Sulfur retention in an oxy-fuel bubbling fluidized bed combustor: Effect of coal rank, type of sorbent and O_2/CO_2 ratio

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HIGHLIGHTS

- The optimum temperature for sulfur retention in oxy-fuel fluidized beds is 900–925 °C.
- The sulfur retentions with the dolomite are higher than with the limestones.
- Sulfur retention depends on sulfur content of the coal.
- O_2/CO_2 ratio hardly affects sulfur retention.
- A decrease in the sorbent particle size produces an increase in sulfur retention.

ARTICLE INFO

ABSTRACT

In this work, SO_2 retention via calcium-based sorbents added in a continuous bubbling fluidized bed combustor ($\sim$3 kW$_{th}$) operating in oxy-fuel combustion mode is analyzed. Tests were performed at different operating temperatures with three sorbents, two limestones and one dolomite, and with three coals, ranging from lignite to anthracite, to analyze the influence of coal rank, type of sorbent, sorbent particle size, and O_2/CO_2 feeding ratio on the sulfation process.

It was found that the combustor temperature had a strong influence on the limestones sulfur retention with a maximum at 900–925 °C. The behavior of the limestones was qualitatively similar with the three coals, attaining the highest sulfur retention values working with the lignite and the lowest working with the bituminous coal. On the contrary, with the dolomite the sulfur retention was hardly affected by the combustion temperature and the sulfur retentions attained were higher than with the limestones. The sulfur retention increased with diminishing the Ca-based sorbent particle size, and it was hardly affected by the O_2/CO_2 ratio fed into the combustor.

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1. Introduction

Nowadays, there is a great public awareness about the emissions of pollutant gases into the atmosphere from large power plants. The release of CO_2 and SO_2 gases from coal combustion to generate electric power causes serious environmental problems. The former contributes to the build-up of greenhouse gases and the latter to acid rain formation.

According to the IPCC 2005 [1], CO_2 capture and storage technologies could be promising to mitigate CO_2 emissions from large power plants into the atmosphere. The development of CO_2 capture technologies to obtain an outlet gas stream in energy generation processes with high CO_2 concentration seems to be one of the most reliable solutions to slow down the increase of CO_2 in the future. Currently, there are several types of CO_2 capture technologies, oxy-fuel combustion being one of them. Oxy-fuel combustion consists of burning the fuel with a mix of pure oxygen and a part of recycled flue gas, mainly composed of CO_2 (after steam condensation) [2–4]. Therefore, the CO_2 concentration in the flue gas may be enriched up to 95%, making possible an easy CO_2 recovery.

There are different types of boilers to perform this process. Fluidized bed (FB) combustors, and particularly circulating fluidized bed (CFB) combustors, are very promising for the oxy-fuel process because as well as having a great versatility to burn fuels (either fuel-lean or blend of coal with other fuels such as biomass or wastes) they allow the in-situ flue gas desulfurization via Ca-based sorbents added into the combustor, such as limestone or dolomite. This could be an advantage since sulfur containing species mean a risk of corrosion and could have impacts on the furnace, during ash collection, CO_2 compression, transport and storage [5,6]. Currently, the CFB oxy-fuel combustion technology is gaining interest. Alstom

[7], VTT and Foster Wheeler [8], Metso [9], Czestochowa University of Technology [10], Canmet Energy [6,11–13], and Fundación Ciuden [14] have carried out oxy-fuel combustion experimental tests with CFB combustors at scales up to 30 MW$_{th}$.

Canmet Energy research group has successfully worked with two CFB combustors of 100 kW$_{th}$ [11,12,15] and 0.8 MW$_{th}$ [6,13] with flue gas recycle. They found lower sulfur retention via calcium sorbents addition in oxy-fuel combustion than in air combustion conditions at about ~850 °C. However, further increases of temperature led to the enhancement of the sulfur retention in oxy-fuel combustion, that is, once the conditions were shifted from direct to indirect sulfation. Their results strongly support the point of view that oxy-fuel combustion technology has the same advantages as air-fired CFB. Nevertheless, the test experiences showed that operating in the oxy-fuel mode led to increase corrosion as a consequence of higher sulfur concentrations in the flue gas [6]. SO$_2$ concentration in the oxy-fuel mode was up to four times higher compared to the air firing mode. They suggested that the combustion mode affected limestone performance for sulfur removal and that this impact depended on combustion temperature as well as on fuel characteristics.

Our research group has performed experimental tests in a thermogravimetric analyzer (TGA) [16], in a batch fluidized bed reactor [17], and in a continuous bubbling fluidized bed (BFB) combustor (~3 kW$_{th}$) [18,19] to analyze the effect of temperature on the SO$_2$ retention by limestones under oxy-fuel operating conditions. It was observed that the main effect of increasing the CO$_2$ concentration in the combustor was to shift the CaCO$_3$ decomposition to CaO at higher temperatures. An optimum temperature with respect to sulfur retention in oxy-fuel conditions was found to be around 900–925 °C whereas in oxygen enriched air combustion the optimum temperature was around 850–870 °C.

In industrial plants, the SO$_2$ in the flue gas can be removed before or after the stream recirculation. In this work, the SO$_2$ retention via calcium-based sorbents added into a continuous BFB combustor (~3 kW$_{th}$) operating in the oxy-fuel combustion mode is analyzed simulating an inlet gas composition similar to one obtained when the gas cleaning is carried out before stream recirculation. Nevertheless, the effect of the SO$_2$ recirculation was analyzed in a previous paper [19]. Tests were performed at different operating temperatures with three sorbents, two limestones and one dolomite, and with three coals, ranging from lignite to anthracite. In addition, the influence of the sorbent particle size and O$_2$/CO$_2$ feeding ratio in the sulfation process is also analyzed.

2. Experimental section

2.1. Materials

To study the sulfation process, two Spanish coals, a lignite and an anthracite, and a Colombian bituminous coal were selected as fuels. The coals were crushed and sieved in a range of the particle size between 0.2 and 1.2 mm. Table 1 shows the proximate and ultimate analysis of the coals. Moreover, two Spanish limestones, and one Spanish dolomite were used as calcium-based sorbents for sulfur retention. The particle size of the sorbents was in the range of 0.3–0.5 mm, except for the tests where the sorbent particle size was analyzed. Table 2 gives the chemical analysis and the main physical properties of the sorbents.

To control the residence time of the sorbent in the fluidized bed combustor, inert silica sand with a particle size of 0.2–0.6 mm was also fed along with the fuel and the sorbent during the tests.

2.2. Experimental installation

The experimental installation consisted of a fluidized bed combustor (~3 kW$_{th}$) and different auxiliary systems for gas supply, solid feeding, solid recovering, and gas analysis. Fig. 1 shows a schematic diagram of the installation.

The combustor consisted of a stainless steel reactor of 9.5 cm i.d. and 60 cm height and a freeboard of 15 cm i.d. and 50 cm height. The height of the solids in the BFB was kept constant at 40 cm. The reactant gases, air, CO$_2$, and O$_2$, were supplied from bottle cylinders by means of electronic mass-flow controllers to simulate typical gas compositions entering the reactor in oxy-firing mode.

The gases were introduced into the reactor through a gas distributor plate and the solids by means of water-cooled screw feeders located just above the distributor plate. The O$_2$, CO$_2$, CO, and SO$_2$ concentrations at the exit of the combustor were continuously analyzed after water condensation by on-line gas analyzers. The installation was described in detail in a previous paper [19]. Table 3 shows the feeding rates of solids and the flow rate of gases used in the tests.

2.3. Procedure

To start-up, the bed was filled with ~1.8 kg of silica sand and hot air was fed through a gas pre-heater to reach the coal ignition temperature. Then, the coal feeding started and the bed temperature went on increasing due to the coal combustion. After reaching the desired temperature, the preheating system was turned off, the air was replaced by the typical oxy-fuel gas mixture, O$_2$/CO$_2$, sand and a coal/limestone mixture were fed into the bed and a heat exchanger was introduced into the bed to control the temperature. Once a stable operation was attained, it was maintained to reach up to the steady state operation for SO$_2$ retention. An important feature of the tests carried out in the continuous unit was the certainty that the results were obtained under steady state conditions. This aspect was commented in detail in a previous paper [18].

SO$_2$ retentions (SR) were calculated by Eq. (1) as the molar fraction of sulfur retained by the bed solids with respect to the sulfur contained in the coal feeding.

$$SR(\%) = \frac{(F_{0,coal} x_{S,coal}/M_S) - Q_{out} \cdot C_{SO2,out}}{F_{0,coal} x_{S,coal}/M_S} \cdot 100 \quad (1)$$

being $F_{0,coal}$ the coal feeding rate, $x_{S,coal}$ the coal sulfur content, M_S the molecular weight of S, $C_{SO2,out}$ the SO$_2$ concentration in the flue gas at the exit of the reactor (dry base), and Q_{out} the gas flow rate at the reactor exit (dry base). Q_{out} was calculated by means of a mass balance, considering the coal and gas feeding flow rates and the flue gas composition. $C_{SO2,out}$ was considered as an average value of the measurements taken during the whole test duration in steady state conditions. The average concentrations of the other gases during the test were also taken into account and were calculated in the same

Table 1
Proximate and ultimate analysis of coals.

	Lignite	Anthracite	Bituminous
Proximate analysis (wt%)			
Moisture	12.6	2.3	5.2
Ash	25.2	31.7	12.9
Volatiles	28.7	5.6	32.7
Fixed C	33.6	60.4	49.2
Ultimate analysis (wt%, wet)			
C	45.43	59.64	65.63
H	2.50	1.67	4.06
N	0.65	0.93	1.5
S	5.17	1.52	0.77
LHV (kJ/kg)	16,252	21,807	25,398