Coal combustion in a 50 kW_{th} Chemical Looping Combustion unit: seeking operating conditions to maximize CO₂ capture and combustion efficiency

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Abstract

In-situ Gasification Chemical-Looping Combustion (*iG-CLC*) with coal has been proposed as a low-cost process for the capture of CO₂ during the energy generation. Previous experimental works have highlighted that high CO₂ capture efficiency, close to 100 %, can be achieved. However, a certain amount of unburnt gases (mainly CH₄, CO and H₂) are present in the CO₂ stream. These gases can be treated in an oxygen polishing step placed downstream from the CLC unit where they are burnt with pure oxygen, which defines the so-called oxygen demand for the process. The aim of this work was to optimize the performance of the *iG-CLC* process with coal in order to minimize oxygen demand while maintaining CO₂ capture at high levels. Ilmenite was used as the oxygen carrier to burn a bituminous coal in a 50 kW_{th} CLC unit, which consisted of a fuel reactor, an air reactor and a carbon stripper unit between them. The fuel reactor temperature, solids inventory in the fuel reactor, solids circulation rate, coal feeding rate and carbon stripper efficiency were varied, and the CO₂ capture efficiency and oxygen

1 demand were calculated for each set of operating conditions. The effect of the fuel reactor
2 temperature was higher on the CO₂ capture than on the oxygen demand, with a temperature
3 close to 1000 °C advisable in order to reach CO₂ capture rates higher than 90 %. In order to
4 further increase CO₂ capture, the efficiency of char separation in the carbon stripper was
5 increased. The solids circulation flow rate and the coal feeding rate -which define the oxygen
6 carrier-to-fuel ratio-, in addition to the solids inventory in the fuel reactor, showed a strong
7 influence on the combustion efficiency. Thus, the total oxygen demand was able to be
8 decreased from 10 % to 7 % by increasing the oxygen carrier-to-fuel ratio from 1.1 to 1.5 and
9 the solids inventory from 450 to 720 kg/MW_{th}. However, an increase in the circulation rate
10 showed a detrimental effect on CO₂ capture, which could be offset by increasing the carbon
11 stripper efficiency.

12
13 **Keywords:** Carbon dioxide capture; Chemical Looping Combustion; coal; ilmenite;
14 optimization.

1. Introduction

The combustion of fossil fuels for power generation is responsible for a major increase in the greenhouse gases concentration in the atmosphere, mainly carbon dioxide (CO₂), which is predicted to have a severe impact on the Earth's temperature (IPCC, 2013). Carbon Capture and Storage (CCS) has been identified an important strategy in the fight for the stabilization of such CO₂ concentrations in the atmosphere (EASAC, 2013). One novel CO₂ capture technology is the Chemical-Looping Combustion (CLC) process, which allows the capture of CO₂ in combustion processes at low cost and with a low energy penalty (Rubin et al., 2012).

In CLC technology, the oxygen needed for fuel combustion is supplied by an oxygen carrier, usually a metal oxide, which circulates between the fuel reactor and air reactor. In CLC with solid fuels, the fuel is physically introduced into the fuel reactor, where it is mixed with the oxygen carrier. An outline of the CLC technology with solid fuels is shown in Fig. 1. The fuel is burnt in the fuel reactor, and CO₂ and steam are mainly obtained as combustion products. Contact is avoided between the air and the fuel, which means that CO₂ capture is inherent to the process. The global chemical reaction of the CLC process and the enthalpy released during fuel combustion are the same as those of conventional combustion with air.

In recent years, there has been an important advance in the development of CLC with solid fuels through two processes: *in-situ* Gasification Chemical Looping Combustion (iG-CLC) and Chemical Looping with Oxygen Uncoupling (CLOU) (Adanez et al., 2012; Lyngfelt, 2014). Relevant recent works have been performed in CLC units in the 10 kW_{th} to 3 MW_{th} interval (Shen et al., 2009; Abdulally et al., 2012; Linderholm et al., 2012; Sozinho et al., 2012; Xiao et al., 2012; Cao et al., 2014; Markström et al., 2014; Thon et al., 2014; Abad et al., 2015a; Bayham et al., 2015; Ströhle et al., 2015).

The iG-CLC concept involves steam and/or recycled CO₂ being supplied to the fuel reactor as fluidizing and gasifying agents. The *in-situ* gasification of solid fuel (e.g. coal) takes place

within this reactor; see reactions (R1-R3). The oxidation of the evolved gases from coal is subsequently produced by gas-solid reaction with the oxygen carrier (M_xO_y); see reactions (R4-R6). The water-gas shift (WGS) reaction can also be of importance in the product distribution; see reaction (R7). The reduced oxygen carrier (M_xO_{y-1}) is transported to the air reactor, where oxidation with the oxygen from air takes place, preparing it for the start of a new cycle; see reaction (R8).

Gasification in *i*G-CLC is the limiting step for coal conversion. It may allow some unconverted char particles to be able to reach the air reactor within the oxygen carrier stream exiting from the fuel reactor. Once the char particles are in the air reactor, they are oxidized to CO_2 which is eventually released to the atmosphere together with the air reactor exhaust gases; see reaction (R9). This situation could decrease the CO_2 capture efficiency of the *i*G-CLC process. A carbon separation step was proposed in order to avoid the by-pass of unconverted char particles into the air reactor; see Fig. 1 (Cao and Pan, 2006). The fraction of carbon in unconverted char particles is affected by coal reactivity (Cuadrat et al., 2012a; García-Labiano et al., 2013;

Mendiara et al., 2014), but in general, the efficiency of the carbon separation system is a key parameter in order to obtain high CO₂ capture rates (Kramp et al., 2012; Abad et al., 2013a). Separation can be carried out in a carbon stripper by taking advantage of the different fluid dynamic properties of char and oxygen carrier particles. The use of a high-efficiency carbon stripper has been successfully proven in a 100 kW_{th} CLC unit (Markström et al., 2013) in order to obtain high CO₂ capture rates (Abad et al., 2013b).

Fig. 1. Diagram showing the influence of operating conditions on both CO₂ capture efficiency and total oxygen demand in the iG-CLC process.

Furthermore, complete combustion of gases generated in the fuel reactor is not usually achieved. Several technological improvements have been proposed and analysed in order to achieve complete combustion (Gayán et al., 2013). Among these, the oxygen polishing step

1 downstream from the fuel reactor uses pure oxygen to burn the unconverted products, e.g. CO,
2 H₂ and CH₄; see Fig. 1 (Lyngfelt, 2014). The total oxygen demand parameter, Ω_T , defined by
3 Cuadrat et al. (2012b) evaluates the amount of oxygen needed in the oxygen polishing unit,
4 which allows a quick assessment of combustion efficiency. Total oxygen demand has been
5 decreased in existing *iG*-CLC units by increasing the solids inventory in the fuel reactor or by
6 using highly reactive oxygen carriers (Mendiara et al., 2012). In this regard, ilmenite can be
7 considered a benchmark material owing to its extensive use as an oxygen carrier. Total oxygen
8 demand was able to be decreased from ~10 % to ~7 % when the inventory of ilmenite was
9 increased from 1000 to 2000 kg/MW_{th} (Cuadrat et al., 2012a, 2012b; Linderholm et al., 2012).
10 Selecting results obtained with 1500 kg/MW_{th}, total oxygen demand could be lowered from ~9
11 % with ilmenite to ~7.6 %, ~6 % and 2 % by using Mn-ore, Fe-ESF or Fe-ore as oxygen
12 carrier, respectively (Linderholm et al., 2012; Mendiara et al., 2013, 2014). In addition, the use
13 of a Cu-based oxygen carrier showed impressive results by taking advantage of the oxygen
14 uncoupling property in the CLOU process burning coal or biomass (Abad et al., 2012; Adánez-
15 Rubio et al., 2013, 2014).

16 Fig. 1 also shows the main parameters in the *iG*-CLC process that can affect both CO₂ capture
17 efficiency and total oxygen demand. The coal conversion rate, residence time of solids in the
18 fuel reactor and carbon stripper efficiency will affect CO₂ capture efficiency, while oxygen
19 carrier reactivity and oxygen availability in the fuel reactor (by means of both solids circulation
20 and solids inventory) will affect the total oxygen demand. The operating variables influencing
21 every parameter are also shown.

22 Despite the considerable efforts made in the development of CLC technology with solid fuels,
23 it is clear that there is a need to better understand the behaviour of the *iG*-CLC process with
24 solid fuels. In a previous work carried out in a 50 kW_{th} CLC unit, 88 % of CO₂ capture and 8.5
25 % of total oxygen demand were obtained with a solids inventory in the fuel reactor of 470

kg/MW_{th} (Abad et al., 2015a). The operating conditions should be optimized in order to maximize the carbon conversion in this CLC unit. Parametric studies from modelling results (Abad et al., 2013a, 2013b; García-Labiano et al., 2013) showed that the fuel reactor temperature, solids circulation rate and solids inventory in the fuel reactor had an important role in the total oxygen demand. The increase in the carbon stripper efficiency contributed to the improvement of the CO₂ capture efficiency, but the solids circulation rate had to be limited to the lowest possible values. In order to achieve high CO₂ capture efficiency with low total oxygen demand values, a trade-off must be reached between all the operating conditions (Abad et al., 2015b).

The aim of this work was to evaluate the relative significance of several parameters on the performance of the *i*G-CLC process with coal. For this, bituminous coal combustion experiments were conducted in a 50 kW_{th} CLC unit using ilmenite as the oxygen carrier. The effect of the fuel reactor temperature, solids inventory in the fuel reactor, carbon stripper efficiency and solids circulation rate was studied on both CO₂ capture efficiency and combustion efficiency.

2. Experimental

2.1. Materials

Ilmenite was selected as the oxygen carrier to be used in the 50 kW_{th} CLC unit at ICB-CSIC. The ilmenite in this work came from Norway and was extracted by Titania A/S from a natural ore. This kind of ilmenite was first evaluated for the CLC of solid fuels by Leion et al. (2008) and has been successfully used with coal in CLC units ranging from 0.5 to 1 MW_{th} (Cuadrat et al., 2011; Linderholm et al., 2012; Marktröm et al., 2013; Abad et al., 2015a; Ströhle et al., 2015).

The oxygen carrier particles were exposed to thermal treatment at 950 °C in air for 2 hours to remove any possible moisture and as a pre-oxidation treatment. Thereafter, the particles were sieved to the particle size interval +100-300 µm. After calcination, ilmenite particles have two active phases, hematite (Fe₂O₃) and pseudobrookite (Fe₂TiO₅), which are able to transport oxygen from the air reactor to the fuel reactor. An increase in the ilmenite reactivity was observed with the number of redox cycles, both using gaseous and solid fuels (Adánez et al., 2010; Cuadrat et al., 2012c). Thus, ilmenite particles were activated prior to the experimental campaign burning coal. The activation was performed in the 50 kW_{th} CLC unit in continuous hot fluidization for approximately 100 h (Abad et al., 2015a). Table 1 shows the main properties of the activated ilmenite particles. Fe₂O₃ and Fe₂TiO₅ are reduced to magnetite (Fe₃O₄) and ilmenite (FeTiO₃) in the *i*G-CLC process through reactions (R10-R15), and the ilmenite and magnetite are oxidized during the oxidizing step; see reactions (R16-R17) (Abad et al., 2011). The oxygen transport capacity, R_{OC} , was calculated considering these redox systems.

A South African bituminous coal with medium volatile matter content (mvb) (ASTM, 1998) was fed into the fuel reactor during the experimental campaign. The diameter of the coal particles was in the +100-300 μm interval. Table 2 shows the proximate and ultimate analyses of the coal. In addition, this table also shows the lower heating value and the oxygen demand of the coal. The oxygen demand of the coal (Ω_{SF}) represents the stoichiometric mass of oxygen required for coal combustion (Abad et al., 2013a).

Table 1. Main properties of the activated ilmenite particles.

XRD main phases	Fe_2TiO_5 , Fe_2O_3 , TiO_2
Particle diameter (μm)	100-300
Crushing strength (N)	2.7
Oxygen transport capacity, R_{OC} (wt. %)	4.0
Skeletal density (kg/m^3)	4200
Porosity (%)	18.0
Specific surface area (m^2/g)	0.4

Table 2. Main characteristics of the South African bituminous coal.

Proximate analysis (wt. % raw matter)		Ultimate analysis (wt. % raw matter)	
Moisture	3.5	C	66.3
Volatile matter	25.5	H	3.6
Fixed carbon	55.3	N	1.8
Ash	15.7	S	0.5
		O ^a	8.6
LHV (kJ/kg)	24930		
Ω_{SF} (kg O/kg coal)	2.0		

^a Oxygen by difference

2.2. *Experimental setup*

An experimental campaign was performed in a 50 kW_{th} CLC unit for solid fuels, designed by and erected at ICB-CSIC (Abad et al., 2015a). The unit was designed to operate both in *iG*-CLC and CLOU modes. The design thermal power was 20 kW_{th} for *iG*-CLC mode and 50 kW_{th} for CLOU mode. The difference in thermal power is due to the better performance of CLOU with respect to *iG*-CLC on the basis of CO₂ capture and combustion efficiency (Adánez et al., 2013).

A layout of the CLC unit is shown in Fig. 2, and its main dimensions are given in Table 3. The CLC unit is based on two interconnected circulating fluidized bed reactors, the fuel and air reactors, and a carbon stripper between them. The air reactor is characterized by: (1) a wide part at the bottom, which is always full of solids; and (2) a riser with high gas velocity to entrain solids to the cyclone. This design allows the flow rate of solids at the outlet to be the same as that found at the inlet because there is no accumulation of solids observed in the air reactor. The design of the carbon stripper is that of a bubbling fluidized bed reactor for ilmenite particles, although lighter and/or smaller char particles can be elutriated. Elutriated char particles are routed to the mid-part of the fuel reactor, where they are discharged. The fuel reactor was operated in the turbulent fluidizing regime. In addition, a secondary gas flow can be fed to the riser of the fuel reactor whenever a higher solids flux is required. A baffled gravitational settling chamber is located downstream from the fuel reactor cyclone in order to recover particles escaping from the cyclone.

The design of the CLC unit includes a double loop seal after the fuel reactor cyclone to split up the outlet solids stream from the fuel reactor. A fraction of solids is deviated to the carbon stripper but other fraction can be recirculated to the fuel reactor. The solids circulation rate is controlled by setting the gas velocity in the part of the double loop seal that empties into the carbon stripper (see Fig. 2: green chambers). In this way, an independent control of the solids

circulation rate can be achieved owing to the flexibility that exists in the split flow ratio between the two streams exiting from this unit (Basu et al., 2009). Also, the direct measurement of global solids circulation rate and the measurement of internal solids circulation to the fuel reactor can be performed by means of two diverting solids devices situated below the cyclones. The coal is fed at the bottom of the fuel reactor through a screw feeder system. More information about the design of the CLC unit can be found elsewhere (Abad et al., 2015a).

Fig. 2. Layout of the ICB-CSIC-s50 plant facility for the CLC of solid fuel.

Table 3. Main design parameters of the 50 kW_{th} CLC facility.

	Fuel Reactor	Air Reactor	Carbon Stripper
Height (m)	4.00	4.60	0.71
Diameter bottom (m)	0.10	0.30	0.15
Diameter top (m)	0.08	0.10	-

Differential pressure gages are distributed throughout the CLC unit in order to gauge the pressure drop between different points of the reactors. The solids inventory value in each reactor is estimated through these devices. The fuel reactor, air reactor, carbon stripper and double loop seal are electrically heated by independent furnaces in order to achieve the adequate temperature. The temperature measurement is carried out by means of thermocouples located within the fluidized beds in both reactors.

An online gas analyser system is used to analyse the concentration of main gases exiting from both the fuel reactor (CO_2 , CO , H_2 and CH_4) and the air reactor (O_2 , CO_2 and CO). The CO_2 , CO and CH_4 concentration are measured by means of non-dispersive infrared (NDIR) analyser (Siemens Ultramat 23). The H_2 concentration is measured by thermal conductivity detector (Maihak S710/THERMOR). The O_2 concentration is determined using a paramagnetic analyser (Siemens 23/Oxymat 6). All data are collected by means of a data logger connected to a computer.

2.3. Procedure

Steam was fed as the fluidizing agent into both the bottom of the fuel reactor and the carbon stripper. Steam was also tapped to act as the coal gasifying medium. The steam flow supplied to the fuel reactor was maintained at 7000 $\text{L}_\text{N}/\text{h}$, while the steam flow fed to the carbon stripper was varied in the range from 2900 to 9900 $\text{L}_\text{N}/\text{h}$ in order to achieve the gas velocity required in the unit for each test. Furthermore, a steam flow of 2500 $\text{L}_\text{N}/\text{h}$ was introduced into the bottom of the riser of the fuel reactor to guarantee an adequate transport of solids to the cyclone. In the air reactor, air was used as fluidizing agent and to re-oxidize the reduced oxygen carrier coming from the carbon stripper. The air flow was maintained at a constant value of 50000 $\text{L}_\text{N}/\text{h}$. Nitrogen was introduced into all loop seals as the fluidizing agent.

The global solids circulation flow rate was measured inside the diverting solids valve located below the air reactor cyclone, while the entrained solids flow from the fuel reactor was

1 measured inside the corresponding device located below the fuel reactor cyclone. In some
2 cases, the entrained flow of solids from the fuel reactor was higher than desired circulation rate.
3 Consequently, the fluidization conditions in the double loop seal were modified in order to
4 modify the internal recirculation flow to the fuel reactor, and hence to fit the desired circulation
5 rate to the air reactor. Therefore, the flow introduced into the part of the double loop seal that
6 empties into the fuel reactor (Fig. 2: blue chambers) was 120 L_N/h. However, the flow supplied
7 to the other part of the double loop seal (Fig. 2: green chambers) was modified to between 950
8 and 1500 L_N/h. The temperature in the fuel reactor was modified while the air reactor
9 temperature was maintained at 950 °C. The total inventory of ilmenite existing into the CLC
10 unit was in the 88-92 kg range. The total inventory in the CLC unit affected the solids
11 inventory in the fuel reactor; thus it could be fitted to the target value. Table 4 shows the main
12 operating conditions used in CLC unit burning South African coal. A total of twelve tests at
13 steady state were carried out by varying the operating conditions. These tests were distributed
14 into different series, from I to VI, in order to rationally analyse the effect of the different
15 operating conditions on CO₂ capture and combustion efficiency. The ilmenite was subjected to
16 a total of around 50 hours of continuous hot fluidization, of which 30 hours corresponded to
17 coal combustion in *iG*-CLC mode.

18 Series I-IV were mainly devoted to analyse the influence of the carbon stripper efficiency on
19 the CO₂ capture rate by means of varying the gas velocity in the carbon stripper. Note that the
20 temperature was varied in Series I and III. Complementarily, Series V was performed to
21 evaluate the effect of the solids circulation rate itself on CO₂ capture. Finally, Series VI was
22 designed in order to obtain similar CO₂ capture rates to those values obtained in previous tests
23 by changing several operating conditions, i.e. fuel reactor temperature, gas velocity in carbon
24 stripper, solids circulation rate and coal feeding rate.

1 **Table 4.** Operating conditions and main results obtained in the *i*G-CLC unit.

Series		I		II	III			IV	V				V ₂
Test		1	2	3	4	5	6	7	8	9	10	11	12
Operating conditions													
T_{FR}	°C	944	990	1006	964	982	990	990	905	963	970	990	962
$\dot{m}_{OC}$	kg/h	140	140	140	150	150	150	150	100	100	100	100	75
$\dot{m}_{SF}$	kg/h	2.5	2.5	2.5	2.0	2.0	2.0	2.0	1.8	1.8	1.8	1.8	1.0
m_{FR}^*	kg/MW _{th}	253	306	443	522	525	481	478	680	535	506	466	722
τ_{FR}	s	138	170	230	168	170	156	156	303	239	225	207	240
ϕ	-	1.1	1.1	1.1	1.5	1.5	1.5	1.5	1.1	1.1	1.1	1.1	1.5
Power	kW _{th}	17.5	17.5	17.5	13.5	13.5	13.5	13.5	12.5	12.5	12.5	12.5	6.9
T_{CS}	°C	926	945	972	943	958	962	961	900	955	957	969	953
$u_{g,inCS}$	m/s	0.20	0.20	0.35	0.50	0.50	0.50	0.70	0.35	0.35	0.35	0.35	0.35
Main results (evaluating parameters)													
η_{CC}	%	66.1	75.5	89.8	81.2	87.9	89.5	90.0	62.9	80.9	83.1	88.6	89.7
X_C	%	58.2	70.0	87.7	76.9	84.0	87.2	87.9	54.4	76.5	79.2	86.2	87.5
Ω_T	%	9.1	9.1	9.8	6.5	7.0	8.2	8.6	8.3	8.2	8.2	9.6	7.1
$\eta_{comb,FR}$	%	85.6	87.5	88.4	91.3	91.2	90.3	90.1	86.4	89.1	89.3	88.8	91.7
η_{SF}	%	88.1	91.0	91.7	89.2	87.9	92.9	93.6	89.0	88.7	88.5	94.3	94.0
ξ_{Cfix}	%	14.2	10.7	10.0	13.0	14.5	8.6	7.6	13.2	13.5	13.8	6.9	7.2

These tests were also used to analyse the effect of the operating conditions on combustion efficiency. Thus, the coal feeding rate was somewhat lower in Series III and IV to increase the oxygen carrier-to-fuel ratio (ϕ), while the specific solids inventory in the fuel reactor, m_{FR}^* , was significantly lower in Series I. Test 12 in Series VI was useful in order to have additional information for the evaluation of the effect of different operating conditions on combustion efficiency when the CO₂ capture rate was maintained roughly constant.

2.4. Data evaluation

The evaluation of the available oxygen in the oxygen carrier circulated from the air reactor to the fuel reactor is carried out by using the oxygen carrier-to-fuel ratio (ϕ), which is determined by Eq. 1. The ϕ parameter is defined as the amount of available oxygen in solids transported from the air reactor (assuming their complete oxidation in the air reactor) divided by the stoichiometric oxygen demanded by the solid fuel fed.

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

In order to evaluate the performance of the CLC unit, the flow of every gas compound in the gas streams from fuel and air reactors was estimated by finding the concentration of every compound and the N₂ flow existing in the gas streams, in a similar way to that performed in previous works (Cuadrat et al., 2011; Mendiara et al., 2014; Abad et al., 2015a).

A carbon balance was calculated in order to verify the fate of carbon existing in the fed solid fuel. The carbon in coal can be released in volatile matter, gasified within the fuel reactor, burnt in the air reactor, or elutriated in the form of unconverted char particles escaping from the fuel reactor cyclone. The fraction of carbon in coal converted in both the fuel and the air reactor was evaluated by means of the solid fuel conversion (η_{SF}), calculated by Eq. 2:

$$\eta_{SF} = \frac{(F_{CH_4} + F_{CO} + F_{CO_2})_{outFR} + (F_{CO_2})_{outAR}}{\dot{m}_{SF} \cdot f_{C,SF} / M_C} \quad (2)$$

The carbon in coal was split between the carbon in volatiles and the fixed carbon in char. The coal could be assumed to have been fully devolatilized, and that the carbon in volatiles was fully released in the fuel reactor. Thus, the carbon not detected in gases may have been related to the carbon in elutriated char particles resulting from an incomplete separation of solids in the cyclone. The fraction of carbon fixed in escaping char particles from the fuel reactor cyclone, $\xi_{C,fix}$, was calculated as:

$$\xi_{C,fix} = \frac{F_{C,elutr}}{\dot{m}_{SF} \cdot f_{C,fix} / M_C} \quad (3)$$

The carbon flow in elutriated particles was calculated as the difference between the fed carbon and the carbon in both the fuel and air reactors exhaust gas streams:

$$F_{C,elutr} = \frac{\dot{m}_{SF} \cdot f_{C,SF}}{M_C} - \left[(F_{CO_2} + F_{CO} + F_{CH_4})_{outFR} + (F_{CO_2})_{outAR} \right] \quad (4)$$

Additionally, $F_{C,elutr}$ was also obtained by analysing the carbon content in solids recovered in the baffled gravitational settling chamber. The $F_{C,elutr}$ values obtained by these two methods were compared to evaluate the confidence of the carbon balance confidence.

CO₂ capture efficiency (η_{CC}) is defined as the fraction of the carbon converted to gas in the fuel reactor with respect to the total carbon converted to gas in both the fuel and the air reactors:

$$\eta_{CC} = \frac{(F_{CO_2} + F_{CO} + F_{CH_4})_{outFR}}{(F_{CO_2} + F_{CO} + F_{CH_4})_{outFR} + (F_{CO_2})_{outAR}} \quad (5)$$

Captured CO₂ is related to the carbon contained in the volatile matter and the carbon in the char being gasified. Therefore, the CO₂ capture efficiency calculated according to Eq. (5) depended on the fraction of carbon in char that was gasified. The conversion of carbon in char, X_C , in the

fuel reactor was calculated as the flow of fixed carbon converted to gas in the fuel reactor divided by fixed carbon converted in the CLC unit, i.e. the fixed carbon in the coal discounting the elutriated carbon:

$$X_{Char} = \frac{(F_{CO_2} + F_{CO} + F_{CH_4})_{outFR} - F_{C,vol}}{\dot{m}_{SF} \cdot f_{C,fix} / M_C - F_{C,elutr}} \quad (6)$$

The gasified carbon was calculated as the difference between the carbon converted to gas in the fuel reactor and the carbon from volatile matter; see numerator in Eq. (6). The carbon proceeding from volatile matter was calculated from the ultimate and proximate analysis of the coal as the difference between the total carbon and the fixed carbon; see Table 2.

η_{CC} and X_{Char} were calculated considering the carbon that was able to be converted in the CLC unit. Thus, the elutriated carbon flow, $F_{C,elutr}$, was not considered; however, the flow of char being converted in the iG-CLC unit was considered in order to provide a proper evaluation of the char conversion potential in the fuel reactor, as was previously reported (Mendiara et al., 2013, 2014).

Once the coal was gasified (R1-R3), the gasification products and volatile matter were oxidized to CO_2 and H_2O (R4-R6) in the fuel reactor. The fuel conversion to CO_2 and H_2O was assessed by means of two parameters: combustion efficiency in the fuel reactor ($\eta_{comb,FR}$) and total oxygen demand (Ω_T), following the methodology used in previous works (Cuadrat et al., 2011, 2012a, 2012b; Mendiara et al., 2013, 2014; Thon et al., 2014; Abad et al., 2015a). The combustion efficiency in the fuel reactor was defined as the fraction of the coal converted in the fuel reactor which was oxidized to CO_2 and H_2O :

$$\eta_{comb,FR} = 1 - \frac{(4F_{CH_4} + F_{CO} + F_{H_2})_{outFR}}{\dot{m}_{SF} \cdot \Omega_{SF} / M_O - 2(F_{C,elutr} + F_{CO_2 outAR})} \quad (7)$$

Combustion efficiency in the fuel reactor is related to the oxygen demand (Ω_{OD}), which has been defined as $\Omega_{OD}=1-\eta_{comb,FR}$ by other authors (Linderholm et al., 2012; Markström et al., 2013).

The total oxygen demand, Ω_T , is defined as the fraction of the stoichiometric oxygen required to fully burn the coal which would be demanded by the unconverted gases exiting from the fuel reactor to be converted to CO_2 and H_2O :

$$\Omega_T = \frac{(4F_{CH_4} + F_{CO} + F_{H_2})_{outFR}}{\dot{m}_{SF} \cdot \Omega_{SF} / M_O} \quad (8)$$

The $\eta_{comb, FR}$ and Ω_T parameters are somehow related, but they are complementary; thus, Gayán et al. (2013) reported a mathematical expression to calculate the oxygen demand ($\Omega_{OD}=1-\eta_{comb,FR}$) as a function of Ω_T . However, the Ω_T value is only influenced by the unconverted gases exiting from the fuel reactor, and gives a quick idea of how much oxygen would be required for combustion of gases in an oxygen polishing step compared to the oxy-fuel combustion process. Nevertheless, the combustion efficiency in the fuel reactor was related to the actual conversion of gases evolved in the fuel reactor, i.e. volatile matter and gasification products. At this point, it was not possible to know the relevance of unconverted gasification products present in the H_2 and CO measured. However, it could be assumed that CH_4 came from volatiles generated at the bottom bed of the fuel reactor. Assuming a distribution of volatile products given by Matthesius et al. (1987), the amount of CH_4 produced during the pyrolysis of the coal could be calculated. Thus, the bituminous coal burnt in the experimental campaign generated $f_{CH_4} = 0.0626$ kg of CH_4 per kg of coal fed into the fuel reactor. Therefore, by knowing the amount of CH_4 (from the coal) fed into the fuel reactor and the flow of this gas exiting from the fuel reactor, CH_4 conversion could be calculated by Eq. (9):

$$X_{CH_4} = \frac{(F_{CH_4})_{outFR}}{\dot{m}_{SF} \cdot f_{CH_4} / M_{CH_4}} \quad (9)$$

An important concept in *iG*-CLC is the specific solids inventory in the fuel reactor, m_{FR}^* , because it represents a good parameter with which to compare different oxygen carriers used in CLC independently of the power fed to the *iG*-CLC unit (Abad et al., 2007). The specific solids inventory was estimated from the pressure drop measurements in the fuel reactor, calculated by Eq. (10) considering the two different sections of the fuel reactor: bottom bed and riser.

$$m_{FR}^* = \frac{1}{P_{th}} m_{OC,FR} = \frac{1}{P_{th}} \left[\left(\frac{\Delta P \cdot S}{g} \right)_{bot} + \left(\frac{\Delta P \cdot S}{g} \right)_{top} \right] \quad (10)$$

3. Results and discussion

An experimental campaign burning a South African bituminous coal with ilmenite as oxygen carrier was performed in a 50 kW_{th} CLC unit in *iG*-CLC mode. The fuel reactor temperature, the solids circulation rate, the solids inventory into the fuel reactor and the carbon stripper efficiency were varied in order to assess their effects on the CO₂ capture efficiency and the combustion efficiency of the CLC process.

The unit operation was smooth and the response to a gas flow change was quite quick. The solid flows and pressure drops were kept constant during the stable operation time. By way of example, Fig. 3 shows the temporary evolution of the temperatures and the gas concentrations in both the fuel and air reactors during Series III (Tests 4-6), where the fuel reactor temperature was varied; see Table 4. Steady state was usually reached in less than 30 min after temperature modification, with roughly constant concentration values of CO₂, CO, H₂ and CH₄ in the fuel reactor, and oxygen and some CO₂ in the air reactor.

Fig. 3. Time evolution of temperatures and concentration of gases in both fuel and air reactors during Series III (Tests 4-6). Gas concentration values in the fuel reactor are given in N₂-free and dry basis.

The evaluating parameters defined by Eqs. (2)-(8) were calculated by using the concentration of gases in both the fuel and air reactor streams during the tests carried out. Table 4 shows the main relevant parameters obtained in *i*G-CLC mode. The solid fuel conversion values were in the range 88.1-94.3 %, which means that about 6-12 % of carbon in coal escaped from the cyclone as unconverted char before having the chance to be gasified in the fuel reactor. Ideally,

the solid fuel conversion should be close to 100 % which would have been achieved by using a more efficient cyclone. Nevertheless, the high solid fuel conversion values reached in this unit compared to other CLC units (Abad et al., 2013b; Ströhle et al., 2015) allows us to be confident of the combustion efficiency reached for the gases produced in the coal gasification. These results can most likely be attributed to the coarser coal particles used in this work (+100-300 μm) compared to previous works (~40-90 μm) (Markström et al., 2013, 2014). Nevertheless, the coarser coal particle size may have hindered the char separation from the oxygen carrier particles in the carbon stripper. Thus, CO_2 capture rates were lower than values obtained in other works (Markström et al., 2013, 2014), but values as high as 90 % were obtained. It is worth highlighting that low total oxygen demands in the range of 6.5-9.8 % were reached.

3.1. Assessment of CO_2 capture efficiency

3.1.1. Effect of fuel reactor temperature on CO_2 capture

The fuel reactor temperature was varied in three experimental series (Series I, III and V). Note that each series had a different set of operating conditions, such as the solids circulation rate, coal feeding rate or gas velocity in the carbon stripper. However, the set of operating conditions inside a series was kept roughly constant, excepting the solids inventory which was somewhat affected by temperature. Fig. 4 shows the values of the CO_2 capture efficiency as a function of fuel reactor temperature for these tests. CO_2 capture monotonically increases with fuel reactor temperature. This is a usual finding in the *i*G-CLC process, both in CLC units whether or not they include a carbon stripper, owing to the increase in the conversion rate of char gasification (Berguerand et al., 2009; Shen et al., 2009; Cuadrat et al., 2011, 2012a; Sozinho et al., 2012; Mendiara et al., 2013, 2014; Ge et al., 2015; Ma et al., 2015). The highest CO_2 capture rates were obtained for Series III and V, indicating that the gas velocity in the carbon stripper and the solids circulation rate influenced the coal conversion in the fuel reactor. The effect of these parameters will then be analysed in Sections 3.1.2 and 3.1.3, respectively. CO_2 capture rates of

about 90 % were obtained at a fuel reactor temperature of 990 °C. With the trend observed in Series III and V, it can be estimated that a temperature of 1010 °C could be high enough to reach CO₂ capture rates higher than 95 %. However, that temperature was not reached in this experimental campaign.

Fig. 4. Effect of the fuel reactor temperature on the CO₂ capture efficiency. Series I (◆), Series III (●) and Series V (▼).

Table 5 shows the inventory and the distribution of the ilmenite particles within the fuel reactor for these two series. Note that the rise of the char conversion caused an increase in the gas velocity within the fuel reactor because a higher amount of gasification products was generated. This fact could explain the decrease in the solids inventory in the fuel reactor with increasing temperature (see Table 4: Series III and V). Most of the oxygen carrier particles were located in the bottom part of the fuel reactor. But with the increase in the fuel reactor temperature, part of these solids rose from the bottom to the top of the fuel reactor. This may be due to the gases

produced in *iG*-CLC process with coal, most of which are generated in the bottom part of the fuel reactor. Nevertheless, CO₂ capture increased with temperature although the solids inventory was monotonically decreasing. This fact could be highlighted due to the presence of the carbon stripper. Note that the mean residence time of char particles in the fuel reactor was not only affected by the solids inventory in the fuel reactor, but also by the char separation efficiency in the carbon stripper.

Table 5. Inventory and distribution of ilmenite particles in the fuel reactor (Series III and V).

Series	Test	T_{FR} (°C)	ΔP_{FR} (kPa)		m_{FR}^* (kg/MW _{th})		$m_{OC.FR}$ (%)	
			Bottom	Top	Bottom	Top	Bottom	Top
III	4	964	6.5	3.1	401	121	77	23
	5	982	6.3	3.5	389	136	74	26
	6	990	5.4	3.8	334	147	69	31
V	8	905	7.4	4.4	494	186	73	27
	9	963	5.8	3.5	387	148	72	28
	10	970	5.3	3.6	354	152	70	30
	11	990	4.7	3.6	314	152	67	33

3.1.2. Effect of the carbon stripper efficiency on the CO₂ capture

The effect of the carbon stripper efficiency on the CO₂ capture efficiency was evaluated by comparing results obtained in Series I-IV, where the gas velocity in the carbon stripper was varied. However, the efficiency of the carbon stripper separating char particles from the oxygen carrier could not be calculated at this time, and the gas velocity $u_{g,CS}$ was used as the parameter influencing the CO₂ capture. It can be expected that an increased gas velocity may promote the preferential elutriation of the lighter and smaller particles: the char in this case. Fig. 5 shows the variation of CO₂ capture with the fuel reactor temperature at different gas velocities in the

carbon stripper. In Series I, a low gas velocity in the carbon stripper (0.20 m/s) was used as the starting value to scan from the lowest to the highest values. In this case, the CO₂ capture efficiency was low both at 945 and 990 °C, because the gas velocity was not high enough to entrain a relevant amount of char particles from the carbon stripper. The gas velocity in the carbon stripper was subsequently increased to 0.35 m/s in Series II, and the corresponding CO₂ capture efficiency was greatly improved by 14 %, until $\eta_{CC} = 89.8\%$ was achieved. Although the temperature was also increased to 1006 °C, it can be seen that the effect of the gas velocity in the carbon stripper was more relevant than the trend in increasing temperature.

Fig. 5. CO₂ capture efficiency vs. fuel reactor temperature for series using different gas velocity in the carbon stripper. Series I (◆); Series II (▼); Series III (●); Series IV (▲).

In order to evaluate the potential of the increase in gas velocity in the carbon stripper on the CO₂ capture improvement, the gas velocity was raised to 0.5 and 0.7 m/s; see Series III and IV. The increase to 0.5 m/s gave an additional rise in the CO₂ capture efficiency of 5 %. Thus, a

CO₂ capture efficiency of 89.5 % was achieved at a fuel reactor temperature of 990 °C. However, a further increase in the gas velocity to 0.7 m/s barely improved CO₂ capture. Therefore, the increase in the gas velocity in the carbon stripper has a fundamental effect in order to reach high CO₂ capture efficiency. Moreover, an increase in gas velocity could cause a relevant fraction of ilmenite particles to also become entrained from the carbon stripper, which is undesirable. Thus, the gas velocity in the carbon stripper must be several times higher than the terminal velocity of the char particles (~0.1 m/s), but it must be below the terminal velocity of the oxygen carrier particles (~1m/s) in order to achieve a suitable separation between both types of particles (Abad et al., 2015b). A gas velocity in the carbon stripper of 0.5 m/s seems to be adequate to optimize this unit.

3.1.3. Effect of the solids circulation rate on the CO₂ capture

The solids circulation rate was modified within the 75-150 kg/h interval. In this section, results obtained in Series II, V and VI are compared because the solids circulation rate was different in each series, but the gas velocity in the carbon stripper was constant. Note that the gas velocity in the carbon stripper affected the CO₂ capture; see Section 3.1.2. Thus, results in Series II, V and VI were not affected by differences in the carbon stripper efficiency Fig. 6 shows the values of CO₂ capture efficiency as a function of the fuel reactor temperature obtained in these series. Clearly, the CO₂ capture efficiency in the unit increased as the solids circulation rate was decreased. A rise in the CO₂ capture efficiency of 5 % is estimated when the solids circulation flow drops from 140 to 100 kg/h. Furthermore, when the solids circulation rate was decreased from 100 to 75 kg/h, the CO₂ capture increased by 10.8 %. The solids circulation rate affects CO₂ capture efficiency because a lower solids flux rate means a higher residence time values for the char particles in the fuel reactor (Cuadrat et al., 2012b; Mendiara et al., 2013). More importantly, there is also an increase in the residence time in the carbon stripper which can affect carbon stripper efficiency (Sun et al., 2015), and hence CO₂ capture. Thus, it can be

1 speculated that the separation between char and oxygen carrier particles was improved when
2 the load of solids to the carbon stripper was decreased.

3
4 **Fig. 6.** CO₂ capture efficiency vs. fuel reactor temperature for series with different solids
5 circulation flow rate. Series II (·▲·); Series V (·▼·); and Series VI (·■·).

6
7 Therefore, it was confirmed that a decrease in the solids circulation rate increases CO₂ capture
8 efficiency. However, the solids circulation rate is related to the oxygen carrier-to-fuel ratio, ϕ ,
9 which should be above unity to transport enough oxygen to permit complete fuel oxidation. In
10 this sense, the ϕ value should be maintained as low as possible, but conditioned by $\phi > 1$. Thus,
11 if a higher CO₂ capture is desired, then the carbon stripper operation should be improved, e.g.
12 by increasing the gas velocity and having a more efficient carbon stripper. Such action can be
13 analysed by comparing results obtained in Tests 6 and 11; see Table 4. Thus, increasing the gas
14 velocity in the carbon stripper in Test 6 could compensate for the increase in the solids
15 circulation rate compared to Test 11, thus reaching a similar CO₂ capture efficiency value. In

addition, note that the solids circulation rate in Series VI was decreased but ϕ was maintained at a value of $\phi = 1.5$ by decreasing the coal feeding rate. This means that the specific size of the carbon stripper by thermal power was increased. This factor must be considered in the design of a CLC unit (Abad et al., 2015b; Sun et al., 2015).

Finally, it was proved that CO_2 capture efficiency can be adjusted by varying the temperature, the residence time of the oxygen carrier particles within the fuel reactor and carbon stripper (through variation in the solids circulation rate) and the carbon stripper separation efficiency (through variation in the gas velocity). Thus, similar CO_2 capture rates were achieved in Tests 3, 6, 11 and 12.

3.2. Assessment of total oxygen demand

The total oxygen demand calculated by Eq. 8 depends both on the flow of unconverted gases into the fuel reactor and the solid fuel feeding rate. Previous results and theoretical models (Cuadrat et al., 2012b; García-Labiano et al., 2013) showed that the factors with a major influence on the total oxygen demand are fuel reactor temperature, oxygen carrier-to-fuel ratio, ϕ , and the specific solids inventory in the fuel reactor, m_{FR}^* . Note that when other operating conditions, such as fuel power or solids circulation rate was varied, but with ϕ and m_{FR}^* kept constant, the total oxygen demand values recorded were practically equal; see Table 4. For example, the total oxygen demand values for Tests 3 and 11 were 9.8 and 9.6 %, respectively.

3.2.1. Effect of fuel reactor temperature on total oxygen demand

Fig. 7 shows the total oxygen demand when the fuel reactor temperature was varied in Series I, III and V. The total oxygen demand was different in every series because other operating conditions were varied at the same time. Thus, Series I, characterized by a low solids inventory, showed a relatively high value of $\Omega_T = 9.1$ %, which was unaffected by the temperature. In contrast, Series III was characterized by a higher oxygen carrier-to-fuel ratio, showing the

lowest total oxygen demand values ($\Omega_T = 6.5\text{--}8.2\%$). It is clear that the reaction rate of ilmenite increased with temperature (Abad et al., 2011). But in general, the total oxygen demand was barely affected by the fuel reactor temperature when a particular series was analysed, with a slight increase in the total oxygen demand at the highest temperatures in Series III and V. In order to analyse these results, the effect of the solids inventory and the amount of gases released in the fuel reactor must be considered.

Fig. 7. Effect of the fuel reactor temperature on the total oxygen demand (Ω_T) and on the combustion efficiency in the fuel reactor ($\eta_{\text{comb,FR}}$). Series I (◆), Series III (●) and Series V (▼).

On the one hand, the reacting gases originate from both gasification products (CO and H₂) and the volatile matter (CH₄, CO and H₂). The volatile matter fraction can be considered constant with this temperature variation. Considering CH₄ as a characteristic compound in volatile matter, CH₄ conversion can give us some information about the effect of temperature on the

volatile matter oxidation by the oxygen carrier; see Table 6. It can be seen that CH_4 represents the major contributor to the total oxygen demand, followed by CO, which is considered an intermediate product of the CH_4 conversion as well as gasification product (Abad et al., 2013a). This fact suggests that the oxidation of volatile matter by ilmenite is more difficult than the oxidation of the gasification products. This fact agrees with the lower reactivity of CH_4 with respect to CO and H_2 (Abad et al., 2011) and the poorer contact with oxygen carrier particles of volatile matter compared to gasification products, as was shown previously by modelling results (Abad et al., 2013a; García-Labiano et al., 2013). The effect of temperature on CH_4 conversion is clearly seen when results obtained in Test 8 are analysed. In this test the CH_4 conversion was low, which could be attributed to the low reactivity of CH_4 with ilmenite at 900 °C. But the reactivity of ilmenite with CH_4 greatly increases with temperature (Abad et al., 2011); thus, CH_4 conversion was increased from 63.2 % to 70.4 % when the temperature was increased from 904 to 963 °C.

However, the amount of gasification products evolved in the fuel reactor increased with the temperature; see Section 3.1.1. Considering volatile matter conversion was improved by temperature, a higher flow of unconverted gasification products must be present in the exhaust gas to justify that the total oxygen demand was unaffected by temperature. Due to the different definition used for the combustion efficiency parameter, it can be seen that the combustion efficiency increased with temperature. This fact suggests that combustion of gasification products was improved by temperature in order to justify higher combustion efficiency values, which agrees with the higher reaction rate of ilmenite with temperature (Abad et al., 2011). In addition, the improvement in conversion of gasification products with the temperature increase was more relevant than for volatile matter conversion.

On the other hand, the solids inventory was varied little, or even somewhat increased, in the cases where total oxygen demand was not varied with the temperature. Thus, the increase in the

total oxygen demand obtained at the highest temperatures was related to experiments carried out with low solids inventory values, where m_{FR}^* was lower than 500 kg/MW_{th}. A preliminary evaluation of the effect of solids inventory and oxygen carrier to fuel ratio can be made by comparing results obtained in Series I, III and V. Clearly, CH₄ conversion increased with both the increase in solids inventory and oxygen carrier-to-fuel ratio; see Table 6. Note the low CH₄ conversion when the solids inventory was below 500 kg/MW_{th}.

Table 6. Gas concentration exiting from the fuel reactor (dry basis and N₂-free), contribution of unburnt gases on total oxygen demand and CH₄ conversion.

Series	Test	Gas concentration from FR (%)				Contribution on the Ω_T (%)			Methane conversion (%)
		CO ₂	CO	H ₂	CH ₄	CO	H ₂	CH ₄	X_{CH_4}
I	1	78.6	15.4	1.7	4.4	44.4	4.8	50.8	63.2
	2	81.1	13.9	1.5	3.5	47.1	5.0	47.9	65.3
II	3	83.2	11.2	2.4	3.2	42.6	9.3	48.1	62.4
III	4	87.1	8.9	1.6	2.4	44.3	7.8	47.9	74.9
	5	86.5	8.8	2.4	2.3	43.2	11.8	45.0	75.2
	6	85.6	9.6	2.3	2.5	43.8	10.5	45.7	69.9
IV	7	86.0	8.0	3.3	2.7	36.1	14.6	49.2	66.3
V	8	81.0	10.6	3.9	4.5	32.7	11.9	55.4	63.2
	9	83.7	10.4	3.1	2.8	41.9	12.6	45.5	70.4
	10	83.8	10.3	3.1	2.8	42.1	12.8	45.1	70.4
	11	83.7	10.1	3.3	2.9	40.4	13.1	46.5	62.4
VI	12	89.3	6.2	1.8	2.7	33.2	9.5	57.3	69.5

Because the amount of generated gases in the fuel reactor can affect combustion efficiency, the effect of other operating parameters on total oxygen demand was evaluated by using results

obtained in tests where similar CO₂ capture rates were achieved, e.g. Series III and V or Tests 3, 6, 11 and 12.

3.2.2. *Effect of the oxygen carrier-to-fuel ratio (ϕ) on total oxygen demand*

Two series of experiments (Series III and V) were carried out with modification of the solids circulation rate while maintaining a similar coal feeding rate. The corresponding ϕ values were 1.5 and 1.1, respectively. Note that the CO₂ capture efficiency obtained for the two series was practically the same because of the different gas velocities used in the carbon stripper; see Fig. 4. Thus, the amount of gasification products evolved in the fuel reactor was similar in these two series, and therefore it has no influence on this evaluation. Figs. 7 and 8 show that the total oxygen demand decreased significantly when the ϕ parameter increased from 1.1 to 1.5. By comparing results obtained with similar specific solids inventories, it can be concluded that the oxygen carrier-to-fuel ratio has a relevant influence on total oxygen demand; see Fig. 8. The total oxygen demand decreased by 18 % because of the effect of the increase in the ϕ parameter from 1.1 to 1.5. Moreover, an increase in CH₄ conversion was evidenced at higher ϕ values, which suggests that volatile matter conversion was improved at a higher solids circulation flow rate; see Table 6.

In other works (Abad et al., 2013b; Markström et al., 2013), the solids circulation flow rate did not influence total oxygen demand. However, tests in those works were carried out at higher oxygen carrier-to-fuel ratios, usually in the 2.5-5 interval, with lower fuel conversion values and higher total oxygen demand values ($\Omega_T = 10\text{-}12\%$). Under those conditions, the variation in the solids conversion was low; and a variation in the ϕ parameter barely affected oxygen carrier reactivity (Abad et al., 2007). As a conclusion, the potential of the oxygen carrier-to-fuel ratio to improve the combustion efficiency of the *iG*-CLC process would be limited to low ϕ

values such as used in this work, as was predicted in a previous modelling work (García-Labiano et al., 2013).

Fig. 8. Effect of the oxygen carrier to fuel ratio (ϕ) and solids inventory into the fuel reactor on the total oxygen demand. Test 3 (•◆•); Test 6 (•●•); Test 11 (•▼•); and Test 12 (•■•).

3.2.3. Effect of the solids inventory in the fuel reactor on total oxygen demand

Setting the amount of oxygen carrier in the fuel reactor entailed some difficulties because this may depend on several parameters. A trade-off between several operating conditions (e.g. solids circulation rate, input thermal power, gas velocity in the carbon stripper or fuel reactor temperature) was necessary in order to achieve a constant specific solids inventory but with similar oxygen carrier-to-fuel ratio and CO₂ capture values. Tests 6 and 12 fulfilled such conditions.

In Test 6, the solids inventory in the fuel reactor was 481 kg/MW_t, and the total oxygen demand was $\Omega_T = 8.2\%$. Fig. 8 shows that total oxygen demand decreased by 15.5 % until Ω_T

= 7.1 % when the solids inventory was increased up to 722 kg/MW_{th}. In this case, the increase in the solids inventory in the fuel reactor produced a decrease in the contribution of gasification products on total oxygen demand, while CH₄ conversion was barely changed; see Table 6. This fact was related to the rise of the dense zone in the bottom part of the fuel reactor when the solids inventory was increased. This part of the reactor is more efficient at oxidizing gasification products than volatile compounds (García-Labiano et al., 2013).

In general, the contribution of gasification products on total oxygen demand would be lower than the relevance of the unconverted compounds from volatile matter. In order to increase combustion efficiency in the fuel reactor, a number of design improvements have been proposed (Guío-Pérez et al., 2014; Lyngfelt and Leckner, 2015) and modelled (Gayán et al., 2013) in order to increase the combustion efficiency of volatile matter. Some of such improvements will be implemented and evaluated in the 50kW_{th} CLC unit in future works.

The results obtained in this work suggest that the performance of the *iG*-CLC process can be improved by optimizing operating conditions in the fuel reactor and the carbon stripper.

4. Conclusions

The evaluation of the *in-situ* Gasification Chemical Looping Combustion (*iG*-CLC) process with coal was performed through the analysis of the effect of the main operating conditions on CO₂ capture and combustion efficiency. Ilmenite was used as the oxygen carrier to burn a bituminous coal in a 50 kW_{th} CLC unit. Fuel reactor temperature, solids circulation flow rate, carbon stripper efficiency and solids inventory in the fuel reactor were varied in order to achieve high CO₂ capture efficiency with low total oxygen demand.

After evaluating the effect of the main operating variables on CO₂ capture and on total oxygen demand, the following conclusions were obtained:

- CO₂ capture efficiency was fundamentally influenced by fuel reactor temperature, solids circulation rate and carbon stripper efficiency. Thus:
 - The increase in fuel reactor temperature notably improves CO₂ capture owing to the increase of char conversion in the fuel reactor. The temperature set in the fuel reactor must be as high as possible (≥ 1000 °C) in order to achieve higher char conversion and consequently CO₂ captures close to 100 %.
 - CO₂ capture decreased when the solids circulation rate was increased because a greater amount of char particles reached the carbon stripper.
 - Carbon stripper efficiency was improved by increasing the inlet gas velocity. Thus, CO₂ capture efficiency was increased because the residence time of the char particles in the fuel reactor was raised. CO₂ capture rates of around 90 % were obtained even for the highest solids circulation rate used in this work.
- Total oxygen demand was strongly affected by both the oxygen carrier-to-fuel ratio (ϕ) and the solids inventory in the fuel reactor. The total oxygen demand related to unconverted products from volatile matter was higher than the total oxygen demand related to gasification products. Also, some effects of fuel reactor temperature were evidenced. Thus:
 - The increase in fuel reactor temperature improved combustion efficiency, which was evident both for gasification products and volatile matter.
 - The increase in the oxygen carrier-to-fuel ratio improved combustion efficiency; thus lower total oxygen demand values were achieved at higher oxygen carrier-to-fuel ratios. Specifically, total oxygen demand decreased by 18 % when the ϕ value was increased from 1.1 to 1.5. The conversion increase of CH₄ from volatile matter was highly relevant for the decrease in total oxygen demand.
 - Total oxygen demand was decreased by the rise in the solids inventory in the fuel reactor. In this case, the increase in the conversion of gasification products (CO and H₂) was

mainly responsible for the improvement. A minimum total oxygen demand of $\Omega_T = 7.1 \%$ was reached with 722 kg/MW_{th} in the fuel reactor.

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Nomenclature

$f_{C,SF}$	carbon content in solid fuel
f_{CH_4}	methane content in volatile matter from the solid fuel (kg CH_4 per kg solid fuel)
F_i	molar flow of compound i (mol/s)
$F_{C,fix}$	carbon flow in fixed carbon (mol/s)
$F_{C,vol}$	carbon flow in volatile matter (mol/s)
$F_{C,elutr}$	elutriated carbon flow exiting from the fuel reactor (mol/s)
$\dot{m}_{OC}$	solids circulation flow rate (kg/s)
$m_{OC,FR}$	solids inventory in the fuel reactor (kg)
m_{FR}^*	specific solids inventory in the fuel reactor (kg/MW _{th})
$\dot{m}_{SF}$	coal feeding rate (kg/s)
M_C	atomic weight of carbon ($12 \cdot 10^{-3}$ kg/mol)
M_O	atomic weight of oxygen ($16 \cdot 10^{-3}$ kg/mol)
M_{CH_4}	atomic weight of methane ($16 \cdot 10^{-3}$ kg/mol)
$n_{C,coll}$	carbon content in the elutriated char collected (mol)
P_{th}	thermal power (MW)
R_{OC}	oxygen transport capacity (kg oxygen per kg of oxygen carrier)
S	cross sectional of a reactor (m^2)
T	temperature ($^{\circ}C$)
u_g	gas velocity (m/s)
X_C	carbon conversion in char

1	X_{CH_4}	methane conversion
2		
3	Greek symbols	
4	ΔP	pressure drop (Pa)
5	ϕ	oxygen carrier-to-fuel ratio
6	η_{CC}	carbon capture efficiency
7	$\eta_{comb,FR}$	combustion efficiency in the fuel reactor
8	η_{SF}	solid fuel conversion
9	$\eta_{C,elut}$	fraction of total carbon being elutriated
10	$\xi_{Cfix, elut}$	fraction of fixed carbon being elutriated
11	τ_{FR}	Mean residence time of solids in the fuel reactor (s)
12	Ω_{OD}	oxygen demand of the gases into the fuel reactor
13	Ω_{SF}	oxygen demand of the coal (kg oxygen per kg solid fuel)
14	Ω_T	total oxygen demand
15		
16	Subscripts	
17	AR	air reactor
18	CS	carbon stripper
19	FR	fuel reactor
20	in	inlet
21	out	outlet
22	bott	bottom part
23	top	top part
24		
25	Acronyms	
26	CCS	CO ₂ Capture and Storage
27	CLC	Chemical Looping Combustion
28	CLOU	Chemical Looping with Oxygen Uncoupling
29	iG-CLC	<i>in-situ</i> Gasification Chemical Looping Combustion
30	LHV	Lower Heating Value (kJ/kg coal)
31	WGS	Water Gas Shift
32	XRD	X-Ray Diffraction
33		

Appendix. Evaluation of elutriated char during continuous operation

The elutriated char was produced because one part of the solids flux that reached the fuel reactor cyclone was not recovered as a result of a leak from the CLC unit. The losses due to elutriated char may have affected the calculated CO₂ capture efficiency and, in particular, influenced the evaluation of total oxygen demand. A lower char flow exiting from the cyclone would have caused an increase in the total oxygen demand because the char gasification products would be increased. Thus, an evaluation of the amount of elutriated char was performed.

The design of the 50 kW_{th} CLC unit included a particle collector system downstream from the fuel reactor cyclone. This system consisted of a baffled gravitational settling chamber and a wet scrubber. After every working day, the outlet pipe from the fuel reactor cyclone was cleaned in order to collect the deposited solids in a particle collector system. The particulates collected in the wet scrubber were then dried.

The fraction of carbon in elutriated solids was achieved through an ultimate analysis. The carbon content of two representative samples collected from both the gravitational settling chamber and the wet scrubber was calculated. The carbon fraction in the elutriated solids was estimated as the sum of the averages of the two values of carbon fraction obtained at each collection point. The fraction of coal that was elutriated carbon or the carbon elutriated fraction, $\eta_{C,elut}$, was calculated as:

$$\eta_{C,elut} = \frac{n_{C,coll}}{\left(\dot{m}_{SF} \cdot C_{SF} / M_C \right) \cdot t_{comb}} \quad (A1)$$

where $n_{C,coll}$ was the number of carbon mols in the solids collected and t_{comb} the combustion time in the CLC unit for the tests during which $n_{C,coll}$ was collected. Thus, the carbon elutriated

fraction represents the carbon in the elutriated char with respect to the total carbon in the fed coal.

Once the elutriated carbon was calculated, a carbon balance could be calculated considering all the carbon containing streams exiting from the CLC unit:

$$\eta_{C,exit} = \eta_{SF} + \eta_{C,elut} \quad (A2)$$

Fig. A1 shows the carbon balance for every test performed in the CLC unit. In general, the carbon balance values observed were close to or higher than 95 % with respect to the carbon fed into the fuel reactor. Thus, the results obtained in this work showed a good reliability with respect to the carbon balance and the values of total oxygen demand calculated.

Fig. A1. Carbon balance for every test carried out in the CLC unit. η_{SF} (■); $\eta_{C,elut}$ (□).

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