NO and N_2O emissions in oxy-fuel combustion of coal in a bubbling fluidized bed combustor.

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ABSTRACT

Emissions from coal oxy-fuel combustion are receiving significant attention during the last years. This paper is focused on the analysis of fuel-N emissions in fluidized bed combustion systems. Experiments were carried out in a bubbling fluidized bed unit in the temperature interval 850-950ºC. Different coals (anthracite, bituminous and lignite) were used as fuels and different sorbents were employed for in-bed sulphur retention. In the experiments, NO, N_2O and NO_2 were measured. NO_2 was not detected in any of the operating conditions. The influence of temperature on NO and N_2O emissions was the same as in conventional combustion: NO emission increased as temperature increased while N_2O emission decreased. Nevertheless, the total fuel-N conversion to nitrogenous species seemed to be lower than in combustion with air. As in air-firing combustion, the highest levels of NO and N_2O were registered with the highest rank coals. The Ca-sorbent was found to have a key role on NO reduction via catalytic reaction and this catalytic effect seemed not to be affected by the high CO_2 levels present in oxy-fuel combustion. Also, the moisture content in the coal affected the NO formation, which decreased

with an increase in the coal moisture content. A similar effect was observed by increasing the oxygen concentration fed to the combustor.

Keywords: combustion; coal; CO_2 capture; oxy-fuel; NO, N_2O

1. Introduction

Oxy-fuel combustion is one of the CO_2 capture technological options with more retrofitting possibilities for already existing power plants. Therefore, several aspects related to the changes in oxy-fuel combustion compared to conventional combustion have been analyzed during last years. Considering that the use of coal is likely to continue or even increase through the 21st century [1], many of the research studies were related to oxy-fuel pulverized coal combustion (PC) [2]. However, oxy-fuel combustion of coal in fluidized bed combustors (FBCs) received relatively little attention. Combustion of coal in a circulating fluidized bed (CFB) has been investigated from mid-1980s [3]. This combustion technology brought some advantages compared to conventional PC. CFB combustion was introduced as a very flexible technology, allowing to burn a wide range of fuels with relatively low NO_x and SO_2 emissions. Working under oxy-fuel mode, the CFB technology could report additional advantages. A higher oxygen concentration in the combustion chamber and a reduction in the area of CFB boilers up to 50% [4] could be achieved due to the better control of combustion temperature by the solids recirculation. This would make possible a significant reduction of the amount of recycled flue gas.

One of the important aspects in coal combustion is the formation of pollutant compounds, especially SO_2 and nitrogen oxides such as NO, NO_2, commonly referred as NO_x, and N_2O. The formation of NO_x in conventional combustion systems can take place through fixation of molecular nitrogen in the combustion air or from nitrogen chemically bound in the fuel [5]. At the typical temperatures used in CFB combustors (800-900ºC), NO formation mainly comes from the oxidation of the nitrogen present in the fuel. However, the low combustion

temperatures used to enhance SO_x/NO_x control are responsible for the relatively high level of N_2O emissions observed in these combustion systems. Most values range from 50 to 200 ppm, while in natural-gas and oil-fired turbines these values are, in general, less than 2 ppm and in PC boilers, levels are below 20 ppm in most cases [6]. N_2O enhances the greenhouse gas effect due to its high radiative forcing compared to CO_2 and its long atmospheric lifetime. Besides, it plays an important role in depletion of the ozone layer. These high N_2O emissions observed in CFB combustion of coal and the potential environmental damage associated to them lead to an intense research on N_2O formation and destruction mechanisms [7].

The NO and N_2O chemistry in FBCs is quite complex and involves numerous reactions, both homogeneous and heterogeneous. In general, N_2O/NO formation and destruction in a FBC can be summarized as follows [3,8]. Once coal is fed to the FBC, volatile release takes place. During devolatilization, fuel nitrogen is split between the volatiles and the char generated. The fraction of fuel-N retained in char after devolatilization depends on several factors, such as temperature and type of coal. About 60% or more of fuel-N was found to be retained in char during pyrolysis at temperatures relevant to fluidized-bed combustion [9]. The main volatile nitrogen species are hydrogen cyanide, HCN, and ammonia NH_3. When the fuel volatiles are oxidized in the gas phase at FBC temperatures, HCN is predominantly converted into N_2O, whereas NH_3 is an important source of NO [6-7], although in both cases, N_2 is also formed. During combustion, the char nitrogen is oxidized to NO and N_2O and partly reduced to N_2. In the process of N_2O formation some NO could be consumed in the pores of the char particles and externally. Small amounts of HCN and NH_3 might be also formed in char oxidation, which can take part in the reduction of NO and N_2O.

The heterogeneous reactions refer to both catalytic and non-catalytic reactions. The most active catalytic surfaces among those normally present in a bed of burning coal are the char and calcined limestone (CaO). By effect of the active surfaces, the selectivity of HCN to NO formation increases and the oxidation of NH_3 to NO is enhanced. NO can also be consumed by

NH$_3$ or reduced by CO catalysed by char and other active surfaces [10]. The non-catalytic NO/N$_2$O reduction on the surface of char has also been studied. For different chars, Rodriguez-Mirasol et al. [11] observed that NO and N$_2$O reduction on char surface was influenced by the origin of the coal (lignite char was the most active) and the presence of other combustion gases which may create active sites for NO/N$_2$O reduction. CO and N$_2$O enhanced the NO reduction on char surfaces. Nevertheless, CO did not enhance decomposition of N$_2$O. The importance of the reaction mechanisms highlighted above depends on the specific operating conditions, fuel type used, and the type of materials present in the fluidized bed.

In oxy-fuel mode, few studies have analyzed to date the coal-N chemistry under fluidized bed combustion conditions. It was speculated that under oxy-fuel combustion, CO$_2$ diminishes NH$_3$ formation and increases HCN [12]. However, HCN oxidation was observed to be inhibited by the presence of high CO$_2$ concentration levels [13]. Therefore a reduction in NO$_x$ and N$_2$O emissions under oxy-fuel combustion compared to conventional combustion would be expected. Hosoda and Hirama [14] observed a reduction in the conversion of fuel-N to NO$_x$ and N$_2$O in a bubbling fluidized-bed (BFB) with recycled flue gas. In their experiments, NO$_x$ decreased linearly with increasing CO$_2$. Lupiáñez et al. [15-16] performed experiments in a 90 kW$_{th}$ BFB reactor under oxy-fuel conditions and observed that the limestone with the lower SO$_2$ retention capacity showed the higher impact on NO emissions for all of the O$_2$/CO$_2$ atmospheres tested. They also observed that the higher the bed temperature and O$_2$ excess, the higher the NO emissions, and compared to conventional air combustion, oxy-fuel tests resulted in lower values of fuel−N conversion ratios. Similar results were found by Jia et al. [4] who observed that the NO$_x$ emissions in a mini-CFB resulted lower than in air-firing mode at temperatures as high as 950ºC and even much lower than for oxy-fuel PC. Our group [17], in experiments performed in a BFB where flue gas recirculation was simulated, observed 60-70% reduction of the recycled NO to N$_2$ and N$_2$O, the latter representing less than 5% of NO conversion.

The objective of the present paper is to further contribute to the analysis of NO/N_2O formation/destruction under oxy-fuel combustion conditions in fluidized beds. Experiments were performed in a 3 kW_{th} experimental BFB unit under different operating parameters, such as temperature, type of coal, type and size of Ca-sorbent and oxygen concentration in the feeding, in order to investigate their effect on the NO/N_2O emissions.

2. Experimental

2.1 Materials

Three different coals were used in this work: a Spanish anthracite from "El Bierzo", a Spanish lignite from Teruel and a Colombian bituminous coal "El Cerrejón". The 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 these coals.

Different calcium-based sorbents were used in the experiments: two limestones (Granicarb and Horcallana) and one dolomite (Sierra de Arcos). Table 2 gives the analysis of these sorbents, together with the porosity and the apparent density of the sorbents. The particle size of the limestones and dolomite was in the range of 0.3–0.5 mm. In all the cases, inert silica sand with a size 0.2–0.6 mm was fed together with the coal and the calcium sorbent during all the tests to control the residence time of the sorbent in the fluidized bed reactor. Similar operating conditions were maintained in all the experiments except indicated. The ratio O_2/CO_2 was 35/65, the fluidized bed combustor temperature was set to 925ºC and the Ca/S molar ratio, influencing sulphur retention by the calcium sorbent, was set to 3 for the limestones and 2 for the dolomite.

2.2 Experimental setup

All the experiments were performed in a BFB combustor (3 kW_{th}) at Instituto de Carboquímica (ICB-CSIC). Figure 1 shows a schematic diagram of the installation. Details about this setup and the experimental procedure can be found elsewhere [18].

The coal feeding rates were controlled to keep the O_2 concentration at 3.75 ± 0.75 vol.% at the combustor exit (dry basis). The gaseous product stream was continuously analyzed after water condensation by on-line gas analyzers. CO_2, CO, and SO_2 concentrations were measured in a Non-Dispersive Infra-Red analyzer (NDIR, Siemens/Ultramat 23), O_2 concentration in a paramagnetic analyzer (Siemens/Oxymat 6), NO, N_2O, and NO_2 concentrations in an infrared gas analyzer, via Fourier transform infrared (FTIR, Temet CX 4000). In any case NO_2 was detected.

3. Results and Discussion

The analysis of the influence of operating parameters on NO and N_2O emissions in a BFB combustor burning coal under oxy-fuel mode is divided into different sections:

3.1 Effect of temperature

Regarding the levels of the different nitrogen compounds, there is a general agreement about the effect of the fluidized bed temperature on NO and N_2O emissions in conventional air combustion. As the temperature increases N_2O emissions decrease while NO exhibits the opposite trend [7]. There is a temperature window for N_2O formation around 750-950ºC [19]. In an oxidizing environment, the reason for the decrease of N_2O emissions at high temperatures lies in the intermediate species, as NCO [19-20]. It was observed that NCO reacts mainly to NO at high temperatures and to N_2O at lower temperatures [19-20]. Nevertheless, some authors claim that the amount of N_2 produced during combustion is independent of temperature [9]. This represents that the sum of fuel-N conversions to N_2O and NO can be considered constant through the range of temperatures typical for FBC, although the emission levels of NO and N_2O varied with temperature. Changes in the temperature resulted in a trade-off between both nitrogen oxides: the emission levels of one pollutant increase at the expense of the other [20]. On the other hand and compared to conventional air-combustion, a reduction in the total conversion of fuel-N to NO_x and N_2O in the oxy-fuel fluidized bed coal combustion has been reported [14].

The first set of experiments analyzed the influence of temperature on the NO and N_2O emissions. Figure 2 shows the NO and N_2O levels reached with the three different coals and "Granicarb" limestone as sorbent. The evolution of NO in Figure 2(A) follows the same trend as in air-firing combustion, NO emissions increase as temperature increases, except for the case of lignite, where the effect of temperature seems to be soften. Figure 2(B) shows the corresponding results for N_2O. In this case and for all coals, the N_2O emissions decrease with temperature. Nevertheless, the amount of fuel-N converted to NO and N_2O, shown in Figure 2(C), can be considered as roughly constant with temperature for all the coals as it was observed before under air combustion conditions by Pels et al. [9]. According to the results, it can be estimated that around 20%, 17%, and 13% of coal-N was converted to NO and N_2O in the case of the experiments with anthracite, bituminous coal, and lignite respectively. In the work presented by Pels et al. [9], experiments were conducted in a quartz fluidized bed in the temperature range 900-1300 K. In this work, the percentage of fuel-N converted to these nitrogenous species was larger, around 67% for anthracite, 50% for bituminous coals and 45% for lignite. Therefore and according to these results, a reduction in the total fuel-N conversion to NO and N_2O in fluidized bed combustion under oxy-fuel conditions was observed in our experiments. It should be noted that in the experiments by Pels et al. [9] no sorbent was present together with the coal in the fluidized bed while "Granicarb" limestone was introduced with the coal in the present oxy-fuel experiments.

3.2 Effect of the type of coal

3.2.1 Effect of the coal rank

The correlation between coal rank and NO/N_2O emissions has been also studied. In air combustion, Pels et al. [9] observed a rank dependence for the total fuel-N conversion, with higher-rank coals clearly showing higher conversions to NO and N_2O. Coal rank seems to affect more the conversion of fuel-N to N_2O than to NO [9]. Amand and Leckner [21] commented that

low rank coals (sub-bituminous and lignite) with higher volatile content show higher release of fuel-N in the form of NH_3 and the main part of this NH_3 may be oxidized to NO or N_2. On the other hand, higher rank coals (anthracite) with lower volatile content tend to retain an important part of fuel-N as nitrogen char. The nitrogen char is released as NO within the pores of the char and the NO formed can be reduced within the pores of the char to N_2 [21]. These authors [21] also comment that the volatile-N would contain a fraction of HCN which can evolve to N_2O and that N_2O can be formed by incomplete reduction of NO on char surfaces. The reduction of the N_2O formed would be less in the combustion of low-volatile than in high-volatile fuels [22]. According to this, the conversion of fuel-N to N_2O in air combustion usually increases with coal rank [6,9,22,23]. However, some changes in this trend could be expected working under oxy-fuel conditions due to the effects of the high CO_2 concentration on NH_3 formation and HCN oxidation. As mentioned before, high CO_2 concentration diminishes NH_3 formation and increases HCN [12], while HCN oxidation may be inhibited by CO_2 [13].

Figure 2 also shows the influence of the coal type on the NO and N_2O emissions recorded in the fluidized bed combustion experiments under oxy-fuel conditions. The highest levels of NO and N_2O at the outlet of the fluidized bed in Figure 2 (A and B) corresponded to the experiments with the highest rank coals, i.e. the Spanish anthracite "El Bierzo" and the bituminous Colombian coal "El Cerrejón", although the NO and N_2O concentration values were slightly higher for the bituminous coal, i.e. for the coal with a higher N-fuel content. Therefore, no change in the trend observed under air combustion was observed in the oxy-fuel experiments regarding the influence of coal rank on N_2O emissions.

Another aspect influencing the nitrogen chemistry in the fluidized beds is the nature of the ashes present, which may depend on the type of coal used. In general, it can be said that some metal oxides present in the ashes positively affects NO/N_2O reduction [24]. Fe_2O_3 and MgO demonstrated activity for N_2O decomposition. However, oxides based on Al, or Si exhibited lower activities [25]. In our experiments, lignite and anthracite are the coals with the highest ash

content (see Table 1). According to the coal flow used in the experiments (576 g/h for anthracite and 700 g/h for lignite), the amount of ashes in the fluidized bed in both cases would be similar. Table 1 shows the composition of the ashes of the three coals used in the fluidized bed experiments (anthracite, bituminous and lignite). As it can be seen, the major components of the ashes are Al_2O_3 and SiO_2 as they represent around 65-75% of the ashes. Nevertheless, important quantities of Fe_2O_3 and MgO are present, especially in the case of lignite, which can have some influence on the nitrogen chemistry, favouring NO and N_2O reduction.

3.2.2 Effect of the moisture content of the coal

In oxy-fuel combustion, there are two different possibilities for flue gas recirculation to the combustion chamber: wet and dry recirculation. In a previous paper, the authors analyzed the effect of water vapour recirculation on the emission of SO_2, NO and N_2O [17] and observed that the recirculation of steam decreased NO emissions and almost did not affect N_2O and SO_2 emissions. However, the recirculation of steam did not improve the reduction of the recirculated NO. Thus, it was concluded that the recirculation of steam only influenced NO formation but once it was formed, the contribution of steam to the minimization of NO emission was very small.

To further investigate these results and to analyze how much the water initially present in the coal influenced the NO and N_2O emissions under oxy-fuel combustion in FBCs, the moisture content of two of the coals used, anthracite and lignite, was modified. According to the composition presented in Table 1, anthracite was the coal with the lowest moisture content, which was increased from 2.3% to 5.2% by impregnation of a known amount of water using a sprayer. Lignite presented the highest moisture content (12.6%). Therefore, it was dried in a muffle at 110ºC until the moisture content decreased to 4.1%.

Experiments were run as explained in the experimental section. When stable conditions were reached, the coal with modified moisture was introduced. Figure 3(A) shows the results

corresponding to anthracite and Figure 3(B) those corresponding to lignite regarding NO concentration in dry basis. In the case of anthracite, once the "wet" anthracite was introduced, the NO concentration decreased around 75 vppm and remained stable in that value. In the experiment with "dry" lignite, the opposite trend was observed. When "dry" lignite was fed, an increase of 30 vppm in NO concentration was recorded. Although it is not shown in Figure 3, it should be mentioned that no effect on N_2O concentrations was observed during these experiments, the measured N_2O concentrations being about 72±4 and 28±5 vppm for anthracite and lignite respectively. Therefore, it can be concluded that the moisture in the coal has a similar effect on the reduction of NO as the recirculation of steam.

3.3 Effect of the calcium-based sorbent

3.3.1 Effect of addition of Ca-sorbent and type of sorbent

Ca-sorbents are added to the FBCs for *in-situ* desulfurization as CaO reacts with SO_2 to be converted into $CaSO_4$. The addition of Ca-sorbents to FBCs results of great effectiveness in SO_2 emission reduction during coal combustion. In full-scale CFB units, sulphur retentions up to 90% have been reached with Ca/S ratios of 2-2.5 [26]. However, the presence of Ca-sorbents in FBCs has been proved to affect the nitrogen chemistry in conventional combustion. The Ca-sorbent has a beneficial effect on reducing N_2O emissions while the opposite trend is observed in the NO level [27-29]. The catalytic activity of a Ca-sorbent decreases during sulphation due to a loss in porosity and a lower activity of the $CaSO_4$ formed. In order to obtain the same degree of desulfurization during combustion, Ca-sorbents with high sulphur capacity must be present in a lower concentration than Ca-sorbents with low sulphur capacity. Thus, the importance of the sorbent to the nitrogen chemistry may be higher when a Ca-sorbent with a low sulphur capacity is used [30]. Nevertheless, the opposite effect has been reported under oxy-fuel combustion experiments [15].

The presence of a Ca-sorbent affects several aspects of the NO/N_2O chemistry under conventional combustion [7,31]:

i) Conversion of coal volatile-N to NO and N_2O: CaO is an active catalyst for oxidation of NH_3 to NO. Nevertheless, the presence of H_2O and SO_2 can inhibit this oxidation process [32-33], while CO_2 has not been observed to affect the catalytic oxidation of NH_3 [34].

ii) N_2O decomposition: CaS and CaO are better catalyst for reduction of N_2O than $CaSO_4$ and $CaCO_3$. N_2O easily decomposes over CaO both at oxidizing and reducing conditions [30,35]. N_2O decomposition over calcined limestone was inhibited by H_2O, CO_2 [33,36] and SO_2 [32]. The existence of two types of active sites on calcined limestone has been proposed to explain the different effect of H_2O and CO_2 on NH_3 oxidation and N_2O decomposition, respectively. NH_3 and O_2 would be adsorbed on one type of active sites and N_2O would be adsorbed on the second type. H_2O will adsorb on all sites, while CO_2 would be adsorbed on the same sites as N_2O. Thus, CO_2 would affect N_2O decomposition and not NH_3 oxidation [34].

iii) NO reduction: NO can be reduced by CO on CaO. The CO_2 present in the gas can poison catalytic sites and limit NO reduction [30]. The level of SO_2 can also affect this NO reduction mechanism. It has been observed that the CO oxidation was moderately inhibited by the presence of SO_2 due to a decrease in the radical inventory [37]. If CO oxidation is inhibited, the increase in CO concentration would favour the reduction of NO on CaO and also on the char surfaces [38].

Prior to the comparison of the results obtained with the different sorbents used in this work, the influence of Ca-sorbent addition was analyzed using limestone. A test without and with limestone addition was carried out using the anthracite as fuel and the "Granicarb" limestone (Ca/S=3) as sorbent. The SO_2, CO, NO and N_2O concentrations measured in the experiments are shown in Figure 4. As it can be seen, after feeding the limestone, the SO_2 concentration began to decrease to almost reach the stationary state, the NO concentration increased around 40 vppm and the CO and N_2O concentrations slightly decreased, around 50 and 12 vppm respectively. The

oxy-fuel results in Figure 4 confirm some of the observations made in conventional combustion and summarized above. The introduction of limestone would favour NH_3 oxidation on CaO to produce NO. Besides, the introduction of limestone decreases SO_2 concentration and therefore CO oxidation is less inhibited, leading to a slight decrease in CO concentration. If less CO is present, the catalytic reduction of the NO formed will be less favoured, which would also favour the NO increase observed in Figure 4. A lower value of SO_2 concentration will also favour N_2O decomposition, as observed in this experiment, because N_2O decomposition is inhibited by SO_2 [32].

Figure 5 shows the effect of the type of sorbent fed to the combustor on the SO_2, NO and N_2O emissions under oxy-fuel conditions. In Figure 5(B), NO emissions decreased following the sequence: "Sierra de Arcos" dolomite > "Horcallana" limestone > "Granicarb" limestone. It can also be observed how this decrease in the NO emissions is correlated with an increase in the SO_2 emission values which are shown in Figure 5(A). It seems that NO chemistry is influenced by the presence of SO_2, capable of inhibiting the NH_3 oxidation to NO and CO oxidation. According to this, the lowest NO emissions would correspond to the sorbent with the lowest sulphur retention capacity, as it was described for conventional combustion in air. In addition, the highest NO emissions obtained with the dolomite, even using a lower Ca/S molar ratio, could be due to the fact that the pores in dolomite are not blocked with $CaSO_4$ as fast as in limestones because the presence of MgO in dolomite contributes to maintain the porosity of the material. Therefore CaO remains more accessible than in the case of limestone. On the other hand, some studies reported that MgO in dolomite can also contribute to the catalytic reduction of NO with CO [39] although this effect was not seen in our experiments. The inhibiting effect of SO_2 on N_2O decomposition is not clearly appreciated in any of the conditions tested in Figure 5(C).

In the previous section, it was speculated that the effect of the amount of water vapour on decreasing NO formation shown in Figure 3 could be explained by the influence of the sorbent present in the bed. A larger fraction of water vapour in the combustor could inhibit the oxidation

of NH_3 to NO on CaO active sites minimizing NO formation. In order to investigate this possibility, an additional test with steam recirculation and without feeding limestone to the combustor was carried out at the same experimental conditions as those described in a previous paper [17]. As it can be seen in Figure 6, when steam was introduced a sharp decrease in NO emission was observed. This reduction was very similar to that observed in the test with limestone addition. Therefore, it could be concluded that wet recirculation would produce a great decrease in the NO concentration in comparison with dry recirculation in a FBC independently of the presence of a Ca-based sorbent. It can also be observed that the change in the CO and N_2O concentrations was almost negligible as in the test with limestone addition [17].

3.3.2 Effect of the particle diameter of the sorbent and the residence time

Figure 7 shows the effect of the mean particle size of the sorbent used on NO and N_2O emissions together with the corresponding SO_2 concentration recorded in the experiments. In this case, the sorbents used were "dolomite "Sierra de Arcos" and "Granicarb" limestone. Again, the correlation between NO emissions and SO_2 concentration in the bed could be observed. The larger the particle diameter of the sorbent, the higher the SO_2 concentration and unconverted CaO, as the SO_2 diffusion in the sorbent pores is less favoured. As mentioned before, higher SO_2 concentrations are linked to lower NO emission values. The effect of SO_2 can also be observed in the values of N_2O. The higher the SO_2, the higher the inhibition effect on N_2O decomposition and therefore, slightly higher N_2O emissions are observed.

Figure 8 shows the effect of the mean residence time of solids on NO and N_2O emissions using "Granicarb" limestone as sorbent. In the experiments, the residence time was increased by decreasing the flow of sand introduced to the fluidized bed, which leads to a higher fraction of sorbent in the bed. On one hand, as can be observed in Figure 8, the increase in the residence time decreases the concentration of SO_2 which results in the increase of NO emissions. Furusawa et al. [38] also observed a decrease in NO reduction with increased residence time of the solids

in the fluidized bed under conventional combustion with air. On the other hand, the effect of the mean residence time of solids on N_2O emissions was almost negligible.

3.4 Effect of the oxygen concentration

In conventional air combustion, Åmand and Leckner [21] determined that an increase in the oxygen concentration increased N_2O and NO emissions, but the increase seemed to be larger for N_2O than for NO. Some authors corroborated this finding [19]. Nevertheless, Collings et al. [23] pointed that the effect of an oxygen concentration increase is stronger at lower than at higher temperatures.

Figure 9 shows the corresponding results obtained in the FBC operating under oxy-fuel mode with anthracite as fuel and "Granicarb" limestone as sorbent. In all the cases, the experiments were designed so that around 3.75 ± 0.75 vol.% oxygen concentration was reached in the outlet stream of the fluidized bed. Considering this, an increase in the oxygen introduced was compensated with an increase of the coal flow rate being introduced. Therefore, if the amount of coal introduced increases the NO and N_2O concentrations expressed in vppm also increases. However, when the concentrations are normalized (expressed in mg/MJ), these concentrations decrease with the increase in the inlet oxygen concentration because more unconverted char could be present in the bed and this would favour NO reduction on the char surface. Nevertheless, N_2O emissions seem to be less affected by the changes in the initial oxygen concentration than NO.

4. Conclusions

The influence of different parameters affecting NO and N_2O emissions under oxy-fuel combustion in a fluidized bed reactor was analyzed using different coals as fuels (anthracite, bituminous and lignite) and Ca-based sorbents (limestones and dolomite) and compared with the findings already observed in literature for conventional combustion using air.

In the oxy-fuel combustion experiments, NO and N_2O emissions followed the same trend with temperature as in air-firing combustion: NO emission increased as temperature increased while N_2O emissions decreased. Besides, as it was the case in combustion using air, the highest levels of NO and N_2O at the outlet of the fluidized bed correspond to the experiments with the highest rank coals. However, a reduction in the total fuel-N conversion to NO and N_2O in fluidized bed combustion under oxy-fuel conditions was observed.

The moisture content in the coal had a similar effect on the reduction of NO as the recirculation of steam. An increase in the coal moisture content decreased NO emissions and hardly affected N_2O emissions. The same effect was observed by increasing the oxygen concentration fed to the combustor.

The calcium-based sorbent was proved to play a role in the NO and N_2O chemistry also under oxy-fuel combustion conditions. As it was observed in conventional combustion with air, the sulphur retention capacity of the different sorbents was the most influencing characteristic, as it affected the final SO_2 concentration and the amount of free CaO present in the fluidized bed. The lowest NO emissions corresponded to the sorbent with the lowest sulphur retention capacity. In general, the N_2O emission values were not as affected by the changes in SO_2 concentration as NO emission values. Besides, it was found that an increase in the sorbent particle size and a decrease in the sorbent residence time decreased the NO emissions. Finally, the high levels of CO_2 in the oxy-fuel experiments seem not to affect the catalytic activity of the sorbent in any of the experimental conditions tested.

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