Development of a Mn-Fe-Ti based Oxygen Carrier in Chemical Looping Combustion with Coal

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Abstract

Due to its price and availability, coal is positioning as an increasingly important fuel for the near future. Many research efforts are focused on clean coal technologies, especially on the minimization of greenhouse gas emission. In this sense, CO_2 capture and storage from coal combustion is a mid-term solution to stabilize CO_2 atmospheric concentration. The recently developed Chemical Looping Combustion (CLC) technology facilitates inherent CO_2 capture in coal combustion processes. The oxygen needed for the coal oxidation is provided by an oxygen carrier, normally a metal oxide, circulating between two interconnected fluidized bed reactors. In the fuel reactor the coal is oxidized to CO_2 and H_2O while the carrier is reduced. CO_2 in the product stream can be easily captured, once the water has been condensed. The reduced oxygen carrier is then transported to the air reactor and re-oxidized in air. If coal is used as fuel, the coal and oxygen carrier are physically mixed in the fuel reactor and H_2O and/or CO_2 are used as gasifying agents. Then, gasification products are oxidized in-situ by reacting with oxygen carrier particles

This work analyzes the development of a Mn-Fe-Ti based oxygen carrier in the combustion of coal in a 500 W_{th} continuous unit. Combustion tests were carried out for 20 hours at 900 ºC both in the fuel and air reactors and the oxygen concentration fed into the air reactor was the necessary to reach an oxygen concentration leaving of the air reactor about 4-6%. Benefits on combustion efficiency were found with high solids circulation rates. A total oxygen demand of 3.6 % was obtained using ϕ values higher than 2.5.

Keywords: CO_2 capture, combustion, coal, chemical looping combustion, Mn-Fe-Ti oxides

1. Introduction

Despite an increasing commitment in many countries to low- or zero carbon sources, the energy sector continues to emit greenhouse gases and pollutants at a rate that has profound consequences for the environment and human health. Global coal demand grows by 15% to 2040 through current low cost prices, which is estimated in 550 million tons of oil equivalent in the period 2013-2035. This fact together with the rise of the rest of fossil fuels demand will cause an increase of CO_2 emissions with an average annual growth rate by 0.7% during this period (IEA, 2014).However, the reduction of 50% of the global CO_2 emissions is necessary to limit the long-term global average temperature rise around 2 ºC by the year 2035. Carbon Capture and Storage (CCS) is seen as one of the more important reduction measures for large CO_2 stationary point sources (Markewitz et al., 2012). Chemical-Looping Combustion (CLC)

is a young carbon capture technology highlighting by to be much cheaper that current other carbon capture technologies (Rubin et al., 2012).

The CLC is based in two reactor so-called fuel and air reactors with an oxygen carrier continuously circulating between them. In the fuel reactor, the fuel combustion happens using oxygen available in the oxygen carrier, usually being a metal oxide. In the air reactor, the oxygen carrier is regenerated by oxidation with air. The total chemical reaction and combustion enthalpy is the same than in normal combustion with air. The oxygen carrier is able to transport the oxygen from air to fuel while the contact between the air and the fuel is avoided. In the fuel reactor, CO_2 and steam are mainly obtained as combustion products, which facilities CO_2 capture once the water has been condensed. The CO_2 capture is inherent to the process due to that a separation step would no longer be necessary. In the CLC with solid fuels, the fuel is physical introduced and mixed with the oxygen carrier within the fuel reactor. A scheme of the CLC technology with solid fuels is shown in Fig.1.
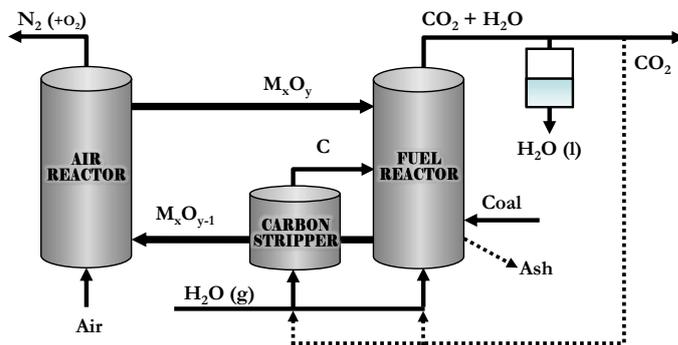

Fig. 1. Scheme of CLC processes with solid fuels

During the last decade, the development of the CLC with solid fuels has meaning an important advance from the hand of two processes: *in-situ* Gasification (*i*G-CLC) and Chemical Looping with Oxygen Uncoupling (CLOU) (Adánez et al., 2012; Lyngfelt, 2014).

In the *i*G-CLC concept, steam and/or recycled CO_2 are supplied to the fuel reactor as gasifying agents. In-situ gasification of solid fuel (e.g. coal) takes place into the fuel reactor, as well as subsequent oxidation of the gasification products generated by gas-solid reactions with the oxygen carrier (M_xO_y). The reduced oxygen carrier (M_xO_{y-1}) is sent to the air reactor where it is oxidized with oxygen from air being found ready to start a new redox cycle again.

In *i*G-CLC, the gasification is a slow step during the coal conversion. This fact may cause that the stream of the reduced oxygen carrier particles that arrives at the air reactor containing unconverted char particles from fuel reactor. Once the char particles reach the air reactor they are oxidized to CO_2, which decreases the CO_2 capture efficiency significantly. One solution to avoid it without increasing the fuel reactor size in excess can be to include a carbon separation step (e.g. carbon stripper) between both fuel and air reactors (Kramp et al., 2012). Despite the implantation of this improvement, complete combustion of gases in the fuel reactor has not been reported in exiting *i*G-CLC facilities. Some solutions to oxidize the unconverted compounds have been proposed by Gayán et al. (2013)

The CLOU concept was developed based on the use of metal oxides with the capacity of release gaseous oxygen in the fuel reactor. Thereby, solid fuel combustion with the gas phase oxygen avoiding the slow gasification step (Mattisson et al., 2009). Besides, these metal oxides can be regenerated at high temperatures. Copper and manganese oxides were identified as the most promising compounds to be used as oxygen carrier for CLOU (Mattisson et al., 2009) The CLOU concept was demonstrated by Abad et al. (2012) in a 1.5 kW_{th} unit burning a bituminous coal with a Cu-based oxygen carrier. Complete coal combustion and CO_2 capture rates close to 100% were reached.

Nevertheless, manganese oxides have recently focused attention because it is cheaper than copper oxides. However, traditional Mn-based oxygen carrier supported on inert materials, e.g. ZrO_2, did not show oxygen uncoupling properties (Abad et al., 2006; Johansson et al., 2006; Zafar et al., 2007). On the contrary, Mn-based perovskites or spinels have shown suitable characteristics for CLOU (Rydén et al., 2014). Thus, fuel conversion was improved by the oxygen uncoupling capacity with $CaMnO_{3-\delta}$ based oxygen carrier, both for gaseous (Källén et al., 2013; Cabello et al., 2014) and solid fuels (Schmidt et al., 2014). High circulation rates were required in order to take advantage of the oxygen uncoupling capacity (Cabello et al, 2014; Abad et al, 2014; de Diego et al., 2014). In recent years a great interest has arisen in the use of manganese and iron mixed oxides as oxygen carrier due to their potential use in CLOU mode. Azimi et al. (2013a) reported a theoretical binary phase diagram of these oxides suggesting the range from molar ratio between the oxides that can be attractive for CLOU mode. Other authors also have reported studies with these combined oxides (Azimi et al., 2013b; 2014; Källén et al., 2014; Larring et al., 2014). These oxygen carriers have shown good oxygen uncoupling properties during the combustion of coal in batch reactors, provided that the oxygen carrier particles were completely reduced.

In this work a mixture of manganese, iron and titanium oxides has been used to preparation of oxygen carrier particles by spray drying to assess their performance in a continuous CLC unit with coal. Oxygen carrier circulation rate was varied to analyze the effect of the oxygen carrier to fuel ratio on the combustion efficiency. In all tests performed, the air used as oxidation agent of the oxygen carrier particles in the air reactor was mixed with a N_2 stream before to be introduced at the bottom of the bubbling bed in order to achieve oxygen concentrations leaving of the air reactor on the range 4-6%, such as it occurs in a traditional coal combustion energy plant. The final aim was the evaluation of the *i*G-CLC process considering an air excess similar to the conditions of the traditional coal combustion.

2. Experimental

2.1 Materials

A manganese-iron-titanium mixed oxide has been used as oxygen carrier in this work. The oxygen carrier particles were prepared by spray drying and manufactured by the VITO (Flemish Institute for Technological Research) in Belgium using Mn_3O_4 (Strem Chemical, Inc), Fe_2O_3 and TiO_2 (Panreac, Prs) as metal oxides. The Mn_3O_4, Fe_2O_3 and TiO_2 contents were 60, 33 and 7 wt.%, respectively. The particles were exposed to double thermal processing in air atmosphere. First they were calcined 12 hours at 1075 ºC and subsequently the particles were sieved to particle size suitable (+100-300μm). Thereafter, the particles with this size were exposed to a second calcination at 1200 ºC during 2 hours in order to achieve a higher crushing strength. Table 1 shows the main properties of this oxygen carrier called Mn60FeTi7_1200. The oxygen transport capacity, R_{OC}, was determined in a thermogravimetric analyzer (CI Electronics Ltd.). R_{OC} is defined as the mass fraction of the material being transferable oxygen when the oxygen carrier particles are reduced. The crushing strength was determined using a Shimpo FGN-5X crushing strength apparatus. It was taken the average value of 20 measurements of the force needed to fracture a particle. The skeletal density of the material was measured with a Micromeritics AccuPyc II 1340 helium picnometer. Particle porosity was measured by Hg intrusion in a Quantachrome PoreMaster 33. 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 Cu Kα radiation equipped with a graphite monochromator. The main crystalline phases found by XRD analysis were $MnFeO_3$ and Fe_2TiO_4. This

material showed magnetic properties, which would facilitate its separation from ash in the CLC process.

Table 1: Main properties of Mn60FeTi7_1200

R_{OC} (%)	5.9
Crushing Strength (N)	2.0
Skeletal density (kg/m^3)	4630
Porosity (%)	9.5
XRD main phases	$MnFeO_3$, Fe_2TiO_4

A Colombian bituminous coal, so-called "Cerrejón", has been used as fuel. From previous experiences in our group, this coal presents a high swelling behavior. In order to avoid the appearance of these plastic properties in the coal, a thermal pre-treatment for its pre-oxidation was performed. The coal particles were calcined at 180 ºC during 24 hours in air atmosphere (Pis et al., 1996). Table 2 shows the proximate and ultimate analyses of the pre-treated coal. The lower heating value was 21900 kJ/kg and the oxygen demand of coal (Ω_{coal}) was 1.85 kg of oxygen per kg of coal. The coal particles were fed into the fuel reactor with a diameter of +200-300 µm.

Table 2: Main characteristics of pre-treated "Cerrejón" coal (stabilized humidity by exposition to the atmosphere)

Proximate analysis (wt.% raw matter)		Ultimate analysis (wt.% raw matter)	
Moisture	2.3	C	65.8
Volatile matter	33.0	H	3.3
Ash	8.8	N	1.6
Fixed carbon	55.9	S	0.6
		O^a	17.6

^{a} Oxygen by difference

2.2 Experimental setup and procedure

2.2.1 Determination of oxygen transport capacity

The oxygen transport capacity, R_{OC}, of the Mn60FeTi7_1200 was determined through Temperature Programmed Reductions and Oxidations (TPRs and TPOs) in a TGA. TPRs were carried out in three types of environment: high-purity N_2, 15 vol. % H_2 (N_2 to balance) and 15 vol. % CH_4 (with 20 vol. % H_2O and N_2 to balance). TPOs were performed with two different oxygen concentrations: 21 vol. % (air) and 5 vol. % (diluted air). In every test, about 50 mg of new fresh oxygen carrier particles was loaded on a platinum basket, and a gas flow of 25 l$_N$/h was fed. Every sample was heated to 400 ºC in air where no reaction was observed. After, the desired reducing atmosphere was introduced while the material was heating from 400 ºC up to 1000 ºC at a constant rate of 20 ºC/min where they remained during 10 minutes. Subsequently, the oxidizing gas was introduced into the reactor and then the temperature was

decreased at a constant rate of 8 ºC/min down to 400 ºC. After, a new sequence of other TPR followed by other TPO from 400 ºC was repeated.

2.2.2 Tests in a 500 W$_{th}$ CLC facility for coal combustion

Experimental tests were performed in a continuously operated 500 W$_{th}$ CLC plant for solid fuels. A layout of CLC unit is shown in Fig.2. This CLC unit is based on two interconnected bubbling fluidized bed reactors, the fuel (1) and air (3) reactors, connected by a loop seal (2) to avoid the mixing between the air from air reactor and the gases from fuel reactor. The fuel reactor has an internal diameter of 50 mm with a bed height of 200mm. The coal (9) is fed in the bottom of the fuel reactor through two screw feeder system (10). The oxygen carrier is reduced in the bottom of the fuel reactor by gas-solid reaction with the coal gasification products and the gases generated during coal devolatilization. Steam was fed as gasifying medium. Subsequently, the oxygen carrier particles are lead to the air reactor where are re-oxidized with the oxygen from air. The air reactor has an internal diameter of 80 mm with a bed height of 100 mm. The air used as fluidizing agent in the air reactor was mixed with a N$_2$ stream before to be introduced in the bottom of the bubbling bed. This action allows the oxygen concentration leaving the air reactor in the range 4-6% such as it occurs in a traditional coal combustion process. The oxygen concentration supplied into the air reactor was around 8 vol.%. In the air reactor, the top part is based in a narrow riser (4) with an internal diameter of 50mm to guarantee the solids circulation flow rate. A high efficiency cyclone (5) recovered the particles in a solid reservoir (7) which avoids mixing atmospheres between the fuel reactor and the riser. The solids flow returning to the fuel reactor is regulated by a solids control valve (8). The measurement of solids circulation flow rate between air and fuel reactors can be performed through a diverting solids device (6) situated below the cyclone. A filters system (12) is included after air reactor cyclone as well as a condensation step (11) of gas exiting from fuel reactor. This system allows gather any fine oxygen carrier particles and the fly ash.

At the beginning of the experimental runs, 2.75 kg of Mn60FeTi7_1200 was introduced into the CLC unit. The solids inventory into the fuel reactor was around 0.65 kg. The temperatures both in the fuel reactor as in the air reactor were maintained at about 900 ºC. The steam flow used in the fuel reactor was 130 L$_N$/ h, corresponding to a gas velocity of 0.08 m/s at 900 ºC. The oxygen carrier to fuel ratio (ϕ) represents the amount of oxygen required in the fuel reactor to oxidize the coal to CO$_2$ and H$_2$O and is determined by means of the Eq. 1. The ϕ parameter is defined as the amount of the oxygen available in the fuel reactor, which is transported by the oxygen carrier flow from the air reactor respect the stoichiometric oxygen demand of the coal fed (Ω_{coal}).

$$\phi = \frac{R_{OC} \cdot \dot{m}_{OC}}{\dot{m}_{coal} \cdot \Omega_{coal}} \tag{1}$$

where $\dot{m}_{OC}$ is the oxygen carrier circulation flow rate, and $\dot{m}_{coal}$ the coal fedding rate.

In the air reactor the total flow supplied was 1980 L$_N$/h, corresponding to a gas velocity of 0.47 m/s at 900ºC. To achieve this flow, an air flow (754 L$_N$/h) and a N$_2$ flow (1226 L$_N$/h) were mixed.
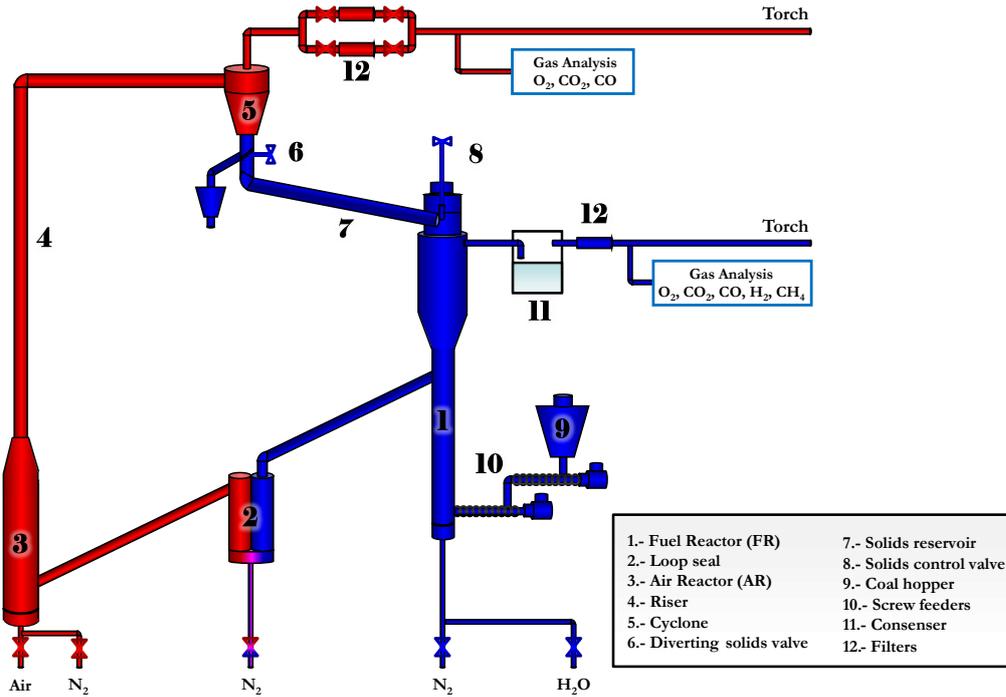
Fig. 2. Layout of the 500 kW$_{th}$ CLC Plant facility at ICB-CSIC-s1

Table 3 shows the main operating conditions used in *i*G-CLC unit burning coal. Oxygen carrier circulation flow and coal feeding rate were varied to analyze the effect of ϕ parameter on the performance of the system in a wide interval (ϕ=1.1-7). In total, the Mn60FeTi7_1200 particles have been subjected to around 40 hours of continuous hot fluidization of which 20 hours were of coal combustion. For the analysis of gases, an online gas analyzer system was used. The values of the CO_2, CO and CH_4 dry basis concentration were measured by means of non-dispersive infrared (NDIR) analyzer (Siemens Ultramat 23 and Maihak S710). The H_2 concentration in dry basis was measured by thermal conductivity detector (Maihak S710/THERMOR). The O_2 concentration was determined using a paramagnetic analyzer (Siemens 23/Oxymat 6). All data were collected by means of data logger via wifi to the computer.

Table 3. Operating conditions in the 500 W$_{th}$ CLC Unit for solid fuels

Test	1	2	3	4	5
$\dot{m}_{OC}$ (kg/h)	2.7	3.2	4.7	7.6	18.4
$\dot{m}_{coal}$ (g/h)	78.0	82.0	80.0	93.0	80.0
ϕ	1.1	1.2	1.9	2.6	7.3
Solids inventory (kg/MW$_{th}$)	1393	1325	1359	1169	1317
Thermal power (W)	475	499	487	566	487

3. Results and discussion

3.1. Oxygen transport capacity, R_{OC}

The oxygen transport capacity (R_{OC}) of the Mn60FeTi7_1200 material has been determined with several reacting atmospheres (N_2, H_2 and CH_4) as well as two oxygen concentration (21 vol. % and 5 vol. %). R_{OC} can be defined as the mass difference between the oxidized and reduced states of the oxygen carrier, which is calculated by means of Eq. 2:

$$R_{OC} = \frac{m_o - m_r}{m_o} \tag{2}$$

where m_o and m_r are the masses of the oxidized and reduced state of the oxygen carrier, respectively. Through TPR and TPO experiments the mass of the reduced and oxidized forms of the oxygen carrier could be obtained in different both reducing as oxidizing atmospheres. Fig. 3 shows the normalized mass-loss variation (ω) during TPR and TPO tests. The W represents the fraction of mass lost during reduction or oxidation and can be calculated as:

$$\omega = \frac{m}{m_o} \tag{3}$$

According to Eqs. 2 and 3, the oxygen transport capacity can be calculated as:
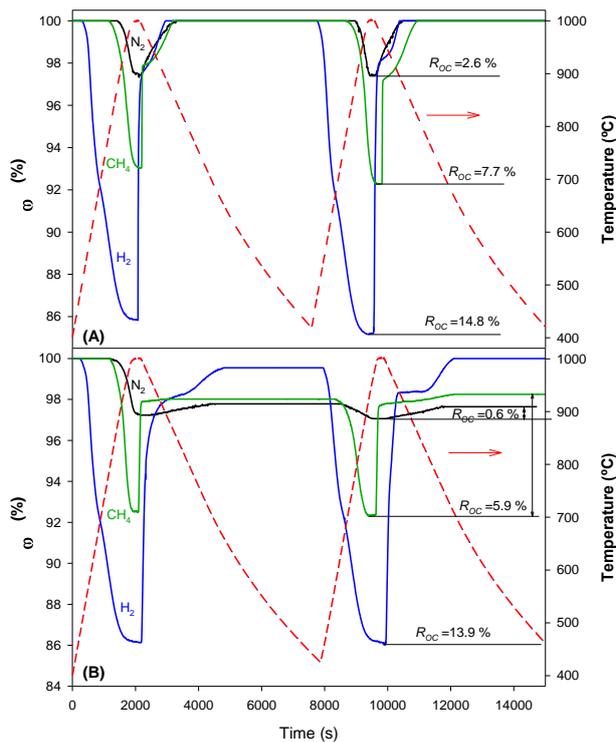
$$R_{OC} = 1 - \omega_r \tag{4}$$

Fig. 3. Normalized mass-loss profiles for TPRs (20 ºC/min) in 100 vol. % high-purity N_2, 15 vol. % H_2 and 15 vol. % CH_4 and for TPOs (8 ºC/min) in: (A) 21 vol. % O_2; (B) 5 vol. % O_2, as well as temperature evolution.

Three different gases were used as reducing atmosphere because for every gas a different R_{OC} can be obtained depending of reduction grade of the particles; (see eq. 5-8). In N_2 medium only the gaseous oxygen release is observed due to temperature (5). So, it can be evaluated the oxygen transfer capacity of material in CLOU mode. In H_2 atmosphere, the maximum oxygen transfer capacity can be obtained because both the manganese as the iron are reduced to the maximum (5-7). In presence of CH_4, the manganese is reduced to MnO (5-6) but the

iron only is reduced to Fe_3O_4 (8). In CLC technology, when a Fe-based oxygen carrier is used should only reduction to Fe_3O_4 is suitable for CLC because the subsequent reduction to FeO or Fe is thermodynamically unfavorable (Abad et al., 2007). Therefore using CH_4, the R_{OC} in CLC can be obtained.

$$3Mn_2O_3 \leftrightarrow 2Mn_3O_4 + \tfrac{1}{2}O_2 \tag{5}$$

$$Mn_3O_4 \leftrightarrow 3MnO + \tfrac{1}{2}O_2 \tag{6}$$

$$Fe_2O_3 \leftrightarrow 2Fe + \tfrac{3}{2}O_2 \tag{7}$$

$$3Fe_2O_3 \leftrightarrow 2Fe_3O_4 + \tfrac{1}{2}O_2 \tag{8}$$

When a 21 vol. % O_2 was used as oxidizing atmosphere (Fig. 3A), all oxygen transfer capacity of the particles is recuperated after two TPRs following by two TPO for three reducing gases. Besides, the R_{OC} values are slightly the same or higher that the theoretical values in all cases (Adánez et al., 2004). In the CLC process, the aim is that the oxygen concentration leaving the air reactor is on the range 4-6%. Therefore, 5 vol. % O_2 concentration in TPOs has also been used (Fig. 3B). It shows that not fully oxygen transfer capacity is recuperated after second TPO. After the reduction using high-purity N_2, the Mn60FeTi7_1200 is not able to achieve the fully oxidize state reaching only an oxygen transfer capacity of 0.6 %. It can be due because the oxygen concentration during the oxidation step is insufficient to fully oxidation (5). The same may be seen when H_2 or CH_4 as reacting agents are fed into the reactor. Both curves have a similar behavior during the TPOs. For example for the CH_4 curve, it can be seen a first fast step corresponding to the reverse of reactions 6 and 8, and a second slow step corresponding to the reverse reaction (5) as seen by Lambert et al., 2009. The total oxygen transfer capacity of this material is obtained with the curve of CH_4/5 vol. % O_2 reaching a value of 5.9%.

3.2. Coal combustion in the 500 W_{th} CLC unit

A campaign burning a bituminous Colombian coal has been performed in order to assess the behavior of Mn60FeTi7_1200 as oxygen carrier in CLC. During electric heating period, nitrogen as fluidizing agent was used in the fuel reactor and diluted air (8 vol. % O_2) as fluidizing agent and oxidizing medium was fed in the bottom of the air reactor. Thus, a non-realistic high oxidation of the oxygen carrier was avoided, as it was discussed in section 3.1.Once reached the desired temperature, steam was introduced into the fuel reactor as gasifying agent and then, coal was fed into the bottom of the fuel reactor through a system of two screw feeders. Nitrogen as fluidizing agent was always used in the loop seal. As an example, Fig 4 shows the evolution of the temperatures and the gas concentrations in both the fuel and air reactors both before and after the coal fedding. Air and fuel reactor temperatures were maintained at 900 ºC. A continuous oxygen concentration of 1.9% was released in the fuel reactor before of the coal combustion. Few minutes after coal injection started, steady state was reached with roughly constant concentration values of CO_2, CO, H_2 and CH_4 in the fuel reactor and oxygen and some CO_2 in the air reactor.

Fig. 5 shows the values of the carbon capture efficiency and the total oxygen demand versus the ϕ parameter obtained for tests 1-5; see Table 3.
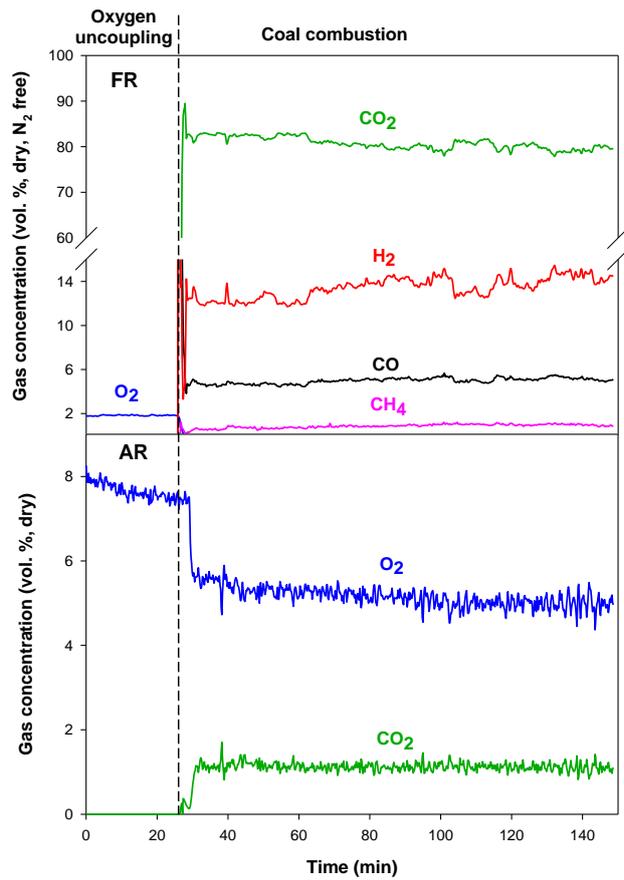
Fig. 4. Evolution of gas concentrations in both fuel and air reactors during Test 1 at 900 ºC

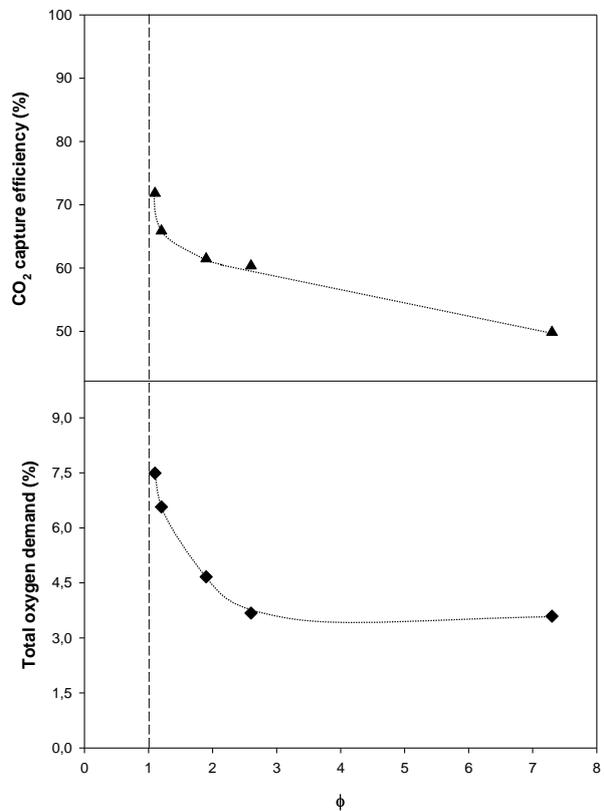

Fig. 5. CO_2 capture efficiency and total oxygen demand versus ϕ parameter

The CO_2 capture efficiency can be defined as the fraction of the carbon introduced into the fuel reactor that is converted to gas in both the fuel and air reactors. Fig. 5 shows that CO_2 capture decreased with the rise of the ϕ parameter, which depended of the oxygen carrier circulation flow (see eq. 1). Logically, the larger is the oxygen carrier circulation flow higher amount of unconverted char particles can escape from the fuel reactor reaching the air reactor, where unconverted char was burned to CO_2. This action could lead to a significant decrease on the CO_2 capture efficiency. It is clear that during these experiments it was not observed a beneficial effect due to the oxygen uncoupling property of the oxygen carrier (eq. 5) because otherwise it would be expected higher CO_2 capture values. So, the use of a carbon stripper as for iG-CLC is needed in order to achieve higher CO_2 capture efficiency. Then, this material could be compared with other cheaper oxygen carrier tested in continuous operation in iG-CLC with bituminous coal. Higher CO_2 capture efficiencies were obtained with Mn60FeTi7_1200 with respect to the ilmenite (Cuadrat et al., 2011), and similar values were achieved compared both with red-mud and Fe-ore (Mendiara et al., 2013; 2014).

The total oxygen demand represents the fraction of oxygen required to fully oxidize the unconvertered gases exiting the fuel reactor to CO_2 and H_2O with respect to the oxygen demand of the coal fuel fed. Fig. 5 shows clearly that the total oxygen demand decreased with the rise of the ϕ parameter achieving lower oxygen demand values with ϕ values higher than 2.5. Therefore, it was very influenced by the solids circulation rate. But draws attention the different behavior of this material respect other cheaper material (Cuadrat et al., 2011; Mendiara et al, 2013; 2014) during the coal combustion with lower ϕ values. This may be due to the small fraction of available oxygen in particles which can be transferred *via* oxygen uncoupling mechanism. Thus, for low ϕ values, the variation of the solids conversion was high, and the relative amount of oxygen transferred via oxygen uncoupling was low; see Fig.3. But the relative relevance of this fraction of oxygen increased with the ϕ parameter, which can cause that the total oxygen demand was strongly decreased during the increase of the ϕ parameter from 1 to 2.5. Thus, large solids circulation rates are necessary in order to reach a high reactivity of the material and lower the oxygen demand. If Mn60FeTi7_1200 is compared with the other cheaper material used as oxygen carrier, it can see than lower oxygen demand was obtained respect to the ilmenite (Cuadrat et al., 2001) and similar values were achieved than with red-mud (Mendiara et al., 2013).

4. Conclusions

A Mn-Fe-Ti based oxygen carrier has been evaluated in a 500 W_{th} continuous iG-CLC unit. Experiments were performed burning a bituminous Colombian coal at 900 ºC. The oxygen concentration fed into the air reactor was the necessary to reach an oxygen concentration leaving of the air reactor about 4-6% such as it occurs in a traditional coal combustion energy plant. The oxygen carrier particles have been subjected to around 40 hours of continuous hot fluidization of which 20 hours were of coal combustion. The increase of the oxygen carrier circulation flow was a decrease on the CO_2 capture efficiency. The inclusion of a carbon stripper could suppose an improvement in order to increase the CO_2 carbon efficiency. However the solids circulation flow rate was highly beneficial to reach high combustion efficiency in the process. The oxygen demand obtained was around 3.5 % for ϕ values higher than 2.5.

About the oxygen carrier used in this work, it did not show a relevant oxygen uncoupling capability to convert char particles under the conditions used in this work, i.e. low air excess ratios in the air reactor. Low oxidation rate at 900 ºC with 5% O_2 was observed. To reach full oxidization of this material, lower oxidation temperatures or higher oxygen partial pressure in the air reactor should be necessary.

5. Acknowledgements

6. References

Abad A., Mattisson A., Lyngfelt A., Rydén M., 2006. Chemical-looping combustion in a 300 W continuously operating reactor system using manganese-based oxygen carrier. Fuel 85, 1174-1185.

Abad A., Adánez J., García-Labiano F., de Diego L.F., Gayán P., Celaya J., 2007. Mapping on the range of operational conditions for Cu-, Fe- and Ni-based oxygen carriers in chemical-looping combustion. Chem. Eng. Sci. 62, 533-549.

Abad A, Adánez-Rubio I., Gayán P., García-Labiano F., de Diego L.F., Adánez J., 2012. Demonstration of chemical-looping with oxygen uncoupling (CLOU) process in a 1.5 kW_{th} continuously operating unit using a Cu-based oxygen-carrier. Int. J. Greenhouse Gas Control 6, 189-200.

Abad A, Gayán P., de Diego L.F., García-Labiano F., Adánez J., 2014. Modelling a CLC process improved by CLOU and validation in a 120 kW unit. 11th Int. Conf. on Fluidized Bed Technology, Beijing, China..

Adanez J., de Diego L.F., Garcia-Labiano F., Gayán P., Abad A., Palacios J.M., 2004. Selection of Oxygen Carrier for Chemical-Looping Combustion. Energy Fuels 18, 371-377.

Adanez J., Abad A., Garcia-Labiano F., Gayan P., de Diego L.F., 2012. Progress in Chemical-Looping Combustion and Reforming technologies. Prog. En. Comb. Sci. 38, 215-282.

Azimi G., Rydén M., Leion H., Mattisson T., Lyngfelt A., 2013a. $(Mn_zFe_{1-z})_yO_x$ Combined Oxides as Oxygen Carrier for Chemical-Looping with Oxygen Uncoupling. AIChE J. 59, 582-588.

Azimi G., Leion H., Rydén M., Mattisson T., Lyngfelt A., 2013b. Investigation of Different Mn-Fe Oxides as Oxygen Carrier for Chemical-Looping with Oxygen Uncoupling (CLOU). Energy Fuels 27, 367-377.

Azimi G., Leion H., Mattisson T., Rydén M., Snijkers F., Lyngfelt A., 2014. Mn-Fe Oxides with Support of $MgAl_2O_4$, CeO_2, ZrO_2 and Y_2O_3-ZrO_2 for Chemical-Looping Combustion and Chemical-Looping with Oxygen Uncoupling. Ind. Eng. Chem. Res. 54, 10358-10365.

Cabello A., Abad A., Gayán P., de Diego L.F., García-Labiano F., Adánez J., 2014. Effect of Operating Conditions and H_2S Presence on the Performance of $CaMg_{0.1}Mn_{0.9}O_{3-\delta}$ Perovskite Material in Chemical Looping Combustion (CLC). Energy Fuels 28, 1262-1274.

Cuadrat A., Abad A., García-Labiano F., Gayán P., de Diego L.F., Adánez J., 2011. The use of ilmenite as oxygen-carrier in a 500 W_{th} Chemical-Looping Coal Combustion Unit. Int. J. Greenhouse Gas Control 5, 1630-1642.

de Diego L.F., Cabello A., Abad A., Gayán P., García-Labiano F., Adánez J., 2014. Reduction and Oxidation Kinetics of a $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ Oxygen Carrier for Chemical-Looping Combustion. Energy Fuels 28, 1262-1274.

Gayán P., Abad A., de Diego L.F., García-Labiano F., Adánez J., 2013. Assessment of technological solutions for improving chemical looping combustion of solid fuels with CO_2 capture. Chem. Eng. J. 233, 56-69.

International Energy Agency (IEA), 2014. Special Report: World Energy Investment Outlook, Paris, France.

Johansson M., Mattisson T., Lyngfelt A., 2006. Investigation of Mn_3O_4 with stabilized ZrO_2 for chemical-looping combustion. Chem. Eng. Res. Des. 84, 807-818.

Källén M., Hallberg P., Rydén M., Mattisson T., Lyngfelt A., 2014. Combined oxides of iron, manganese and silica as oxygen carrier for chemical-looping combustion. Fuel Process. Technol. 124, 87-96.

Kramp M., Thon A., Hartge E.-U., Heinrich S., Werther J., 2012. Carbon Stripper - A Critical Process Step in Chemical-Looping Combustion of Solid Fuels. Chem. Eng. Technol. 35, 1-12.

Larring Y., Braley C., Pishahang M., Andreassen K.A., Bredesen R., 2014. Evaluation of Fe-Mn oxide system for CLC. Chemical Looping Process. In: 3rd Int. Conf. Chemical Looping, Göteborg, Sweden.

Lambert A., Delquié C., Clémençon I., Comte E., Lefebvre V., Rousseau J., Durand B., 2009. Synthesis and characterization of bimetallic Fe/Mn oxides for chemical looping combustion. Energy Procedia 1, 375-381.

Lyngfelt A., 2014. Chemical-looping combustion of solid fuels - Status of development. Applied Energy 113, 1869-1873.

Markewitz P., Kuckshinrichs W., Leitner W., Lissen J., Zapp P., Bongartz R., Schreiber A., Müller T.E., 2012. Worldwide innovations in the development of carbon capture technologies and the utization of CO_2. Energy Environ. Sci. 5, 7281-7305.

Mattisson T., Lyngfelt A., Leion H., 2009. Chemical-looping with oxygen uncoupling for combustion of solid fuels. Int. J. Greenhouse Gas Control 3, 11-19.

Mendiara T., de Diego L.F., García-Labiano F., Gayán P., Abad A., Adánez J., 2013. Behaviour of a bauxite waste material as oxygen carrier in 500 W_{th} CLC unit with coal. Int. J. Greenhouse Gas Control 17, 170-182.

Mendiara T., de Diego L.F., García-Labiano F., Gayán P., Abad A., Adánez J., 2014. On the use of a highly reactive iron ore of Chemical Loopin Combustion of different coals. Fuel 126, 239-249.

Pis J.J., Centeno T.A., Mahamud M., Fuertes A.B., Parra J.B., Pajares J.A., Bansal R.C., 1996. Preparation of active carbons from coal. Part I: Oxidation of coal. Fuel Process. Technol. 47, 19-38.

Rubin E.S., Mantripragada H., Marks A., Versteeg P., Kitchin J., 2012. The outlook for improved carbon capture technology. Prog. En. Comb. Sci. 38, 630-671.

Rydén M., Leion H., Mattisson T., Lyngfelt A., 2014. Combined oxides as oxygen-carrier material for chemical-looping with oxygen uncoupling. Applied Energy 113, 1924-1932.

Schmitz M., Linderholm C.J., Lyngfelr A., 2014. Perfonmance of Calcium Manganate as Oxygen Carrier in Chemical Looping Combustion of Biomass in a 10 kW pilot. 3rd Int. Conf. on Chemical Looping Combustion, Göteborg, Sweden.

Zafar Q., Abad A., Mattisson T., Gevert B., Strand M., 2007. Reduction and oxidation kinetics of Mn_3O_4/Mg-ZrO_2 oxygen carrier particles for chemical-looping combustion. Chem. Eng. Sci. 62, 6556-6567.