-fuel CFBC with the limits set out in the European Union's Industrial Emissions Directive [Directive, 2010], which states that, *for emissions of the VOCs where the mass flow of the sum of the compounds is greater than, or equal to, 10 g/h, a total sum emission limit value of 2000 µg/Nm³ shall be complied with*, Table 6 shows that VOC emission rates from our oxy-fuel CFBC operation conform to this directive with the exception of results from the test CB-5 for benzene. Interestingly, much earlier work with a commercial-scale air-fired CFBC burning coal generally supported the idea that organic emissions are very low, with benzene being among the highest VOC emission [Cianciarelli, 1989; Mortazavi, 1996]. In this case it appears that neither oxy-firing nor K doping has made any significant difference to this outcome, but it is clear that attention should be paid to benzene emissions, although the one very high value, if it is not an artefact, could possibly be explained by the much smaller size of this unit compared with the 0.8 MW_{th} scale of the CFB results provided by the Tan et al. work [2013] or operational problems in the test CB-5. As in the case of the work done by Tan et al. [2013], high benzene levels are also associated with slightly elevated toluene levels.

Table 6. Hydrocarbon Emissions

VOC ($\mu\text{g}/\text{Nm}^3$)	CB-3	CB-5	CB-7	CB-9
Dichlorodifluoromethane (FREON 12)	0.54 - 0.90	< 82	<42	<9.5
Chloromethane	11.6 - 11.9	12 - 73	<31	3.6 - 10.4
Vinyl Chloride	<0.44	< 57	<27	<6.2
Bromomethane	6.3	8.9 – 70.1	4.6 - 35.8	0.79 - 7.55
Chloroethane	27	2.1 – 38.8	<19	<4.3
Trichlorofluoromethane (FREON 11)	0.18 - 0.40	0.22 - 41.0	<21	0.34 - 4.85
Acetone (2-Propanone)	20	5.5 – 189	3.8 - 97.2	1.4 - 21.7
1,1-Dichloroethylene	<0.37	<45	<23	<5.2
Iodomethane	12	6.4 – 67.5	1.7 - 32.8	<7.1
Carbon Disulphide	9.7	14900	104 - 158	11 - 23
Methylene Chloride (Dichloromethane)	<0.64	<78	<40	<9.0
1,1-Dichloroethane	<0.40	<49	<25	<5.7
trans-1,2-Dichloroethylene	<0.34	<41	<21	<4.7
cis-1,2-Dichloroethylene	<0.34	<41	<21	<4.7
Chloroform	<0.37	<45	<23	<5.2
1,2-Dichloroethane	<0.23	<29	<15	<3.3
Methyl Ethyl Ketone (2-Butanone)	11	<148	<75	<17
1,1,1-Trichloroethane	<0.47	<57	<29	<6.6
Carbon Tetrachloride	<0.54	<66	<34	<7.6
Benzene	137	117000	3060	797
1,1,2-Trichloroethane	<0.54	<66	<34	<7.6
1,2-Dichloropropane	1.3 - 1.5	<45	<23	<5.2
Trichloroethylene	<0.37	<45	<23	<5.2
Dibromomethane	<0.34	<41	<21	<4.7
Bromodichloromethane	<0.37	<45	<23	<5.2
cis-1,3-Dichloropropene	<0.34	<41	<21	<4.7
trans-1,3-Dichloropropene	<0.23	<29	<15	<3.3
Dibromochloromethane	<0.30	<37	<19	<4.3
Methyl Isobutyl Ketone	1.7 - 2.0	<78	0.5 - 39.9	<9.0
Methyl Butyl Ketone (2-Hexanone)	7.9 - 8.4	<127	<65	<15
Toluene	8.6 - 8.8	7680	97	30.9 - 31.2
Ethylene Dibromide	<0.34	<41	<21	<4.7
Tetrachloroethylene	<0.6	<74	<38	<8.5
Chlorobenzene	0.55 - 0.74	<45	<23	<5.2
1,1,1,2-Tetrachloroethane	<0.34	<41	<21	<4.7
Ethylbenzene	1.6 - 1.9	386	<29	8.1 - 8.4
m/p-Xylene	4.5	298	<31	<7.1
Styrene	2.0 - 2.2	2040	<25	<5.7
o-Xylene	1.2 - 1.4	73 – 74	<31	<7.1
Bromoform	<0.47	<57	<29	<6.6
1,1,2,2-Tetrachloroethane	<0.47	<57	<29	<6.6
1,2,3-Trichloropropane	<0.5	<61	<31	<7.1
1,3-Dichlorobenzene	<0.67	<82	<42	<9.5
1,4-Dichlorobenzene	<0.67	<82	<42	<9.5

1,2-Dichlorobenzene	<0.67	<82	<42	<9.5
CB-3: (air-fired)				
CB-5: (oxy-fired, 25% O ₂)				
CB-7: K doping (oxy-fired, 30% O ₂)				
CB-9: K doping and limestone addition (oxy-fired, 30% O ₂ ; Ca/S = 3)				

3.4 Bed Solid, Fly Ash and Deposit Probe Results

Bed ash and fly ash samples were taken at the end of co-combustion experiments for Tests no. 3-1, 3-2 and 3-3 which were nominal 24 h runs. At the end of each run, bed ash was separated into three groups according to particle size and they were exposed to XRF and XRD analyses. XRF analyses of three different particle ranges of bed ash are given in Table 7.

Table 7. XRF Analysis of Bed Ash

		Particle Size of Bed Ash		
		0.6-0.85 mm	0.85-2 mm	> 2mm
Test no. 3-1	CaO, wt%	1.46	15.42	40.68
	SO ₃ , wt%	2.34	9.42	17.61
	LOF	0	3.04	15.53
Test no. 3-2	CaO, wt%	1.46	15.42	40.68
	SO ₃ , wt%	2.34	9.42	17.61
	LOF	0	3.04	15.53
Test no. 3-3	CaO, wt%	1.46	15.42	40.68
	SO ₃ , wt%	2.34	9.42	17.61
	LOF	0	3.04	15.53

LOF: loss on fusion

What is clear from these results at 850°C is that the Ca component in the bed ash for Test no. 3-2, where limestone was used is in the form of CaCO₃ as indicated by the high loss on fusion (LOF) result and this has been confirmed by QXRD data, which show negligible CaO content in Test no. 3-2, (Table 8). For Test no. 3-3 (at 915°C), Table shows a negligible CaCO₃ content in the bed material.

Table 8. QXRD Composition as a Function of Bed Particle Size Range

		Particle Size of Bed Ash		
		0.6-0.85 mm	0.85-2 mm	> 2mm
Test no. 3-2	Calcite, wt%	54.9	73.4	60.2
	Lime, wt%	0.6	0.2	0.3
Test no. 3-3	Calcite, wt%	-	-	0.8
	Lime, wt%	10.9	18.5	39.1

For the fly ash, CaO content for Test no. 3-2 is 14.5% (34.6% sulphated) and the LOF is 10.8%, while for Test no. 3-3, the CaO content is higher at 28.1%, but this material is 37.8% sulphated and the LOF is lower at 8.1%. QXRD results for these tests give the fly ash anhydrite content as 34.6%, and the calcite content as 18.8%, with the remaining compounds being small amounts of quartz (7%), magnetite (8.3%) and hematite (4.4S%) for Test no. 3-2. For Test no. 3-3, the anhydrite content according to QXRD results is 54.5%, with a lime content of 6.2%, and a calcite content of 10.5%, and the only iron compounds being hematite, at a concentration of 5.3% and magnetite at 6.4%.

Probe results are given in Table 9. What is interesting about these results is that the primary component of the deposit is anhydrite, and that there is only a small amount of K-containing material in the form of microcline in any of the deposits. In the K doping experiments fly ash contains between 1.5 and 2.5% K expressed as K_2O , compared with a value of 0.9% for the coal ash, and values for the bed ash of around 0.2 to 1.5% for all runs. However, this cannot totally rule out the possibility that some of the K is depositing elsewhere in the system.

Table 9. QXRD Result for Deposits on Deposit Sampling Probe

Chemical Compound		Test no. 3-1 (wt%)	Test no. 3-2 (wt%)	Test no. 3-3 (wt%)
Hematite, syn	Fe_2O_3	20.0	11.0	7.8
Anhydrite	$CaSO_4$	13.0	33.8	36.9
Magnesianoferrite, syn	$MgFe_2O_4$	5.6	12.7	4.9
Forsterite, syn	$Mg_2(SiO_4)$	9.8	8.8	9.7
Calcite	$CaCO_3$	1.0	13.2	7.7
Quartz, low	SiO_2	1.3	5.0	1.8
Lime, syn	CaO	0.6	1.5	5.9
Microcline	$K(AlSi_3)O_8$	2.7	4.2	2.4
	Crystallinity (%)	54.0	90.2	77.1
	Amorphous (%)	46.0	9.8	22.9

Similar tests carried out in a 0.1 m dia. air-fired CFBC in Turkey identified high concentrations of potassium calcium sulphate (30-70%), using an identically designed air-cooled probe as in this work, also operating at a temperature of 550°C. However, no such compound is apparent in these deposits, which suggests there is either a difference between oxy- and air-fired combustion, or the doping technique produces different results.

4 Conclusions

In the case of flue gas emissions for the combustion and co-combustion of Spanish lignite and wood pellets, the effect of the share of wood pellets in the fuel mixture on CO_2 , CO, SO_2 , and NO_x emissions was investigated. These results suggest increasing biomass share in the fuel mixture had no impact on NO_x emissions, and only a small positive impact on CO emissions. As expected, SO_2 emissions decreased with an increase in the share of wood pellets in the fuel mixture.

Experiments with K doping of the biomass did not show any significant effect on gas emissions, as expected, and the deposits formed were comprised principally of anhydrite, with a low amount of a K component (microcline). As the K levels in the fly ash were only slightly elevated in the K doping experiments this means we cannot completely rule out the possibility that K is depositing elsewhere in the system.

SO₂ emissions increased from about 300 ppm (air firing, 21% O₂ with 50% biomass addition) to 2300 ppm when the co-combustion test (50% wood pellets) was conducted with 25% O₂. This increase is due to flue gas recycle and one might conclude that this can also be explained in part by the high partial pressure of CO₂ in the combustor which, in turn, promotes direct sulphation. However, increasing the bed temperature to 915°C also increased the SO₂ emissions, even though at the higher bed temperature the sulphation must have been by the indirect route. The O₂ percentage in the gas had no significant effect on NO_x emission. Increasing the O₂ percentage in the gas supplied to the base of the combustor appeared to cause some increase in CO emission. Finally, while an increase in the operating temperature from 850°C to 915°C increased the SO₂ emissions it did not significantly affect the CO and NO_x emissions. Overall, these experiments suggest that co-firing biomass in CFBC in an oxy-fuel environment poses no special problems, which is in line with other, albeit limited work on pilot oxy-fuel CFB plants that has been generated.

Hydrocarbon emissions were also low, with the exception of benzene, as was anticipated based on previous CFBC results. A general conclusion can be drawn from these results, namely that there is simply a dearth of studies on emissions of oxy-fired CFB plants operating in the co-firing mode and, in particular, information on organic emissions of which this study and an earlier study by Natural Resources Canada - CanmetENERGY on its 0.8 MW_{th} CFBC unit appear to be the only two public domain studies currently available.

Acknowledgment

The financial support provided to this project by the Turkish Scientific and Technical Research Council-TUBITAK-2214 (2011/2) is greatly appreciated as is the support of Natural Resources Canada – CanmetENERGY, where the test work was carried out and which hosted Dr. Varol during the course of this work.

5 References

1. Al-Jeboori, M.J., Nguyen, M., Dean, C. and Fennell, P.S., Improvement of Limestone-based CO₂ Sorbents for Ca Looping by HBr and Other Mineral Acids, *Industrial and Engineering Chemistry Research*, 52, 1426-1433, 2013.
2. Anthony, E.J. and Granatstein, D.L., Sulfation Phenomena in Fluidized Bed Combustion Systems, *Progress in Energy and Combustion Science*, 27, 215-236, 2001.
3. Anthony, E.J. and Hack, H., Oxy-fired Fluidized Bed Combustion: Technology prospects and new developments, Chapter 5 (pg. 867-894) in *Fluidized Bed Technologies for Near-Zero Emission Combustion and Gasification*, F. Scala (ed.), Woodhead Publishing, London, UK, 2013.
4. Bui, M., Fajardy, M., MacDowell, N., "Bio-Energy with CCS (BECCS) Performance Evaluation: Efficiency Enhancement and Emissions Reduction, *Applied Energy* 195, 289-302, 2017.
5. Cianciarelli, D., Characterization of Semi-Volatile Organic Emissions from the Chatham 20 MW Circulating Fluidized Bed Demonstration Unit, Environment Canada Report, File 4030-7-15, January 1989.
6. Cormos, C-C., Oxy-combustion of Coal, Lignite and Biomass: A Techno-economic Analysis for a Large-Scale Carbon Capture and Storage Project in Romania, *Fuel*, 169, 50-57, 2016.
7. Demirbas, M.F., Evaluation of Olive Cake for Bio Oil, *Energy Sources, Part A, Recovery, Utilization and Environmental Effects*, 31, 1236-1241, 2009.
8. Directive 2010/75/Eu of The European Parliament and of The Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control), *Official Journal of the European Union*, 17.12.2010.
9. Duan, L., Duan, Y., Zhao, C., and Anthony, E.J., NO emissions during co-firing in an Oxy-fuel Circulating Fluidized Bed Combustor, *Fuel*, 150, 8-13, 2015.
10. <https://www.epa.gov/sites/production/files/2015-12/documents/0031.pdf> accessed November 2017.
11. García-Labiano, F., Rufas, A., De Diego, L.F., Obras-LoCERTALES, M.D.L., Gayán, P., Adánez, J., Calcium-based Sorbents Behaviour during Sulphation at Oxy-Fuel Fluidized Bed Combustion Conditions, *Fuel*, 90, 3100-3108, 2011.
12. Jia, L., Tan, Y., Wang, C. and Anthony, E.J., Experimental Study of Oxy-Fuel Combustion and Sulfur Capture in a Mini-CFBC, *Energy & Fuels*. 21, 3160–3164, 2007.
13. Jia, L., Tan, Y. and Anthony, E.J., Emissions of SO₂ and NO_x during Oxy-Fuel CFB Combustion Tests in a Mini-Circulating Fluidized Bed Combustion Reactor, *Energy & Fuels*. 24, 910–915, 2010.
14. Jia, L., Tan, Y., McCalden, D., Wu, Y., He, I., Symonds, R. and Anthony, E.J., Commissioning of a 0.8 MW_{th} CFBC for Oxy-Fuel Combustion, *International Journal of Greenhouse Gas Control*, 7, 240-243, 2012.
15. Leckner, B., Co-Combustion – A Summary of the Technology, AGS Pathways report 2007:E3.
16. Leckner, B. and Karlsson, M., Gaseous Emissions from CFB Combustion of Wood, Biomass and Bioenergy, 4, 379-389, 1993.
17. Lu, D.Y., Hughes, R.W., Anthony, E.J. and Manovic, V., Sintering and Reactivity of CaCO₃ based Sorbents for Insitu CO₂ Capture in Fluidized Beds under Realistic Calcination Conditions, *Journal of Environmental Engineering*, 135, 404-410, 2009.
18. Lupiáñez, C., Guedea, C., Bolea, I, Luis, I., Díez, L.I. and Romeo, L.M., Experimental study of SO₂ and NO_x emissions in fluidized bed oxy-fuel combustion, *Fuel Processing Technology*, 106, 587–594, 2013.
19. Lupion, M., Alvarez, I., Otero, P., Cortes, V.J., Kuivalainen, R., Lantto, J., Hotta, A. and Hack H., 30 MW_{th} Ciudad Oxy—CFB Boiler- First Experience, GHGT-11, *Energy Procedia*, 2013.
20. Mortazavi, R., Characterization of Semi-Volatile Organic Compounds (SVOCs) and Volatile Organic Compounds (VOCs) from the Point Aconi Coal-Fired Power Plant, Environment Canada Report PMD/96-7, 1996.

21. Romeo, L., Diaz, L.I., Guedea, I. Bolea, I., et al., Design and operation assessment of an oxyfuel fluidized bed combustor, *Experimental Thermal and Fluid Science*, 35, 477-484, 2011.
22. Singh, R.I. and Kumar, R., Current Status and Experimental Investigation of Oxy-Fired Fluidized Bed, *Renewable and Sustainable Energy Reviews*, 61, 398-420, 2016.
23. Stanmore, B.R. and Gilot, P. Review—Calcination and Carbonation of Limestone during Thermal Cycling for CO₂ Sequestration, *Fuel Processing Technology*, 86, 1707 – 1743, 2005.
24. Symonds, R.T., Champagne, S., Ridha, F.N. and Lu, D.N., Attrition of CaO-based pellets in a 0.1MW_{th} dual fluidized bed pilot plant for post-combustion CO₂ capture, *Powder Technology*, 291, 60-65, 2016.
25. Toftengard, M., Brix, J., Jensen, P.A., Glarborg, P. and Jensen, A.D., Oxy-fuel Combustion of Solid Fuels, *Progress in Energy and Combustion Science*, 36, 581-625. 2010.
26. Tan, Y., Jia, L. and Anthony, E.J., Experiences and Results on a 0.8 MW_{th} Oxy-fuel Operation Pilot-Scale Circulating Fluidized Bed, *Applied Energy*, 92, 343-347, 2012.
27. Tan, Y., Jia, L. and Wu, Y., Some Combustion Characteristics of Biomass and Coal Cofiring under Oxy-Fuel Conditions in a Pilot-Scale Circulating Fluidized Combustor, *Energy & Fuels*. 27, 7000, 2013.
28. Varol, M., Investigation of Combustion Characteristics of Biomass and Coal Mixtures in a Circulating Fluidized Bed Combustor, PhD Thesis, Middle East Technical University, Turkey, September 2013.
29. Varol, M., Atimtay, A.T., Olgun, H., Atakül, Emission Characteristics of Co-Combustion of a Low-Calorie and High-Sulfur Lignite Coal and Wood Pellets in a Circulating Fluidized Bed Combustor: Part 1. Effect of Excess Air Ratio, *Fuel*, 117, 792-800, 2014a.
30. Varol, M., Atimtay, A.T., Olgun, H., Emission Characteristics of Co-Combustion of a Low-Calorie and High-Sulfur Lignite Coal and Wood Pellets in a Circulating Fluidized Bed Combustor: Part 2. Effect of Secondary Air and Its Location, *Fuel*, 130, 1-9, 2014b.