Full Length Article

Effect of co-firing on emissions and deposition during fluidized bed oxy-combustion

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HIGHLIGHTS

- Oxy-combustion of anthracite and corn stover blends is experimentally characterized in a lab-scale reactor.
- SO_2 emissions are affected by the chlorine content in the biomass while NO_x are more dependent on operating conditions.
- In comparison to air combustion, oxy-firing increases the chlorine detected in fly ashes.
- Deposition rates are affected by the KCl content in the corn rather than the firing atmosphere.
- $K_2Ca(SO_4)_2$ and $K_3Na(SO_4)_2$ are found in deposits for the more severe conditions.

ARTICLE INFO

ABSTRACT

The relevance of coal oxy-firing in fluidized bed reactors has increased during the last years as an alternative for the development of CO_2 capture technologies. The addition of biomass in the fuel blend is well-known in conventional combustion, but few experiences are found under oxy-combustion conditions. This paper discusses the results obtained when oxy-firing anthracite and corn stover in a lab-scale fluidized bed, paying attention to pollutant emissions, deposition rates and composition of the ashes. While SO_2 emissions are affected by the chlorine content supplied with the biomass, NO_x are much more dependent on operating conditions in a similar way to conventional combustion. As concerns the ash composition, chlorine is detected in fly ashes while the bed solids are mostly composed by aluminosilicates. Oxy-firing increases the chlorine detected in fly ashes in comparison to the air-fired tests. Deposition rates are barely modified by the O_2/CO_2 atmosphere; severe deposition is only detected for the blend with the highest chlorine content. Mixed Ca-K sulfates are found in deposits, minimizing the risk of chlorine-induced corrosion.

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1. Introduction

During the last years, an important effort has been done to demonstrate oxy-firing as a feasible technology for capturing CO_2 in power stations [1,2]. Firstly on pulverized burners [3,4] and later on fluidized bed reactors [2,5], O_2/CO_2 combustion shows promising solutions to reduce the CO_2 emissions.

The application of oxy-firing on fluidized bed reactors offers the inherent advantages of this kind of technology, i.e. fuel flexibility, moderate combustion temperature and low pollutant emissions. Moreover, fluidized bed reactors do not require the development of new burners suitable for the oxidizer composition, since they are able to operate with high O_2 concentration [6–9] which favours smaller boilers and ancillaries [1].
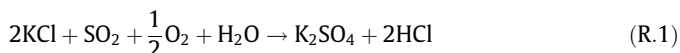
Biomass combustion widens the energy use of residues, with a neutral CO_2 contribution. The possibility of burning 100% biomass in fluidized beds has been demonstrated under conventional combustion conditions [10,11]. Nevertheless, the heterogeneous chemical composition of the biomasses requires a detailed analysis to avoid several inconveniencies during the operation [12–14]. Some elements as alkali or chlorine promote the formation of deposits on heat exchangers tubes, which enhance corrosion and diminish heat transfer.

Co-firing is conceived as a way to introduce biomass in large-scale coal-fired plants, but the synergies between the mineral matter of the fuels have to be well determined. Aho and

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Ferrer [15] studied the effect of coal ashes composition on the chlorine deposition during co-firing experiments in fluidized bed, reporting significant influences for the coals with higher contents in Al, Si and S. In this way, KCl from biomass mineral matter can follow reactions (R.1) and (R.2), in presence of sulfur oxides from the coal:

$$2KCl + SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow K_2SO_4 + 2HCl \qquad (R.1)$$

$$2KCl + SO_3 + H_2O \rightarrow K_2SO_4 + 2HCl \qquad (R.2)$$

Then, HCl is released in the gas-phase as result of the KCl transformation and K_2SO_4 is found in the deposits. While fouling propensity by K_2SO_4 is increased in comparison to potassium aluminosilicates, corrosion promoted by KCl can be to the contrary attenuated.

Co-firing can also affect the NO_x emissions in comparison to coal combustion. Even though NO_x formation is more sensitive to combustion conditions (temperatures and O_2 concentrations), the volatile content and composition can also play a role. Therefore, the trends reported by previous works show a wide variety of behaviours [16,17]. For fluidized beds, it can be stated that the lower the volatile matter of the fuels and the lower the N-bound in the volatiles, the lower the NO_x emissions. This is due to several reasons: (a) in the dense phase, char particles participate in NO_x-reduction mechanisms [18,19], (b) in the diluted phase, volatiles oxidation increases the temperature and then the NO_x formation rates.

Few experiences are reported so far as concerns oxy-combustion of coal and biomass blends. Jurado et al. [20] carried out some experiments in a pulverized burner highlighting the relevance of the increase of corrosive species in the reactor due to dry-FGR (Flue Gas Recycling) and a similar amount on sulfur in the deposits formed. Ekvall et al. [21] simulated oxy-co-firing in a pulverized burner reporting a high influence of H_2O and SO_2 in FGR to control sulfation of alkali compounds, while the increase of HCl inhibits the alkali sulfation ratio. Regarding fluidized bed experiments, Tan et al. [22] demonstrated the suitability of fluidized bed reactors to carry out oxy-co-firing with low pollutant emission, including VOCs. Duan et al. [23] studied the influence of operational parameters (temperature, O_2 concentration and primary oxidant fraction) on NO_x emissions: the higher the three parameters, the higher the NO emitted.

Aiming at increasing the available results related to oxy-co-firing in fluidized bed units, this paper reports an experimental investigation carried out firing anthracite and corn stover in a lab-scale oxy-fired bubbling fluidized bed. Discussion is focused in the effect of adding corn stover with different chlorine contents on the gaseous emissions (SO_2, NO_x, HCl) and the ashes composition, as well as the deposits characterization.

2. Experimental work

2.1. Facility

The experiments were run in CIRCE fluidized bed laboratory (Fig. 1). The reactor is 2.5 m height and its inner diameter is 0.203 m. The facility can be operated under conventional combustion or under oxy-firing conditions, then feeding O_2 and CO_2 from commercial cylinders. Fuel is fed by regulated endless screws and bed temperature is controlled by four water-cooled probes. The installation is fully instrumented with temperature and pressure meters. The uncertainties of the measurements are: 1% full-scale for the thermocouples and 2% full-scale for pressure sensors. More details about the facility can be found elsewhere [24,25].

An air-cooled deposition probe (AISI304) was introduced at 80 cm over distributor to gather the deposits formed during the experiments. The probe consists of two concentric tubes, 16 mm and 36 mm inner diameter respectively. Compressed air is introduced through the inner tube and flows back through the outer tube. The probe is equipped with three thermocouples (air inlet temperature, air outlet temperature and probe tip temperature). The air-cooling flowrate is regulated by a PID controller to keep the probe temperature within the range 450–500 °C, resembling the performance of a superheater tube. A removable coupon is placed near the tip probe that can be replaced for each experimental condition. Once every test is finished, the coupon is removed for analysis and a new one is placed in the probe.

To detect the chlorine in the gas-phase, a suction system can be inserted at 90 cm over the distributor. A gas sample of 0.4 m³/h is conveyed through three consecutive impingers containing Na_2CO_3 dissolution (0.1 M), respectively named Trap1, Trap2 and Trap3. This is done to ensure the complete capture of sulfates and chlorine (HCl + Cl_2) of the gas sample. The $SO_4^=$ and Cl^- concentrations in every trap are determined by ion chromatography in a Metrohm Chromatograph equipped with a Metrosep A Supp 5 column.

Gas analyser takes on-line samples from the flue gas circuit to measure the content of CO_2, CO, SO_2 and NO (NDIR sensors) and O_2 (paramagnetic sensor). The uncertainty of these measurements is 1% full-scale.

2.2. Fuels

The selected fuels for the co-firing experiments were anthracite and corn stover. The former because of the large amount of reserves available at Northwest Spain, the latter due to the growing interest in valorising domestic agricultural residues for energy use. Table 1 shows their ultimate and proximate analysis and heating value, as well as ash composition obtained by ICP. It is worth mentioning the very different content in volatiles, as well as the differences in the ash content and composition: the major components found in the coal ashes are Al and Si, while the biomass shows a larger content in K.

Semi-quantitative analysis of the mineral matter was performed by XRD, confirming the presence of aluminosilicates (48% wt.), quartz (47% wt.) and pyrite (5% wt.) in the anthracite, and sylvite (KCl, 56% wt.), Ca-Mg carbonates (30% wt.), quartz (10% wt.) and halite (NaCl, 4% wt.) in the corn stover. No sulfates were detected in the original ashes.

Corn stover possesses a significant content in chlorine, which is an outstanding specificity in relation to fouling and corrosion phenomena. Since the chlorine content in the original samples was low (0.35%) in comparison to the ranges available in other works [26–28], the received stuff was doped with KCl in order to increase its chlorine concentration. Doping was carried by spraying the particles of corn stover with the KCl solution, followed by a natural drying to stabilize moisture. Then, three different contents were finally tested during the experiments: 0.35% (as received), 1% and 2%.

2.3. Experimental matrix

Table 2 shows the experimental conditions during the co-firing tests. They can be divided in two groups according to the fluidizing gas: air-firing (A1–A2) and 30/70% O_2/CO_2 oxy-firing (O1–O5). Most of the tests were carried out for 80/20 coal-to-biomass energy ratio, except test O3 when the amount of biomass was reduced. The corn stover supplied covered three different chlorine contents: 0.35%, 1% and 2%. The addition of limestone was also included in tests O4 and O5, with molar ratio Ca/S = 2.5. Limestone is typically used in fluidized bed reactors to get in-situ capture of SO_2 by sulfation. Ca/S molar ratios usually range 2–6, depending on the sulfur content of the coal. For the tested anthracite in this paper, previous experiences have shown Ca/S = 2.5 as a reasonable
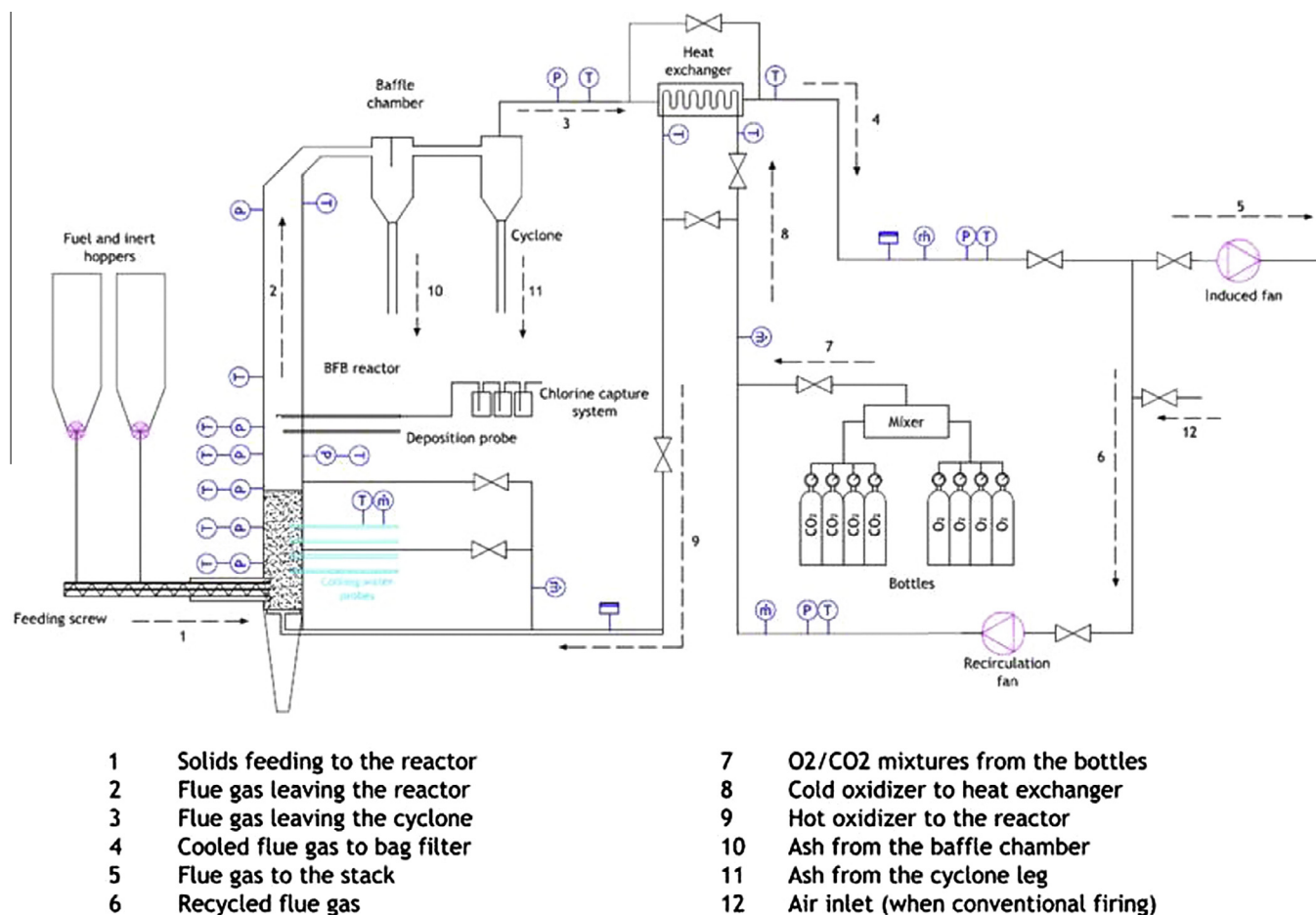
Fig. 1. CIRCE oxy-fired fluidized bed facility.

1	Solids feeding to the reactor
2	Flue gas leaving the reactor
3	Flue gas leaving the cyclone
4	Cooled flue gas to bag filter
5	Flue gas to the stack
6	Recycled flue gas
7	O2/CO2 mixtures from the bottles
8	Cold oxidizer to heat exchanger
9	Hot oxidizer to the reactor
10	Ash from the baffle chamber
11	Ash from the cyclone leg
12	Air inlet (when conventional firing)

Table 1
Fuel analysis, heating value and ash composition, as received.

	Anthracite	Corn stover
Proximate analysis (%)		
Moisture	2.42	6.18
Ash	31.30	5.50
Volatiles	6.71	70.68
Fixed carbon	59.57	17.64
Ultimate analysis (%)		
C	59.27	43.3
H	2.01	5.82
N	0.91	0.57
S	1.58	0.11
Cl	–	0.35
LHV (kJ/kg)	21 620	15 438
Ashes (%)		
Al_2O_3	24.78	1.36
CaO	2.83	8.72
Fe_2O_3	8.26	6.08
K_2O	3.22	27.90
MgO	1.56	3.27
Na_2O	0.70	0.22
SiO_2	47.20	29.81
TiO_2	0.99	0.80
P_2O_5	–	3.81
MnO_2	–	0.14

Table 2
Experimental conditions during the tests.

Test #	Fluidizing gas	Coal to biomass ratio	Ca/S	Chlorine in corn (%)
A1	Air	80/20	0	0.35
A2	Air	80/20	0	1
O1	30/70% O_2/CO_2	80/20	0	1
O2	30/70% O_2/CO_2	80/20	0	2
O3	30/70% O_2/CO_2	90/10	0	1
O4	30/70% O_2/CO_2	80/20	2.5	0.35
O5	30/70% O_2/CO_2	80/20	2.5	1

value [6]. Thermal input was similar during all the tests, around 30 kW. For each test, operating data were on-line recorded every two seconds during at least one hour and a half of stable conditions.

2.4. Instrumental techniques

The composition and morphology of the sampled particles was studied by means of scanning electron microscopy (SEM) in a Hitachi S-3400N microscope equipped with a SDD-EDX detector Rontec XFlash. The phase composition of the crystalline species of the samples was investigated applying X-ray diffraction (XRD)

using a Siemens Bruker D8 Advance Series 2 diffractometer set to select Cu Kα radiation. The diffraction angle scanned was 20–70° 2θ using a step size of 0.05° 2θ/s. The determination of soluble chlorides in selected ashes was performed following the CEN/TS 15105 standard for solid biofuels: the sample is heated in a closed container at 120 °C for 1 h, and the concentration of chloride is determined by Ion-Chromatography (IC).

3. Results and discussion

3.1. Gas phase

Table 3 shows the mean values for the bed T_b and freeboard T_{fb} temperatures during the experiments, as well as the flue gas composition – in dry basis – leaving the reactor. Bed temperatures were kept in the range 850–900 °C by means of the water-cooled probes (see Fig. 1). Differences are due to variations in the fuel feeding and the cooling water flowrates. Freeboard temperatures also depend on the fluidizing gas flowrate, as the O_2 concentration in flue gases reveals. Emissions of NO and SO_2 have been corrected to a common reference (6% O_2) and normalized to mg/MJ unit.

According to the results shown in Table 3, the higher the chlorine content in the corn stover, the lower the SO_2 emitted, both under air-firing mode (A1 vs A2) and oxy-firing mode (O1 vs O2, and O4 vs O5). This is linked to the sulfur detected in the solid phase, as shown later. SO_2 emissions can be affected by the different bed temperatures during the tests, but in our case this extent is very limited. For the tests without limestone addition, desulfurization does not happen and then temperature influence can be neglected. For the tests with limestone addition, O4 and O5, desulfurization is carried out by direct sulfation, i.e. non-calcining conditions, and the bed temperature difference (847 °C vs 870 °C) does not explain the SO_2 increase. As concerns the differences in freeboard temperatures, SO_2 oxidation rates to SO_3 are small in fluidized bed units and barely affected within our temperature ranges. In consequence, it can be concluded that evolution of SO_2 emissions is mostly related to the chlorine content in the corn stover.

Another observation is the increase of SO_2 emissions when the coal-to-biomass ratio is increased (O1 vs O3). This is the logical trend according to the sulfur content in the fuels, but some works have observed the opposite [22] due to the self-retention capacity of the coal ashes. This is not our case, provided that Ca, Mg and K contents in anthracite ashes are low.

A slight reduction of SO_2 emissions is observed if air-fired A2 is compared to oxy-fired O1, the rest of conditions being the same. Since no limestone was added in those tests, the only explanation can be related to the enhancement of sulfur oxidation to SO_3 under oxy-combustion [29,30]. Finally, limestone addition leads to desulfurization efficiency over 80% (comparing test O5 to test O1).

No direct relation between the chlorine content in the corn stover and the NO emissions can be inferred from the experimental results. Comparing O1 and O2, the reduction of NO is mainly explained by the lower oxygen excess. The same can be stated if test A2 is compared to test O1: the expectable reduction of normalized NO emission (in mg/MJ) under oxy-firing is hidden

by the higher oxygen excess during the O1 test. The effect on NO emissions due to the different values of bed and freeboard temperatures can be neglected, since fuel-NO_x is the governing mechanism and mostly depends on the oxygen partial pressure.

The effect of the coal-to-biomass ratio is negligible, if the NO figures of tests O1 and O3 are compared. In fact, the NO_x emissions when firing 100% anthracite are also very similar, according to the results already available in reference [31] for the same facility. Therefore, the NO emission remains almost the same at least for the range 0–20% of corn in the feedstock. Limestone and lime are proved to act as catalysts for nitrogen oxidation in fluidized beds [31–33]. This, together with high oxygen excess, lead to the largest values of NO emissions observed for tests O4 and O5.

During the oxy-tests O1, O3 and O5 (1% chlorine in the corn), an aliquot of flue gas was suctioned from the freeboard inlet and conveyed to the Cl^- and $SO_4^=$ capture system, already described in Section 2.1. Ionic concentrations in the three in-cascade traps were quantified by ion chromatography. These results are shown in Table 4, mainly serving as a comparison of the chlorine presence in the flue gas for the O1, O3 and O5 experiments.

A clear correspondence can be seen between SO_2 emissions reported in Table 3 and $SO_4^=$ concentration detected in Table 4. As concerns the chlorine, the comparison of results for test O1 vs O3 confirms that lower share of corn stover (O3) yields less chlorine concentration in the gas phase. On the other hand, the results for O5 unexpectedly show lower Cl^- concentrations than the observed for the test O1 – same conditions but without feeding limestone. This will be explained later by the higher presence of chlorine in the solid phase for the test O5.

3.2. Composition of ashes

3.2.1. Bed ashes

The analysis carried out by means of SEM-EDX to determine the composition of bed ashes reveals they are mainly composed by the initial silica sand and fuel ashes; raw and sulfated limestone particles were also detected in experiments O4 and O5. The composition of representative bed ash obtained by surface EDX is shown in Table 5.

No relevant differences in surface composition are detected when comparing air combustion vs oxy-firing: A1 ash is similar to O4, A2 to O1, O3 and O5. No sulfur is detected in tests without limestone supply, thus pointing out a negligible extent of the self-retention by fuel ashes. On the other hand, a trend of potassium enrichment can be shown for those experiments with 1% Cl in corn stover respect to the 0.35% Cl, both for air and oxy conditions, what is coherent with previous experiences [34].

Other relevant result is the absence of chlorine in the bed ashes, in accordance with the high volatility of KCl. For sorbent particles, EDX analysis of partially sulfated limestone in test O5 (Fig. 2) also confirms the absence of chlorine related to calcium ($CaCl_2$).

3.2.2. Fly ashes

The composition of fly ashes sampled during all the experiments is shown in Table 6, according to the results obtained

Table 3
Bed and freeboard temperatures, and composition of flue gases leaving the reactor.

Test #	T_b (°C)	T_{fb} (°C)	O_2 (%)	CO_2 (%)	NO (mg/MJ)	SO_2 (mg/MJ)
A1	861	555	4.94	12.57	105	906
A2	857	509	5.19	15.49	68	623
O1	850	566	8.04	91.78	132	571
O2	900	631	2.27	97.46	73	453
O3	865	550	4.99	92.81	123	705
O4	847	581	13.40	86.49	172	120
O5	870	568	11.76	88.20	149	105

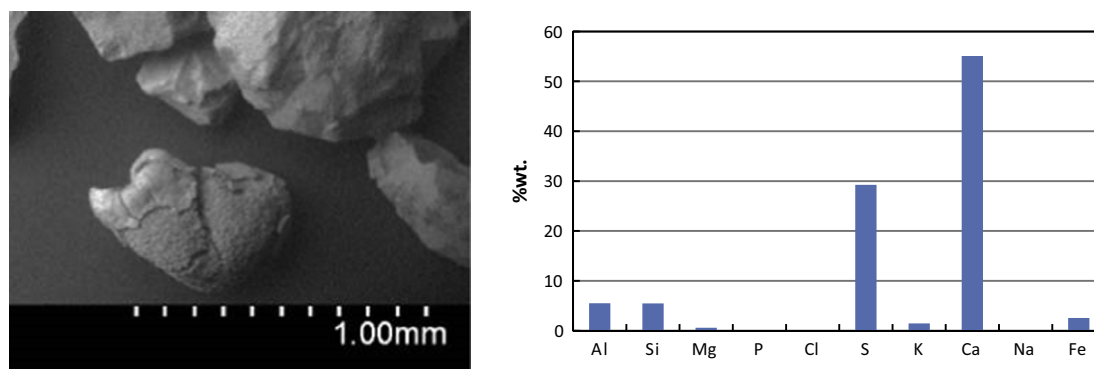**Table 4**
Ionic concentrations (ppm) in the alkaline dissolutions of the three in-cascade traps.

Test #	Ion	Trap 1	Trap 2	Trap 3
O1	Cl^-	>300	0	0
	$SO_4^=$	1688	53.8	7.3
O3	Cl^-	68.4	0	0.7
	$SO_4^=$	3143	77.1	3.5
O5	Cl^-	87.5	30	1.8
	$SO_4^=$	524	187	7.3

Table 5
Surface weight composition (%) of main elements in representative bed ashes for the tests with 0.35% and 1% chlorine.

Test #	Na	Mg	Al	Si	S	K	Ca	Fe	K/Al	K/Si
A1	1.86	1.79	30.10	51.15		10.44	2.02	2.64	0.35	0.20
A2	1.05	1.87	32.87	41.74		14.17	3.44	4.87	0.43	0.34
O1	0.00	3.64	26.39	28.63		12.71	6.44	22.18	0.48	0.44
O3	1.66	2.00	22.84	25.72		12.93	12.27	22.57	0.57	0.50
O4	1.98	2.00	29.07	46.92	0.30	11.45	3.26	5.02	0.39	0.24
O5	2.94	2.50	24.32	31.56	1.00	10.23	22.99	4.46	0.42	0.32

Fig. 2. Composition of a partially sulfated limestone particle from test O5.

Table 6
Surface weight composition (%) of main elements in fly ashes and soluble chloride content (%).
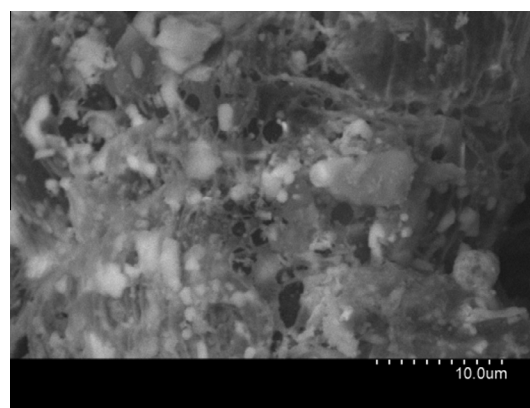
Test #	Al	Si	K	S	Na	Mg	Ca	Fe	Cl	Soluble Cl
A1	24.91	34.93	8.59	3.68	–	3.78	11.08	11.94	–	–
A2	32.64	44.78	12.87	1.14	1.26	1.46	3.37	2.47	–	–
O1	22.50	31.91	8.55	1.60	1.66	3.22	15.40	12.57	0.78	0.210
O2	21.52	29.93	11.61	3.80	–	2.30	18.42	10.81	1.60	0.535
O3	22.24	33.78	11.14	1.94	0.81	3.31	14.14	10.26	1.23	–
O4	36.18	43.97	4.11	0.86	0.53	1.08	6.27	6.28	–	0.002
O5	15.77	28.80	10.17	2.66	1.31	2.40	23.00	14.02	1.86	0.660

by SEM-EDX (normalized to inorganic elements, i.e. excluding C and O). They are mainly composed by calcium and potassium aluminosilicates, but the presence of sulfur and chlorine is also detected for some experiments.

On the contrary than in the bed ashes, the presence of chlorine in fly ashes was expected due to condensation of the gaseous chlorine compounds and some KCl on the unburned fuel particles elutriated from the reactor. The comparison between O1 and O2 reveals an increase of chlorine in the fly ashes of the latter, which is in accordance with the increase of chlorine concentration in corn stover fed. No chlorine was detected for the tests run under air-fired conditions.

The sulfur reported in Table 6 was not bound in the ashes, but occurred as condensed potassium sulfates. These sulfates were also detected in some of the deposition particles, and its formation is explained hereinafter (Section 3.3.2).

A deeper analysis of soluble chlorides in fly ashes was performed following the standard CEN/TS 15105 by ion chromatography (IC). Values obtained are also shown in Table 6, which are in good agreement to those obtained by EDX. Fly ash from experiment O5 is richer in chlorine than that from O2, despite the lower initial chlorine content in the corn stover fed (1% vs 2%), and it is also richer than fly ash from O1, the same conditions (1%) except the limestone supply. SEM-EDX analysis of the O5 cyclone-ashes has confirmed that KCl is found as small condensed crystals (Fig. 3). This can be explained by the lower concentration of SO_2 along the reactor, leading to a lower rate of KCl dissociation.

Fig. 3. SEM image of cyclone fly ashes, test O5.

Accordingly, the concentration of HCl sampled during O1 was significantly higher than the observed during O5, as already reported in Table 4.

3.3. Deposits onto the probe

3.3.1. Deposition rates

After every test, the probe inserted in the reactor showed a different qualitative range of deposition: from no deposition to

Table 7
Deposition rates after the tests and deposition indexes.

Test #	Deposit on probe	Al + Si/Na + K	S/Cl	S*/Cl
A1	No deposit	10.18	14.65	
A2	Thin fouling	8.76	5.02	
O1	Fouling	8.76	5.02	
O2	Thick deposit	7.26	2.61	
O3	Thin fouling	14.77	11.35	
O4	No deposit	10.18	14.65	2.93
O5	Thin fouling	8.76	5.02	1.00

Table 9
Normalized composition (%) of deposit particles.

Test #	Al	K	S	Na	Ca	Cl
O1	1.00	1.37	0.85	0.47	0.28	0
O2	1.00	2.11	1.12	0.22	0.93	0.52
O3	1.00	0.49	0.45	0.13	0.23	0
O5	1.00	0.63	0.77	0.14	0.66	0

		% mass (sq)
a	sylvite KCl	8
b	syngenite $K_2Ca(SO_4)_2$	47
c	aphthalite $K_3Na(SO_4)_2$	23
d	quartz SiO_2	9
e	hematite Fe_2O_3	4
h	anhydrite $CaSO_4$	8

Fig. 5. XRD of the deposits (test O2) and semiquantitative composition.

Fig. 4. Fouling on deposition probe after test O1 (right side).

thick scales, as presented in Table 7. No deposits were found in experiments A1 and O4 (0.35% chlorine in the corn stover). A thick and stubborn deposition layer and corrosion scale on the probe tip was found after experiment O2 (2% chlorine in corn stover), formed by condensed compounds but also some elutriated solids.

Fouling without corrosion was found in the rest of the tests (1% chlorine in corn stover), comprising a thin loose layer of reddish aluminosilicate material: very scarce and irregular (thin fouling) for the tests A2, O3 and O5, while ampler and more uniformly distributed during test O1, as depicted in Fig. 4.

Table 7 also presents a set of composition indexes. The first ratio measures the amount of aluminum and silicon to alkali content in fuel, as Na and K [35]. Both elements are easily retained in aluminosilicates, which implies the release of chlorine [36]. Values over 10 would assure free-chlorine deposits. This condition is observed during the co-combustion with the original corn stover (0.35% Cl, tests A1 and O4) and with the highest coal-to-biomass ratio (90/10, test O3).

S/Cl index relates the sulfur to chlorine content in the fuel. Values of S/Cl higher than 4 are considered adequate to avoid the presence of chlorine in the deposits [15]. Provided that sorbent was added during test O4 and O5, sulfur actually available in the gas phase is related to the index S*/Cl (taking into account the desulfurization efficiency). According to that, the presence of chlorine in the deposits would only be expected in the case of corn stover with 2% Cl (test O2) and the test run with added limestone (O4 and O5). This condition is observed during the co-combustion with the original corn stover (0.35% Cl, tests A1 and O4) and with the highest coal-to-biomass ratio (90/10, test O3). A detailed description of the deposits found is given in the next sections.

3.3.2. Deposits characterization

The composition of the samples taken from the deposition probe was analyzed by SEM-EDX, as reported in Table 8. One of the first findings is than chlorine is only detected for test O2, which is in agreement with the S/Cl index. On the contrary, chlorine is not found during test O5 despite the value of the S*/Cl index is below 4. According to the values provided in Table 6, condensed KCl was significantly present in the O5-fly ashes but not in the deposits onto the probe.

The elements Al and Si come from the coal mineral matter, deposited as fine aluminosilicates, likely with a fraction of the K detected. The elements K, Na, Ca and S are related to the deposition of salts. Fe(part), Cr and Ni belong to the metallic substrate, indicating a low degree of coverage. Table 9 shows the concentration of the main elements found in the deposits, but normalized to the Al-content in atomic basis.

The semiquantitative results in Table 9 indicate that the O2 deposits are rich in KCl and calcium and potassium sulfates. Test
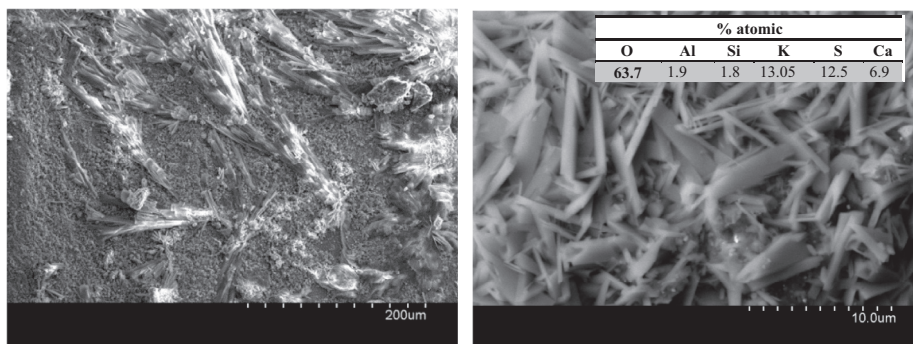
Table 8
Surface weight composition (%) of elements in the deposits.

Test #	Al	Si	K	S	Na	Mg	Ca	Fe	Cr	Ni	Cl
O1	10.54	12.62	20.93	10.61	4.24	1.95	4.50	18.58	11.33	4.70	0
O2	10.25	12.88	31.27	13.62	1.89	1.09	14.42	7.52	0	0	7.05
O3	12.61	14.86	9.01	6.67	1.39	2.10	4.47	41.27	3.46	3.49	0
O5	9.44	12.33	8.64	8.61	1.15	1.63	9.46	40.51	5.26	2.96	0

			% atomic		
O	Al	Si	K	S	Ca
63.7	1.9	1.8	13.05	12.5	6.9

Fig. 6. (a) Left-side: SEM micrograph of probe surfaces in test O2 after solids removal, (b) Right-side: detailed SEM-EDX of the crystals with atomic composition.

O3, with the lowest biomass ratio, shows the lower amount of deposited salts. Deposits on O1 probe are composed mainly by potassium sulfate, whereas its presence is lower in O5 due to the addition of limestone.

Deposits from O2 probe were removed by gently brushing and a sample of loose particles was obtained. It was analyzed by XRD, and results are presented in Fig. 5. The assignation by JPDC database confirms the presence of sylvine –KCl–, but the absence of arkanite –K_2SO_4–: main peaks detected are syngenite –$K_2Ca(SO_4)_2$– and aphtalite –$K_3Na(SO_4)_2$–. These sulfates are commonly found in biomass combustion [37,38]. The software Diffract Eva v4.0 was used to obtain the semiquantitative elemental composition also inserted in Fig. 5. Calcium in deposits comes from the corn stover mineral matter, where it is finely dispersed as organically bounded or as oxalates in the organic matter. For the combustion temperatures, organic calcium can be transformed into CaO aerosols that may react with available SO_2 and condense as sulfates.

Underneath the loose deposits, SEM identified crystalline structures grown from bare metallic surfaces (see Fig. 6). EDX composition is shown in the insert of Fig. 6b, providing a stoichiometry of $K_2Ca(SO_4)_2$. No molten or sticky KCl phase is found here; on the contrary, well-formed K-Ca sulfate structures indicate that they were originated in the gas-phase as aerosols that condense onto the probe (working at 450 °C). These structures were not found in the deposits taken after the O1, O3 and O5 tests.

For a long-term exposure, the mixed Ca-K sulfates would develop into Ca-K trisulfate which is less aggressive in terms of metal degradation than $K_3Fe(SO_4)_3$ formed from K_2SO_4 [39]. The formation of potassium-metal trisulfate from K_2SO_4 deposits is considered the main source of metal surfaces corrosion under oxy-combustion [40]. Most of the studies on biomass oxy-co-firing have used the synthetic ash recoat approach for corrosion tests studying the K-Cl-S system [41]. Nevertheless, other elements from biomass mineral matter may play a role in deposits formation since aerosols composition greatly varies with the chemical composition of the fuel used [42,43]. In the present case, the Ca-K sulfates found under oxy-co-firing conditions indicate that the alkaline deposits are formed by heterogeneous condensation onto the metallic probe, not molten but solid and crystallized, which eventually decreases the risks of deposit growing by an adhesion mechanism.

4. Conclusions

An experimental characterization of anthracite and corn stover co-firing under air and oxy-combustion has been conducted in a lab-scale fluidized bed reactor, with special focus to the influence of the chlorine content supplied with the biomass on emissions, ashes composition and deposition characteristics.

As concerns emissions, SO_2 is confirmed to be dependent on the chlorine content of the biomass, both under air combustion and oxy-combustion. The higher the chlorine, the lower the SO_2 emitted. Sulfur is then observed in the solid phase, forming sulfates. This extent is logically lower when limestone is supplied to the reactor. On the other hand, NO_x emissions are barely affected by the chlorine in the corn stover and the biomass ratio (at least, in the range 0–20%). NO_x is much more sensitive to the oxygen excess, in a similar way to conventional combustion.

No chlorine was detected in the solids taken from the bed bottom. As for the fly ashes, chlorine was not detected for air-fired tests but was for oxy-firing tests as KCl (except for the lower Cl content in the biomass). The observed trend is the expectable: the higher the chlorine in the corn stover, the higher the chlorine detected in the fly ashes. If limestone is supplied to capture SO_2, the presence of chlorine in fly ashes is enhanced and the concentration in the gas-phase is consequently reduced.

Finally, deposition was observed and characterized for the tests with 1% Cl (thin fouling) and 2% (thick deposition). The presence of crystallized non-sticky mixed Ca-K sulfates onto the deposition probe was identified for the test with the highest initial content of KCl in the biomass. For the conditions studied, there is not a severe risk of chlorine-induced corrosion under oxy-co-firing of anthracite and corn stover.

Summing up, and according to the insights obtained from the experimental campaign, it is concluded that fluidized bed oxy-firing of anthracite and corn stover is feasible from an operational point of view, with biomass ratios up to 20%. There is a positive synergy due to corn addition, since chlorine can contribute to sulfur retention. Nevertheless, the chlorine content in the biomass should not be over 1% since fouling rate and corrosion risk could be enhanced. Limestone addition with a molar ratio Ca/S = 2.5 yields a remarkable desulfurization efficiency, provided that original fuels showed a low sulfur content.

Acknowledgements

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