

Performance of CLOU process with a Cu-Mn oxygen carrier for the combustion of different types of coal with CO₂ capture

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Abstract

The Chemical Looping with Oxygen Uncoupling (CLOU) process is a Chemical Looping Combustion (CLC) technology that allows the combustion of solid fuels with inherent CO₂ separation by using oxygen carriers based on metal oxides. This technology has low energy penalty and thus low CO₂ capture costs. In CLOU, the oxygen carrier must be able to release gaseous oxygen which limit the availability of metal oxides for this process. In this work, the suitability of oxygen carrier particles containing 34 wt.% CuO and 66 wt.% Mn₃O₄ (active phase Cu_{1.5}Mn_{1.5}O₄) prepared by granulation was investigated in a continuous 1.5 kW_{th} rig during CLOU combustion of different rank coals (two sub-bituminous and a lignite). The effect of the different coals in the combustion and CO₂ capture efficiencies at different oxygen carrier to coal ratios was studied. It was found that full combustion can be reached independently of the coal used. However, CO₂ capture efficiencies were highly determined by the coal rank. Finally it was found that work with oxygen carrier to coal ratios higher than 4 and the low oxygen carrier conversion both in the fuel and air reactors decreasing the effect of

the chemical stress in the attrition rate; therefore it is clearly beneficial for the lifetime of the oxygen carrier particles to operate with low ΔX between fuel and air reactors.

Keywords: CO₂ capture, coals, CLOU, mixed oxide, copper, manganese.

1. Introduction

Chemical Looping Combustion (CLC) option to burn solid fuel is the Chemical Looping with Oxygen Uncoupling (CLOU) process. Metallic oxides used as oxygen carriers for CLOU process have the property to release gaseous oxygen at the operation temperatures. In the fuel reactor, the O₂ (g) released by the oxygen carrier burn directly the solid fuel feed in. In addition, the oxygen carrier for CLOU process must be regenerated by air in the air reactor. Three single metal oxides have the properties needed for CLOU process: CuO/Cu₂O, Mn₂O₃/Mn₃O₄, and Co₃O₄/CoO [1].

Mattisson [2] and Imtiaz et al. [3] have done reviews of CLOU materials. This review included Cu-based [4, 5], and mixed oxides based oxygen carriers: Cu-Mn [6, 7], Mn-Fe [8] and Mn-Si [9]. Among the developed materials, one spray dried particles with a 60 wt.% of CuO were analyzed in a CLOU unit of 1.5 kW_{th} where the proof of CLOU concept was demonstrated using different coal ranks and biomass [10-12]. With these particles was also analyzed the fate of the Sulphur and its effect in the CO₂ capture efficiency [13], as well the fate of Sulphur, Nitrogen and Mercury with a similar oxygen carrier [14]. The oxygen carrier did not show decrease of reactivity or agglomeration. However, the oxygen carrier needs improvement due to an important decrease in the crushing strength and an increase of its porosity [15]. On the other hand, oxygen carriers based on Mn has some advantages respect to Cu-based materials: operate at lower temperatures due to the fact that the O₂ partial pressure

at equilibrium for the Mn_2O_3/Mn_3O_4 is higher than for CuO/Cu_2O ; and also Cu materials are more expensive than Mn ones. However, the necessity of decrease the temperature in the air reactor around 800 °C to regenerate the Mn_3O_4 to Mn_2O_3 makes Mn-based materials unsuitable for use on an industrial scale [16-18]. So, nowadays the main effort to continue with the development of CLOU process is to find a suitable oxygen carrier for the process with high reactivity with solid fuels, high oxygen release rate and low attrition rate.

Cu-Mn mixed oxides has a good perspective of future for CLOU process due to the fact that oxygen release at lower temperature than Cu-based oxygen carriers [7]. Some studies have studied different Cu-Mn oxygen carriers prepared by co-precipitation [7], extrusion [19] or freeze drying [6]. They found that the Cu-Mn mixed oxides was able to generate gaseous oxygen up to 700 °C and have good reactivity with CH_4 but CO was present in the outlet stream. Depending on the Cu-Mn mixed oxide phase formed during the oxygen carrier preparation: $CuMn_2O_4$ [7, 20] or $Cu_{1.5}Mn_{1.5}O_4$ [19, 21], the oxygen release can occur by two different reactions:



Moreover, oxygen carrier derived from the commercial hopcalite, Carulite 300®, was analyzed as CLOU oxygen carrier by Adánez-Rubio et al. [21]. They found that the hopcalite derived oxygen carrier was able to completely burn coal by CLOU process to CO_2 and H_2O in a batch fluidized bed reactor at low temperatures. Nevertheless, hopcalite derived oxygen carrier showed a reduction in the particle crushing strength with the operation time, reaching values under 1N, indicating that the particles need an improvement in their physical

properties. Thus the oxygen carrier derived from commercial material was not considered adequate for CLOU process.

Based on the hopcalite composition, a new Cu-Mn oxygen carrier for CLOU process named Cu₃₄Mn₆₆-GR (34 wt.% CuO and 66 wt.% Mn₃O₄) was developed in our research group ICB-CSIC prepared by spray granulation [22]. This material showed a high reactivity with coal and char in a batch fluidized bed reactor, allowing complete combustion of the coal to CO₂ and H₂O [22]. Moreover, the Cu₃₄Mn₆₆-GR showed a low attrition rate (0.005 %/h, which corresponds to a particle lifetime of 20000 h), which is 18 times lower than the attrition rate of the hopcalite derived oxygen carrier [21]. This material was also tested in a continuous CLOU unit of 1.5 kW_{th} burning subbituminous Chilean coal, where the effect on combustion and CO₂ capture efficiencies of the fuel reactor temperature, coal feeding rate, solid circulation rate, fluidization agent and O₂ available in the air reactor were analyzed [23]. It was found that with fuel reactor temperatures higher than 800 °C complete combustion of coal was obtained. The CO₂ capture was higher than 90 % at low operation temperatures as 850 °C in the fuel reactor, reaching 96.2 % at 875 °C [23]. On the other hand, the oxygen carrier to fuel ratio (ϕ) is a fundamental parameter to obtain high CO₂ capture efficiencies. Higher values of ϕ produced higher char conversion rates in the fuel reactor, because the oxygen generation rate of this oxygen carrier highly depends on the reduction conversion. Note that a higher value of ϕ resulted in less reduction conversion, higher oxygen generation rate, higher char conversion rate and higher CO₂ capture efficiency [22, 23]. This results was opposite to what was found for a Cu-based oxygen carrier [10]. The use of steam as fluidizing agent did not show any substantial improvement in the CO₂ capture efficiency in the process with respect to N₂. Finally, it was found that in the air reactor it is necessary use an air excess ratio

of 4 to obtain high CO₂ capture efficiencies [23]. From this previous work, optimized conditions were found for the Cu₃₄Mn₆₆-GR material, namely fuel reactor temperature of 850 °C, air excess ratio of 4, and oxygen carrier to fuel ratio >4 in order to allow high CO₂ capture efficiencies. The aim of this work is study the effect of high value of the oxygen carrier to fuel ratios with coals of different rank in a CLOU continuous unit with the oxygen carrier Cu₃₄Mn₆₆-GR under optimized operating conditions. Possible chemical and physical changes in oxygen carrier particles were evaluated after operation at optimized conditions.

2. Experimental

2.1. Oxygen carrier

The material used was a Cu-Mn mixed oxide prepared by spray granulation in a spouted bed system. Oxygen carrier particles were manufactured at Institute of Carboquímica using Mn₃O₄ (STREM, PRS) and CuO (Panreac, PRS) as raw materials. The CuO content was 34 wt.% and the Mn₃O₄ was 66 wt.%. After particle formation in a spouted lab unit (Procell, Glatt), the particles were calcined for 2 h at 1125 °C. From now on the oxygen-carrier was named as Cu₃₄Mn₆₆-GR. Table 1 shows the main properties of the oxygen carrier. The particle size was +0.1-0.3 mm.

Table 1: Properties of Cu-Mn oxygen carrier used in this work: fresh and used after 50 h of continuous operation.

	Fresh	Used 50 h
XRD main phases	Cu _{1.5} Mn _{1.5} O ₄ , Mn ₃ O ₄	Cu _{1.5} Mn _{1.5} O ₄ , Mn ₃ O ₄ , Mn ₂ O ₃
Composition (wt.%)	72% Cu _{1.5} Mn _{1.5} O ₄ 28% Mn ₃ O ₄	72% Cu _{1.5} Mn _{1.5} O ₄ 23% Mn ₃ O ₄

		5% Mn ₂ O ₃
Oxygen transport capacity for CLOU, R_{OC} (wt.%)	4.0	4.0
Crushing strength (N)	1.9	1.2
Skeletal density of particles (kg/m ³)	4100	4700
AJI (%)	3.0	5.3
Porosity (%)	12.1	18.7
Specific surface area, BET (m ² /g)	<0.5	1.0

2.2. Oxygen carrier characterization

Physical and chemical characterization of the prepared oxygen carrier (Cu₃₄Mn₆₆-GR) was carried out by different techniques. The oxygen transport capacity, R_{OC} , was calculated as a function of the composition of the particles after the calcination step. The crushing strength was determined by measuring the force needed to fracture a particle using a Shimpo FGN-5X crushing strength apparatus. The crushing strength was taken as the average value of at least 20 measurements of particles with size diameter between 0.1 to 0.3 mm. In this case crushing strength represents the value of the mixture of oxygen carrier, char and ashes present in the fuel reactor. Attrition resistance was determined using a three-hole air jet attrition tester ATTRI-AS (Ma.Tec. Materials Technologies Snc) configured according to the ASTM-D-5757 standard [24]. The weight loss of fines was recorded after 1 h and 5 h of operation, respectively. Equation (3) shows the AJI value as the percentage of fines after a 5 h test.

$$AJI = \frac{m_{5h}}{m_s} \quad (3)$$

where m_{5h} is the mass of fines after 5 h collected from the attrition test rig, and m_s the mass of sample loaded into the apparatus (nominally 50 g). In the case of the CLOU process, the presences of ashes in the fuel reactor bed together with oxygen carrier particles make the AJI analysis somewhat difficult. After the AJI test an ICP analysis was carried out on the particles

to know the amount of Cu and Mn, from the filter and the bed, with this it is possible to know the ash present in the recovered and in the initially tested material.

The skeletal density was determined by He pycnometry in a Micromeritics AccuPyc II 1340. The surface area of the oxygen carrier was determined by the Brunauer-Emmett-Teller (BET) method by adsorption/desorption of nitrogen at 77 K in a Micromeritics ASAP-2020 (Micromeritics Instruments Inc.), and the pore volume were measured by Hg intrusion in a Quantachrome PoreMaster 33. The identification of crystalline chemical species was carried out by X-ray diffraction (XRD) pattern were collected by a Bruker D8 Advance X-ray powder diffractometer equipped with an X-ray source with a Cu anode working at 40 kV and 40 mA and an energy-dispersive one-dimensional detector. The diffraction pattern was obtained over the 2θ range of 10° to 80° with a step of 0.019° . The assignation of crystalline phases was performed on base of Joint Committee on Powder Diffraction Standards. DIFFRAC.EVA software supports a reference pattern database derived from Crystallography Open Database (COD) and The Powder Diffraction File (PDF) for phase identification. Quantitative XRD analysis of the crystalline phase was performed by Rietveld refinement using TOPAS software.

The main phase determined by XRD is $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$, so the mixed oxide was formed from the separate oxides during the oxygen carrier calcination step. Following the hopcalite derived oxygen carrier composition [21], to prepare the Cu₃₄Mn₆₆-GR particles a relation 2:1 of Mn to Cu was used. As the main phase obtained is $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$, the molar ratio between Cu:Mn in the active phase is 1:1, and thus it remains an excess of Mn_3O_4 in the particles. However, it reduces the oxygen transport capacity for CLOU, because it is difficult to regenerate Mn_3O_4 to Mn_2O_3 in oxygen carriers based exclusively on Mn oxide [17, 25, 26] due to the low temperature in the air reactor needed for regeneration. Therefore, the fresh oxygen carrier

particles used in this work had a composition of 72 wt.% of $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ and 28 wt.% of Mn_3O_4 determined by quantitative XRD analysis by TOPAS software.

2.3. Coals

Three different coals were used for CLOU experiments with $\text{Cu}_{34}\text{Mn}_{66}$ -GR oxygen carrier. A lignite from Teruel basin (Spain), two medium volatile bituminous coals from South Africa (MVB_SA) and Russia (MVB_R) were used with the aim to cover a wide range of coals. Main properties of selected coals (proximate and ultimate analysis and LHV) are shown in Table 2. Note the high ash and sulphur contents of lignite coal. The coal particle size used for this study was +0.2-0.3 mm.

Table 2. Properties of coals used in this work.

	Medium Volatile Bituminous (South Africa)	Medium Volatile Bituminous (Russia)	Lignite (Spain)
Proximate Analysis (wt.%)			
Moisture	4.2	5.8	12.6
Volatile matter	25.5	32.0	28.6
Fixed carbon	55.9	52.1	33.6
Ash	14.4	10.1	25.2
Ultimate Analysis (wt.%)			
C	69.3	65.8	45.4
H	3.9	4.6	2.5
N	1.9	2.0	0.6
S	0.9	0.5	5.2
O	5.4	11.3	8.5
LHV (kJ/kg)	25500	26600	16250
Ω_{coal} (kg O_2 /kg coal)	2.0	1.8	1.2

2.4. Experimental setup

A schematic view of the setup used is shown in Figure 1. The set-up was basically composed of two interconnected fluidized bed reactors –the air and fuel 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 in the system. A diverting solids valve located below the cyclone allowed for the measurement of the solids flow rates at any time. Therefore, this design allowed us to control and measure the solids circulation flow rate between both reactors. A detailed description of the continuous unit can be found in Abad et al. [10].

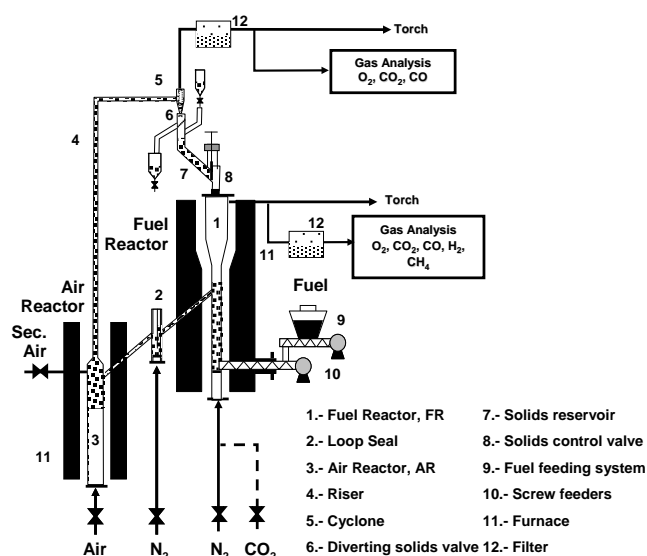


Figure 1. Schematic view of the ICB-CSIC-s1 unit.

The fuel reactor temperature was fixed at 850 °C, the gas flow was 250 L_N/h, corresponding to a gas velocity of ~ 0.15 m/s. Coal is fed by a double screw feeder at the bottom of the bed just above the fuel reactor distributor plate in order to maximize the time that the fuel and volatile matter is in contact with the bed material. A small N₂ flow (24 L_N/h) is introduced at the beginning of the screw feeder to avoid any possible reverse gas flow. Reduced oxygen carrier particles overflowed into the air reactor through fluidized bed loop seal, a N₂ flow of 90 L_N/h was introduced in the loop seal. Considering the optimized conditions determined for Cu₃₄Mn₆₆-GR [23], the oxidation of the carrier took place in the air reactor with a mixture of air/N₂ flow of 2100 L_N/h (14 vol% O₂ inlet, 8 vol% O₂ outlet). The operation temperature in

the air reactor was 800 °C. In addition, a secondary air flow (600 L_N/h) was introduced at the top of the bubbling bed to help particle entrainment.

The total oxygen carrier inventory in the system was 3 kg, being about 1 kg in the fuel reactor. CO, CO₂, H₂, CH₄ and O₂ concentration in the fuel reactor outlet stream and CO, CO₂ and O₂ from the air reactor were continuously recorded. For CH₄, CO and CO₂ a nondispersive infrared (NDIR) analyzers (Siemens Ultramat 23) were used; a paramagnetic analyzer (Siemens Ultramat 23 and Oxymat 6) was used for O₂ concentration measurement and a thermal conductivity detector (Siemens Calomat 6) was used for H₂.

2.5. Experimental planning

Table 3 shows a compilation of the main variables used in each test. Totally, the same batch of oxygen carrier particles was used during 50 h of hot fluidization conditions, whereof 25 h with coal combustion. The temperature in the fuel reactor was maintained at 850 °C. The temperature in the air reactor was fixed at 800°C. To obtain high values of the oxygen carrier coal ratio the coal feeding rate was fixed at low values and high solids circulation rates were used. The coal feeding rate was varied as a function of the coal type between 0.032 and 0.046 kg/h, which corresponds to a power input between 230 and 340 W_{th}. The solid circulation rate was varied between 8 and 20 kg/h. With these values the oxygen carrier to coal ratio, ϕ , was varied from 4.8 to 11.1. The oxygen carrier to fuel ratio (ϕ) was defined by the following equation [27]:

$$\phi = \frac{\text{Oxygen supplied by the oxygen carrier}}{\text{Oxygen demanded by the fuel for full combustion}} \quad (4)$$

Table 3. Main Data for Experimental Tests in the CLOU Prototype

Coal	Test	\dot{m}_{OC} (kg/h)	\dot{m}_{coal} (kg/h)	Power (W)	$m_{S,FR}$ (kg)	ϕ	m_{FR}^* (kg/MW _{th})
South Africa	S01	20	0.032	230	1.2	8.3	5400
South Africa	S02	18	0.032	230	1.2	7.7	5400
South Africa	S03	14	0.032	230	1.2	6.6	5400
South Africa	S04	9	0.032	230	1.2	5.2	5400
Russia	R01	20	0.046	340	1.2	7.6	3600
Russia	R02	18	0.046	340	1.2	6.9	3600
Russia	R03	14	0.046	340	1.2	5.4	3600
Russia	R04	12	0.046	340	1.2	4.8	3600
Lignite	L01	18	0.035	160	0.94	11.1	5600
Lignite	L02	15	0.035	160	0.94	8.6	5600
Lignite	L03	13	0.035	160	0.94	7.4	5600
Lignite	L04	8	0.035	160	0.94	4.9	5600

3. Data evaluation

To analyze the performance of the CLOU process, the combustion efficiency in the fuel reactor and the CO₂ capture efficiency were calculated. Calculations are based on the molar flow of every gas analyzed, F_i , which is determined from the measured concentration. Mass balances were checked and a closing about 95 % was found for the carbon balance.

The combustion efficiency in the fuel reactor was calculated through the ratio between the oxygen required to fully burn unconverted gases (CH₄, CO and H₂) at the fuel reactor exit and the oxygen demanded by coal converted in the fuel reactor. Thus, the oxygen demanded by

the carbon bypassed to the air reactor, $F_{CO_2,AR}$, is subtracted to the oxygen demanded by coal in the denominator. Therefore, the combustion efficiency in the fuel reactor was calculated as:

$$\eta_{comb,FR} = 1 - \frac{4F_{CH_4,outFR} + F_{CO,outFR} + F_{H_2,outFR}}{\frac{1}{M_{O_2}} \cdot 2\Omega_{coal} \dot{m}_{coal} - 2F_{CO_2,outAR}} \quad (5)$$

The CO₂ capture efficiency, η_{CC} , was defined as the fraction of the carbon initially present in the coal fed in which is actually at the outlet of fuel reactor as CO₂. This is the actual CO₂ captured in the CLOU system; the remaining is exiting in the air reactor outlet.

$$\eta_{CC} = 1 - \frac{F_{CO_2,outAR}}{F_{CO_2,outFR} + F_{CO,outFR} + F_{CH_4,outFR} + F_{CO_2,outAR}} \quad (6)$$

The carbon capture efficiency depends on the conversion of char in the fuel reactor. The conversion of char in the fuel reactor, $X_{char,FR}$, was calculated considering the carbon contained in the coal fed remaining in the char, i.e. fixed carbon, and the carbon not converted in the fuel reactor, which exits as CO₂ from the air reactor.

$$X_{Char,FR} = \frac{f_{C_{Fix}} \cdot \dot{m}_{coal} - M_C \cdot F_{CO_2,outAR}}{f_{C_{Fix}} \cdot \dot{m}_{coal}} \quad (7)$$

4. Results

4.1. Combustion and CO₂ capture efficiency

To investigate the effect of the oxygen carrier to fuel ratio in the CLOU process for the combustion of different rank coals, several test were done in a CLOU continuous unit, ICB-CSIC-s1. As oxygen carrier was used the material Cu34Mn66-GR prepared by granulation. The effect of the coal rank and the oxygen carrier to fuel ratio on the combustion and CO₂

capture efficiencies were investigated. The oxygen carrier to coal ratio, ϕ , was varied from 4.8 to 11. A total of 50 h of operation were done in the CLOU continuous unit.

The composition of the gases at the fuel and air reactor outlet streams were determined for every experimental test. As example, in Figure 2 it can be seen the gas concentration (dry basis) measured for experiments carried out with Medium Volatile Bituminous coal from Russia. Different oxygen carrier to fuel ratios were tested, and at least 50 min of stable condition were considered.

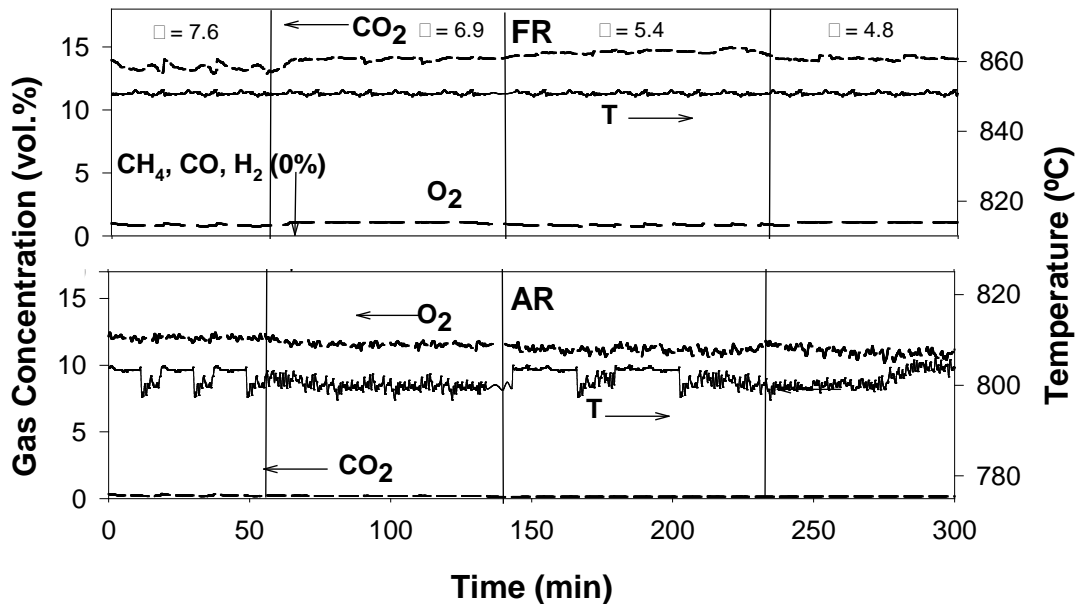


Figure 2. Evolution of the gas composition in the air and fuel reactor as oxygen carrier to fuel ratio was varied for Russian MVB coal. Experimental tests R01-R04. $T_{FR} = 850 \text{ }^\circ\text{C}$; $\dot{m}_{coal} = 0.046 \text{ kg/h}$.

When the solid circulation rate was varied to change the oxygen carrier to fuel ratio, a period of transition appear and the next stable steady state was reached in around 10 min. At steady state, the temperature and gas concentration at the outlet stream of both reactors were stable during the whole test. The carbon and oxygen mass balance were accurate (closing $> 95\%$). Therefore, the loss of elutriated char particles from the fuel reactor was negligible. Also, when

the steady state was reached, the oxygen transferred in the fuel reactor from the oxygen carrier to the fuel was equal to the oxygen recovered in the air reactor by the oxygen carrier oxidation with air.

As it can be seen in Figure 2, there were not unburnt products in the fuel reactor outlet stream. This result was observed for all coal tested. The only gases present in the fuel reactor outlet were CO₂, H₂O, O₂ and N₂ (introduced as fluidizing agent). Thus, it can be observed in Figure 2 that the volatiles of the coal were fully burnt to CO₂ and H₂O in the fuel reactor by reaction with the O₂ released by the Cu-Mn mixed oxide reduction. Moreover, the rate of oxygen release was enough to supply an excess of O₂(g) that exit with the combustion gases in the fuel reactor stream. Small fractions of SO₂ and NO were present in the gases coming from sulphur and nitrogen of the different coals. However, these compounds were not evaluated in this work.

Combustion and CO₂ capture efficiencies were analyzed for all the coals studied, see Figure 3(a). Complete combustion to CO₂ and H₂O of coal in the fuel reactor was found for all coals and in all experimental conditions used. However, the coal rank affects the CO₂ capture efficiency. For lignite, CO₂ capture efficiency was very high (near 100%) and higher than for both medium volatile bituminous coals. Similar CO₂ capture efficiencies were obtained for both MVB coals of the same rank, being slightly higher for Russian coal (MVB_R) due to the lower amount of fixed carbon in its composition with respect to the South African coal (MVB_SA); see Table 2.

In order to change the value of oxygen carrier to fuel ratio and maintain the oxygen carrier inventory in the fuel reactor, the oxygen carrier circulation rate was varied. It was observed with Cu-based oxygen carrier that an increase in the oxygen circulation rate had a negative effect in the CO₂ capture effect due to the increase the unconverted char transferred to the air

reactor [10]. However, for both medium volatile coals a maximum was found. At low oxygen carrier to fuel ratios the CO₂ capture efficiency increased, reaching a maximum with a further decrease of the CO₂ capture efficiency with ϕ . At such conditions, is highly relevant the improvement of the oxygen uncoupling process as the oxygen carrier is less reduced [22, 23]. Both coals have very similar characteristics and for both the maximum of CO₂ capture efficiency was close. For South African coal the maximum CO₂ capture occurred around values of $\phi=6.6$ and from Russia coal $\phi=5.4$, see Figure 3(a). With ϕ higher than these values, the CO₂ capture efficiency decrease due to the fact that it is more important the increase of the amount of unburnt char transferred to the air reactor than the increase of the O₂ available in the fuel reactor, as it was the case for Cu-based material [10].

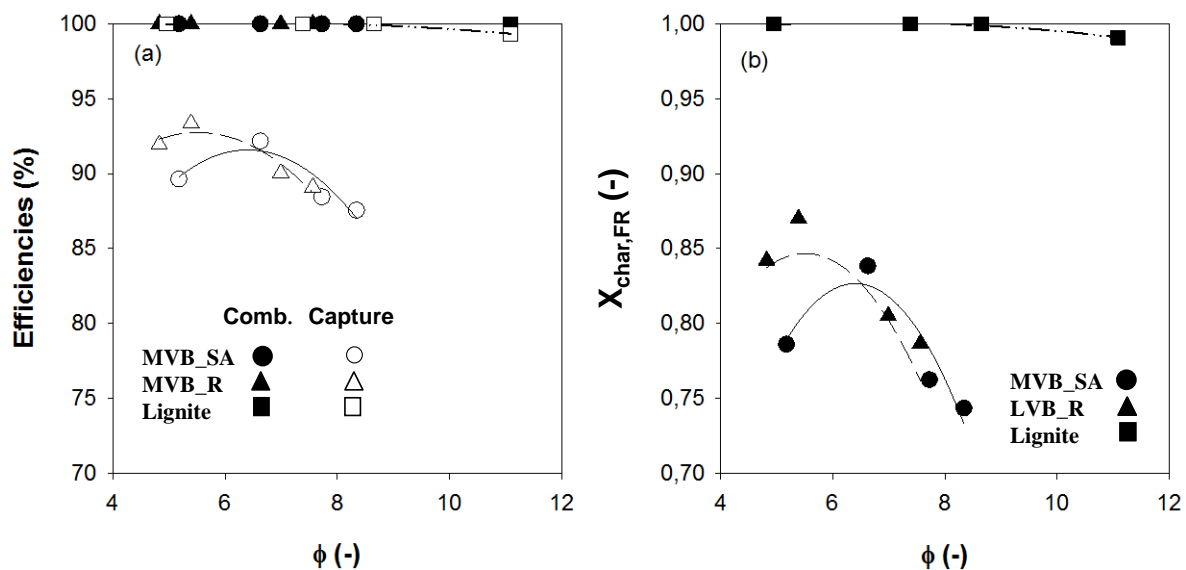


Figure 3. (a) Combustion efficiency in the fuel reactor and CO₂ capture efficiency and (b) char conversion, as a function of the fuel reactor temperature obtained with different coals.

In Figure 3(b) it can be seen the evolution with ϕ of char conversion in fuel reactor for the different coals. With ϕ values lower than the maximum, when increase the oxygen carrier to fuel ratio, increase the char conversion because the oxygen carrier is able to release more

gaseous oxygen. However at the same time when ϕ increases the residence time of char particles in fuel reactor decreases and this increases the amount of char transferred to the air reactor, and thus CO₂ capture efficiency decreases. At values after the maximum this effect is more important than the increase of the oxygen carrier reactivity and the CO₂ capture decreases.

On the other hand, for high reactive coals, as lignite, the oxygen carrier to coal ratio has lower relevance, as it can be seen in Figure 3(a). This coal is so reactive that in a wide interval of oxygen carrier to fuel ratios the CO₂ capture efficiency was 100%. It is necessary to reach ϕ values higher than 10 to observe a slight decrease of the CO₂ capture efficiency, which decreases to 99.3%. This is due to the high reactivity of the lignite char [10]. Thus, it is necessary to have a big decrease of the char residence time to observe a decrease in the char conversion and observe an increase of the unbunrt char transferred to the fuel reactor, see Figure 3(b). Probably, with lower oxygen carrier inventories and residence times of the solids in the fuel reactor, that are needed to obtain CO₂ capture efficiencies lower than 100%, it would be also possible to observe a maximum in the CO₂ capture efficiency as a function of ϕ [28].

Regarding the maximum values of CO₂ capture obtained for the different coals remark that were higher than 90%, and a 100% for Lignite. To increase the maximum values of CO₂ capture efficiencies over 95% for both medium volatiles bituminous coals it would be necessary to increase the fuel reactor temperature or to use a carbon stripper that recovers the unbunrt char that exits from the fuel reactor to the air reactor, and return it to the fuel reactor to burn the char completely [11].

4.2. Oxygen carrier attrition resistance

After 50 h of continuous operation burning different rank coals the oxygen carrier particles were analyzed to evaluate their durability. The joint evaluation of the AJI parameter and the crushing strength is a good indicator to know the resistance of the particles [29]. It is very significant that the value of crushing strength of the particles was higher than 1, more specifically 1.2, which is a requirement for suitable operation of an oxygen carrier in fluidized beds [29, 30]. In previous works with a Cu-based oxygen carrier in a CLOU continuous unit, the crushing strength of the particles showed a very significant decrease of this value below values of 1 after 40 h of operation time [15].

Considering this good value of crushing strength of the particles, these were analyzed by an ASTM standard D5757 method [24] to know their attrition resistance. The Cu₃₄Mn₆₆-GR fresh particles showed an AJI value of 3%, after 50h of operation in the continuous unit the AJI increase to 7.2, see Table 1. This value of the AJI test is slightly higher than the reference value to select a scalable material for FCC process ($AJI \leq 5\%$) [29].

In a previous work, the same oxygen carrier was used in the continuous CLOU unit with other operation condition, different fuel reactor temperature and ϕ values. For this batch of oxygen carrier particles the AJI test together with the crushing strength analysis were carried out. The AJI value after 30 h of operation burning subbituminous Chilean coal with low values of oxygen carrier to fuel ratios ($\phi < 3$) was 15, and the crushing strength of the particles was 0.8N.

This clearly indicates the effect of the chemical stress in the attrition rate of oxygen carriers. At low oxygen carrier conversion by the redox process, the attrition rate clearly decreases: $AJI = 7.2$ at $\phi > 4$ and $AJI = 15$ when $\phi < 3$. These values correspond to $\Delta X_{red} < 0.25$ and $\Delta X_{red} < 0.33$ respectively. Therefore, continuous operation with values of oxygen carrier to fuel

ratio, ϕ , higher than 4, reduces the chemical stress and it is beneficial for the lifetime of the oxygen carrier particles for CLOU process.

4.3. Oxygen carrier characterization

Solid samples from the air and fuel reactor after 50 h of continuous operation in the ICB-CSIC-s1 unit were characterized by different techniques. The main properties of the used oxygen carrier particles can be seen in Table 1. It can be seen that the used sample porosity has been increased from 12.1 to 18.7% and also appeared an increase in the specific surface area, BET. These changes in the particles structures could be related with the decrease on the crushing strength from 1.9 to 1.2.

The XRD analysis of the particles used shows that the main phase is $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$, equal than in the fresh ones. Together to the $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ were detected Mn_3O_4 and a small amount of Mn_2O_3 . Mn_2O_3 was also detected in the experiments in a batch fluidized bed reactor for solid fuels by Adánez-Rubio et al. [22]. Also, the XRD analysis of the samples showed that the amount of $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ was stable after 50h of continuous operation.

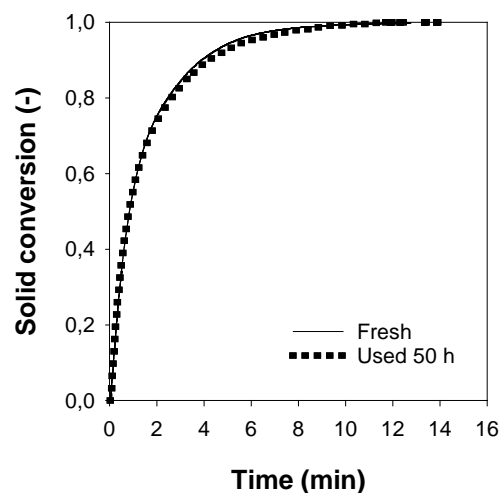


Figure 4. Conversion vs time curves for oxygen uncoupling reaction for fresh and used particles. Reduction in N_2 and oxidation in air at 950 °C in TGA.

Reactivity of oxygen uncoupling step for the fresh and used particles were determined in a TGA at 950 °C, using N₂ during the reduction and air for the oxidation. The reactivity data was obtained from the variation of mass of the sample during the redox cycles as a function of time. The oxygen carrier reduction conversion was calculated as $X_{red} = (m_{ox}-m)/R_{OC}\cdot m_{ox}$, where m is the mass of sample at each time, m_{ox} is the mass of the fully oxidized sample, and R_{OC} is oxygen transport capacity. Figure 4 shows the oxygen carrier conversion curves for the oxygen release period for fresh and used samples. It can be seen that both the reduction reactivity and the R_{OC} were maintained by the used oxygen carrier particles, even when a high sulphur content coal (5.2 wt.% S in lignite) was evaluated in the CLOU continuous unit.

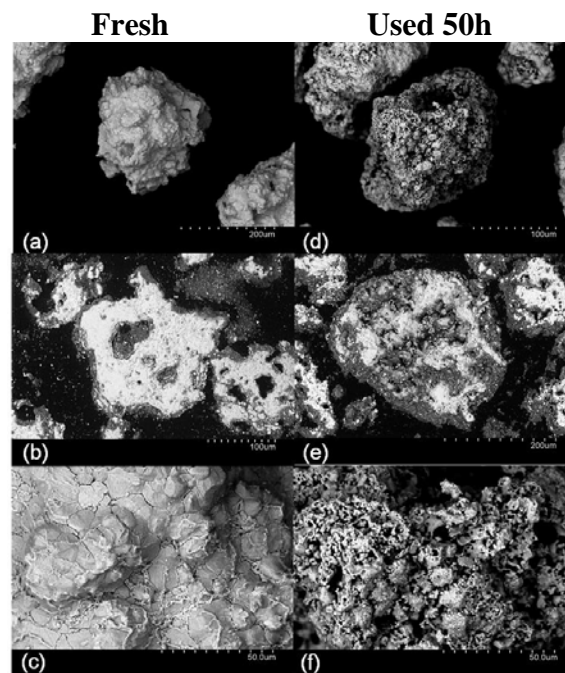


Figure 5. SEM images of fresh (left) and used particles after 50 h in the continuous CLOU unit: (a, d) image of the particles; (b, e) cross section of a particle; (c, f) surface image of the oxygen carrier particle.

Figure 5 shows the SEM images of fresh and used particles after 50 h of continuous operation. In Figure 5 (c and f) it can be seen that after the combustion of coal in the continuous unit, a granular shape was formed in the surface of the particles. This behaviour has been observed previously by Adánez-Rubio et al. [22] using the Cu₃₄Mn₆₆-GR oxygen

carrier in two batch fluidized bed reactors. They found that this change was increased by the increase of the reduction conversion of the particles and could be related with the chemical stress. In Figure 5(f) it can be seen that this change is more pronounced than in previous work where the oxygen carrier was only tested in a batch fluidized bed reactor.

5. Conclusions

The performance of the combustion of different rank coals was carried out in a CLOU continuous unit with a Cu-Mn mixed oxide as oxygen carrier (Cu₃₄Mn₆₆-GR) prepared by spray granulation in a spouted bed system. The effect of the coal rank and the oxygen carrier to fuel ratio on the combustion and CO₂ capture efficiencies were investigated. The oxygen carrier to coal ratio, ϕ , was varied from 4.8 to 11.

Complete combustion of all coals to CO₂ and H₂O in the fuel reactor was achieved. Regarding the maximum values of CO₂ capture obtained for the different coals, remark that CO₂ capture efficiency were higher than 90% for both medium volatile bituminous coals, and a 100% for Lignite. For both medium volatile coals a maximum in the CO₂ capture efficiency as a function of the oxygen carrier to fuel ratio was reached. Both coals have very similar characteristics and for both the maximum of CO₂ capture efficiency were close. For South African coal the maximum CO₂ capture is around values of $\phi=6.6$ and from Russian coal $\phi=5.4$. With ϕ higher than these values, the CO₂ capture efficiency decrease due to the fact that it is more important the increase of the amount of unburnt char transferred to the air reactor than the increase of the O₂ available in the fuel reactor.

For high reactive coals, as lignite, the oxygen carrier to coal ratio has lower relevance. This coal is so reactive that in a broad interval of oxygen carrier to fuel ratios the CO₂ capture

efficiency was 100%. It is necessary to reach ϕ values higher than 10 to observe a slight decrease of the CO₂ capture efficiency, decreasing to 99.3%.

After 50 h of continuous operation it is very significant that the value of crushing strength of the particles was higher than 1, more specifically 1.2. Moreover, AJI value after 50 h of operation was 7.2, which is acceptable as a CLOU scalable material. Therefore, the continuous operation with values of oxygen carrier to fuel ratio, ϕ , higher than 4 is beneficial for the lifetime of the oxygen carrier particles for CLOU process. This clearly indicates the effect of the chemical stress in the attrition rate of oxygen carriers. At low oxygen carrier conversion by the redox process the attrition rate clearly decreases: AJI = 7.2 at $\phi > 4$ and AJI = 15 when $\phi < 3$. These values correspond to $\Delta X_{\text{red}} < 0.25$ and $\Delta X_{\text{red}} < 0.33$ respectively.

In summary, the oxygen carrier has shown a very good behavior in the combustion of coals of different rank. CO₂ capture efficiencies were higher than 90% at low fuel reactor temperatures (850 °C) and complete combustion of the coals to CO₂ and H₂O were obtained. Moreover, the crushing strength found and the AJI test value in the used particles is a suitable value, so it can be concluded that these particles are a good oxygen carrier for coal combustion by CLOU process.

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6. Nomenclature

Symbols

F_i	Molar flow of compound i (mol/s)
$f_{C,fix}$	Mass fraction of fix carbon in coal (-)
M_i	Atomic or molecular weigh of i elements or compound (kg/mol)
m	Mass of the sample at each time in TGA (kg)
\dot{m}_{coal}	Mass-based flow of coal fed-in to the fuel reactor (kg/s)
\dot{m}_{OC}	Solids circulation rate (kg/s)
m_{ox}	Mass of the oxygen carrier sample fully oxidized (kg)
$m_{s,FR}$	Mass of solids in the fuel reactor (kg)
R_{OC}	Oxygen transport capability (-)
$X_{Char,FR}$	Char conversion (-)

Greek letters

η_{CC}	Carbon capture efficiency (-)
$\eta_{comb,FR}$	Combustion efficiency in the fuel reactor (-)
ϕ	Oxygen carrier to fuel ratio (-)
Ω_{coal}	Stoichiometric mass of O_2 to convert 1 kg of coal (kg/kg)

Acronyms

AR	Air reactor
BET	Brunauer-Emmett-Teller
CLC	Chemical Looping Combustion

CLOU Chemical Looping with Oxygen Uncoupling

FCC Fluid catalytic cracking

FR Fuel reactor

OC Oxygen carrier

TGA Thermogravimetric analyzer

XRD X-ray diffractometer

Subscripts

outAR Outlet stream from air reactor

outFR Outlet stream from fuel reactor

7. References

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