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Release of pollutant components in CLC of lignite

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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 the past years, significant advances have been achieved in the combustion of both gaseous and solid fuels. Nevertheless, pollutant gas emissions from CLC systems have received little attention. This paper focuses on sulphur, nitrogen and mercury emissions during lignite combustion 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. 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. The higher the temperature, the more H₂S converted to SO₂. In the air reactor, the sulphur in the unconverted char was released as SO₂. Regarding the emission of nitrogen in coal, most of the nitrogen was found as N₂ at the outlet of the fuel reactor. No NH₃ or HCN were registered and only small amounts of NO were detected. The nitrogen contained in the char reaching the air reactor was released as NO. Mercury speciation was also analyzed and the ratio Hg²⁺/Hg⁰ determined. In the fuel reactor, the major mercury species was Hg⁰ and in the air reactor Hg²⁺. The incorporation of a carbon separation unit between fuel and air reactors would help to reduce the sulphur emissions in the air reactor and comply with the current legislation for power generation systems.

Keywords: combustion, coal, CO₂ capture, chemical looping, ilmenite, emissions

1. 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 (IPCC, 2007). 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 technology which allows CO₂ capture from power plants at low cost (Eide et al., 2005). The process is based on the oxygen transfer from air to fuel by means of a solid oxygen carrier avoiding direct contact between fuel and air. The oxygen carrier is normally a metal oxide. The most common configuration for chemical looping combustion is two interconnected fluidized beds, identified as fuel and air reactors, with the oxygen carrier material circulating between them. 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 so that a new redox cycle can be started.

CLC allows the combustion of both gaseous and solid fuels. 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 (Cao et al., 2006). In the second, the solid fuel is burned with the gaseous oxygen released by the oxygen carrier in the fuel reactor. This process is referred as Chemical Looping with Oxygen Uncoupling (CLOU) (Mattisson et al., 2009). This paper focuses on the first alternative, denoted as *iG*-CLC.

Recent research activities in *i*G-CLC have been focused on three main aspects. The first one is finding the adequate oxygen carrier. Some oxygen carrier losses are expected in the drainage of 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. Among them, ilmenite has been commonly used (Adánez et al., 2012). The second aspect is the optimization of the fuel gasification, as it is already known that the gasification of the solid fuel is the limiting step of this process (Dennis et al., 2006; Leion et al., 2007; Cuadrat et al., 2011). The presence of unconverted char in the solid stream at the fuel reactor outlet 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 (Cao et al., 2006). Finally, the minimization of unburned products at the fuel reactor outlet is another focus of interest. The presence of unburned compounds reduces the energetic efficiency of the CLC process. The use of an oxygen-polishing step downstream where pure oxygen would be used to burn these compounds is a widespread solution, although some other alternatives are possible (Gayán et al., 2013).

1.1 Pollutants in coal combustion: S, N and Hg

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, nitrogen or mercury. Traditionally, three different types of sulfur can be considered in coal: pyritic, sulphate (disulfides and sulfates) and organic sulfur (bond to the hydrocarbon matrix). The amount of organic sulfur is dependent on the coal rank although it 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 (Attar, 1978). Further oxidation of these species leads to SO₂ formation, which has been found to be responsible for the acid rain. During the coal particle devolatilization, fuel-N is distributed between volatiles and char. The distribution of nitrogen between char and volatiles, as well as the volatile composition, depends mainly on the fuel structure and the temperature (Glarborg et al., 2003). At temperatures typical for fluidized bed combustion, HCN together with NH₃ and HNCO can be released during pyrolysis from fuel-bound nitrogen, in particular for low rank coals and biomass. These species can be oxidized to NO_x or, depending on the stoichiometry or fuel-N concentration, they may be converted to N₂ (Glarborg et al., 2003). The collective term NO_x represents NO, NO₂ and N₂O. 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 conventional combustion processes, mercury in coal evaporates yielding Hg⁰, HgO and HgCl₂. The amount of each species in the gas phase depends on how the mercury is bonded in coal and on the compounds also present in the gaseous stream, mainly particulates and chlorine (Olson and Mibeck, 2005). Hg⁰ is the thermodynamically stable form in the highest temperature regions of combustors and gasifiers and remains the dominant form in the relatively reducing conditions of a gasification flue gas. If temperature decreases, Hg⁰ will react to form Hg²⁺ compounds (Galbreath and Zygarlicke, 1996). In case of existence of a wet flue gas desulphurization unit (FGD), the oxidized mercury would be removed there. Hg⁰ is more difficult to control because of its high vapour pressure and low water solubility. Once emitted through the stack, it may remain in the atmosphere and is likely to enter the food chain with the risk of affecting human health.

1.2 The relevance of pollutants in CLC

Compared to conventional combustion, the concern about H₂S, SO₂, NO_x and Hg⁰/Hg²⁺ formation in CLC systems is not only environmental but also operational. Two gaseous

streams exit from an *i*G-CLC unit: (i) a CO₂-concentrated stream from the fuel reactor and (ii) a lean-air stream from the air reactor. Char in the fuel reactor is gasified while char in the air reactor is burned. This difference can affect the release of pollutants in both reactors. The presence of pollutants in the gas stream from the air reactor can be managed similarly to the case of conventional combustion. The gaseous outlet stream from the air reactor is emitted directly to the atmosphere. This means that the amounts of sulphur, nitrogen and mercury compounds exiting the air reactor should comply with the current legislation for pollutant emissions from power generation systems. In the Directive 2010/75/UE, the limit for SO₂ and NO_x emission from power generation plants burning solid fuels up to 300 MW_{th} is set to 200 mg/Nm³ (6% O₂ vd.). The only reference for mercury can be found in this Directive for incineration systems. In this case, the maximum mercury emission is set to 0.05 mg/Nm³ (normalized to 10% O₂ vd. in the outlet stream).

The presence of other components than CO₂ (not only pollutants) in the CO₂ stream is important regarding the quality of the CO₂. The final composition of the CO₂ stream depends on the fuel, the combustion technology and the CO₂ capture process used (post-combustion, pre-combustion and oxyfuel capture) (Anheden et al., 2004). In order to lay out recommendations about CO₂ quality not only the origin of the captured CO₂ but also the transportation means (pipeline, shipping) and the storage location (geological or ocean storage) should be taken into account. Some of the first specifications for CO₂ quality were intended for Enhanced Oil Recovery (EOR) applications. The specifications for the CO₂ stream were case-specific. The Weyburn Pipeline (IPCC, 2005) and Gullfalks¹ experiences

¹ CO₂ supply report: document prepared by Elsam A/S, Kinder Morgan CO₂ Company L.P., NewEnergyStatoil
<http://www.co2.no/download.asp?DAFID=17&DAAID=6>.

can be cited as examples. The European project ENhanced CAPture of CO₂ (ENCAP)² updated the knowledge gained during last years and presented a guideline about CO₂ quality. More recently, the work conducted as a part of the Euroepan 6th Framework Programme DYNAMIS³ completed the guidelines summarized in the ENCAP project giving new recommended values for the other components found in the CO₂ stream (de Visser et al., 2008). In this case, the recommendations were intended for pipeline transportation. Table 1 shows the specifications given for different components.

The presence of other compounds in CO₂ streams is associated with additional energy requirements in the CO₂ transport and storage chain. These compounds may shift the boundary of the two-phase region to higher pressures and therefore higher operating pressures are required to maintain CO₂ in dense phase (de Visser et al., 2008). The transport capacity would be also reduced because these impurities occupy volume. Moreover, the impurities would lower the CO₂ density and therefore the storage capacity. Other effects of the presence of other compounds in the CO₂ stream are the risk of corrosion and hydrate formation, together with free water formation (EASAC, 2013). Mercury is known to accumulate and attack aluminium components. Corrosion can be also caused when CO₂ or H₂S are dissolved in water forming carbonic and hydrosulfuric acid, respectively. Actually, the joint presence of CO₂ and H₂S is more corrosive than H₂S alone (de Visser et al., 2008). Besides, H₂S, CO₂ and CH₄ can form hydrates with water which can plug the line and cause damage equipment. Regarding free water formation, there is no general agreement on the limit for water content in the CO₂ stream. Water content should be controlled more strictly when CO₂ is transported at low temperatures and pressures (de Visser et al., 2008). Besides

² ENCAP project. Enhanced capture of CO₂. 6th framework program. Contract number: SES6-CT-2004-502666.
<http://www.encapco2.org/index.htm>

³ Website DYNAMIS www.dynamis-hypogen.com

the operational issues highlighted above, health and safety considerations are also important when toxic compounds are present in the CO₂ stream. In case of sudden leakages of the transportation pipeline, the release to the atmosphere of compounds such as H₂S or CO represents a risk due to their toxicity. The limit values for their concentration in the CO₂ stream were also set to control the airborne concentration of the toxic compounds (de Visser et al., 2008). As it can be observed in Table 1, despite the high toxicity of mercury no recommendations for the mercury content in the CO₂ stream are included.

Sulfur, nitrogen and mercury emissions from solid fuel fired systems have been largely investigated under conventional combustion conditions during the last decades, but pollutant emission in CLC combustion of solid fuels has received little coverage in literature (Shen et al., 2010; Song et al., 2012, 2013). Shen et al. (2010) used a NiO/Al₂O₃ 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 H₂S transformation to SO₂. The increase of SO₂ in the fuel reactor accelerated the reaction of SO₂ to form COS. Moreover COS concentration in the fuel reactor increased with the fuel reactor temperature. In the air reactor, the exit gas contained SO₂ from the unconverted char being burned and from Ni₃S₂ oxidation. This sulfide is formed in the fuel reactor due to the reaction of H₂S with NiO, especially at high temperatures. Although Shen et al. (2010) point to a regeneration of the oxygen carrier in the air reactor, other authors indicated that part of the sulphur remained in the solid and total regeneration was not possible (Dueso et al., 2012). This fact together with the high toxicity of the nickel makes that Ni-based oxygen carriers were not considered suitable for *i*G-CLC. Compared to nickel, the use of Cu- or Fe-based oxygen carriers could reduce sulphur emissions from the air reactor (Forero et al., 2010; Cabello et al., 2013). Song et al. (2012, 2013) studied the fate of fuel-N in experiments with anthracite and bituminous

coal using two different oxygen carriers, i.e. NiO/Al₂O₃ and hematite. They concluded that N₂ was the only product of nitrogen transfer from fuel-N in the fuel reactor due to NO reduction and the consumption of NO_x precursors (HCN and NH₃). They observed that the concentration of N₂ 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 slightly increased when the fuel reactor temperature increased from 850 to 950°C. To date, the fate of mercury in a CLC system has not been analyzed. Therefore no information about mercury speciation in CLC is already available in literature.

1.3 Objective

The objective of the present work is the evaluation of the distribution of sulphur, nitrogen and mercury between fuel and air reactors during *i*G-CLC of Spanish lignite together with the identification of the main species in the gaseous streams. Lignite was chosen as fuel due to its high reactivity and high sulphur content. The measurement of the different pollutants will be performed simultaneously, which is the novelty of this work compared to others available in literature. This will allow to consider for the first time the synergetic effects that may be present. Besides, an evaluation of the measures needed to fulfil pollutant emission laws and attain certain CO₂ quality will be done based on the results obtained in the continuous unit.

2. Experimental

2.1 Materials used

Ilmenite has been one of the most used oxygen carriers for *in situ* gasification-CLC of coal (Berguerand and Lyngfelt, 2008; Bidwe et al., 2011; Cuadrat et al., 2011; Schwebel et al., 2012). 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 Fe₂O₃ and Fe₂TiO₅.

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 +100-300 μm . An increase in ilmenite reactivity has been observed with the number of redox cycles (Cuadrat et al., 2011). Thus, the sample used in this work was previously activated so that 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 2. Spanish lignite (+200-300 μm) was used as fuel in the experiments. Table 3 shows the proximate and ultimate analyses of the coal together with the low heating value.

2.2 Experimental setups and procedures

2.2.1 Continuous unit

The coal combustion experiments were performed at the ICB-CSIC-s1 unit, previously used in other works from our research group. The scheme of the setup is presented in Figure 1. Detailed description of the experimental unit can be found elsewhere (Cuadrat et al., 2011).

In the present experiments, the ilmenite inventory introduced at the beginning of the experiments was 3.3 kg, corresponding to 0.7 kg of ilmenite in the fuel reactor. The steam flow to the fuel reactor was 200 $\text{L}_\text{N}/\text{h}$, corresponding to a velocity of 0.14 m/s at 900°C. In the air reactor the total primary air flow was 1800 $\text{L}_\text{N}/\text{h}$ (corresponding to a velocity of 0.45 m/s at 900°C). The secondary air flow was 400 $\text{L}_\text{N}/\text{h}$. The nitrogen flow in the loop seal was 100 $\text{L}_\text{N}/\text{h}$. Lignite feeding rate was about 50 g/h, which determines a steam to carbon molar ratio of 3.5 during the experiments. In order to measure the circulation flow rate of the oxygen carrier, a diverting solid valve (6) at the outlet of the cyclone after the air reactor was placed. Using this valve, the circulation flow rate was measured and controlled to be about 7 kg/h. These conditions ensure that the operation is over stoichiometric conditions, so that there is enough oxygen supply by the oxygen carrier. The oxygen carrier to fuel ratio (ϕ) is

commonly used to compare the oxygen supplied by the circulating oxygen carrier to the oxygen needed to burn the fuel:

$$\phi = \frac{\dot{m}_{OC} \cdot R_{OC}}{\Omega_{SF}} \quad (1)$$

In this case, values of ϕ around 3 were used in the experiments. 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 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. CO, CO₂, H₂, and CH₄ concentration in the fuel reactor outlet stream and CO, CO₂ and O₂ at the air reactor outlet were determined. The analyzers used in the measurements are included in Table 4. The analysis of sulphur, nitrogen and mercury species required different instrumentation, also included in Table 4. Oxidized mercury was retained in KCl impingers with 1M KCl placed in a bath at 0°C (Ontario Hydro Method). Sampling of gaseous mercury (Hg⁰ and Hg²⁺) was performed during 30 minutes at steady state.

2.2.2 Batch fluidized bed

Some experiments were performed in order to better understand sulphur release in the continuous unit and especially the fate of the pyritic sulphur in lignite. The release of sulphur from lignite during pyrolysis and gasification processes under conditions similar to those in the fuel reactor of the CLC unit was analyzed in a batch fluidized bed reactor. Details about the fluidized reactor can be found elsewhere (Mendiara et al., 2013). The reactor was loaded with 300 g of silica sand (+200-300 µm) which act as an inert. The lignite coal (20 g) was introduced in the silica sand bed with the help of a fuel chute. The temperature in the bed was increased up to 900°C at 20 K/min in nitrogen atmosphere (200 L_N/h) and the products

resulting from lignite pyrolysis were burned in a post-combustion chamber located after the fluidized bed reactor. The combustion of the volatiles in this chamber took place at 800°C and 10% O₂. After condensing the steam, the resulting products were sent for analysis. Once the temperature reached 900°C, the fluidizing agent was changed from nitrogen to steam. The products of char gasification at 900°C were then burned in the post-combustion chamber and the products registered. Char gasification lasted until no CO₂ signal could be detected in the product gas. Then, steam was replaced by air in order to burn any char that could still remain in the bed.

3. Results and Discussion

3.1 CLC performance: carbon capture and combustion efficiency

The objective of this work is to further investigate the fate of sulphur, nitrogen and mercury in coal in an *i*G-CLC unit. Prior to any other analysis, the performance of the *i*G-CLC system burning Spanish lignite with ilmenite as oxygen carrier was evaluated. The main compound at the fuel reactor outlet was CO₂ and its percentage in the product stream increased with temperature. In all cases the CO₂ concentration was below 90% (N₂ free dry basis). Unburned compounds, mainly CO, H₂ and CH₄ were also detected. The total oxygen demand (Ω_T) compares the oxygen required to fully oxidize unconverted gaseous compounds in the fuel reactor with the oxygen required to burn the coal fed to CO₂ and H₂O. As unconverted compounds H₂, CO, CH₄ and H₂S are considered. The total oxygen demand allows a fast evaluation of the amount of oxygen that would be required to reduce the unburned in the fuel reactor stream in an oxygen polishing step.

$$\Omega_T = \frac{0.5 \cdot F_{CO,FR} + 2 \cdot F_{CH_4,FR} + 0.5 \cdot F_{H_2,FR} + 1.5 \cdot F_{H_2S,FR}}{(\dot{m}_{SF} \cdot \Omega_{SF} / M_{O_2})} \quad (2)$$

The total oxygen demand values are presented in Figure 2. The oxygen demand decreased when the temperature increased from 5.7% at 875°C to 4.5% at 930°C. The total oxygen

demand reported by Cuadrat et al. (2012) was larger, between 7-8% in the 870-920°C temperature range. This is due to the different solid inventories used by Cuadrat et al. (2012) (1770 kg/MW_{th}) and that used in the present experiments (2700 kg/MW_{th}). The ilmenite supplies a larger amount of oxygen in the fuel reactor which contributes to a better combustion of CO, H₂ and CH₄.

Some carbon is emitted in the air reactor as CO₂, corresponding to the char particles with low residence time in the fuel reactor to be gasified. The char conversion in the fuel reactor (X_{char}) was calculated as the fraction of carbon in the char which is released to the fuel reactor exhaust gas stream:

$$X_{char} = \frac{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} - F_{C,vol}]}{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} + F_{CO_2,AR} - F_{C,vol}]} \quad (3)$$

The gasified char in the fuel reactor was calculated as the 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. The carbon captured in an *i*G-CLC system depends on the carbon contained in the volatiles and the carbon in the char converted. The carbon capture efficiency (η_{CC}) represents the removal of carbon that would otherwise be emitted to the atmosphere. The carbon capture efficiency is then defined as the quotient between the carbon in the gases exiting the fuel reactor and the carbon in gases from both fuel and air reactors. Only CH₄, CO and CO₂ were considered, as the amount of tars and hydrocarbons heavier than CH₄ was proved to be negligible.

$$\eta_{CC} = \frac{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR}]}{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} + F_{CO_2,AR}]} \quad (4)$$

where $F_{i,FR}$ is the i species molar flow in the fuel reactor inlet/outlet stream. $F_{CO_2,AR}$ is the CO_2 flow in the air reactor. Figure 2 shows the values of the carbon capture and char conversion obtained at different fuel reactor temperatures. High carbon capture efficiencies were expected due to the high volatile content of the lignite (Cuadrat et al., 2012). As it is observed, the carbon capture efficiency increased with temperature from 82% at 875 °C to 93% at 930°C. Char conversion values were calculated and increased from 74.2% at 875°C to 89.3% at 930°C due to the increase in the char gasification rate with temperature.

3.2 Fate of sulphur

Part of the sulphur contained in lignite is quickly released as gaseous compounds in the pyrolysis taking place in the fuel reactor. The rest remains in the char generated and can be released in the fuel reactor as char is gasified or in the air reactor as part of the ungasified char reaches the air reactor.

3.2.1 Sulphur distribution in fuel and air reactors

After measuring the different sulphur compounds present at the gaseous outlet of fuel and air reactors, the sulphur distribution was determined. Figure 3 presents the weight percentage of the sulphur measured which was released as gaseous compounds in the fuel and air reactors at different fuel reactor temperatures. At any of the temperatures tested, more than 90% of the sulphur in gases was released in the fuel reactor. This percentage increased with temperature and the amount of sulphur released in the air reactor decreased in parallel. As it was already shown before in Figure 2, char conversion is more favoured at high fuel reactor temperatures and this leads to a lower amount of char reaching the air reactor. If less char is transported to the air reactor, the sulphur contained in it and therefore released in the air reactor will decrease with the fuel reactor temperature.

3.2.2 Sulphur compounds in fuel and air reactors

Figure 4 shows the evolution of the sulphur gaseous species in the fuel reactor for different fuel reactor temperatures. In the fuel reactor of an *i*G-CLC system, H₂S, SO₂, COS and CS₂ could be present in the outlet stream. The presence of COS might be favoured by the presence of CO and CO₂. However, only H₂S and SO₂ were detected as main sulphur species in the temperature interval 875-930°C. No COS or CS₂ were identified under the experimental conditions used. The gaseous sulphur species liberated (mainly H₂S) may react with the oxygen carrier particles forming new more oxidized sulphur species. The molar ratio between H₂S and SO₂ depended on the fuel reactor temperature. As temperature increases, the char conversion increases and the H₂S/SO₂ molar ratio slightly decreases from 0.33 to 0.23. At high temperatures, both volatile release and char gasification are favoured, as well as the reaction of the gaseous products formed in these processes with the oxygen carrier particles. The fact that the H₂S/SO₂ molar ratio decreases with the increase in temperature can be explained by the enhancement in the conversion of H₂S from both volatiles and char gasification to SO₂ at high temperatures. This trend has been observed before for other species reacting with oxygen, i.e. H₂, CO and CH₄.

In the air reactor, sulphur emissions are originated in the combustion of the unconverted char reaching the air reactor. Therefore, the only sulphur species detected was SO₂. The SO₂ concentration measured at the outlet of the air reactor decreased from 65 to 20 ppm as the fuel reactor temperature increased. The enhancement of char conversion in the fuel reactor reduced the amount of char transferred to the air reactor. The SO₂ emission values reached around 450 mg/Nm³ (6% O₂) at 930°C. This value is above the EU legal limit established for power plants up to 300 MW_{th} (200 mg/Nm³, 6% O₂). Lower SO₂ emissions could be reached if the fuel reactor temperature was increased.

3.2.3 Sulphur splitting

Figure 5 presents the weight percentages corresponding to the sulphur released in the gaseous streams from both fuel and air reactors. In average, the percentages of sulphur released as gaseous compounds in both reactors oscillates around 75 wt.% of the total sulphur in the coal fed. Therefore, there is approximately 25% of the sulphur in the coal fed which has not been measured. Further investigations were conducted to determine the fate of this sulphur. There are several possibilities:

i. Sulphur retention by the ashes: It has been already reported that the CaO present in the ashes of this lignite is capable of retaining sulphur during combustion by the formation of CaSO_4 (Adánez-Rubio et al., 2014). The ash content in this lignite is high (25.2%) and the CaO content in the ashes is 6.5%. Considering this, de Diego et al. (2013) calculated that the self-retention capacity of the lignite ashes would justify the retention of 10-15% of the sulphur fed with coal. This estimated percentage has been incorporated to Figure 5.

ii. Pyritic sulphur present in the lignite ashes: Lignite ashes contain pyritic sulphur. In the continuous unit, the combustion of this pyritic sulphur could take place once the char reaches the air reactor, as no oxygen is present in the gaseous atmosphere of the fuel reactor. However, the combustion rate of pyritic sulphur at the temperature conditions of the air reactor is low. The residence time of ash particles in the air reactor in the continuous unit would not be enough for the pyrite in coal ashes to be completely burned and the pyritic sulphur may escape unburned from the CLC system together with the fly ashes. It is worth noting that most ashes are not separated by the cyclone and are recovered in filters downstream the air reactor. To confirm this hypothesis, analyses were done to the fly ashes collected in the continuous unit and pyritic sulphur was found. In order to investigate the

amount of pyritic sulphur in lignite, an experiment was conducted in a batch fluidized bed reactor. The methodology followed was described before in the experimental section. Figure 6 shows the concentration profiles of the main products (CO, CO₂, SO₂) all along the different processes (pyrolysis, gasification and oxidation) after being oxidized in the post-combustion chamber. The temperature selected for the experiment was 900°C, as it is an intermediate value for the temperature interval used in this work. During the pyrolysis step, there is a maximum in SO₂ (1300 ppm) and CO₂ (2.5%) concentration when temperature approximately reaches 400°C. Both maximum are associated with the volatile release from lignite. The amount of sulphur measured during this period corresponds to 22.1% of the sulphur fed with the coal introduced in the bed. In the steam gasification step, 46.8% of the initial sulphur was emitted. The molar S/C ratio was calculated and it remained approximately constant during the steam gasification, close to a value of 0.03. This fact indicates that both carbon and sulphur seem to be gasified simultaneously and at similar rate. Finally, SO₂ release was observed during the period when air was introduced as fluidizing agent. The sulphur emitted during oxidation represented around 4.6% of initial sulphur. This value was considered as an indication of the amount of pyritic sulphur contained in lignite ashes, which were the only coal fraction present in the bed at that moment. Figure 5 included the percentage of pyritic sulphur determined through the experiment in the batch fluidized reactor. Further analyses about the origin of the inorganic sulphur in this lignite showed that no sulphides or sulphates were present. It is then speculated that the sulphur released during steam gasification is mainly organic sulphur.

iii. Sulphur retention by the oxygen carrier: A thermodynamic study on the formation of iron-sulphur solid species by reaction with the ilmenite was carried out considering the experimental conditions in the continuous unit. The software HSC Chemistry 6.1 was used in

the thermodynamical calculations⁴. According to this study, the formation of FeS in the fuel reactor during ilmenite reduction is not favoured above stoichiometric conditions. Therefore, no sulphur retention by the oxygen carrier is expected in these experiments. The thermodynamic predictions were confirmed by the SEM-EDX analysis to used ilmenite samples. The analysis on the surface of the particles did not evidence the presence of sulphur, therefore it was assumed that all the sulphur in coal was either released in the volatiles or retained in the lignite char or ash. An activation of ilmenite after the combustion of fuels with high sulphur content has been reported in the literature (Moldenhauer et al., 2013). Therefore, the ilmenite particles were analyzed after 55 hours of continuous hot fluidization to check any change that may occur in their reactivity and no differences were found with respect to the sample before use. Besides, it is known that the transport capacity of ilmenite (R_{OC}) may decrease with the number of redox cycles, as a consequence of the migration of Fe_2O_3 to the external part of the particle when ilmenite was highly reduced (Adánez et al., 2010). The transport capacity of the calcined and used ilmenite was determined in experiments in a TGA at 950°C using as reducing mixture 5% H_2 + 40% H_2O , so that the final reduced form was Fe_3O_4 . In this case, no changes were detected after operation and the oxygen transport capacity remained 4.3% what agrees with results previously reported (Cuadrat et al., 2011).

Once all the possible non-measured contributions to the sulphur balance were included in Figure 5, the sulphur balance closed around 95% on average, which can be considered as good result. Possible SO_3 emission in the air reactor was not measured, although it is believed that formation of SO_3 in the air reactor would have minor importance regarding the sulphur balance to the whole CLC unit. It has been reported that only fractions below 4% of the total

⁴ HSC Chemistry 6.1, Chemical reaction and equilibrium software with thermochemical database and simulation module, Outotec Research Oy, Pori, Finland; 2008.

sulphur present as SO_2 can be converted to SO_3 in combustion processes (Spörl et al., 2013). According to this, the formation of SO_3 could represent 0.3% of the total sulphur fed.

3.3 Fate of nitrogen

The presence of N_2 in the combustion atmosphere at high temperatures favours the formation of NO_x (thermal NO_x) as it has been observed in conventional combustion. However, this contribution to NO_x formation is not present in CLC, as no N_2 enters in the fuel reactor gases. Therefore only the nitrogen in the fuel can be present in the fuel reactor, either N_2 or NO_x . In order to avoid N_2 in the gases fed to the system CO_2 was used to fluidize the loop seal and in the screw feeder.

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 the case of molecular nitrogen, it could be formed both from homogeneous reactions in the gas phase or due to NO reduction by the char particles present in the fuel reactor. As it was done with sulphur emissions, the presence of the abovementioned species was analyzed both in the fuel and air reactors. In this case, data were only available at 875 and 930°C. Most of the nitrogen in coal was found in the fuel reactor outlet and this partition does not seem to be notably affected by temperature. Different nitrogen compounds were detected and are detailed next.

3.3.1 Nitrogen in fuel and air reactors

Figure 7 (A) shows the splitting of the nitrogen contained in the lignite fed in the experiments at 875 and 930°C, respectively. In both experiments most of the nitrogen fed was detected in the gaseous phase in fuel and air reactors. On average, it can be said that 92% of the nitrogen in lignite was measured, which can be considered as a good closure for the nitrogen balance. At the fuel reactor outlet, only traces of NH_3 and HCN were identified using the mass spectrometer, but in such a low amount that could not be quantified. It seems that the NH_3

and HCN generated in lignite devolatilization were oxidized by the oxygen carrier particles at the temperatures tested. This is in line with the results reported by Song et al. (Song et al., 2012, 2013), who after a thermodynamic study assuming fuel reactor temperatures between 600-1000°C, concluded that both species could be oxidized by Fe_2O_3 yielding NO. Then, NO can evolve or not to N_2 , following homogeneous (gas phase) and heterogeneous reactions. The only NO_x detected and quantified was NO. The analyses showed that N_2O was not formed during these processes and only traces of NO_2 were identified by the mass spectrometer. The major nitrogenated species observed in the fuel reactor was N_2 (0.21-0.24 vol. %). According to these results, around 99% of the nitrogen measured in the fuel reactor was in the form of N_2 .

In the air reactor the nitrogen contained in the unconverted char was released as NO. No trace of N_2O or NO_2 was detected. Figure 7 (B) presents the results obtained in the air reactor with more detail. The amount of NO present in the outlet stream depended on the fuel reactor temperature and is correlated with the evolution of the carbon flow reaching the air reactor. The lower the amount of char being burned there, the lower the level of NO emissions. At the highest temperature tested (930°C), the value of NO emissions was 74 mg/ Nm^3 (6% O_2), lower than the 200 mg/ Nm^3 (6% O_2) limit set by EU legislation.

3.4 Fate of mercury

Mercury measurements at the outlet of both fuel and air reactors were performed in order to analyze the fate of mercury when lignite was used as fuel. During the analyses, the temperature in the fuel reactor was 910°C. The mercury present in the fines at the outlet of the air reactor was determined. These solids were mainly coal ash and no mercury was found during the analysis. The initial mercury content of lignite was 0.10 mg Hg/kg. Around 31.5% of this amount was released in the fuel reactor while 67.7% was liberated in the air reactor. In

conventional combustion, most of the mercury in coal is vaporized once coal is fed into the combustion chamber. However, a significant amount of mercury remained in the char after devolatilization in the CLC experiments. This char was transferred to the air reactor where it was burned and the rest of the mercury released. The reason for this important difference with combustion processes may lay in the different atmospheres present in a boiler and in the fuel reactor of a CLC system. In this case, char is gasified in the fuel reactor, although gasification products are oxidized *in situ* by the oxygen carrier. It has been previously observed that in coal gasification environments, where steam is present in high proportion, mercury release was suppressed (Sekine et al., 2008). This mercury partition between fuel and air reactors corresponds to total mercury emissions of 15.5 and 2.1 $\mu\text{g}/\text{Nm}^3$, respectively. Both values are expressed in dry basis. Although there is no legislation already available for Europe, the mercury concentration in the air reactor is quite low. As a guideline, the mercury emission limit from incineration systems is indicated. According to Directive 2010/75/UE, the maximum mercury emission in these installations is set to 0.05 mg/Nm^3 . The concentration value found for the air reactor was 25 times lower. The speciation of mercury was also determined for each of the reactors. In the fuel reactor, the ratio $\text{Hg}^0/\text{Hg}^{\text{total}}$ was 0.75 and in the air reactor it was 0.46. These results indicate that the major species in the fuel reactor was Hg^0 . In the air reactor, the amount of Hg^{2+} was slightly higher than that corresponding to Hg^0 . Further analysis would be required to understand the reasons for the speciation in both reactors and will be the subject of ongoing investigation in our research group.

4. Assessment on pollutant emissions and CO₂ quality

As in any other power generation unit, the emissions to the atmosphere in the air reactor should be under the limits imposed by legislation for different pollutants. Legislation for combustion systems has been set for both SO₂ and NO_x, although in our experiments SO₂ was

the only pollutant with a concentration at the outlet of the air reactor exceeding that allowed (200 mg/Nm³, 6% O₂). Therefore, this analysis will focus on these pollutants. All the sulphur and nitrogen emissions in the air reactor originate from the char transported from the fuel reactor. Therefore, an interesting measure to be taken in order to reduce the emissions from the air reactor would be to improve char conversion in the fuel reactor, so that less char is burned in the air reactor. This can be done by means of a carbon separation unit located between fuel and air reactors. The effect of the efficiency of the carbon separation unit (η_{CSS}) on carbon capture has been described before (Mendiara et al., 2013). This time the effect of its incorporation on pollutant emissions in the air reactor will be investigated. For that purpose, a simple model based on carbon balances to the fuel reactor and carbon separation unit was used to estimate the emission levels reached for different efficiencies of the carbon separation unit (Mendiara et al., 2013). The model considers the char gasification rate at the corresponding temperatures and using that value, first the char conversion and then the carbon capture efficiency are calculated for different η_{CSS} values. Once the char conversion is known, the estimation of the emissions in the air reactor can be done with the ultimate analysis of lignite char.

Figure 8 presents the results obtained using this model for lignite and ilmenite at a temperature in the fuel reactor of 930°C. First of all, it can be seen that the incorporation of a carbon separation unit increased the char conversion and carbon capture efficiency which was already high for lignite. The efficiency of the carbon separation unit has been reported to be 0.98 during operation in a 100 kW_{th} CLC unit (Abad et al., 2013). As a consequence, less char is reaching the air reactor in those conditions. Therefore, the concentration values of SO₂ and NO in the air reactor decreased when the efficiency of the carbon separation unit was higher. If $\eta_{CSS}=0.98$ is considered, then the emission values in the air reactor can be estimated

as 9.8 mg/Nm³ SO₂ and 1.0 mg/Nm³ NO (both at 6% O₂ excess). These SO₂ and NO emissions are well below the legal limits. Therefore, considering the estimation of emissions presented, it can be said that, with the incorporation of a carbon separation unit in the CLC system no problems with SO₂ emissions in the air reactor may be expected.

Following the results presented above regarding the composition of the gaseous stream at the outlet of the fuel reactor, some considerations about CO₂ quality can be elaborated. Different compounds have been found in the CO₂ stream (CO, H₂, CH₄, H₂S, SO₂, N₂, NO_x and Hg⁰/Hg²⁺). The values of these compounds in the experiment at the highest temperature (930°C) have been included in Table 1 (dry N₂ free basis) in order to compare with the recommendations given by de Visser et al. (2008) for CO₂ quality. The conclusions obtained in the comparison are qualitatively the same as in the case that a carbon separation unit would be used. As it can be observed, the amounts of CH₄, N₂, H₂ and NO_x are under the specification limits. However, there are an excess of unburned CO and sulphur compounds at the fuel reactor outlet compared to the recommended values. The CO concentration is more than 20 times that allowed and the CO₂ concentration does not reach the required 95.5%. The values of H₂S and SO₂ are more than 10 and 100 times those specified, respectively. In the case of mercury no limits were suggested. Therefore, the CO₂ stream leaving the fuel reactor should be subjected to several treatments in order to adequate the content of these compounds to the values needed for safe transport and storage.

First of all, unconverted gases (especially CO) should be burned. Different alternatives have been recently proposed to increase the combustion efficiency in CLC of solid fuels. Among them, the highest reduction in the unconverted gases emitted was reached using a secondary fuel reactor at the fuel reactor outlet (Gayán et al., 2013). The next step would be the removal of the sulphur compounds. Absorption processes to selectively remove H₂S from process

streams containing carbon dioxide are based on methyldiethanolamine (MDEA). The reaction rate of MDEA with CO₂ is lower than with H₂S therefore no much CO₂ is absorbed by this amine (Rogers et al., 1998). The removal of SO₂ can be carried out using the same technology as in air-fired combustion. One of the most widely used is the wet flue gas desulfurization (FGD). In this process, SO₂ is removed using limestone slurry. The performance of this technology has been already tested with flue gases from oxyfuel combustion (Hansen et al., 2011). It is interesting to remind that Hg²⁺ could be eliminated in the FGD unit (Stergaršek et al., 2008). Elemental mercury could be adsorbed using the activated carbon injection (ACI) technology (Pavlish et al., 2003). Finally, the CO₂ stream should be dried and then compressed.

5. Conclusions

The fate of sulphur, nitrogen and mercury was evaluated at different fuel reactor temperatures in the combustion of lignite in a continuous *i*G-CLC unit using ilmenite as oxygen carrier. High carbon capture efficiencies were obtained in the 875-930°C temperature interval. The sulphur, nitrogen and mercury emissions 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 presence of COS or CS₂ was not detected. The molar H₂S/SO₂ ratio slightly decreased with the fuel reactor temperature, indicating that H₂S consumption maybe favoured by 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. The incorporation of a carbon separation unit in the *i*G-CLC system allowed to comply with the legal emission limits for SO₂ in the air reactor. Regarding the fate of nitrogen in coal, N₂

was the main compound in the fuel reactor. It represented around 99% of the nitrogen measured in the fuel reactor. In the air reactor, the nitrogen released by the unconverted char was emitted as NO at a lower level than the legislation limit. A third of the mercury fed with coal was released in the fuel reactor mainly as Hg^0 , whereas in the air reactor higher amounts of Hg^{2+} were found. In order to ensure adequate quality of the CO_2 stream produced in the fuel reactor, conversion of unburned gases and $\text{H}_2\text{S}/\text{SO}_2$ removal should be addressed.

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738 **Nomenclature**

739 $F_{CO_2,AR}$: carbon dioxide molar flow in the air reactor (mol/s)

740 $F_{i,FR}$: i species molar flow in the fuel reactor inlet/outlet stream (mol/s)

741 $F_{C,vol}$: carbon flow from the volatile matter (mol/s)

742 M_{O_2} : molar mass of molecular oxygen (0.032 kg/mol)

743 $\dot{m}_{OC}$: mass-based solid circulation rate (kg/s)

744 $\dot{m}_{SF}$: coal feeding rate (kg/s)

745 R_{OC} : oxygen transport capacity

746 X_{char} : char conversion

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748 Greek symbols

749 ϕ : oxygen carrier to fuel ratio

750 Ω_{SF} : coal oxygen demand (kg oxygen/kg coal)

751 Ω_T : total oxygen demand

752 η_{CC} : carbon capture efficiency

753 η_{CSS} : carbon separation efficiency in the carbon separation unit

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Figure 6. Evolution with time of the main products from lignite pyrolysis and steam gasification at 900°C

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915 **Tables**

916 **Table 1.** Concentration of different compounds at the fuel reactor outlet

Component	DYNAMIS CO ₂ quality recommendations (de Visser et al., 2008)	Present work (930°C)	Units
H ₂ O	500	-	ppmv
H ₂ S	200	2692	ppmv
CO	2000	42567	ppmv
O ₂	Aquifer < 4 EOR 0.0001-0.001	-	vol%
CH ₄	Aquifer < 4 EOR < 2	1.2	vol%
N ₂ , Ar, H ₂	< 4 (all non-condensable gases)	0.3 (N ₂) ^a 2.9 (H ₂)	vol%
SO ₂	100	11693	ppmv
NO _x	100	42	ppmv
CO ₂	> 95.5	89.1	vol%

917 ^a Only nitrogen formed from fuel-N is considered

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Table 2. Main properties of activated ilmenite particles

Activated ilmenite	
XRD phases	Fe ₂ TiO ₅ , Fe ₂ O ₃
Crushing strength (N)	3.2
Oxygen transport capacity(%)	4.3
Particle density (kg/m ³)	4100
Porosity (%)	18.7
BET Surface (m ² /g)	0.8

944 **Table 3.** Proximate and ultimate analyses of the Spanish lignite (wt %)

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Carbon	45.4	Moisture	12.5
Hydrogen	2.5	Ash	25.2
Nitrogen	0.6	Volatile matter	28.6
Sulfur	5.2	Fixed carbon	33.6
Oxygen ^a	9.9		
LHV (kJ/kg)	16252		

946 ^a By difference

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963 **Table 4.** Equipment used in the measurement of different pollutants

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Species	Measurement method	Instrument (supplier)
CO, CO ₂ , CH ₄	Nondispersive infrared	Maihak S710/UNOR
O ₂	Paramagnetism	Maihak S710/OXOR-P
H ₂	Thermal conductivity	Maihak S710/THERMOR
SO ₂	Infrared	Siemens Ultramat 23
H ₂ S, COS, CS ₂	Gas chromatography	Varian 3400-CX GC (PORAPAK-Q column)
		Flame photometric detector (FPD)
NH ₃ , HCN	Mass spectrometry	Pfeiffer
NO _x	FTIR	Temex CX 4000
Hg ⁰ (g)	Cold vapour atomic absorption spectroscopy	VM3000 from MCI
Hg ²⁺ (impingers)	Gold amalgam atomic absorption spectroscopy	LECO AMA254
Hg (p)		

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