Coal combustion with a spray granulated Cu-Mn mixed oxide for the Chemical Looping Oxygen Uncoupling (CLOU) process

Iñaki Adánez-Rubio, Alberto Abad*, Pilar Gayán, F. García-Labiano, Luis F. de Diego, Juan

Adánez

Instituto de Carboquímica (ICB-CSIC), Dept. of Energy & Environment, Miguel Luesma

Castán 4, 50018, Zaragoza, Spain

**Corresponding Author: abad@icb.csic.es*

Abstract

The Chemical Looping with Oxygen Uncoupling (CLOU) process is a form of Chemical Looping Combustion (CLC) technology that enables the combustion of solid fuels by means of oxygen carriers that release gaseous oxygen in the fuel reactor, i.e. with oxygen uncoupling capability. In recent years, tests have found several Cu-based, Mn-based and mixed oxide oxygen carriers with suitable properties for the CLOU process. Among them, Cu-Mn mixed oxides show high reactivity and high O₂ equilibrium concentration at temperatures of interest for coal combustion. In this work, proof of concept was demonstrated by burning coal with Cu-Mn mixed oxides in a 1.5 kW_{th} CLOU unit for the first time. The effect of fuel reactor temperature, solids circulation flow, fluidization agent in the fuel reactor (inert N₂ or steam as gasifying agent), and excess air in the air reactor on combustion efficiency and CO₂ capture rate was analysed. The results showed that high combustion efficiency and CO₂ capture are feasible using this material at relatively low fuel reactor operating temperatures. Therefore, the developed Cu-Mn mixed oxide was a suitable material for use as an oxygen carrier for the CLOU combustion of solid fuels. Optimum operating conditions were determined for this oxygen carrier with regard to the oxygen circulation rate and air reactor conditions for the regeneration of the oxygen carrier.

Keywords: CO₂ capture; coal; CLOU; mixed oxide; copper; manganese.

1 Introduction

The Chemical Looping with Oxygen Uncoupling (CLOU) process is a form of Chemical Looping technology for the combustion of solid fuel with inherent CO₂ separation using oxygen carriers. CLOU technology may be particularly suitable for solid fuels such as coal. This process uses an oxygen carrier that is capable of generating gaseous oxygen at high temperatures, enabling the solid fuel to react in the fuel reactor with the gaseous oxygen generated by the oxygen carrier. To be suitable for the CLOU process, oxygen carriers need to be capable of generating gaseous oxygen by decomposition in the fuel reactor, but also to be regenerated by oxidation with air in the air reactor. Three metal oxide systems have suitable properties for use as oxygen carriers in the CLOU process: CuO/Cu₂O, Mn₂O₃/Mn₃O₄ and Co₃O₄/CoO [1]. Reviews of CLOU materials were conducted by Mattisson [2] and Imtiaz [3], which included Cu-based oxygen carriers [4-6] and oxygen carriers based on mixed oxides: Cu-Mn [7-9], Mn-Fe [10-12], Mn-Si [13], Mn-Fe-Si [14] and Ca-Mn based perovskites [15-17]. Most of these works focused on the evaluation of the materials at an early stage (e.g. evaluation in TGA or tests in batch reactors), and few materials were found to show the properties required for use in a CLOU unit with solid fuels, namely Cu-Mn-based and Ca-Mn-based materials [17, 18].

Among the more promising materials, a Cu-based oxygen carrier (prepared by spray drying with 60 wt.% CuO and 40 wt.% MgAl₂O₄ as inert) was first tested by burning coal and biomass in a 1.5 kW_{th} continuous CLOU unit [18-22] due to its high reactivity and good oxygen uncoupling capability [23]. Mn-based oxygen carriers showed a lower oxygen transport capacity but were able to work at lower temperatures because the Mn₂O₃/Mn₃O₄

system has a higher equilibrium partial pressure of oxygen than CuO/Cu₂O. Also, materials containing manganese are more economical than those containing copper. Nevertheless, Mn-based materials are not suitable for industrial use because it is necessary to decrease the air reactor temperature to 800 °C in order to regenerate the Mn₃O₄ to Mn₂O₃, which decrease the kinetics of the process [24-26]. Consequently, Cu-based oxygen carriers are excellent materials for oxygen uncoupling, but they are expensive owing to the high Cu-content required, whereas Mn-based oxygen carriers are not suitable for CLOU.

In the development of materials based on Cu-Mn mixed oxides, attention was initially focused on overcoming the problems derived from the use of either Cu or Mn-based oxygen carriers. Cu-Mn mixed oxides have great potential because their high reactivity and thermodynamic properties causes them to release O₂ at lower temperatures than those needed for CuO/Cu₂O. Depending on the mixed oxide phase formed during preparation of the oxygen carrier, either CuMn₂O₄ [8, 27] or Cu_{1.5}Mn_{1.5}O₄ [28-30], oxygen release can occur by means of two different reactions:

There are some works focused on the study and development of Cu-Mn materials for the CLOU process. Pour et al. [7] studied five different Cu-Mn oxygen carriers prepared by freeze drying with a CuO load of between 5 and 61 wt.%. They found that Cu-Mn materials were able to release gaseous O₂ at temperatures above 700 °C. Hosseini et al. [8] studied different oxygen carriers with varying proportions of Mn and Cu prepared by co-precipitation. They found that a ratio of 75 wt.% of Mn₃O₄ and 25 wt.% CuO in the oxygen carrier gives the best properties for the CLOU process. Also, the O₂ concentration released by the active phase CuMn₂O₄ in the oxygen carrier particles decreased with conversion to CuMnO₂, see reaction

(1). Azad et al. [28] studied Cu-Mn oxygen carriers prepared by extrusion with 69.2 wt.% Mn_2O_3 and 30.8 wt.% CuO. They observed that the Cu-Mn oxygen carrier behaved well when burning CH_4 , but that CO was present in the reactor outlet gas stream as an unburnt product.

Recently, a Cu-Mn material derived from a commercially available hopcalite, Carulite 300®, was studied for use as an oxygen carrier by Adánez-Rubio et al. [29] based on a $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ mixed oxide. Hopcalite can be prepared by different methods at laboratory and industrial scale to be used for the catalytic oxidation of CO at ambient temperature [31]. They found that the mixed oxide derived from hopcalite was capable of releasing O_2 at low temperatures (800 °C), which allowed the complete conversion of coal to CO_2 and H_2O in a batch fluidized bed reactor. However, the hopcalite-derived oxygen carrier showed a broad reduction in particle crushing strength with operating time. Therefore, the oxygen carrier derived from the commercial material required the improvement of its physical properties in order to become suitable for the CLOU process.

In short, Cu-based and Cu-Mn-based materials show sufficiently high reactivity for the oxygen uncoupling reaction. A Cu-based material was tested in a CLOU unit burning solid fuels and excellent results were obtained with regard to CO_2 capture and combustion efficiency [18-21]. However, the mechanical strength and physical stability of these materials was eventually reduced, which would result in high attrition rates and low lifetime values for these oxygen carriers [22]. Currently, the main efforts in the development of the CLOU process are being made to find an oxygen carrier with the following characteristics: high oxygen release rate and a low attrition rate.

In this sense, the suitability of a new Cu-Mn oxygen carrier named Cu34Mn66-GR (34 wt.% CuO and 66 wt.% Mn_3O_4), prepared by spray granulation, was evaluated for use in the CLOU process [30]. This oxygen carrier showed sufficiently high reactivity for oxygen release, allowing complete combustion of coal during its preliminary evaluation in a batch fluidized

bed reactor. This material also demonstrated good fluidization behaviour, presenting no agglomeration problems and with a low attrition rate in repeated N₂-air redox cycles (0.005 %/h, which corresponds to a particle lifetime of 20000 h). The attrition rate was 18 times lower than the value obtained in the same batch fluidized reactor using the hopcalite-derived oxygen carrier [29]. According to recommendations made in a previous work [32], the low attrition rate and ASTM attrition test index (AJI) value, together with the stable crushing strength of the particles, made this Cu-Mn oxygen carrier suitable for operation in fluidized bed reactors. Adánez-Rubio et al. [30] concluded that the granulated Cu-Mn oxygen carrier was a promising material to be scaled-up for coal combustion in a CLOU unit. Nevertheless, the proof of concept of this material in a CLOU unit would be a key stage for the evaluation and subsequent development of oxygen carrier material: preparation by a scalable industrial method, i.e. granulation, and testing in an experimental unit.

The aim of this work was to investigate the performance of the Cu-Mn mixed oxide oxygen carrier prepared by spray granulation in a CLOU system for the first time. The combustion of coal was carried out in a 1.5 kW_{th} CLOU unit. The effect of fuel reactor temperature, residence time of solids in the fuel reactor, coal feed rate, fluidization agent and oxygen concentration in the air reactor on the CO₂ capture and combustion efficiency was investigated. A temperature range of 800-875 °C was used for the combustion. The results obtained were analysed and discussed in order to understand the CLOU process burning coal with the Cu₃₄Mn₆₆-GR oxygen carrier, in order to facilitate the scale-up of the process.

2 Experimental section

2.1 Materials

2.1.1 Oxygen carrier

The oxygen carrier particles, based on a Cu-Mn mixed oxide, were manufactured at the Instituto de Carboquímica (ICB-CSIC) by means of spray granulation in a spouted bed system (ProCell LabSystem, Glatt). Powders of Mn_3O_4 (STREM, PRS) and CuO (Panreac, PRS) were used as precursors, and these were mixed at a proportion of 34 wt.% CuO and 66 wt.% Mn_3O_4 . The atomic ratio between the Mn and Cu particles was 2:1 in order to achieve a composition similar to that of the hopcalite-derived oxygen carrier [29]. After their formation in a spouted laboratory unit, the particles were calcined for 2 h at 1125 °C and sieved in the +0.1–0.3 mm interval. The oxygen carrier was named Cu₃₄Mn₆₆-GR and its main properties are shown in Table 1 [30].

2.1.2 Oxygen carrier characterization

Chemical and physical characterization of the prepared particles was performed using different methods. A Shimpo FGN-5X was used to measure crushing strength, defined as the force needed to fracture a particle. Crushing strength was taken as the average value of at least 20 measurements of particles with a size diameter of between 0.1 and 0.3 mm. He picnometry was used to determine skeletal density in a Micromeritics AccuPyc II 1340. BET specific surface area was determined by adsorption/desorption of nitrogen at 77 K in a Micromeritics ASAP-2020 (Micromeritics Instruments Inc.). Mercury intrusion in a Quantachrome PoreMaster determined pore volumes. An X-ray diffraction (XRD) pattern was collected by a Bruker D8 Advance X-ray powder diffractometer. Quantitative XRD analysis of the crystalline phase was performed by Rietveld refinement using TOPAS software.

The main phase determined by XRD was $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ with an excess of Mn_3O_4 remaining in the particles. The mixed oxide was formed from the individual oxides during calcination step. The Cu:Mn atomic ratio was 1:1 in the oxygen carrier active phase due to the fact that the main phase formed was $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$. On the other hand, regeneration of Mn_3O_4 to Mn_2O_3 became difficult because the necessary air reactor temperature was near to 800 °C [25, 33, 34]. The observed oxygen transport capacity was 4.0 wt.%, which was below the theoretical value of 4.5 wt.% following reaction (2) and considering Mn_3O_4 as an inert for the CLOU process [30].

2.1.3 Solid fuel

A Chilean subbituminous coal from the Mina Invierno on Riesco Island, Chile, was used for CLOU combustion with the oxygen carrier. Ultimate and proximate coal analyses are shown in Table 2. Coal particles of +200-300 μm in size were used in the experimental work.

2.2 Experimental set-up

Figure 1 is a diagram of the experimental 1.5 kW_{th} CLOU unit. The CLOU unit comprised two fluidized bed reactors -the air and fuel reactors- connected by a fluidized loop seal. A riser was used to transport solids from the air to the fuel reactor. A cyclone was used to separate solids from the air reactor outlet, which were recirculated to the fuel reactor by a solids circulation rate control valve. A diverting solids valve located below the cyclone was used to measure solids circulation flow rates at any time during operation. This system made possible to measure and control the solids circulation flow rates between reactors. Coal was fed into the bottom of the bed by a system comprising a series of two screw feeders, designed to prevent the pyrolysis of the coal before it entered the fuel reactor. Thus, the first screw feeder, which was directly connected to the fuel reservoir, allowed the coal feed rate to be controlled by varying its rotational speed. The second screw feeder was operated at high rotational speed to minimize the residence time of coal inside it. In addition, this screw feeder

was water-cooled to prevent the undesired heating of coal in the feeding system. A detailed description of the continuous unit can be found in Abad et al. [18].

The fuel reactor was fluidized with N₂ for an accurate analysis of the results [18]. In some cases, steam was added to evaluate the effect of the fluidizing medium. The gas flow was 250 NI/h, corresponding to a gas velocity of ~0.15 m/s. To avoid reverse gas flow in the screw feeders, a small N₂ flow (24 NI/h) was introduced at the beginning of the faster screw feeder. A U-shaped fluidized bed loop seal was used to prevent the gas from mixing between reactors while allowing the transport of the oxygen carrier to the air reactor. The loop seal was fluidized with a N₂ flow of 90 NI/h. The oxygen carrier was regenerated in the air reactor with an air flow of 2100 NI/h, which was fed through the distributor plate. In some experiments, the gas flow to the air reactor was a mixture of N₂ and air to analyse the effect of the oxygen concentration in the oxygen carrier regeneration. To improve particle entrainment from the bottom bed to the riser, a secondary air flow (600 NI/h) was introduced into the upper part of the air reactor.

The total inventory of oxygen carrier in the unit was 2.8 kg, of which 0.7 kg corresponded to the fuel reactor. The concentration of CO, CO₂, H₂, CH₄ and O₂ in the fuel reactor outlet stream and of CO, CO₂ and O₂ exiting from the air reactor were continuously recorded. Non-dispersive infrared (NDIR) analysers (Siemens Ultramat 23) were used for CH₄, CO and CO₂; a paramagnetic analyser (Siemens Ultramat 23 and Oxymat 6) was used to measure O₂ concentration; and a thermal conductivity detector (Siemens Calomat 6) was used for H₂.

2.3 Experimental planning

Table 3 shows the main operating variables used in the different experimental tests. The same batch of oxygen carrier particles were used for a total of 62 h under hot fluidization conditions, 30 h of which involved coal combustion.

Chilean subbituminous coal was fed into the fuel reactor, and the combustion efficiency of coal in the CLOU system was analysed. The fuel reactor temperature was varied from 800 °C to 875 °C (T01-T05). The temperature in the air reactor was maintained at around 800 °C. The coal feed rate was in the range of 65-175 g/h, which corresponded to a power input range of 340-915 W_{th} in tests T06-T09, whereas the solids circulation rate was varied from 2.4 to 13.8 kg/h (T10-T13). The effect of the fluidization agent was studied using steam (T14). Finally, the oxygen concentration available in the air reactor, and its effect on combustion and CO₂ capture efficiencies, was also studied (T15-T18). Oxygen concentration determines the air excess ratio, λ , calculated according equation (3).

$$\lambda = \frac{\text{Oxygen flow in air}}{\text{Oxygen demand of the fuel for full combustion}} = \frac{0.21F_{\text{air}}M_{\text{O}_2}}{\Omega_{\text{coal}}\dot{m}_{\text{coal}}} \quad (3)$$

The fuel reactor temperature in tests T01-T18 was higher than the air reactor temperature. This condition could be achieved in a CLOU unit because the overall combustion process in the fuel reactor is exothermic [7, 28-30]. However, depending on the energy integration of a CLC unit, the temperature in the fuel and air reactors could be approximately the same [35]. To evaluate this condition, the temperature in the air reactor was increased to 850 °C (T19). In all the experiments, the oxygen carrier to fuel ratio, ϕ , defined by equation (4), varied between 0.6 and 2.9. The oxygen carrier to fuel ratio was defined by the following equation:

$$\phi = \frac{\text{Oxygen supplied by the oxygen carrier}}{\text{Oxygen demand of the fuel for full combustion}} = \frac{R_{\text{OC}}\dot{m}_s}{\Omega_{\text{coal}}\dot{m}_{\text{coal}}} \quad (4)$$

2.4 Data evaluation

Combustion and CO₂ capture efficiencies were calculated to analyse the performance of the CLOU process. The measured concentration of every gas analysed was used to calculate their molar flow, F_i , from which the mass balances were calculated. Carbon and oxygen mass

balances were checked, with closure at about 95 %. Unbalanced carbon was assumed to be present in the unconverted char elutriated from the fuel reactor, $F_{C,elut}$.

Combustion efficiency in the fuel reactor, $\eta_{comb,FR}$, was calculated as a function of the oxygen required to burn the unconverted gases in the fuel reactor outlet (CH_4 , CO and H_2) and the oxygen demand of the coal converted in the fuel reactor (coal fed minus elutriated carbon, $F_{C,elut}$, and carbon bypassed to the air reactor, exiting as CO_2 , $F_{CO_2,outAR}$). Thus, the combustion efficiency in the fuel reactor was calculated as:

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

CO_2 capture efficiency, η_{CC} , was defined as the fraction of carbon in the fuel reactor outlet related to the carbon converted in the CLC unit which was actually found both at the fuel and air reactor outlet. The remaining carbon was non-converted in the CLC unit, e.g. because it was elutriated.

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

CO_2 capture efficiency is dependent on the conversion of char in the fuel reactor, $X_{char,FR}$, which was calculated considering the carbon content of the char fed in, i.e. fixed carbon, which exits in the fuel reactor outlet stream; elutriated carbon; and the carbon transferred to the air reactor, which exits as CO_2 .

$$X_{char,FR} = \frac{f_{C,fix} \cdot \dot{m}_{coal} - F_{C,elut} - M_C \cdot F_{CO_2,outAR}}{f_{C,fix} \cdot \dot{m}_{coal} - F_{C,elut}} \quad (7)$$

The char conversion rate was calculated as:

$$(-r_C) = \frac{X_{char,FR}}{\tau_{char,FR}} \quad (8)$$

where $\tau_{\text{char,FR}}$ is the mean residence time of particles of char in the fuel reactor. This is associated with the mean solids residence time in the fuel reactor according to the following equation:

$$\tau_{\text{char,FR}} = \tau_{\text{FR}}(1 - X_{\text{char,FR}}) \quad (9)$$

3 Results

To determine the behaviour of a CLOU system with the Cu₃₄Mn₆₆-GR oxygen carrier, different experimental tests burning coal were conducted in the 1.5 kW_{th} continuous unit. The gas composition at the exit gases of fuel and air reactors was determined. As an example, Figure 2 shows the evolution of gas concentrations (dry basis) over time found in experiments T01-T05 at different temperatures in the fuel reactor of 800-875 °C. The solids circulation rate was kept at a mean value of 8.6 kg/h, whereas the coal feed rate was 0.120 kg/h. The oxygen carrier to fuel ratio was 1.8, as defined by equation (3). Each experiment was maintained at a steady state for a period of at least 1 h, with uniform temperature and gas concentrations at the outlet. Changes of temperature were fast and the steady state was quickly reached.

CH₄, CO and H₂ were only detected in the gases exiting the fuel reactor in the experiment performed at 800 °C. Unburnt products were not detected in experiments conducted at higher temperatures (T02-T05). Thus, CO₂, H₂O and O₂ were the only gases, together N₂ introduced as fluidizing gas, found at temperatures higher than 820 °C. Unburnt products are typically associated with inefficient conversion of volatile matter in this pilot unit [36]. This indicates that combustion of volatiles to CO₂ and H₂O was complete using the Cu-Mn mixed oxide owing to the rapid combustion with gaseous oxygen generated from the decomposition of Cu_{1.5}Mn_{1.5}O₄ (CLOU process) and/or the high reactivity of the oxygen carrier with gases (CLC process). Note that in these experiments, regeneration of the oxygen carrier in the air reactor was boosted by having a large amount of excess air ($\lambda = 4$) as well as a lower

temperature than that of the fuel reactor [30]. Note that this condition would be feasible in a CLOU unit given the exothermicity of the combustion in the fuel reactor.

Complete combustion was also observed in the experiments performed with a low coal feed rate (T06-T07), but the oxygen generation rate was high enough in these cases to supply an excess of gaseous oxygen (O_2), which exited together with the combustion gases from the fuel reactor. At higher coal feed rates, the oxygen release was enough to burn the coal, but no excess gaseous O_2 was detected at the fuel reactor exit.

3.1 Effect of fuel reactor temperature

Figure 3 shows the combustion and CO_2 capture efficiencies and char conversion, as a function of fuel reactor temperature. Complete combustion of the coal to CO_2 and H_2O , i.e. $\eta_{comb,FR} = 100\%$, was observed in the fuel reactor at temperatures higher than $800\text{ }^\circ\text{C}$. However, at $800\text{ }^\circ\text{C}$, there were some unburnt products in the fuel reactor exit gas flow, with CH_4 , CO and H_2 concentrations near $1\text{ vol.}\%$. In this case, combustion efficiency decreased to a value of 82.7% .

On the other hand, CO_2 capture efficiency in a CLOU system is determined by char conversion in the fuel reactor, due to the unburnt char being transferred to the air reactor where it is burnt and emitted to the atmosphere. In Figure 3, the positive effect of fuel reactor temperature on CO_2 capture efficiency can be observed, which increases from 69.8% to 91.7% with an increase of $50\text{ }^\circ\text{C}$ in the fuel reactor temperature. When the fuel reactor temperature reached $875\text{ }^\circ\text{C}$, the value of CO_2 capture efficiency increased to 96.3% . This high value of CO_2 capture efficiency is especially remarkable given the relatively low temperature used in the fuel reactor. In a previous work with a Cu-based oxygen carrier in the same continuous CLOU unit, it was found that a fuel reactor temperature of $910\text{ }^\circ\text{C}$ (Spanish lignite) and $920\text{ }^\circ\text{C}$ (South African medium volatile coal) was necessary to reach this high value of CO_2 capture efficiency [19]. These high CO_2 capture efficiencies with fuel reactor temperatures

below 900 °C are due to the fact that Cu-Mn mixed oxides are able to generate high gaseous O₂ concentrations between 800 and 900 °C [29, 30], improving coal combustion at these temperatures. Char conversion increases as temperature increases, as also shown in Figure 3. Thus, by increasing the fuel reactor temperature, char combustion rates were higher and a lower amount of unburnt char was transferred to the air reactor.

3.2 Effect of power input

Figure 4 shows the effect of the coal feed rate on combustion and CO₂ efficiencies, and on char conversion. Changes in the coal feed rate varied both the oxygen carrier to fuel ratio, ϕ , and specific solids inventory in the fuel reactor, m_{FR}^* . Although the coal feed rate had a lower effect than the fuel reactor temperature, an effect on CO₂ capture efficiency can be appreciated that is directly related to char conversion in the fuel reactor, see Figure 4. With low coal feed rates of between 0.065 and 0.093 kg/h (340-450 W_{th}), characterized by a value of $\phi > 2$ and an oxygen carrier inventory in the fuel reactor higher than 1000 kg/MW_{th}, the oxygen carrier was able to completely burn the coal with a CO₂ capture efficiency higher than 99 %, and the oxygen release rate was also high enough to supply an excess of gaseous oxygen (O₂), which exited together with the combustion gases.

However, when the coal feed rate was increased, CO₂ capture efficiency decreased due to the decrease in char conversion in the fuel reactor. This effect was due to the decrease in the value of ϕ and the oxygen carrier inventory; see Table 2. By decreasing both parameters, the conversion of the oxygen carrier in the fuel reactor is increased. With the Cu₃₄Mn₆₆-GR oxygen carrier, the O₂ release rate (and thus char conversion) depended on oxygen carrier conversion, as higher the oxidation degree of oxygen carrier resulted in higher oxygen concentration by oxygen uncoupling [30]. Figure 5 shows that for ϕ values about 1.2 and 1.3, the char conversion rate was 2-4 %/s. However, when the oxygen carrier to fuel ratio and the

oxygen carrier inventories increased to over $\phi > 2$ and $m_{FR}^* > 1000 \text{ kg/MW}_{th}$ (T06-T07), the char conversion rate rose to values of close to 100 %/s. In these tests (T06-T07) there was gaseous oxygen in the fuel reactor exit gas stream together with CO_2 and H_2O , which suggests that oxygen was released at a higher rate than that at which it was being consumed by the coal. Therefore, in order to obtain high CO_2 efficiencies, it would be necessary to work with ϕ values higher than 2, but also oxygen carrier inventories in the fuel reactor $\geq 1000 \text{ kg/MW}_{th}$.

3.3 Effect of oxygen carrier to fuel ratio

From the results produced by experiments T06-T09, a study of the oxygen carrier to fuel ratio, ϕ , was performed with a solids inventory in the fuel reactor $\sim 1000 \text{ kg/MW}_{th}$. Figure 6 shows combustion and CO_2 capture efficiencies and char conversion as a function of the solids circulation flow rate. Combustion efficiency in the fuel reactor was 100 % in all cases. A slight increase in CO_2 capture and char conversion can also be observed with the solids circulation flow rate. This result for a Cu-Mn mixed oxide was contrary to those obtained for a Cu-based material in the same unit [18], and is more similar to the results obtained for CLC with gaseous fuels [37]. For this Cu-Mn mixed oxide oxygen carrier, the availability of oxygen to burn coal was limited by the oxygen generated by the oxygen carrier, which depended on the oxygen carrier reduction conversion. Thus, although an increase in the solids circulation rate reduced the residence time of the solids in the fuel reactor, the increase in the oxygen availability was more beneficial for coal combustion.

Complete combustion and high CO_2 capture rates were still achieved even though the oxygen carrier to fuel ratio was lower than 1 (T10). Under such conditions, the oxygen required to burn the fuel is higher than the oxygen supplied by the oxygen uncoupling mechanism; see reaction (2). In order to meet the oxygen demand, reduction of free Mn_3O_4 to MnO , or even further reduction of CuMnO_2 to Cu and MnO , may occur by means of the direct reaction of the oxygen carrier with gaseous compounds, such as the H_2 , CO or CH_4 evolved in the fuel

reactor during coal conversion. Nevertheless, the CLOU process is improved as more oxygen becomes available via the oxygen uncoupling mechanism, i.e. by increasing the solids circulation rate.

3.4 Effect of solids inventory in the fuel reactor

In addition, the effect of the oxygen carrier inventory can be analysed independently of the oxygen carrier to fuel ratio, ϕ , by comparing tests T07 and T11. Both tests had the same fuel reactor temperature (850 °C) and value of ϕ (≈ 2). By increasing the oxygen carrier inventory to over 1000 kg/MW_{th}, CO₂ capture efficiency was increased from 95 % (T11: 961 kg/MW_{th}) to 99.6 % (T07: 1190 kg/MW_{th}). Therefore, this result shows that specific solid inventories $\geq$ 1000 kg/MW_{th} would be necessary in order to achieve CO₂ capture rates above 95 %.

3.5 Effect of fluidization agent

The effect of the fluidization agent in the fuel reactor was also evaluated by using pure steam as the fluidizing agent (T14). Figure 6 shows the combustion and CO₂ capture efficiencies and char conversion during experiments carried out with steam in the fuel reactor. Under these conditions, char conversion showed a slightly increase, increasing CO₂ capture efficiency, while complete combustion was maintained in the fuel reactor. Therefore, the use of steam as a fluidizing agent in the fuel reactor did not produce a substantial improvement in of coal combustion performance in the CLOU process.

3.6 Effect of oxidation conditions in the air reactor

The effect of the oxygen concentration available to regenerate the oxygen carrier in the air reactor on the conversion of char and the CO₂ capture efficiency was analysed in experiments T15-T18. The air excess ratio (λ) varied between 4 and 1.1. Figure 7 shows the effect of the oxygen concentration used at the air reactor inlet to oxidize the oxygen carrier on combustion and CO₂ efficiencies and char conversion. It can be seen that the use of a flow of air with up

to 14 vol.% O₂ at the air reactor inlet (λ between 4 and 2.6), CO₂ capture efficiency and char conversion were unaffected, remaining at around 97 % and 0.96, respectively. With an inlet concentration of O₂ lower than 10 vol.% ($\lambda = 2$), CO₂ capture efficiency decreased significantly due to the decrease in char conversion in the fuel reactor.

An explanation for the behaviour observed in Figure 7 is that a low oxygen concentration in the air reactor implies the incomplete oxidation of the oxygen carrier due to the oxidation rate being decreased [29, 30]. In a previous work with this oxygen carrier (Cu₃₄Mn₆₆-GR), it was determined that the concentration of oxygen released during the oxygen uncoupling stage decreased when the oxygen carrier was less oxidized [30]. Therefore, lower char conversion is achieved with a lower concentration of oxygen released inside the fuel reactor. With lower values of char conversion in the fuel reactor, more unburnt char is transferred to the air reactor, decreasing CO₂ capture efficiency. Thus, when the oxygen concentration at the air reactor inlet was 8 vol.%, and $\lambda = 1.4$, oxygen uncoupling capability was reduced. But the oxygen in particles available for oxygen uncoupling was high enough to achieve high coal conversion when the O₂ concentration at the air reactor inlet was 14 vol.%, corresponding to an air excess ratio of $\lambda = 2.6$.

In addition, with an oxygen concentration at the air reactor inlet of 6 vol.% ($\lambda = 1.1$), the air reactor temperature was increased to 850 °C (T19). Results obtained under these conditions were similar to those obtained in experiment T18; see Figure 7. This result indicates the low effect of air reactor temperature on the oxidation kinetics of this material.

4 Discussion

The results obtained from the experimental campaign offer valuable information for the further development of the CLOU process with oxygen carriers based on Cu-Mn mixed oxides.

With regard to combustion efficiency, the presence of unburnt products from the fuel reactor should not be expected if the fuel reactor temperature is kept above 800 °C. During real application, the fuel reactor temperature would be influenced by the air reactor temperature, which was mostly fixed at 800 °C in this work to achieve good regeneration of the oxygen carrier. Achievable temperatures in the fuel reactor would be somewhat higher due to the exothermicity of the overall process that takes place during coal combustion, and would be determined by a heat balance to the CLOU unit and heat losses [38].

Thus, complete combustion was achieved regardless of the operating conditions used, even with a low solids inventory (584 kg/MW_{th}), low oxygen carrier to fuel ratios (even with $\phi < 1$) or low air excess ratios ($\lambda = 1.1$). Complete combustion can be explained by the highly efficient oxygen uncoupling mechanism in action when burning coal; however, the high reactivity of the Cu-Mn material with gases, such as H₂, CO and CH₄, is also relevant whenever oxygen uncoupling capability is limited, e.g. when $\phi < 1$.

This fact represents a great advantage for CLOU over the in-situ Gasification Chemical Looping Combustion (iG-CLC) process [37], for which the materials used do not have the oxygen uncoupling capability. In iG-CLC, coal must be gasified in the fuel reactor, and the presence of unburnt compounds, such as CO, H₂ and CH₄, is expected because of the low reactivity of materials used, together with the poor contact the volatile matter and gasification products have with the oxygen carrier [36]. An additional oxygen polishing step is required in order to achieve complete combustion, which would be avoided through the use of materials

with oxygen uncoupling capability, i.e. in CLOU. However, any presence of oxygen in the CO₂ stream must be removed in order to prevent pipeline corrosion in the CO₂ transport system [39]. Therefore, it would be preferable to achieve conditions at which the oxygen concentration could be minimized at the fuel reactor exit. Nonetheless, the separation of O₂ from a CO₂ stream seems to be a standard operation, e.g. in the oxy-fuel combustion process, which could be accomplished without great difficulty in the compression and purification unit (CPU) [40].

However, operating conditions can greatly affect CO₂ capture. CO₂ capture in our work was governed by the char conversion rate, which was mainly driven by the oxygen uncoupling mechanism. Thus, CO₂ capture was boosted by improving the oxygen uncoupling process in the fuel reactor, e.g. by increasing the fuel reactor temperature to above 820 °C, the oxygen carrier to fuel ratio to above 2, and the air excess ratio to above 2. Also, a solids inventory higher than 1000 kg/MW_{th} is recommended in order to achieve high CO₂ capture rates.

It is worthy of note that in the case of Cu-Mn oxygen carriers, the conditions in the air reactor affect the degree to which the oxygen carrier is oxidized, which eventually affects its oxygen uncoupling capability in the fuel reactor and, consequently, CO₂ capture. This fact has not been observed in other materials, with or without, oxygen uncoupling capability [18-21, 36, 41], given that oxygen carrier regeneration is usually a fast process and one that is easy to achieve in pilot units. Even so, high values of CO₂ capture efficiency (>85 %) were obtained in the pilot unit with air excess ratio values in the 1.1-1.4 interval. In any case, the performance of the Cu-Mn oxygen carrier in a CLOU unit with a proper air reactor design would be improved compared to the results achieved in this work. The reason for this is that ambient air would be used in the air reactor of a CLOU unit instead of diluted air. The use of diluted air was required in the 1.5 kW_{th} CLOU unit to vary the air excess ratio, while maintaining the total gas flow, in order to entrain the solids to the riser. As a consequence, the average oxygen

concentration in the air reactor is lower when diluted air is used, and a higher oxidation conversion of the oxygen carrier would be expected if ambient air was used.

For practical reasons, the values selected for operating conditions may result in limited CO₂ capture, while still achieving complete combustion in the fuel reactor. For example, air excess ratio values close to 1.5 or solids inventory values of around 500 kg/MW_{th} would be recommended. In these cases, the use of a carbon separation system [36], e.g. a carbon stripper, will be required in order to achieve CO₂ capture efficiencies higher than 95 %, even with highly reactive coals such as the subbituminous Chilean coal used here. From results presented in this work, an estimation can be made of CO₂ capture in the presence of a carbon separation system. Taking test T17 as a reference, where $\eta_{CC} = 85 \%$, the char conversion rate was estimated to be $(-r_c) = 0.013 \text{ s}^{-1}$ by using equation (8). Considering the efficiency of the carbon separation system, η_{CSS} , CO₂ capture can be calculated by [23, 42]:

$$\eta_{CC} = 1 - \frac{f_{C,fix}}{f_{C,coal}} \left[\frac{\dot{m}_s^* (1 - \eta_{CSS})}{(-r_c) m_{FR}^* + \dot{m}_s^* (1 - \eta_{CSS})} \right] \quad (10)$$

where $\dot{m}_s^*$ is the specific solids circulation rate, corresponding to 3 kg/s per MW_{th} for test T17. Thus, the estimated CO₂ capture increases with the specific solids inventory and the efficiency of the carbon separation system; see Figure 8. In addition, to achieve a specific CO₂ capture value, the efficiency of the carbon separation system needs to increase as the solids inventory decreases. Through a combination of suitable solids inventory values and carbon separation system efficiency, CO₂ capture values higher than 95 % could be achieved under such conditions.

At an industrial scale, steam and/or CO₂ could be considered as the fluidizing medium in the fuel reactor. Steam is highly recommended when oxygen carriers without the oxygen uncoupling capability are used, as in the *i*G-CLC process [36]. However, steam generation has a negative impact on the energetic efficiency of the process and the use of CO₂ is

recommended wherever possible [43]. This is the case of the CLOU process with Cu-based materials [41] or with Cu-Mn as shown here. In CLOU, CO₂ would be used as the fluidizing gas, since no differences are expected with respect to the results obtained with steam or N₂ because the gasification rate of char with CO₂ is usually lower than that obtained with steam. Therefore, wet or dry CO₂ could be used as the fluidizing gas, taking into account the recirculation of hot or cold exhaust gases, respectively; however, the performance of the CLOU unit in terms of CO₂ capture and combustion efficiency is not expected to be affected by this decision.

Furthermore, an industrial-scale fuel reactor is usually designed to operate as a circulating fluidized bed reactor in the turbulent or fast fluidization regime [43, 44], instead of the bubbling regime used in the 1.5 kW_{th} CLOU unit. Thus, the gas velocity would be considerably higher, e.g. 1-4 m/s, than the gas velocity used in this work, ~0.15 m/s, which would modify the solids distribution and gas-solid contact in the reactor. In a circulating fluidized bed, the gas-solid contact is improved in the freeboard, which would improve the gas conversion [45, 46]. In this case, lower amounts of solids would be required to achieve complete combustion in the fuel reactor, and the solids inventory used in this work could be used to create a safe design for a CLOU unit. Nevertheless, future work at higher scale would be required before the scale-up of the CLOU process, which is planned for the 50 kW_{th} Chemical Looping unit at ICB-CSIC [47].

5 Conclusions

Combustion of coal was performed in a 1.5 kW_{th} CLOU system for 30 h using a Cu-Mn mixed oxide as an oxygen carrier. At temperatures higher than 800 °C in the fuel reactor, unburnt compounds were not present at the outlet of the fuel reactor in all cases. The reaction

products were CO₂ and H₂O, with some excess O₂ supplied by the oxygen carrier. In most of the cases, the CO₂ capture efficiency was higher than 90 %. Char combustion was improved at higher temperatures, reaching 94 % conversion at 875 °C. Under these conditions, CO₂ capture efficiency values obtained were as high as 96.2 %.

The oxygen carrier to fuel ratio, ϕ , is a fundamental parameter for obtaining high CO₂ capture efficiencies, because the rate of oxygen generation of this oxygen carrier depends on the degree of its reduction. Thus, high oxygen carrier to fuel ratio values ($\phi > 2$) produce high char conversion rates in the fuel reactor and consequently the CO₂ capture was improved. Moreover, CO₂ capture rates close to 100% were reached when the oxygen carrier inventory in the fuel reactor was in the region of 1000 kg/MW_{th}.

CO₂ capture was increased to above 95 % by increasing the air excess ratio, which was likely related to enhanced oxygen carrier regeneration in the air reactor. However, if the air excess ratio was restricted to $\lambda = 1.4$, CO₂ capture was limited to approximately 85 % in this CLOU unit.

The implementation of a carbon separation system in a CLOU unit would be key to achieving CO₂ capture rates close to 100 % if a low solids inventory in the fuel reactor (<1000 kg/MW_{th}) and a low air excess ratio (e.g. in the 1.1-1.4 interval) are considered in the design of a CLOU unit at an industrial scale. Complete combustion in the fuel reactor would be still expected under these conditions. Also, the use of recirculated dry or wet CO₂ as the fluidizing agent in the fuel reactor is recommended at an industrial scale.

The results obtained in this work have shown that the use of the granulated Cu₃₄Mn₆₆-GR oxygen carrier is suitable for coal combustion by the CLOU process. The use of the Cu-Mn mixed oxide would allow the amount of CuO in the oxygen carrier particles to be reduced, lessening the operating costs of the CLOU process.

Acknowledgements

This work was supported by the Spanish Ministry of Economy, Industry and Competitiveness (MINECO Project: ENE2013-45454-R, ENE2014-56857-R and ENE2016-77982-R) and the European Union FEDER funds. Our thanks to Ing. Konrad Holscher from Mina Invierno Chile, for supplying the subbituminous coal.

Notation

Symbols

$f_{C,coal}$	carbon fraction in coal (-)
$f_{C,fix}$	Fixed carbon fraction in coal (-)
F_i	Molar flow of compound i (mol/s)
M_i	Atomic or molecular mass of i elements or compound (kg/mol)
$\dot{m}_{coal}$	Mass flow rate of coal fed into the fuel reactor (kg/s)
m_{FR}	Solids inventory in the fuel reactor (kg)
m_{FR}^*	Specific solids inventory in the fuel reactor (kg/MW _{th})
$\dot{m}_s$	Solids circulation rate (kg/s)
$\dot{m}_s^*$	Specific solids circulation rate (kg/s per MW _{th})
$(-r_C)$	Char conversion rate (s ⁻¹)
R_{OC}	Oxygen transport capability (kg oxygen per kg of oxygen carrier)
T	Temperature (°C)
$X_{char.FR}$	Char conversion in the fuel reactor (-)

Greek letters

ϕ	Oxygen carrier to fuel ratio (-)
η_{CC}	CO ₂ capture efficiency (-)
$\eta_{comb,FR}$	Combustion efficiency in the fuel reactor (-)
η_{CSS}	Efficiency of the carbon separation system (-)
λ	Air excess ratio (-)
$\tau_{char.FR}$	Mean residence time of char particles in the fuel reactor (s)
τ_{FR}	Mean residence time of solids in the fuel reactor (s)
Ω_{coal}	Stoichiometric mass of O ₂ to convert 1 kg of coal (kg/kg)

Subscripts

AR	Air reactor
C,elut	Elutriated carbon
FR	Fuel reactor
in	Inlet
out	Outlet

Figure captions

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

Figure 2. Evolution of the gas composition in the air and fuel reactors as the temperature in the fuel reactor was varied. Experimental tests T01-T05. $\dot{m}_S = 8.6$ kg/h; $\dot{m}_{\text{coal}} = 0.120$ kg/h.

Figure 3. Combustion (---●---) and CO₂ capture (---▲---) efficiencies and char conversion (---Δ---) at different fuel reactor temperatures.

Figure 4. Combustion (---●---) and CO₂ capture (---▲---) efficiencies and char conversion (---Δ---) at different coal feed rates.

Figure 5. Char conversion rate as a function of the oxygen carrier to fuel ratio (ϕ). Oxygen carrier inventory in the fuel reactor: (●) < 1000 kg/MW_{th}; (▲) > 1000 kg/MW_{th}. $T_{FR} = 850$ °C. Experiments: T06-T10.

Figure 6. Combustion (---●---; ■) and CO₂ capture (---▲---; ▼) efficiencies and char conversion (---Δ---; ▽) at different solids flow rates with N₂ or steam as the fluidizing agent, respectively.

Figure 7. Combustion (---●---) and CO₂ capture (---▲---) efficiencies and char conversion (---Δ---) as a function of the oxygen concentration available to regenerate the oxygen carrier in the air reactor. Combustion (■) and CO₂ capture (▼) efficiencies and char conversion (▽) at 850 °C in the air reactor.

Figure 8. CO₂ capture (η_{CC}) estimation as a function of the efficiency of the carbon separation system (η_{CSS}) for different specific solids inventory in the fuel reactor. Conditions for test T17.

Table captions

Table 1. Properties of the fresh Cu-Mn granulated oxygen carrier.

Table 2. Properties of the Chilean subbituminous coal used in this work (as received).

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Table 1. Properties of the fresh Cu-Mn granulated oxygen carrier.

XRD main phases	$\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$, Mn_3O_4
Oxygen transport capacity for CLOU, R_{OC} (wt.%)	4.0
Crushing strength (N)	1.9
Skeletal density of particles (kg/m^3)	4100
AJI (%)	3.0
Porosity (%)	12.1
Specific surface area, BET (m^2/g)	<0.5

Table 2. Properties of the Chilean subbituminous coal used in this work (as received).

Proximate Analysis (wt.%)		Ultimate Analysis (wt.%)	
Moisture	14.2	C	52.4
Ash	15.3	H	5.24
Volatile matter	34.6	N	0.77
Fixed carbon	35.9	S	0.2
		O*	11.9
LHV (kJ/kg)	18900		

* Calculated by difference

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

Test	T _{FR} (°C)	H ₂ O (vol.%)	T _{AR} (°C)	[O ₂] _{inAR} (%)	λ (-)	ϕ (-)	$\dot{m}_s$ (kg/h)	$\dot{m}_{coal}$ (kg/h)	Power (W)	m _{FR} (kg)	m _{FR} [*] (kg/MW _{th})
T01	800	0	800	21	4	1.8	8.6	0.120	625	0.64	989
T02	820	0	800	21	4	1.8	8.6	0.120	625	0.60	959
T03	850	0	800	21	4	1.8	8.6	0.120	625	0.61	988
T04	860	0	800	21	4	1.8	8.6	0.120	625	0.61	968
T05	875	0	800	21	4	1.8	8.6	0.120	625	0.60	961
T06	855	0	800	21	4	2.9	8.2	0.065	342	0.60	1775
T07	855	0	800	21	4	2.1	8.2	0.093	490	0.58	1190
T08	855	0	800	21	4	1.3	8.2	0.165	867	0.60	700
T09	855	0	800	21	4	1.2	8.2	0.175	913	0.53	584
T10	850	0	800	21	4	0.6	2.4	0.120	625	0.62	980
T11	850	0	800	21	4	1.9	9.2	0.120	625	0.60	961
T12	850	0	800	21	4	2.1	10	0.120	625	0.65	1000
T13	850	0	800	21	4	2.8	13.8	0.120	625	0.70	1100
T14	855	100	800	21	4	1.2	6	0.120	625	0.58	910
T15	855	0	800	21	4	1.5	7.5	0.125	657	0.76	1100
T16	855	0	800	14	2.6	1.5	7.5	0.125	657	0.65	995
T17	855	0	800	8	1.4	1.7	7.5	0.125	657	0.63	960
T18	855	0	800	6	1.1	1.8	7.5	0.125	657	0.60	925
T19	855	0	850	6	1.1	1.9	7.5	0.125	657	0.60	925

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