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Optimum temperature for sulphur retention in fluidised beds working under oxy-fuel combustion conditions

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Abstract

Oxy-fuel combustion is one of the leading options for power generation with CO_2 capture. The process consists of burning the fuel with a mixture of nearly pure oxygen and a CO_2-rich recycled flue gas, resulting in a product flue gas from the boiler containing mainly CO_2 and H_2O. Among the possible boiler types, fluidised bed combustors are very appropriate for the oxy-fuel process because they allow the in-situ desulphurisation by feeding Ca-based sorbents into the combustor.

In this work, the effect of the temperature of the combustor on the retention of the SO_2 generated in the combustion of two coals with very different sulphur content (a lignite and an anthracite) has been studied. The experimental facility used was a bubbling fluidised bed (BFB) combustor of ~3 kW_{th}. Tests were conducted under oxy-fuel combustion mode and also under enriched-air combustion mode for comparison reasons. A Spanish limestone "Granicarb" was used as Ca-based sorbent for sulphur retention. The temperatures tested were between 800 and 970 ºC using Ca/S molar ratios between 0 and 3.

It was found that in BFB combustors operating under oxy-fuel combustion conditions the optimum temperature to achieve the highest sulphur retention was 900-925 ºC, whereas operating with enriched air the optimum combustion temperature was 850-870 ºC. Working at the optimum temperature, the SO_2 retentions were lower in oxy-fuel

combustion than in enriched air combustion conditions. It was also observed that working with lignite there was 10-15% of sulphur retention by coal ashes, however, working with anthracite the sulphur retention by coal ashes was negligible. This finding was independent of the combustion mode used, oxy-fuel or enriched air.

1. Introduction

The emission of gases into the atmosphere from burning fossil fuels, mainly coal, in large power plants causes important environmental problems. The CO_2 produced in combustion process has been recognised as one of the major contributors to the build-up of greenhouse gases in the atmosphere and, in addition, sulphur in coal is oxidised to SO_2, which contributes to acid rain formation.

The capture and storage of CO_2, emitted in large quantities from power plants, is considered an option to be explored in the medium term for reducing CO_2 levels released to the atmosphere. Oxy-fuel combustion is one of the possibilities under investigation within the different options for CO_2 capture [1-3]. This technology uses for combustion pure O_2 (instead of air used in conventional combustion) mixed with CO_2-rich recycled flue gas, and so, the flue gas stream from the boiler finally produced is highly concentrated on CO_2. After condensing water and a cleaning step, the CO_2 can be stored.

Among the possible boiler types, fluidised bed (FB) combustors are very appropriate for the oxy-fuel process because they allow the in-situ desulphurisation of the flue gas by feeding Ca-based sorbents into the combustor, such as limestone or dolomite. This could be an advantage since sulphur containing species mean a risk of corrosion and could have impacts in the furnace, during ash collection, CO_2 compression, transport and storage [4,5]. Other well known advantages are the possibility of burning a wide range of fuels and the relatively low NOx emissions achieved [6-7]. It is also believed that oxy-fuel circulating fluidised bed (CFB) combustors could be an important candidate for new coal fired power plants, mainly because the circulation of solids in the combustor can help to an effective control of the temperature [5-11]. This will permit the use of high oxygen concentrations in the combustor, thus reducing the area of the CFB combustor, as well as the amount of recycled flue gas, thus reducing the size of some subsequent equipments and power consumption [10]. Other important advantage

is the efficiency improvement, mainly due to the strong mixing in the furnace and longer residence times of solids that allows a good carbon burnout.

The development of the oxy-fuel combustion technology in CFB combustor is currently growing. Alstom [10], VTT and Foster Wheeler [11], Metso [12], Czestochowa University of Technology [7], and Canmet Energy [5,8,9,13] have experimented in oxy-fuel combustion with CFB combustors at scales up to 4 MW_{th}. The Fundación Ciuden [14] in Spain is developing two plants able to operate from conventional air combustion to oxy-fuel combustion. One is a 20 MW_{th} PC boiler and the other is a CFB combustor of 15 MW_{th} operating in air-mode and 30 MW_{th} operating in oxy-mode. The research group of Canmet Energy [8-9] is involved in testing a CFB combustor of 100 kW_{th} with flue gas recycle. Operating at ~850 ºC, they found lower sulphation in oxy-fuel combustion than in air combustion conditions, but the sulphation improved working with a petroleum coke by increasing the operation temperature, that is, changing from direct to indirect sulphation. However, the same effect was not confirmed working with coals. Recently this group has successfully converted and operated a conventional 0.8 MW_{th} pilot-plant to oxy-fuel firing [5,13]. Their results strongly support the view that this technology offers all of the advantages of air-fired CFB. However, the test experiences showed that operating the pilot-scale unit over a long period under oxy-fuel mode led to enhanced corrosion due to higher sulphur concentrations in the flue gas [5]. SO_2 concentration under oxy-fuel mode was up to four times higher compared to air firing mode. They concluded that limestone performance for sulphur removal was impacted by the combustion mode, and that this impact depended on fuel characteristics as well as on combustion temperature.

Our research group have recently carried out several tests in a thermogravimetric analyser (TGA) and in a batch fluidised bed reactor to analyse the behaviour of limestones for SO_2 retention under oxy-fuel operating conditions [15-16]. We found that the major effect of increasing the CO_2 concentration in the reacting gas was to shift the $CaCO_3$ decomposition to CaO until a higher temperature. The higher temperature needed to work in conditions of indirect sulphation with increasing CO_2 contents had a negative influence on the sulphation conversion reached by the limestones. It was concluded that the optimum temperature for sulphur retention in oxy-fuel combustion mode in FB reactors was incremented up to ~925 ºC from the 850 ºC normally used at conventional air combustion conditions. This conclusion seems in good agreement with

the results found by Canmet Energy working in its CFB combustors [5,9]. However, more work should be carried in continuous fluidised bed reactors to confirm this conclusion.

The objective of this work was to determine the optimum operating temperature to achieve the maximum sulphur retention in fluidised bed reactors working under oxy-fuel operating conditions. Tests were carried out in a continuous bubbling fluidised bed (BFB) combustor (~3 kW_{th}) operating with limestone under calcining or non calcining conditions. Two coals of different rank and sulphur content were used. The effect of Ca/S molar ratio with respect to the sorbent sulphation process was also analysed.

2. Experimental section

2.1. Materials

Two Spanish coals, an anthracite and a lignite with a high sulphur content, were selected for this study. Both coals were 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 coals. Sulphur in coal can exist in both inorganic and organic forms. The inorganic sulphur is mostly pyrite and/or marcasite, together with small amounts of sulphates depending on the level of oxidation of the coal. The organic sulphur exists either in aromatic rings or in aliphatic functional groups. The distribution between organic and pyritic sulphur depends on the rank and total sulphur content of the coal [17]. The release of the sulphur to form SO_2 in the oxy-fuel combustion process can depend on the sulphur distribution. So, it is also included in Table 1 the different forms of the sulphur and the composition of the coal ashes. In this case, all the sulphur present in the anthracite was as pyritic form meanwhile sulphur present in lignite was distributed in three forms. The analysis of the ashes shows that both coals contained some CaO, which could contribute to the reduction of the SO_2 emissions.

For sulphur capture tests, a high purity Spanish limestone “Granicarb” (97.1 wt.% $CaCO_3$) was used as Ca-based sorbent. Table 2 gives the analysis of the Granicarb limestone. Particle size of the limestone was in the range of 0.3-0.5 mm. The porosities of the raw and after calcination sorbent were 3.7 % and 49 %, respectively.

In addition, inert silica sand of size 0.2-0.6 mm was fed together with the coals and the limestone during all the tests to decrease the residence time of the sorbent in the fluidised bed reactor, as it will be commented later.

2.2. Experimental installation

The experimental installation of ~3 kW_{th} consisted of a fluidised bed combustor and different auxiliary systems for gas supply, solid feeding, solid recovering, and gas analysis. Figure 1 shows a schematic diagram of the installation.

The combustor consisted of a stainless steel reactor of 10 cm i.d. and 60 cm height and a freeboard of 15 cm i.d. and 50 cm height. The height of solid in the BFB was maintained constant at 40 cm. A heat exchanger located inside the bed allowed us the perfect control of temperature. This heat exchanger could be moved vertically through the reactor, modifying the contact surface inside the bed and extracting the needed heat from the combustor to reach the desired temperature.

The reactant gases, air, CO_2, and O_2, were supplied from bottles by mass-flow controllers to simulate typical gas compositions entering into the reactor in oxy-fuel combustion conditions. These gases were fed into the reactor through a distributor plate. A linear gas velocity of 40 cm/s (calculated at 850 ºC) at the inlet of the bed was used during all the tests. An air pre-heater allowed introducing hot air inside the reactor during the start-up of the plant.

The solids were fed to the reactor by means of water-cooled screw feeders located just above the distributor plate. To assure a constant Ca/S molar ratio, 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 the coal pyrolysis and the plugging of the pipe. Other screw feeder controlled the 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 was sent to the stack. The gas composition at the exit of the combustor was analysed continuously after water condensation by on-line gas analysers. CO_2, CO and SO_2 concentrations were measured in a Non-Dispersive

Infra-Red analyser (NDIR, Siemens/Ultramat 23), and O_2 concentration in a paramagnetic analyser (Siemens/Oxymat 6).

The facility was equipped with pressure sensors and thermocouples to know the pressure drop and temperatures along the installation. General process data (temperatures, pressures, mass flow of gases, gas composition, etc.) were continuously recorded by a computer.

2.3. Procedure

For star-up, the bed was filled with ~1.8 kg of sand. Figure 2 shows the typical evolution of temperature and gas composition during the start-up of the installation until reaching stable operating conditions. Hot air was introduced through the gas pre-heater to heat the bed up to the ignition temperature of the coal (~400 ºC). At this temperature, the coal feed started and the bed temperature rose rapidly due to the combustion of the coal. Neither sand nor sorbent was fed during this step. During this step, O_2 concentration decreased and CO_2, CO, and SO_2 appeared as combustion products. CO concentration was high at the lowest temperatures, due to the bad combustion, but as the temperature went on the CO concentration decreased. When the temperature set point was reached and the initial charge of coal (without limestone) spent, the sand and the coal/limestone mixture were fed into the bed, the preheating system was turn off, the air was replaced by the desired O_2/CO_2 or O_2/N_2 mixture, and the heat exchanger was introduced into the bed to control the temperature. The total time for the start-up of the plant was about 3-4 hours. Once stable operating conditions were reached, these conditions were maintained until reaching steady state operation for SO_2 retention. This aspect will be commented in detail later.

The SO_2 retention (SR) was calculated by equation (1) as the molar fraction of sulphur retained by the bed solids with respect to the sulphur fed into the bed.

$$SR(\%) = \frac{\left(F_{0,coal} x_{S,coal} / M_{SO2}\right) - Q \cdot C_{SO2}}{F_{0,coal} x_{S,coal} / M_{SO2}} .100 \qquad (1)$$

being $F_{0,coal}$ the feeding coal rate, $x_{S,coal}$ the coal sulphur content, M_{SO2} the molecular weight of SO_2, C_{SO2} the SO_2 concentration in the flue gas, and Q the gas flow rate at the exit of the reactor. The SO_2 concentration was considered as an average value of those measured along the whole duration of the test in steady state conditions. Q was

calculated by means of a mass balance, considering the coal and gas flow rates fed to the combustor and the flue gas composition.

2.4. Steady state conditions for SO_2 retention.

An important feature of the tests carried out in continuous units is the certainty that the results are obtained under steady state conditions. In our installation, considering the fluidised bed dimensions, the coal and limestone feeding rates (with a Ca/S molar ratio of 3 and without feeding sand), and assuming that the coal ashes are not elutriated out of the combustor, the mean residence time of solids in the bed was estimated by equation (2) to be about 7 hours when operating with anthracite and 4 hours with the lignite.

$$t_R(h) = \frac{W_{bed}}{F_{ash} + F_{limestone}} \qquad (2)$$

Of course, the mean residence time of non-elutriable solids will be higher when the Ca/S molar ratio would be lower than 3 and because an important fraction of ash will be elutriated out of the combustor and collected by the cyclone (this fact was observed in the experiments). So, mean residence times between 5 and 20 hours, or even higher, would be normal for typical tests in our installation.

To be sure that steady state conditions have been reached, it is considered that the weight of solids fed to the bed should be at least 2-2.5 times the weight of solids existing in the bed, which gives operating times of 10-50 hours, out of our experimental possibilities. To reduce the mean residence time of the solids inside the fluidised bed up to about 2 hours, 0.9 kg/h of sand was fed into the reactor in all of the tests. In this way, after reaching stable conditions, the steady state for SO_2 retention was reached in 4-5 hours and maintained at least for 1 hour for each experimental data.

3. Results

Coal combustion tests with and without limestone addition were carried out in a BFB combustor working in oxy-fuel combustion conditions with oxygen concentrations at the inlet of 27 and 35 vol.% O_2. In addition, similar experiments were also carried out under enriched air conditions to know the effect of the reaction atmosphere.

Tables 3 and 4 summarize the experiments carried out with the two coals including the operating conditions (temperature, Ca/S molar ratio, and O_2 concentration), as well as the O_2 in the flue gas and the SO_2 emissions measured in each case. These data correspond to the average values recorded during at least 1 hour working under steady state operation, which gives a total of about 50 hours in steady state and about 300 hours of total continuous operation in the plant (including the time to reach the steady state).

To calculate both the SR and the power developed by the facility, a combustion efficiency of 100 % has been considered. This simplification was made because the carbon combustion efficiencies determined by solid analysis were always >99 % working with the lignite and >98 % working with the anthracite. These combustion efficiencies were determined in the tests carried out without limestone addition taking into account the carbon fed to the combustor and the losses of carbon in the solids collected in the cyclone and in the solids collected in the drainage deposit.

3.1. Influence of temperature.

In practice, FB combustors are usually operated in the 800-950 ºC range, under overall oxidising conditions [18]. Some researchers [19-20] have found that the optimum temperature for sulphur retention was nearly 850 ºC under conventional air combustion in FB combustors. These operating conditions are characterised by low CO_2 concentrations in the flue gas (up to 16%). However, the CO_2 concentration in oxy-fuel operating conditions is significantly higher than in air combustion, up to 90%, which will affect to the Ca-based sorbent behaviour inside the bed.

When a Ca-based sorbent is added to a FB combustor, temperature is one of the most important parameters affecting the SO_2 retention process because sorbent calcination is highly dependent on the temperature and CO_2 concentration through the thermodynamic equilibrium curve of $CaCO_3$ calcination, as it can be observed in Figure 3.

The conditions existing in FB combustors during conventional combustion with air lead to a previous sorbent calcination (R1) and to the sulphation of calcines (R2), i.e. indirect sulphation:

$$CaCO_3 \rightleftharpoons CaO + CO_2 \qquad \text{(R1)}$$

$$CaO + SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons CaSO_4 \quad \text{(R2)}$$

In oxy-fuel combustion, CO_2 concentration in the flue gas may be enriched up to values as high as 90%. Therefore, the sorbent can be surrounded by CO_2 concentrations ranging from 40 to 90 % during their stage in the FB reactor. Under so high CO_2 concentrations, the sorbent can behave in two ways depending on the temperature (see Figure 3). At 850 ºC, the sulphur retention will be produced under direct sulphation (R3), being necessary higher temperatures to operate under indirect sulphation (R1 and R2).

$$CaCO_3 + SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons CaSO_4 + CO_2 \quad \text{(R3)}$$

To analyse the effect of temperature on SR, several tests were carried out maintaining constant the Ca/S molar ratio and the O_2 concentration at the inlet of the reactor. Tables 3 and 4 give the SO_2 emissions measured in the tests and Figure 4 shows the effect of temperature on SR for the two coals working with enriched air and in oxy-fuel combustion conditions.

Working with enriched air, the SR increased with increasing temperature up to a maximum of 850-870 ºC for both coals and then, a further increase in temperature caused a decrease in SR values. These results are in accordance with other authors who affirm the existence of a maximum sulphur capture efficiency at about 850 ºC working in atmospheric FB combustors systems under air combustion conditions [18]. Lin [21] has summarised several of the reasons proposed as responsible of this maximum which, include: sorbent sintering at high temperatures, resulting in lower porosity and surface area, hence reducing the overall conversion of the limestone; SO_2/SO_3 equilibrium determines the maximum, with higher temperatures reducing the availability of SO_3 for reaction with CaO; and high temperatures enhances sulphation rate which causes small pores to become blocked preventing the entry of SO_2/SO_3 to the inner part of the calcined limestone particle.

Comparing the results obtained working with air and under oxy-fuel operating conditions, it is clear that oxy-fuel combustion conditions shift the maximum in SR from ~850 to 900-925 ºC. These results are in good agreement with the results obtained in previous works of our research group where the sulphur retention capacity of the limestone “Granicarb” was analysed in a TGA and in a batch FB reactor under different operating conditions [15-16]. In these works, it was found that the effect of the

temperature was different for the direct and indirect sulphation reactions. In direct sulphation or non-calcining conditions, the sulphation reaction rate rose with increasing the temperature (until reach calcining conditions). On the contrary, in conditions of indirect sulphation or calcining conditions, the sulphation reaction rate increased with increasing the temperature up to 900-925 ºC and then decreased. The sulphation conversions achieved under indirect sulphation were always higher than those achieved under direct sulphation. As shown in Figure 3, the high partial pressure of CO_2 in oxy-fuel shifts the decomposition of $CaCO_3$ to higher temperatures. Therefore, at temperature of 850 ºC under oxy-fuel combustion leads to direct sulphation, being necessary temperatures higher than 900 ºC to be indirect sulphation. As a consequence, the maximum sorbent conversion was reached at temperatures about 900-925 ºC.

It can be also seen in Figure 4 that operating at the optimal temperature for each case, enriched air or oxy-fuel, the SR obtained in oxy-fuel combustion was lower than that obtained in enriched air combustion conditions, probably because the higher temperature needed for the sorbent calcination caused an increase of the sinterisation of the limestone.

Figure 5 shows a comparison between the SR obtained working at the same operating conditions with the lignite and the anthracite. It can be observed that the behaviour of the limestone was qualitatively similar with both coals, but higher SR values, and so higher limestone sulphation conversions, were achieved working with the lignite. It has to be noted that lignite and anthracite have very different sulphur content, being much higher that of lignite (see Table 1). Previous studies carried out under oxy-fuel combustion conditions in a TGA [15] and in a batch FB reactor [16] demonstrated that the sulphation conversion of the sorbent increased as the SO_2 concentration increased. The higher SO_2 concentration present in the FB combustor during lignite combustion was therefore the responsible of the higher SR values achieved in the plant with this coal.

3.2. Influence of the Ca/S molar ratio

As it is well know, the utilisation of Ca-based sorbents for SR in FB boilers is not complete due to the pore blockage produced by $CaSO_4$ formation. In the typical operating conditions used in FB combustors, the sulphation reaction usually takes place

at the external surface and around the pores of the sorbent particles. Since the molar volume of $CaSO_4$ is higher than the molar volume of $CaCO_3$ or CaO, the pores are blocked and the inner part of the particles remains essentially unsulphated [18]. This is usually valid for both direct and indirect sulphation. Therefore, an important parameter in the SR process is the Ca/S molar ratio used in the combustor. This Ca/S molar ratio has to be necessarily higher than 1 in order to achieve a significant SO_2 retention.

Figure 6 compares the SR achieved working with the lignite and the anthracite under oxy-fuel operating conditions at different Ca/S molar ratios. As expected, an increase in the Ca/S molar ratio produced a higher SR in all range of temperatures studied. The effect of the temperature was similar for the different Ca/S molar ratios used, with maximum values at 900-925 ºC.

When a Ca-based sorbent is fed into a combustor, the SR is normally attributed to the effect of the sorbent. However, it is known that not all the sulphur contained in the coal is emitted as SO_2 either because it is already in sulphates form [17] or because coal ashes retain part of the SO_2 released [22-24].

In this work, to know the real SO_2 emissions derived from the combustion of the coals used, and to determine therefore the retention capacity of the coal ashes, combustion experiments without limestone addition (Ca/S=0) were performed at different temperatures both in oxy and enriched air mode. The results obtained are shown in Figures 6 and 7. It can be observed that all the sulphur contained in the anthracite was emitted as SO_2 during its combustion; however, a part of the sulphur contained in the lignite was not emitted as SO_2. It seems that some of the SO_2 generated during the combustion of the lignite was retained by its ashes, as it will be commented later. In addition, the SR produced by the coal ashes was almost the same working with enriched air and under oxy-fuel combustion conditions.

In the experiments carried out with the lignite, the SR produced by coal ashes was around 10-15%, and slightly decreased with increasing the temperature. Taking into account the ash content and the CaO present in the coal ashes (see Table 1), the maximum SR that can be achieved by this CaO was calculated to be 18 %. Therefore, the utilization of this CaO was around 60-80 %, probably because part of the CaO was elutriated with the ashes out of the combustor. In the case of the anthracite, the SR produced by ashes was negligible. However, taking into account the ash content and the CaO present in the coal ashes in this coal, it was calculated that the maximun retention

that can be achieved by this CaO would be 38 %. Therefore, it seems that the Ca present in the ashes is not in a form able to retain sulphur.

To analyse these results in more detail, ashes of both coals were produced in a muffle oven to study their capacity for SR. Samples of these ashes were introduced in a TGA, heated at 900 ºC, and then $CO_2/O_2/SO_2$ was fed to simulate typical oxy-fuel operating conditions. The lignite ashes increased 10.5 % in weight, whereas the anthracite ashes did not increase in weight. Both results are in accordance with the experimental results obtained in the BFB combustor.

3.3. Effect of mean residence time of the limestone

Some previous works on sorbent sulphation with long reaction times [15,25] have demonstrated that the residual activity of the sorbents after pore plugging can be very important. However, as it was previously commented in the experimental section, an important feature of the tests carried out in this work was the certainty that the results were obtained under steady state conditions. For that, 0.9 kg/h of sand was fed into the reactor in all of the tests. At these conditions, the mean residence time of the solids inside the fluidised bed was about 2 hours. However, average residence times in industrial FB combustors are clearly much higher than those used here, with values as high as 10-20 hours [26-28].

To analyse the effect on the SR of the mean residence time of the limestone in the combustor, two tests were carried out with both coals at 925 ºC. For that, after reaching steady-state conditions with a mean residence time of the solids of 2 hours, the sand feeding was diminished from 0.9 to 0.2 kg/h to increase the residence time of the solids inside the bed. Figure 8 shows the evolution of the SO_2 concentration during these tests. It can be observed that an important decrease in the SO_2 concentration was obtained as a consequence of the increase of the sorbent inventory in the bed as well as the increase of the residence time of the sorbent. However, it must be remarked that in these tests the steady-state was not achieved and no quantitative data can be obtained, although the trend is clear.

Figure 9 shows the sorbent sulphation conversion obtained in a TGA in a previous work as a function of the reaction time working with the Granicarb limestone (dp=0.3-0.5 mm, 3000 vppm SO_2, 900 ºC, and 60 vol.% CO_2) [15]. Considering this plot as

representative of the sorbent sulphation pattern exhibited by the limestone in the BFB combustor, an important increase in sorbent sulphation (ΔX) can be achieved by increasing the residence time as it would be usual in industrial FB combustors.

It can be concluded therefore that the results showed in this paper are very useful from a qualitatively point of view to determine the optimum operating temperature working under oxy-fuel combustion in FB with respect to the SR process. However, it is expected that the SR achieved in industrial units would be higher than those obtained in this work. So, tests of increasing solids residence time in the combustor under steady state conditions would be needed to confirm this issue.

4. Conclusions

Combustion tests were carried out in a ~3 kW_{th} continuous BFB combustor with two coals and one limestone as sulphur sorbent under oxy-fuel and enriched-air combustion conditions to optimise the operating temperature with respect to the sulphur retention process in FB combustors.

It was found that sorbent calcination had a strong effect on SO_2 retention under oxy-fuel combustion conditions. The SO_2 retention was higher working at calcining (indirect sulphation) than at non-calcining (direct sulphation) operating conditions. The optimum FB combustor temperature from of point of view of SR shifted from 850-870 ºC in combustion with enriched air to 900-925 °C in oxy-fuel combustion mode. Working at the optimum temperature for each combustion mode, the SO_2 retentions obtained in oxy-fuel combustion were lower than those obtained under air combustion.

As it is obvious, an increase in the Ca/S molar ratio produced an increase in SO_2 retention in all range of temperatures. In addition, an important effect of coal ashes on SO_2 retention was determined for the lignite, meanwhile the SO_2 retention achieved by the anthracite ashes was negligible.

The results showed in this paper are very useful from a qualitatively point of view to determine the optimum operating temperature working under oxy-fuel combustion in FB with respect to the SO_2 retention process. However, it is expected that the SO_2 retention achieved in industrial units with longer residence time of solids would be higher than those obtained in this work.

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Captions for Tables

Table 1. Analysis of coals and its ashes.

Table 2. Limestone characteristics.

Table 3. Tests carried out and experimental results obtained under oxy-fuel operating conditions.

Table 4. Tests carried out and experimental results obtained under enriched air operating conditions.

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Figure 3. Thermodynamic equilibrium curve of $CaCO_3$ calcination.

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Figure 9. Sulphation conversion of the Granicarb limestone in a TGA during long reaction time. dp=0.3-0.5 mm, 3000 vppm SO_2, 900 ºC, and 60 vol.% CO_2

Table 1. Analysis of coals and its ashes.

	Coals	
	Lignite	Anthracite
Proximate analysis (wt %)		
Moisture	12.6	1.0
Ash	25.2	31.6
Volatiles	28.7	7.6
Fixed C	33.6	59.9
Ultimate analysis (wt %, dry)		
C	45.43	59.64
H	2.50	1.67
N	0.65	0.93
S	5.17	1.52
Sulphate	1.05	0.02
Pyritic	1.76	1.50
Organic (by diff.)	2.36	0.00
LHV* (kJ/kg)	16252	21807
Ash Composition (wt%)		
Al_2O_3	24.81	24.93
CaO	6.54	2.73
Fe_2O_3	20.05	10.22
K_2O	1.38	4.18
MgO	1.44	1.84
Na_2O	0.15	0.94
SiO_2	41.00	51.47
TiO_2	0.80	0.94

*Low Heating Value.

Table 2. Limestone characteristics.

Composition (wt %)	
$CaCO_3$	97.1
$MgCO_3$	0.2
Na_2O	1.1
SiO_2	<0.1
Al_2O_3	<0.1
Fe_2O_3	<0.1
Porosity (%)	
Raw	3.7
Calcined*	49

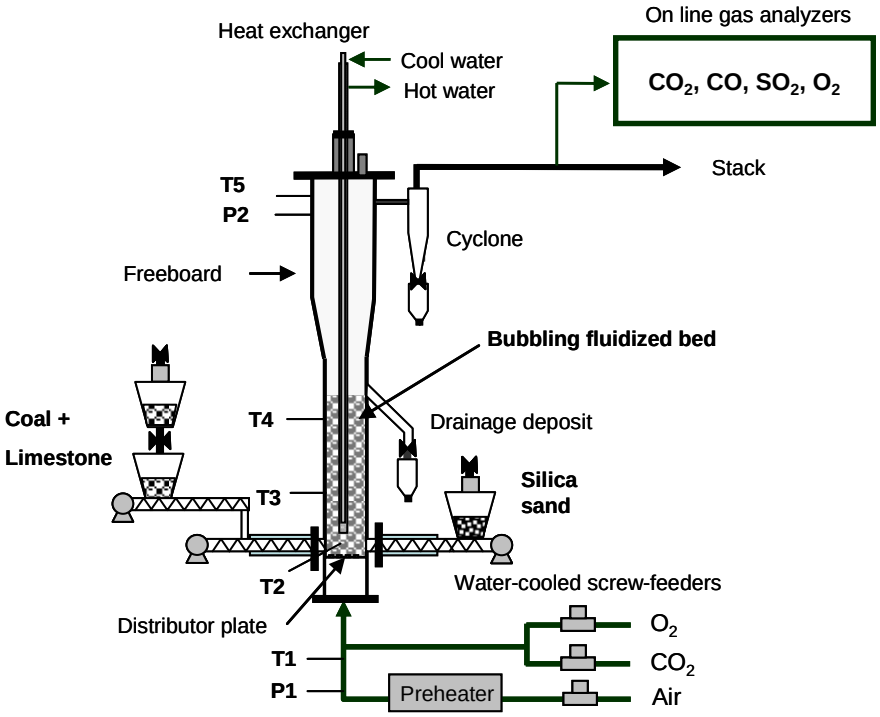
* Calcined in N_2 atmosphere at 900 ºC during 10 minutes.

Table 3. Tests carried out and experimental results obtained under oxy-fuel operating conditions.

Exp.	Ca/S	T (ºC)	O_2 / CO_2 (%)	O_2 in flue gas (% d.b)	SO_2 emitted (ppm/kW_{th})	Power (kW_{th})
Lignite						
OX-1	0	800	27 / 73	3.9	3028	2.4
OX-2	0	850	27 / 73	3.8	3050	2.4
OX-3	0	900	27 / 73	3.9	3147	2.4
OX-4	0	950	27 / 73	3.1	3234	2.5
OX-5	2	800	27 / 73	3.8	2439	2.4
OX-6	2	850	27 / 73	3.0	2180	2.5
OX-7	2	900	27 / 73	3.7	1486	2.4
OX-8	2	925	27 / 73	3.7	1427	2.4
OX-9	2	950	27 / 73	3.7	1782	2.4
OX-10	2	925	35 / 65	3.6	1405	3.2
OX-11	3	850	35 / 65	5.0	1843	3.1
OX-12	3	875	35 / 65	4.1	1196	3.2
OX-13	3	900	35 / 65	3.8	770	3.2
OX-14	3	925	35 / 65	3.5	828	3.2
OX-15	3	950	35 / 65	4.3	1123	3.2
Anthracite						
OX-16	0	850	35 / 65	4.3	778	3.4
OX-17	0	900	35 / 65	3.9	771	3.5
OX-18	0	950	35 / 65	3.8	795	3.5
OX-19	2	850	35 / 65	4.3	592	3.4
OX-20	2	900	35 / 65	3.8	351	3.5
OX-21	2	925	35 / 65	3.6	332	3.5
OX-22	2	945	35 / 65	3.7	400	3.5
OX-23	2	970	35 / 65	3.6	507	3.5
OX-24	3	820	35 / 65	4.0	585	3.5
OX-25	3	850	35 / 65	3.8	533	3.5
OX-26	3	875	35 / 65	3.6	408	3.5
OX-27	3	900	35 / 65	3.5	293	3.5
OX-28	3	900	35 / 65	3.4	266	3.5
OX-29	3	925	35 / 65	3.5	305	3.5
OX-30	3	925	35 / 65	3.7	268	3.5
OX-31	3	940	35 / 65	3.6	330	3.5
OX-32	3	950	35 / 65	3.2	369	3.6
OX-33	3	970	35 / 65	3.7	437	3.5

Table 4. Tests carried out and experimental results obtained under enriched air operating conditions.

Exp.	Ca/S	T (ºC)	O_2 / CO_2 (%)	O_2 in flue gas (% d.b)	SO_2 emitted (ppm/kW_{th})	Power (kW_{th})
Lignite						
A-1	0	800	27 / 73	5.0	2974	2.3
A-2	0	850	27 / 73	4.0	3153	2.4
A-3	0	900	27 / 73	4.7	3227	2.3
A-4	0	950	27 / 73	4.0	3096	2.4
A-5	2	800	27 / 73	4.4	1238	2.3
A-6	2	850	27 / 73	4.6	932	2.3
A-7	2	900	27 / 73	4.5	1179	2.3
A-8	2	925	27 / 73	4.6	1533	2.3
A-9	2	950	27 / 73	3.3	1895	2.4
Anthracite						
A-10	0	850	35 / 65	3.6	780	3.5
A-11	0	900	35 / 65	3.7	782	3.5
A-12	3	820	35 / 65	4.0	447	3.5
A-13	3	850	35 / 65	3.8	176	3.5
A-14	3	870	35 / 65	3.6	174	3.5
A-15	3	920	35 / 65	3.7	238	3.5
A-16	3	970	35 / 65	3.6	360	3.5



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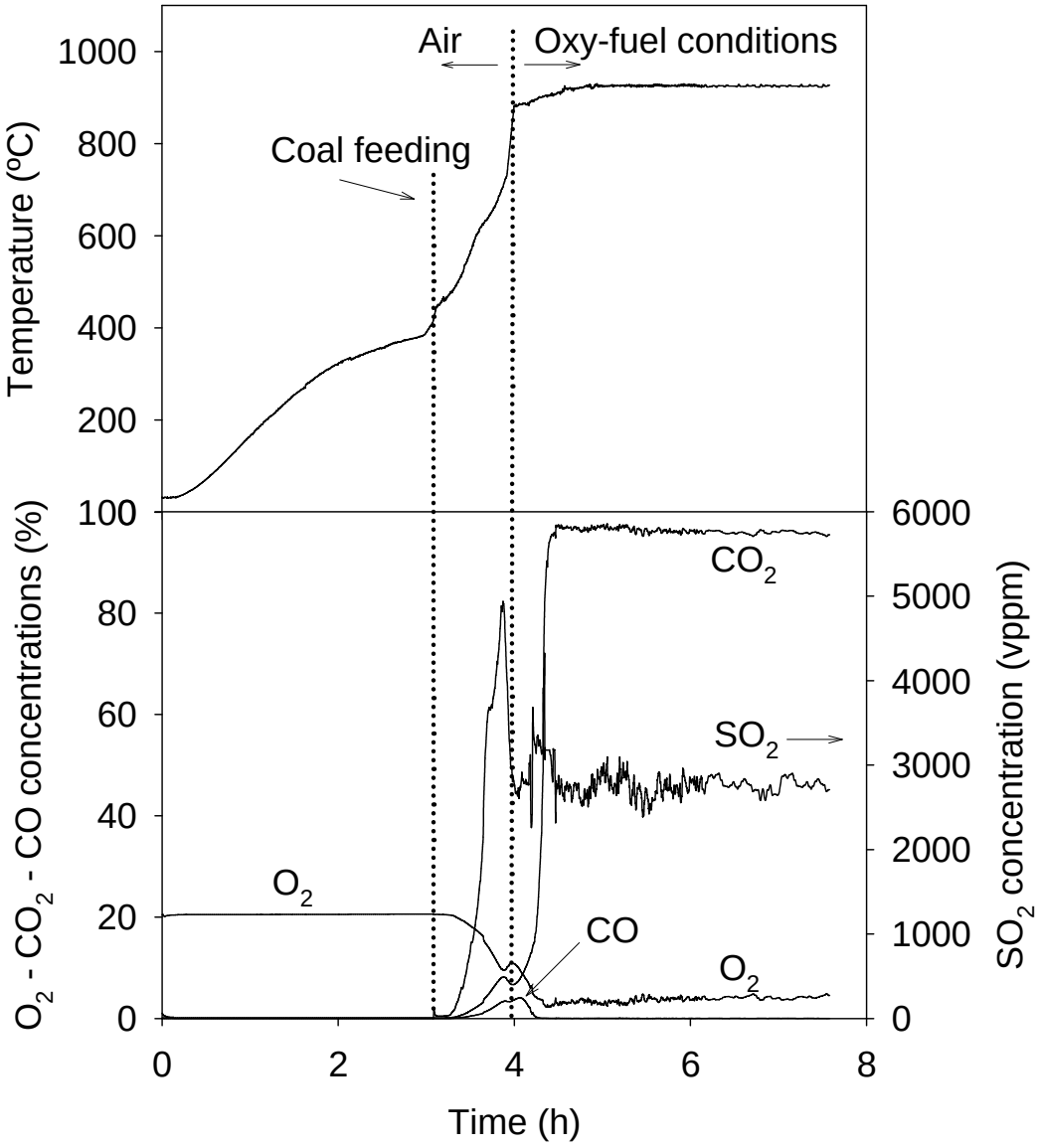

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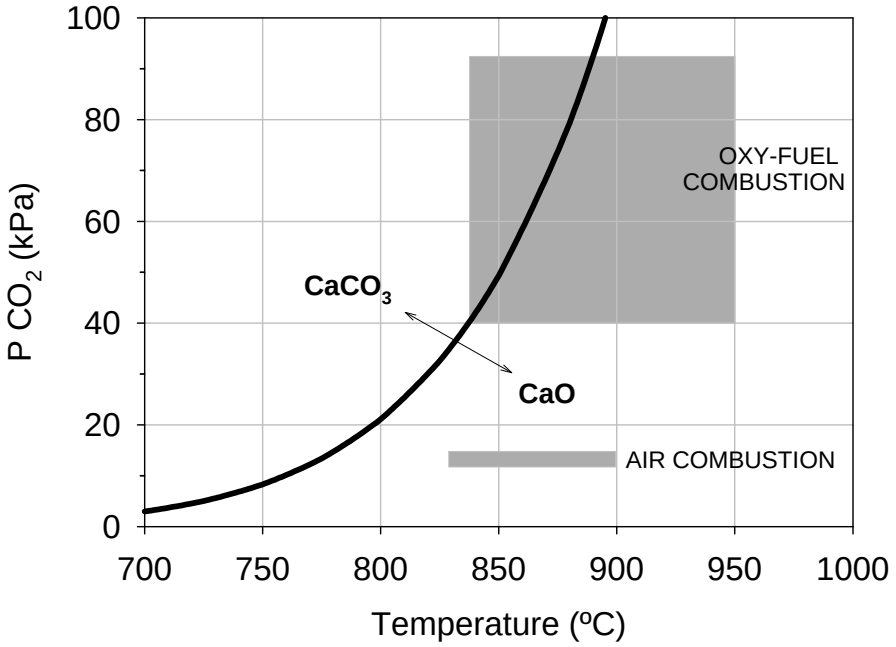

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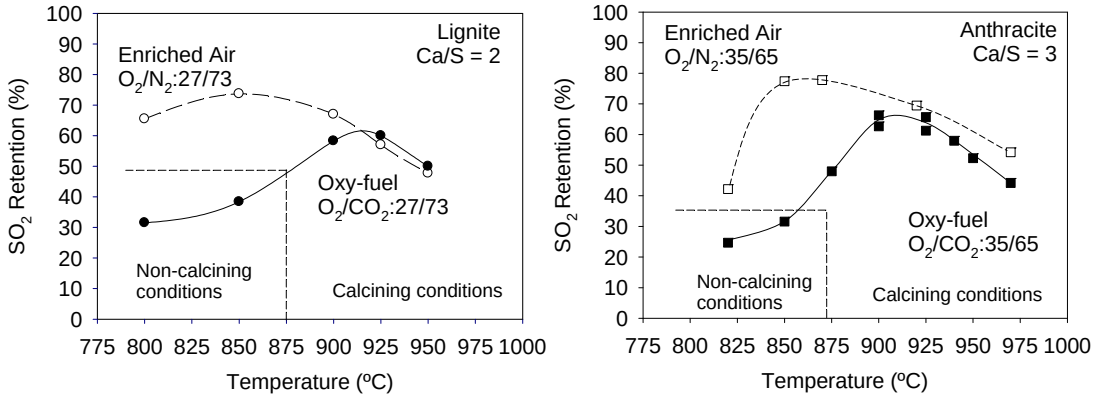

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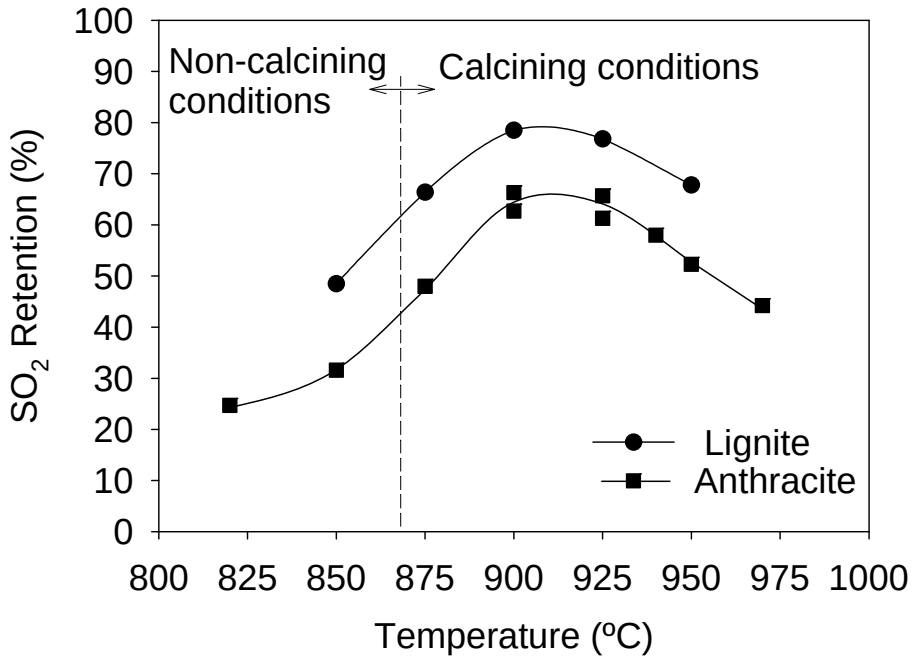

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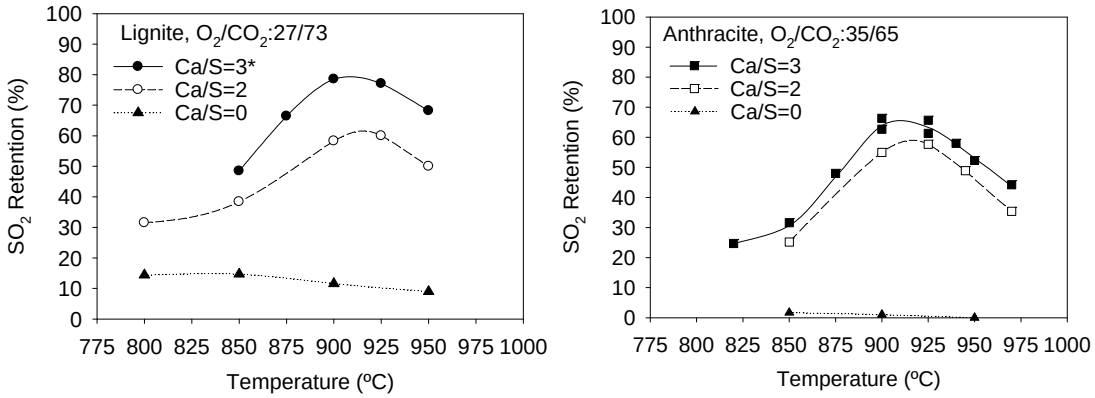

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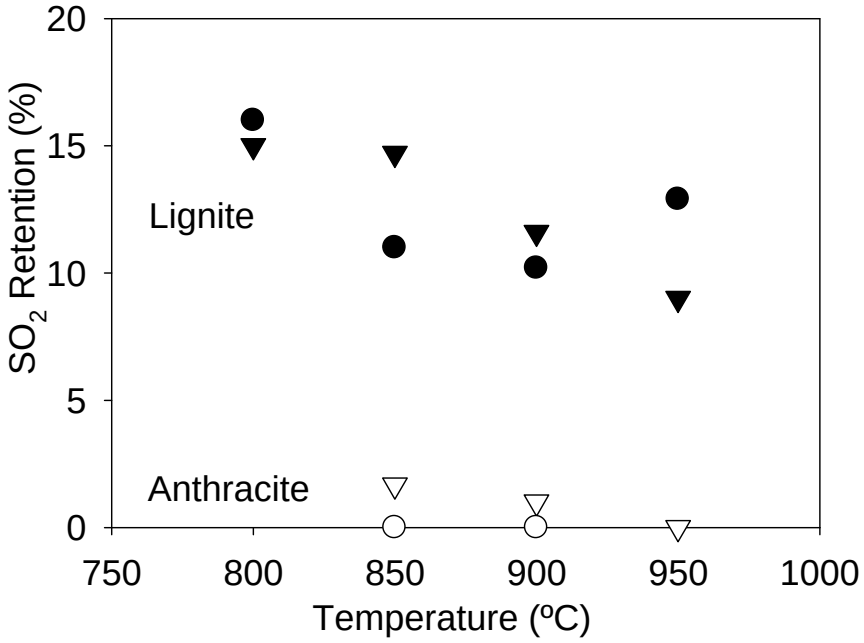

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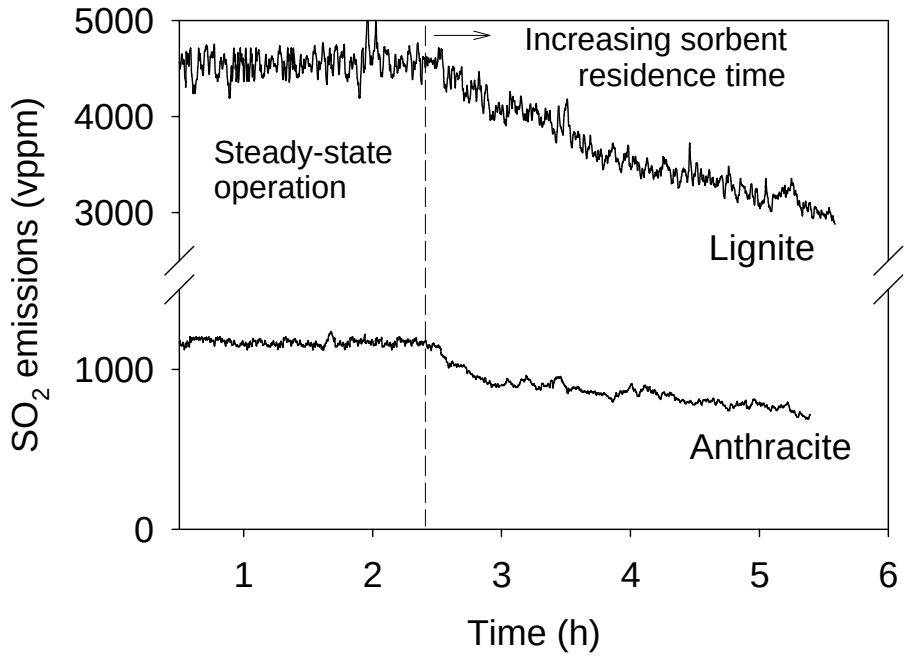

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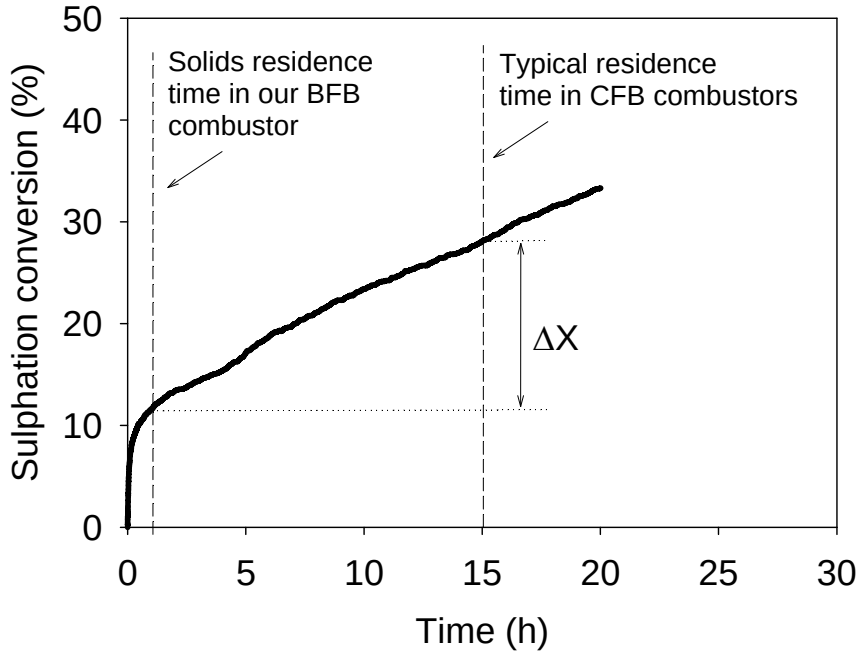

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