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Full Length Article

CLOU process performance with a Cu-Mn oxygen carrier in the combustion of different types of coal with CO_2 capture

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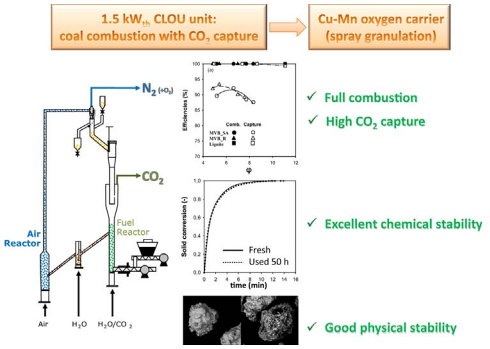
GRAPHICAL ABSTRACT



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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 CO_2 separation by using oxygen carriers based on metal oxides. This technology has a low energy penalty and thus low CO_2 capture costs. The oxygen carrier used in the CLOU process must be able to release gaseous oxygen, an aspect that limits the availability of metal oxides for this process. This work investigated the suitability of an oxygen carrier containing 34 wt% CuO and 66 wt% Mn_3O_4 (active phase $Cu_{1.5}Mn_{1.5}O_4$) prepared by granulation regarding the CO_2 capture, combustion efficiency and lifetime of the particles. The effect of the different types of coal (two sub-bituminous and a lignite) on combustion and CO_2 capture efficiencies by CLOU was studied at different oxygen carrier to coal ratios in a continuous 1.5 kW$_{th}$ rig. It was found that full combustion could be reached regardless of the coal used. However, CO_2 capture efficiencies were highly determined by coal rank. Finally, it was found that working with oxygen carrier to coal ratios higher than $\phi = 4$, which corresponded to values of the variation of the oxygen carrier conversion lower than $\Delta X_{oc} = 0.25$, decreased the effect of chemical stress on the attrition rate. Therefore, it is clearly beneficial for the lifetime of oxygen carrier particles to operate with low variations of the oxygen carrier conversion (ΔX_{oc}) between fuel and air reactors.

1. Introduction

A promising Chemical Looping Combustion (CLC) option for burning solid fuel is the Chemical Looping with Oxygen Uncoupling (CLOU) process. Metallic oxides used as oxygen carriers for the CLOU process must be able to release gaseous oxygen at operating temperatures. The O_2 (g) released by the oxygen carrier in the fuel reactor directly burns the solid fuel fed into it. In addition, the oxygen carrier for

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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 weight of i elements or compound (kg/mol)
m	Mass of the sample at each time in TGA (kg)
m_{5h}	Mass of fines after 5 h collected from the attrition test rig (kg)
m_s	Mass of sample loaded into the apparatus (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 fully oxidized oxygen carrier sample (kg)
$m_{s,FR}$	Mass of solids in the fuel reactor (kg)
m^*_{FR}	Specific solids inventory in the fuel reactor (kg/MW_{th})
R_{OC}	Oxygen transport capability (–)
T	Temperature (°C)
$X_{char,FR}$	Char conversion in the fuel reactor (–)
X_{red}	Oxygen carrier conversion for the reduction reaction (–)

Greek letters

ΔX_{oc}	Variation of the oxygen carrier conversion (–)
η_{CC}	CO_2 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

AJI	Air Jet Index
AR	Air reactor
BET	Brunauer-Emmett-Teller
CLC	Chemical Looping Combustion
CLOU	Chemical Looping with Oxygen Uncoupling
FCC	Fluid catalytic cracking
FR	Fuel reactor
ICP	Inductively coupled plasma
OC	Oxygen carrier
TGA	Thermogravimetric analyser
XRD	X-ray diffractometer

Subscripts

C,elut	Carbon elutriated
outAR	Outlet stream from air reactor
outFR	Outlet stream from fuel reactor

CLOU process must be able to be regenerated by air in the air reactor. Three single metal oxides have the properties required for the CLOU process: CuO/Cu_2O, Mn_2O_3/Mn_3O_4 and Co_3O_4/CoO [1]. Mattisson [2] and Imtiaz et al. [3] conducted reviews of CLOU materials. These reviews included Cu-based oxygen carriers [4,5] and the mixed-oxide-based oxygen carriers Cu-Mn [6,7], Mn-Fe [8] and Mn-Si [9].

Among the developed materials, one consisting of spray dried particles with 60 wt% CuO was analysed in a CLOU unit of 1.5 kW_{th}, with it the proof of CLOU concept was demonstrated using different coal ranks and biomass [10–12]. These particles were also used to analyse the fate of sulphur and its effect on CO_2 capture efficiency [13], and the fate of sulphur, nitrogen and mercury was also analysed with a similar oxygen carrier [14]. This Cu-based oxygen carrier did not show any decrease in reactivity or agglomeration. However, it required improvement due to an important reduction in crushing strength and an increase in its porosity [15].

Mn-based oxygen carriers show some advantages with respect to Cu-based materials: they operate at lower temperatures owing to the fact that the partial pressure of O_2 at equilibrium for the Mn_2O_3/Mn_3O_4 is higher than it is for CuO/Cu_2O [1]; and Cu-based materials are more expensive than Mn-based ones. However, the need to decrease the temperature in the air reactor to around 800 °C to regenerate the Mn_3O_4 to Mn_2O_3 makes Mn-based materials unsuitable for use on an industrial scale CLOU process [16–18].

Cu-Mn mixed oxides show good prospects for the CLOU process because they release oxygen at lower temperature than Cu-based oxygen carriers do [7]. A number of works have studied different Cu-Mn oxygen carriers prepared by co-precipitation [7], extrusion [19] and freeze drying [6]. They found that Cu-Mn mixed oxides were able to generate gaseous oxygen above 700 °C and had good reactivity with CH_4, but CO was found to be 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], oxygen release can occur by means of two different reactions:

$$3CuMn_2O_4 \leftrightarrow 3CuMnO_2 + Mn_3O_4 + O_2 \tag{1}$$

$$2Cu_{1.5}Mn_{1.5}O_4 \leftrightarrow 3CuMnO_2 + O_2 \tag{2}$$

Moreover, an oxygen carrier derived from the commercially prepared hopcalite, Carulite 300®, was analysed as a CLOU oxygen carrier by Adánez-Rubio et al. [21]. It was found that the hopcalite-derived oxygen carrier was able to completely burn coal in the CLOU process to CO_2 and H_2O in a batch fluidized bed reactor at low temperatures. Nevertheless, it showed a reduction in particle crushing strength with the operation time, reaching values under 1 N, which indicated that the physical properties of the particles need improvement. Thus, the oxygen carrier derived from this commercial material was not considered suitable for the CLOU process.

The main efforts currently being made to continue the development of CLOU is to find a suitable oxygen carrier for the process with high mechanical strength and physical stability in order to show low attrition rates, but still having a high oxygen release rate. A new Cu-Mn oxygen carrier for the CLOU process named Cu34Mn66-GR (34 wt% CuO and 66 wt% Mn_3O_4, granulated particles), based on the composition of hopcalite, was developed by our ICB-CSIC research group and prepared by spray granulation [22]. This material showed high reactivity with coal and char in a batch fluidized bed reactor, allowing complete combustion of the coal to CO_2 and H_2O. Moreover, the Cu34Mn66-GR showed an attrition rate (0.005%/h, corresponding to a particle lifetime of 20,000 h) that was 18 times lower than that of the hopcalite-derived oxygen carrier [21]. This material was also tested in a 1.5 kW_{th} continuous CLOU unit burning sub-bituminous Chilean coal, where the effect on combustion and CO_2 capture efficiencies of the fuel reactor temperature, coal feeding rate, solid circulation rate, fluidization agent and O_2 available in the air reactor were analysed [23]. It was found that complete combustion of coal was obtained with fuel reactor temperatures higher than 800 °C. CO_2 capture was higher than 90% at operating temperatures as low 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 for achieving high CO_2 capture efficiencies. Higher ϕ values produced higher char conversion rates in the fuel reactor, because the oxygen generation rate of this oxygen carrier is highly dependent on the reduction conversion. Note that a higher ϕ value resulted in lower reduction conversion, a higher oxygen generation rate, higher char conversion rate and higher CO_2 capture efficiency [22,23]. These results were contrary to what was found for a Cu-based oxygen carrier [10]. The use of steam as a fluidizing agent did not show