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Use of Chemical-Looping processes for coal combustion with CO_2 capture

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Abstract

Chemical-Looping Combustion, CLC, is one of the most promising processes to capture CO_2 at a low cost. It is based on the transfer of the oxygen from air to the fuel by using a solid oxygen carrier that circulates between two interconnected fluidized-bed reactors: fuel and air reactors. The CO_2 capture is inherent to this process, as the air does not get mixed with the fuel. In this work two options are evaluated in a 1 kW_{th} continuously operated unit for coal fueled Chemical-Looping. The first one is the gasification of coal in the fuel reactor –*in-situ* Gasification Chemical-Looping Combustion (*i*G-CLC)–. Ilmenite or a bauxite waste material is used as oxygen carrier. The second one is the combustion of coal in the fuel reactor by using oxygen carriers which release gaseous oxygen –Chemical-Looping with Oxygen Uncoupling (CLOU)–. A Cu-based material is used in this mode. Coals ranging from anthracite to lignite were used. Complete combustion was always reached in CLOU mode, whereas unburnt compounds were present in *i*G-CLC. Both in *i*G-CLC and CLOU processes the CO_2 capture increased with temperature and decreased with the coal rank. The highest CO_2 capture rate was obtained for lignite, being 93% for *i*G-CLC and 99% for CLOU, even without a carbon separation system. The key aspects for the good performance of *i*G-CLC and CLOU processes are analyzed through the performance results obtained with different coals.

Keywords: CLC; CLOU; coal; combustion; CO_2 capture; ilmenite; iron; copper

1. Introduction

Chemical-Looping Combustion (CLC) is one of the most promising technologies to carry out CO_2 capture at low cost. A CLC system is based on the use of an oxygen carrier which transfers the oxygen necessary for the fuel combustion from the air to the fuel. Frequently, a CLC system is composed by two interconnected fluidized bed reactors, the air reactor and the fuel reactor, and the oxygen carrier circulating between them. In CLC, the fuel is introduced to the fuel reactor where it is converted by the

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oxygen carrier to produce CO_2 and H_2O. The spent oxygen carrier must be transported to the air reactor to be oxidized by air and then start a new cycle. The CO_2 capture is inherent to this process, as the air does not get mixed with the fuel. A review of CLC processes has been recently done by Adanez et al. [1].

The use of coal in CLC is very attractive in future sceneries with restriction in CO_2 emissions, since coal will keep on being a main energy source in the medium-term. In the so-called solid fuelled-CLC the solid fuel is physically mixed with the oxygen carrier in the fuel reactor. Two options have been proposed, depending on how the solid fuel is converted. The *in-situ* Gasification Chemical-Looping Combustion (*i*G-CLC) involves the *in-situ* gasification of the fuel in the fuel reactor by H_2O and/or CO_2 [2]. The gasification step is the limiting step in the coal conversion in the fuel reactor. To overcome the slow gasification stage in the *i*G-CLC, the Chemical-Looping with Oxygen Uncoupling (CLOU) process was proposed by Mattisson and coworkers [3]. In CLOU an oxygen carriers that dissociated to produce gaseous oxygen is used, so the solid fuel conversion goes via fast combustion. Moreover, in CLOU the fluidization gas can be recycled CO_2, reducing in this way the steam duty of the plant and energy penalty.

The main reactions involved in each process are depicted in Fig. 1. The most relevant chemical processes during coal conversion in the *i*G-CLC process are showed in reactions (1-4), and the corresponding processes for the CLOU mode includes reaction (1), followed by (5-6). Both in *i*G-CLC and CLOU the char must be highly converted in the fuel reactor to avoid leaking of char particles to the air reactor where they would be burnt with air. This fact would reduce the CO_2 capture efficiency because CO_2 emitted from the air reactor is not captured. As a consequence of the ashes present in the solid fuel it is necessary the draining of ashes from the system to avoid its accumulation in the reactors. However, the drain stream will also contain some amount of oxygen carrier. Thus, a partial loss together with the fuel ashes is expected and low cost materials or materials readily separable from the ashes are desirable.

$$\text{Coal} \rightarrow \text{Volatile matter} + \text{Char(C)} \tag{1}$$

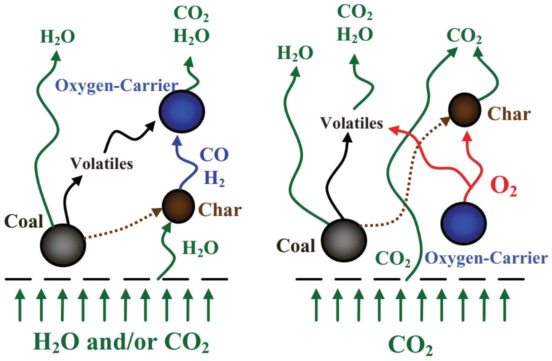
$$\text{Char(C)} + H_2O \rightarrow H_2 + CO \tag{2}$$

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

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

$$Me_xO_y \rightarrow Me_xO_{y-1} + ½\,O_2 \tag{5}$$

$$\text{Char(C)} + \text{Volatile matter} + (n + m/2)\,O_2 \rightarrow n\,CO_2 + m\,H_2O \tag{6}$$



iG-CLC (solid fuel) **CLOU (solid fuel)**

Fig. 1. Main processes involved in fuel reactor for the *i*G-CLC and CLOU modes.

Mainly low cost materials have been analyzed for the *i*G-CLC process by several authors [1]. The most used material was ilmenite, which is a mineral mainly composed of $FeTiO_3$. There are an interesting number of recent studies showing an acceptable performance of ilmenite as oxygen carrier in CLC. Leion et al. [4] analyzed the reactivity of ilmenite in a batch fluidized bed, obtaining high conversion of CO and H_2 but moderate conversion of CH_4. Adánez et al. [5] found that ilmenite gains reactivity with the redox cycles, and eventually the reactivity was maintained constant. Good performance of ilmenite has been proven for *i*G-CLC with coal in continuously operated units ranging from 500 W_{th} [6] to 10 kW_{th} [7]. The effect of the operating variables on the *i*G-CLC was investigated by Cuadrat et al. [8,9] working with coals of different rank from lignite to anthracite. Temperatures above 1000 °C [7] and values of the oxygen carrier to fuel ratios slightly above the stoichiometric value are beneficial to maximize the carbon capture in the *i*G-CLC process [8]. Recently it has started the use of ilmenite in a 100kW_{th} unit at Chalmers University of Technology [10] and 1 MW_{th} unit at TU Darmstadt [11].

In the CLOU process, the material used as oxygen carrier must have suitable thermodynamic properties for oxygen uncoupling. Three metal oxide systems have been so far identified: CuO/Cu_2O, Mn_2O_3/Mn_3O_4, and Co_3O_4/CoO [3]. In general, Cu-based materials have faster release of oxygen than Mn-based particles [12]. From a screening study, a Cu-based oxygen carrier 60 wt.% CuO supported on $MgAl_2O_4$ was selected according to its high reactivity, low attrition rate and avoidance of agglomeration during successive redox cycles [13]. This material was used to demonstrate the proof of CLOU concept with coal in a 1.5 kW_{th} unit located at ICB-CSIC (Spain) [14]. The temperature (900-960ºC), coal feeding rate and solids circulation flow rate was varied to analyze the effect of the kinetics of the processes, the solids inventory per MW_{th} and the residence time of particles in the fuel reactor, respectively, on the CLOU performance. In all cases, unburnt volatile matter was not present in the fuel reactor outlet, which was composed by CO_2 and H_2O with the equilibrium O_2 concentration at the operating temperature. Coal conversion in the fuel reactor was limited by the char combustion, which was mainly affected by the temperature and the mean residence time. In spite of the lack of carbon stripper in the CLOU unit, the carbon capture was always higher than 97% even when the solids inventory was as low as 235 kg/MW_{th}.

The objective of this work is to do a comprehensive comparison of the *i*G-CLC and CLOU processes based on the experimental results obtained with different coals in the CLC-CLOU unit existing in ICB-CSIC. Results obtained at several fuel reactor temperatures and with different type of coals are used, and a discussion based on the carbon capture and combustion efficiency is done.

2. Experimental

2.1. Materials

Two materials are used as oxygen carriers for *i*G-CLC: ilmenite and a Fe-enriched *sand fraction* (71 wt.% Fe_2O_3) from bauxite digestion (Fe-ESF). Ilmenite was initially activated during 3 hours of continuous operation [6]. The Fe-ESF was supplied by Alcoa Europe-Alumina Española S.A. Prior to its use, the sample was calcined at 1200ºC for stabilization purposes. The material used for CLOU mode was a Cu-based oxygen carrier prepared by spray drying (Cu60MgAl). Oxygen carrier particles were manufactured by VITO (Flemish Institute for Technological Research, Belgium). The CuO content was 60 wt.%. Details about composition and physical properties of these materials are shown in Table 1 and references [6,14,15].

Three different coals were used for *i*G-CLC and CLOU experiments. A Lignite from Teruel basin (Spain), a Bituminous coal from South Africa, and an Anthracite from El Bierzo (Spain) were used with the aim to cover a wide range of coals. Main properties of selected coals are showed in Table 2. The coal particle size used for this study was +0.2–0.3 mm with all fuels.

Table 1. Characterization of oxygen carrier particles.

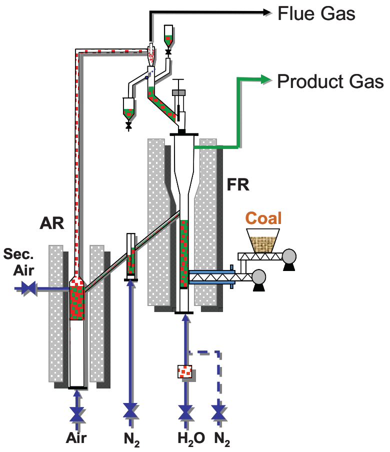
	Ilmenite	Fe-ESF	Cu60MgAl
XRD main phases	Fe_2TiO_5, Fe_2O_3, TiO_2	Fe_2O_3, β-Al_2O_3	CuO, $MgAl_2O_4$
Particle diameter (μm)	+150-300	+150-300	+100-200
Crushing strength (N)	2.0	2.8	2.4
Oxygen transport capacity, R_{OC}, (%)	3.9	2.4	6.0
Porosity (%)	18.0	3.7	16.1
Skeletal density (kg/m^3)	4200	4500	4600
Specific surface area, BET (m^2/g)	0.4	0.1	0.5

Table 2. Properties of coals used in this work.

	Anthracite	Bituminous	Lignite
Proximate Analysis (wt.%)			
Moisture	1.0	4.2	12.6
Volatile matter	7.5	25.5	28.6
Fixed carbon	59.9	55.9	33.6
Ash	31.6	14.4	25.2
Ultimate Analysis (wt.%)			
C	60.7	69.3	45.4
H	2.1	3.9	2.5
N	0.9	1.9	0.6
S	1.3	0.9	5.2
LHV (kJ/kg)	21900	25500	16250

2.2. Experimental set-up

A schematic view of the experimental set-up is shown in Fig. 2. The set-up was basically composed of two interconnected fluidized-bed reactors joined by a loop seal, a riser for solids transport from the air reactor to the fuel reactor, a cyclone and a solids valve to control the solids circulation flow rate between both reactors. A diverting solids valve located below the cyclone allowed the measurement of the solids flow rates at any time. Thus, this design allowed us to control and measure the solids circulation flow rate. The gas velocity at 900ºC in the fuel-reactor was 11 cm/s and 60 cm/s for the air-reactor. Coal is fed in by a two-step screw feeder at the bottom of the bed right above the fuel reactor distribution plate in order to maximize the time that the fuel and volatile matter is in contact with the bed material. The ash particles remaining after char combustion were not retained by the cyclone and were collected in a reservoir downstream. Thus, ashes were not accumulated in the system. The absence of a carbon stripper facilitates the interpretation of the effect of these operational conditions on the results obtained, specially the effect of the mean residence time. CO, CO_2, H_2, CH_4, and O_2 were analyzed in the exiting streams from the air and fuel reactors. Higher hydrocarbons (C2-C5) were analyzed by chromatography and the amount of tar was analyzed following a tar protocol. More information is given in [6,14].



FUEL REACTOR	
Inner diameter	5 cm
Bed height	20 cm
LOOP SEAL	
Inner diameter	50 mm
AIR REACTOR	
Inner diameter	8 cm
Bed height	10 cm

Fig. 2. Schematic diagram of the ICB-CSIC-s1 facility for coal-fuelled *i*G-CLC and CLOU.

The performance of the *i*G-CLC and CLOU processes is assessed by evaluating two parameters: the carbon capture efficiency and the combustion efficiency in the fuel reactor. The carbon capture efficiency, η_{CC}, is defined as the fraction of carbon exiting in the fuel reactor outlet gas stream. The combustion efficiency in the fuel reactor is defined as the percentage of the oxygen demanded by the effective coal that is supplied by the oxygen carrier in the fuel reactor.

$$\eta_{CC} = \frac{\left(F_{CH_4} + F_{CO} + F_{CO_2}\right)_{outFR}}{\left(F_{CH_4} + F_{CO} + F_{CO_2}\right)_{outFR} + \left(F_{CO_2}\right)_{outAR}} \tag{7}$$

$$\eta_{comb,FR} = 1 - \frac{\left(4F_{CH_4} + F_{CO} + F_{H_2}\right)_{outFR}}{2\Omega_{coal}\dot{m}_{coal} - 2\left(F_{CO_2}\right)_{outAR}} \tag{8}$$

Ω_{coal} being the he stoichiometric mol of O_2 to convert 1 kg of coal to CO_2 and H_2O.

3. Results

In the *i*G-CLC mode, ilmenite was mainly used as oxygen carrier, whereas Cu60MgAl material was used for CLOU. To consider specific characteristics of both processes, different residence times in the fuel reactor were used, around 16 min in *i*G-CLC (~1500 kg/MW_{th}) while 7 min were used for CLOU (~900 kg/MW_{th}). Additional experiments were carried out in *i*G-CLC mode using Fe-ESF with anthracite as fuel. In this case, mean residence time of solids in the fuel reactor was 11 min (2000 kg/MW_{th}).

Differences between *i*G-CLC and CLOU are evident when results are compared. Fig. 3 shows the comparison on the carbon capture efficiency obtained for different coals as a function of the fuel reactor temperature. As much for *i*G-CLC as for CLOU the carbon capture was higher when the temperature was increased because the gasification or combustion rate was enhanced. Carbon capture is much higher in CLOU because the char is converted faster when it is burnt with gaseous O_2 than when it is gasified by H_2O. In both *i*G-CLC and CLOU, the type of coal affected to the carbon capture efficiency.

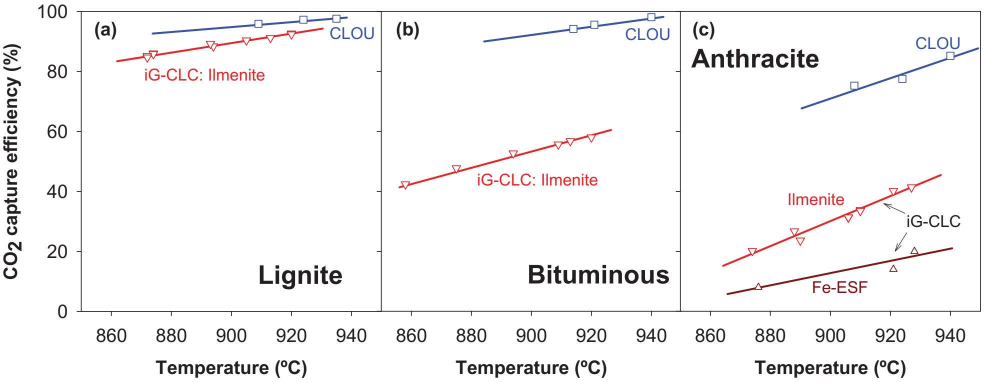


Fig. 3. Carbon capture efficiency in *i*G-CLC or CLOU as a function of the fuel reactor temperature.

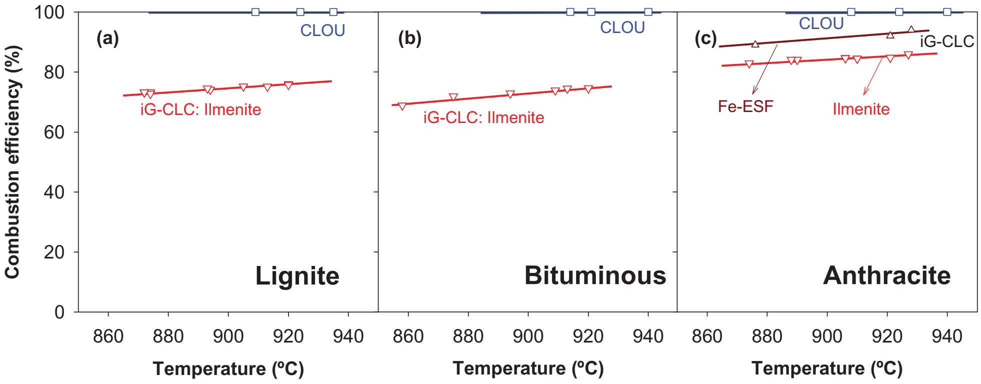


Fig. 4. Combustion efficiency in *i*G-CLC or CLOU as a function of the fuel reactor temperature.

In general, the carbon capture followed the order Lignite > Bituminous > Anthracite. Since the carbon from the volatiles exits with the fuel reactor outlet stream, that fraction of carbon is always captured. Thus, the carbon capture efficiency depends on the fraction of carbon in the volatile matter and on the char conversion rate. So, less reactive coals gave lower carbon capture. More in detail, the type of coal showed a high effect on the carbon capture in *i*G-CLC with ilmenite. So, at 920°C the carbon capture was as high as 93% with Lignite and it was reduced to 58% and 40% with the Bituminous coal and Anthracite, respectively. In the CLOU mode high carbon capture efficiency was obtained for Lignite and Bituminous coal (η_{CC} = 97% at 935°C with both coals). Nevertheless, lower values were obtained for Anthracite (η_{CC} = 84% at 940°C).

Experiments in *i*G-CLC mode were carried out with anthracite using a more reactive material: Fe-ESF. In this case, the carbon capture was lower than with ilmenite. The main factor affecting the carbon capture was the lower residence time of solids in the fuel reactor with Fe-ESF. This fact was because the higher solids circulation rate with Fe-ESF due to its lower oxygen transport capacity compared to ilmenite, see Table 1. The oxygen carrier reactivity would have little influence on the carbon capture efficiency [16].

The Lignite showed the highest carbon capture efficiency, being the difference obtained between *i*G-CLC and CLOU of low relevance at high temperatures. On the contrary, Bituminous coal and Anthracite showed higher differences when *i*G-CLC and CLOU performance was compared.

Fig. 4 shows the combustion efficiency in the fuel reactor for all fuels tested at the different temperatures in *i*G-CLC and CLOU modes. Results on CLOU with the Cu-based oxygen carrier showed that full combustion of coal to CO_2 and H_2O was reached for all coals tested. On the contrary, unburnt gases exit from the fuel reactor in *i*G-CLC with ilmenite; CH_4, CO and H_2 were the only unburnt compounds found. Any tarry material or higher hydrocarbons were fully converted by the oxygen carrier. Correspondingly the combustion efficiency was lower than 100%. The combustion efficiency in *i*G-CLC mode was higher for solid fuels with lower volatile content, but it was slightly affected by the reactor temperature. Also, the use of a more reactive oxygen carrier in *i*G-CLC mode, as Fe-ESF is, increased the combustion efficiency in 9%, see Fig. 4(c). Note that a higher solids inventory was used per MW_{th} with Fe-ESF, which can contribute to an increase in the range 3-6% in the combustion efficiency [16,17], the rest being attributable to the higher reactivity of Fe-ESF. But the low values of combustion efficiency in *i*G-CLC are not fully justified by the reactivity of the oxygen carrier. Ilmenite has enough high reactivity to fully convert gasification products to CO_2 and H_2O [5]. However, unburnt compounds in CLC with coal mainly proceed from volatiles generated during coal devolatilization [6]. This fact explains the higher value of combustion efficiency found for anthracite, which was due to the lower volatile content of this fuel. So, the way that gases are converted in *i*G-CLC or CLOU has influence on combustion. In *i*G-CLC volatiles must diffuse until solids to react, whereas in CLOU oxygen from oxygen carrier reacts in gas phase with gases. This is a more effective way for gas conversion.

4. Discussion

The carbon capture efficiency, the combustion efficiency in the fuel reactor and the separation of ash from the oxygen carrier are the key factors that must be maximized for the development of an optimized *i*G-CLC or CLOU process. From results above showed, the combustion efficiency was complete for the CLOU mode, whereas unburnt compounds were always present in *i*G-CLC both with ilmenite or Fe-ESF as oxygen carrier. In CLOU mode, complete combustion would be still possible even lowering the solids inventory to 60 kg/MW_{th} [18]. On the contrary, in *i*G-CLC it is not worth to increase the solids inventory above 2000 kg/MW_{th} to improve the combustion efficiency [16]. Different possibilities have been proposed to process the unburnt compounds. The use of a more reactive oxygen carrier has a residual effect on this improvement, unless the gain in reactivity is important [17]. A second fuel reactor downstream where exhaust gases are fed can be used. From a preliminary study, a solids inventory of 45 kg/MW_{th} should be necessary in the second reactor [16] to reach complete combustion of gases. Improve the gas-solid contact in the fuel reactor or the separation and recirculation of unburnt compounds can be also other options. Finally, if any of the above solution becomes valid, an oxygen polishing step could be added to the fuel reactor down-stream. Thus, unburnt components are fully burnt to CO_2 and H_2O with pure oxygen, being necessary an air separation unit (ASU) of small size. In conditions in the ICB-CSICs1 unit, the oxygen demand was 5-9% of the oxygen required by coal combustion with ilmenite; some lower (3-7%) with Fe-ESP as oxgyen carrier. In CLOU process, oxygen polishing would not be required but fuel reactor gases contains some oxygen which has to be taken into account.

The carbon capture efficiency was higher for CLOU process than for *i*G-CLC. No further actions would be needed to reach values of $\eta_{CC} \approx 98\%$ when high reactive coals are used in CLOU. However, the residence time of char should be increased when low reactive coals are used in CLOU, but in any case for the *i*G-CLC mode. The carbon capture efficiency was limited by the char conversion rate in the fuel reactor. Table 3 shows the char conversion rate in the fuel reactor for different coals and processes. Model simulations indicated the relevance of a carbon separation system (e.g. a carbon stripper) on the carbon capture efficiencies [19]. The carbon stripper separates char particles away from oxygen carrier particles which are returned to the fuel reactor, whereas oxygen carrier particles are left to pass to the air reactor with minor amounts of char.

Table 3. Carbon capture efficiency, combustion efficiency in the fuel reactor and char conversion rate obtained using ilmenite or Fe-ESF in *i*G-CLC or Cu60MgAl in CLOU with several coals. T = 930ºC.

	Anthracite			**Bituminous**		**Lignite**	
	Ilmenite	Fe-ESF	Cu60MgAl	Ilmenite	Cu60MgAl	Ilmenite	Cu60MgAl
Solids inventory (kg/MW$_{th}$)	1400	2000	900	1380	1000	1770	850
Mean residence time (min)	16	11	7	16	7	16	7
Carbon Capture (%)	42	20	80	60	98	93	98
Combustion efficiency FR (%)	85	94	100	75	100	76	100
Char conversion rate (%/min)	3.7	3.6	40	5.0	360	55	400

Considering a carbon separation system, the carbon capture efficiency can be calculated as a function of the carbon separation system efficiency (η_{CSS}), the solids inventory in the fuel reactor ($m_{s,FR}$), the solids circulation flow rate ($\dot{m}_{OC}$), the carbon content (f_C) and fixed carbon ($f_{C,fix}$) in coal [20].

$$\eta_{CC} = \frac{f_C - f_{C,fix}}{f_C} + \frac{f_{C,fix}}{f_C}\left[1 - \frac{\dot{m}_{OC}\left(1-\eta_{CSS}\right)}{\left(-r_C\right)m_{s,FR} + \dot{m}_{OC}\left(1-\eta_{CSS}\right)}\right] \tag{9}$$

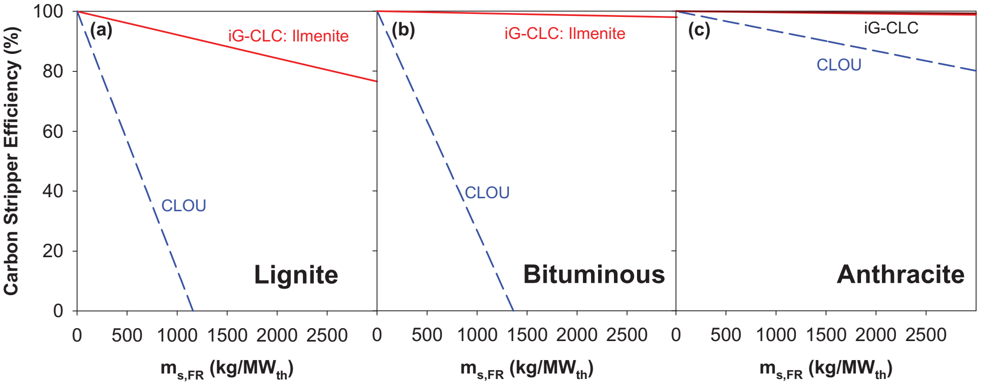


Fig. 5. Efficiency of the carbon stripper required for a carbon capture of 98% as a function of the solids inventory in the fuel reactor for *i*G-CLC and CLOU processes. T$_{FR}$ = 930ºC. Oxygen carrier to fuel ratio: ϕ = 1.5.

Thus, the solids inventory and the efficiency of the carbon separation system can be calculated to obtain a certain value of the carbon capture efficiency for every oxygen carrier-coal pair. Fig. 5 shows the efficiency of the carbon stripper (η_{CSS}) required to reach a carbon capture of η_{CC} = 98% for different coals. The η_{CSS} value required decreases as the solids inventory in the fuel reactor increases. Nevertheless, it is necessary a highly efficient carbon stripper (η_{CSS}>98%) in the *i*G-CLC mode with low reactive coals (bituminous and anthracite) if the solids inventory was limited to 2000 kg/MW$_{th}$ at maximum. Lower is the requirement for the carbon striper using lignite in *i*G-CLC or in the CLOU mode. It is worthy to note that 60 kg/MW$_{th}$ of Cu60MgAl material in CLOU mode should be enough to avoid unburnt compounds from the fuel reactor. However, a higher solids inventory is required depending on the efficiency of the carbon separation system. Thus, if a carbon stripper is not present, 1000-1500 kg/MW$_{th}$ should be necessary to reach a carbon capture efficiency of 98% in CLOU with lignite or bituminous coal.

The use of CLOU process for solid fuel combustion using oxygen carriers that can release oxygen at high temperature is a promising alternative to *i*G-CLC which does not need an oxygen polishing step and reach very high carbon capture efficiencies specially with reactive coals. A cornerstone in the successful development of CLOU process is the oxygen carrier material. It is necessary the development of resistant and cheap materials with CLOU properties that can be easily separated from coal ashes.

5. Conclusions

The performance regarding the carbon capture and combustion efficiency for CLOU was better than for *i*G-CLC. Whereas complete combustion was reached in CLOU mode, the incomplete combustion in *i*G-CLC process requires the use of additional actions, e.g. an oxygen polishing step. The characteristics of coal have an important effect on combustion and gasification processes and it is expected that also affect to *i*G-CLC and CLOU processes. The use of coals with high volatile content or highly reactive during the gasification or combustion reaction enhances the carbon capture efficiency of the process. In order to reach high carbon capture efficiency, the existence of the carbon separation system is imperative in the *i*G-CLC mode for all type of coals and in CLOU mode with low reactive coals, e.g. anthracite. Nevertheless, the use of a carbon separation system is also recommended in CLOU mode with lignite or bituminous coal.

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