Improving the efficiency of Chemical Looping Combustion with coal by using ring-type internals in the fuel reactor

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Abstract

Chemical Looping Combustion (CLC) with solid fuels has been widely developed by using two interconnected fluidized beds, the fuel reactor and the air reactor, with an oxygen carrier continuously circulating between them. Experience gained in this process shows that high CO₂ capture values can be reached. However, complete combustion of the fuel is not achieved, with some H₂, CO and CH₄ as the main unconverted compounds in the combustion products from the fuel reactor. It is believed that the combustion efficiency can be increased by improving the gas-solid contact in the fuel reactor. In this work, the solids distribution in the fuel reactor was modified by using ring-type internals with the objective of enhancing the gas-solid contact. Two experimental campaigns were carried out in a 50 kW_{th} CLC unit burning a bituminous coal with ilmenite particles in the temperature interval of 900–1000 °C. The first campaign was conducted with the original riser of the fuel reactor, which was characterized by a smooth section from bottom to top. For the second campaign, three ring-type internals were implemented in the riser in order to modify the solids distribution in the fuel reactor. The presence of the internals had a beneficial effect on the coal combustion. The major benefit was an improved oxidation of volatile matter in the form of CH₄ and the full conversion of H₂. As a result, the total oxygen demand decreased by 20 %, from 12.2 % to 9.8 %, with the implementation of the internals.

Keywords: CO₂ capture; Chemical Looping Combustion; coal; ring-type internals.

1. Introduction

Carbon dioxide Capture and Storage (CCS) is a required action to drastically reduce the CO₂ emissions in energy generation from fossil fuels [1]. However, the high cost of the CO₂ capture process could dissuade the implementation of CCS, making difficult the achievement of the goal of the Paris Agreement, i.e. limiting the increase of the global average temperature below 2 °C by 2100 [2].

Chemical Looping Combustion (CLC) has a great potential to reduce the economic and energetic cost of CO₂ capture for energy generation [3]. The CLC concept is based on the transference of oxygen from the air to the fuel by using a solid oxygen carrier, usually a metal oxide (M_xO_y). In this way, fuel can be oxidized to CO₂ and H₂O in a nitrogen free environment. This allows pure CO₂ stream to be obtained at low-cost, since after an easy condensation step, a stream highly concentrated on CO₂ is ready to transport and storage [4]. In one preferred configuration, the oxygen carrier is continuously circulating between two interconnected fluidized bed reactors called fuel and air reactors [5]. Thus, an oxidized oxygen carrier is able to provide oxygen for combustion inside the fuel reactor, while it is regenerated to its initial oxidized state with the oxygen in air supplied to the air reactor.

Coal combustion via CLC has been extensively studied by means of the *in-situ* Gasification Chemical Looping Combustion (*iG*-CLC) process [6,7]; see Fig. 1. In *iG*-CLC, coal devolatilization and gasification happens inside the fuel reactor with H₂O or CO₂ fed to the fuel reactor; see reaction R1. Then, gasification products are oxidized by the oxygen carrier to CO₂ and H₂O; reaction R2. The reduced oxygen carrier, M_xO_{y-1}, is transported to the air reactor where it is regenerated with oxygen in air -reaction R3- to be later used in the fuel reactor again.

Fuel reactor:

Air reactor:

Fig. 1. Scheme of *iG*-CLC process for coal combustion.

There is great experience around worldwide operating continuous CLC units with solid fuels, which has driven to significant advances on *iG*-CLC [7]. In most cases, low cost materials, such as natural ores or industrial wastes, have been used as oxygen carriers. Despite their lower reactivity compared to synthetic materials, the use of low cost materials is popular due to the expected high make-up flow to replace the oxygen carrier lost together the required ash purge.

Coal gasification has been identified as the limiting step during the fuel conversion in the fuel reactor [8]. As a consequence, unconverted char particles could reach the air reactor together the oxygen carrier stream. Then, they will burn to CO_2 -reaction R4- with the corresponding decrease in the CO_2 capture efficiency. This issue has been solved by including a carbon separation unit between the fuel and air reactors [9-12], reaching CO_2 capture values close to 100%.

Another relevant issue in *iG*-CLC is the appearance of unburned gases, mainly CO , H_2 and CH_4 , at the fuel reactor outlet [7]. Lyngfelt and Leckner [13] proposed to oxidize them in an oxygen

polishing unit with pure oxygen; see Fig. 1. But this implies an economic and energy penalty on the overall process. The optimization of the operating conditions can improve the combustion efficiency, but a relevant fraction of unburnt products is still present in the CO₂ stream [11]. Some options have been suggested to increase the combustion efficiency of the process, including:

- Using more reactive oxygen carrier materials was proposed as one of the more efficient way to improve the combustion efficiency [14]. In this sense, the performance of synthetic materials overcomes those of natural ores. Thus, the use of a highly reactive Cu-based material developed by ICB-CSIC [15] has been tested in a 25 kW_{th} CLC unit at TUHH, improving the combustion efficiency achieved with ilmenite [16]. In this case, materials easily separable from the ash particles would be advised, e.g. using the magnetic properties of the Mn-Fe redox system for the design of oxygen carriers [17] or supporting materials [18].
- Implementing a secondary fuel reactor [19]. Thus, the combustion efficiency has been improved by splitting the solids in the fuel reactor in two compartments [20,21]. In this sense, the use of up to 5 compartments has been proposed [22].
- Recirculating unburnt products to the fuel reactor [23]. Different alternatives have been modelled, the best option being the recirculation of a fraction of the exhaust gases to the carbon stripper [24].
- Improving the gas-solid contact in the fuel reactor [25]. Experimental works in cold flow models showed that the use of ring-type internals in the fuel reactor modifies the distribution of solids to make it more homogeneous with height [25,26]. At low gas velocities characteristics of the bubbling regime, the fuel reactor can be considered as one reactor split in different compartments by the internal as it was discussed above [21,22]. In this case, the fuel reactor is characterized by a counter-flow of falling solids and ascending gas [25,26]. However, at high velocities the solids entrainment is promoted, but the core-nucleus structure in the fast fluidization regime is disturbed [27]. It would be expected that the gas-solid contact could be promoted in the dilute

region. Theoretical calculations showed that the modification of the solids distribution in the fuel reactor by using ring-type internals can reduce the amount of unburnt products by 35 % [24], but not experimental confirmation has been done.

The objective of this work is to assess the effect of the presence of ring-type internals in the fuel reactor on performance of the *i*G-CLC process for coal. Two experimental campaigns were conducted in a continuously operated CLC pilot plant for solid fuels. The first campaign was made with the original riser of the fuel reactor, which is characterized by a smooth section from the bottom to top. For the second campaign, three ring-type internals were implemented in the fuel reactor in order to modify the solids distribution. Experimental conditions were selected in order to analyse the effect of the presence of ring-type internals on the CO₂ capture and the combustion efficiency of the CLC process with coal.

2. Experimental

2.1. Materials

The oxygen carrier used in this work was Norwegian ilmenite from Titania A/S Company. Oxygen carrier particles, in the 0.1-0.3 mm size, were exposed to thermal treatment in air at 950 °C for 2 hours as a pre-oxidation stage, since the material was received in its reduced form, i.e. FeTiO₃. Table 1 shows the main physicochemical characteristics of activated ilmenite particles [28]. Ilmenite has been extensively used as oxygen carrier in CLC with coal, and can be considered a reference material [7].

A Russian bituminous coal from the “Taldinsky” mine was used as fuel. Coal was crushed and sieved to obtain particles in the 0.1-0.3 mm interval. Table 1 shows the proximate and ultimate analyses of the coal. The lower heating value is LHV = 26640 kJ/kg and the oxygen demand for its combustion is $\Omega_{sf} = 2.0$ kg of oxygen per kg of coal.

Table 1. Main properties of ilmenite particles and “Taldinsky” bituminous coal.

Ilmenite [28]		“Taldinsky” bituminous coal (wt%) [29]	
Main XRD phases	Fe ₂ TiO ₅	Moisture	5.8
	Fe ₂ O ₃	Ash	10.1
	TiO ₂	Volatile matter	32.0
Crushing strength (N)	2.0	Fixed carbon	52.1
Oxygen transport capacity, R_{OC} (%)	3.9	C	65.8
Skeletal density (kg/m ³)	4200	H	4.0
Porosity (%)	18.0	N	2.0
		S	0.5

2.2. Chemical Looping Combustion facility

The experimental facility was a CLC pilot plant for solid fuels located at ICB-CSIC [30]; see Fig. 2(a). This facility was designed to operate in both *i*G-CLC and CLOU modes. The nominal thermal power was 20 kW_{th} for *i*G-CLC mode and 50 kW_{th} for CLOU mode. In this work, the unit was operated in *i*G-CLC mode by using ilmenite as oxygen carrier.

The CLC unit mainly consists of two interconnected circulating fluidized beds, being the fuel and air reactors, and one carbon stripper being a bubbling fluidized bed. The fuel reactor is designed with two parts: bottom bed (0.10 m inner diameter, 1.2 m height) and upper part (0.08 m inner diameter, 2.8 m tall). The gas velocity in both sections of the fuel reactor is the adequate to operate in the turbulent regime, supporting the required solids circulation rate in the unit. Originally, the riser of the fuel reactor was designed with a regular internal side [30]. Following, geometrical constrictions were implemented inside in order to increase the amount of solids in the dilute zone of the fuel reactor to enhance the gas-solid contact. Thus, three ring-type internals were placed throughout of the riser, maintaining a distance between two consecutive rings of 0.7 m; see Fig. 2(b). These internals were designed according with results obtained by Guío-Pérez et al. [26]. The rings were wedge-shaped designed, with the opening section being the 60% of the reactor cross-section; see Fig. 2(c).

Fig. 2. (a) Layout of the 50 kW_{th} CLC facility [30]; (b) detail of the fuel reactor with indication of position of ring-type internals; (c) detail of section of one ring-type internal.

Coal is fed at the bottom of the fuel reactor through a double screw feeder system to maximize the contact between the volatile matter and the oxygen carrier particles. The CLC unit is not expected to be auto-thermal due to heat losses associated to the unit size. Then, the fuel reactor, air reactor, carbon stripper, and loop seals are heated by separate furnaces. Different thermocouples in the fuel and air reactors, as well as in the carbon stripper, have been included in order to monitor the temperature of these reactors. Likewise, several differential pressure gauges are distributed throughout CLC facility in order to measure the pressure drop between different points of the unit. This allows solids inventory to be estimated in each reactor, which is useful to determine the specific solids inventory in the fuel reactor. Two solids diverter valves are used to measure directly the solids flux exiting from both the fuel and air reactors. The solids circulation flow rate could be modified by acting on the double loop seal (D-LS). Thus, the solids exiting from the fuel reactor could be divided in two streams: (1) the main stream to the carbon stripper, corresponding to the

circulating solids between the air and fuel reactors; and (2) solids internally recirculated to the fuel reactor. More detailed information about the design of the CLC unit can be found elsewhere [30]. The concentration of CO, CO₂, H₂, and CH₄ in the fuel reactor outlet stream and CO₂ and O₂ from the air reactor was continuously recorded by specific gas analysers. The concentrations of the C-based gases are measured using a non-dispersive infrared analyzer (Siemens Ultramat 23), whereas a thermal conductivity detector (Maihak S710/THERMOR) and a paramagnetic analyzer (Siemens 23/Oxymat 6) are used to measure the H₂ and O₂ concentrations, respectively.

2.3. Experimental conditions

Both the fuel reactor and the carbon stripper were fluidized by H₂O, which acts as fluidizing medium and gasifying agent. The steam flow in the carbon stripper was set at 5 Nm³/h, which supposes an inlet gas velocity in the carbon stripper of 0.35 m/s at 950 °C. The total steam flow fed to the fuel reactor was maintained at 10 Nm³/h. In most of the tests this flow was divided, being introduced 7 Nm³/h at the bottom part and 3 Nm³/h as secondary gas; see Fig. 2(b). In some tests, the steam total flow (10 Nm³/h) was only fed at the bottom part. The gas velocity at the bottom part was 1.2–1.8 m/s, while it was about 5 m/s at the upper part. Note that gas flow to the carbon stripper is also added to the gas flow in the upper part of the fuel reactor.

Constant air flow of 40 Nm³/h was supplied in the air reactor in order to act as fluidizing and oxidizing agent, corresponding to a gas velocity of 0.7 m/s at the bottom and of 6.0 m/s at upper of this reactor. Nitrogen was selected as fluidizing medium into all loop-seals of the facility.

In total, 14 tests at steady state were carried out in two experimental campaigns: (1) the first one corresponding to a reference Series R (tests 1–6) by using the original riser of the fuel reactor without internals; and (2) the second campaign corresponding to Series I-1, I-2 and I-3 (tests 7–14) where the ring-type internals were implemented inside the riser of the fuel reactor; see Table 2. Series I-1 was characterized by a low amount of solids in the fuel reactor, mainly being in the bottom part. Then, the transference of solids to the upper part was enhanced either by increasing the

solids inventory (Series I-2) or by increasing the gas velocity in the bottom part (Series I-3).

Table 2. Operating conditions and evaluating parameters for the experimental campaigns conducted in the CLC unit using ilmenite as oxygen carrier.

Internals	Series	Test	$T_{FR,bottom}$ (°C)	$T_{FR,upper}$ (°C)	$u_{g,FRbottom}$ (m/s)	Power (kW _{th})	$\dot{m}_{OC}$ (kg/h)	ϕ (–)	m_{FR}^* (kg/MW _{th})
NO	R	1	905	910	1.0	14.0	125	1.3	520
		2	960	955	1.1	14.0	125	1.3	535
		3	970	972	1.1	14.0	125	1.3	485
		4	985	990	1.2	14.0	125	1.3	475
		5	990	988	1.2	14.0	125	1.3	400
		6	1000	985	1.2	14.0	125	1.3	325
YES	I-1	7	910	965	1.0	12.5	80	0.9	270
		8	970	1030	1.1	12.5	80	0.9	225
YES	I-2	9	910	930	1.0	14.8	140	1.3	420
		10	970	967	1.1	14.8	140	1.3	480
		11	990	980	1.2	14.8	140	1.3	400
		12	1000	985	1.2	14.8	140	1.3	435
YES	I-3	13	950	975	1.7	17.0	115	1.0	320
		14	970	990	1.8	17.0	115	1.0	260

Experimental conditions were selected in order to perform a proper comparison of the CO₂ capture and the combustion efficiency obtained with and without internals. For this, it was considered that the fuel reactor temperature was mainly affecting to the CO₂ capture, while the solids circulation flow rate and the solids inventory in the fuel reactor were the main operating conditions affecting to the combustion efficiency [11]. Thus, the fuel reactor temperature was varied in the 900-1000 °C interval. The carbon stripper temperature was maintained at a value similar than in the fuel reactor. The air reactor temperature was maintained at 950 °C. Solids circulation rate, $\dot{m}_{OC}$, was varied in the 55-200 kg/h interval by acting on the D-LS. The effect of $\dot{m}_{OC}$ was evaluated by means of the oxygen carrier to fuel ratio, ϕ , defined as the flow of oxygen available inside the fuel reactor divided by the flow of oxygen required to achieve complete fuel combustion [7]. The specific solids inventory in the fuel reactor, m_{FR}^* , was varied between 225 and 535 kg/MW_{th}, which was estimated

by means of the measurement of the pressure drop in the fuel reactor [11].

2.4. Evaluating parameters

Performance on *i*G-CLC process was assessed through four evaluating features: solid fuel conversion, CO₂ capture efficiency, combustion efficiency in the fuel reactor and total oxygen demand, following the standardized nomenclature proposed by Adánez et al. [7] and calculated from Eqs. (1)-(4).

$$X_{sf} = \frac{\text{carbon in gases from FR and AR}}{\text{carbon in solid fuel}} = \frac{(F_{CO_2} + F_{CO} + F_{CH_4})_{FR} + F_{CO_2,AR}}{\left(\frac{1000}{12}\right) \cdot \dot{m}_{sf} \cdot x_C} \quad (1)$$

$$\eta_{CC} = \frac{\text{carbon in gases from FR}}{\text{carbon in gases from FR and AR}} = \frac{(F_{CO_2} + F_{CO} + F_{CH_4})_{FR}}{(F_{CO_2} + F_{CO} + F_{CH_4})_{FR} + F_{CO_2,AR}} \quad (2)$$

$$\eta_{comb,FR} = 1 - \frac{\text{ox. needed to burn unconverted gases}}{\text{ox. demanded by fuel converted in FR}} = 1 - \frac{[F_{H_2} + F_{CO} + 4F_{CH_4}]_{FR}}{\left[\frac{1000}{16}\right] \dot{m}_{sf} \Omega_{sf} - 2[F_{CO_2,AR} + F_{C,elut}]} \quad (3)$$

$$\Omega_r = \frac{\text{oxygen needed to burn unconverted gases}}{\text{oxygen needed to burn solid fuel}} = \frac{(F_{CO} + F_{H_2} + 4F_{CH_4})_{FR}}{\left(\frac{1000}{16}\right) \cdot \dot{m}_{sf} \cdot \Omega_{sf}} \quad (4)$$

The solid fuel conversion, X_{sf} , represents the fraction of carbon in solid fuel that is converted to gaseous compounds in the CLC unit, i.e. both in the fuel and air reactors. Carbon flow not detected in gaseous streams is assumed to be present in the unconverted char particles not recovered by the fuel reactor cyclone, being considered as elutriated carbon, $F_{C,elut}$. The CO₂ capture efficiency, η_{CC} , represents the fraction of carbon in gases actually exiting from the fuel reactor. The carbon flow exiting from the fuel reactor depends on the char being gasified in the fuel reactor, which is evaluated through the fraction of carbon in char converted in the fuel reactor, $x_{char,FR}$, calculated by Eq. (5). The generated gases in the fuel reactor, both in volatile matter and gasification products, must be oxidized to CO₂ and H₂O by reacting with oxygen carrier particles. The degree of oxidation of these gases is evaluated with the combustion efficiency in the fuel reactor, $\eta_{comb,FR}$. Often, this parameter is expressed as the oxygen demand in the fuel reactor, i.e. $\Omega_{FR} = 1 - \eta_{comb,FR}$.

Complementary, the total oxygen demand, Ω_T , describes the combustion efficiency by an intuitive definition: the fraction of oxygen required to fully oxidize unburnt gases from fuel reactor with respect to the stoichiometric oxygen required to fully oxidize the fuel.

$$x_{char,FR} = \frac{\text{fixed carbon converted in FR}}{\text{fixed carbon in solid fuel}} = \frac{(F_{CO_2} + F_{CO} + F_{CH_4})_{FR} - \left[\left(\frac{1000}{12} \right) \cdot \dot{m}_{sf} \cdot (x_C - x_{fc}) \right]}{\left[\left(\frac{1000}{12} \right) \cdot \dot{m}_{sf} \cdot x_{fc} \right]} \quad (5)$$

The gas flow of every gaseous compound, F_i , was calculated from the measured gas concentrations and the total gas flow exiting from each reactor, which was determined by means of a N_2 balance following the methodology described in previous works [11,17,28].

3. Results and discussion

Two experimental campaigns burning “Taldinsky” coal with ilmenite was ongoing in the CLC unit. A total of 50 h of continuous circulation of solids at hot conditions were gathered, of which 28 h corresponded to combustion tests. Table 3 shows the values calculated for the evaluating parameters for the 14 tests performed in the CLC unit. Tests in Series R were performed with the original fuel reactor without ring-type internals, while three ring-type internals were implemented in the fuel reactor for the Series I-1 to I-3.

In general, high solid fuel conversions, in the 84-98 % interval with an average value of 92 %, were found regardless of the implementation of the internals inside the fuel reactor. This supposes an average percentage of elutriated coal of 8 %, which is relatively low compared to results found in the literature [7], and agrees with the range of values observed in a previous work burning other bituminous coal [11]. Following, the evaluating parameters will be discussed to assess the effect of the presence of ring-type internals on the performance of the *i*G-CLC process.

Table 3. Evaluating parameters, gas concentration at the fuel reactor, contribution of unconverted gases to the total oxygen demand, and methane conversion.

Series	Test	X_{sf}	η_{CC}	$x_{char,FR}$	Ω_{FR}	Ω_T	Gas concentration at the FR outlet (% , dry and N ₂ -free)				Contribution to the Ω_T (%)			X_{CH_4}
		%	%	%	%	%	CO ₂	CO	H ₂	CH ₄	CO	H ₂	CH ₄	%
R	1	92.3	70.4	55.8	16.4	11.9	77.9	12.8	3.4	5.9	32.0	8.5	59.6	50.3
	2	95.5	84.2	75.3	14.7	12.1	80.9	11.5	2.8	4.7	34.9	8.6	56.5	51.9
	3	96.1	88.2	80.8	14.1	12.4	81.4	11.4	2.7	4.5	34.4	8.3	54.8	50.8
	4	92.9	90.0	79.3	13.3	11.8	81.4	11.6	2.9	4.1	35.2	8.7	49.7	55.9
	5	93.7	92.0	82.6	13.9	12.6	81.0	11.9	2.7	4.4	37.1	8.4	54.5	51.8
	6	92.9	92.3	82.0	13.9	12.5	80.6	12.3	2.7	4.3	38.2	8.4	53.4	52.9
I-1	7	86.5	77.7	58.6	24.6	17.4	71.2	18.3	3.9	6.6	37.8	8.1	54.1	44.7
	8	98.0	93.3	89.2	20.1	18.6	60.8	24.8	4.0	4.5	53.2	8.5	38.3	46.7
I-2	9	94.0	72.6	59.9	13.9	10.0	80.8	14.5	0.1	4.6	43.9	0.3	55.8	60.5
	10	91.5	77.8	63.6	13.4	10.0	82.0	11.9	1.7	4.4	38.3	5.4	56.3	60.4
	11	86.7	80.7	64.1	13.0	9.7	82.7	11.1	2.0	4.3	36.8	6.6	56.6	61.3
	12	86.3	80.8	63.8	12.7	9.5	82.4	11.6	2.0	3.9	39.5	6.9	53.6	64.3
I-3	13	83.8	78.4	56.7	14.8	10.3	76.5	19.5	0.0	4.0	55.1	0.0	44.9	67.4
	14	96.2	81.2	72.4	13.4	10.8	79.3	17.2	0.0	3.5	55.1	0.0	44.9	65.8

3.1. CO₂ capture efficiency

Fig. 3 shows the variation of the CO₂ capture as a function of the fuel reactor temperature for the four experimental series shown in Table 2. An increase of the CO₂ capture efficiency with temperature was observed in all cases, which is related to the calculated increase in the fraction of carbon in char converted in the fuel reactor, $x_{char,FR}$. Thus, CO₂ capture efficiency greater than 90 % was achieved at a fuel reactor temperature higher than 980-990 °C in Series R and I-1, but lower values were found for Series I-2 and I-3.

During the experimental campaign without internals inside the fuel reactor, Series R, a maximum CO₂ capture value of 92.3 % was obtained at 1000 °C. This value is still far from those obtained in a 100 kW_{th} CLC unit at Chalmers (η_{CC} ~99 %), where the char separation was highly efficient due to advanced design of the carbon stripper, with four compartment individually fluidized, and the lower size of coal particles (~0.04 mm) [9]. Nevertheless, the fraction of char converted in the fuel reactor was relatively high because the solid fuel conversion, X_{sf} , was significantly high, i.e. the fraction of char not recovered by the cyclone was low. The fraction of char converted in the fuel reactor could

have an effect on the combustion efficiency in the fuel reactor, and will be discussed later.

Fig. 3. CO₂ capture efficiency as a function of the fuel reactor temperature for tests conducted without internals (closed symbols) and with internals (open symbols).

Some differences on the CO₂ capture efficiencies were observed when the ring-type internals were implemented inside the fuel reactor (Series I-1, I-2 and I-3), which can be justified by differences in the fluid dynamics and solids distribution in the fuel reactor; see Table 4 and Fig. 4. Higher CO₂ capture values were obtained in Series I-1 than in Series R. In this case, a low amount of solids was present in the whole fuel reactor, corresponding to values of the specific solids inventory about 250 kg/MW_{th}. As a consequence, the fraction of solids in the upper part of the fuel reactor was low, and a high temperature profile in the fuel reactor was found; see Table 2. The high temperature in the upper part of the fuel reactor could promote the char conversion, thus achieving higher values of the CO₂ capture.

Fig. 4. Pressure profile in the fuel reactor in tests at 970 °C for selected test in Series R, I-1, I-2 and I-3. The gas velocity and distribution of solids between the bottom and upper part is also indicated. The gas flow at 1.2 m includes secondary flow and gas from carbon stripper.

Table 4. Specific solids inventory and distribution of the ilmenite particles in the fuel reactor, as well as temperature difference between the bottom and the upper parts.

Series	Test	$\Delta T_{upper-bottom}$ (°C)	ΔP_{FR} (kPa)		m_{FR}^* (kg/MW _{th})		Distribution of solids in the fuel reactor (%)	
			Bottom	Upper	Bottom	Upper	Bottom	Upper
R	1	+5	6.4	3.4	392	128	75	25
	2	-5	6.6	3.4	405	130	76	24
	3	+2	5.9	3.3	360	125	74	26
	4	+5	5.1	4.3	311	164	65	35
	5	-2	4.8	2.9	290	110	72	28
	6	-15	3.5	3.0	210	115	65	35
I-1	7	+55	3.9	0.3	255	15	95	5
	8	+60	3.0	0.2	217	8	96	4
I-2	9	+20	5.5	3.2	310	110	73	27
	10	-3	6.5	3.2	366	114	76	24
	11	-10	5.5	2.6	310	90	77	23
	12	-15	6.2	2.4	350	85	80	20
I-3	13	+25	5.2	1.9	260	60	81	19
	14	+20	4.4	1.4	218	42	83	17

On the contrary, lower CO₂ capture rates were observed in Series I-2, where the solids inventory in the CLC unit was increased compared to Series I-1. In this case, the solids distribution was significantly varied from the reference case without internals, i.e. Series R; but in both Series R and I-2 a homogeneous temperature in the whole fuel reactor was found. Fig. 4 shows that a gradual decrease in the gauge pressure with the reactor height was observed in absence of internals, which corresponds to a gradual decrease in the solids concentration. However, in Series I-2 solids were mainly accumulated at the bottom bed and above the second internal. This fact suggests char particles are being accumulated at the upper part due to the different solids distribution caused by the presence of the internals, as well as the accumulation of solids in a position close to the reactor exit [25]. This situation could facilitate the elutriation of char particles, decreasing their residence time in the fuel reactor. The solids stream leaving the fuel reactor would be concentrated in char, which entails that the char separation efficiency decreases inside the carbon stripper [31]. This behaviour was predicted by modelling the implementation of internals in the fuel reactor [24].

In Series I-3 the secondary flow was removed, and all the gas was fed by the distributor plate of the fuel reactor. As a consequence, the amount of solids in the fuel reactor decreased due to a higher gas velocity in the bottom part, and also the fraction of solids at the upper region was lower; see Table 4. Solids were still accumulated above the second internal (see Fig. 4) which can justify the lower CO₂ capture rates compared to Series R. But a temperature gradient was observed which could explain the higher CO₂ capture rate achieved in Series I-3 compared to Series I-2.

From these results, it can be stated that the use of ring-type internals in the fuel reactor decreases the CO₂ capture rate because of accumulation of solids in a position close to the reactor exit. A highly efficient carbon stripper would be required to recover the high CO₂ capture efficiency reached in Series R.

3.2. Total oxygen demand

Series R (tests 1-6) were initially carried out with the original riser of the fuel reactor, i.e. without internals, in order to establish the combustion efficiency at the reference conditions. The effect of the implementation of constrictions inside the fuel reactor on the combustion efficiency will be made in a suitable way by comparing the results obtained in Series I-1, I-2 and I-3. Here, both the total oxygen demand, Ω_T , and the combustion efficiency in the fuel reactor, $\eta_{\text{comb,FR}}$, are the parameters used to evaluate the combustion efficiency of the CLC unit; see Eqs. (3) and (4). Fig. 5 shows that both Ω_T and $\eta_{\text{comb,FR}}$ were affected by the presence of internals in the fuel reactor, as well as by variations of other operating conditions, such as the oxygen carrier to fuel ratio or the specific solids inventory in agreement with previous results obtained in this CLC facility [11]. If we pay attention to the values of the total oxygen demand, it was obtained an average value of $\bar{\Omega}_T = 12\%$ for tests performed without internals in the fuel reactor, i.e. Series R. In Series I-1, $\bar{\Omega}_T$ increased to values about 18 % although the internals were installed. However, it cannot be said that the presence of internals had a negative effect on total oxygen demand, but the increase in total oxygen demand was caused by other effects. Thus, both the oxygen carrier to fuel ratio and specific solids inventory were lower in Series I-1 ($\phi = 0.9$ and $m_{FR}^* \approx 250 \text{ kg/MW}_{\text{th}}$) compared to Series R ($\phi = 1.3$ and $m_{FR}^* \approx 400\text{-}500 \text{ kg/MW}_{\text{th}}$), which it is well known to affect negatively to the oxygen demand [11,32]. But more interestingly is the analysis of the solids distribution in the fuel reactor; see Fig. 4. At conditions used in Series I-1, i.e. low solids inventory and low gas velocity in the bottom part, most of solids were in this region. Low presence of solids in the upper part of the reactor was observed, where the internals were installed. Therefore, solids were not accumulated above the internals and could not be effective for the fuel oxidation.

In order to achieve similar solids inventories than in Series R, more solids were added to the CLC unit. Thus, Series I-2 was performed with the similar ϕ and m_{FR}^* values than in Series R. Comparing

results obtained in these Series, it can be observed a decrease in the average value of the total oxygen demand from $\bar{\Omega}_T = 12.2\%$ without internals to $\bar{\Omega}_T = 9.8\%$. This means an average decrease of 20 % in the oxygen demand with the implementation of the internals in the fuel reactor. This value is in line with the potential Ω_T reduction predicted by implementing internals in the fuel reactor [24]. In Series R and I-2, the oxygen carrier to fuel ratio was the same, and not only the amount of solids in the fuel reactor was similar but also the distribution of solids between the bottom and upper parts of the reactors was similar; see tests 3 and 10 in Fig. 4. But there is a relevant difference in the solids distribution: while in Series R there is a uniform decrease in the solids concentration with the reactor height, in Series I-2 there is an accumulation of solids above the second internal, as it was expected considering fluid dynamics results from a cold flow model [25,26]. Likely, this fact promoted a better gas-solid contact at the upper part of the reactor, which enhanced the conversion of unburned gases in this section.

Fig. 5. Total oxygen demand and combustion efficiency in the fuel reactor as a function of the fuel reactor temperature for tests conducted without internals (Series R: $\blacktriangle$) and with internals (Series I-1: $\circ$; I-2: $\square$; I-3: $\diamond$).

Then, solids at the bottom part of the reactor seems to be less effective oxidizing gasification products, as it was predicted from modelling results [14,32,33]. In order to decrease the amount of solids in the bottom part, the gas flow from the distributor plate was increased from 7 to 10 m³/h (STP), avoiding the secondary gas flow. As a result, the amount of solids both in the bottom and upper parts decreased, as well as the solids circulation rate. But accumulation of solids above the second internal was still observed; e.g. see test 14 in Fig 4. Thus, the total oxygen demand increased from $\bar{\Omega}_T=9.8$ % in Series I-2 to $\bar{\Omega}_T=10.5$ % in Series I-3. Interesting is the fact that the total oxygen demand in Series I-3 was still lower than in Series R, suggesting that the performance was improved by the use of internals even when there were lower values of ϕ and m_{FR}^* .

As it was shown, the total oxygen demand decreased with the use of internals in the CLC unit. However, one can think that these results could be influenced by a lower char conversion in the fuel reactor, related to a lower CO₂ capture when the internals were installed; see Fig. 3 and Table 3. To evaluate this issue, it is interesting to analyse the evolution of Ω_T jointly to $\eta_{comb,FR}$ as the char conversion in the fuel reactor varied, following a method previously developed [7]. In the four Series carried out in this work the total oxygen demand, Ω_T , was barely affected by the fuel reactor temperature. This means that the flow of unburnt products were roughly the same regardless the temperature in the reactor. However, the combustion efficiency in the fuel reactor, $\eta_{comb,FR}$, showed a slight increase with the fuel reactor temperature. This means that the gases generated in the fuel reactor, i.e. volatile matter and char gasification products, are better oxidized as the temperature was higher. The different trend between Ω_T and $\eta_{comb,FR}$ is related to the different oxidation degree of volatile matter and char gasification products. The amount of char gasification products increased with temperature, as the char conversion in the fuel reactor increased. Thus, an increase of $\eta_{comb,FR}$ with temperature would be related to a better combustion of char gasification products compared to volatile matter. In this way, if most of unburnt products were from volatile matter, Ω_T would be

roughly constant, as it is. Considering the values of Ω_T , Ω_{FR} and $x_{char,FR}$ in Table 3, the combustion efficiency of volatile matter, $\eta_{comb,v}$, and char gasification products, $\eta_{comb,g}$, can be calculated from the following expression [7]:

$$A = (1 - \eta_{comb,v}) + (1 - \eta_{comb,g}) \cdot B \quad \text{with} \quad A = \frac{\Omega_{char}(1 - x_{char,FR})}{\Omega_{vol} \left[\frac{1}{\Omega_T} - \frac{1}{\Omega_{FR}} \right]} \quad \text{and} \quad B = \frac{\Omega_{char}}{\Omega_{vol}} x_{char,FR} \quad (6)$$

Fig. 6 shows the B vs. A plot and the corresponding linear regression by least squares approximation. Results of the combustion efficiency of volatile matter and char gasification products are shown in Table 5. The uncertainty of these values may be high due to the lack of a relevant number of available results. Note that in some cases two data are only used for the regression. However, when all the results obtained in this work are evaluated together, additional information about the combustion of volatile matter and gasification products can be extracted from this analysis, which can be compared to other results, e.g. the conversion of methane.

As expected from the previous discussion, a high combustion degree of char gasification products is calculated, with values of $\eta_{comb,g}$ above 90 % in all Series. Lower is the combustion efficiency of volatile matter, which is also affected by the presence of internals in the fuel reactor. Thus, $\eta_{comb,v}$ values of 67.1 and 51.1 % are calculated for Series R and I-1, i.e. where there was no either internals or accumulation of solids above the internals. Then, the presence of internals caused an increase in the combustion efficiency of volatile matter, but higher for Series I-2 ($\eta_{comb,v} = 78.3$ %) than for Series I-3 ($\eta_{comb,v} = 70.6$ %) due to the different values of ϕ and m_{FR}^* ; see Table 2.

Considering CH_4 as a marker of volatile matter content, it is observed that most of the contribution to the total oxygen demand is due to the presence of this gas; see Table 3. The conversion of CH_4 in the fuel reactor was calculated assuming the generation of 0.0704 kg CH_4 per kg of coal [34], and it is shown in Tables 3 and 5. In general, the methane conversion has the trend followed by $\eta_{comb,v}$, and it is improved by the presence of internals.

Fig. 6. Determination of combustion efficiency of volatile matter and gasification products following Eq. (6) for the four Series carried out in this work.

Table 5. Values of combustion efficiency of gasification products, $\eta_{\text{comb,g}}$, and volatile matter, $\eta_{\text{comb,v}}$, according to Eq. (6) and results shown in Fig. 6, and CH_4 conversion.

Series	$\eta_{\text{comb,g}}$ (%)	$\eta_{\text{comb,v}}$ (%)	$\bar{X}_{\text{CH}_4}$ (%)
R	90.8	67.1	52.3
I-1	92.3	51.1	45.7
I-2	91.2	78.3	61.6
I-3	95.5	70.6	66.6

The different combustion efficiency of volatile matter and gasification products can be explained because of differences on reactivity and gas-solid mixing, as it was previously discussed in works modelling the fuel reactor behaviour [14,35]. Char particles are well mixed with oxygen carrier particles. Therefore, char gasification products (CO and H_2) are mainly generated in the emulsion phase, where can easily react with ilmenite particles. However, volatile matter is mainly evolved in bubbles or plumes in the bottom region with poor contact with oxygen carrier particles. The gas-

solid contact is somewhat improved in the dilute region, where is mainly converted. In this line, the presence of internals enhances the gas-solid contact in the dilute region. In addition, low values of H_2 are detected in the presence of internals, which is related to the high reactivity of this gas with ilmenite compared to reactivity with CO or CH_4 [36]. In this sense, the low reactivity of ilmenite with CH_4 justifies the high fraction of total oxygen demand coming from CH_4 . Because of this, the effect of internals on the fluid dynamics of the fuel reactor improves the combustion efficiency of the CLC process.

It was determined that the volatile matter was more difficult to oxidize than the char gasification products, and the enhancement of the gas-solid contact is a relevant issue to promote the conversion of volatile matter. This fact can be of high relevance with fuels with a high volatile content, such as biomass. In this case, the combustion efficiency could be improved by implementing internals but without negatively affect to the CO_2 capture due to the high reactivity of char from biomass. This hypothesis will be evaluated in future works with biomass as fuel. In addition, the potential of using ring-type internals on the improvement of the combustion efficiency could be higher in CLC units with taller fuel reactors, as it was predicted from modelling results [24]. However, the studies carrier out about the effects of internals on the reactor fluid dynamics is mostly restricted to cold flow models [25-27]. The potential of this solution at large-scale should be evaluated during the scale-up of the CLC process, considering technological options in order to disturb the core-annulus structure of the circulating fluidized bed and distributing the solids along the riser.

4. Conclusions

Two experimental campaigns were conducted in the continuously operated 50 kW_{th} CLC pilot plant for solid fuels to evaluate the effect of ring-type internals in the fuel reactor on the performance of coal combustion by CLC. The presence of internals modified the solids distribution in the fuel reactor, which affected to the total oxygen demand. The presence of the internals had a beneficial

effect on the coal combustion. Thus, the total oxygen demand decreased from 12.2 % to 9.8 %, corresponding to a decrease of 20 %. It was concluded that conversion of volatile matter was improved by the presence of the internals, because the conversion of CH_4 was improved up to 25 %. Also, gasification products were highly converted, as shown the fact that very low H_2 concentration values were achieved.

Acknowledgements

This work was supported by the Spanish Ministry of Economy, Industry and Competitiveness (projects ENE2014-56857-R and ENE2016-77982-R), the Spanish National Research Council (CSIC project: 2017-80E035), the EU project ACCLAIM (RFCP-CT-2012-00006) and the European Regional Development Fund (ERDF).

5. Nomenclature

F_i	molar flow of compound i (mol/s)
$F_{C,elut}$	carbon flow in the char elutriated (mol C/s)
$\dot{m}_{OC}$	solids circulation flow rate (kg/s)
m_{FR}^*	specific solids inventory into the fuel reactor (kg/MW _{th})
$\dot{m}_{sf}$	rate of solids feeding (kg/s)
R_{oc}	oxygen transport capacity of the oxygen carrier (kg oxygen per kg oxygen carrier)
T	temperature (°C)
u_g	gas velocity (m/s)
X_{CH_4}	methane conversion (-)
$x_{char,FR}$	fraction of carbon in char converted in the fuel reactor (-)
X_{sf}	solid fuel conversion to gas (-)
x_C	carbon fraction in coal (-)
x_{fc}	fixed carbon in coal (-)

Greek symbols

ΔP	pressure drop (Pa)
$\Delta T_{upper-bottom}$	temperature difference between the upper and the bottom parts of the fuel reactor (°C)
ϕ	oxygen carrier-to-fuel ratio (-)
η_{CC}	CO ₂ capture efficiency (-)
$\eta_{comb,FR}$	combustion efficiency in the fuel reactor (-)
$\eta_{comb,v}$	combustion efficiency of the volatile matter (-)
$\eta_{comb,g}$	combustion efficiency of the char gasification products (-)
Ω_{char}	oxygen demand of char (kg oxygen per kg solid fuel)
Ω_{sf}	oxygen demand of the coal (kg oxygen per kg solid fuel)
Ω_{FR}	oxygen demand in the fuel reactor (-)
Ω_T	total oxygen demand (-)
Ω_{vol}	oxygen demand of volatile matter (kg oxygen per kg solid fuel)

Acronyms

AR	Air reactor
CCS	Carbon capture and Storage
CLC	Chemical Looping Combustion
CLOU	Chemical Looping with Oxygen Uncoupling
FR	Fuel reactor
iG-CLC	<i>in-situ</i> Gasification Chemical Looping Combustion
LHV	Lower Heating Value (kJ/kg)
OC	Oxygen carrier
XRD	X-Ray Diffraction

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