



The role of limestone during fluidized bed oxy-combustion of coal and biomass



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HIGHLIGHTS

- Indirect sulfation of limestone yields high desulphurization efficiency but increases NO emissions.
- Bed agglomeration is not found, even for the highest temperature (925 °C).
- Limestone fragmentation largely influences the desulphurization efficiency.
- Sulfation ratios of the alkali chlorides are consistent with HCl and SO₂ concentrations in the gas-phase.
- In comparison to air-firing, oxy-firing reduces the corrosion risk and does not affect deposition.

ARTICLE INFO

Article history:

Received 19 July 2016

Received in revised form 4 November 2016

Accepted 6 November 2016

Available online 14 November 2016

Keywords:

Oxy-combustion

Limestone

Emissions

Deposition

Biomass

Fluidized beds

ABSTRACT

The interest in bio-CCS technologies is growing due to their potential to reduce CO₂ emission in power generation. Oxy-co-firing in fluidized-bed units is one of the available techniques to develop bio-CCS, offering wide fuel flexibility and low SO₂ and NO_x emissions. This paper discusses the results of an experimental campaign carried out in a lab-scale fluidized bed reactor. The work focuses on the influence of limestone when oxy-firing blends of lignite and corn stover. Two different types of limestone with two Ca:S molar ratios were tested, and operational conditions were selected to compare the mechanisms governing desulphurization. Emissions of SO₂, NO and HCl, together with deposition rates and ash mineralogy are studied in the paper. SO₂ capture increases with the Ca:S ratio and bed temperature, but to a different extent depending on the limestone fragmentation. The amount of NO emitted rises with the Ca:S ratio and the presence of calcined limestone (indirect desulphurization). The HCl concentration in the gas phase is dominated by alkali sulfation. Finally, the conditions for the highest desulphurization efficiency diminished the deposition rates, but increased the risk for chlorine-induced corrosion.

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1. Introduction

Among the carbon capture and storage technologies (CCS), oxy-firing is one of the nearly commercially available solutions [1–3]. The investment during the last few years has allowed demonstration-scale facilities to be commissioned in which the feasibility of oxy-firing has been proved [4–7]. Nevertheless, important research efforts are still ongoing concerning its efficiency, emissions and fuel-related issues [8–12].

Oxy-combustion was initially developed and scaled-up in pulverized fuel units, but now oxy-fired fluidized bed boilers are of similar size. The latter offers the additional capability of burning low rank fuels with good efficiency. This includes combustion of

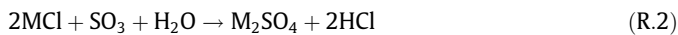
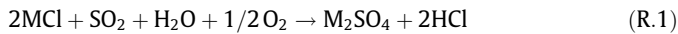
residual biomass, which implies CO₂-neutral power generation [13–15]. Bio-CCS technologies based on the combination of residual biomass combustion and permanent CO₂ removal are considered to be negative emission concepts [16–18].

Despite the use of residual biomass for power generation can result in environmental benefits related to SO₂ and NO_x emissions [19,20], several operational issues arise related to its mineral matter composition. The release of alkali metals, which are mainly present in herbaceous biomasses, promotes condensation on water-tube surfaces, limiting the heat transfer efficiency. Additionally, alkali chlorides in deposits interact with Fe and Cr, accelerating corrosion of heat exchangers in boilers [21–24]. In the case of fluidized bed units, interactions with silicates (in the sand) increase the risk of bed agglomeration. To reduce these difficulties, some researchers have explored the addition of alumina, dolomite, kaolin or limestone in the bed inventory [14].

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The co-combustion of coal and residual biomass has been found to decrease agglomeration and corrosion risks compared to firing biomass alone [25–27]. The effectiveness of co-firing in preventing deposition of alkali chlorides is due to sulphur in coal since SO₂ and SO₃ react with alkali chlorides, yielding alkali sulphates ((R.1) and (R.2)):

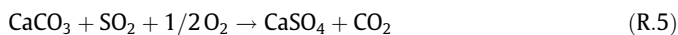


These mechanisms reduce the interaction between the bed material and alkali metals, lessening the deposition of alkali chlorides [28]. The formation of alkali sulphates is not desirable from the point of view of heat transfer since fouling may be increased, but at least the risk of tube corrosion is reduced.

In fluidized bed reactors, SO₂ and SO₃ available for (R.1) and (R.2) are usually limited by in-situ desulphurization due to sorbent addition, generally limestone. Depending on the operational conditions, desulphurization can be carried out following two different mechanisms. When limestone is calcined, yielding CaO (R.3), it retains SO₂ following reaction (R.4):



This two-step mechanism, also called indirect capture, is typically found in atmospheric fluidized beds under conventional combustion. However, under oxy-firing conditions, with higher CO₂ concentrations, calcination can be inhibited [29] and SO₂ reacts with CaCO₃ by means of a direct capture mechanism (R.5):



At typical bed temperatures (~850 °C), direct capture is the governing mechanism for SO₂ retention. Direct capture is slower than indirect desulphurization mainly due to the smaller pores of limestone compared to those of lime, so this process is controlled by the diffusion of SO₂ in the particle and in the product layer [30]. Accordingly, other studies have found that indirect capture offers the highest desulphurization efficiencies also under oxy-firing conditions, but for an optimum temperature in the range of 900–925 °C [31,32].

On the other hand, some researchers have investigated the effect of co-firing in O₂/CO₂ atmospheres. Skeen et al. [33] studied the effect of co-firing sawdust and coal in a pulverized burner, reporting a sharp increase in emissions of NO with the O₂ concentration in the primary oxidizer stream. Rianza et al. [34] added biomass to coal in an entrained-flow reactor to study ignition and NO emission. Moroñ and Rybak [35] and Pickard et al. [36] reported a reduction of NO_x and SO₂ emissions during co-firing under O₂/CO₂ atmospheres. Jurado et al. [37] highlighted the relevance of increasing the concentration of corrosive substances due to recycled flue gases, while Ekvall et al. [38,39] injected KCl into a pulverized fuel reactor, obtaining a higher alkali sulfation in oxy-firing mode than in air-firing mode.

Nevertheless, there are few experiences to date concerning oxy-firing of coal and biomass in fluidized bed facilities. Tan et al. [40] conducted oxy-co-firing experiments to demonstrate the viability of this technology and characterize pollutant emission. Duan et al. [41] focused on NO_x emission, observing dependencies similar to oxy-firing of coal alone. Kosowska-Golachowska et al. [42] studied the influence of the fluidizing gas composition in combustion, reducing burn-out time and increasing temperature with the highest O₂ concentration.

There is a lack of research addressing oxy-firing of coal with residual biomass in fluidized bed reactors, and this paper aims to increase knowledge in this field. In particular, there are no reported

works regarding the influences of limestone and the desulphurization mechanisms when coal and biomass are fired together. This paper describes and discusses the experimental results of oxy-firing campaign with lignite and corn stover, encompassing gaseous emissions, the ash composition and the characterization of deposits.

2. Experimental setup

2.1. Experimental facility

The experimental campaign was conducted in a 100 kW_{th} fluidized bed. Fig. 1 shows an updated scheme of the plant after a recent refurbishment. The height of the reactor is 3500 mm, and the inner diameter is 205 mm. The unit can be operated under air-firing and oxy-firing modes, using O₂/CO₂ mixtures from commercial gas cylinders. The bed temperature is controlled by means of four water-cooled probes, whereas the freeboard is electrically heated to maintain the temperature. Fuels and sorbents are fed from hoppers by means of independent screw feeders.

The operational parameters are measured by thermocouples, pressure sensors and flow-meters and are continuously recorded. The flue-gas composition is provided on-line by a gas analyser. CO, CO₂, SO₂ and NO concentrations are measured by NDIR (non-dispersive infrared) sensors. A paramagnetic sensor is used to measure O₂ concentration. The measurement uncertainties are 1% for the temperature sensors, 2% for the pressure sensors and 1% for the gas analyser cells.

To simulate deposition on the superheater tubes, an air-cooled probe can be inserted at 800, 2000 or 3300 mm over the distributor plate. A removable coupon made of AISI Type 304 stainless steel is placed in the tip of the probe for further SEM-EDX analysis of the deposits. The probe is equipped with a thermocouple and a PID controller, which determines the air flow-rate required to maintain the prescribed surface temperature.

Gas samples can be taken while on-load at 800, 2000 and 3100 mm over the distributor plate. Each sample is conveyed through three impingers with a 0.1 M Na₂CO₃ solution that retains chlorides, fluorides, sulphates and nitrates. The chlorine concentration in the impinger solution is determined by ion chromatography. Solids can also be gathered while on-load from the bed bottom, the baffle chamber and the cyclone.

2.2. Fuels and sorbents

The coal selected for the experiments was Spanish lignite, which has a very high sulphur and ash content (see Table 1). The mean particle size was 0.7 mm, with particle sizes between 0.3 and 1.0 mm.

Corn stover, with 0.35% chlorine content as received, was the herbaceous biomass selected for the experiments. Aiming to test the influence of the chlorine content, the corn stover was doped with a KCl solution to increase the concentration up to 1% Cl. The apportioned KCl was dispersed onto the biomass surface as 1 μm crystals identified by SEM (Fig. 2). For that particle size, it has been claimed that in-flight sulfation is achievable at the short gas residence times typical of combustion systems [43]. The resulting biomass was ground and sieved to obtain a fraction between 1.0 and 2.0 mm.

As regards the sorbents, two domestic limestones with high CaCO₃ contents (>97%) were selected: Granicarb limestone and Bahoto limestone. The mean particle size was approximately 0.6 mm for both. Silica sand was the inert constituent of the bed at the beginning of each test, with the same mean particle size.

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