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Comparative Evaluation of the Performance of Coal Combustion in 0.5 and 50 kW$_{th}$ Chemical Looping Combustion units with ilmenite, redmud or iron ore as oxygen carrier

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Abstract

Chemical Looping Combustion (CLC) is one of the most promising technologies to achieve the CO_2 capture at a low economic and energetic penalty. In CLC the combustion is split in two steps: fuel combustion assisted by an oxygen carrier in the fuel reactor, and oxygen carrier regeneration in the air reactor by oxygen in air. Usually, the air and fuel reactors are interconnected fluidized beds, with the oxygen carrier circulating between them. Thus, the CO_2 capture is inherent to the CLC process. The use of solid fuels in CLC is attracting great attention due to coal is the most abundant fuel, and burning biomass with CO_2 capture would allow to reduce the atmospheric CO_2 concentration. The *in situ* Gasification CLC (*i*G-CLC) allows the conversion of the solid fuel by performing both gasification and combustion of gasification products in the fuel reactor. In *i*G-CLC complete combustion is not reached, and an oxygen polishing step is required downstream by using a small fraction of pure oxygen.

In this work, an overview of the operational experience in ICB-CSIC is presented. Results obtained in 0.5 kW$_{th}$ and 50 kW$_{th}$ CLC units burning different coals with ilmenite, redmud or iron ore are compiled and critically compared. Insights were obtained in order to achieve high CO_2 capture and combustion efficiency values. Eventually, the use of ring-type internals in the fuel reactor of the 50 kW$_{th}$ CLC unit was accomplished to promote the gas-solid contact, thus increasing the combustion efficiency.

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1. Introduction

Chemical Looping Combustion (CLC) technology is recently attracting attention as a promising technology to reduce the associated economical costs and energy penalty of the CO_2 capture process [1]. In CLC the oxygen required for fuel combustion is supplied by an oxygen carrier, normally a particulate metal oxide. This process is usually carried out in two interconnected fluidized bed reactors, the fuel and air reactors, with the oxygen carrier continuously circulating between them. In the fuel reactor, fuel is oxidized to CO_2 and H_2O, while in the air reactor it is re-oxidized by air before starting a new cycle. Thus, the fuel is not mixed with air, and a concentrated CO_2 stream is obtained after the fuel combustion.

Chemical Looping Combustion (CLC) of solid fuels is based on the direct feeding of the fuel, e.g. coal or biomass, into the fuel reactor, where it is devolatilized and *in situ* gasified in the so-called *in situ* Gasification CLC (*i*G-CLC). A conceptual diagram of processes happening in the fuel reactor is presented in Fig. 1. In the *i*G-CLC concept, coal gasification is an intermediate step for coal conversion; see reactions (1)-(3). Usually, steam is preferred to be used as gasifying agent, but CO_2 gasification can also happen due to the formation of CO_2 as a combustion product. In the same fuel reactor, oxidation of gasification products by reacting with oxygen carrier particles occurs; see reaction (4). In addition, the water-gas shift reaction can modify the composition of gases; see reaction (5). Usually, complete combustion is not reached, and an oxygen polishing step is required downstream in order to allow complete combustion to CO_2 and H_2O by using a small fraction of pure oxygen; see Fig. 2 [2,3].
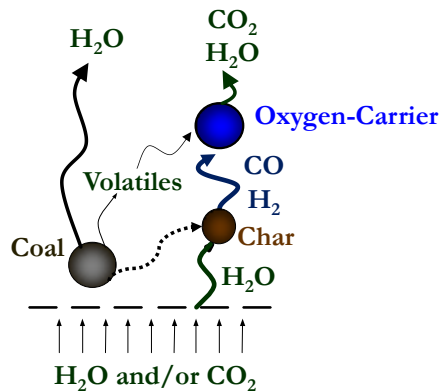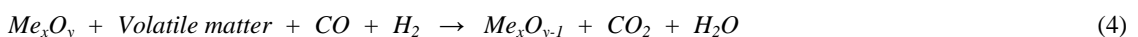

Fig. 1. Scheme of main chemical processes involved in the fuel reactor of *i*G-CLC.

$$Coal \; \rightarrow \; Volatile \; matter \; + \; char(C) \tag{1}$$

$$Char(C) \; + \; H_2O \; \rightarrow \; CO \; + \; H_2 \; + \; ash \tag{2}$$

$$Char(C) \; + \; CO_2 \; \rightarrow \; 2\,CO \; + \; ash \tag{3}$$

$$Me_xO_y \; + \; Volatile \; matter \; + \; CO \; + \; H_2 \; \rightarrow \; Me_xO_{y-1} \; + \; CO_2 \; + \; H_2O \tag{4}$$

$$CO \; + \; H_2O \; \leftrightarrow \; CO_2 \; + \; H_2 \tag{5}$$

$$Me_xO_{y-1} \; + \; \tfrac{1}{2}\,O_2 \; \rightarrow \; Me_xO_y \tag{6}$$

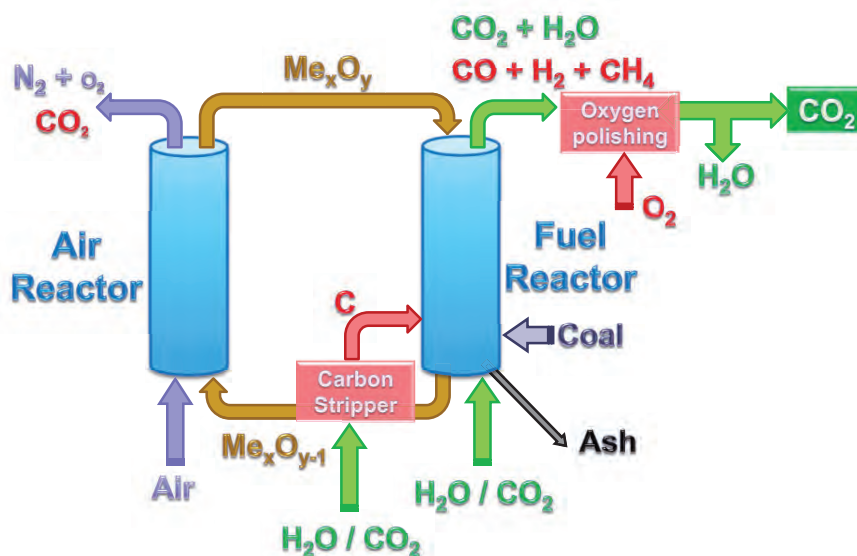$$C \; + \; O_2 \; \leftrightarrow \; CO_2 \tag{7}$$

Fig. 2. Scheme of the *i*G-CLC process with coal.

The reduced oxygen carrier is transported to the air reactor where is regenerated by air; see reaction (6). However, some unconverted char particles can be present in the oxygen carrier stream, which will be burnt in the air reactor; see reaction (7). The CO_2 generated in the air reactor is not captured, so it would be desirable that unconverted char particles did not reach the air reactor. The use of a carbon separation system, such a carbon stripper, has been proposed for this purpose [4]. In the carbon stripper char particles are separated from oxygen carrier, and they are recirculated to the fuel reactor.

In *i*G-CLC, ash generated after coal conversion must be drained from the system to avoid its accumulation. As coal is mixed with oxygen carrier, the purge stream may contain both ash and oxygen carrier particles. A make-up stream must be added to replace oxygen carrier lost in the purge stream. Therefore, low cost materials are usually used as oxygen carrier in *i*G-CLC [2,3]. Ilmenite, Fe-ores or Mn-ores have been frequently used in CLC units.

Experience has been gained in the combustion of coal in CLC units ranging from 0.5 kW_{th} to 3 MW_{th} [3]. Highly relevant results were obtained in units of 100 kW_{th} at Chalmers University of Technology [5], 1 MW_{th} at Darmstadt University of Technology [6] and 3 MW_{th} by Alstom USA [7]. High CO_2 capture rates were obtained when the bypass of char particles to the air reactor was blocked. But unburnt products were always present in the CO_2 stream, demanding as much as the 15-20 % of the total oxygen required to burn the coal in the oxygen polishing step.

At ICB-CSIC, two CLC units are available to burn solid fuels with a nominal thermal power of 0.5 kW_{th} and 50 kW_{th}. Several campaigns have been performed in these units burning different types of solid fuels, including coals and biomasses, with several oxygen carriers [8-19]. In this work, results obtained in these units are revisited and a comparison is done depending on the CLC unit, the type of solid fuel and the type of oxygen carrier. Useful information is extracted in order to maximize the CO_2 capture and combustion efficiency of the *i*G-CLC process.

2. Experimental

2.1. Oxygen carriers

Ilmenite was initially selected as oxygen carrier in the 0.5 kW CLC unit due to its suitable reactivity, oxygen transport capacity, crushing strength and avoidance of agglomeration [20]. Due to its wide use in CLC with coal, ilmenite was also tested in the 50 kW CLC unit burning bituminous coals. Then, more reactive materials were tested in the 0.5 kW CLC unit such as redmud and Tierga iron ore [21]. Table 1 shows the main chemical characteristics of

these materials, as well as data related to their use in the 0.5 kW and 50 kW CLC units. Redmud is a residue from the aluminum production from bauxite. The selected redmud fraction to be the oxygen carrier was referred as iron enriched sand fraction (Fe-ESF).

In addition to Fe-based materials, Cu- and CuMn-based materials were tested in the 0.5 kW unit in the so-called Chemical Looping with Oxygen Uncoupling (CLOU) mode [22]. The CLOU process takes advantage of the generation of gaseous oxygen (O_2) by the oxygen carrier at the fuel reactor conditions. Finally, a MnFe mixed oxide was also used in the 0.5 kW unit. It was determined that conversion of coal with this material was mainly via CLC, but some oxygen could be transferred via oxygen uncoupling, corresponding to the Chemical Looping aided with Oxygen Uncoupling (CLaOU). In these cases, the power of the small facility was increased up to 1.5 kW for CLOU conditions. Results obtained with these materials will be briefly discussed and they are included in Table 1.

Table 1. Oxygen carriers used in the 0.5 kW and 50 kW units, including CLOU materials.

Oxygen carrier	Active phases	R_{OC} (wt.%)[1]	Facility	Solid fuels[2]	Combustion time (h)	Refs.
Ilmenite	Fe_2TiO_5, Fe_2O_3	4.0	0.5 kW CLC	A, B, L	100	[8-11]
			50 kW CLC	B	100	[17-19]
Redmud (Fe-ESF)	Fe_2O_3	2.0	0.5 kW CLC	A, B, L	50	[12,13]
Tierga iron ore	Fe_2O_3	2.0	0.5 kW CLC	A, B, L, Bio	160	[14-16]
$CuO/MgAl_2O_4$	CuO	6.0	1.5 kW CLOU	A, B, L, Bio	85	[23-26]
$CuO/Fe_2O_3/MgAl_2O_4$	CuO	5.0	1.5 kW CLOU	L	35	[27]
Cu-Mn mixed oxide	$Cu_{1.5}Mn_{1.5}O_4$	4.0	1.5 kW CLOU	sB	16	[28]
Mn-Fe mixed oxide	$(Mn_{0.66}Fe_{0.33})_2O_3$	7.7	0.5 kW CLaOU	B	10	[29]

[1]R_{OC}: oxygen transport capacity

[2] A: anthracite; B: bituminous coal; sB: subbituminous coal; L: lignite; Bio: biomass

2.2. 0.5 kW$_{th}$ CLC unit

The 0.5 kW$_{th}$ CLC unit comprised two interconnected fluidized bed reactors, (1) and (3) in Fig. 3, heated by electric furnaces (11). The fuel reactor (1) and the air reactor (3) were connected by a fluidized bed acting as loop seal (2). A riser (4) transported solids from the air to the fuel reactor. A cyclone recovered the entrained solids (5) and sent them to a deposit. A solids valve controlled the solids flow fed from this deposit to the fuel reactor (8). A diverting solid valve (6) enabled the measurement of the solid flow rates at any time. The fuel reactor consisted of a bubbling fluidized bed (50 mm ID). Solid fuel was fed with a screw feeder (9) at the bottom of this bed and just above the fuel reactor distributor plate. In most of cases, the fuel reactor was fluidized with steam which also acted as gasifying agent, but H_2O/CO_2 mixtures were used in specific experiments.

This unit does not have a carbon stripper. However, the absence of a carbon stripper in this unit facilitated the interpretation of the effect of different operating conditions on the results obtained. More information about this facility can be found elsewhere [8-16].
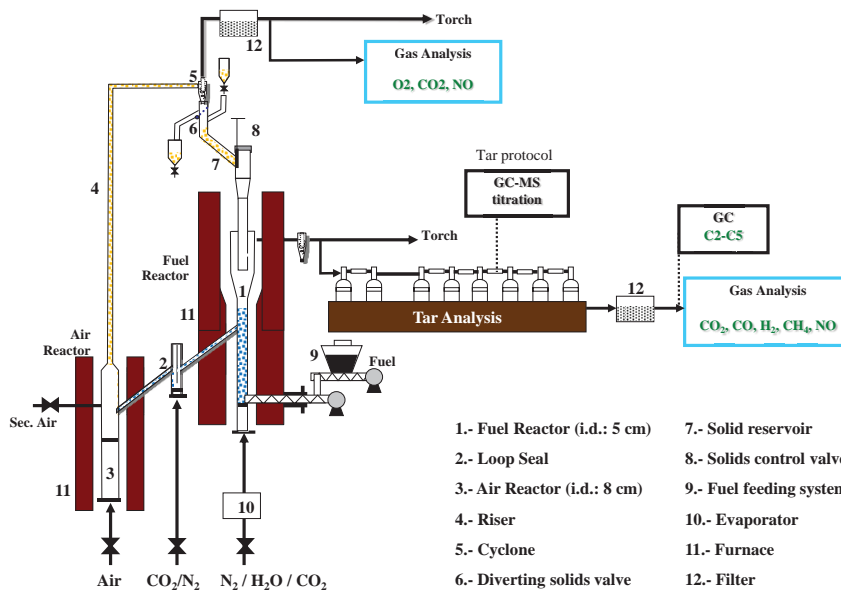
Fig. 3. Layout and picture of the 0.5 kW$_{th}$ CLC unit (ICB-CSIC-s1) plant facility for the CLC of solid fuel.

2.3. 50 kW$_{th}$ CLC unit

The design of the 50 kW$_{th}$ CLC unit was based on two interconnecting circulating fluidized beds reactors, being the fuel and air reactors; see Fig. 4. Also, a carbon stripper was included in order to minimize the flow of char entering to the air reactor. The carbon stripper was identified as a key element in order to reach high CO$_2$ capture rates. In addition, a double loop seal after the fuel reactor cyclone was designed to allow a stable solids circulation between fuel and air reactors with independent control. The measurement of solids circulation between both reactors can be performed by means of two diverting solids devices located downstream the fuel and air reactor cyclones.

This CLC facility 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. The unit was designed to operate both in CLC of coal assisted by *in-situ* gasification (*i*G-CLC) and in CLOU mode. 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 CLC on the basis of CO$_2$ capture and combustion efficiency [30,31].

The dimensions of the reactor are defined by the design values of solids inventory and gas velocity. Design data are shown in Table 2. The height of air and fuel reactors were determined in order to arrange all the elements of the CLC unit. Thus, the air reactor height was 4.6 m, whereas the fuel reactor was 4.0 m tall. More information about the design of the CLC unit can be found elsewhere [17-19].

Table 2. Oxygen carriers used in the 0.5 kW$_{th}$ and 50 kW$_{th}$ units, including CLOU materials.

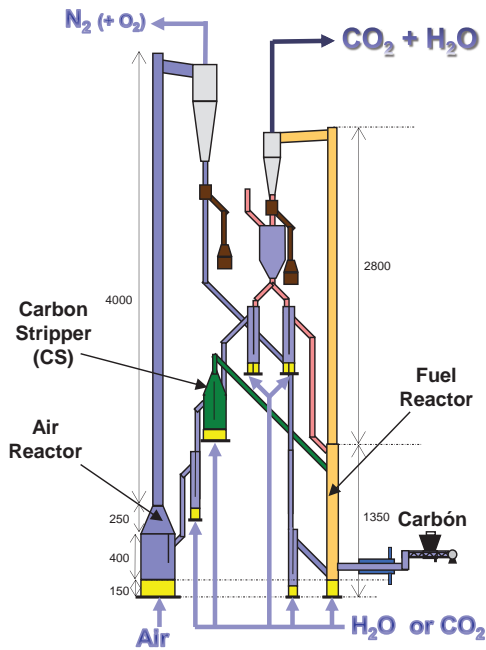|	Fuel Reactor	Air Reactor	Carbon Stripper
Height (m)	4.0	4.6	0.71
Diameter bottom (m)	0.10	0.30	0.15
Diameter up (m)	0.08	0.10	--

Fig. 4. Layout and picture of the 50 kW$_{th}$ CLC unit (ICB-CSIC-s50) plant facility for the CLC of solid fuel.

In *i*G-CLC mode, the solid fuel is converted by *in-situ* gasification. Thus, the fuel reactor was fluidized by H$_2$O, which acts as fluidization medium and gasification agent. The solid fuel was fed through a screw feeder system just above the distributor plate in the fuel reactor. It is intended to convert the fuel to CO$_2$ and H$_2$O, minimizing the unburnt compounds.

3. Results

The 0.5 kW$_{th}$ and 50 kW$_{th}$ CLC units were operated in *i*G-CLC mode. Ilmenite, redmud and Tierga iron ore were used as oxygen carriers in the 0.5 kW$_{th}$ facility burning different solid fuels (anthracite, bituminous coal, lignite and biomass). But ilmenite has been the only material used in the 50 kW$_{th}$ plant burning bituminous coals; see Table 1. In general, steam was used as fluidizing gas, which also acted as gasifying medium. Results obtained are presented in the form of CO$_2$ capture and total oxygen demand. The total oxygen demand is a useful parameter to evaluate the combustion efficiency of the CLC unit [3].

3.1. CO$_2$ Capture

Captured CO$_2$ in a CLC unit is related to carbon in gaseous compounds exiting the fuel reactor. Any CO$_2$ from the air reactor would be diluted in N$_2$ and, therefore, will be not captured. Results in coal combustion carried out in the 0.5 kW$_{th}$ CLC unit showed that the CO$_2$ capture mainly depended on both the temperature and mean residence time of solids in the fuel reactor. Fig. 5 shows most of results obtained in this unit burning bituminous coals with ilmenite, redmud or iron ore as oxygen carrier. The use of different materials as oxygen carrier barely affected to the CO$_2$ capture rate. But it was clear the increase in the CO$_2$ capture by increasing the fuel reactor temperature and/or the mean residence time in this reactor. This fact was due to more char was gasified due either to an increase of the gasification rate by increasing the temperature or more time to be gasified as the mean residence time was increased. Note that CO$_2$ capture was dependent on the char conversion in the fuel reactor, X_{char}, by the following equation:

$$\eta_{CC} = f_{c,vol} + X_{char} f_{C,fix} = \left(1 - f_{c,fix}\right) + X_{char} f_{C,fix} \tag{8}$$

$f_{c,vol}$ anf $f_{c,fix}$ being the fraction of carbon in volatile matter and fixed carbon, respectively. Thus, all carbon existing in volatile matter is captured, while only carbon in char being gasified in the fuel reactor is captured. In the 0.5 kW$_{th}$ CLC unit, unconverted char passed to the air reactor where it was burnt by oxygen in air, given non-captured CO_2.

Fig. 5 shows also results obtained in the 50 kW$_{th}$ CLC unit. In this case, the mean residence time of solids in the fuel reactor was lower than in the 0.5 kW$_{th}$ CLC, but a higher temperature in the fuel reactor was reached. Interestingly, the CO_2 capture in the 50 kW$_{th}$ CLC unit was significantly higher than that achieved in the 0.5 kW$_{th}$ CLC unit. In this case, the presence of a carbon stripper in the 50 kW$_{th}$ CLC unit was critical in order to obtain high CO_2 capture rates (~90%) with low residence time of solids in the fuel reactor. The carbon stripper separated unconverted char particles from the oxygen carrier stream exiting the fuel reactor. The oxygen carrier was left to follow the way to the air reactor to be regenerated, while unconverted char particles were recirculated to the fuel reactor. Thus, char particles had more time to be highly converted in the fuel reactor.
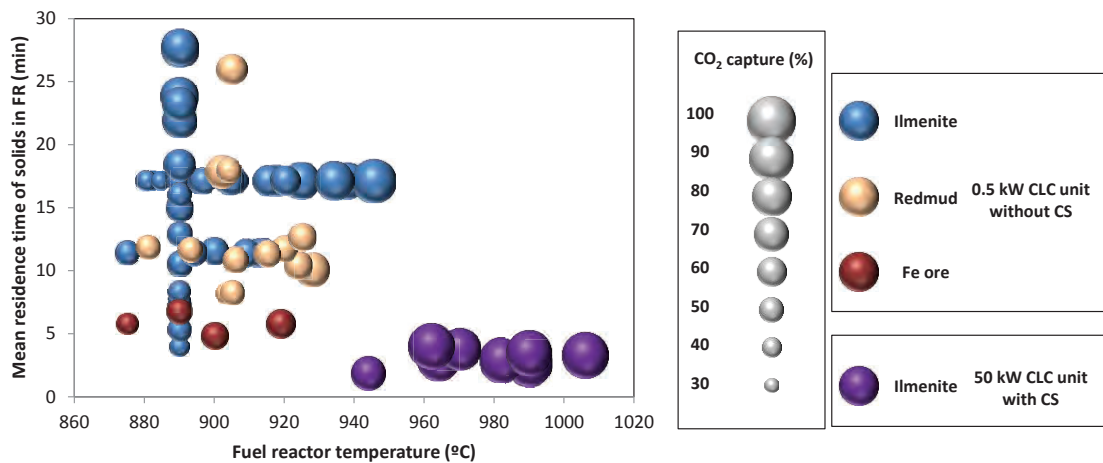

Fig. 5. CO_2 capture achieved in the 0.5 kW$_{th}$ and 50 kW$_{th}$ CLC units as a function of the temperature and the mean residence time of solids in the fuel reactor. Fuel: bituminous coal. Data compiled from [8-19]. Size of spheres indicates the CO_2 capture.

As the CO_2 capture depends on the char conversion in the fuel reactor, it is logical to think that the reactivity of the coal may affect to the CO_2 capture. Indeed, this fact was revealed by using different coals ranging from anthracite to lignite in the 0.5 kW$_{th}$ CLC unit; see Fig. 6. The CO_2 capture follow the coal reactivity sequence, i.e. lignite > bituminous > anthracite. It is remarkable the high degree of CO_2 capture obtained with the lignite due to the high reactivity for steam gasification. On the contrary, poor values of CO_2 capture was obtained with the low reactive anthracite. Thus, it is mandatory a highly efficient carbon stripper to allow CO_2 capture rates close to 100% for bituminous coals and anthracite. Results obtained in the 50 kW$_{th}$ CLC unit burning bituminous coals with ilmenite confirm the beneficial effect of the carbon stripper on the CO_2 capture, despite the short residence time of solids in the fuel reactor.

In Fig. 6, it is highlighted that the use of ilmenite, redmud or iron ore barely affected to the CO_2 capture. This results is related to the fact that in all cases char gasification happens in an environment enriched in H_2O and CO_2, and the solid-solid reaction between char and oxygen carrier particles is not relevant at the existing conditions in the fluidized bed acting as fuel reactor [32]. Thus, while gasification rate was increased by the presence of an oxygen carrier [33], the increase in the oxygen carrier reactivity (Fe ore > redmud > ilmenite) has low effect on a further increase of the char gasification rate [21].

Additionally, some experiments were carried out with different $H_2O:CO_2$ mixtures, ranging from pure H_2O to pure CO_2 [9,10,12]. The use of CO_2 negatively affected the CO_2 capture with anthracite and bituminous coals. But this effect was of lower relevance with the highly reactive lignite, and CO_2 capture values higher than 90% were achieved by using CO_2 as fluidizing agent in the fuel reactor. Therefore, choosing lignite as fuel would allow the use of recycled CO_2 in the fuel reactor, avoiding the penalty related to the steam generation for the fuel reactor. In addition, the efficiency of the carbon stripper on separating char particles could be lower than that required for other fuels with lower reactivity. The use of CO_2 was also proven to be valid for several biomasses [15,16]. In this case, CO_2 capture close to 100% was achieved in the 0.5 kW$_{th}$ CLC unit without the presence of a carbon stripper.
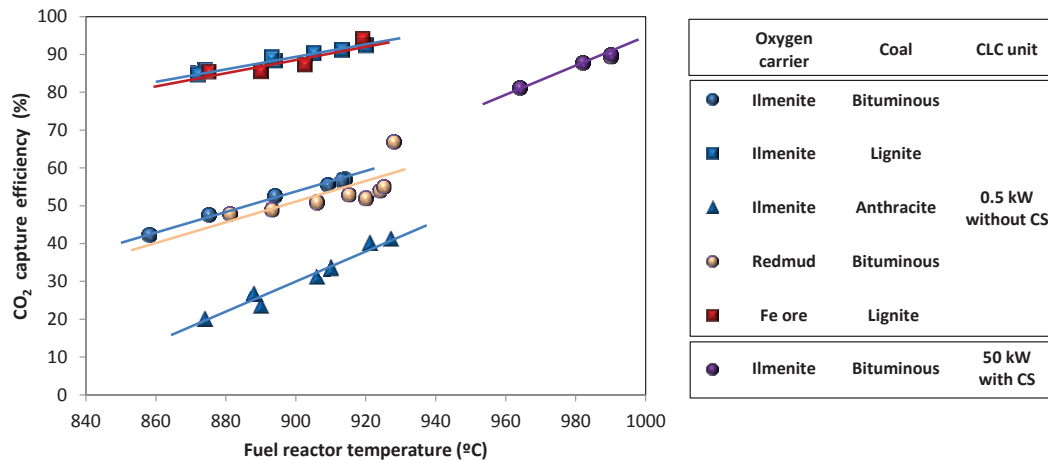

Fig. 6. CO_2 capture as a function of the fuel reactor temperature for different oxygen carriers and coals achieved in 0.5 kW$_{th}$ and 50 kW$_{th}$ units. Mean residence time of solids in the fuel reactor was about 10 min in the 0.5 kW$_{th}$ unit, and 3 min in the 50 kW$_{th}$ unit. Data compiled from [8-19].

3.2. Combustion efficiency

In general, unburnt products are always present in the CO_2 stream exiting the fuel reactor. These products, mainly H_2, CO and CH_4, affect to the CO_2 purity and must be treated before the CO_2 compression step. Thus, an oxygen polishing step, downstream the fuel reactor, has been proposed to achieve the complete oxidation of these compounds by using pure oxygen. Considering the oxygen required in this polishing step, the combustion efficiency in the 0.5 kW$_{th}$ and 50 kW$_{th}$ CLC units is usually evaluated by means of the total oxygen demand parameter, Ω_T, defined as the stoichiometric oxygen required in the oxygen polishing step related to the stoichiometric oxygen required for the entire combustion of coal [2,3].

Results obtained in the 0.5 kW$_{th}$ CLC unit revealed that the coal particle size, the oxygen carrier to fuel ratio, ϕ, and the solids inventory in the fuel reactor, i.e. mass of solids per MW$_{th}$ of fuel, had a relevant effect on the total oxygen demand. Fig. 7 shows that the oxygen demand was increased when coal in the 75-125 μm size interval was used; while the oxygen demand was noticeably decreased when coarser particles of coal (125-200 or 200-300 μm) were used. This effect is related to the fluid dynamic characteristics of the fuel reactor. In the 0.5 kW$_{th}$ CLC unit the fuel reactor is a bubbling fluidized bed, where segregation of particles can happen. Thus, light and small char particles can float up over the denser and bigger oxygen carrier particles. In addition, the presence of char particles would be promoted in the freeboard as the particle size of char was decreased. Anyway, CO and H_2 from char particles being gasified in the upper part of the reactor have not the chance to react with oxygen carrier particles, thus increasing the amount of unburnt products in the CO_2 stream. This fact was minimized by using coarser coal particles, which could be better mixed with oxygen carried particles. At these conditions, it was determined that unburnt products come mainly from volatile matter, which could be evolved in the form of plumes of volatiles with poor contact with oxygen carrier particles. However, gasification products were highly converted by the oxygen

carrier [8]. In this case, char gasification happens mainly in the emulsion phase, and gasification products had a good contact with oxygen carrier particles.
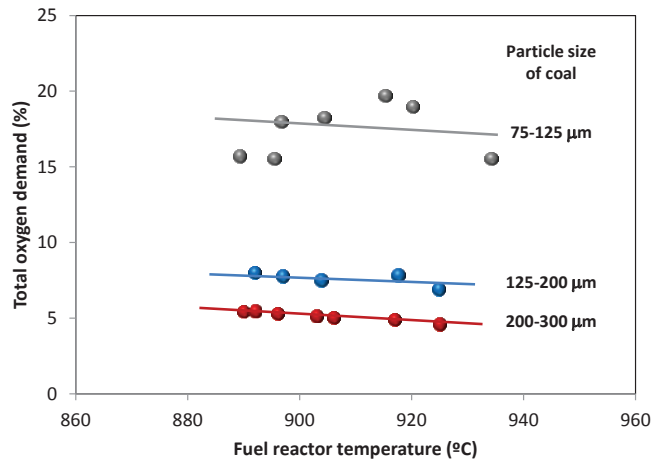

Fig. 7. Total oxygen demand as a function of the fuel reactor temperature obtained with ilmenite in the 0.5 kW$_{th}$ CLC unit for different coal particle sizes. Data compiled from [8]

As a consequence, the volatile matter content of the solid fuel affected to the oxygen demand of gases in the 0.5 kW$_{th}$ CLC unit. Fig. 8 shows the total oxygen demand obtained for different coals using ilmenite, redmud or iron ore as oxygen carrier. Focused on the type of coal, the oxygen demand was higher for lignite and lower for anthracite, corresponding to coal with high and low volatile matter content, respectively. Namely, the amount of volatile matter by-passed in volatile plumes was higher as the volatile matter in coal increased. This fact was especially relevant for fuels with a huge amount of volatile matter, such as biomass [15,16]. In addition, the effect of the oxygen carrier reactivity was also relevant. The oxygen demand decreased as the reactivity of the oxygen carrier increased. Thus, oxygen demand values as low as 2 % were achieved by using a highly reactive iron ore burning a bituminous coal.
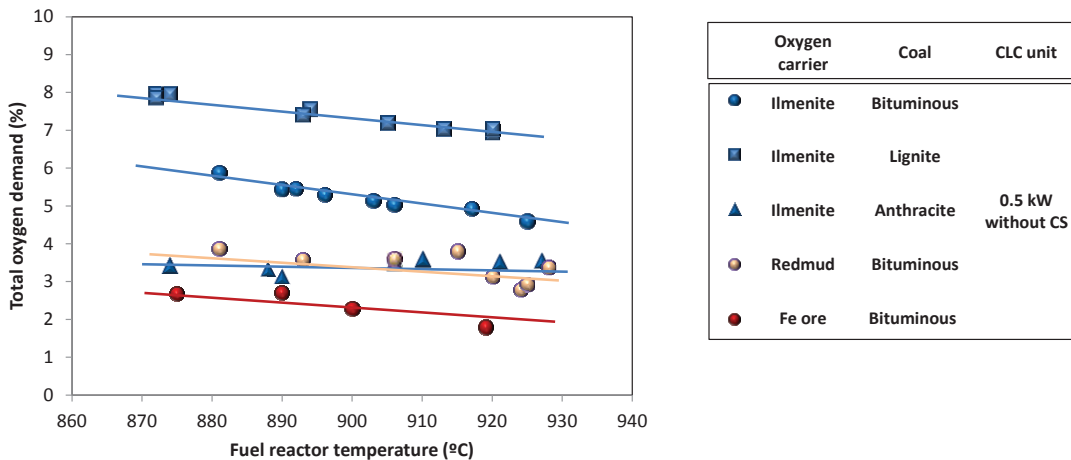

Fig. 8. Total oxygen demand as a function of the temperature for different oxygen carriers and coals in the 0.5 kW$_{th}$ CLC unit. Specific solids inventory in fuel reactor was 2400, 1770 and 1400 kg/MW for bituminous coal, lignite and anthracite, respectively. Data compiled from [8-16].

The effect of both the oxygen carrier to fuel ratio, ϕ, and the solids inventory in the fuel reactor on the total oxygen demand is shown in Fig. 9. The oxygen demand was considerably decreased from 13% to 9% as the solids inventory increased from 1500 kg/MW$_{th}$ to values of around 2000 kg/MW$_{th}$. But the increase of the oxygen carrier to fuel ratio was of lower relevance when over-stoichiometric conditions were reached, i.e. $\phi > 1$. Note that the average reactivity of the oxygen carrier slightly increased with the ϕ number [34]. But this increase could not be efficiently exploited in the fuel reactor due to a poor contact between volatile matter and oxygen carrier particles. However, the use of more reactive oxygen carrier particles, i.e. redmud or iron ore, was beneficial for the combustion of volatile matter, especially for the CO conversion. Thus, the oxygen demand decreased as the reactivity of the oxygen carrier increased.
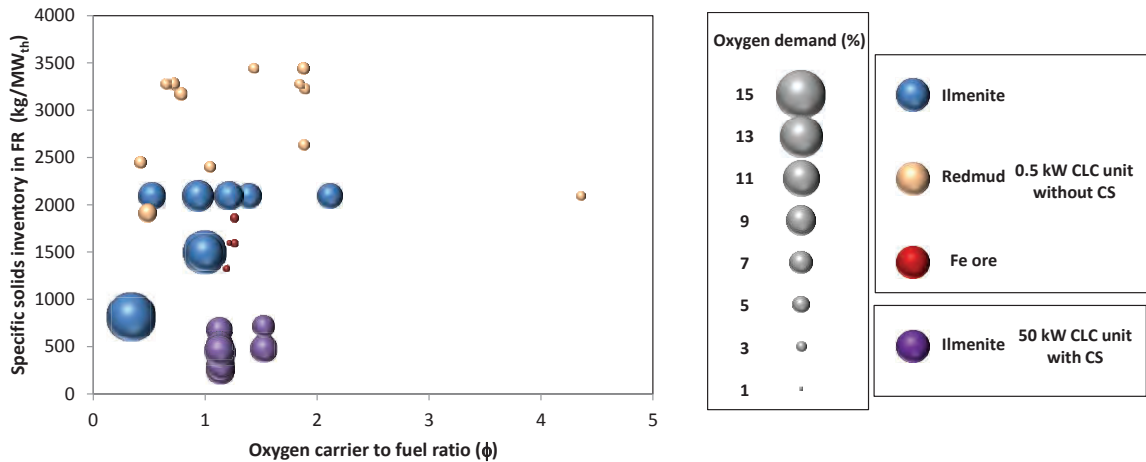

Fig. 9. Total oxygen demand achieved in the 0.5 kW$_{th}$ and 50 kW$_{th}$ CLC units as a function of the specific solids inventory in the fuel reactor and the oxygen carrier to fuel ratio, ϕ. Solid fuel: bituminous coal. Data compiled from [8-19]. Size of spheres indicates the oxygen demand.

In comparison, improved results about oxygen demand were obtained in the 50 kW$_{th}$ CLC unit; see Fig. 9. In general, the total oxygen demand using ilmenite as oxygen carrier was in the Ω_T = 6-9% interval for oxygen carrier to fuel ratio values and solids inventory ranging from ϕ = 1-2 and 250-700 kg/MW$_{th}$. In this case, the fuel reactor in the 50 kW$_{th}$ CLC unit was a circulating fluidized bed, being operated in the turbulent regime. So, both oxygen carrier and char particles are entrained from the bottom bed to the fuel reactor cyclone. The existing dilute region was more effective converting volatile matter than the bubbling fluidized bed in the 0.5 kW$_{th}$ CLC unit. But char particles were gasified in the riser. As a consequence, both volatile matter and gasification products were present in the exhaust gases from the fuel reactor [35]. Following a new methodology proposed in other work [3], it was determined that the combustion efficiency of volatile matter and gasification products were around 80-90%, which agrees with theoretical calculations by using a validated fuel reactor model [36].

The solid fuels used in the 50 kW$_{th}$ CLC unit were two similar bituminous coals (South African and Taldinsky) crushed and sieved in the 100-300 μm size. Considering the fuel reactor is a circulating fluidized bed, modelling results predicted that a decrease in the coal particle size would decrease the CO$_2$ capture if the efficiency of the carbon separation efficiency was relatively low, e.g. 90% [37]. In this case, a lower amount of coal would be converted in the fuel reactor and the oxygen demand would decrease. However, if the efficiency of the carbon stripper was high enough to achieve CO$_2$ capture close to 100%, the oxygen demand may increase for lower coal particle sizes due to an increase of the char concentration in solids in the dilute region. In addition, the cyclone could not recover most of unconverted char from the fuel reactor [5,36].

3.3. Actions to improve the combustion efficiency

From the experimental work carried out in the 0.5 and 50 kW$_{th}$ CLC units it was concluded that it is possible to decrease the oxygen demand by operating in the turbulent regime instead of the bubbling regime. In addition, design parameters and operating conditions such as solids inventory, oxygen carrier to fuel ratio, fuel reactor temperature or type of oxygen carrier can be selected in order to achieve a low value of oxygen demand. However, despite all efforts the oxygen demand was not decreased to values close to zero for reasonable conditions, e.g. a specific inventory of solids lower than 1000 kg/MW$_{th}$ in the fuel reactor. Several options could be feasible in order to achieve a further decrease of the oxygen demand in the 50 kW$_{th}$ CLC unit. Such options include:

- To optimize operating conditions. In a previous work, it was determined that a fuel reactor temperature of 1000 °C, a solids inventory of 500-700 kg/MW$_{th}$ and an oxygen carrier to fuel ratio of ϕ =1.5-2 are realistic conditions in order to minimize the oxygen demand [18]. Following, mass balances to the *i*G-CLC unit are presented in order to evaluate the feasibility of these conditions. The oxygen carrier to fuel ratio depends on the oxygen transport capacity of the oxygen carrier and the solids circulation flow, the last being limited by fluid dynamics restrictions. Thus, the solids flux, G_s, in kg m^{-2}s^{-1} and the oxygen carrier to fuel ratio, ϕ, are related by:

$$G_s = \frac{\phi \Omega_{sf}}{S_r R_{OC} LHV} \tag{9}$$

Ω_{sf} being the oxygen demanded by coal (kg oxygen per kg coal), R_{OC} the oxygen transport capacity of the oxygen carrier and *LHV* the lower heating value of the coal (MJ per kg coal). The riser cross-section was assumed to be S_r =0.2 m^2/MW$_{th}$ [38]. ,Fig. 10(a) shows that the solids flux increases with the f number and as R_{OC} of the oxygen carrier decreases. Considering an upper limit for the solids flux of 80 kg m^{-2}s^{-1} [34], it can be seen that the use of the iron ore is restricted to a maximum value of ϕ = 4, which is high enough to achieve low oxygen demand. Lower solids flux would be required for ilmenite due to its higher R_{OC} value. Therefore, there is not fluid dynamic restrictions to the use of Fe ore or ilmenite to achieve the intended solids circulation rate for the target of ϕ = 1.5-2.

In addition, the solids inventory and the solids circulation rate define the mean residence time of solids in the fuel reactor, t_{FR}, which affected to the CO_2 capture; see Fig. 5.

$$t_{FR} = \frac{m_{FR}^*}{G_s S_r} = \frac{m_{FR}^* R_{OC} LHV}{\phi \Omega_{sf}} \tag{10}$$

m_{FR}^* being the specific inventory of solids in the fuel reactor (kg oxygen carrier per MW$_{th}$). Thus, considering a suitable value of ϕ = 2 for the iron ore, the residence time of solids in the fuel reactor would be 1 min or 1.6 min for 500 and 750 kg/MW$_{th}$, which could allow achieving high CO_2 capture with an efficient carbon stripper; see Fig. 10(b). For ilmenite, the residence time of solids in the fuel reactor would be doubled; see Fig. 10(c). But the required residence time of char in the fuel reactor 15-25 min to achieve high CO_2 capture values (>80 % in Fig. 5) would not be achieved if a carbon separation unit was not considered in the design of a CLC plant, unless a huge amount of solids was used in the fuel reactor.

- To use a more reactive oxygen carrier than ilmenite: future work will be done by using highly reactive materials such as the Tierga iron ore or manganese ore from Gabon previously selected from a screening work [39].

- To use of oxygen carriers with oxygen uncoupling capability. The Chemical Looping with Oxygen Uncoupling (CLOU) was proposed as an efficient way to convert coal by chemical looping process. In this case, the oxygen carrier is able to generate gaseous oxygen (O_2) in the fuel reactor, thus allowing the combustion of coal with oxygen in a similar way that happen with air. The proof of the CLOU concept was performed in the 0.5 kW$_{th}$ unit

with a Cu-based oxygen carrier (60 wt.% CuO, 40 wt.% $MgAl_2O_4$) [23] and excellent results were obtained with different fuels even increasing the thermal power of the unit up to 1.5 kW [23-26]. Complete combustion of coal to CO_2 and H_2O was achieved, while CO_2 capture close to 100% was obtained for reactive coals. The use of a carbon stripper would be still advised for low reactive coals. Later, similar results were obtained by using a similar material modified by addition of Fe and a Mn-Cu material [27,28]. Other kind of interesting materials are Mn-Fe mixed oxides [40]. In this case, a Mn-Fe material modified by addition of Ti showed excellent behavior in the 0.5 kW$_{th}$ unit [29]. In this case, the coal conversion in the fuel reactor involved both the oxygen uncoupling mechanism and the characteristics gas-solid reactions of *i*G-CLC. The process was called Chemical Looping with aided Oxygen Uncoupling (CLaOU) and was highly dependent on the oxidation conditions in the air reactor. Moreover, these Mn-Fe-Ti materials showed magnetic properties, which could facilitate its separation in the purge stream to extract ash [41].
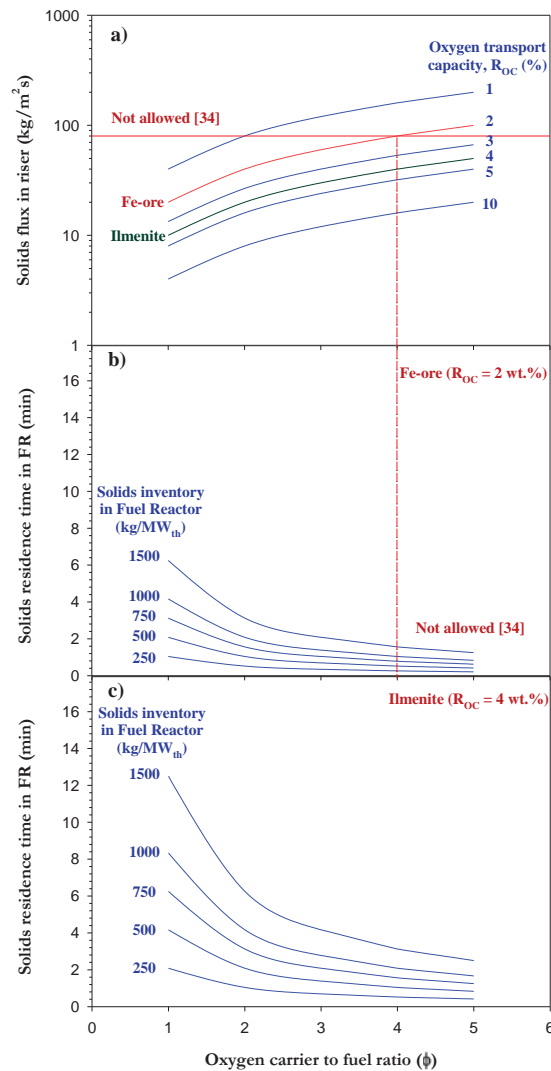

Fig. 10. (a) Solids flux, G_s, vs. oxygen carrier to fuel ratio, ϕ, depending on the oxygen transport capacity of the oxygen carrier; and mean residence time of solids for (b) iron ore and (c) ilmenite as a function of ϕ for different solids inventory values in the fuel reactor.

- To modify the design of the CLC unit. Several technological solutions were modelled to evaluate the potential on the reduction of the oxygen demand in a CLC unit [42]. These options were: (1) the use of internals in the fuel reactor to improve the gas-solid contact; (2) to recirculate gases to the fuel reactor or the carbon stripper; and (3) to use a secondary fuel reactor, which can be i) another reactor fed by gases exiting the fuel reactor, ii) the carbon stripper, or iii) the fuel reactor itself if coal is fed into the carbon stripper. A scheme of the different options is shown in Fig. 11. Among these options, the oxygen demand could be decreased by 35% with the use of internals, by 40-70% by recirculating gases, or by 50-95% by using a secondary fuel reactor. Although the potential to decrease the oxygen demand by using internals would be limited, this option is easy to implement in the 50 kW$_{th}$ CLC unit. Results obtained by using ring-type internals are discussed in the following section.
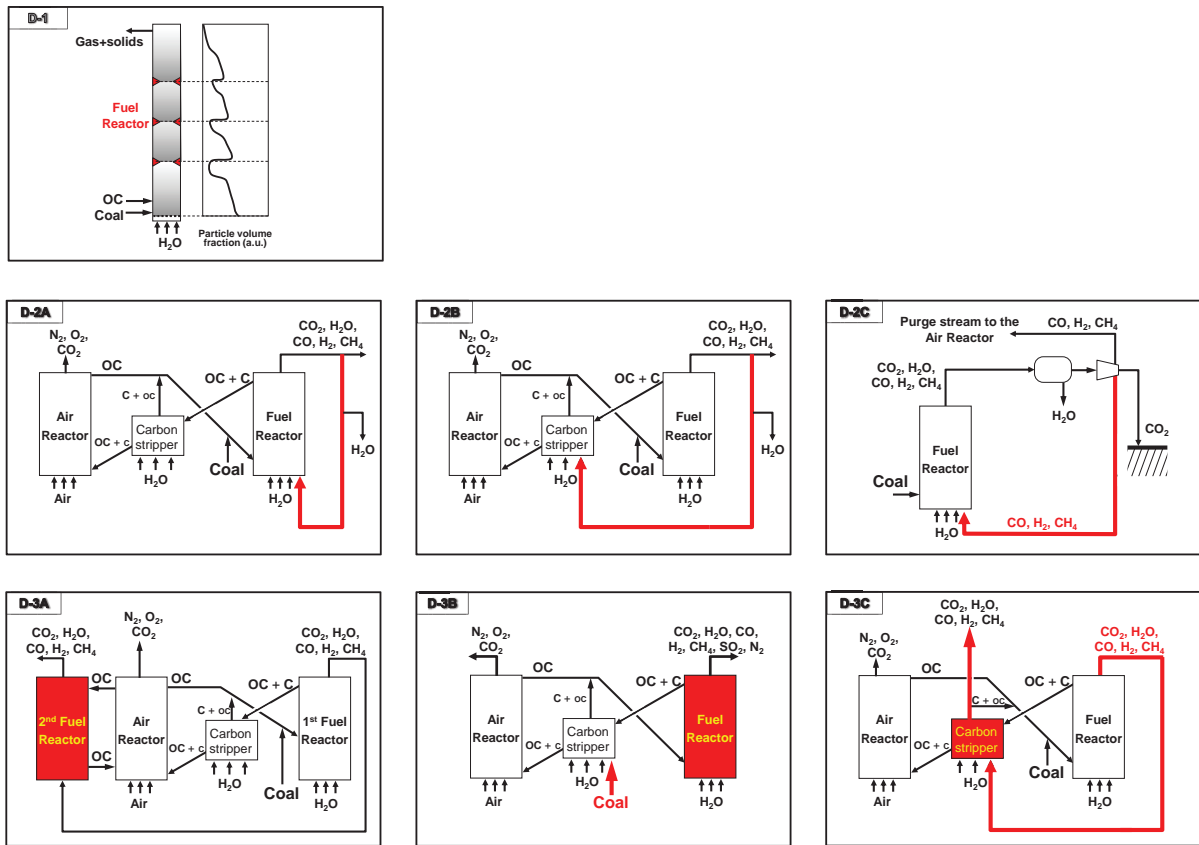

Fig. 11. Diagrams of the different configurations for the improvement of the *i*G-CLC process [42].

3.4. Use of ring-type internals in the 50 kW CLC unit

Three ring-type internals were implemented in the fuel reactor. The ring-type internals were designed according with results obtained at Vienna University of Technology [43]. The rings were wedge-shaped designed, with the opening section being the 60% of the reactor cross-section; see Fig. 12(a). The distance between two consecutive rings was 0.7 m; see Fig. 12(b). Two experimental test series were accomplished burning "Taldinsky" coal, i.e. without and with internals, to assess the effect of the presence of the internals on the performance of the CLC unit.
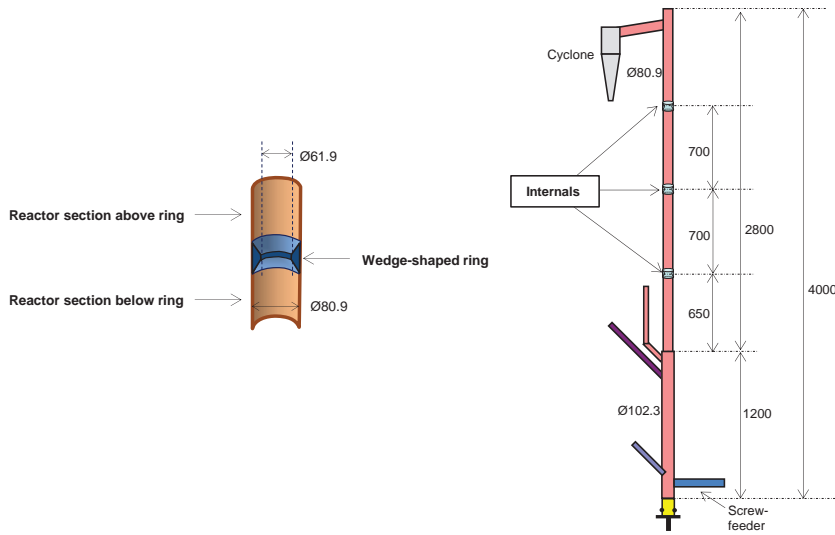
Fig. 12. (a) Detail of a wedge-shaped ring implemented in the fuel reactor; and (b) Scheme of the fuel reactor showing the position of the ring-type internals in the 50 kW$_{th}$ CLC unit. Units in mm.

Fig. 13 shows the CO_2 capture and total oxygen demand values obtained during these experimental campaigns. The CO_2 capture efficiency was scarcely affected by the presence of ring-type internals. The small differences observed could be due to the lower amount of solids in the whole fuel reactor in experiments carried out with internals rather than the presence of internals itself. More interesting was the decrease in the oxygen demand when the internals were implemented. So, the oxygen demand was 12 % aprox., in the conditions used, before the implementation of the internals. The solids inventory was 500-540 kg/MW$_{th}$. But the oxygen demand decreased to 10 % aprox. when experiments were carried out with the ring-type internals in the fuel reactor. In this case, the solids inventory was in the 260-420 kg/MW$_{th}$ interval.
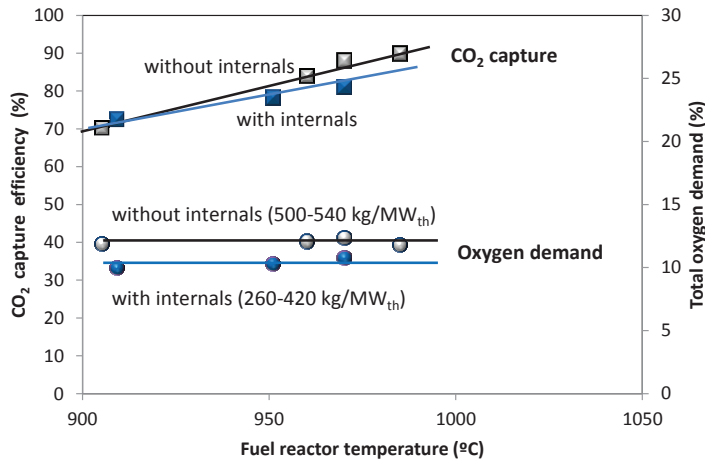

Fig. 13. .CO_2 capture and total oxygen demand as a function of the temperature in the 50 kW$_{th}$ CLC unit obtained without and with internals in the fuel reactor. Data compiled from [19].

In a previous work the oxygen demand was increased by 2-3 points when the solids inventory decreased from ~500 kg/MW$_{th}$ to ~250 kg/MW$_{th}$. This fact suggests that the oxygen demand without internals could be about 14-15 % with 250 kg/MW$_{th}$, which would represent that the presence of internals would decrease the oxygen demand in 4-5 points. Thus, the oxygen demand would be decreased by ~30%, which agrees with the expected improvement from theoretical calculations [42]; see previous section.

The ring-type internals modified the solids distribution in the fuel reactor. Thus, the solids concentration was increased above the internals, allowing a better contact between gas and solids. As a consequence, the combustion of both, the volatile matter and gasification products was improved. It was deduced that gasification products were highly converted, as it was the case for a bubbling fluidized bed; while the combustion efficiency of CH$_4$ from volatile matter was improved from 50% without internals to 60-65% with internals [19].

3.5. Environmental issues

The concern on the environmental issues is relevant when coal is used as fuel due to the generation of some contaminants in the exhaust gases such as SO$_x$, NO$_x$ and Hg [11,13]. In addition, a fraction of the oxygen carrier can be mixed together the ash. Thus, the oxygen carrier must not present toxicity or risk for the environment in order to avoid the contamination of ash by dangerous products [44]. All these issues were addressed considering the oxygen carriers used in the 0.5 kW$_{th}$ CLC unit, i.e. ilmenite, redmud and Tierga iron ore.

Regarding sulphur emissions, relevant results were obtained burning lignite with high-sulphur content. In this case, high char conversion was achieved in the fuel reactor and, consequently more than 90 % of the sulphur in coal was released in the fuel reactor as H$_2$S or SO$_2$. The presence of COS or CS$_2$ was not detected. H$_2$S would be oxidized to SO$_2$ in the oxygen polishing step. The presence of SO$_2$ in the CO$_2$ stream to be compressed transported and stored in geologic formations must be addressed. In the air reactor, sulphur was released as SO$_2$ and the emission level was related to the amount of unconverted char being burned in the air reactor. The legal emission limits for SO$_2$ in the air reactor would be easily reached using a coal with a lower amount of sulphur [11].

Thermal NO$_x$ are not generated in the CLC process due to combustion is carried out without flame. In addition, most of nitrogen in the coal was evolved as N$_2$ the fuel reactor. In the air reactor, the nitrogen released by the unconverted char was emitted as NO at a lower level than the legislation limit [11].

Mercury from coal evolved in the CO$_2$ stream can originate problems in the heat transfer surfaces existing in the CO$_2$ processing unit. It was found that about 40-55 % of Hg was emitted in the fuel reactor, mainly as Hg^0 [13]. Also, some Hg^{2+} was found in exhaust gases from the air reactor, but no major problems with mercury emissions from the air reactor are anticipated if the legislation corresponding to incineration systems is considered as reference.

Also, the spent oxygen carrier must be evaluated regarding the environmental impact for the disposal in a landfill. Ilmenite and the Fe-ore used in the 0.5 kW$_{th}$ CLC unit were characterized with this purpose and they were classified as stable nonreactive hazardous waste [44]. The main environmental concern arose from the high chromium content of the redmud (Fe-ESF). However, this would not represent a drawback itself due to redmud is considered originally as a hazardous waste, with a problematic management. Note that if redmud was used as oxygen carrier, it was giving an industrial use to this problem waste.

4. Conclusions

Relevant results obtained in 0.5 kW$_{th}$ and 50 kW$_{th}$ CLC units at ICB-CSIC has been revisited and critically compared. The use of a carbon separation system, such as a carbon stripper disposed in the 50 kW$_{th}$ CLC is a key element to reach high CO$_2$ capture efficiency. In this case, the required solids residence time of solids in the fuel reactor to achieve CO$_2$ capture rates above 90 % can be achieved with realistic solids inventory in the fuel reactor and solids circulation flow for different oxygen carriers.

The complete combustion in the fuel reactor was not achieved, and some unburnt compounds (mainly H$_2$, CO, CH$_4$) were present in the CO$_2$ stream. The fluidization in the bubbling regime of the fuel reactor allowed a high degree of oxidation of gasification products, but poor conversion of volatile matter was achieved. The conversion of volatile matter was improved with ilmenite as oxygen carrier when the fuel reactor was a circulating fluidized bed,

thus decreasing the oxygen demand of the *i*G-CLC process. The oxygen demand could be decreased to $\Omega_T = 12$ % by selecting suitable operating conditions in the fuel reactor, and a further decrease to $\Omega_T = 9$ % was achieved by including ring-type internals. An additional decrease in the oxygen demand can be expected by using more reactive materials, such as redmud or iron ore, or even complete combustion could be reached using materials with oxygen uncoupling capability (CLOU).

Finally, no major environmental drawbacks are expected in the *i*G-CLC process regarding SO_x, NO_x, Hg emissions, or even disposal in landfill of spent oxygen carrier.

Acknowledgements

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