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Behaviour of a bauxite waste material as oxygen carrier in a 500W_{th} CLC unit with coal

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Abstract

This paper is focused on the Chemical Looping Combustion (CLC) of coal. Under this configuration, coal is fed directly into the fuel reactor where coal is gasified and the gaseous products react with the oxygen carrier. In CLC of coal it is especially interesting to consider low cost oxygen carriers as some losses of solid material may occur during the ashes drainage. The performance as oxygen carrier of a Fe-enriched sand fraction (Fe-ESF) generated in the alumina production from bauxite is evaluated in this work. The experiments were carried out in a continuous 500W_{th} unit using a bituminous coal. Different variables affecting the process were analyzed, such as the temperature in the fuel reactor, coal feeding rate, solid circulation flow and composition of the gasifying gas. High combustion efficiencies in the fuel reactor (around 90%) were obtained at all the temperatures tested. Low oxygen demand (<5%) values were also obtained in the temperature interval tested (880-930°C). Higher temperatures or the use of a carbon separation system would be needed to have high carbon capture efficiencies. Regarding OC performance, good results were found. During 40 hours of continuous operation, the attrition rate was adequate and no agglomeration problems were detected. The reactivity of the oxygen carrier slightly increased as well as the porosity. Compared to ilmenite, the most tested oxygen carrier material so far for this process, the Fe-ESF material provided lower oxygen demand at the fuel reactor outlet and higher oxygen transfer rates in similar experimental conditions, which makes Fe-ESF an interesting alternative for CLC processes with coal.

Keywords: combustion, coal, CO₂ capture, chemical looping, bauxite waste

1. Introduction

The Intergovernmental Panel on Climate Change (IPCC) has recently referred the relationship between the observed increase in global average temperatures since the mid-20th century and the increase in anthropogenic greenhouse gases (GHG) concentrations in the atmosphere (IPCC, 2007a). Emissions of the GHGs covered by the Kyoto Protocol increased by about 70% from 1970 to 2004, with carbon dioxide (CO₂) being the largest source, having grown by about 80% (IPCC, 2007b). The largest growth in CO₂ emissions has come from power generation.

Most scenarios project that the supply of primary energy will continue to be dominated by fossil fuels until at least the middle of the present century (IPCC, 2005). Currently, coal is filling much of the growing energy demand of developing countries, such as China and India, where energy-intensive industrial production is growing rapidly and large coal reserves exist. Without additional measures, the intensified use of coal would substantially increase CO₂ emissions unless there was very widespread deployment of Carbon Capture and Storage (CCS) (IEA, 2010). Interest has been increasing in the carbon sequestration option because it is compatible with the large energy production and delivery infrastructure now in place. In the first step of the chain, capture technologies allow the separation of CO₂ from combustion. Among them, Chemical Looping Combustion (CLC) has recently emerged as a promising technology that facilitates CO₂ inherent separation at low cost (Eide et al., 2005).

In CLC, the oxygen needed for fuel combustion is supplied by an oxygen carrier, normally a metal oxide, which circulates between two interconnected fluidized-bed reactors: the fuel and air reactors (Adánez et al., 2012). The oxygen carrier is reduced in the fuel reactor and the

fuel is oxidized. The gaseous product from the fuel reactor is composed of the combustion products, i.e. CO₂ and steam. Once water is condensed, an almost-pure CO₂ stream is obtained. The reduced oxygen carrier is re-oxidized with air in the air reactor and sent back to the fuel reactor to start a new redox cycle.

The application of this technology to solid fuels, especially coal, has been the subject of research in the last years. CLC of coal can be carried out under different configurations (Adánez et al., 2012). One of them is based on the *in-situ* gasification of the solid fuel in the fuel reactor. In this process, coal is fed directly into the fuel reactor and mixed with the oxygen carrier. The coal is gasified by steam or CO₂, which also act as fluidizing agents, according to the following reaction scheme:

The oxygen carrier reacts with the gases produced in reactions (1)-(3) to produce CO₂ and water as products:

After reaction in the fuel reactor, the reduced oxygen carrier reaches the air reactor, where it is re-oxidized again using air.

Coal gasification is the rate limiting step in this process (Cuadrat et al., 2012b; Dennis et al., 2006; Dennis and Scott, 2010; Leion et al., 2007). CO and H₂ are well-known inhibitors of

the char gasification reactions (Johnson, 1981). Therefore the continuous consumption of the gasification products by reaction with the oxygen carrier increases the gasification rate of the char (Cao and Pan, 2006; Cuadrat et al., 2012b; Leion et al., 2007, 2008b). Several studies point to high temperatures (around 1000°C) in order to achieve high char gasification rates (Berguerand and Lyngfelt, 2009a, 2010; Berguerand et al., 2011; Cuadrat et al., 2011; Leion et al., 2008b). High temperatures would also enhance the CO and H₂ conversion by the oxygen carrier but in a lower extent (Shen et al., 2009). If the combustion of the coal devolatilization/gasification products is not complete some energy would be lost as unburnt compounds (CO, H₂, CH₄, volatiles) in the combustion gases from the fuel reactor. To avoid the loss in efficiency, highly reactive oxygen carriers or excess solids inventory could be used but the improvement would not be significant if there is not a good gas-solid contact in the fluidized bed acting as fuel reactor (Adánez et al., 2012). Some strategies have been proposed to convert the unburnt compounds. They include an oxygen polishing step to complete gas combustion, the separation and recirculation of unburnt compounds or a fuel reactor in series.

The slow coal gasification rate may cause that the solid stream exiting from the fuel-reactor contains some unconverted char together with the oxygen-carrier and ash. Once the unconverted char reaches the air reactor it reacts with air to produce CO₂. This loss of carbon in the air reactor decreases significantly the CO₂ capture efficiency of the process and therefore it should be avoided. To increase the residence time of char particles in the fuel reactor, without excessively increasing the reactor size, the use of a carbon separation unit after the fuel reactor has been proposed (Cao and Pan, 2006). In this unit, char particles are separated from the oxygen carrier particles using their different fluidization properties. Char particles are recirculated to the fuel reactor.

The use of CO₂ as gasifying agent would be desirable because no energy consumption for steam production would be required as carbon dioxide can be recirculated from the flue gases. However, it is known that dry gasification rates are lower than steam gasification rates, especially for high rank coals and therefore it is possible that there has to be a limited percentage of CO₂ in the gasifying stream in order to maintain a high gasification rate (Cuadrat et al., 2012b, 2012c; Leion et al., 2009).

One of the present and future challenges of the CLC technology is to find suitable oxygen carrier materials able to perform multiple redox cycles without losing their chemical and physical properties: high oxygen transport capacity, high reactivity and selectivity to CO₂ and H₂O, high mechanical strength to resist the stress associated with the circulation of the particles in the CLC system, high resistance to attrition and absence of agglomeration. Besides, it is desirable that the oxygen carrier material is environmentally friendly, easy to dispose once depleted and also cost competitive. In the case of the CLC with coal, these two last aspects are especially important as some oxygen carrier losses are expected in the drainage of the coal ashes. Considering this, Fe- and Cu-materials are preferred for their use in this process better than Ni-based materials due to their toxicity. Moreover, Fe-based materials with magnetic properties are preferred for the use with coal as they could be separated from the ashes.

A number of studies have recently demonstrated CLC of coal during continuous operation in CLC units ranging from 500 W_{th} to 100 KW_{th} using Fe-based oxygen carriers (Berguerand and Lyngfelt, 2008a, 2008b, 2009a, 2009b; Berguerand et al., 2011; Cuadrat et al., 2011; Markström et al., 2012; Wu et al., 2010). Most of them used as oxygen carrier a natural mineral called ilmenite, mainly composed of FeTiO₃. Good reactivity to CO and H₂ was

observed working with this material in the temperature interval 900-1000°C as well as very low tendency for attrition/fragmentation and no signs of agglomeration. However, as it was previously observed for other Fe-based materials, the reactivity to methane was lower (Abad et al., 2011; Cuadrat et al., 2012a; Leion et al., 2008a). Cuadrat et al. (2012a) also found that ilmenite reactivity increased with the number of redox cycles using both gaseous and solid fuels (Cuadrat et al., 2012a, 2012b). Some authors operated a 10 kW_{th} Chemical-Looping combustor with ilmenite using coal and petroleum coke as solid fuels (Berguerand and Lyngfelt 2008a, 2008b, 2009a, 2009b, 2011; Linderholm et al., 2012). Good performance of the CLC concept for solid fuels was described and they concluded that ilmenite appeared to be a suitable material to be used for solid fuel combustion in a CLC system. CO₂ capture efficiencies ranged 60-96% depending on the reactivity of the solid fuel used. Lower values were observed for petroleum coke. They verified the effect of the fuel reactor temperature on the carbon capture and the solid fuel conversion and concluded that high temperatures enhance both. Unburnt tars or hydrocarbons were not present in the fuel reactor outlet in experiments in a 500 W_{th} CLC unit using ilmenite, with the exception of CH₄ which was found at low concentration (Cuadrat et al., 2011). Besides, it was proved that unburnt compounds (CO, H₂ and CH₄) came mainly from unconverted volatile matter. Similar carbon capture efficiencies to those obtained by Berguerand and Lyngfelt (Berguerand and Lyngfelt 2008a, 2008b, 2009a, 2009b) were observed. Oxygen demand values between 5-15% were found using Cerrejón bituminous coal. Recent results in a 100 kW_{th} continuous unit at Chalmers University revealed that high carbon capture efficiencies (close to 100%) can be attained using highly-efficient cyclones (Markström et al., 2012). The oxygen demand reported was similar to those obtained by Cuadrat et al (Cuadrat et al., 2011, 2012c).

Other Fe-based materials have been also used as oxygen carriers such as a natural iron ore (hematite). Wu et al. (Wu et al., 2010) operated a continuous 1 kW_{th} CLC reactor and obtained similar values of coal combustion efficiency than those of a highly reactive Ni-based oxygen-carrier (Shen et al., 2010). More recently, biomass as solid fuel was evaluated by Shen et al. (2009) in a continuous 10 kW_{th} CLC combustor using an oxygen-carrier prepared from iron oxide powders.

In our research group, we evaluated different low-cost Fe-based materials as potential oxygen carriers for CLC with coal (Mendiara et al., 2012b). Among them, several studies were dedicated to analyze the behaviour of a Fe-enriched sand fraction (Fe-ESF) obtained in the production of alumina from bauxite via the Bayer process. This material is mainly consisting of hematite, although the Fe₂O₃ content may vary with the origin of the raw bauxite. Fe-ESF reactivity with gaseous fuels was first analyzed (Mendiara et al., 2012a). This material reacted faster with H₂ than with CO and CH₄, and the reaction rates obtained in TGA experiments, were similar to those obtained using a synthetic Fe₂O₃/Al₂O₃ oxygen carrier. An increase in the reactivity of this material with the number of redox cycles was observed both using gaseous (Mendiara et al., 2012a) and solid fuels (Mendiara et al., 2013b). The use of Fe-ESF with solid fuels was also investigated in a batch fluidized bed reactor using char from coal as fuel. Fe-ESF showed high combustion efficiencies of the gases generated during the gasification of the corresponding char at all temperatures tested and in experiments with different fuels (Mendiara et al., 2013a).

As a further step in the evaluation of this material as oxygen carrier for the CLC process with coal, this work presents a detailed study of the behaviour in a continuous unit. Except for ilmenite, most of the studies using Fe-based oxygen carriers with solid fuels have only

focused on the influence of the fuel reactor temperature on the performance of the process. However, the aim of this work is to carry out a comprehensive study of the influence on the CLC performance of most of the main variables of the process. The effect of operating conditions such as the fuel reactor temperature, coal feeding rate, solid circulation rate and the gasifying agent on the combustion efficiency and the extent of gasification in the fuel reactor will be investigated. Besides, the possible changes undergone by the Fe-ESF particles with time will be evaluated. The conclusions drawn from this work will give a complete picture of the advantages of using Fe-ESF as oxygen carrier for CLC with coal.

2. Experimental

2.1 Materials used

The material used in this work as oxygen carrier was supplied by Alcoa Europe-Alúmina Española S.A. As mentioned before, this potential oxygen carrier is an Fe-based residue generated after bauxite digestion in the alumina production via the Bayer process. The sample used here corresponds to the so-called Fe-enriched sand fraction (Fe-ESF), which refers to particles with a size larger than 150 μm . The Fe-ESF sample was dried at room temperature for 72 hours and then sieved to +100-300 μm . After this, the dried sample was calcined at 1200°C during 18 h to completely oxidize the sample and increase the mechanical strength (Mendiara et al., 2012a).

The main chemical and physical properties of the material are shown in Table 1. The active Fe_2O_3 content was determined in a TGA using 15% H_2 at 950°C, and therefore, this percentage corresponds to the amount of iron reducible species, which are the species to take

part in the chemical looping process. The oxygen transport capacity, R_{OC} , is defined as the mass fraction that can be used in the oxygen transfer.

$$R_{OC} = \frac{m_o - m_r}{m_o} \quad (8)$$

where m_o and m_r are the mass of fully oxidized and reduced Fe-ESF sample, respectively.

The value of the oxygen transport capacity, R_{OC} , depends on the final oxidation state after reduction. Only the transformation from hematite (Fe_2O_3) to magnetite (Fe_3O_4) may be applicable for industrial CLC systems, due to thermodynamic limitations. Further reduction to wustite (FeO) or Fe would increase the equilibrium concentrations of CO and H_2 (Abad et al., 2007) worsening the CO_2 purity obtained in the fuel reactor. Besides, some authors have found agglomeration problems in the bed associated with the oxidation of wustite in air (Cho et al., 2006; Rydén et al., 2010). Thus, the reduction to FeO or Fe should be prevented in a CLC system. The identification of crystalline chemical species was carried out by powder X-ray diffraction (XRD) patterns acquired in an X-ray diffractometer Bruker AXS D8ADVANCE using Ni-filtered $\text{Cu K}\alpha$ radiation equipped with a graphite monochromator. The XRD analysis of the calcined sample confirmed that Fe_2O_3 and $\beta\text{-Al}_2\text{O}_3$ were the major components. Some minor amounts of other oxides such as Na_2O (4.0%), TiO_2 (4.0%) and SiO_2 (1.5%) were detected by ICP. The force needed to fracture a particle was determined using a Shimpo FGN-5 crushing strength apparatus as the average of 20 different measurements. Particle porosity was measured by Hg intrusion in a Quantachrome PoreMaster 33. The skeletal density of the particles was measured with a Micromeritics AccuPyc II 1340 helium picnometer. Brunauer-Emmett-Teller (BET) surface area value was measured and a low value was obtained.

A bituminous Colombian coal “El Cerrejón” was used as fuel (+200-300 μm). Due to its strong swelling tendency, agglomeration of the fluidized bed can take place. Therefore, the coal was subjected to a thermal pre-treatment for pre-oxidation (180°C in air for 28 hours). Ultimate and proximate analysis of the pre-treated bituminous coal is shown in Table 2, together with the low heating value.

2.2 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 (Abad et al., 2012; Cuadrat et al., 2011). The scheme of the setup is presented in Figure 1. In this experimental unit there are two interconnected fluidized bed reactors, (1) and (3) in Figure 1, 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).

The fuel reactor is a bubbling fluidized bed (50 mm ID and 200 mm bed height). An screw feeder (9) is used to feed the coal at the bottom of this bed and above the fuel reactor distributor plate. This design increases the time that volatile matter is in contact with the oxygen carrier in the fuel reactor bed. A small nitrogen flow was introduced to the screw feeder in order to avoid gas backflow from the fuel reactor. The fuel reactor is fluidized by steam, which also gasifies the coal introduced. In some experiments, CO₂ or mixtures steam/CO₂ were introduced as fluidizing/gasifying gases. An U-shaped fluidized bed loop seal (50 mm ID), fluidized with nitrogen, transfers the reduced oxygen carrier particles to the air reactor so that the gaseous atmospheres in the fuel and air reactors are not mixed. Together with the reduced oxygen carrier, unconverted char particles may be transported to the air reactor. This constitutes a loss of carbon and therefore a decrease in the CO₂ capture

efficiency of the process. A carbon separation system could be placed after the fuel reactor outlet to recover unconverted char particles and return them to the fuel reactor. However, the absence of a carbon separation system facilitates the interpretation of the effect of different operational conditions on the experimental results.

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 and the gaseous stream was sent up the riser (4) to the stack through a high-efficiency cyclone (5) and a filter (12). The particles collected by the cyclone were sent to a solid reservoir (7). This oxygen carrier reservoir is also a loop seal to avoid the leakage of gas between the fuel reactor and the riser. In the solid reservoir, a solid valve (8) allowed to control the solid flow rate. It was also possible to measure the solid flow rate by means of a diverting solid valve (6).

The total solid inventory in the system inventory was 3 kg and the solid level in the fuel reactor was fixed to around 0.9 kg of Fe-ESF. 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 2100 L_N/h (corresponding to a velocity of 0.5 m/s at 900°C). The secondary air flow was 480 L_N/h. The sum of the primary and secondary air flow gives a gas velocity in the riser around 2 m/s. The nitrogen flow in the loop seal was 90 L_N/h. The fuel reactor temperature was varied from 870 to 930°C while in the air reactor was maintained at 950°C. Different experiments were carried out varying the fuel reactor temperature, the solid circulation rate, the coal feed rate and the gasifying agent used. **Table 3** summarizes the conditions tested. A total of 40 hours of continuous operation feeding fuel and 55 hours of continuous fluidization were registered. Once stable conditions were reached, they were maintained during at least 30

minutes. 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 were used for CO, CO₂, and CH₄ concentration determination; a paramagnetic analyzer was used for O₂ concentration measurement and a thermal conductivity detector was used for H₂. All data were collected by means of a data logger connected to a computer. In some selected experiments the tar amount present in fuel reactor product gases was determined following the tar protocol (Simell et al., 2000). Besides, the presence of higher hydrocarbons was also tested using sampling bags. The samples were taken at the outlet of the fuel reactor and analyzed by gas chromatography.

2.3. Data evaluation

The objective is to analyze the performance at different conditions of the CLC process with coal and Fe-ESF as oxygen carrier using the measured values of gas concentration at the outlet of the reactors, the coal feeding rate and solid circulation rate. The absence of a carbon separation system facilitates this analysis.

Two main parameters are defined in order to evaluate the fuel reactor performance: the carbon capture efficiency and the combustion efficiency in the fuel reactor. The difference between the carbon present both in the fuel and air reactor exhaust gases and the carbon in the coal introduced revealed that there was elutriation of char produced in the fuel reactor. In an industrial plant, this char would be collected in a cyclone and reintroduced in the fuel reactor. All the calculations presented hereafter considered the effective char 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}) is defined as the fraction of the carbon introduced converted to gas in the fuel reactor. Only CH₄, CO and CO₂ were considered, as the amount of tars and hydrocarbons heavier than CH₄ was negligible.

$$\eta_{CC} = \frac{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR}]_{out} - [F_{CO_2,FR}]_{in}}{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} + F_{CO_2,AR}]_{out} - [F_{CO_2,FR}]_{in}} \quad (9)$$

where $F_{i,FR}$ is the i species molar flow in the fuel reactor inlet/outlet stream. For the experiments using CO₂ as fluidization agent, the inlet CO₂ flow must be subtracted. $F_{CO_2,AR}$ 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:

$$X_{char} = \frac{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} - F_{C,vol}]_{out} - [F_{CO_2,FR}]_{in}}{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} + F_{CO_2,AR} - F_{C,vol}]_{out} - [F_{CO_2,FR}]_{in}} = \frac{F_{C,char,eff} - F_{CO_2,AR}}{F_{C,char,eff}} \quad (10)$$

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 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 combustion efficiency in the fuel reactor ($\eta_{comb,FR}$) is a measure of the gas conversion in the fuel reactor. It is defined as the fraction of oxygen demanded by the volatile matter and gasification products that is supplied by the oxygen carrier in the fuel reactor. It is therefore dependent on the reaction rate of Fe-ESF particles with the gaseous fuels and on the amount of gases generated, i.e. the volatile matter content of the fuel and the char conversion. The oxygen supplied by the oxygen carrier in the fuel reactor is calculated through the oxygen containing species in the product gas. The combustion efficiency in the fuel reactor was calculated as:

$$\eta_{comb,FR} = \frac{[0.5 \cdot F_{H_2O,FR} + F_{CO_2,FR} + 0.5 \cdot F_{CO,FR}]_{out} - [0.5 \cdot F_{H_2O,FR} + F_{CO_2,FR} + 0.5 \cdot O_{coal,eff}]_{in}}{O_{2demand,coal,eff} - F_{CO_2,AR}} \quad (11)$$

where $O_{coal,eff}$ is the flow of oxygen contained in the effective coal introduced.

$O_{2demand,coal,eff}$ is the oxygen flow needed to completely burn the fuel and is calculated with the volatile matter in the coal feed and the effective char flow. The steam flow is calculated from a hydrogen balance in the fuel reactor.

From the value of the combustion efficiency, a value for the oxygen needed for complete combustion of the gases in the fuel reactor could be calculated. However and regarding practical applications, it would be more interesting to calculate the oxygen demand for the whole process. The oxygen demand represents the fraction of oxygen required in the oxygen polishing step after the fuel reactor compared with the oxygen needed to burn the same amount of fuel. Thus, the oxygen demand is not affected by the char conversion, as it is referred to the needs of oxygen to burn all the amount of fuel introduced to the system.

Considering this, the total oxygen demand (Ω_T), evaluates the performance of the combustion

process in this unit and is defined as the fraction of oxygen lacking to achieve a complete combustion to CO₂ and H₂O of the fuel reactor product gas in comparison to the oxygen demand of the effective introduced coal, $O_{2,demand,coal,eff}$.

$$\Omega_T = \frac{O_{2,demand,gases,FR}}{O_{2,demand,coal,eff}} = \frac{0.5 \cdot F_{CO,FR} + 2 \cdot F_{CH_4,FR} + 0.5 \cdot F_{H_2,FR}}{O_{2,demand,coal,eff}} \quad (12)$$

The oxygen carrier to fuel ratio (ϕ) was used to compare the oxygen supplied by the circulating oxygen carrier to the oxygen needed to burn the fuel:

$$\phi = \frac{F_{OC} \cdot R_{OC}}{\Omega_{SF}} \quad (13)$$

where F_{OC} is the solid circulation rate and Ω_{SF} is the amount of oxygen necessary to burn the solid fuel introduced expressed as kg oxygen/kg coal·s. Stoichiometric conditions are represented by an oxygen carrier to fuel ratio equal to one.

The rate of oxygen transferred by the Fe-ESF ($-r_O$), is also calculated as the oxygen gained in the oxygen-containing gases (CO, CO₂ and H₂O), divided by the amount of oxygen carrier in the fuel reactor ($m_{OC,FR}$):

$$(-r_O) = \frac{([0.5 \cdot F_{H_2O,FR} + F_{CO_2,FR} + 0.5 \cdot F_{CO,FR}]_{out} - [0.5 \cdot F_{H_2O,FR} + F_{CO_2,FR} + 0.5 \cdot F_{CO,FR}]_{in}) \cdot M_{O_2}}{m_{OC,FR}} \quad (14)$$

The mean residence time of the Fe-ESF particles is also estimated assuming that the char and ash present in the fuel reactor are low and perfect mixing of the oxygen carrier particles:

$$t_{m,OC} = \frac{m_{OC,FR}}{F_{OC}} \quad (15)$$

If there was no char elutriation in the fuel reactor, the residence time of the Fe-ESF material and the char particles would be the same, but as some char particles may escape from the bed, the residence time of the char particles would be lower. This value is calculated as the mass of char in the fuel reactor, $m_{char,FR}$, divided by the char flow that exits the fuel reactor, which is the sum of carbon in the elutriated particles $C_{char,elutr}$ and the carbon flow from the char to the air-reactor $C_{char,AR}$.

$$t_{m,char} = \frac{m_{char,FR}}{C_{char,AR} + C_{char,elutr}} \quad (16)$$

The rate of char conversion, $(-r_C)$, was calculated assuming the fuel reactor as a continuous stirred tank reactor.

$$\frac{F_{CO_2,AR}}{F_{C,chargeff}} = \frac{1}{(-r_C) \cdot t_{m,char} + 1} \quad (17)$$

3. Results and Discussion

A detailed study of the influence of different variables on the performance of CLC of coal using Fe-ESF was carried out in order to consider this material as an alternative oxygen

carrier. The variables analyzed are the fuel reactor temperature, the coal feeding rate, the solids circulation rate and the composition of the fluidizing/gasifying mixture. A bituminous Colombian coal with a high volatile content is used as fuel.

3.1 Effect of the fuel reactor temperature

The first analysis of the performance of the Fe-ESF as oxygen carrier is the effect of the fuel reactor temperature. Steam is used as fluidizing/gasifying agent. As an example, Figure 2 presents the concentrations (dry basis and N₂ free) of the main product gases detected at the outlet of both fuel and air reactors in a typical experiment where the fuel reactor temperature was varied. The experiment was performed at stoichiometric conditions, i.e oxygen carrier to fuel ratio equal to one ($\lambda = 1$). As it can be seen in Figure 2, the steady state after any change in temperature was fast reached. The steady state for each operating condition was maintained during at least 30 minutes. Temperatures in Figure 2 varied between 880 and 925°C. In this temperature range, the main component of the fuel reactor outlet was CO₂. CO, H₂ and CH₄ were also detected as not fully oxidized products of devolatilization and char gasification. In order to test the presence of C₂-C₄ hydrocarbons, some samples were analyzed in a GC and no hydrocarbons higher than methane were detected. Tar measurements in the outlet stream of the fuel reactor were also done, according to the tar protocol (Simell et al., 2000). After reaching steady state at the corresponding temperature, the product gases from the fuel reactor were flowed during one hour through two impingers at 0°C and another six at -18°C so that both moisture and tar could be collected by absorption in isopropanol. These analyses showed that there were no tars in the fuel reactor outlet flow. From the previous results, it can be concluded that all the hydrocarbons higher than methane generated in coal pyrolysis were reformed or partially/fully oxidized by the Fe-ESF. In the air reactor,

CO₂ was detected as the combustion product of the char that was not gasified in the fuel reactor and transferred to the air reactor.

Figure 3 shows the evolution of CO₂, CO, H₂ and CH₄ averaged concentration (dry basis N₂ free) with temperature. The CO₂, CO and H₂ concentrations registered were far from the corresponding to the WGS equilibrium at the corresponding temperature. The CO₂ values increased with temperature from 85.2 to 92.3%. However, the CO, H₂ and CH₄ concentrations decreased with temperature CO (3.2-1.8%), H₂ (9.2-4.8%) and CH₄ (2-1%). If temperature increases, gasification reactions are favoured and the amount of gases generated is higher. However, the rise in temperature also increases the reaction rate between these gases and the oxygen carrier particles. If the concentration of CO and H₂ is decreased, the inhibition effect on the char gasification rate of both gases, especially H₂, losses intensity and the char gasification proceeds faster. The combination of the effects previously described leads to the increase on the CO₂ concentration and the decrease of the concentration values of CO, H₂ and CH₄. Figure 4 shows the carbon capture efficiency (η_{CC}), char conversion (X_{char}) and combustion efficiency in the fuel reactor ($\eta_{Comb,FR}$) in experiments at different temperatures. The carbon capture efficiency increased with temperature from 44.5% at 880°C up to a value of 67% at the highest temperature tested (930°C). The amount of carbon converted to gas in the fuel reactor increases as the amount of char gasified increases. This is the reason why the increase in the carbon capture efficiency is related to the increase in the char conversion with temperature also observed in Figure 4. At 880°C, only 19.8% of the char in the fuel reactor was gasified while the extent of char conversion at 930°C was 57%. If char conversion in the fuel reactor is higher, less char will reach the air reactor, therefore increasing the carbon capture efficiency. To further increase the values of the carbon capture efficiency, higher temperatures in the fuel reactor would be needed in order to speed up the

char gasification process. It is interesting to note that the values presented here were obtained without the presence of a carbon separation system. The effect of the use of a carbon separation system on the performance of the CLC process with coal has been analyzed elsewhere (Cuadrat et al., 2012b, 2012e). Higher efficiencies of the carbon separation system lead to higher char conversion values and carbon capture efficiencies.

Figure 4 also shows the combustion efficiency in the fuel reactor for the different temperatures. The efficiency values were high in all the cases and increased with temperature from 86.8% at 880°C to 93.1% at 930°C. The values of the oxygen demand decrease with temperature from 4.7% at 880°C to 3% at 930°C. It is expected that higher temperatures would even reduce this value of oxygen demand.

3.2 Effect of the coal feeding rate

To evaluate the effect on the performance of the CLC process of the coal feeding rate, the rest of the variables were maintained constant. As can be seen in Table 3, the fuel reactor temperature was 905°C and the oxygen carrier circulation rate was set to 10.6 kg/h. All the experiments were performed using steam as gasifying agent. In all the experiments, there was an excess of both oxygen and steam so that they did not limit the reaction rate. The oxygen carrier to fuel ratio was always above stoichiometric conditions ($\lambda = 1.1 - 2.4$) and in all the cases the steam to fixed carbon ratio was over 2.6. The coal feeding rate was varied between 59 and 165 g/h, which correspond to a thermal power of 292-610 W_{th}.

Figure 5 summarizes the main results obtained. As explained before, these results consider the effective carbon flow fed to the system. Since the circulation rate of Fe-ESF is fixed, the residence time of the oxygen carrier in the fuel reactor is the same in all the experiments,

around 4.5 minutes. The corresponding amount of Fe-ESF in the fuel reactor also remained constant. As there are more gases to be burnt by the same amount of Fe-ESF, the conversion of those gases may decrease. In [Figure 5](#), a slight decrease in the combustion efficiency in the fuel reactor from 89 to 86% was registered. The differences in char conversion were not large for a significant change in the coal feeding rate, which is almost tripled. The reason behind is that the differences in the residence time values for the char particles in the fuel reactor are not large enough to significantly affect char conversion. These values vary between 1.1 and 1.8 minutes. Finally, it is interesting to note that the values of the oxygen demand were lower than 10% in all the experiments performed. They increased with the effective carbon fed from 4% to 7%.

3.3 Effect of the solids circulation rate

In the analysis of the influence of the solid circulation rate, the fuel reactor temperature was maintained at 905°C. All the experiments were done using steam as fluidizing agent. The solid circulation rate varied between 2 and 20.6 kg/h. These rates correspond to values of the oxygen carrier to fuel ratio ($\square$) between 0.5 and 6, i.e. between conditions where the Fe-ESF did not transport the oxygen needed to fully oxidize the fuel and conditions where there was an excess of oxygen. The main parameters showing the process performance are presented in [Figure 6](#). As it can be seen in [Figure 6 \(A\)](#), the carbon capture efficiency decreases as the oxygen carrier to fuel ratio is higher, i.e, the solid circulation rate is higher, as previously observed by other researchers ([Berguerand and Lyngfelt 2010](#), [Cuadrat et al., 2012c](#)). This decrease is steeper for values of $\square$ lower than the unity. For higher $\square$ values the carbon capture did not experience significant variations. This trend is parallel to that showed by the char conversion. Once the temperature has been fixed, the extent of char conversion depends on the residence time of the char particles in the fuel reactor. The residence time is inversely

related to the solid circulation rate and therefore, the $\square$ value (Cuadrat et al., 2012c). Figure 6 (B) shows the link between residence time and $\square$. If the oxygen carrier circulates at a low rate between the fuel and air reactors, the residence time of the oxygen carrier in the fuel reactor will be higher and therefore the residence time of the char particles, so higher char conversion extent would be expected and therefore lower value of $F_{CO_2,AR}$. According to Figure 6 (B), the residence time almost doubles when $\square$ decreases from 1 to 0.5. However, the higher the value of $\square$, the lower the differences in the residence time, which result in small differences in the char conversion or carbon capture efficiency. Also in Figure 6 (A) the combustion efficiency in the fuel reactor is represented. The combustion efficiency was not significantly affected by the change in the solid circulation rate for values of $\square$ higher than 1. In all the cases, the values obtained were high, around 90%. However, a slight decrease to 88% was observed for $\square \sim 0.5$, because there was not enough oxygen available to burn the fuel. The values of the oxygen demand (Ω_T) were also calculated for the different experiments performed, but were not much affected by the solid circulation rate. The average estimated value was 4%.

3.4 Effect of the gasification agent: steam/CO₂ mixtures

The use of CO₂ from recirculated flue gases in the gasifying gas fed to the fuel reactor is interesting, as it would reduce the energy needs related to steam generation. The possibility of using CO₂ will depend on the type of coal used as fuel (Cuadrat et al., 2012d). In this case, all the experiments presented were performed at 930°C.

Figure 7 shows the carbon capture efficiency and combustion efficiency in the fuel reactor for steam and CO₂ mixtures. As expected, the carbon capture efficiency decreased as more CO₂ was present in the gasifying mixture, due to a slower conversion of the char particles in the

reaction with CO₂. The value of the carbon capture efficiency decreases linearly with the amount of CO₂ introduced in the feed. At the same temperature, the carbon capture using steam as gasifying agent was 67% and using CO₂ was 42.3%, which corresponds to a decrease percentage around 37%. If a gasifying mixture 70:30 (H₂O:CO₂ molar ratio) was used, the decrease in the carbon capture is 15%.

The gasifying gas used does not affect much the volatile release and therefore the unburnt products at the outlet of the fuel reactor. Considering that there is good contact between the gases and oxygen carrier and the high reactivity of the Fe-ESF oxygen carrier, it is not expected that the combustion efficiency changes significantly in these experiments. As it can be seen in **Figure 8**, the combustion efficiency was not affected. The average value for the combustion efficiency in the fuel reactor was 94%. According to this value, the Fe-ESF was able to burn most of the gases produced in the devolatilization/gasification in any case. The present results confirm the need to limit the amount of CO₂ fed in order to maintain the adequate performance of the process in case that a bituminous coal is used as a fuel. A 70:30 H₂O:CO₂ molar ratio could be considered as adequate for operation, as it would not excessively affect the performance of the CLC system (40 hours).

3.5 Characterization of the Fe-ESF material during operation in the continuous unit

As a part of the evaluation of the suitability of the Fe-ESF as oxygen carrier for the CLC process with coal, both the possible changes in physical and chemical properties of the oxygen carrier particles were studied during the experiments in the continuous unit. For that purpose, several samples were extracted from the fuel and air reactor and the filters at the fuel and air reactor outlet streams at different operating times and further characterized by

different techniques. It is also interesting to highlight that no defluidization or agglomeration problems of the Fe-ESF material were detected during the experiments here presented.

The first aspect to be analyzed was the composition of the samples after their use in the continuous unit. Samples were extracted from the air reactor at different times of operation (from 0.5 to 38 hours). They were analyzed using XRD to determine the major solid crystalline phases. In all samples, Fe_2O_3 and $\beta\text{-Al}_2\text{O}_3$ were the only compounds, i.e. no new compounds were formed during the experiments. The active iron content in samples extracted after 15.3 and 27 hours of operation was determined in the experiments in a TGA using 15% H_2 at 950°C. The iron content in fines elutriated from the installation after 4.5 and 32 hours of operation was also determined using this experimental procedure. In all the cases, both in the samples from the air reactor and from the fines, the amount of Fe_2O_3 determined was 58%, the same as in the calcined Fe-ESF. No changes in composition were observed and therefore the value of the oxygen transport capacity (R_{OC}) remained constant.

As mentioned before, the reactivity of the Fe-ESF material increased with the number of redox cycles in TGA or batch fluidized-bed experiments (Mendiara et al., 2012a, 2013b). In this work, the activation of the Fe-ESF is evaluated during operation in the continuous unit. In order to compare with the results obtained in the previous works, the reactivity of the extracted samples was evaluated at 950°C with 5% H_2 + 40% H_2O in a TGA apparatus. The conversion for reduction, X_r , and oxidation, X_o , was calculated from the mass variations registered in TGA as:

$$X_r = \frac{m_o - m}{m_o - m_r} = \frac{m_o - m}{R_{OC} m_o} \quad (18)$$

$$X_o = 1 - X_r = \frac{m - m_r}{R_{OC} m_o} \quad (19)$$

where m is the instantaneous mass of the sample and m_o and m_r are the mass of fully oxidized and reduced oxygen carrier, respectively.

Figure 8 compares the final activation state reached by an Fe-ESF sample in a TGA using hydrogen and in a batch fluidized bed reactor using char from bituminous coal as fuel with the conversion curves obtained for the samples extracted from the continuous unit at different operating times. All the results presented in Figure 8 were obtained in a TGA at 950°C using hydrogen as reducing agent. Figure 8 (A) shows the results for the reducing period. As it can be observed, the reactivity slightly increases with time during operation. However, after 40 hours, the reactivity showed by the Fe-ESF is far from that obtained for the samples activated in a batch fluidized bed using char as fuel and closer to that displayed by the fresh sample. This fact is attributed to the low conversion values of the Fe-ESF obtained in the continuous unit compared to those reached in both the batch reactor and the TGA apparatus with gaseous fuels. Figure 8 (B) shows the corresponding results for the oxidation period. Again, the gain in reactivity with time was very little and the final reactivity is more similar to that of the fresh Fe-ESF. It seems that the activation of the Fe-ESF in the continuous unit is a very slow process and would take longer times than those tested in this work.

Figures 9 and 10 present the evolution with time of different characteristics of the Fe-ESF material. Figure 9 presents the evolution with time in the porosity of the oxygen carrier. According to the analyses performed, the pores in the oxygen carrier are in the macroporous range (> 50 nm). It can be observed that the pore size distribution of the Fe-ESF material changes considerably during operation compared to the fresh material. The mean pore size shifts to macropores of smaller size. The porosity increases from a value of 3.7% to 22% after

40 hours of operation. The increase in the porosity could be related to the slight increase in the reactivity of the sample observed in the TGA experiments with samples extracted after different hours of operation. Figure 10 shows the SEM images of calcined and used Fe-ESF after 15.3 and 40 hours of operation. The above mentioned increase in porosity can be also checked in Figures 10 (A) to (C). Another interesting result obtained from the SEM analysis is that no indication of coal ash melting on the oxygen carrier surface was found.

In Figure 11, the effect of the operating time on the averaged crushing strength of the particles extracted from the continuous unit was analyzed. As a reference, a continuous line for a crushing strength value equal to 1 N is included in the graph. From the experience gained up to date from the relationship between crushing strength and lifetime of the particles in a continuous unit, it is believed that values considerable lower than 1 N might be too soft for long-time circulation. The calcined Fe-ESF particles present an initial crushing strength of 4.3 N, which is high enough to operate in a CLC system. However, this value decreases with time. After 55 hours of hot fluidization, the crushing strength is half of the initial value (around 2 N). Note that the values in Figure 11 are averaged values and in most of the cases they presented high standard deviation (up to 1.5 N). Fine particles ($< 40\ \mu\text{m}$) were lost during operation and retained in the filters at the outlet of the reactors. It was estimated that the attrition rate was similar to that reported before for this material in experiments in a batch fluidized bed reactor (Mendiara et al., 2012a), i.e. 0.2 %/h. This attrition rate can be considered as a moderate value and would correspond to an averaged lifetime of 500 h. The adequacy of this lifetime to the needs of the CLC system will depend on the composition and the behaviour of the coal ashes. If ashes are not entrained as fly ashes, then it is necessary a draining stream to avoid accumulation in the system. This will reduce the lifetime of the oxygen carrier. Besides, both the decrease in the crushing strength with time and the attrition

rate of the Fe-ESF material would imply a frequent need of fresh oxygen carrier in the CLC system but it would be compensated by the fact that the Fe-ESF material is a residue, available in large quantities at no cost, what would make the oxygen carrier needs feasible.

4. Evaluation of the performance of Fe-ESF in a continuous unit

The results previously presented in this paper for Fe-ESF in the continuous CLC unit indicate that it could be an advantageous material to be used as oxygen carrier in the further scale-up of the CLC process with coal. So far, mostly ilmenite has been proposed as oxygen carrier for this process. In this section, the results obtained in this work are compared to those obtained using ilmenite in the same CLC rig and for the same bituminous Colombian coal, (Cuadrat et al., 2011, 2012c) in order to highlight the improvements in the CLC performance that the use of Fe-ESF could bring.

Figure 12 presents the values of oxygen demand together with the carbon capture efficiency at different fuel reactor temperatures for ilmenite and Fe-ESF. The experiments were performed with a solids inventory in the fuel reactor of 3140 kg/MW_{th} in the case of ilmenite and 2850 kg/MW_{th} for the Fe-ESF material. The results were obtained under stoichiometric conditions ($\phi = 1$). As it can be seen in Figure 12 (A) the oxygen demand decreases with temperature for both oxygen carriers. However, lower values of oxygen demand were always obtained using Fe-ESF regardless of the temperature. In this case the oxygen demand was always lower than 5%. At 930°C, the oxygen demand with ilmenite was 5% while it was 3% for Fe-ESF. This could be explained by the higher reactivity of the Fe-ESF to the main gases present in the fuel reactor (CO, H₂, CH₄) compared to ilmenite (Mendiara et al., 2012a). In order to further compare the results for ilmenite and the Fe-ESF the rate of oxygen transfer ($-r_O$) was calculated. In both cases, the rate of oxygen transferred from the oxygen carrier to the gaseous fuels increases as temperature increases. At 930°C the value of ($-r_O$) for Fe-ESF is

$2.1 \cdot 10^{-5}$ kg O₂/s·kg oxygen carrier, around 1.5 times that obtained for ilmenite. Besides a rate index, expressed in %/min, can be obtained from the TGA experiments for the reaction of an oxygen carrier with different gases. This value has been used before as a mean to compare the reactivity of different oxygen carriers. In the work of Mendiara et al. (2012b), the rate indexes for several Fe-based potential oxygen carriers for CLC with coal were presented. The rate index in the reaction with hydrogen at 950°C for ilmenite after used in the 500W_{th} continuous unit was 7.9 %/min while in the present work a value of 8.7 %/min for Fe-ESF was calculated, higher than that observed for ilmenite in the same conditions. Finally, note that the lower values of oxygen demand reached with Fe-ESF were obtained with lower solids inventory compared to ilmenite. This fact would allow smaller fuel reactor size using Fe-ESF with the additional advantage of fewer requirements in the oxygen polishing step.

Figure 12 (B) compares the values of carbon capture efficiency obtained for different fuel reactor temperatures using ilmenite and Fe-ESF. The values obtained at low temperatures are similar but in both cases they increase with temperature as char gasification is more favoured at higher temperatures. However, the increase is steeper for ilmenite and higher differences are expected at temperatures around 1000°C. This could be explained by the different values of oxygen transport capacity (R_{OC}) of the materials, 4% for ilmenite and 2.4% for Fe-ESF. To transfer the same amount of oxygen to the fuel, the solids circulation rate needed with ilmenite is lower (2.1 kg/h) than with Fe-ESF (5.4 kg/h). As a consequence, the residence time of the char particles in the fuel reactor using ilmenite will be higher than with Fe-ESF, which has a significant effect on the char conversion and the carbon capture efficiency. The rate of char conversion, ($-r_C$), was also calculated at 930°C using both materials and resulted 14.3% and 19.2% for ilmenite and Fe-ESF, respectively. If Fe-ESF is the bed material the rate is slightly higher than when ilmenite was used. Thus, the gasification reaction seems to

be enhanced in some extent by this more reactive material, but still the residence time in the fuel reactor should be high enough. In order to increase the residence time of the char particles in the fuel reactor without excessively increasing its size a carbon separation unit can be used (Cao et al, 2006). This unit allows the separation of the oxygen carrier and the unconverted char particles, which are returned back to the fuel reactor. With the incorporation of the carbon separation system, the differences in the carbon capture efficiency between ilmenite and Fe-ESF would be notably reduced.

Figure 13 shows the values of the combustion efficiency reached in the fuel reactor at different temperatures using ilmenite and Fe-ESF. Again the higher reactivity of the Fe-ESF material compared to ilmenite becomes visible. In both cases, the combustion efficiency increases with temperature, but the values registered are always higher for Fe-ESF. At 930°C, the combustion efficiency for ilmenite is around 82% while it is 93% for the Fe-ESF material. Besides the differences in the reactivity of both materials, the water-gas-shift (WGS) reaction can be also playing a role:

Ilmenite was not capable of catalyzing this shift reaction (Cuadrat et al., 2012b). However, the Fe-ESF oxygen carrier is able to catalyze the conversion of the unreacted CO to CO₂ according to the WGS, while the H₂ formed rapidly reacts with the oxygen carrier (Mendiara et al., 2013b). This would favour a higher conversion of the gases generated in coal combustion and therefore higher combustion efficiencies.

Not only is the CLC performance improved with the use of Fe-ESF. There are also advantages if the evolution of the properties of both carriers during operation is compared. The Fe-ESF presents an interesting advantage compared to ilmenite. It was observed that ilmenite undergoes a migration phenomenon of the iron oxide present towards the external part of the particle while the core is titanium enriched. That segregation leads to a gradual decrease in the oxygen transport capacity of ilmenite (Adánez et al., 2010). However, as it was explained before, no changes in R_{OC} were observed after 40 hours of operation with Fe-ESF in the continuous unit.

If all the all the issues summarized in this section are considered, this Fe-ESF material can be regarded as an interesting alternative to ilmenite in CLC applications to coal combustion.

5. Conclusions

An iron-based residue from alumina production (Fe-ESF) was tested as oxygen carrier in a 500W_{th} continuous CLC unit using bituminous coal as fuel. The influence on the performance of this material of different operational parameters was tested in order to asses the feasibility of this material as potential oxygen carrier.

High combustion efficiencies up to 90% were obtained. The main unburnt products detected in the outlet stream of the fuel reactor were CO, H₂ and CH₄.

The oxygen demand was less than 5% in all conditions. To obtain high values of the carbon capture efficiency, temperatures higher than 950°C would be required. The change in the coal feeding rate did not affect significantly the values of the combustion and carbon capture efficiency in the experimental conditions used. However, the solids circulation rate, i.e the residence time of the solids in the fuel reactor, was critical in order to obtain adequate values

of the carbon capture efficiency. The composition of the gasifying gas fed to the fuel reactor also proved to be important to maintain a high efficiency in the carbon capture. Using CO₂ as gasifying agent, a decrease in the carbon capture efficiency around 37% was observed.

Therefore, the amount of CO₂ present in the feeding should be limited.

During operation, no defluidization or agglomeration problems were detected with the Fe-ESF material and the oxygen transfer capacity was maintained constant. The porosity of the oxygen carrier increased with time while the value of crushing strength decreased. Although frequent replacement is expected, the attrition rate observed allowed continuous operation in a CLC system. The lifetime of the Fe-ESF was adequate although it would also depend on the ash drainage needs.

In comparison to ilmenite, lower oxygen demand and higher oxygen transfer rates were observed for the Fe-ESF material. Considering all the results presented in this work, it can be concluded that this low cost material seems to be an advantageous alternative for ilmenite in CLC processes with coal.

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Nomenclature

$C_{char, elutr}$: carbon in the elutriated particles (kg/s)

$C_{char, AR}$: carbon flow from the char to the air reactor (kg/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)

F_{OC} : solid circulation rate (kg/s)

m : instantaneous mass of oxygen carrier sample (kg)

$m_{char, FR}$: mass of char in the fuel reactor (kg/s)

m_o : mass of fully oxidized oxygen carrier sample (kg)

M_{O_2} : oxygen molar weight (kg/mol)

$m_{OC, FR}$: mass of oxygen carrier in the fuel reactor (kg)

m_r : mass of fully reduced oxygen carrier sample (kg)

$O_{coal, eff}$: flow of oxygen contained in the effective coal (mol/s)

$O_{2\ demand, coal, eff}$: oxygen flow needed to completely burn the fuel (mol/s)

$(-r_c)$: instantaneous rate of char conversion (s^{-1})

$(-r_O)$: rate of oxygen transferred from the oxygen carrier to the fuel (mol/s)

R_{OC} : oxygen transport capacity

$t_{m, OC}$: mean residence time of the oxygen carrier in the fuel reactor (s)

$t_{m, char}$: mean residence time of char in the fuel reactor (s)

X_{char} : char conversion

X_r : conversion for the reduction of the oxygen carrier

X_o : conversion for the oxidation of the oxygen carrier

Greek symbols

ϕ : oxygen carrier to fuel ratio

Ω_{SF} : oxygen necessary to burn the solid fuel (kg oxygen/kg coal·s)

Ω_T : total oxygen demand

η_{CC} : carbon capture efficiency

$\eta_{comb, FR}$: combustion efficiency in the fuel reactor

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Tables

Table 1. Characterization of the Fe-ESF material

	Calcined
Fe ₂ O ₃ (% wt)	58 ^a
XRD main phases	Fe ₂ O ₃ , β -Al ₂ O ₃
Crushing strength (N)	4.3
Oxygen transport capacity, R_{OC} , (%)	2
Porosity (%)	10
Skeletal density (kg/m ³)	4266
Specific surface area, BET (m ² /g)	0.1

^a Determined by TGA

Table 2. Ultimate and proximate analyses of bituminous Colombian coal “El Cerrejón” (% weight)

Ultimate analysis		Proximate analysis	
Carbon	65.8	Moisture	2.3
Hydrogen	3.3	Ash	8.8
Nitrogen	1.6	Volatile matter	33.0
Sulfur	0.6	Fixed carbon	55.9
LHV (kJ/kg)	21900		

Table 3. Experimental conditions used

$T_{FR}, ^\circ\text{C}$	Coal feed, g/h	Fuel power, W_{th}	Solid circ. Rate, kg/h	t_{res} , solids in FR (min)	$\frac{\text{Gasif.agent}}{\text{Fixed C}}, \text{mol/mol}$	Gasification mixture, vol.%H ₂ O
870-930	66.9	400	5.4	11.5	4	100
905	59-165	292-610	10.6	4	3.9 - 2.6	100
905	52.3	314	2 – 20.6	18 – 2.1	4.5	100
930	52.3	314	4.7	10	4.5	100;70;0