

Fate of pollutant components during chemical looping combustion of coal

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Abstract

The recently developed Chemical Looping Combustion technology (CLC) is nowadays considered an interesting option to capture CO₂ at low cost in fossil fuelled power plants. In this technology, the oxygen needed for combustion is supplied by an oxygen carrier, normally a metal oxide, avoiding the mixture of the fuel and air. In the past years, significant advances have been achieved in the combustion of both gaseous and solid fuels. Nevertheless, pollutant emission from CLC systems has received little attention. This paper focuses on the study of sulphur and nitrogen emissions in the combustion of a lignite in a 500 W_{th} CLC unit. Ilmenite was used as oxygen carrier, as it is one of the most common materials used for CLC of solid fuels. Emissions from both fuel and air reactors were studied. The main sulphur species detected in the fuel reactor were H₂S and SO₂. The amount and proportion depended on the temperature of the fuel reactor. At high temperatures, low H₂S/SO₂ molar ratios were observed. Regarding nitrogen emissions, no NH₃, HCN or N₂O were registered in the fuel reactor. N₂ was the major product from fuel-N originated in the fuel reactor, together with small amounts of NO and NO₂. In the air reactor, sulphur and nitrogen were released from unconverted char as SO₂ and NO, respectively.

Introduction

In recent years, the concentration of different greenhouse gases in the atmosphere has increased significantly compared to pre-industrial levels. The major contribution to this increment corresponds to carbon dioxide [1]. The increase of CO₂ atmospheric concentration has been linked to global warming and this fact has awoken the interest in the mitigation of its emission. New technologies have been developed to facilitate CO₂ capture and subsequent storage (CCS).

Chemical Looping Combustion (CLC) is an emerging CCS technology which allows CO₂ capture from power plants at low cost [2]. The process is based on the transfer of oxygen from air to the fuel by means of a solid oxygen carrier avoiding direct contact between fuel and air. The oxygen carrier is normally a metal oxide, which circulates between two reactors, identified as fuel and air reactors. In the fuel reactor, the combustion of the fuel takes place while the oxygen carrier is reduced, yielding CO₂ and water. Once water is condensed, the outlet gas of the fuel reactor consists of an almost pure CO₂ stream. The reduced oxygen carrier is then transferred to the air reactor, where it is re-oxidized in air, before starting a new redox cycle. The net combustion heat released in this process is the same as in usual combustion.

The most common configuration for chemical looping combustion is two interconnected fluidized beds. This configuration allows the combustion of both gaseous and solid fuels [2]. There are two alternatives to burn a solid fuel in a CLC system. In the first, the solid fuel is gasified *in-situ* in the fuel reactor using steam or CO₂ as fluidization agents and the oxygen carrier particles react with the gaseous products of coal devolatilization/gasification, as shown in Figure 1.

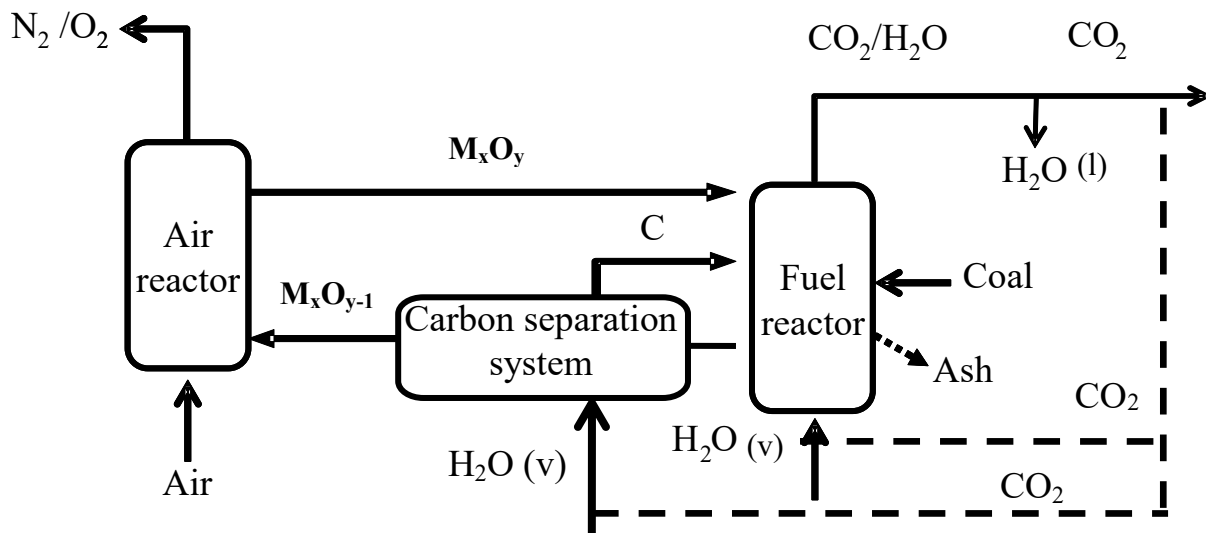


Figure 1. *In situ* Gasification Chemical Looping Combustion process.

(- - - -) Optional streams to replace H₂O (v) by CO₂ in the fluidizing gas of fuel reactor and/or the carbon separation system

In the second, the solid fuel is burned with the gaseous oxygen released by the oxygen carrier in the fuel reactor (Chemical Looping with Oxygen Uncoupling, CLOU). This paper focuses on the first alternative. Recent research activities in CLC with gasification *in-situ* of the solid fuel dealt with two main aspects. The first is finding the adequate oxygen carrier. In *iG-CLC*, some oxygen carrier losses are expected together with fuel ashes. Therefore, low-cost oxygen carriers are preferred. From the studies performed until now, Fe-based minerals or industrial residues are the most promising candidates [2]. Among them, ilmenite has been commonly used. The second aspect is the optimization of the fuel gasification, as it is the limiting step of this process [3-5]. The presence of unconverted char in the solid stream at the outlet of the fuel reactor implies a decrease in the carbon capture efficiency of the process. Once the char reaches the air reactor, it is burnt there releasing CO₂ that is not captured. Therefore, char conversion in the fuel reactor should be as high as possible. One of the options already being investigated is the incorporation of a carbon separation unit between fuel and air reactors where unconverted char could be separated from the oxygen carrier particles and recirculated back to the fuel reactor [6].

Another important aspect during the combustion process is the fate of different elements commonly present in coal which can lead to pollutant formation, such as sulfur and nitrogen. Traditionally, two different types of sulfur can be considered in coal: inorganic (disulfides and sulfates) and organic sulfur (bond to the hydrocarbon matrix). The amount of organic sulfur is usually one-half to one-third of the total sulfur. At high temperatures, most of the sulfur in coal is released as H₂S and CS₂ [7]. The further oxidation of these species leads to SO₂ formation, which has been found to be responsible for the acid rain.

Fuel-bound nitrogen represents the main source of nitrogen oxides (NO_x) in most solid fuel combustion systems. The collective term NO_x represents NO , NO_2 and N_2O . Nitric oxide and nitrogen dioxide are also acid rain precursors and participate in the generation of photochemical smog, while nitrous oxide is a greenhouse gas. During the coal particle devolatilization, the fuel-N is distributed between the volatiles and char. The distribution of nitrogen between char and volatiles, as well as the volatile nitrogen composition, depends mainly on the fuel structure and the temperature [8]. At temperatures typical for fluidized bed combustion, HCN together with NH_3 and HNCO can be released during coal pyrolysis, in particular for low rank coals and biomass. These species can be oxidized to NO or, depending on the stoichiometry or fuel-N concentration, they may be converted to N_2 [8].

Sulphur and nitrogen emissions from solid fuel fired systems have been largely investigated in conventional combustion conditions during the last decades, but pollutant emission in CLC combustion of solid fuels has received little coverage in literature. Up to date, only few studies dealing with sulfur and nitrogen compounds emission in coal combustion can be found in literature [9-13]. Regarding sulfur compounds emission, Berguerand and Lyngfelt [13] performed experiments using a petroleum coke as fuel and ilmenite as oxygen carrier. They calculated the total concentration of the sulfur-containing gases (SO_2 and H_2S) assuming that the S/C ratio in the petcoke that they used as fuel was the same as in the gas leaving the fuel reactor. The H_2S content was deduced from the measured SO_2 content. The ratio $\text{SO}_2/\text{C}_{\text{tot}}$ was presented as an indication of the H_2S conversion to SO_2 . From the laboratory measurements, they concluded that most of the sulfur released was associated with the char conversion. Shen et al. [9] used a $\text{NiO}/\text{Al}_2\text{O}_3$ oxygen carrier to burn coal in a 1 kW_{th} prototype. They analyzed sulfur emissions both in fuel and air reactors and observed that a high fuel reactor temperature favored H_2S transformation to SO_2 . The increase of SO_2 in the fuel reactor accelerated the reaction of SO_2 to form COS [14]. Therefore, COS concentration in the fuel reactor increases with the fuel reactor temperature.

Song et al. [10,11] studied the fate of fuel-N in experiments with an anthracite and a bituminous coal using two different oxygen carriers, i.e. $\text{NiO}/\text{Al}_2\text{O}_3$ and hematite. They concluded that N_2 was the only product of fuel-N conversion in the fuel reactor due to NO reduction and the consumption of NO_x precursors (HCN and NH_3). They observed that the concentration of N_2 in the fuel reactor exit gas increased with the fuel reactor temperature. They also analyzed NO_x emissions in the air reactor and determined that the proportion of char-N converted to NO in the air reactor increased when the fuel reactor temperature increased from 850 to 950°C .

The concern about H_2S , SO_2 and NO_x formation in CLC systems is not only environmental due to the harmful emissions to the atmosphere, but also operational. The presence of these compounds in the outlet stream of the fuel reactor can also affect the quality of CO_2 to be transported and stored, still subject of research. Therefore, the aim of the present work will be to analyze the sulfur and nitrogen release in the fuel and air reactors in a continuous 500W_{th} CLC unit burning a Spanish lignite and using ilmenite, a Fe-based oxygen carrier material.

Experimental

Materials used

Ilmenite has been one of the most used oxygen carriers in *iG*-CLC of coal [15-18]. The ilmenite used in this work was provided by the Norwegian company Titania A/S and was

extracted from a natural ore. The active phases in ilmenite are Fe_2O_3 and Fe_2TiO_5 . The ilmenite was received in its reduced form, FeTiO_3 . Therefore it was calcined in air at 950°C during 24 hours to ensure complete oxidation. Then it was sieved to a particle size of $+100\text{-}300\ \mu\text{m}$. An increase in ilmenite reactivity has been observed with the number of redox cycles, both using gaseous and solid fuels [5,19]. The batch sample used in this work was previously activated. Therefore, the reactivity of ilmenite during all the tests can be considered as constant. The main properties of the activated ilmenite used are summarized in Table 1.

Table 1. Main properties of activated ilmenite particles

	Activated ilmenite
XRD phases	Fe_2TiO_5 , Fe_2O_3 , TiO_2
Crushing strength (N)	2.0
Oxygen transport capacity (%)	4
Particle density (kg/m^3)	4200
Porosity (%)	18
BET Surface (m^2/g)	0.4

A Spanish lignite ($+200\text{-}300\ \mu\text{m}$) was used as fuel in the experiments. Table 2 shows the proximate and ultimate analyses of the coal.

Table 2. Proximate and ultimate analyses of lignite

	(wt %)		(wt %)
Moisture	12.5	Carbon	45.4
Ash	25.2	Hydrogen	3.9
Volatile matter	28.6	Nitrogen	0.6
Fixed carbon	33.6	Sulfur	5.2
		Oxygen	7.2

Experimental setup and procedure

The coal combustion experiments were performed at the ICB-CSIC-s1 unit, previously used in other works from our research group [16]. The scheme of the setup is presented in Figure 2. This experimental unit was composed of two interconnected fluidized bed reactors, (1) and (3) in Figure 2, electrically heated by their corresponding furnaces (11). The fuel reactor (FR) (1) and the air reactor (AR) (3) are connected by a fluidized bed acting as loop seal (2), a riser (4) for solids transport from the air to the fuel reactor, a cyclone to recover the entrained solids (5) and a solid valve (8) to control the solid flow fed to the fuel reactor.

The fuel reactor consisted of a bubbling fluidized bed (50 mm ID and 200 mm bed height). Coal is fed by a screw feeder (9) at the bottom of this bed and above the fuel reactor distributor plate in order to maximize the time that volatile matter is in contact with the oxygen carrier in the bed. In order to avoid gas backflow from the fuel reactor, a small nitrogen flow was introduced to the screw feeder. In the fuel reactor, the oxygen carrier is reduced by the volatile matter and the CO and H_2 produced in coal gasification. The fuel-reactor is fluidized by steam, which acts also as a gasifying agent.

The reduced oxygen carrier particles overflow through a U-shaped fluidized bed loop seal (50 mm ID) to the air reactor, avoiding mixing gaseous atmospheres between fuel and air reactors. The loop seal was fluidized using nitrogen. Preliminary results showed that about 65% of the N₂ introduced to fluidize the loop seal derived to the fuel reactor and the rest to the air reactor. Due to this design, unconverted char particles may be transported together with the oxygen carrier to the air reactor, decreasing the CO₂ capture efficiency of the process. To avoid this loss of carbon, a carbon stripper could be placed after at the fuel reactor outlet. However, the absence of a carbon stripper facilitates the interpretation of the effect of different operational conditions on the results obtained, which is the aim of this work.

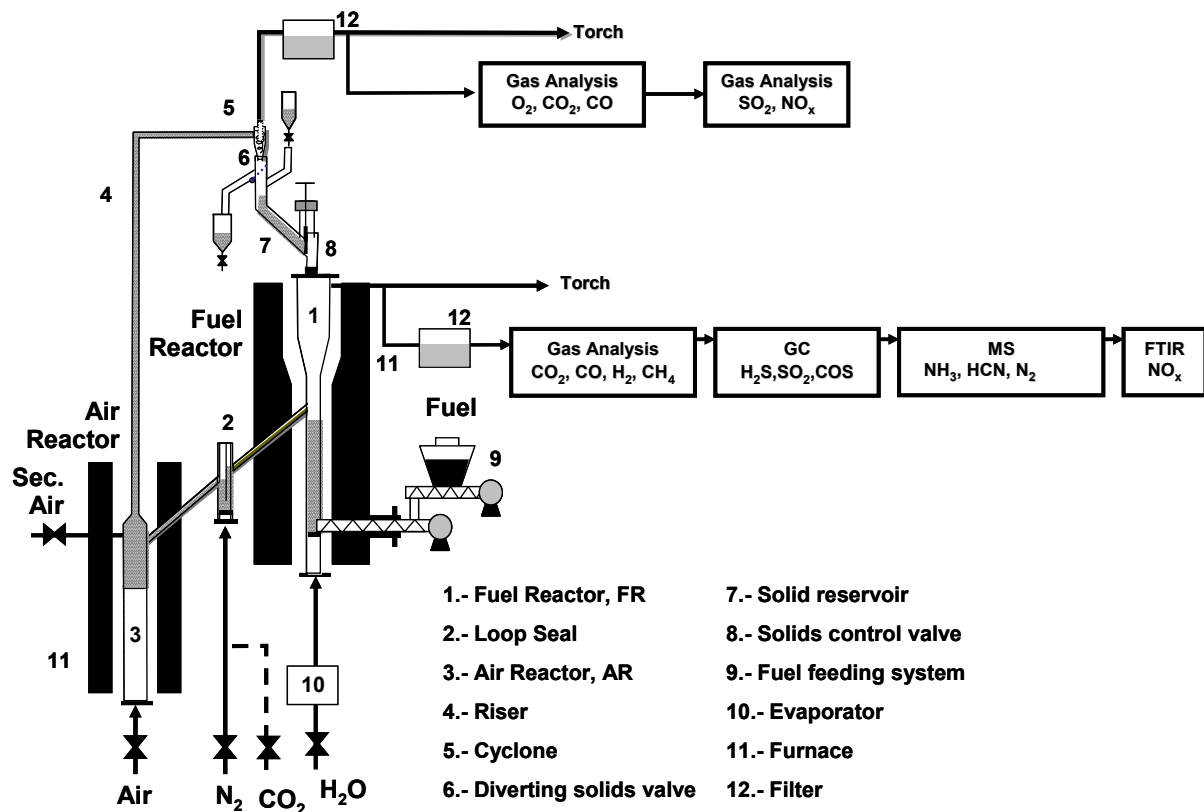


Figure 2. Experimental unit ICB-CSIC-s1

The reduced oxygen carrier is re-oxidized in the air reactor (80 mm ID and 100 mm bed height). Secondary air was introduced at the top of the bubbling bed to help particle entrainment. The outlet stream from the air reactor was sent up the riser to the stack through a high-efficiency cyclone and a filter. The oxidized solid particles recovered by the cyclone were sent to a solid reservoir (7) which acts as a loop seal avoiding the leakage of gas between the fuel reactor and the riser. The solid flow rate of regenerated oxygen carrier to the fuel reactor was controlled using a solid valve placed in the solid reservoir. A diverting solid valve (6) allowed the measurement of the solids flow rates at any time.

CO, CO₂, H₂, and CH₄ concentration in the fuel reactor outlet stream and CO, CO₂ and O₂ from the air reactor were continuously recorded. Nondispersive infrared (NDIR) analysers (Maihak S710/UNOR) were used for CO, CO₂, and CH₄ concentration determination; a paramagnetic analyzer (Maihak S710/OXOR-P) was used for O₂ concentration measurement and a thermal conductivity detector (Maihak S710/THERMOR) was used for H₂. The

analysis of sulphur and nitrogen species required different instrumentation. SO₂ was determined using an infrared Siemens Ultramat 23 analyzer. For the determination of H₂S and COS a gas chromatograph (Varian 3400-CX GC) equipped with a PORAPAK-Q packed column for chromatographic separation and a sulfur-specific flame photometric detector (FPD) was used. NH₃, HCN and N₂ were measured with a quadrupole mass spectrometer from Pfeiffer, while NO_x were determined using an FTIR spectrometer Temex CX 4000.

The ilmenite inventory was 3 kg. The solid level in the fuel reactor was fixed, corresponding to 0.7 kg of ilmenite sample. The steam flow to the fuel reactor was 200 L_N/h, corresponding to a velocity of 0.14 m/s at 900°C. In the air reactor the total primary air flow was 1800 L_N/h (corresponding to a velocity of 0.45 m/s at 900°C). The secondary air flow was 400 L_N/h. Considering both primary and secondary air flows, the gas velocity in the riser was 2 m/s. The nitrogen flow in the loop seal was 100 L_N/h. The circulation flow rate was measured and controlled to be about 7 kg/h and the coal flow was about 50 g/h. These conditions ensure that the operation is over stoichiometric conditions, so that there is enough oxygen supply by the oxygen carrier. During operation, temperatures in the fuel reactor bed and freeboard, air reactor bed and riser were monitored as well as the pressure drops in selected points in the system, such as the fuel reactor bed, the air reactor bed and the loop seal. The temperature in the air reactor was maintained at around 950°C and the fuel reactor temperature was varied from 875 to 930°C. The fuel reactor freeboard temperature was kept constant at about 910°C in all the experiments. A total of 35 hours of continuous operation feeding fuel and 55 hours of continuous fluidization were registered.

Data evaluation

Two main parameters are defined in order to evaluate the combustion performance: the carbon capture efficiency and the oxygen demand. All the calculations presented considered the effective coal fed to the system. Thus, the carbon balance considered the carbon exiting the fuel reactor as gaseous compounds and the carbon in the char transported to the air reactor and burned to yield CO₂.

The carbon capture efficiency (η_{CC}) represents the removal of carbon that would otherwise be emitted to the atmosphere. The carbon capture efficiency is defined as the fraction of the carbon introduced converted to gas in the fuel reactor. Only CH₄, CO and CO₂ were considered.

$$\eta_{CC} = \frac{F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR}}{F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} + F_{CO_2,AR}} \quad (1)$$

where $F_{i,FR}$ is the i species molar flow in the fuel reactor inlet/outlet stream and $F_{CO_2,AR}$ is the CO₂ gas flow in the air reactor.

The carbon captured in the system is the carbon contained in the volatiles and the carbon in the char that is gasified. Thus, the carbon capture efficiency depends on the fraction of char that has been gasified. The char conversion (X_{char}) is defined as the fraction of carbon in the effective char fed to the fuel reactor which is released to the fuel reactor exhaust gas stream:

$$X_{char} = \frac{F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} - F_{C,vol}}{F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} + F_{CO_2,AR} - F_{C,vol}} = \frac{F_{C,char,eff} - F_{CO_2,AR}}{F_{C,char,eff}} \quad (2)$$

The gasified char in the fuel reactor was calculated as difference between the carbon in the outlet gases of the fuel reactor and the carbon flow coming from the volatile matter, $F_{C,vol}$. The carbon content in the volatiles is directly calculated using the ultimate and proximate analysis of the coal as the difference between the total carbon in coal and the fixed carbon. $F_{C,char\ eff}$ is the carbon in the effective char flow introduced in the CLC system and is calculated by means of the carbon mass balance in the plant.

The oxygen demand (Ω) refers to the oxygen needed to convert H_2 , CO and CH_4 in the outlet gas from the fuel reactor to CO_2 and H_2O . Therefore, the oxygen demand evaluates the efficiency of the combustion process and is defined as the fraction of oxygen lacking to achieve a complete combustion to CO_2 and H_2O of the fuel reactor product gas in comparison to the oxygen demand of the introduced coal, $O_{2,demand,coal}$.

$$\Omega = \frac{O_{2,demand,gases,FR}}{O_{2,demand,coal}} = \frac{0.5 \cdot F_{CO,FR} + 2 \cdot F_{CH_4,FR} + 0.5 \cdot F_{H_2,FR}}{O_{2,demand,coal}} \quad (3)$$

Results and Discussion

CLC performance

The performance of lignite combustion in the CLC system can be evaluated through the carbon capture efficiency and the oxygen demand. The evolution of both parameters with the fuel reactor temperature is presented in Figure 3. The carbon capture efficiency increased with temperature from 82% at 875 °C to 93% at 930°C. Char conversion values were also calculated and varied between 74.2% at 875°C and 89.3% at 930°C. As lignite presents high volatile content compared to other higher-rank coals, high carbon capture efficiencies can be expected [20].

The oxygen demand values in Figure 3 decreased when the temperature increased from 5% at 875°C to 4.1% at 930°C. It is known that the contact between volatile matter and oxygen carrier particles in the fuel reactor bed is a determinant variable to obtain high combustion efficiencies in the fuel reactor and thus, low oxygen demand [21]. Most of the volatiles are released in a plume, so that it is possible that some of them escape as unburnt.

Fate of sulphur

The lignite used in the experiments presents high sulphur content. As mentioned before, sulphur compounds in the gaseous products from both fuel and air reactors were analyzed. Figure 4 summarizes the main results for sulphur emissions.

In the fuel reactor, H_2S , SO_2 and COS could be present in the outlet stream. The presence of COS might be favoured by the presence of CO and CO_2 . However, only H_2S and SO_2 were detected as main sulphur species at all temperatures tested. The molar ratio between H_2S and SO_2 depended on temperature. Figure 4(A) presents the evolution of this ratio with temperature, together with the corresponding char conversion values. As temperature increases, the char conversion increases and the H_2S/SO_2 molar ratio slightly decreases. According to these results, higher temperatures would favour the conversion of H_2S , from both volatiles and char gasification, to SO_2 .

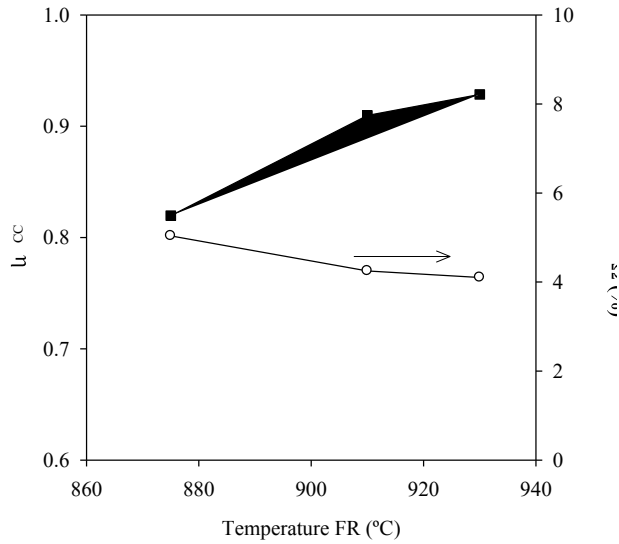


Figure 3. Carbon capture efficiency (η_{CC}) and oxygen demand (Ω) at different temperatures in the fuel reactor

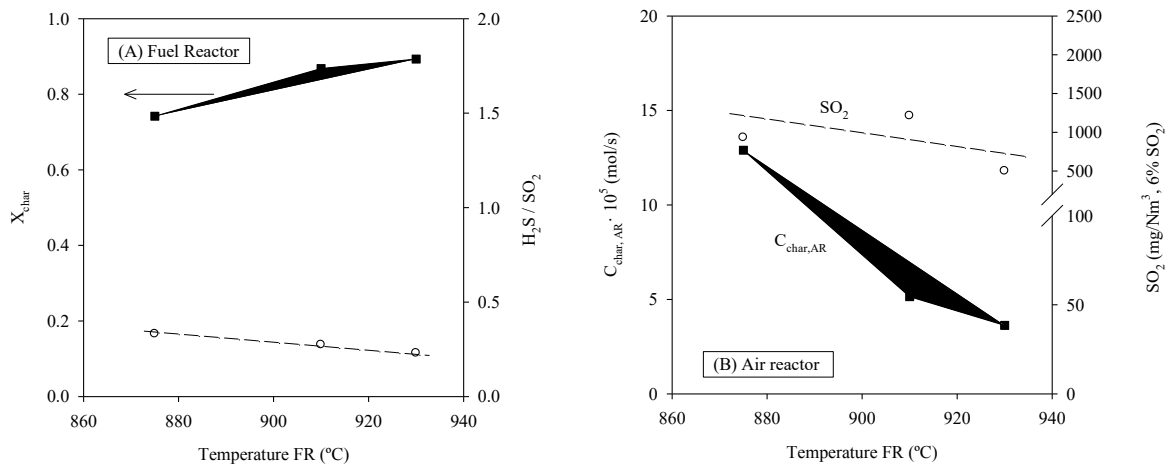


Figure 4. (A) Char conversion and H_2S/SO_2 molar ratio in the fuel reactor and (B) Carbon molar flow and SO_2 emissions in the air reactor at different fuel reactor temperatures

Figure 4(B) presents the analysis of sulphur emissions in the air reactor. In this case, sulphur emissions are originated in the combustion of the unconverted char reaching the air reactor. Therefore, the only sulphur species detected was SO_2 . Figure 4(B) shows the carbon molar flow reaching the air reactor and the SO_2 emissions (mg/Nm^3 , 6% O_2) as a function of the fuel reactor temperature. As the fuel reactor temperature increases, more char is converted in the fuel reactor and less carbon reaches the air reactor. Correspondingly, the SO_2 emissions decrease to a value of $500 mg/Nm^3$ (6% O_2) at the highest temperature. Lower SO_2 emissions could be reached if the fuel reactor temperature increases.

It is also interesting to analyze the sulphur distribution between fuel and air reactors. Figure 5 presents the percentage of the total sulphur fed which was released in the fuel and air reactors at different fuel reactor temperatures. At any of the temperatures tested, more than 90% of the sulphur was released in the fuel reactor. The percentage of sulphur released in the fuel reactor increased with temperature. Therefore, the amount of sulphur released in the air reactor decreased with temperature.

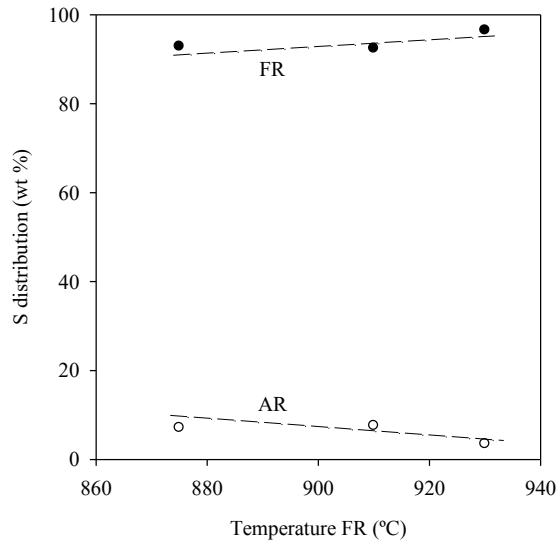


Figure 5. Sulfur emission distribution in fuel and air reactors

Fate of nitrogen

The nitrogen present in the lignite may be released during devolatilization as NH_3 or HCN . Depending on the combustion conditions, these nitrogenated species can evolve to N_2 or NO_x . In order to carry out a nitrogen balance, N_2 as inert was avoided in all the gas fed to the system. Therefore, CO_2 was used to fluidize the loop seal and to avoid the backflow in the screw feeder. As it was done with sulphur emissions, the presence of the abovementioned species was analyzed both in the fuel and air reactors. The main results are presented in Figure 6.

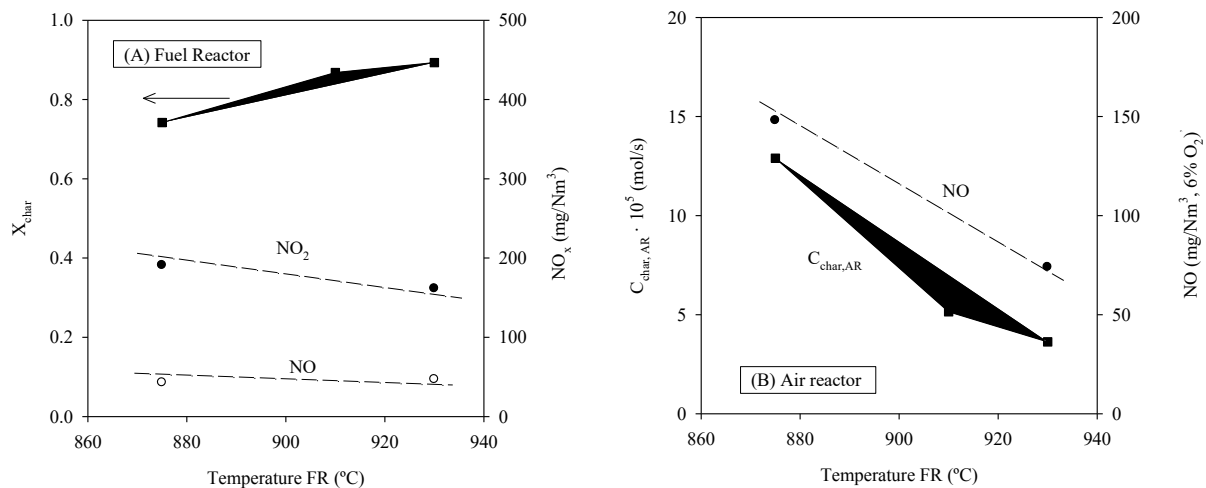


Figure 6. (A) Char conversion and NO_x content in the fuel reactor and (B) carbon molar flow and NO emissions in the air reactor at different fuel reactor temperatures

Figure 6(A) shows the corresponding results for the fuel reactor. Only traces of NH_3 and HCN were identified. NO and NO_2 were detected in very little amounts, but no N_2O . Therefore, the major nitrogenated compound observed was N_2 . Around 92% of the nitrogen fed was converted to N_2 in the fuel reactor. This in accordance with previous results reported by Song et al. [10,11]. Figure 6(B) presents the results obtained in the air reactor, where the nitrogen contained in the unconverted char was released as NO . No trace of N_2O or NO_2 was

detected. The amount of NO present in the outlet stream depends on the fuel reactor temperature and decreases to a value of 74 mg/Nm³ (6% O₂).

Conclusions

The fate of sulphur and nitrogen was evaluated at different fuel reactor temperatures in the combustion of lignite in a 500W_{th} CLC unit using ilmenite as oxygen carrier. The sulphur and nitrogen compounds present in both fuel and air reactors were analyzed. Regarding sulphur emissions, more than 90% of the sulphur in coal was released in the fuel reactor as H₂S or SO₂. The molar H₂S/SO₂ ratio slightly decreased with the fuel reactor temperature. In the air reactor, sulphur was released as SO₂ and the emission level was related to the amount of unconverted char being burned in the air reactor. Regarding the fate of nitrogen in coal, N₂ was the main compound in the fuel reactor. It represented around 92% of the nitrogen fed. In the air reactor, the nitrogen released by the unconverted char was emitted as NO.

Acknowledgments

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Nomenclature

$C_{char, AR}$: carbon flow from the char to the air reactor (mol/s)
 $F_{CO_2, AR}$: carbon dioxide molar flow in the air reactor (mol/s)
 $F_{i, FR}$: i species molar flow in the fuel reactor inlet/outlet stream (mol/s)
 $F_{C, vol}$: carbon flow from the volatile matter (mol/s)
 $F_{C, char\ eff}$: carbon in the effective char flow (mol/s)
 $O_2\ demand, coal$: oxygen flow needed to completely burn the fuel (mol/s)
 R_{OC} : Oxygen transport capacity
 X_{char} : char conversion

Greek symbols

Ω : oxygen demand

η_{CC} : carbon capture efficiency

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