Design and operation of a 50 kW_{th} Chemical Looping Combustion (CLC) Unit for Solid Fuels

Alberto ABAD*, Raúl PÉREZ-VEGA, Luis F. de DIEGO, Francisco GARCÍA-LABIANO, Pilar GAYÁN, Juan ADÁNEZ

Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, E-50018 Zaragoza, Spain

**Corresponding Author: abad@icb.csic.es*

Abstract

A Chemical Looping Combustion (CLC) unit for solid fuels has been designed, erected and operated. The design was based on a thermal power of 20 kW_{th} for *in-situ* Gasification Chemical Looping Combustion (iG-CLC) or 50 kW_{th} for Chemical Looping with Oxygen Uncoupling (CLOU). Fuel and air reactors are two interconnected circulating fluidized beds reactors, with the coal being fed at the bottom of the fuel reactor to maximize the contact between the volatile matter and the oxygen carrier particles. A carbon stripper has been included between fuel and air reactors to increase the CO₂ capture rates. In this unit, the char particles are separated from the oxygen carrier particles and recirculated to the fuel reactor. The solids flow exiting from the fuel reactor is split into two different streams by using a double loop seal down the fuel reactor cyclone. One goes to the carbon stripper and the other is recirculated to the fuel reactor. In this way it is possible to have an independent control of solids inventory in the fuel reactor and the global solid circulation flow rate between fuel and air reactors. First operational results at steady state have been obtained with stable operation in iG-CLC mode during combustion of a bituminous coal with ilmenite being the oxygen

carrier. A CO₂ capture value of 88% at 991 °C and a total oxygen demand value of 8.5% were obtained with a solids inventory in the fuel reactor of 470 kg/MW_{th}.

Keywords: CO₂ capture; CLC; CLOU; Coal; Design.

1 Introduction

In Chemical Looping Combustion (CLC) with solid fuels, the fuel is physically mixed with the oxygen carrier. A scheme of the CLC with solid fuels is shown in Fig. 1. The oxygen needed for fuel combustion is supplied by an oxygen carrier, normally a metal oxide, which circulates between the so-called fuel and air reactors. In the fuel reactor, the fuel is oxidized to CO₂ and H₂O, which facilitates CO₂ capture once the water has been condensed. The reduced oxygen carrier is then transported to the air reactor where it is re-oxidized before starting a new cycle. The net chemical reaction and combustion enthalpy is the same as in conventional combustion. CO₂ capture is inherent to this process, as the air is not mixed with the fuel. Significant advances have been made in the development of CLC using solid fuels in recent years by means of two processes: *in-situ* gasification CLC (*iG*-CLC) and Chemical Looping with Oxygen Uncoupling (CLOU) [1,2].

Fig. 1. Reactor scheme of CLC processes with solid fuels.

In the *iG*-CLC concept coal is fed directly to the fuel reactor and mixed with the oxygen carrier. Steam and/or recycled CO₂ are supplied to the fuel reactor as fluidizing agents. In-situ

gasification of coal occurs, generating volatile matter and gasification products, which are oxidized by gas-solid reactions with the oxygen carrier. Gasification is the limiting step for coal conversion. The slow coal gasification rate may cause that the solids stream exiting from the fuel reactor contained some unconverted char together with the oxygen carrier and ash. Once the unconverted char reaches the air reactor it is burnt with air to produce CO₂, which could significantly decrease the CO₂ capture efficiency of the process. To increase the residence time of char particles in the fuel reactor, without excessively increasing the reactor size, a carbon separation unit is included after the fuel reactor. This unit can be designed as a carbon stripper, where char particles are separated from the oxygen carrier particles and recirculated to the fuel reactor using their different fluidization properties. In addition, complete combustion of gases from the fuel reactor has not been reached in existing *iG-CLC* units. Some strategies have been proposed to convert the unburnt compounds. They include an oxygen polishing step to complete gas combustion, the separation and recirculation of unburnt compounds or a secondary fuel reactor in series [3].

The CLOU concept was developed based on the use of oxygen carrier materials which can release gaseous oxygen and thereby allow the solid fuel to be burnt with gas phase oxygen [4]. These materials can also be regenerated at high temperatures. Complete combustion and CO₂ capture rates close to 100% have been found in a 1.5 kW_{th} CLOU unit due to the fast combustion of coal with gaseous oxygen generated *in-situ* in the fuel reactor [5].

To date, several design concepts have been developed for *iG-CLC* ranging from 10 kW_{th} to 3 MW_{th} units, but no operation at scale higher than 1.5 kW_{th} have been reported for CLOU [1]. Major differences between CLC systems were found in the fuel reactor design. In some cases, the fuel reactor included a bubbling- or spout-fluid bed [6-8]; but in other cases, a fuel reactor at the high velocity fluidization regime is preferred [9-11]. Thus, the cross-sectional area per power unit is minimized. Among the latter, a 100 kW_{th} unit [9] allowed stable operation with ilmenite and CO₂ capture rate values close to 100% were obtained because of the high

efficient carbon stripper included [12]. CO₂ capture rates of 97-98% were obtained. However, the combustion efficiency in the fuel reactor was about 80-85%, due to a low solids inventory in the fuel reactor (300-400 kg/MW_{th}), which results in a relevant fraction of unconverted gases in the fuel reactor. Note that theoretical calculations recommended values ranging from 750 to 1500 kg/MW_{th} in order to have a trade-off between combustion efficiency and ilmenite inventory [12-14]. The solids inventory in the fuel reactor and the solids circulation rate is uncoupled by using a circulation riser. However, a relatively high steam flow is required in the carbon stripper and the circulation riser, which result in high values, between 3 and 4, of steam to fixed carbon ratio.

Two different CLC units have been operated at the MW_{th} scale. A 1 MW_{th} unit [10] was designed for solids inventory values about 200-300 kg/MW_{th}. The solids circulation flow rate between the air and fuel reactors could be modified by means of a screw conveyor attached to the loop seal below the air reactor cyclone. Later, the screw conveyor was replaced by an L-valve [15]. Thus, the amount of solids in the fuel reactor would be directly linked to the solids circulation rate. During preliminary operation, steam to fixed carbon ratio was about 2. Another CLC unit, 3 MW_{th}, [11] was characterized by a direct hydraulic link between the bottom of fuel and air reactors. The hydraulic link allowed high CO₂ capture rates to be achieved without the necessity of a carbon stripper. This system is similar to that found in a 120 kW_{th} CLC unit for gaseous fuels [16], where the amount of solids in the fuel and air reactors were closely dependent on the gas velocity and the solids circulation flow rate.

The objective of this work was to design and built a flexible CLC unit for solid fuels, which could be operated at 20 kW_{th} in *i*G-CLC and 50 kW_{th} in CLOU mode. The design of the concept is based on two interconnected circulating fluidized beds reactors. Independent control of solids circulation flow rate and solids inventory in the fuel and air reactors is intended with the proposed design. Thus, direct relation between operational conditions and performance of the CLC unit could be easily evaluated. This unit allows investigating the

performance of the *i*G-CLC and CLOU processes burning different fuels (lignite, bituminous coal and biomass) using different oxygen carrier materials (Fe-based minerals or copper-based oxygen carrier). Preliminary results obtained during combustion of a bituminous coal with ilmenite by *i*G-CLC are presented showing carbon capture efficiencies and oxygen demands.

2 Design of the 50 kW_{th} CLC unit

2.1 Introduction to design

A layout of the CLC unit for solids fuels is shown in Fig. 2. It is based on two interconnected circulating fluidized bed reactors, the air and fuel reactors, and a carbon stripper, being a bubbling fluidized bed. The carbon stripper improves the carbon capture efficiency by recovering char particles that escape from the fuel reactor. The design includes a double loop seal after the fuel reactor cyclone to split the solids stream before reaching the carbon stripper. A fraction of solids is allowed to go to the carbon stripper but another fraction is recycled to the riser of the fuel reactor. In this way it is possible to reach one independent control of solid circulation in fuel reactor from the global solid circulation flow. Moreover, the measurement of solids circulation between fuel and air reactors can be performed by means of two diverting solid devices located below the cyclones.

Ilmenite ($d_p=0.17$ mm; $\rho_p=3710$ kg/m³) and a Cu-based material (60 wt.% CuO and 40 wt.% MgAl₂O₄; $d_p=0.17$ mm; $\rho_p=3860$ kg/m³) were considered as oxygen carriers for *i*G-CLC and CLOU, respectively; while a South African bituminous coal ($d_p=0.10$ mm; $\rho_p=1000$ kg/m³) was assumed the solid fuel for design calculations. The oxygen carriers have been successfully tested in continuously operated *i*G-CLC [9,17-20] and CLOU units [5,21-23]. For design conditions, the nominal thermal power was 20 kW_{th} for *i*G-CLC mode and 50 kW_{th} for CLOU mode. The difference of nominal power is because the better performance of CLOU with respect to *i*G-CLC on the basis of CO₂ capture and combustion efficiency

[24]. The solids inventory in the fuel reactor was set to 20 kg in *iG*-CLC, corresponding to 1000 kg/MW_{th}. This solids inventory value was estimated as the amount of oxygen carrier to balance the trade-off between the increase of pressure drop and the decrease in oxygen demand caused by an increase of solids in the reactor [12,14]. In CLOU, the same amount of solids corresponded to 400 kg/MW_{th}, which has been considered a suitable value from previous works [5, 24-26].

Fig. 2. Layout of the 50 kW_{th} CLC Plant facility at ICB-CSIC-s50

Different types of coals, ranging from lignite to anthracite, as well as biomass, can be used as fuel. Mass balances, fluid dynamics considerations and the performance of the fuel reactor predicted by a theoretical model previously developed [13] were taken into account for the design of the CLC unit. The solids circulation flow rate, reactor temperatures, solids inventory in the fuel reactor, steam requirements and air flow were determined. Design of the carbon stripper, loop seals, and the cyclone system was also considered.

The design was done on the basis of the operation both in *iG-CLC* and *CLOU* modes. The solid fuel feeding point was just above the distributor plate in the fuel reactor. It is intended to convert the fuel to CO₂ and H₂O, minimizing the unburnt compounds. To maximize the solid fuel conversion, the fuel reactor temperature was assumed to be 1000 °C in *iG-CLC* [9, 12-14, 17] and 950 °C in *CLOU* [5, 21,23]. The CLC unit is not expected to be auto-thermal due to heat losses associated with the unit size. The fuel reactor, air reactor, carbon stripper, and loop seals are electrically heated by independent furnaces.

2.2 Design parameters

The dimensions of the reactor are defined by the design values of the pressure drop, solids inventory and gas velocity. Design data are shown in Table 1. The cross sectional area corresponded to 0.39 m²/MW_{th} in *iG-CLC* and 0.16 m²/MW_{th} in *CLOU*.

Table 1. Main design parameters of the 50 kW_{th} Unit

Operation mode	<i>iG-CLC</i>			<i>CLOU</i>		
Power (kW _{th})	20			50		
Reactor	FR	AR	CS	FR	AR	CS
Height (m)	4.15	4.80	0.71	4.15	4.80	0.71
Diameter (cm)*	10.2/8.1	30.0/10.2	15.0	10.2/8.1	30.0/10.2	15.0
Solids inventory (kg)	20	55	8	20	55	8
ΔP (kPa)	25	15	4.5	25	15	4.5
$u_{g,in}$ (m/s)	1.0	0.40	0.35	1.0	0.90	0.35
$u_{g,out}$ (m/s)	4.00	4.00	0.35	5.50	9.00	0.35
Stoichiometric $G_{S,FR}$ (kg·m ⁻² ·s ⁻¹)	7.5	-	-	12.5	-	-
Designed $G_{S,FR}$ (kg·m ⁻² ·s ⁻¹)	30	11	-	50	18	-

2.2.1 Fuel reactor and Double loop seal

The fuel reactor can be fluidized by H_2O , CO_2 or mixtures of these gases. The gas flow fed to the bottom part of the fuel reactor was fixed in order to operate with a gas velocity in the bottom bed just above the terminal velocity of oxygen carrier particles; see Fig. 3 [27]. When the gases from coal conversion together with the gas stream from the carbon stripper were considered, the gas velocity was estimated to be 4 m/s in *i*G-CLC and 5.5 m/s in CLOU. Under these conditions, the solids flux to the fuel reactor cyclone was estimated to be 30 $kg \cdot m^{-2} \cdot s^{-1}$ in *i*G-CLC and 50 $kg \cdot m^{-2} \cdot s^{-1}$ in CLOU [16], which are higher values than those required for stoichiometric conditions, i.e. 7.5 $kg \cdot m^{-2} \cdot s^{-1}$ in *i*G-CLC and 12.5 $kg \cdot m^{-2} \cdot s^{-1}$ in CLOU. Stoichiometric conditions were defined by a value of the oxygen carrier to fuel ratio $\phi = 1$. The ϕ parameter was defined as the flow of oxygen available in the circulating solids stream divided by the flow of oxygen required to achieve complete fuel combustion.

The maximum oxygen carrier to fuel ratio achievable in the CLC unit was estimated to be $\phi = 4$. However, ϕ values between 1 and 2 are preferable to maximize the CO_2 capture rate. For design conditions ϕ was selected to be 2, which means that the solids circulation flow to the air reactor must be lower than the solids flow exiting the fuel reactor. Thus, the double loop seal (LS-D) must be operated to direct the solids circulation towards the carbon stripper, and subsequently to the air reactor, at the desired value. The LS-D system is designed in order to divide the solids stream from the fuel reactor cyclone in two: (1) solids to the carbon stripper, and then to the air reactor, in order to fulfill the required solids circulation flow rate between air and fuel reactors; and (2) excess of solids was recirculated to the fuel reactor. In this way, the residence time of solids, including unconverted char particles, is maximized whereas the solids circulation flow rate between the air and fuel reactors was guaranteed. The use of a

double loop seal was considered to be an improvement with respect to existing CLC units for solid fuels. Another important feature is the possibility to have a direct measurement of the solids flux exiting from both the fuel and air reactors by means of the respective solids circulation measurement devices.

Fig. 3. Fluidization regime in the flow map adapted from [27]. $u^* = Re/Ar^{1/3}$; $d_p^* = Ar^{1/3}$

2.2.2 Carbon stripper

The carbon stripper separates the unconverted char particles from the oxygen carrier according to their different fluid dynamic properties. Char particles are lighter and smaller than oxygen carrier particles and can be elutriated from the carbon stripper and recirculated to the fuel reactor using an appropriate fluidization flow, whereas the oxygen carrier particles are left to pass to the air reactor via loop seal LS-CS. Char particles are recirculated to the bottom bed of the fuel reactor, well above the distributor plate. The carbon stripper can be

fluidized by steam and/or CO₂. In industrial operation is preferable to use CO₂ to fluidize this reactor, thus minimizing the steam duty of the CLC unit [28]. The temperature in carbon stripper was set to 950 °C. No attempts have been made to optimize the design of a carbon stripper to minimize the solids inventory. However, high carbon separation efficiency was reached. Here, the carbon stripper was designed as a bubbling bed (0.3 m height and 0.15 m diameter) and the residence time of solids was estimated to be 100 s when $\phi = 2$. The gauge pressure at the carbon stripper must also account for the pressure drop in the riser of the fuel reactor. Considering the inlet point of solids entrained from the carbon stripper to the fuel reactor, the additional pressure drop to be overcome in the fuel reactor was 10 kPa. The gas velocity in this unit must be higher than terminal velocity of char particles ($u_{t, char} = 0.1$ m/s), but lower than terminal velocity of oxygen carrier particles ($u_{t, OC} = 1$ m/s); see Fig. 3. A gas velocity in the carbon stripper of 0.35 m/s seems to be suitable to reach an effective separation of char particles from oxygen carrier particles.

2.2.3 Air reactor

In the air reactor, the oxygen carrier is regenerated with air. The air reactor was designed to achieve complete oxidation of the oxygen carrier (mean residence time $t_{mr} = 700$ s), but to guarantee the solids circulation flow rate. To achieve this, a wide bottom bed is followed by a narrow riser. The air flow is set with a 10% excess with respect to that needed to burn the fuel fed in the fuel reactor. A low gas velocity was chosen in the bottom bed (0.4 m/s in *i*G-CLC) to operate in the bubbling fluidization regime. The gas velocity increases up to 4 m/s in the riser due to the decrease in diameter, which allows operation in the fast fluidization regime; see Fig. 3. The solids flux in the riser should be $11 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ for $\phi = 2$, which can easily be reached under these conditions. The solids flux in the air reactor is determined by the solids flux entering from the carbon stripper, which depends on the double loop seal operation.

Higher velocities are required in CLOU, 0.9 m/s in the bottom bed and 9 m/s in the riser, because the unit is designed for a higher thermal power in this mode.

2.2.4 Cyclones and Loop seals

Solids entrained from the air and fuel reactors are separated by respective cyclones and sent to the next element in the CLC unit. The dimensioning of the cyclone is based on a high efficiency standard cyclone with a gas velocity at the cyclone inlet of 15 m/s [29].

Loop seals were included in order to balance the pressure between two connected elements. Thus, the length of the low pressure side of each loop seal is determined by the pressure balance in the system, as shown in Fig. 4. The LS-D must balance an overpressure of 10 kPa in the fuel reactor inlet point from the carbon stripper with respect to the fuel reactor cyclone exit. LS-CS must balance a low pressure difference between the bottom of the air reactor and the upper part of the carbon stripper. LS-AF was carefully designed to balance a high pressure difference between the air reactor cyclone and the bottom part of the fuel reactor, which is 25 kPa. The difference of pressure between both sides of each loop seal must be compensated by a solids column in the side with lower pressure, which must be at least 0.8, 0.4 and 2.0 m for loop seals LS-D, LS-CS and LS-AF, respectively. Estimated pressure drops in each element of the CLC unit for the design conditions can be calculated following continuous lines in Fig. 4.

The final objective of using the loop seals was to avoid the gas mixing between reactors connected by the loop seal and to guarantee the appropriate flow of solids. Thus, loop seal LS-CS avoids the mixing of air and $\text{H}_2\text{O-CO}_2$ in the carbon stripper, whereas loop seal LS-AF hinders the mixing of air and gases from fuel. Loop seal LS-D is necessary to avoid leakage of gas from the carbon stripper to the fuel reactor cyclone. Moreover, this loop seal controls the circulation flow rate of solids between the fuel and air reactors.

The loop seal units were designed as bubbling fluidized beds and were dimensioned to allow a high solids circulation flow rate, i.e. the loop seal must not limit the solids circulation flow

rate. The required solid flux in the loop seals is $16 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ at the oxygen carrier to fuel ratio $\phi = 2$, whereas the maximum capacity may be as high as $300 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ [30].

Fig. 4. Estimated pressure profile in the CLC unit. Dotted lines are elements connected for different loop seals. Continuous lines are pressure versus height in each element.

Note that the pressure at the reactor inlets should account for an additional pressure drop of 30% due to the presence of a distributor plate in the fluidized beds. Finally, the heights of air and fuel reactors were determined in order to arrange all the elements of the CLC unit, including the required column of solids in the loop seals. The air reactor height is 4.65 m and the fuel reactor is 4.0 m tall.

2.3 Relevant parameters in evaluation of coal combustion in the CLC unit

The evaluation of the *iG*-CLC unit was done based on carbon and oxygen balances. Carbon in the fuel can be released in volatile matter, gasified in the fuel reactor, burnt in the air reactor, or elutriated in unconverted char particles escaping from the fuel reactor cyclone. The elutriated char flow ($F_{C,elut}$) has been defined as the difference between the carbon feeding into the fuel reactor and the carbon in the fuel and air reactor exhaust gas streams; see Eq. 1.

$$F_{C,elut} = \frac{m_{SF} \cdot C_{SF}}{M_C} - \left[(F_{CO_2} + F_{CO} + F_{CH_4})_{outFR} + (F_{CO_2})_{outAR} \right] \quad (1)$$

The fraction of carbon in coal converted both in the fuel and air reactor is evaluated by means of the solid fuel conversion (η_{SF}), which can be calculated by means of Eq. 2.

$$\eta_{SF} = \frac{(F_{CH_4} + F_{CO} + F_{CO_2})_{outFR} + (F_{CO_2})_{outAR}}{m_{SF} \cdot C_{SF} / M_C} \quad (2)$$

The solid fuel conversion is the relation between the total flow of gaseous carbon leaving both fuel and air reactors and the total flow of carbon fed into the fuel reactor from solid fuel. Unconverted carbon in the *iG*-CLC unit was elutriated in partially converted char particles.

To evaluate the performance of the *iG*-CLC operation, relevant parameters are used in accordance to previous works [3, 12-14, 18-20, 24, 31,32].

The CO₂ capture efficiency (η_{CC}) has been defined as the fraction of the carbon introduced that is converted to gas in both the fuel and air reactors (Eq. 3).

$$\eta_{CC} = \frac{(F_{CO_2} + F_{CO} + F_{CH_4})_{outFR}}{(F_{CO_2} + F_{CO} + F_{CH_4})_{outFR} + (F_{CO_2})_{outAR}} \quad (3)$$

The CO₂ captured in the unit is the addition of the carbon contained in the volatile matter and the carbon from char gasification. Therefore, the CO₂ capture efficiency calculated according Eq. (3) depends on the fraction of char that has been gasified.

The char conversion in the fuel reactor ($X_{Char,FR}$) is defined as the fraction of fixed carbon converted to gas in the fuel reactor. The calculation of the char conversion was corrected to consider the elutriated char, i.e. the fraction of char particles that was not recovered by the fuel reactor cyclone; see Eq. 4. Thus, the denominator in Eq. 4 was calculated as the fixed carbon in coal discounting the elutriated char. In this way, a proper evaluation of the char conversion potential in the fuel reactor can be done, as it was previously described [31,32] by considering only the amount of char having the chance to be converted in the CLC unit.

$$X_{Char,FR} = \frac{(F_{CO_2} + F_{CO} + F_{CH_4})_{outFR} - F_{C,vol}}{F_{C,fix} - F_{C,elutr}} \quad (4)$$

The volatile matter carbon flow 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.

Besides the coal gasification, the fuel reactor must oxidize the gasification products to CO_2 and H_2O . The conversion of gasification products was evaluated by means of two parameters: the combustion efficiency in the fuel reactor, $\eta_{c,FR}$, and the total oxygen demand, Ω_T . The combustion efficiency in the fuel reactor was defined as the fraction of oxygen demanded by the coal converted in the fuel reactor, i.e. volatile matter and gasification products, that is supplied by the oxygen carrier in the fuel reactor:

$$\eta_{c,FR} = 1 - \frac{(4F_{CH_4} + F_{CO} + F_{H_2})_{outFR}}{\dot{m}_{SF} \cdot \Omega_{SF} / M_O - 2(F_{CO_2,outAR} + F_{C,elutr})} \quad (5)$$

The combustion efficiency in the fuel reactor is related to the oxygen demand, Ω_{OD} , defined by other authors by $\eta_{c,FR} = 1 - \Omega_{OD}$ [9,17].

Finally, the total oxygen demand, Ω_T , is defined as the fraction of stoichiometric oxygen required to fully oxidize the unconverted gases exiting the fuel reactor to CO_2 and H_2O with respect to the stoichiometric oxygen demanded by the solid fuel fed.

$$\Omega_T = \frac{(4F_{CH_4} + F_{CO} + F_{H_2})_{outFR}}{\dot{m}_{SF} \cdot \Omega_{SF} / M_O} \quad (6)$$

2.4 Mathematical predictions in the 50 kW_{th} CLC unit for solid fuels

The performance of the CLC unit with coal as fuel was simulated by using theoretical models for *i*G-CLC and CLOU previously developed and validated against experimental results in 100 kW_{th} *i*G-CLC and 1 kW_{th} CLOU units [12, 25]. “El Cerrejón” Colombian bituminous coal was assumed to be the fuel, which was used in previous experimental works [24]. Fig. 5 shows the CO₂ capture efficiency and the oxygen demand predicted in the CLC unit as a function of the carbon stripper efficiency separating unconverted char particles from the oxygen carrier stream. The oxygen demand was defined as the ratio of oxygen flow required to fully oxidize unconverted gases from the fuel reactor to the stoichiometric oxygen flow for complete coal combustion.

Because of the slow rate of coal gasification, a highly efficient carbon stripper is key to reaching high CO₂ capture rates in *i*G-CLC mode. Moreover, complete combustion was not predicted in the fuel reactor. The total oxygen demand increases as the fuel conversion in the fuel reactor increases due to the increase of the char conversion with the carbon stripper efficiency. Thus, a greater amount of gases is produced in the fuel reactor by char gasification. Assuming the conversion of volatile matter was roughly the same regardless the char converted, the increase in the Ω_T is due to a higher amount of gasification products to be oxidized as the carbon stripper efficiency increased. Therefore, an increase in the carbon stripper efficiency will increase the total oxygen demand [14]. The total oxygen demand predicted in *i*G-CLC increased from 3% to 10% when the carbon stripper efficiency increases from 0 to 1.

The estimated CLOU performance was much better than that predicted for *i*G-CLC. Complete combustion was predicted even when the fuel power was higher (50 kW_{th}) compared to the

value assumed for *i*G-CLC (20 kW_{th}). The fast coal conversion in CLOU via combustion with gaseous oxygen evolved from the oxygen carrier makes it possible to achieve CO₂ capture rates greater than 95% even if poor carbon stripper performance was assumed. These predicted differences between *i*G-CLC and CLOU agree with results previously described from experimental works in a 1 kW CLC unit [24].

Fig. 5. Estimated CO₂ capture, η_{CC} , and total oxygen demand, Ω_T , in the CLC unit for: (a) 20 kW_{th} in *i*G-CLC mode; and (b) 50 kW_{th} in CLOU mode.

3 Performance during coal combustion in *i*G-CLC mode

3.1 Materials used and experimental procedure

An experimental campaign in this CLC unit was conducted using ilmenite as oxygen carrier and a South African bituminous coal. Ilmenite particles diameter was +0.1-0.3 mm. Table 2 shows the main characteristics of coal used, which was ground and sieved in order to use particles in the 0.1-0.3 mm interval. The proximate and ultimate analyses of coal were obtained using stabilized coal exposed to the atmosphere. Stabilized coal was the same which was used in the experiments. In this way, the humidity of the coal was not varied during the experiments carried out for several days.

Table 3 shows the main operating conditions used in the CLC unit. The temperatures of the fuel reactor and carbon stripper were varied while the temperature of the air reactor was maintained at about 950 °C. In addition, pressure drop in fuel reactor for test 1 was higher than for tests 2-4, which was related to a higher amount of solids with the temperature drop. The fuel reactor and carbon stripper were fluidized with steam, although N₂ was used in the loop-seals. The coal feed rate and solids circulation rate were 1.8 and 101 kg/h, respectively, during all tests. These values corresponded to a thermal power of 12.5 kW_{th} and an oxygen carrier to fuel ratio of $\phi = 1.1$.

Table 2. Main characteristics of coal (stabilized humidity by exposition to the atmosphere).

South African bituminous coal (wt.% raw matter)	
Proximate analysis	
Moisture	3.5
Volatile matter	25.5
Ash	15.7
Fixed carbon	55.3
Ultimate analysis	
C	66.3
H	3.6
N	1.8
S	0.5
O ^a	8.6

LHV (kJ/kg)	24930
Ω_{SF} (kg O/kg solid fuel)	2.0
^a Oxygen by difference	

Table 3. Operating conditions in *i*G-CLC unit.

Test	1	2	3	4
Fuel Reactor				
T_{FR} (°C)	905	963	970	991
ΔP_{FR} (kPa)	11.8	9.3	8.9	8.3
$m_{OC,FR}$ (kg/MW _{th})	680	535	506	466
$u_{g,inFR}$ (m/s)	1.0	1.1	1.1	1.1
$u_{g,outFR}$ (m/s)	4.3	4.6	4.6	4.7
Air Reactor				
T_{AR} (°C)	937	943	945	950
ΔP_{AR} (kPa)	3.1	3.2	3.2	3.2
$u_{g,inAR}$ (m/s)	0.9	0.9	0.9	0.9
$u_{g,outAR}$ (m/s)	6.9	6.8	6.9	6.9
Carbon Stripper				
T_{CS} (°C)	900	955	957	969
$u_{g,inCS, in}$ (m/s)	0.34	0.35	0.35	0.36

3.2 Results and discussion

Fig. 6 shows the evolution of the temperatures and gas concentrations in both the fuel and air reactors during heating and start-up until steady state was reached for the operating conditions of Test 4; see Table 3. During initial electrical heating all reactors were fluidized with air. After the desired temperatures in the fuel and air reactors were reached, the fluidizing gas was changed to steam in both the fuel reactor and carbon stripper. Then the coal feeding into the fuel reactor was started and the combustion by *i*G-CLC began. Steady operation was quickly reached, with roughly constant concentration values of CO₂, CO, H₂ and CH₄.

Fig. 6. Evolution of temperatures and gas concentrations in both fuel and air reactors during Test 4.

Table 4 shows the main relevant results obtained in the *i*G-CLC during the South African coal combustion. Fig. 7 shows the CO₂ capture and total oxygen demand values according to the Tests summarized in Table 4.

The solid fuel conversion was very similar with values between 80 and 87% during all tests. The CO₂ capture values increased when the temperature increased reaching a value of 88% when the fuel reactor temperature was 991°C. Thus, the fuel reactor temperature has a high impact on the char conversion, even more considering that the solids inventory in the fuel reactor decreased when the temperature increased; see Table 3. The char conversion into the fuel reactor increased from 51% at 905 °C to 84.7% at 991 °C. It is believed that the effect of the decrease in the solids inventory with temperature (see Table 3) is of lower relevance than the effect of the increase in the temperature, especially for tests 2, 3 and 4. Likely, a lower gas flow in test 1 at 905°C, due to a lower fuel conversion, allowed a higher amount of solids in the fuel reactor.

Table 4. Main relevant parameters in *i*G-CLC

Test	1	2	3	4
η_{CC} (%)	60.7	79.4	81.3	87.6
η_{SF} (%)	83.9	82.0	80.1	87.0
X_{Char} (%)	51.0	74.1	76.5	84.7
$\eta_{c,FR}$ (%)	86.6	89.3	89.5	89.2
Ω_T (%)	7.7	7.5	7.4	8.6

Fig. 7. CO₂ capture, η_{cc} , and total oxygen demand, Ω_T , values during combustion of South African bituminous coal in *i*G-CLC mode.

The total oxygen demand remained practically constant at about of 7.5%. At 991 °C, the value increased one point likely due to the lower solid inventory in the fuel reactor and the higher amount of gasification products to be oxidized. Values of total oxygen demand are even lower than those obtained with ilmenite in a CLC unit with the fuel reactor being operated in the bubbling fluidization regime, where most of unconverted gases came from volatile matter [3, 18-20]. Assuming CH₄ was only formed during devolatilization [33], a mass balance to CH₄ gave a value of the CH₄ conversion of around 70%. CH₄ was the most difficult compound to convert by the oxygen carrier because of its low reactivity with ilmenite, and it accounts for a 50 % of the total oxygen demand in exhaust gases during tests 1-4. This suggests an improved conversion of volatile matter in the dilute region above the dense bed in the fuel reactor of the 50 kW_{th} CLC unit, which operated in the turbulent fluidization regime; see Fig. 3.

The results shown for the first tests carried out in the unit was successful. Low values of oxygen demand were obtained due to the combination of fuel reactor operation in turbulent fluidization regime together the use of a solids inventory around 500 kg/MW_{th} in most of cases. The total oxygen demand obtained was lower than those obtained in other CLC units

with ilmenite being the oxygen carrier [3]. In addition, the oxygen demand would be decreased by increasing the solids inventory above 500 kg/MW_{th}. An optimum value of the solids inventory considering the balance between the increase in the pressure drop and the improvement on combustion efficiency was estimated to be about 700-1000 kg/MW_{th} [12-14]. The CO₂ capture rate increased with fuel reactor temperature, and a value of 88% at 991°C was found. This value could be increased by increasing fuel reactor temperature or optimizing operation in carbon stripper; see Figure 5. Nevertheless, the efficiency of the carbon stripper could not be calculated at this time. Theoretical simulations can be used in order to estimate the efficiency of the carbon stripper [12]. When comparing the total oxygen demand for the same results of CO₂ capture rate, i.e. 85% at 990°C, we obtained $\Omega_T = 7.5\%$ in the experiments and $\Omega_T = 7.3\%$ from predictions in Figure 5, which was a good agreement. For this case, the predicted carbon stripper efficiency was 96%.

Thus, from results obtained in this work is recommended for industrial application a solids inventory higher than 500 kg/MW_{th} to reduce the total oxygen demand of the process, and a high temperature in the fuel reactor (close to 1000°C) as well as a highly efficient carbon stripper to improve the CO₂ capture rate [34]. Considering the required cross-section area and pressure drop in the fuel reactor, the proposed design will allow the operation with the recommended solids inventory [28]. Also, a double loop seal, which was used to control the flow of solids to the carbon stripper and air reactor, is an extended technology in the industry to split a flow of solids.

Future work will be performed in order to optimize coal conversion in the *i*G-CLC operation by improving the carbon stripper operation and by increasing the amount of solids in the fuel reactor. Also, operation in CLOU mode is planned using an oxygen carrier with oxygen uncoupling property, e.g. based on copper or manganese.

4 Conclusions

A CLC unit for solid fuels was designed to operate in both *i*G-CLC and CLOU modes. The unit includes a fuel reactor, an air reactor and a carbon stripper. The use of a double loop seal below the fuel reactor cyclone allows the solids circulation flow rate to be controlled independently of the solids inventory in the fuel reactor. Initial experiments carried out by *i*G-CLC burning a bituminous coal with ilmenite showed high CO₂ capture efficiencies with low oxygen demands for the gases coming from the fuel reactor, in accordance with a model developed for this system. The fuel reactor temperature strongly influenced char conversion, increasing the CO₂ capture when temperature was increased. Oxygen demand was barely affected by fuel reactor temperature.

Acknowledgment

This work was supported by the Spanish Ministry for Science and Innovation (Project ENE2013-45454-R). R. Pérez-Vega thanks for the FPI Fellowship.

Nomenclature

Ar	Arquimedes number ($=d_p^3 \rho_g(\rho_p-\rho_g)g/\mu_g^2$)
C_{SF}	carbon fraction in the solid fuel
d_p	particle diameter (m)
F_i	molar flow of compound i (mol/s)
$G_{S,FR}$	solids flux in the riser ($\text{kg m}^{-2} \text{s}^{-1}$)
$m_{OC,FR}$	solids inventory in the fuel reactor(kg oxygen carrier/MW _{th})
$\dot{m}_{SF}$	feeding rate of the solid fuel (kg/s)

M_i	atomic weight of atom i (kg/mol)
Re	Reynolds number ($=u_g d_p \rho_g / \mu_g$)
T	temperature (°C)
u_g	gas velocity (m/s)
u_t	terminal velocity of particles (m/s)
X_{Char}	char conversion

Greek symbols

ΔP	pressure drop in the reactor (kPa)
ϕ	oxygen carrier to fuel ratio
$\eta_{c,FR}$	combustion efficiency in the fuel reactor
η_{CC}	carbon capture efficiency
η_{SF}	solid fuel conversion
ρ_p	density of particles (kg m ⁻³)
Ω_{OD}	oxygen demand of the fuel reactor
Ω_{SF}	oxygen demand for stoichiometric combustion of coal (kg oxygen per kg solid fuel)
Ω_T	total oxygen demand of unconverted gases in the CLC unit

Subscripts

elutr	elutriated
in	at the inlet

OC oxygen carrier
out at the outlet
vol in volatiles
C_{fix} fixed carbon

Acronyms

AR Air Reactor
CLC Chemical Looping Combustion
CLOU Chemical Looping with Oxygen Uncoupling
CS Carbon Stripper
FR Fuel Reactor
*i*G-CLC *in-situ* Gasification Chemical Looping Combustion
LS Loop Seal
LS-D Double Loop Seal

5 References

- [1] Adanez, J., Abad, A., García-Labiano, F., Gayán, P., de Diego, L.F. (2012), Progress in Chemical-Looping Combustion and Reforming technologies, *Progress in Energy and Combustion Science* **38**, pp. 215-282.
- [2] Lyngfelt, A. (2014), Chemical-looping combustion of solid fuels - Status of development, *Applied Energy* **113**, 1869-1873.
- [3] 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 CO₂ capture, *Chemical Engineering Journal* **233**, pp. 56-69.

- [4] Mattisson, T., Lyngfelt, A., Leion, H. (2009), Chemical-looping with oxygen uncoupling for combustion of solid fuels, *International Journal Greenhouse Gas Control* **3**, pp. 11-19.
- [5] 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, *International Journal Greenhouse Gas Control* **6**, pp. 189-200.
- [6] Shen, L., Wu, J., Xiao, J. (2009), Experiments on chemical looping combustion of coal with a NiO based oxygen carrier, *Combustion and Flame* **156**, pp. 721-728.
- [7] Thon, A., Kramp, M., Hartge, E.-U., Heinrich, S., Werther, J. (2014), Operational experience with a system of coupled fluidized beds for chemical looping combustion of solid fuels using ilmenite as oxygen carrier, *Applied Energy* **118**, pp. 309-317.
- [8] Sozinho, T., Pelletant, W., Stainton, H., Chillou, F., Gauthier, T. (2012), Main results of the 10 kW_{th} pilot plant operation, *2nd International Conference on Chemical Looping*, Darmstadt, Germany.
- [9] Markström, P., Linderholm, C., Lyngfelt, A. (2013), Chemical-looping combustion of solid fuels - Design and operation of a 100 kW unit with bituminous coal. *International Journal Greenhouse Gas Control* **15**, pp. 150-162.
- [10] Ströhle, J., Orth, M., Epple, B. (2014), Design and operation of a 1 MW_{th} chemical looping plant, *Applied Energy* **113**, pp. 1490-1495.
- [11] Andrus, H., Chui, J., Thibeault, P., Edberg, C., Turek, D., Kenney, J., Abdulally, I., Chapman, P., Kang, S., Lani, B. (2012), ALSTOM'S limestone-based (LCL™) Chemical Looping Process, *Proceeding from the 2nd International Conference on Chemical Looping*, Darmstadt, Germany.
- [12] Abad, A., Adánez, J., de Diego, L.F., Gayán, P., García-Labiano, F., Lyngfelt, A. (2013), Fuel reactor model validation: Assessment of the key parameters affecting the

- chemical-looping combustion of coal, *International Journal Greenhouse Gas Control* **19**, pp. 541-551.
- [13] Abad, A., Gayán, P., de Diego, L.F., García-Labiano, F., Adánez, J. (2013), Fuel reactor modelling in chemical-looping combustion of coal: 1. model formulation, *Chemical Engineering Science* **87**, pp. 277-293.
- [14] García-Labiano, F., de Diego, L.F., Gayán, P., Abad, A., Adánez, J. (2013), Fuel reactor modelling in chemical-looping combustion of coal: 2. simulation and optimization. *Chemical Engineering Science* **87**, pp. 173-182.
- [15] Ströhle, J., Orth, M., Epple, B. (2014), Chemical Looping Combustion of Hard Coal in a 1 MW_{th} Pilot Plant Using Ilmenite as Oxygen Carrier, 3rd *International Conference on Chemical Looping*, Göteborg, Sweden.
- [16] Pröll, T., Kolbitsch, P.; Bolhár-Nordenkamp, J.; Hofbauer, H. (2009), A novel dual circulating fluidized bed system for chemical looping processes, *AIChE J.* **55**, pp. 3255-3266.
- [17] Cuadrat, A., Linderholm, C., Abad, A., Lyngfelt, A., Adánez, J. (2011), Influence of Limestone Addition in a 10 kW_{th} Chemical-Looping Combustion Unit Operated with Petcoke, *Energy Fuels* **25**, pp. 4818-4828.
- [18] 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, *International Journal of Greenhouse Gas Control* **5**, pp. 1630-1642.
- [19] Cuadrat, A., Abad, A., García-Labiano, F., Gayán, P., de Diego, L.F., Adánez, J. (2012), Effect of operating conditions in Chemical-Looping Combustion of coal in a 500 W_{th} unit, *International Journal of Greenhouse Gas Control* **6**, pp. 153-163.
- [20] Cuadrat, A., Abad, A., García-Labiano, F., Gayán, P., de Diego, L.F., Adánez, J. (2012), Relevance of the coal rank on the performance of the in situ gasification chemical-looping combustion, *Chemical Engineering Journal* **195-196**, 91-102.

- [21] Adánez-Rubio, I., Abad, A., Gayán, P., de Diego, L.F., García-Labiano, F., Adánez, J. (2013), Performance of CLOU process in the combustion of different types of coal with CO₂ capture, *International Journal of Greenhouse Gas Control* **12**, pp. 430-440.
- [22] Adánez-Rubio, I., Abad, A., Gayán, P., García-Labiano, F., de Diego, L.F., Adánez, J. (2014), The fate of sulphur in the Cu-based Chemical Looping with Oxygen Uncoupling (CLOU) Process, *Applied Energy* **113**, 1855-1862.
- [23] Adánez-Rubio, I., Abad, A., Gayán, P., de Diego, L.F., García-Labiano, F., Adánez, J. (2014), Biomass combustion with CO₂ capture by chemical looping with oxygen uncoupling (CLOU), *Fuel Processing Technology* **124**, 104-114.
- [24] Adánez, J., Gayán, P., Adánez-Rubio, I., Cuadrat, A., Mendiara, T., Abad, A., García-Labiano, F., de Diego, L.F. (2013), Use of Chemical-Looping processes for coal combustion with CO₂ capture, *Energy Procedia* **37**, pp. 540-549.
- [25] Adánez-Rubio, I., Gayán, P., Abad, A., García-Labiano, F., de Diego, L.F., Adánez, J. (2014), Kinetic analysis of a Cu-based oxygen carrier: relevance of temperature and oxygen partial pressure on reduction and oxidation reactions rates in Chemical Looping with Oxygen Uncoupling (CLOU), *Chemical Engineering Journal* **15**, pp. 69-84.
- [26] Adánez-Rubio, I., Abad, A., Gayán, P., de Diego, L.F., García-Labiano, F., Adánez, J. (2012), Identification of operational regions in the Chemical-Looping with Oxygen Uncoupling (CLOU) process with a Cu-based oxygen carrier, *Fuel* **102**, pp. 634-645.
- [27] Bi, H.T., Grace, J.R. (1995), Flow regime diagrams for gas-solid fluidization and upward transport, *International Journal Multiphase Flow* **21**, pp. 1229-1236.
- [28] Abad, A., Adánez, J., Gayán, P., de Diego, L.F., García-Labiano, F., Sprachmann, G. (2014), Conceptual Design of a 100 MW_{th} CLC Unit for Solid Fuel Combustion, *Applied Energy*, submitted for publication.

- [29] Sinnot, R.K. (1983), Chemical Engineering Vol. 6, An Introduction of Chemical Engineering Design, *In Chemical Engineering* series by J.M. Coulson and J.F. Richardson; Pergamon Press; Oxford, England.
- [30] Marx, K., Pröll, T., Hofbauer, H. (2012), Next scale chemical looping combustion: fluidized bed system design for demonstration unit, *21st International Conference on Fluidized Bed Combustion, Naples, Italy*.
- [31] 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 a 500 W_{th} CLC unit with coal, *International Journal of Greenhouse Gas Control* **17**, pp. 170-182.
- [32] 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 in Chemical Looping Combustion of different coals, *Fuel* **126**, pp. 239-249.
- [33] Matthesius, G.A., Morris, R.M., Desai, M.J. (1987), Prediction of the volatile matter in coal from ultimate and proximate analyses, *J. S. Afr. Inst. Min. Metall.* **87(6)**, pp. 157-161.
- [34] 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, *Chemical Engineering Technology* **35**, pp. 1-12.