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Effects of temperature and flue gas recycle on the SO₂ and NO_x emissions in an oxy-fuel fluidized bed combustor

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Abstract

Oxy-fuel combustion consists in burning a fuel with a mixture of nearly pure oxygen and a CO₂-rich recycled flue gas resulting in a product flue gas from the boiler containing mainly CO₂ and H₂O.

In this work, the effect of combustion temperature and flue gas recycle composition on pollutant emissions and on the sulfation process, in order to optimize the SO₂ retention in circulating fluidized beds (CFBC), were analyzed.

The experimental work was carried out with an anthracite coal in a 3 kWth continuous bubbling fluidized bed (BFB) combustor operating in oxy-fuel conditions. It was found that in oxy-combustion conditions in BFB an increase of combustor temperature produced an increase on NO emission and a decrease in the CO and N₂O emissions. The optimum temperature to reach the highest sulphur retention was at 900-925 °C.

Flue gas recirculation was simulated by mixing different gases (CO₂, SO₂, NO, and steam) in different concentrations. It was observed that SO₂ recycle produced an increase on the sulfur retention as a consequence of the higher SO₂ concentration existing in the bed. About 65% of the recycled NO was reduced to N₂, being the NO converted to N₂O lower than 5vol.%. Wet recycle produced an important reduction on NO emission in comparison with dry recycle.

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1. Introduction

Nowadays, there is an important public awareness in relation to the hazard of pollutant gases emission into the atmosphere from fossil fuel combustion to obtain energy. On the one hand, CO₂ gas has been recognized as one of the major contributors to the build-up of greenhouse gases and, on the other hand,

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sulfur and nitrogen content in coal are oxidized to SO_2 and NO_x respectively, which contribute to acid rain formation.

According to IPCC 2005 [1], carbon dioxide capture and storage technologies would be needed to mitigate CO_2 emissions from large power plant into the atmosphere for stabilization of atmospheric greenhouse gas concentrations. Oxy-fuel combustion is a CO_2 capture technology which is characterized by using a mixture of pure O_2 and CO_2 -rich recycled flue gas (instead of air used in conventional combustion) to perform the combustion process. As a consequence, with this technology the CO_2 concentration in the flue gas may be enriched up to 95 vol.% (dry), and therefore an easy CO_2 recovery becomes possible.

Fluidized bed combustors (FBC), and specially circulating fluidized bed (CFB) combustors, are very appropriate for this combustion system. This technology has the advantage that external solid heat exchangers can be used to extract heat from the combustion process [2]. This will permit the use of high oxygen concentrations in the combustor. Moreover, in situ desulfurization of combustion gases, by feeding a low cost sorbent such as limestone [2,3], and relatively low NO_x emissions can be achieved [4,5].

The development of the oxy-fuel combustion technology in CFB combustors is currently growing. Alstom [6], VTT and Foster Wheeler [4], Metso [7], Czestochowa University of Technology [5], and Canmet Energy [2,3,8,9] have experimented in oxy-fuel combustion with CFB combustors at scales up to 4 MW_{th} . Recently, the Fundación Ciuden in Spain has operated in oxy-mode with a CFB combustor of 30 MW_{th} .

The objectives of this work were to analyze the effect of the combustor temperature on pollutant emissions and on the sulfation process, in order to optimize the SO_2 retention in CFB combustors, and to analyze the effect of the flue gas recycled into the reactor on the pollutant emissions working in oxy-firing mode.

2. Experimental

2.1. Materials

A Spanish anthracite coal was selected for this study. The coal was crushed and sieved, and the particle size in the range of 0.2-1.2 mm was used. Table 1 gives the proximate and ultimate analyses of the coal. A high purity Spanish limestone “Granicarb” (97.1 wt.% CaCO_3) was used as calcium-based sorbent for sulfur retention. Particle size of the limestone was in the range of 0.3-0.5 mm. The porosities of the raw and after calcination (in N_2 atmosphere at 900 °C for 10 minutes) sorbent were 3.7 % and 49 %, respectively. Inert silica sand of size 0.2-0.6 mm was fed together with the coal and the limestone during all the tests to control the residence time of the sorbent in the fluidized bed reactor.

Table 1. Analysis of anthracite coal.

Proximate analysis (wt%)		Ultimate analysis (wt%, dry)	
Moisture	2.3	C	61.0
Ash	31.7	H	1.71
Volatiles	5.6	N	0.95
Fixed C	60.4	S	1.55
LHV* (kJ/kg)	21807		

*Lower Heating Value.

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

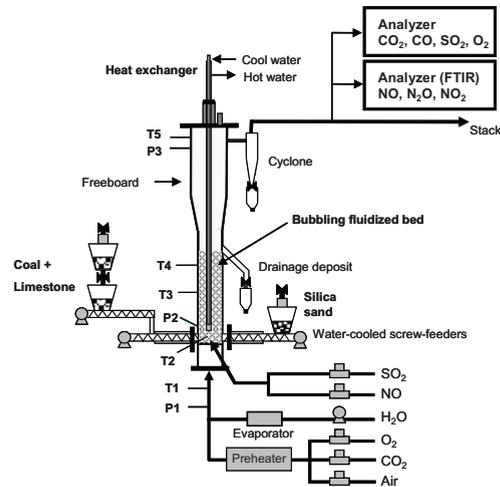


Fig. 1. Oxy-fuel Bubbling Fluidized Bed Combustor at ICB-CSIC. Measurements of temperature (T) and pressure (P).

The combustor consisted of a stainless steel reactor of 0.095 m i.d. and 0.6 m height and a freeboard of 0.15 m i.d. and 0.5 m height. The height of solid in the BFB was maintained constant at 0.4 m. A heat exchanger located inside the bed, which could be moved vertically through the reactor to modify the contact surface inside the bed, allowed us the perfect control of temperature.

The reactant gases, air, CO₂, and O₂, were supplied from cylinders by means of electronic mass-flow controllers to simulate typical gas compositions entering into the reactor in oxy-firing mode. These gases were fed into the reactor through a gas distributor plate. The recirculation of SO₂, NO, and H₂O was simulated by feeding different gas mixtures. H₂O was supplied by a peristaltic pump, subsequently evaporated and fed into the reactor through the gas distributor plate together with the CO₂ and O₂. SO₂ and NO were supplied from cylinders by means of electronic mass-flow controllers just above the gas distribution plate.

The solids were fed to the reactor by means of screw feeders located just above the distributor plate. Coal and sorbent were fed together by means of two screw feeders in series: the first one controlled the coal/sorbent feeding rate and the second one introduced the solid mixture as quick as possible into the bed to avoid coal pyrolysis and plugging of the pipe. Other screw feeder controlled the silica sand fed to the combustor.

The flue gas stream leaving the combustor passed through a high efficiency cyclone to recover the elutriated solids and then it was sent to the stack. The gas composition at the exit of the combustor was analyzed continuously after water condensation by on-line gas analyzers. General process data (temperatures, pressures, flow of gases, gas composition, etc.) were continuously recorded by a computer.

To start-up, the bed was filled with ~1.8 kg of silica sand and hot air was introduced through a gas pre-heater to heat the bed up to the ignition temperature of the coal. The complete procedure was described elsewhere [10].

2.3. Data analysis

Once steady state operating conditions were reached (this aspect was commented in detail in a previous paper [10]), SO₂ retention (SR) was calculated by equation (1) as the molar fraction of sulfur retained by the bed solids with respect to the sulfur fed by the coal into the bed

$$SR(\%) = \frac{(F_{0,coal} \cdot x_{S,coal} / M_S) - Q_{out} \cdot C_{SO_2,out}}{F_{0,coal} \cdot x_{S,coal} / M_S} \cdot 100 \quad (1)$$

being $F_{0,coal}$ the coal feeding rate, $x_{S,coal}$ the coal sulfur content, M_S the molecular weight of S, $C_{SO_2,out}$ the SO₂ concentration in the flue gas at the exit of the reactor, and Q_{out} the gas flow rate at the reactor exit. $C_{SO_2,out}$ was considered as an average value of the measurements taken during the whole test duration in steady state conditions. Steady state was maintained for at least 1 h for each experimental condition.

3. Results

3.1. Influence of the combustor temperature

Combustion tests without feeding SO₂, NO or steam were initially performed at different temperatures between 800 and 950°C. In all cases an inlet gas composition of O₂/CO₂ = 35/65 and a Ca/S molar ratio = 3 were used. The coal feeding rate was controlled to keep the O₂ concentration at 3.75 ± 0.75 vol% (dry basis) at the combustor exit.

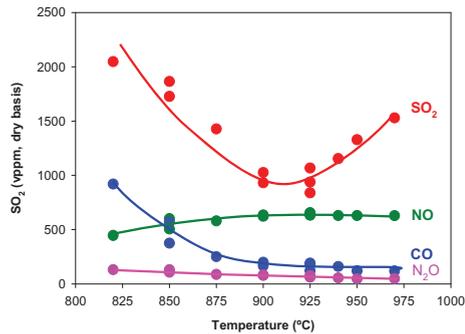


Fig. 2. Effect of temperature on gas pollutant emissions.

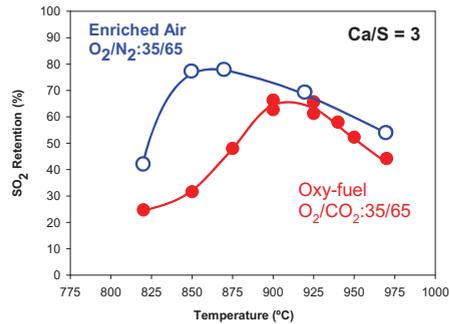


Fig. 3. Effect of temperature on the sulfur retention.

Figure 2 shows the effect of the combustion temperature on the SO₂, CO, NO, and N₂O emissions. NO₂ emission was never detected. The SO₂ emission decreased with increasing temperature up to 900–925 °C and then, a further increase in temperature caused an increase in SO₂ emission. The CO concentration decreased exponentially with rising temperature because the overall coal combustion process improved as the temperature increased. Figure 2 also shows a clear dependence of NO and N₂O emissions with temperature. The NO emission increased with temperature up to 900 °C and then it was

almost constant until 950 °C. On the contrary, the N₂O emission decreased when the combustor temperature increased.

Figure 3 shows the effect of temperature on SR. It is observed that the SO₂ retention was higher working at calcining (indirect sulfation) than at non-calcining (direct sulfation) operating conditions. The optimum combustor temperature from the point of view of SO₂ retention was 900-925 °C in oxy-fuel combustion mode. A comparison of these results with those obtained working with enriched-air [10] shows that oxy-fuel combustion conditions shift the maximum in SR from ~860 °C to 900-925 °C. These results are in good agreement with the results obtained in previous works of our research group where the sulfur retention capacity of the limestone “Granicarb” was analyzed in a TGA [11] and in a batch FB reactor [12] under different operating conditions.

3.2. Effect of the gases recycled with the CO₂.

In the CO₂-rich recycled flue gas, besides CO₂ and O₂, there are other gases in a lower concentration that can affect the pollutant emissions of the combustor [13]. In this section, a summary of the main results of the study of the effect of the recycle of different gases, such as SO₂, NO, and steam, both separately and combined, are showed.

3.2.1. Effect of SO₂ recirculation.

To simulate the flue gas recirculation of SO₂, a flow of this gas was injected just above the gas distributor plate. The pure SO₂ flow rate introduced at each operating condition was approximately the same as the SO₂ that would be recirculated taking into account its concentration at the exit of the combustor. SO₂ concentrations of 900 vppm and 3500 vppm with respect to the inlet gas flow rate at 925 °C and 850 °C, respectively, were injected [13].

It can be seen in Figure 4 that the effect of SO₂ recirculation on the emissions of the other gases depended on the temperature. At 850 °C after SO₂ injection there was an important reduction in the NO concentration and an important increase in the CO concentration at the outlet of the reactor. However, the NO reduction was smaller and the CO increase was negligible at 925 °C. The SO₂ recirculation did not affect N₂O emission at either temperature. The decrease in the NO emission is explained by an increase in CO concentration, since the CO oxidation was moderately inhibited by the addition of SO₂ [14] and the increase in CO concentration favors the reduction of NO on the char surface [15-17].

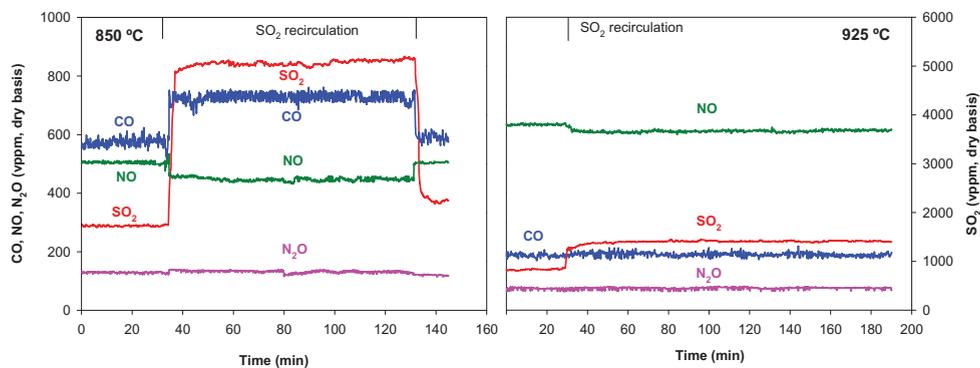


Fig. 4. Effect of SO₂ recirculation on SO₂, CO, NO, and N₂O emissions.

The SO₂ retention with respect to the sulfur fed by the coal was calculated by means of the following expression:

$$SR(\%) = \frac{(F_{0,coal} \cdot x_{S,coal} / M_S) + Q_{in} \cdot C_{SO_2,in} - Q_{out} \cdot C_{SO_2,out}}{F_{0,coal} \cdot x_{S,coal} / M_S} \cdot 100 \quad (2)$$

being $F_{0,coal}$, $x_{S,coal}$, M_S , $C_{SO_2,out}$, and Q_{out} the same as in equation (1), $C_{SO_2,in}$ the SO₂ concentration in the flue gas coming into the reactor, and Q_{in} the gas flow rate at the reactor inlet.

It was found that due to the higher SO₂ concentration the SO₂ retention increased from ~69% to ~81% at 925 °C and from ~34% to ~39% at 850 °C, that is, the Ca utilization was higher after SO₂ injection.

3.2.2. Effect of NO recirculation

The effect of NO recirculation was investigated at two different temperatures, 850 and 925 °C, injecting different flow rates of NO (2 vol.% NO in Ar), which were calculated to be equivalent to 200, 350, 500 and 625 vppm with respect to the inlet gas flow rate. Figure 5 plots the test carried out at 925 °C. The amount of NO reduced was calculated as the difference between the NO concentration in the inlet gas and the increase in the NO concentration in the outlet gas due to NO injection [13]. It was observed that about 60-70% of the NO introduced was reduced, mainly to N₂ (less than 5vol.% of the NO introduced was converted to N₂O), and the reduction rate was almost independent of the initial concentration of NO and temperature. In addition, as can be observed in Figure 5, neither SO₂ nor CO emissions were affected by the NO injection.

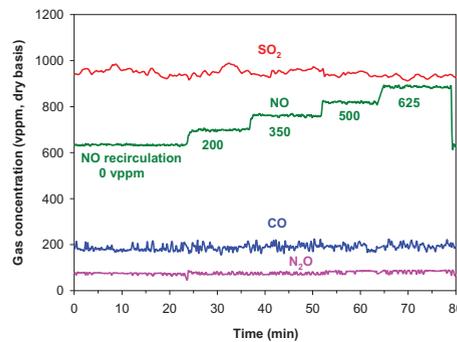


Fig. 5. Effect of NO recirculation on the SO₂, NO, CO, and N₂O emissions. T=925 °C.

3.2.3. Effect of steam recirculation.

Due to wet and dry gas recirculations are possible in oxy-fuel combustors, the effect of steam recirculation on the emission of gases was analyzed. It was simulated replacing CO₂ by H₂O in the inlet gas flow. So, the gas composition fed to the combustor in these tests was 35 vol% O₂, 45-50 vol% CO₂, and 15-20 vol% H₂O.

In all of the tests the gas composition was measured after steam condensation. So, to compare the emissions, the measured gas concentrations for the tests with steam feeding were corrected to the same outlet gas flow as in the tests without steam addition.

As can be seen in Figure 6, at the time of introducing steam, a sharp decrease in NO emission was observed. Therefore, it could be inferred that wet recirculation would produce a great decrease in the NO

concentration in comparison with dry recirculation in a fluidized bed furnace. The change in the CO concentration was negligible and the N₂O concentration increased slightly.

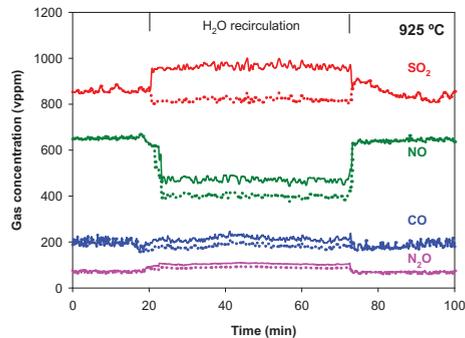


Fig. 6. Effect of steam recirculation on the SO₂, NO, CO, and N₂O emissions. Continuous lines = measured values (dry basis). Dotted lines = corrected values (wet basis), $C_{i,out}(wet) = C_{i,out}(dry) / (1 - C_{H_2O,in})$

Regarding to SO₂ concentration and thus sulfation conversion of the limestone, the effect of H₂O addition on sulfation conversion was very small, both at 850 °C (direct sulfation) and 925 °C (indirect sulfation) [13]. Stewart et al. [18] suggested that the effect of H₂O was negligible in the kinetic-controlled stage and it was especially important in the diffusion-controlled stage with an optimum of water concentration around 15-30 vol%. It must be remarked that the tests of this work were carried out with a mean residence time of solids of ≈ 2 hours and maybe they were not long enough to notice that effect.

3.2.4 Effect of combined recirculations: H₂O/NO, H₂O/SO₂, SO₂/NO, and H₂O/SO₂/NO.

Although the NO emission was lower with H₂O recirculation, the reduction of the NO recycled was almost the same with H₂O and without H₂O recirculation [13]. Therefore, it can be concluded that H₂O recirculation has only influence during the stage of NO formation but once NO is formed, the contribution of the H₂O to minimize the NO emission is very small.

The combined effect of the recirculation of different gases, H₂O/SO₂, SO₂/NO and H₂O/SO₂/NO, in the inlet gas stream on the pollutant emissions was almost the same as the sum of the effects of the recirculation of each gas separately and a synergetic effect among them was not observed.

4. Conclusions

The optimum fluidized bed combustor temperature from the point of view of sulfur retention shifted from ~ 860 °C in combustion with enriched air to 900-925 °C in oxy-fuel combustion mode.

SO₂ recirculation increased the Ca-based sorbent utilization and did not affect N₂O emission. At 850 °C, SO₂ recirculation increased the CO concentration and decreased the NO emission. However, at 925 °C the NO reduction was small and the CO increase was negligible.

About 65% of the recycled NO was reduced to N₂. The formation of N₂O was very small and neither SO₂ nor CO emissions were affected by the NO recirculation.

Steam recirculation produced a sharp decrease in NO emission, a slight increase in N₂O emission, and did not affect the SO₂ and CO emissions.

The combined effect of the recirculation of different gases was almost the same as the sum of the effects of the recirculation of each gas separately and a synergetic effect among them was not observed.

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