



Research paper

On the oxy-combustion of lignite and corn stover in a lab-scale fluidized bed reactor



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ABSTRACT

This paper addresses an experimental investigation concerning oxy-combustion of coal and biomass in a lab-scale fluidized bed reactor. While co-firing has been widely studied under conventional air conditions, few experiences are available to date for O₂/CO₂ atmospheres. The research is focused on SO₂ and NO_x emissions, along with the deposition rates and ashes mineralogy. The influences of the atmosphere (air vs. 30/70% O₂/CO₂), the coal-to-biomass energy input ratio (80/20%, 90/10%), the chlorine mass fraction in the biomass (0.35%, 1%, 2%) and the Ca:S mole ratio (2.5, 4) are reported and discussed in the paper, for two specific fuels: high sulfur lignite and high chlorine corn stover. Concerning SO₂ emissions a correlation among the sulfur and the chlorine contents is clearly detected, being affected by the direct desulfurization mechanism occurring under oxy-firing conditions. The single effect of the chlorine content is found to be almost 1.5% of the desulfurization efficiency. NO_x emissions are otherwise more dependent on oxygen excess and CO concentration in the reactor, rather than the fuel share or the chlorine supplied. Thick deposition is only detected when chlorine content in the corn is 2%. Potassium aluminosilication is found to be enhanced in comparison to potassium sulfation under oxy-firing, especially for the highest Ca:S mole ratio: observed aluminosilication is five times higher when Ca:S ratio is increased from 2.5 to 4. A significant enrichment in iron is also detected for the fly ash composition, with an increase of 30–50% in comparison to air combustion.

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1. Introduction

During the last ten years, oxy-fuel combustion has been proven to be a driving technology towards zero emission power plants [1]. Successful experiences have been reported in pulverized-fuel facilities, as Schwarze Pumpe, Ciuden and Callide [2–6]. Application to fluidized bed boilers has also shown promising results in similar scales [7,8], with the inherent advantages of wide fuel flexibility and low pollutant emissions. According to these developments, oxy-combustion units are ready to get a commercial scale [9].

More recently, biomass has been proposed to be used as main or secondary fuel in oxy-fired units, aiming to develop bio-CCS (Carbon Capture and Storage with biofuels) [10,11]. While conventional combustion of biomass has been extensively studied [12–14], few oxy-combustion experiences are available to date [15]. The

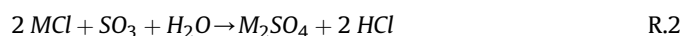
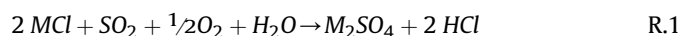
permanent disposal of CO₂ from the combustion of residual biomass contributes to remove CO₂ from the atmosphere, leading to the so-called negative emissions. This enhances the attractiveness of the oxy-combustion technologies.

In comparison to coal, firing biomass shows several challenges mainly related to its chemical composition, strongly affected by issues like harvesting, soil residues or use of fertilisers [16]. Main operational problems are related to the presence of alkalis and chlorine, which promote deposition on heat transfer surfaces and can also yield long-term corrosion [17–20].

Co-firing of coal and biomass can be considered as an intermediate way to mitigate these problems [21], also enabling the feeding of biomass into larger units [22]. Nevertheless, the synergies between the mineral matters of the fuels have to be well determined. The presence of the sulfur in the coal promotes the reactions between sulfur oxides and alkali chlorides, yielding chlorine-free deposits; the reactions (R.1) and (R.2) show this effect:

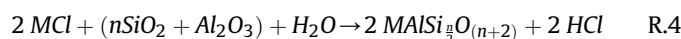
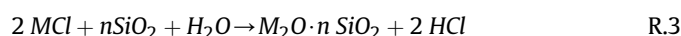
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Following this reduction mechanism, Kassman et al. [23,24] reported the effect of injecting ammonium sulfate, resulting in a decrease of the chlorine detected in the deposits. SO_2 oxidation rate (to SO_3) was suggested by these authors as the limiting factor for the alkali sulfation, since reaction (R.2) eventually controls the process.

On the other hand, alkalis can also be competitively retained in the coal ashes by silication or aluminosilication [21], releasing chlorine to the gas-phase as HCl, according to the reactions (R.3) and (R.4):



According to the results given by Sevonius et al. [25], the extent of reaction (R.3) is very small at fluidized bed conditions and most of alkali retention is due to aluminosilication.

Few results are available in literature concerning co-firing under O_2/CO_2 atmospheres, most devoted to pulverized-fuel burners. Fryda et al. [26] pioneered the research on ash deposition under oxy-fuel conditions, finding out an increase of deposition ratios in comparison to air conditions, but barely affecting the ashes composition. Riaza et al. [27] studied the co-firing of coal and olive residues in an entrained flow reactor, under a variety of O_2/CO_2 atmospheres. They reported an improvement of ignition temperature when biomass was added, and an opposite trend for NO_x emissions: increasing for semi-anthracite but decreasing for bituminous coals. Similar results were reported by Ahn et al. [28]. According to the scheme given by reactions (R.1) and (R.2), Ekvall et al. [29,30] and Jurado et al. [31] respectively found an increase of K_2SO_4 in deposits and a decrease of SO_2 under oxy-firing of coal and biomass.

As concerns the experiences in fluidized bed combustors, most have been focused on emissions. Tan et al. [32] oxy-fired coal and wood pellets, showing a NO decrease with the biomass-to-coal ratio, without a conclusive trend for the SO_2 . Duan et al. [33] found that NO emissions were strongly dependent on O_2 excess and O_2 primary/secondary split, as also happens for coal air- and oxy-firing.

This paper aims at widening the knowledge about oxy-firing of coal and biomass in fluidized bed reactors, focusing the analysis on emissions but also on the behaviour of the solid-phase: deposition ratios and composition, and ashes characterization. This is done for blends of two risky fuels, high-sulfur lignite and high-chlorine corn stover, leading to novel results not available up to now.

2. Experimental setup

2.1. Facility

The tests were conducted in the fluidized bed reactor at CIRCE Laboratories (Fig. 1). The reactor is 2.5 m height and its inner diameter is 0.203 m. Fuel is fed from two independent hoppers, discharging into two variable-speed endless screws. Bed temperature is regulated by water-cooled probes, which can be inserted/extracted on-load. Further details of the facility can be found elsewhere [34–36].

The installation is instrumented with temperature, pressure and flow meters, providing real-time information about the unit performance. Flue gas composition (CO_2 , CO, NO, SO_2 , O_2) is also available, by sampling and analysing at the heat exchanger outlet.

An air-cooled deposition probe can be introduced over the splash zone, in order to characterize the deposits. Probe temperature is controlled to maintain a value within 450–500 °C. A removable coupon is inserted in the tip of the probe, in order to proceed with a subsequent SEM/EDX analysis. Solid samples can be taken during the experiments from the bed bottom, the baffle chamber and the cyclone.

The presence of chlorine in the gas-phase can be determined by conveying samples through three Na_2CO_3 impingers. The sample withdrawal is carried out at 0.9 m over the distributor plate. After every experiment, the contents of the impingers are analysed by ion chromatography (IC) in order to determine the chloride concentration.

2.2. Fuels

The fuels selected for the experimental campaign were lignite and corn stover. The former is high-sulfur, high-ash coal with large reserves in Spain. The latter is an agricultural residue, selected to seek the interactions among chlorine and sulfur compounds.

The coal was supplied by a Spanish mining company. The coal-field is located close to Ariño (Teruel, Spain). The coal was sent to an Italian company in order to mill and sieve it to the required size. Round-trip transportation was done by truck. Once received back, chemical analysis was conducted to random samples of the coal, yielding proximate and ultimate analyses as well as heating values and ash composition (shown in Table 1). According to the classification given by the standard ASTM D388, the coal type is lignite. Its size was in the range 0.3–1 mm, with a mean diameter of 0.7 mm.

The corn stover was supplied by a local farmer from Villamayor (Zaragoza, Spain). Geo-coordinates of the field are 41° 41' 17" N, 0° 45' 45" W. Soil type is silty clay. The specific variety of Zea mays is unknown. Sowing was done during the early spring and harvesting during the early fall (year 2013). Corn stover bales were stored indoors by the farmer. We directly picked up and transported the bales from the field to the lab building. Since Zea mays cultivars cannot be completely specified, there is a reasonable concern that there may be factors that influence the results obtained, and for this reason the work cannot be independently reproduced. But the authors believe that the research exemplifies the effect of the inorganic constituents of both the coal and corn.

Corn stover was milled and sieved between 1 mm and 2 mm. Roughly, half of the initial mass was retained for the experiments. Chemical analysis was conducted to random samples of the sieved stover (results shown in Table 1). Fuels were separately stored in closed containers inside the lab building, at room temperature. The same was done with the limestone and the silica sand used in the tests.

The chlorine content in the corn stock (0.35%) was relatively low in comparison to the values reported in other works [37–39]. For this reason, original corn stover was doped with KCl, increasing the chlorine mass fraction to 1% and 2%. This consequently increased the content of mineral matter in the corn stover (to 6.80% and 8.80% respectively), while the rest of the proximate and ultimate fractions were reduced in proportion. To exclude the effect of the moisture and the ash contents in the fuels, compositions in Table 1 are expressed in dry and ash-free basis.

In order to control SO_2 emissions, Granicarb limestone was added during the tests in different Ca:S mole ratios. This limestone is commercialized by a gravel plant located at Belchite (Zaragoza, Spain). Granicarb limestone is characterized by its high purity and reactivity ($\text{CaCO}_3 > 97\%$). Limestone mean size was 0.6 mm. Silica sand ($\text{SiO}_2 > 99\%$) was used as inert material in the bed, with mean particle size similar to limestone. Bed height was maintained around 400 mm for all the tests.

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