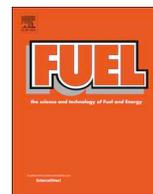




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Evaluation of different strategies to improve the efficiency of coal conversion in a 50 kW_{th} Chemical Looping combustion unit

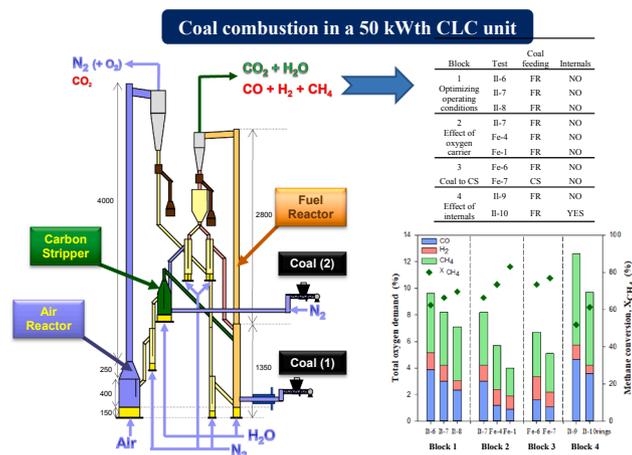
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GRAPHICAL ABSTRACT



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ABSTRACT

Minerals or industrial waste materials are considered promising oxygen carriers for coal combustion through *in-situ* Gasification Chemical Looping Combustion (iG-CLC) process in order to maintain CO₂ capture at low cost. Nevertheless, complete coal combustion to CO₂ and H₂O is usually not achieved and different solutions have been outlined to improve it. The aim of this work is to analyze the potential of two of these strategies: (1) using a more reactive oxygen carrier; and (2) to have two fuel reactors by feeding the coal into the carbon stripper. Coal combustion in a 50 kW_{th} CLC unit was carried out using two oxygen carrier materials, namely Norwegian ilmenite and Tierra iron-ore. Also, an additional test was carried out feeding the coal directly into the carbon stripper of the CLC unit, in contrast with the conventional coal feeding to the fuel reactor. CO₂ capture efficiency was barely affected by the type of oxygen carrier material, but slightly lower values were obtained when coal was fed to the carbon stripper. In contrast, coal combustion efficiency was enhanced by using the iron-ore material, with a potential decrease of the total oxygen demand of 40%, achieving a minimum value of total

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oxygen demand of 4.1%. Also, the total oxygen demand was decreased by 24% when coal was fed to the carbon stripper due to the improvement in the combustion of the volatiles in the fuel reactor. The combination of both strategies has high potential to maximize the coal combustion via iG-CLC process.

1. Introduction

The global energy-related CO₂ emissions are expected to increase by 2040 [1], which makes the implementation of clean combustion technologies to follow on pathway targeted in the Paris Agreement to reach global temperature increases below 2 °C in 2100 necessary [2]. Carbon Capture and Storage (CCS) must play a significant role to drastically reduce CO₂ emissions while fossil fuels are still used [3]. Among the different options for CO₂ capture, Chemical Looping Combustion (CLC) technology allows a relevant decrease in the cost associated with the CO₂ capture [4].

The CLC concept is based on the use of an oxygen carrier to transfer oxygen from the air to the fuel thus preventing the contact between them. In the most common configuration, the oxygen carrier circulates continuously between two interconnected fluidized bed reactors called fuel and air reactors [5]. The oxygen carrier takes oxygen from air in the air reactor. Then, the oxygen carrier provides the required oxygen for the fuel combustion inside the fuel reactor in a N₂-free environment. In this way, a highly concentrated CO₂ stream can be obtained after water condensation.

The CLC process has been intensively developed for the combustion of solid fuels in the last decade, both for coal [6] and biomass [7]. Fig. 1 shows a diagram of the solid fueled CLC process, including the main concerns to be solved. The solid fuel is fed to the fuel reactor, where it is gasified. Because of this, the process is often named *in-situ* Gasification Chemical Looping Combustion (iG-CLC) [6]. Steam and/or recirculated CO₂ may be used as gasifying agent. Then, the gasification products react through gas–solid reactions with the oxygen carrier to produce CO₂ and H₂O.

Several concerns linked to the iG-CLC process of solid fuels have been identified which must be addressed and solved; see red boxes in Fig. 1. Coal gasification has been identified as the limiting step of the solid fuel conversion in the iG-CLC process [8]. Because of this, the use of a carbon separation system between the fuel and air reactors has been proposed to separate unconverted char particles from the oxygen carrier stream exiting from the fuel reactor, thus preventing the loss of CO₂ capture due to the char combustion in the air reactor [9]. For this

purpose, the use of a carbon stripper may separate char particles from the oxygen carrier due to their different fluid dynamic properties, e.g. terminal velocity [10,11]. The carbon stripper design and its operating conditions are critical aspects to achieve a high separation efficiency [12,13].

The use of low-cost oxygen carriers is being adopted as common solution [14] due to the expected losses of oxygen carrier particles during ash draining from the fuel reactor. Among them, minerals and waste materials based on iron and/or manganese oxides have been evaluated as oxygen carriers for coal and biomass combustion by iG-CLC [6]. Incomplete combustion has usually been observed due to the low reactivity of the low-cost oxygen carrier materials and the poor contact between gas and solids in the fuel reactor. This entails that some unburned gases, such as hydrogen, carbon monoxide and methane, dilute the enriched CO₂ stream exiting from the fuel reactor, which reduces its quality for transport and storage. Lyngfelt and Leckner [15] proposed to oxidize them to CO₂ and H₂O through supplying pure oxygen into an oxygen polishing unit; see Fig. 1. This solution implies economic and energy penalties for the overall process, estimated in 0.65 €/ton CO₂ and 0.05% in the efficiency loss, respectively, per each percentage point of decrease in combustion efficiency. Some solutions have been proposed in order to minimize the costs associated to the uncomplete fuel combustion by iG-CLC:

(1) To optimize operating conditions in the fuel reactor: operating parameters such as temperature of the reactors, solids circulation flow rate and solids inventory in the fuel reactor must be determined for each oxygen carrier in order to maximize the combustion efficiency of the iG-CLC process [11,16]. The simulation of the iG-CLC unit with validated models is a powerful tool to determine optimum conditions [17].

(2) To improve the contact between reacting gases and solid particles: volatile matter is the main contributor to the unconverted gases exiting from the fuel reactor [6]. Operating the fuel reactor at turbulent or high velocity regime encourage the gas–solid contact in the dilute zone [18]. Thus, the combustion efficiency achieved in CLC units with a fuel reactor in the bubbling regime [16,19–22] is usually lower than in the cases that it is a circulating fluidized bed [10,11]. Further, different

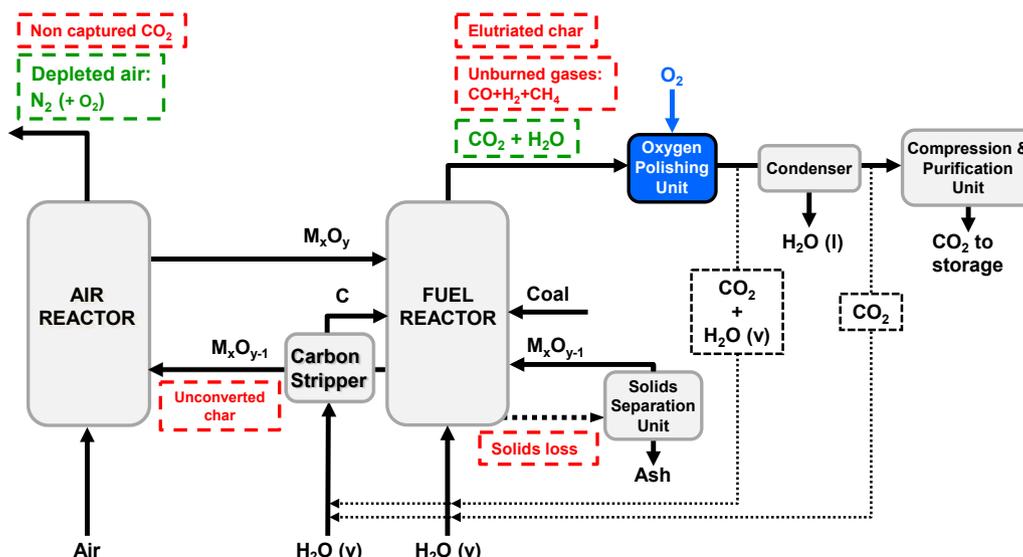


Fig. 1. Scheme of the iG-CLC process, including the potential concerns (red boxes).

Table 1
Main characteristics of the Tierga iron-ore and ilmenite particles.

		Iron-ore	Ilmenite
Particle size	mm	0.1–0.2	0.1–0.3
Oxygen transport capacity, R_{OC}	%	2.5	4.0
Crushing strength	N	5.8	2.7
Porosity	%	26.3	18.0
Skeletal density	kg/m ³	4216	4200

strategies have been proposed in order to achieve a higher conversion of volatiles which includes using a distributor for volatile matter [15], disturbing the core-annulus structure in the dilute region by using ring-type internals [23], implementing a multi-stage fuel reactor [24] or using a secondary fuel reactor [21]. Also, the use of the carbon stripper as a primary fuel reactor has been proposed, being the fuel reactor itself a secondary one [25].

(3) To recirculate exhaust gases to the fuel reactor [26]: this may decrease the unburnt compounds by 70% [25]. In an alternative configuration, complete combustion could be achieved by separating and recirculating unburnt products, but the CO₂ capture would be decreased due to the required purge in this stream to avoid the accumulation of non-condensable N₂ in the CLC unit.

(4) To use highly reactive oxygen carrier materials: ilmenite can be considered as a reference material [27] due to its intensive use in different CLC units of 0.5 [19], 10 [20], 25 [21], 50 [11,22], 100 [10], 1000 [28] and 4000 [16] kW_{th}. However, it is expected that using more reactive materials would increase the combustion efficiency [29]. This fact has been demonstrated when materials more reactive than ilmenite were used, such as a bauxite waste material [30] and iron [31] or manganese ores [16,22,32,33]. Also synthetic materials have shown high potential to improve the combustion efficiency [34,35], but complete combustion could not be achieved in any case [6].

(5) To use materials with oxygen uncoupling capability: materials based on copper or manganese oxides have the capability of releasing gaseous oxygen in the fuel reactor [36], which improves the solid fuel conversion. Among the materials tested are oxygen carriers based on copper [37], copper-manganese mixed oxides [38], manganese-iron mixed oxides [39], manganese-silicon mixed oxides [40], and manganese-based perovskites [41]. To achieve complete fuel combustion a high reactivity is required for the oxygen uncoupling reaction, as well as a high capability to be regenerated in the air reactor. The complete combustion of the fuel has been achieved by using copper or copper-manganese mixed oxides [38,42].

Some of these solutions have been tested in CLC units, namely the use of materials highly reactive or with oxygen uncoupling capability, the implementation of ring-type internals, or the introduction of a secondary fuel reactor. However, the option in which the solid fuel is fed to the carbon stripper has not yet been explored.

In addition, some inconsistencies can be found when results obtained using different oxygen carrier materials are compared. For example, the use of manganese-ores outperformed usually the results achieved with ilmenite [20,22,32,33], but not always [16]. The different variation of the reactivity with redox cycles, increasing for ilmenite [43] but decreasing for manganese-ores [44] may be behind this. In addition, an iron-ore from Tierga mine (Spain) has been found among the low-cost materials with the highest reactivity to be used in iG-CLC [45]. The performance of this material in a 0.5 kW_{th} CLC unit was the best among those low-cost oxygen carriers tested in this unit, including Fe and Mn-based materials [18,31,32]. However, these good results with the Tierga iron-ore could not be achieved in other CLC units [28,46], likely because of the existing operating conditions were not optimized for this material.

The objective of the present work is to evaluate the potential of several options to improve the combustion efficiency of the iG-CLC process using low-cost oxygen carriers. Dedicated experiments were

performed in a 50 kW_{th} CLC unit with the highly reactive Tierga iron-ore, and the results achieved were compared to those obtained previously with ilmenite. The potential to improve the combustion efficiency is evaluated by considering results previously achieved by optimizing the operational conditions or using ring-type internals in the fuel reactor. In addition, the use of the carbon stripper as primary fuel reactor was assessed. For that, a short campaign feeding coal to the carbon stripper was performed, thus implementing one of the most promising technological solutions to reduce the unburnt gases at the fuel reactor outlet.

2. Experimental

2.1. Materials

The highly reactive iron-ore from Tierga mine (Zaragoza, Spain) was supplied by Promindsa [31]. The iron-ore was exposed to thermal treatment at 950 °C in air for 2 h to remove any possible moisture and as a pre-oxidation treatment. Afterward, particles were sieved to obtain a particle size interval 0.1–0.2 mm. Table 1 shows the main properties of the Fe-ore particles. Fe-ore particles contained hematite (76.5 wt% Fe₂O₃) as active phase. The oxygen transport capacity, R_{OC} , was calculated for the Fe₂O₃/Fe₃O₄ redox system, which may be exploited for coal combustion in a fluidized bed reactor [5]. For comparison purposes, experiments were also performed with a Norwegian ilmenite supplied by Titania which has been used in previous works [11,18,19,23]. Properties of ilmenite are shown in Table 1.

A South African bituminous coal was used as fuel. Table 2 shows the proximate and ultimate analyses of the coal, which was crushed and sieved in the 0.1–0.3 mm interval. The low heating value (LHV) was 24930 kJ/kg and the oxygen demand for the coal combustion was $\Omega_{sf} = 2.0$ kg oxygen per kg of coal.

2.2. Chemical looping combustor

An experimental campaign was performed in a CLC unit for solid fuels, which was designed to operate with a thermal power of 20 kW_{th} for iG-CLC and 50 kW_{th} for CLOU [47]. In this work, coal combustion was performed through iG-CLC mode by using ilmenite and iron-ore as oxygen carrier. A layout of the CLC unit is shown in Fig. 2. The unit was based on two interconnected circulating fluidized bed reactors: the fuel and air reactors, connected by different loop seals. Furthermore, this CLC unit contained a carbon stripper located between the fuel and air reactors. The carbon stripper allowed separating the unburned char particles from the oxygen carrier particles in the stream of solids exiting from the fuel reactor due to the selective elutriation of the char particles. The elutriated char particles were sent to the fuel reactor where they could be further gasified. The solids circulation rate may be varied by acting on double loop seal placed downstream the fuel reactor cyclone. In this way, a solids fraction was sent to the carbon stripper while the other fraction may be recirculated to the fuel reactor. In addition, the unit had two solids diverter devices in order to measure the solids flow rate from the reactors.

Coal feeding point was originally located at the bottom of the fuel reactor by means of a double screw feeder system. In addition, an alternative coal feeding point to the carbon stripper was installed in this

Table 2
Proximate and ultimate analysis of South African bituminous coal.

Proximate analysis			Ultimate analysis		
Moisture	wt%	3.5	C	wt%	66.3
Ash	wt%	15.7	H	wt%	3.6
Volatile matter	wt%	25.5	N	wt%	1.8
Fixed carbon	wt%	55.3	S	wt%	0.5

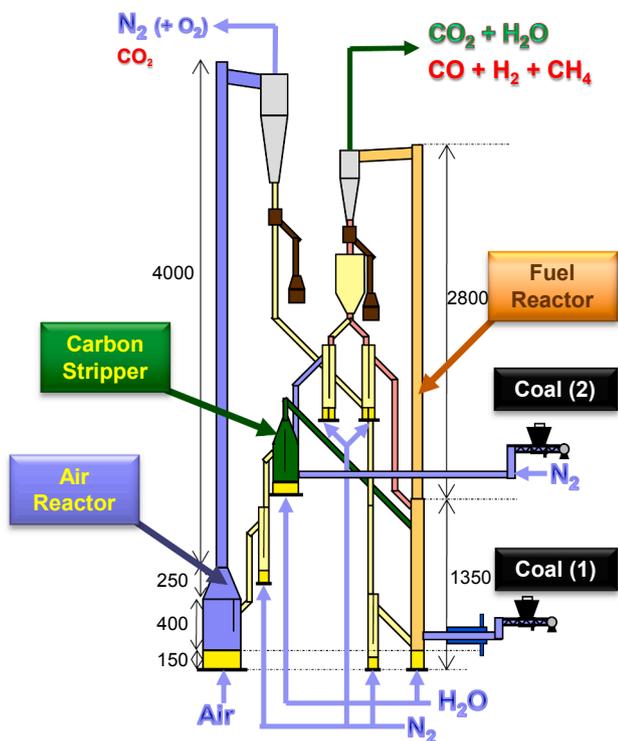


Fig. 2. Layout of the 50 kW_{th} CLC unit (ICB-CSIC-s50) for the combustion of solid fuels [47].

work to evaluate the potential of this option on the combustion efficiency improvement, as Gayán et al. suggested [25]. In this case, coal feeding rate was controlled by using a screw feeder, and then it was injected into the carbon stripper using a nitrogen flow.

The fuel reactor, air reactor, carbon stripper and double loop seal were electrically heated by independent furnaces in order to achieve the desired temperatures. The temperature measurement was carried out by means of thermocouples located within the fluidized bed reactors. Differential pressure gages were distributed throughout the CLC unit in order to measure the pressure drop between different locations in the unit. The solids inventory in each reactor was estimated through

Table 3
Operating conditions and evaluating parameters for the tests conducted in the CLC unit with iron-ore and ilmenite as oxygen carriers.

Test	Oxygen carrier	Coal feeding point	\dot{m}_{sf} (kg/h)	Power input (kW _{th})	T_{FR} (°C)	τ_{FR} (s)	m_{FR}^* (kg/MW _{th})	\dot{m}_{OC} (kg/h)	\dot{m}_{OC}^* (kg/s/MW _{th})	ϕ (-)	η_{CC} (%)	$X_{char,FR}$ (%)	Ω_T (%)	Contribution to Ω_T (%)			X_{CH_4} (%)
														CO	H ₂	CH ₄	
Fe-1	Fe-ore	Fuel reactor	1.8	12.5	923	90	465	220	4.9	1.5	50.6	37.9	4.1	0.9	1.0	2.1	83.0
Fe-2	Fe-ore	Fuel reactor	2.1	14.5	930	75	280	200	3.8	1.0	46.0	30.0	6.3	1.3	1.2	3.8	69.4
Fe-3	Fe-ore	Fuel reactor	2.1	14.5	900	150	510	180	3.5	1.1	52.6	38.1	6.0	1.4	1.5	3.2	74.8
Fe-4	Fe-ore	Fuel reactor	1.8	12.5	924	140	525	160	3.6	1.1	59.9	48.5	5.7	1.2	1.2	3.3	73.4
Fe-5	Fe-ore	Fuel reactor	2.1	14.5	945	190	340	95	1.8	0.7	69.5	60.0	7.3	1.8	1.9	3.7	70.5
Fe-6	Fe-ore	Fuel reactor	2.1	14.5	900	225	485	114	2.2	0.7	60.3	47.6	6.7	1.6	1.7	3.3	73.4
Fe-7	Fe-ore	Carbon stripper	3.4	23.5	937	110	270	200	2.4	0.7	40.2	24.9	5.1	1.1	1.1	2.9	76.8
Fe-8	Fe-ore	Carbon stripper	3.4	23.5	937	85	230	230	2.7	0.8	39.9	27.4	5.6	1.0	1.1	3.5	71.9
Il-1	Ilmenite	Fuel reactor	1.8	12.5	905	303	680	100	2.2	1.1	62.9	54.4	8.3	2.7	1.0	4.6	63.2
Il-2	Ilmenite	Fuel reactor	2.5	17.5	944	138	253	140	2.2	1.1	66.1	58.2	9.1	4.0	0.4	4.6	63.2
Il-3	Ilmenite	Fuel reactor	1.8	12.5	963	239	535	100	2.2	1.1	80.9	76.5	8.2	3.4	1.0	3.7	70.4
Il-4	Ilmenite	Fuel reactor	1.8	12.5	970	225	506	100	2.2	1.1	83.1	79.2	8.2	3.5	1.0	3.7	70.4
Il-5	Ilmenite	Fuel reactor	2.0	13.5	982	170	525	150	3.1	1.5	87.9	84.0	7.0	3.0	0.8	3.2	75.2
Il-6	Ilmenite	Fuel reactor	1.8	12.5	990	207	466	100	2.2	1.1	88.6	86.2	9.6	3.9	1.3	4.5	62.4
Il-7	Ilmenite	Fuel reactor	2.0	13.5	990	156	481	150	3.1	1.5	89.5	87.2	8.2	3.0	1.2	4.0	66.3
Il-8	Ilmenite	Fuel reactor	1.0	6.9	962	240	722	75	3.1	1.5	89.7	87.5	7.1	2.4	0.7	4.1	69.5
Il-9	Ilmenite	Fuel reactor	1.9	14.0	990	161	400	125	2.5	1.3	92.0	82.6	12.6	4.7	1.1	6.9	51.8
Il-10 (internals)	Ilmenite	Fuel reactor	2.0	14.8	990	152	400	140	2.6	1.3	80.7	64.1	9.7	3.6	0.6	5.5	61.3

these measurements. Steam, nitrogen and air were supplied as fluidizing agents to the different reactors by means of specific mass flow controllers.

The concentration of gases exiting from both the fuel reactor (CO₂, CO, H₂ and CH₄) and the air reactor (O₂ and CO₂) was recorded. CO₂, CO and CH₄ concentrations were measured using a non-dispersive infrared (NDIR) analyzer (Siemens Ultramat 23). H₂ concentration was measured by a thermal conductivity detector (Maihak S710/THERMOR). O₂ concentration was determined using a paramagnetic analyzer (Siemens 23/Oxymat 6).

2.3. Procedure and evaluating parameters

Table 3 shows the main operating conditions and results for the tests performed during the experimental campaign with Tierra iron-ore. Selected results with ilmenite as oxygen carrier are also included for comparison purposes [11].

For test with the iron-ore, about 77 kg of this material were introduced in the CLC unit. Air was used as fluidizing medium during the heating period. The target temperature in the air reactor was 1000 °C, while the fuel reactor temperature was varied between 900 and 945 °C. Then, steam was fed to the fuel reactor and carbon stripper, while loop seals were fluidized by nitrogen.

The steam flow to the fuel reactor was 8 m³/h (STP), corresponding to gas velocities at 900 °C of 1.2 m/s at the bottom and 4.2 m/s at the riser. The steam flow to the carbon stripper was about 4.9 m³/h (STP). In the air reactor, air flow was maintained at a constant value of 45 m³/h (STP), which corresponded to gas velocities, at 1000 °C, of 0.8 m/s at the bottom and 7.0 m/s at the riser. A nitrogen flow of 1 m³/h (STP) was supplied to the jet located at the coal feeding system of the carbon stripper when this was used.

The specific solids inventory in the fuel reactor, m_{FR}^* , was in the 230–525 kg/MW_{th} interval. The solids circulation rate was varied between 95 and 230 kg/h, while the coal feeding rate was in the 1.8–3.4 kg/h interval. The relation between the available oxygen in the circulating oxygen carrier and the required oxygen for the coal combustion was evaluated through the oxygen carrier to fuel ratio, ϕ , defined as the oxygen in the solids stream, assuming complete oxidation of the oxygen carrier in the air reactor, divided by the stoichiometric oxygen to burn the coal.

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

The performance of the iron-ore burning coal in the CLC unit was assessed by considering the CO₂ capture efficiency and the total oxygen demand [6]. CO₂ capture efficiency, η_{CC} , evaluates the amount of gaseous carbon at the fuel reactor outlet stream with regard to the total gaseous carbon exiting from the whole CLC unit.

$$\eta_{CC} = \frac{(F_{CO_2} + F_{CO} + F_{CH_4})_{FRout}}{(F_{CO_2} + F_{CO} + F_{CH_4})_{FRout} + (F_{CO_2})_{ARout}} \quad (2)$$

Captured carbon comes from the carbon in volatile matter and fixed carbon being gasified. This entails that η_{CC} is essentially dependent of the amount of char being gasified into the fuel reactor, $X_{char,FR}$. This parameter was calculated as the carbon flow coming from the fixed carbon that is converted to gas into the fuel reactor with regard to the fixed carbon converted in the whole unit.

$$X_{char,FR} = \frac{[(F_{CO_2} + F_{CO} + F_{CH_4})_{FRout}]M_C - [\dot{m}_{sf} \cdot (x_C - x_{fc})]}{[(F_{CO_2} + F_{CO} + F_{CH_4})_{FRout} + (F_{CO_2})_{ARout}]M_C - [\dot{m}_{sf} \cdot (x_C - x_{fc})]} \quad (3)$$

The total oxygen demand, Ω_T , is usually used to evaluate the combustion efficiency of the CLC unit, and it represents the fraction of the oxygen demanded to fully oxidize the unburned gases at the fuel reactor outlet with regard to the oxygen required for full combustion of the coal.

$$\Omega_T = \frac{(0.5F_{CO} + 0.5F_{H_2} + 2F_{CH_4})_{FRout}}{\left(\frac{1}{M_{O_2}}\right) \cdot \dot{m}_{sf} \cdot \Omega_{sf}} \quad (4)$$

An assessment of the uncertainty for several parameters was done considering the accuracy of the apparatus used and the deviation of the measurements. Thus, it was determined that the deviation for the solids circulation rate was about 5%. The uncertainty of the CO₂ capture efficiency and the total oxygen demand was 2%, considering the precision of gas flow controllers (1%) and the confidence level of gas analysers (1%). The values given in Table 3 are the average values of the entire test. The deviation during the test was about 5%, which was higher than the uncertainty in the measurement.

3. Results and discussion

A bituminous coal was combusted via iG-CLC using the highly reactive Tierga iron ore as oxygen carrier. Thermal power was varied between 12.5 and 23.5 kW_{th}. In total, the iron-ore particles were subjected to 60 h of continuous hot fluidization, 30 of them corresponding to coal combustion.

The results obtained were useful to evaluate the performance of this

iron-ore as oxygen carrier and to assess its potential for the improvement of the combustion efficiency compared to what was previously obtained with ilmenite in the same facility. Moreover, two tests were conducted with the coal feeding to the carbon stripper in order to assess the potential of using this device as primary fuel reactor on the combustion efficiency.

3.1. Performance of Tierga iron-ore as oxygen carrier

3.1.1. CO₂ capture efficiency

It is well known that the CO₂ capture efficiency in iG-CLC is mainly ruled by the char conversion in the fuel reactor, which depends on the temperature and mean residence time of solids in the fuel reactor [11]. The experimental campaign was designed to consider the effect of these variables on the CO₂ capture. Fig. 3(a) shows that the CO₂ capture efficiency increased with the fuel reactor temperature, which was related to faster char gasification. In tests performed with iron-ore, the maximum temperature in the fuel reactor was 945 °C, which limited the CO₂ capture to $\eta_{CC} = 70\%$. Considering results from previous work [18], this temperature interval was selected to evaluate the effect of the mean residence time which is better observed when the CO₂ capture was relatively low. However, CO₂ capture values higher than 90% would be expected with fuel reactor temperatures about 1000 °C, as it happened with ilmenite [11].

The CO₂ capture increased as the solids residence time in the fuel reactor was increased from 75 to 90 s for Fe-1 and Fe-2 tests, to 140–190 s for Fe-3, Fe-4 and Fe-5 tests, and to 225 s for Fe-6 test; see Table 3. The effect of the mean residence time, τ_{FR} , may be clearly observed comparing the CO₂ capture in tests Fe-1 and Fe-2, which was higher for the test with the highest value of τ_{FR} . To evaluate the potential of increasing the mean solids residence time to achieve higher CO₂ capture values, the results are plotted as a function of τ_{FR} in Fig. 3(b). Again, an increase of the CO₂ capture with the increase of the mean residence time of solids was observed. This is because a higher amount of char particles were gasified as τ_{FR} increased. However, the τ_{FR} value should be highly increased to achieve CO₂ capture values higher than 90%, e.g. $\tau_{FR} \approx 400$ s at 925 °C. This means that the solids inventory in the fuel reactor must be increased up to 1500 kg/MW_{th}, which seems an excessively large value for industrial scale since values higher than 750 kg/MW_{th} were not recommended [48]. Therefore, it is recommended to increase the fuel reactor temperature in order to achieve high CO₂ capture rates.

The CO₂ capture values achieved with the iron-ore were in line with those obtained with ilmenite; see Fig. 3(a) and 3(b). This fact implies that the oxygen carrier material had a low effect on the char conversion rate, and therefore on the CO₂ capture. From previous results obtained in a batch fluidized-bed reactor in the bubbling regime [31,45], a

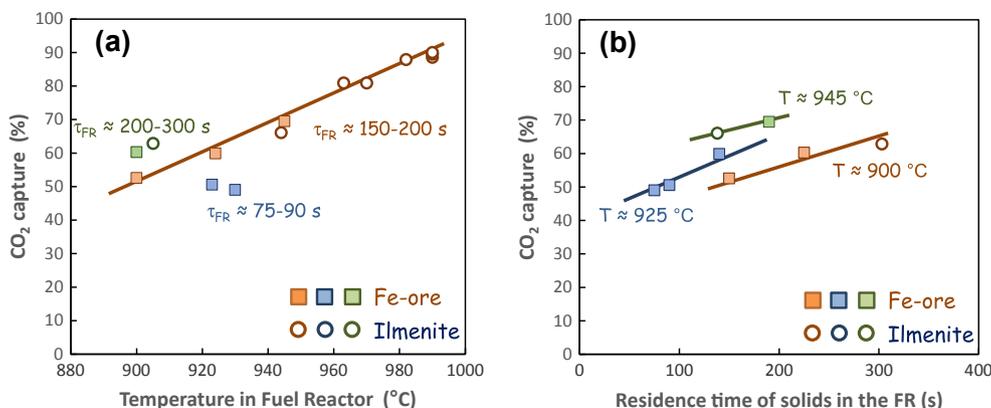


Fig. 3. CO₂ capture efficiency as a function of (a) the fuel reactor temperature and (b) the solids residence time in the fuel reactor. Results with Tierga iron-ore as oxygen carrier (closed symbols) are compared with those obtained with ilmenite [11] (open symbols).

higher char gasification rate would be expected with iron-ore compared to ilmenite due to the lower inhibitory effect of H_2 on the steam gasification with the more reactive iron-ore. However, small differences in the mean H_2 concentration in contact with the oxygen carrier particles in a circulating fluidized bed were deduced from a modelling work [29] because the gasification products are expected to be highly converted in the CLC unit, as it has been previously observed [6,11,23]. In this case, simulation results suggested that a variation in the oxygen carrier reactivity of one order of magnitude is required to observe a relevant effect on the CO_2 capture [29], which is not the case for the iron-ore and ilmenite pair.

3.1.2. Total oxygen demand

The combustion efficiency in the CLC unit is evaluated through the total oxygen demand; see Eq. (4). The total oxygen demand is affected by the availability of oxygen in the fuel reactor, which is evaluated through the oxygen carrier to fuel ratio, ϕ , and the specific solids inventory in the fuel reactor, m_{FR}^* ; see Fig. 4(a) and 4(c). In general, an increase of the ϕ values and the solids inventory entailed a decrease of the total oxygen demand. Nevertheless, the effect of increasing the ϕ value to 1.5 was more relevant than the increase of the solids inventory. Thus, the total oxygen demand decreased by 1.6 points (from 5.7% to 4.1%) when increasing the ϕ parameter from 1.1 to 1.5 with about 500 kg/MW_{th} in the fuel reactor. The lowest value of total oxygen demand was reached in test Fe-1, $\Omega_T = 4.1\%$, which entails a substantial improvement in comparison with those values achieved with ilmenite [11].

The comparison done in Fig. 4(a) and 4(c) are based on the oxygen carrier to fuel ratio, ϕ , as defined by Eq. (1), which is often used to evaluate a single material [6]. However, the oxygen carrier to fuel ratio depends on the oxygen transport capacity of the material. As a consequence, the same value of the oxygen carrier to fuel ratio may be

achieved with different solid circulation rates with different materials. In fact, the lower value of the oxygen transport capacity, R_{OC} , for iron-ore compared to ilmenite makes that the actual solids circulation rate is higher for the iron-ore if the same ϕ value is considered. Note that the physical parameter which can be measured and modified in the CLC unit is the solids circulation rate. Therefore, the use of the specific solids circulation rate, \dot{m}_{OC}^* , is a suitable parameter when several materials want to be compared [32,49]. Fig. 4(b) shows the effect of the specific solids circulation rate on Ω_T . In this case, the differences between ilmenite and iron-ore are reduced in relation to the evaluation against ϕ parameter; see Fig. 4(a). However, the reduction in the total oxygen demand is still relevant when the iron-ore was used. For example, considering values of $m_{FR}^* \approx 500$ kg/MW_{th} and $\dot{m}_{OC}^* \approx 2.2$ kg/s per MW_{th}, the total oxygen demand with ilmenite was 8.2% (test IL-3), and it was reduced to 6.7% (test Fe-6) when iron-ore was used. A further decrease in Ω_T was observed by increasing ϕ or the solids circulation rate, but Ω_T was barely affected by the fuel reactor temperature; see Fig. 4(d).

A deeper analysis on the combustion process was done by analyzing the unburnt compounds at the fuel reactor outlet. Table 3 compiles the contribution to the total oxygen demand of CO , H_2 and CH_4 . The major contributor to the oxygen demand is CH_4 . Considering methane as a characteristic compound of volatile matter, it can be deduced that most of the unburnt products come from the volatile matter, in accordance to previous works [6,11,23]. Note that CO and H_2 are also present in volatiles, and can also be formed as intermediate compounds during CH_4 conversion. Methane in volatiles was calculated to be $x_{CH_4} = 0.0626$ kg CH_4 per kg of South African coal [11]. So, the conversion of methane in the fuel reactor can be calculated as:

$$x_{CH_4} = \frac{M_{CH_4} F_{CH_4}}{\dot{m}_{sf} x_{CH_4}} \quad (5)$$

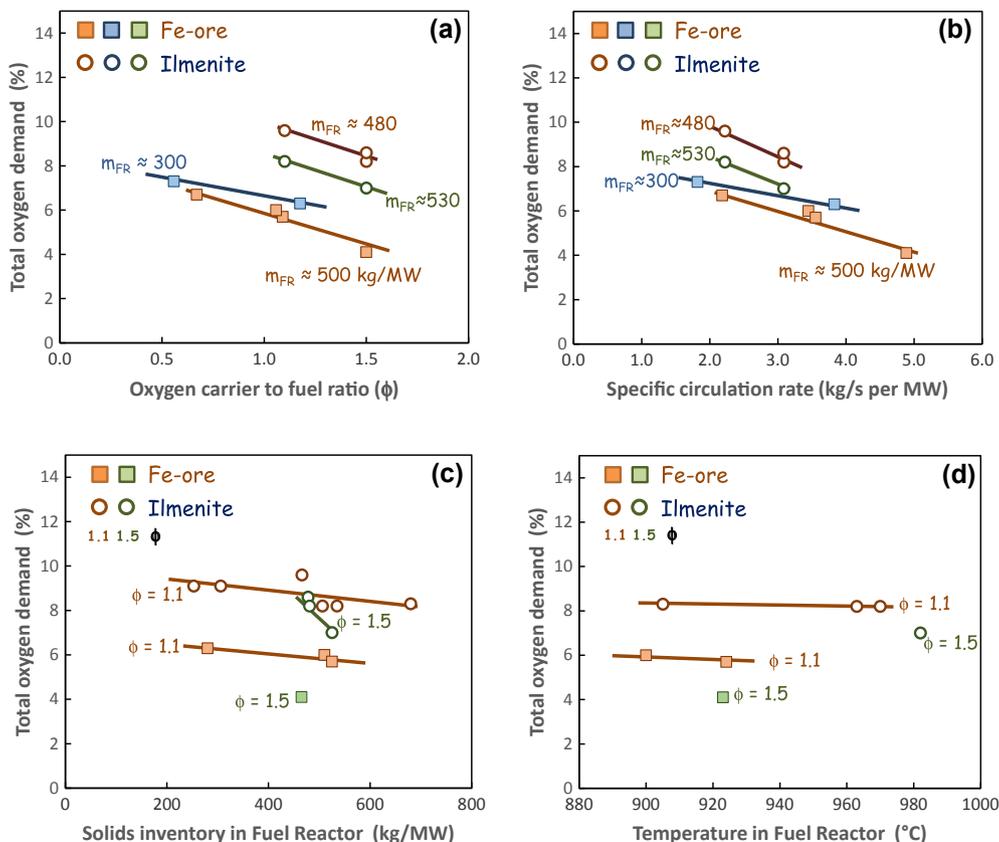


Fig. 4. Total oxygen demand, Ω_T , as a function of (a) oxygen carrier to fuel ratio, ϕ , (b) specific circulation rate, (c) specific solids inventory in the fuel reactor, and (d) fuel reactor temperature.

The methane conversion averaged a value of 74.1% for experiments with iron-ore, higher than the 67.3% found for ilmenite. A comparison of the results obtained at similar operating conditions shows that the methane conversion was 70.4% for ilmenite in test Il-3 and 73.4% for iron-ore in test Fe-6. This corresponds to a scarce decrease of 0.4% in the contribution of the oxygen demand by CH_4 , while the total decrease in Ω_T was 1.5%. This fact suggests that most of the improvement in the combustion of coal was due to a better conversion of CO and H_2 with iron-ore.

3.2. Assessment of coal combustion by using the carbon stripper as primary fuel reactor

Tests Fe-7 and Fe-8 were carried out to assess the effect of using the carbon stripper as primary fuel reactor on the total oxygen demand and CO_2 capture. Operational issues were not found during the whole period with coal feeding to the carbon stripper. The solids circulation rate was not perturbed and similar conditions to those existing feeding coal to the fuel reactor were achieved, even considering that the coal feeding rate was higher in this case, achieving 23.5 kW_{th} .

Fig. 5 compares the results obtained feeding the coal either to the fuel reactor or to the carbon stripper. Feeding coal into the carbon stripper entailed a drop in the CO_2 capture, from 50% to 40% approx, even if the fuel reactor temperature in the event of coal fed to the carbon stripper (937 °C) was higher than that of feeding to the fuel reactor (925 °C). Considering results in Fig. 3(a), the CO_2 capture at 925 °C would be about 5% lower than at 937 °C. The lower CO_2 capture when coal was fed to the carbon stripper might be related with a lower separation efficiency of the carbon stripper. This device was designed with two compartments in which char particles could be elutriated; but only the second compartment could be effective for newly fed particles. Besides, the char to be treated by the carbon stripper is expected to be higher with the coal feeding point in this reactor, which could imply lower carbon separation efficiency [12]. A modification of the carbon stripper design would be advised to prevent a decrease of the CO_2 capture.

The most remarkable result obtained when coal was fed to the carbon stripper was the improvement in the total oxygen demand; see Fig. 5(b). The total oxygen demand was about 5.5% when coal was fed to the carbon stripper and solids inventories in the fuel reactor of about 250 $\text{kg}/\text{MW}_{\text{th}}$. These values can be compared to values about 7.0% with 300 $\text{kg}/\text{MW}_{\text{th}}$ and the coal being fed to the fuel reactor. The methane conversion for these tests were about 70–74% and 72–77% when coal was fed to the fuel reactor and carbon stripper, respectively. But not only methane was better converted, but the oxygen demand for H_2 and CO was also decreased; see Table 3. This implies that the conversion of

volatile matter was improved using the fuel reactor as a secondary reactor.

4. Discussion on different options to improve the combustion efficiency

The experience gained in this work, as well as in previous works [11,23], is of interest to evaluate the potential of different options to improve the combustion efficiency of the iG-CLC process. Fig. 6 compiles relevant results achieved both with ilmenite and iron-ore and grouped in four different blocks for such purpose. In a previous work with ilmenite [11] it was shown that operational conditions could be optimized to minimize the total oxygen demand. Thus, the total oxygen demand could be decreased from 9.6 to 8.2% when the specific circulation rate of solids increased from 2.2 to 3.1 kg/s per MW_{th} . A further decrease of Ω_T to 7.1% was achieved when the specific solids inventory increased from 480 to 720 $\text{kg}/\text{MW}_{\text{th}}$. In this sequence of results (block 1), the methane conversion was improved, as well as the relevance of H_2 in the unconverted gases was decreased.

In block 2, results achieved with iron-ore in test Fe-4 are compared with those of ilmenite in test Il-7, when operating conditions were as similar as possible. The total oxygen demand, Ω_T , was decreased from 8.2 to 5.7% by using iron-ore, which is a more reactive material. Further reduction in the oxygen demand was achieved with the iron-ore by increasing the specific solids circulation rate to 4.9 kg/s per MW_{th} , reaching a minimum Ω_T value of 4.1%. In view of the results previously shown, it would be expected that further improvements may be achieved by increasing the solids inventory in the fuel reactor to 700 $\text{kg}/\text{MW}_{\text{th}}$. Simulation works showed that there is still potential to reduce Ω_T by using more reactive materials [29], but likely this would imply the use of synthetic materials as it was demonstrated in a 25 kW_{th} CLC unit [21,34]. The design of synthetic materials should consider an easy separation of the oxygen carrier from the ash purge stream, e.g. by using metal oxides with magnetic properties [35,39,50] or using supporting materials with magnetic properties [51].

The coal feeding to the carbon stripper has a potential to decrease Ω_T in about 25%, as it is shown comparing test in block 3 in Fig. 6. In this case, Ω_T are higher than other results with iron-ore due to the lower values of m_{FR}^* and m_{OC}^* for these tests. It would be expected even lower Ω_T values if optimum values of solids inventory and circulation rate were used, e.g. $m_{\text{FR}}^* = 500\text{--}700$ $\text{kg}/\text{MW}_{\text{th}}$ and $m_{\text{OC}}^* = 3\text{--}5$ kg/s per MW_{th} .

Besides, the implementation of ring-type internals inside the fuel reactor [23] has demonstrated its potential to reduce Ω_T in the iG-CLC process by 25%; see block 4 in Fig. 6 with ilmenite as oxygen carrier. In this case, higher Ω_T values are obtained because a fuel with higher

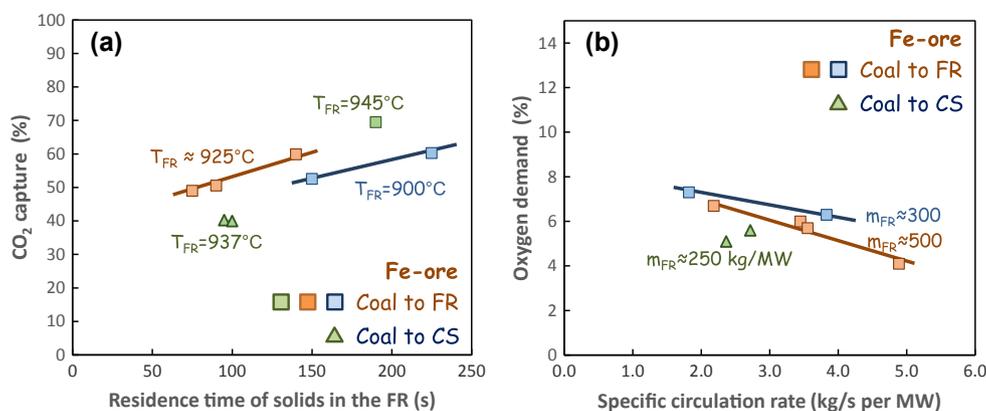


Fig. 5. Effect of the feeding coal point, fuel reactor or carbon stripper, on the (a) CO_2 capture vs. the mean residence time of solids and (b) total oxygen demand vs. the specific circulation rate.

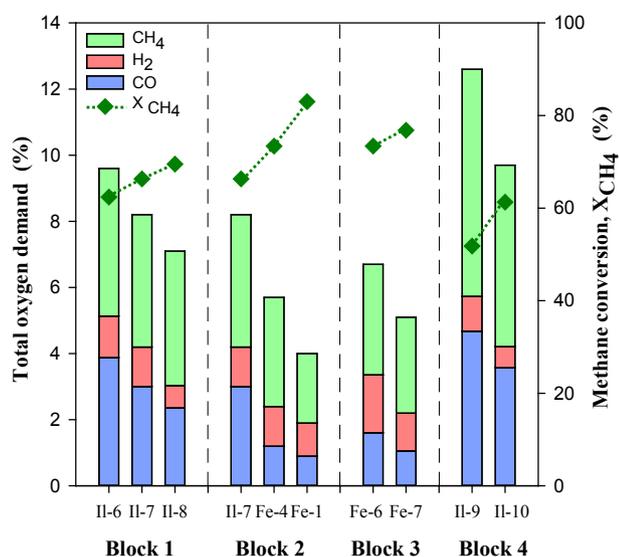


Fig. 6. Potential of different options to decrease the total oxygen demand in the iG-CLC process.

fraction of volatile matter was used. This fact highlights the relevance of implementing solutions to improve the conversion of volatiles. Among other options proposed to improve the combustion efficiency, the use of a secondary fuel reactor has also a high potential to decrease the Ω_T [21]. Both the recirculation of gases and the use of the carbon stripper as a secondary fuel reactor are also alternative to be explored [25]. However, there are still issues to address about the possibility of using all these solutions in iG-CLC units at the industrial scale.

5. Conclusions

Two strategies have been analyzed in this work to improve the coal combustion efficiency in iG-CLC by using Fe-based materials as oxygen carrier.

First, the use of an iron-ore highly reactive in comparison with ilmenite has been analyzed. No major differences were found in the CO₂ capture achieved in the CLC unit regardless of the oxygen carrier, either ilmenite or iron-ore. In contrast, the combustion efficiency was clearly enhanced by using the iron-ore material as oxygen carrier. Under similar and optimized conditions, i.e. about 500 kg/MW_{th} of solids in the fuel reactor and 3.5 kg/s per MW_{th} of solids circulation, the total oxygen demand was 8.2% with ilmenite and 5.7% with iron-ore. A further improvement was observed, $\Omega_T = 4.1$, by increasing the solids circulation to 4.9 kg/s MW_{th}. This was related to an improvement of the conversion of volatiles in the fuel reactor.

Second, a preliminary evaluation of using the carbon stripper as primary fuel reactor has been conducted. In this case, the CO₂ capture was decreased. A more efficient carbon stripper would be required to achieve higher CO₂ capture rates. More interesting was the reduction of the oxygen demand by 25% due to the improvement of volatile matter conversion in the fuel reactor, which acted as a secondary reactor.

The combination of different approaches to improve the combustion efficiency, mostly of volatiles, may have a high potential to minimize the total oxygen demand of the iG-CLC process.

CRediT authorship contribution statement

A. Abad: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **P. Gayán:** Conceptualization, Resources, Visualization, Supervision, Funding acquisition. **R. Pérez-Vega:** Conceptualization, Methodology, Validation, Formal analysis,

Block	1			2			3		4	
Effect of...	Optimizing operating conditions			Oxygen carrier reactivity			Coal to CS		Ring type internals	
Test	Il-6	Il-7	Il-8	Il-7	Fe-4	Fe-1	Fe-6	Fe-7	Il-9	Il-10
Coal feeding	FR	FR	FR	FR	FR	FR	FR	CS	FR	FR
Internals	NO	NO	NO	NO	NO	NO	NO	NO	NO	YES
m_{FR}^* (kg/MW _{th})	466	481	722	481	525	465	485	270	400	400
m_{OC}^* (kg/s·MW _{th})	2.2	3.1	3.1	3.1	3.6	4.9	2.2	2.4	2.5	2.6
ϕ (-)	1.1	1.5	1.5	1.5	1.1	1.5	0.7	0.7	1.3	1.3

Investigation. **F. García-Labiano:** Conceptualization, Methodology, Resources, Supervision, Funding acquisition. **L.F. Diego:** Conceptualization, Methodology, Resources, Funding acquisition. **T. Mendiara:** Conceptualization, Methodology, Resources, Funding acquisition. **M.T. Izquierdo:** Conceptualization, Methodology, Resources. **J. Adánez:** Conceptualization, Methodology, Resources, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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