Chemical looping combustion of biomass: CLOU experiments with a Cu-Mn mixed oxide

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Abstract

Chemical looping combustion (CLC) is a low-cost CO₂ capture technology with a low energy penalty. Bio-energy with CO₂ capture and storage (BECCS) opens up the possibility for negative CO₂ emissions involving the removal of CO₂ already emitted into the atmosphere. The oxygen needed for combustion in CLC processes is supplied by a solid oxygen carrier circulating between the fuel reactor and the air reactor. In this work, the combustion of different types of biomass, such as pine sawdust, olive stones and almond shells, was studied in a continuous 1.5 kW_{th} CLC unit. A mixed Cu-Mn oxide was used as the oxygen carrier. This material releases gaseous oxygen when reduced, resulting in Chemical looping combustion with oxygen uncoupling (CLOU). The released oxygen reacts with both the volatiles and char generated inside the fuel reactor when biomass is fed into it. The oxygen carrier is reoxidized in air inside the air reactor. High CO₂ capture and 100% combustion efficiencies were achieved with this Cu-Mn oxygen carrier. The oxygen concentration inside the air reactor did not affect CO₂ capture efficiency under the studied conditions.

Keywords: CO₂ capture, chemical looping combustion, CLOU, biomass

1 Introduction

Anthropogenic carbon dioxide (CO₂) is the leading contributor to global warming, as a result of the large amounts of this gas emitted from fossil fuel combustion processes and its long residence time into the atmosphere. In order to limit the effects of global warming, the Paris Agreement (2015) [1] established a commitment to limit the global temperature increase to 2 °C or less over the next century. The agreement implies the need to decreasing CO₂ emissions into the atmosphere and even achieving negative CO₂ emissions during the present century. Recent data indicate that CO₂ Capture and Storage (CCS) technologies can contribute about 12% of cumulative emissions reductions needed by around mid-century [2-4]. However, in order to reduce the CO₂ concentration in the atmosphere and not only reduce CO₂ emissions, efforts should be made in the development of negative emissions technologies (NET). Among these, bioenergy with CO₂ capture and storage (BECCS) technologies allow CO₂ to be removed from the atmosphere because of the intrinsic neutral CO₂ balance of biomass and the combination of CCS techniques [5].

The chemical looping combustion (CLC) process is a CCS technology with a reduced energy penalty and low cost associated with CO₂ capture [6]. The oxygen needed for fuel combustion in CLC is supplied by a solid oxygen carrier, thereby preventing air and fuel mixing. The oxygen carrier, typically a metal oxide, circulates between two interconnected reactors, the fuel reactor and air reactor. The fuel in the fuel reactor is burnt to CO₂ and H₂O, while the oxygen carrier is reduced. The reduced oxygen carrier is then transferred to the air reactor, where it is re-oxidized with air [6, 7]. The combination of CLC with biomass as fuel can be considered a promising BECCS technology currently under development [8]. The feasibility of CLC with biomass has mostly been demonstrated in the in-situ gasification chemical looping combustion (iG-CLC) mode. In the iG-CLC mode, a gasifying agent is needed as a fluidizing gas to facilitate reactions between the fuel gasification products and the solid oxygen carrier. Experiments in continuous CLC units with different types of biomass showed that it was possible to reach 100% CO₂ capture efficiency [8, 9]. However, significant amounts of unburnt products, in the range of 10–30%, were detected at the fuel reactor outlet, showing that the combustion efficiency of the process is not optimum. Berdugo

Vilches et al. [10] studied the combustion of commercial wood pellets in a boiler/gasifier loop (with power inputs of 12 MW_{th} and 2–4 MW_{th}, respectively) using two oxygen carriers, ilmenite and a manganese ore. They found combustion efficiencies of around 60% at 830 °C and char conversion of around 0.4. An improvement in the combustion efficiency might be expected working in the so-called chemical looping with oxygen uncoupling (CLOU) mode.

The CLOU process uses an oxygen carrier that releases gaseous oxygen under operation conditions, which presents better combustion kinetics for both char and volatile matter from the solid fuel resulting from gas-gas reactions [11], see reactions (1)-(4).

Few metal oxides present adequate partial pressure of oxygen at conditions relevant for combustion processes (CuO/Cu₂O, Mn₂O₃/Mn₃O₄ and Co₃O₄/CoO) [12]. Among these, Cu-based materials have been the focus of research as their oxygen release is faster than that of Mn-based oxides, and their temperature window for oxygen release is higher than in the case of Mn and Co-based oxides [6]. In order to improve the thermodynamic restrictions associated with manganese, mixed oxides (Mn-Si, Mn-Mg, Mn-Fe, Mn-Cu,) have been proposed. Adding another metal to manganese oxide enables oxidation of the material to be performed at higher temperatures [13-21]. More specifically, the mixed oxide based on Cu-Mn has shown high oxygen uncoupling capability [17]. A synthetic Cu-Mn mixed oxide material was recently developed by Adánez-Rubio et al. [22] and tested in a 1.5 kW_{th} continuous unit using coal as fuel [23, 24]. It showed 100% combustion efficiency, which qualified this oxygen carrier as a potential material for testing in experiments with biomass.

Current experience in biomass combustion in CLOU mode is quite limited. Adánez-Rubio et al. [25] demonstrated the feasibility of CLOU with biomass using a Cu-based oxygen carrier in a 1.5 kW_{th} continuous unit. In that work, 100% CO₂ capture and combustion efficiencies were achieved at 935 °C. Schmitz and Linderholm tested a

perovskite ($\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3.8}$) using a biochar with a very low sulphur content in a 10 kW_{th} unit [26]. High combustion efficiencies and CO_2 capture efficiencies of up to 98% were reached in this case. On the other hand, Wang et al. [27] analysed the behaviour of a Cu-based oxygen carrier supported on olivine (38 wt% CuO) in a batch fluidized bed reactor while burning batches of pine sawdust. CO_2 capture of 99.3% was achieved at 950 °C, together with unburnt products at the outlet gas stream. Hanning et al. [28] studied the combustion of wood char in a batch fluidized with a Mn-Si mixed oxide and Mn-Si-Ti oxygen carriers. They found the CLC reaction to be more important than CLOU with these oxygen carriers.

The aim of this present work was to further analyse the CLC of biomass in CLOU mode with this new Cu-Mn-based oxygen carrier. For this purpose, three different types of biomass were considered and several operating parameters were evaluated.

2 Materials and Methods

2.1 Oxygen carrier

A Cu-Mn mixed oxide was used as oxygen carrier for the CLOU process. The oxygen carrier was prepared by spray granulation in a spouted bed system at ICB-CSIC using CuO (CHEM-LAB) and Mn_3O_4 (Micromax ®, ELKEM). The particles contained 34 wt% CuO and 66 wt% Mn_3O_4 . They were calcined for 2 h at 1125 °C. The active phase in the mixed oxide was $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$. The excess Mn_3O_4 in the particles acted as an inert [22]. Reaction (5) describes the release of gaseous oxygen by the oxygen carrier.

Table 1 shows the main properties of the oxygen carrier. The particle size used was +100-300 μm . This oxygen carrier was given the name Cu34Mn66-GR.

Chemical and physical properties of the oxygen carrier particles (crushing strength, skeletal density, BET surface area, pore volumes, crystalline chemical species) were analysed using different methods. For more information on the analytical techniques used, see Adánez-Rubio et al. [23].

Table 1. Properties of the oxygen carrier used in this work.

XRD main phases	Cu _{1.5} Mn _{1.5} O ₄ , Mn ₃ O ₄
Composition	72 wt% Cu _{1.5} Mn _{1.5} O ₄ 28 wt% Mn ₃ O ₄
Oxygen transport capacity for CLOU, R_{OC} (wt.%)	4.0
Crushing strength (N)	1.9
Skeletal density of particles (kg/m ³)	4100
Air jet index, AJI (%)	3.0
Porosity (%)	12.1
Specific surface area, BET (m ² /g)	<0.5

2.2 Solid fuels

Three different biomasses were tested during the combustion experimental campaign with the oxygen carrier. Scots pine (*Pinus sylvestris*) sawdust is commonly used as a yardstick biomass because of its wide use and distribution. Two different agricultural waste products were also used and compared with the pine sawdust: almond (*Prunus dulcis*) shells and olive (*Olea europaea*) stones. They were selected by taking into consideration annual production [29, 30]. The raw materials were dried and sieved to +500–2000 μm . Properties of the three biomasses are shown in Table 2.

Table 2. Properties of the biomass used in this work.

	Pine sawdust	Almond shells	Olive stones
Proximate Analysis (wt%)			
Moisture	4.2	2.3	9.4
Volatile matter	81.0	76.6	72.5
Fixed carbon	14.4	20.0	17.3
Ash	0.4	1.1	0.8
Ultimate Analysis (wt%)			
C	51.3	50.2	46.5
H	6.0	5.7	4.8
N	0.3	0.2	0.2
S	0.0	0.0	0.0
O	37.8	40.5	38.3
LHV (kJ/kg)	19158	18071	17807

Ω_{SF} (kg O ₂ /kg biomass)	1.5	1.4	1.2
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*Calculated by difference

2.3 Experimental set-up

Figure 1 is a diagram of the ICB-CSIC-s1 unit. The fuel and the air reactors in this facility are bubbling fluidized beds interconnected by means of another fluidized bed that acts as a loop seal. The fuel is continuously fed through a screw feeder into the fuel reactor bed. Once reduced, the oxygen carrier is transferred from the fuel to the air reactor where it is re-oxidized. Oxygen carrier particles at the air reactor outlet are recovered by a cyclone and sent to a deposit. A solids valve provides control of the solids flow sent from this reservoir back to the fuel reactor. The solids circulation rate can be measured by a solids diverter valve. More details concerning the configuration of ICB-CSIC-s1 unit can be found elsewhere [8].

The oxygen carrier inventory into the facility was kept steady at about 3 kg. N₂ was used in the fuel reactor as the fluidizing gas instead of CO₂ in order to improve the accuracy for calculation of the carbon burnt in the fuel reactor. In a previous work, it had been determined that the fluidization agent did not have any influence on the oxygen carrier behaviour [31, 32]. CO, CO₂, H₂, CH₄ and O₂ gas concentrations were measured and recorded at the fuel reactor outlet, as well as those of CO, CO₂ and O₂ at the air reactor outlet. A non-dispersive infrared (NDIR) analyser (Siemens Ultramat 23) was used for CH₄, CO and CO₂; a paramagnetic analyser (Siemens Ultramat 23 and Oxymat 6) was used for O₂ concentration measurement; and a thermal conductivity detector (Siemens Calomat 6) was used for H₂.

Figure 1. Experimental scheme of the ICB-CSIC-s1 unit.

2.4 Experimental planning

Table 3 shows a compilation of the main variables set and measured in each test. The same batch of oxygen carrier particles was maintained during 65 h of hot fluidization conditions, 40 h of which included biomass combustion.

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

Test	T_{FR} (°C)	T_{AR} (°C)	$[O_2]_{inAR}$ (%)	ϕ	$\dot{m}_s$ (kg/h)	$\dot{m}_{SF}$ (kg/h)	Power (W)	$\dot{m}_{FR}^*$ (kg/MW _{th})
P01	850	800	21	7.6	27.2	0.082	435	2200
P02	850	800	21	5.3	19.3	0.082	435	2200
P03	850	800	21	4.7	16.8	0.082	435	2200
P04	850	800	21	2.3	8.7	0.082	435	2200
P05	775	800	21	3.9	22.5	0.14	740	1200
P06	800	800	21	3.9	22.5	0.14	740	1200
P07	825	800	21	3.9	22.5	0.14	740	1200
P08	850	800	21	3.9	22.5	0.14	740	1200

P09	800	800	10	3.9	22.5	0.14	740	1200
P10	800	800	10	3.4	28.5	0.19	1000	900
P11	800	800	10	2.6	28.5	0.25	1330	715
A01	775	800	21	3.0	20.3	0.173	860	1150
A02	800	800	21	3.0	20.3	0.173	860	1150
A03	825	800	21	3.0	20.3	0.173	860	1150
A04	850	800	21	3.0	20.3	0.173	860	1150
O01	775	800	21	3.3	22.5	0.225	1040	760
O02	800	800	21	3.3	22.5	0.225	1040	760
O03	825	800	21	3.3	22.5	0.225	1040	760
O04	850	800	21	3.3	22.5	0.225	1040	760

Mass balances were checked and a closing of about 95% was found for the carbon and oxygen balances. Thus, carbon present in fly ash was of low relevance. The performance of the CLC system was evaluated based on three parameters: combustion efficiency in the fuel reactor, CO₂ capture efficiency and char conversion in the fuel reactor [6].

Combustion efficiency in the fuel reactor is defined as the fraction of oxygen required by the fuel that is supplied by the oxygen carrier in the fuel reactor:

$$\eta_{Comb,FR} = 1 - \frac{4F_{CH_4,outFR} + F_{CO,outFR} + F_{H_2,outFR}}{\frac{1}{M_{O_2}} \cdot 2\Omega_{SF} \cdot \dot{m}_{SF} - 2F_{CO_2,outAR}} \quad (6)$$

where M_{O_2} represents the molecular weight of O₂ (kg/mol); Ω_{SF} is the stoichiometric mass of O₂ to convert 1 kg of biomass (kg/kg); and $\dot{m}_{SF}$ is the biomass rate fed into the fuel reactor (kg/s).

CO₂ capture efficiency (η_{CC}) is defined as the fraction of carbon actually captured at the outlet of the fuel reactor in relation to the total carbon in gases exiting from the chemical looping unit:

$$\eta_{CC} = 1 - \frac{F_{CO_2,outAR}}{F_{CO_2,outFR} + F_{CO,outFR} + F_{CH_4,outFR} + F_{CO_2,outAR}} \quad (7)$$

Char conversion in the fuel reactor ($X_{char,FR}$) shows the ratio between the char converted inside the fuel reactor and the char generated in the fuel reactor when biomass was fed and devolatilized (mainly composed of fixed carbon).

$$X_{Char,FR} = \frac{f_{C_{Fix}} \cdot \dot{m}_{SF} - M_C \cdot F_{CO_2,outAR}}{f_{C_{Fix}} \cdot \dot{m}_{SF}} \quad (8)$$

where $f_{C_{fix}}$ represents the mass fraction of fixed carbon in biomass and M_C is the atomic weigh of carbon (kg/mol).

It is also possible to calculate the char conversion rate, $(-r_{Char})$, by knowing the char conversion in the fuel reactor and the mean residence time of particles of char in the fuel reactor, τ_{char} .

$$(-r_{Char}) = \frac{X_{Char,FR}}{\tau_{Char}} \quad (9)$$

$$\tau_{Char} = \tau_{FR} \cdot (1 - X_{Char,FR}) \quad (10)$$

The air reactor temperature was kept steady at around 800 °C for the entire experimental campaign, and the effect of the oxygen carrier-to-fuel ratio was analysed first. Equation 11 defines the oxygen carrier-to-fuel ratio, ϕ , as the quotient between the oxygen available in the oxygen carrier and the oxygen required for the complete combustion of the fuel. In order to study this, the solids circulation rate was varied between 27.2 and 8.7 kg/h, and a low feed of solid fuel maintained at 0.082 kg/h of biomass (P01–P04).

$$\phi = \frac{\text{Oxygen available in the oxygen carrier}}{\text{Oxygen required for complete solid fuel combustion}} \quad (11)$$

The power input was also analysed, with a pine sawdust feeding rate of between 0.140 and 0.250 kg/h corresponding to a power input range of between 740 and 1330 W_{th} (P09–P11), and the solids circulation rate maintained at about 28.5 kg/h. In addition, the influence of the oxygen available to regenerate the oxygen carrier in the air reactor was analysed by decreasing the oxygen concentration from 21 vol% (P01–P08) to 10 vol% (P09–P11).

3 Results and Discussion

The effect of the temperature in the fuel reactor was analysed and compared between the three biomasses. For this purpose, the fuel reactor temperature was varied between 775 °C and 850 °C for the pine sawdust fuel (P05–P08), almond shells (A01–A04) and olive stones (O01–O04). During the experiments with pine sawdust, the solids circulation rate ($\dot{m}_s$) was 22.5 kg/h, with a solid fuel feed of 0.140 kg/h. The solids circulations rate was of 20.3 kg/h for the almond shells and 22.5 kg/h for the olive stones, with a solid fuel feed of between 0.173 and 0.225 kg/h.

3.1 Pine Sawdust combustion

Biomass combustion by CLOU process was investigated by means of several tests involving the burning of three different biomasses: pine sawdust, almond shells and olive stones. The experiments were carried out in the ICB-CSIC-s1 experimental rig. In the case of pine sawdust, three different parameters were analysed: the oxygen carrier-to-fuel ratio, fuel reactor temperature and power input. A total of 20 h of pine sawdust biomass combustion was carried out with the Cu34Mn66-GR oxygen carrier, without problems of agglomeration.

The gases exiting from the fuel and the air reactors were continuously analysed. Figure 2 shows the gas concentration (dry basis) as a function of the operation time in the pine sawdust experiments, where the effect of the fuel reactor temperature was analysed (P05–P08). The fuel reactor temperature varied between 775 °C and 850 °C, and each temperature was maintained at a steady state for around 60 min. It can be seen that when the fuel reactor temperature was varied, a transition period of around 20 min appear before the new steady state was reached. During the steady state, the temperature and the gas concentration were practically maintained as constants. No unburnt products (CH_4 , CO or H_2) were detected in the outlet gases, even at the lower temperature (775 °C). Therefore, complete combustion of the biomass to CO_2 and H_2O was achieved in the fuel reactor, and all the volatiles were completely converted inside the fuel reactor by the molecular oxygen released by the oxygen carrier.

Figure 2. Evolution of gas composition in the air and fuel reactors as fuel reactor temperature was varied. Experimental tests P05–P08. $\dot{m}_S = 22.5$ kg/h; $\dot{m}_{SF} = 0.140$ kg/h.

It can be seen that an increase in the fuel reactor temperature resulted in an increase in the CO_2 concentration in the fuel reactor outlet gas stream. This was caused by the increase in char conversion inside the fuel reactor that decreased the CO_2 concentration at the air reactor outlet. Also worthy of note is the fact that that no gaseous oxygen was measured at the fuel reactor outlet, contrary to experience in a previous work burning biomass with a Cu-based oxygen carrier [25]. This could be associated with the low fuel reactor temperature, together with the large proportion of volatiles in the biomass composition. However, using this oxygen carrier, CO_2 and H_2O were the only gases detected in the fuel reactor outlet stream, together with a fraction of the N_2 used as fluidizing agent. Moreover, some small amounts of NO_x at ppm level were detected coming from the nitrogen inherent to the biomass. However, evaluation of the nitrogen species was outside the scope of this work.

Figure 3 shows the effect of the oxygen carrier-to-fuel ratio, ϕ , on the combustion and CO_2 capture efficiencies, and on char conversion (P01–P04). In order to achieve high oxygen carrier-to-fuel ratio values, a biomass feed rate of 0.082 g/h ($435 \text{ W}_{\text{th}}$) was set

and the solids circulation rate was varied between 27.8 and 8.7 kg/h. Complete combustion to CO₂ and H₂O was always obtained, together with molecular oxygen, as measured at the fuel reactor outlet. Therefore, the oxygen carrier under these conditions was able to generate enough oxygen, with excess exiting in the fuel reactor stream after fully conversion of the fed-in biomass. CO₂ capture efficiencies of around 100% were achieved. It was necessary to reach ϕ values higher than 7 for the CO₂ capture efficiency to be reduced from 100% to 99.6%. This was due to the high reactivity of the biomass char, which was similar to that of Spanish lignite previously evaluated [25].

With regard to char conversion in the fuel reactor, Figure 3 shows that with ϕ values lower than 7, all the char fed into the continuous unit was converted inside the fuel reactor. With ϕ values higher than 7, the effect of the reduction in the residence time of char and oxygen carrier in the fuel reactor started to become more significant owing to the increase in the solids circulation rate, see Table 3. Moreover, similar behaviour had previously been observed for Spanish lignite; in those experiments it was also necessary to strongly increase the oxygen carrier-to-fuel ratio in order to see a reduction in CO₂ capture efficiency. This change in trend shows the high ϕ values needed to counter the effect of the excess of oxygen generated in the fuel reactor with the increased char entering the air reactor from the fuel reactor [24].

Figure 3. Combustion (●) and CO₂ capture (▲) efficiencies, and char conversion (■) at different oxygen carrier-to-fuel ratio, ϕ , values (P01–P04).

In order to study the effect of the fuel reactor temperature on the biomass combustion by means of the CLOU process, the biomass feed rate was increased from those used in previous tests to 0.140 kg/h (740 W_{th}) and the circulation rate was fixed at 22.5 kg/h, see Table 3. Figure 4 shows combustion and CO₂ capture efficiencies, as well as the char conversion as a function of the fuel reactor temperature (P05–P08). In a similar way to experiments (P01–P04), complete combustion of the biomass to CO₂ and H₂O was achieved for all the temperatures analysed. It is remarkable that complete combustion was even obtained at such a low fuel reactor temperature as 775 °C. The pine sawdust used contained 81% volatile matter; therefore, even with this high volatile matter content, the results showed full combustion of the biomass in all the tests. Note that unburnt compounds were always present at the fuel reactor outlet in the *i*G-CLC process, even if highly reactive materials or high solids inventories were used [8]. Note that incomplete combustion was observed at fuel reactor temperatures lower than 900 °C, with a high amount of CO, in previous experiments with pine using a Cu-based CLOU oxygen carrier [25]. This difference is a result of the low O₂ equilibrium concentration under 900 °C for CuO oxygen carriers without Mn in their composition (at 850 °C, 0.4 vol% for CuO [32] and 2 vol% for Cu_{1.5}Mn_{1.5}O₄ [22]). Interestingly, the present work shows that a Cu-Mn-based oxygen carrier is able to achieve complete combustion of the pine biomass even at 775 °C.

CO₂ capture efficiency depends on how much unburnt char is transferred to the air reactor, where it is burnt emitting CO₂ into the atmosphere. It can be seen that high CO₂ capture efficiency was obtained in all cases. With temperatures higher than 800 °C in the fuel reactor, CO₂ capture efficiencies were higher than 90%, reaching 96.6% at 850 °C. Also, Figure 4 demonstrates the positive effect on CO₂ capture efficiency of fuel reactor temperature. CO₂ capture efficiency increased from 86% to 95% with a 50 °C increase in the fuel reactor temperature. When the fuel reactor temperature reached 850 °C, the value of CO₂ capture efficiency increased to 98%. Under these conditions, CO₂ capture efficiency showed a value as high as 98%, without the use of a carbon separation system, i.e., avoiding the need for a carbon stripper.

Figure 4. Combustion (---●---) and CO₂ capture (---▼---) efficiencies, and char conversion (---■---) at different fuel reactor temperatures for the three different biomasses studied: pine sawdust (P05–P08), almond shells (A01–A04) and olive stones (O01–O04).

Remarkably high CO₂ capture efficiency values were obtained at the relatively low fuel reactor temperatures. Compared to previous experiments carried out in the same continuous unit using a Cu-based oxygen carrier and burning pine sawdust, fuel reactor temperatures higher than 920 °C were necessary in order to achieve similar values of CO₂ capture efficiency [25]. These high CO₂ capture efficiencies at temperatures between 775 °C and 850 °C are due to the fact that the Cu-Mn oxygen carrier is able to generate high concentrations of gaseous oxygen within this window of operation [11, 32], which improves combustion of the biomass. Therefore, the absence of unburnt products together with the high CO₂ capture efficiency highlights the high reactivity of the oxygen carrier for solid fuels combustion [23, 24]. The high CO₂ capture efficiency is associated with fast char conversion by direct combustion with the oxygen released by the oxygen carrier in the fuel reactor. Figure 4 shows char conversion as a function of the fuel reactor temperature. It can be seen that char conversion increased with the fuel reactor temperature. This effect appeared because by increasing the temperature, the char conversion rate in the fuel reactor was also increased, thus the amount of unburnt char transferred to the air reactor was reduced, increasing the CO₂ capture efficiency.

Finally, the effect of the biomass feeding rate (power input) was analysed for the pine sawdust. Figure 5 shows the effect of the power input on the combustion and CO₂ capture efficiencies, and also on char conversion at 800 °C. It can be seen that the effect

of power input was on CLOU performance was lower than that of fuel reactor temperature (P05–P08). However, an influence on CO₂ capture efficiency can be appreciated that is directly related to char conversion in the fuel reactor, see Figure 5. However, when the biomass feeding rate was increased, CO₂ capture efficiency decreased as a result of the reduction in char conversion in the fuel reactor. Under these conditions, when the biomass feeding rate increases, the ϕ value and the oxygen carrier inventory decreases; see Table 3. A decrease in the oxygen carrier-to-fuel ratio value increases oxygen carrier conversion in the fuel reactor, decreasing the rate at which O₂ is released by the Cu-Mn mixed oxide. Thus char conversion depends on oxygen carrier conversion [17]. It is important to highlight that even with a power input of 1330 W_{th} and fuel reactor temperature as low as 800 °C, there was complete combustion of the biomass in the fuel reactor. Higher CO₂ capture efficiencies can be obtained by increasing the temperature to 850 °C, which is an optimum temperature at which to operate the fuel reactor when using the Cu₃₄Mn₆₆-GR oxygen carrier [23].

Figure 5. Combustion (—●—) and CO₂ capture (—▲—) efficiencies, and char conversion (—■—) at different rates of power input (P09–P011). T=800 °C. 10% O₂ in air reactor.

Moreover, the effect of the oxygen concentration available to regenerate the oxygen in the air reactor on CO₂ capture efficiency and char conversion was analysed during tests P09–P11. When comparing experiments P06 and P09, it can be seen that with 10 vol% of O₂ at the air reactor inlet flow (air excess ratio of 2), CO₂ capture efficiency and char conversion were both stable at around 92% and 0.89, respectively. It can be concluded that oxidization is possible in the air reactor with an air excess ratio of 2, as was found previously when burning coal with the Cu₃₄Mn₆₆-GR oxygen carrier.

3.2 Combustion of other biomasses: almond shells and olive stones

Once the main parameters of pine sawdust combustion by the CLOU process were analysed, the combustion of two additional biomasses, almond shells and olive stones, was studied. Both biomasses showed different properties, as seen in Table 2, and it was necessary to know how they would behave in the continuous CLOU unit. This is the first time in the bibliography that biomasses other than pine sawdust have been used as solid fuel in the CLOU process. A total of 20 h of biomass combustion (10 h of combustion with each biomass) were carried out with the Cu₃₄Mn₆₆-GR oxygen carrier, without problems of agglomeration.

For both biomasses the effect on combustion and CO₂ capture efficiency, and char conversion as a function of the fuel reactor temperature was studied. For this purpose, the fuel reactor temperature was varied between 775 °C and 850 °C, see Table 3. The results can be seen in Figure 4. It is remarkable that for both biomasses, as with the pine sawdust experiments, no unburnt gases were found in the fuel reactor outlet, even at the relatively low fuel reactor temperature of 775 °C. This may be associated with the higher oxygen equilibrium concentration at lower temperatures of the Cu-Mn-based oxygen carrier, together with the possible presence of a gas-solid reaction between the oxygen carrier and the volatile matter of biomass, as was previously analysed by Adáñez-Rubio et al. by burning coal in a batch fluidized bed reactor [17, 22].

Focusing on CO₂ capture efficiency, Figure 4 shows that the CO₂ capture efficiency for both biomasses, the almond shells and olive stones, was lower than that achieved for the pine sawdust in the entire fuel reactor temperature interval studied. For both biomasses, as well as in the case of the pine biomass, CO₂ capture efficiency increased with fuel reactor temperature, reaching values higher than 90%. This was because CO₂ capture efficiency is directly related to char conversion and its reactivity: the higher the rate of char conversion in the fuel reactor, the lower the amount of unburnt char transferred to the air reactor and released into the atmosphere. As can be seen in Figure 4, char conversion was lower for almond shells and olive stones in the entire fuel reactor interval temperature studied. Table 2 shows that almond shells and olive stones have a larger proportion of fixed carbon in their compositions (therefore, a larger amount of

char is produced in the fuel reactor) and that more power was fed into the fuel reactor for both biomasses, see Table 3. As Figure 5 shows, the power input has less effect on CO₂ capture efficiency than fuel reactor temperature. Consequently, the difference in char conversion for the different biomasses would be related with the difference in their char reactivity. Also, it can be seen that char conversion is lower for almonds shell than it is for olive stones in the interval 775 °C–800 °C; however, char conversions were similar for both almond shells and olive stones at temperatures higher than 800 °C, with similar CO₂ capture efficiencies achieved for both biomasses. Therefore, for biomasses with lower reactivity than that of pine sawdust, it would be necessary to increase the fuel reactor temperature or to install a carbon stripper to reduce the amount of unburnt char transferred to the air reactor, and thus to increase char combustion reactivity and to increase CO₂ capture efficiency to over 95%.

The char conversion rate was analysed to compare the reactivity of the three different biomasses studied. With the experimental data obtained in the continuous unit, it was possible to calculate the char conversion rate using the Equation (9). Figure 6 shows the char conversion rate as a function of the fuel reactor temperature for the three biomasses studied in this work. Pine sawdust char was the most reactive, as can also be observed in Figure 4 with higher CO₂ capture efficiency values. Moreover, it can be seen that the char conversion rate for the three biomasses increased with fuel reactor temperature. The increase in char conversion was almost linear for almond shells, olive stones and pine sawdust. This enabled CO₂ capture efficiency to reach a value of 98% for the pine biomass, while maximum values of 92.3% and 90.5%, respectively, were obtained for almond shells and olive stones at 850 °C under the selected conditions used.

Figure 6. Char conversion rate for the different biomasses studied as a function of fuel reactor temperature: pine sawdust (●), almond shells (▲), olive stones (■). $\phi = 3.0\text{--}3.9$

It is possible to compare the results obtained by the CLOU process when burning three different biomasses with the results obtained with the *iG-CLC* process. Mendiara et al. [8] performed experiments in a 0.5 kW_{th} unit for the *iG-CLC* process by burning three different biomasses at temperatures between 900 °C and 990 °C. They found that at 900 °C CO₂ capture efficiency was around 90% for almond shells and olive stones and 96% for pine sawdust (920 °C), as in the CLOU process at 850 °C, see Figure 4. In the same study, 100% CO₂ capture efficiency was obtained at 950 °C for all biomasses. However, when considering combustion efficiency in the fuel reactor, in the case of the *iG-CLC* process at all temperatures, oxygen demand (which is directly related with the combustion efficiency in the fuel reactor) was around 10–30% for the interval of temperatures studied. On the contrary, no gaseous unburnt products were found in the gas exit stream of the CLOU process experiments.

4 Conclusions

The operation with three different biomasses was carried out in a 1.5 kW_{th} CLOU system for 65 h (40 h of combustion) using a Cu-Mn mixed oxide as an oxygen carrier

(Cu₃₄Mn₆₆-GR). Gaseous unburnt compounds were not present in the fuel reactor outlet, even at the lowest temperature studied (775 °C) in the fuel reactor, with CO₂, H₂O and O₂ being the only reaction products for the three biomasses studied in this work. When using pine sawdust as fuel, CO₂ capture efficiency was higher than 95% in most of the cases at operating temperatures in the fuel reactor as low as 850 °C.

Throughout the experimental campaign, no unburnt gaseous compounds appeared at the fuel reactor outlet, thus showing that combustion efficiency in the fuel reactor was always 100%. In experiments where the effect of the oxygen carrier-to-fuel ratio, ϕ , was studied, the oxygen carrier was able to generate enough oxygen to release excess into the fuel reactor stream and to fully convert the fed-in biomass. CO₂ capture efficiencies achieved values of around 100%.

Char combustion was improved at higher temperatures, reaching a fuel reactor conversion rate of 96.6% at 850 °C. At this condition, CO₂ capture efficiency showed a value as high as 98%, which therefore meant that the presence of a carbon separation system, i.e. a carbon stripper, could be avoided. The oxygen carrier-to-fuel ratio (ϕ) was found to be a fundamental parameter in order to obtain high CO₂ capture efficiencies. Higher ϕ values led to higher char conversion rates in the fuel reactor. This was due to the fact that the oxygen generation rate of this oxygen carrier depends on its reduction conversion. The lower the reduction conversion, the higher oxygen the generation rate, producing higher char conversion rates and also higher CO₂ capture efficiencies.

The effect of the oxygen available to regenerate the oxygen carrier in the air reactor was also investigated, with O₂ concentrations of 10 vol% at the air reactor inlet (4 vol% in the outlet stream). CO₂ capture did not show a significant decrease. It can be concluded that it is possible to oxidize the oxygen carrier in the air reactor with an oxygen concentration of 10 vol% at the inlet (4 vol% at the outlet) and obtain high CO₂ capture efficiencies.

Complete combustion was also obtained for almond shells and olive stones, and CO₂ capture efficiency increased with fuel reactor temperature, reaching values higher than 90%. As a function of the results obtained, for biomasses with lower reactivity than pine sawdust, it would be necessary to increase the fuel reactor temperature or to install a carbon stripper to reduce the amount of unburnt char transferred to the air reactor, and thereby to increase CO₂ capture efficiency to over 95%. Finally, char conversion rate was analysed to compare the reactivity of the three biomasses studied. The increase in char conversion was almost linear for almond shells, olive stones and pine sawdust. This enabled CO₂ capture efficiency, in the case of the pine biomass, to achieve a value of 98%, while the maximum value obtained for almond shells and olive stones at 850 °C was 92.3% and 90.5%, respectively.

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Notation

Symbols

f_i	Mass fraction of element or compound i (-) in biomass
F_i	Molar flow of compound i (mol/s)
M_i	Atomic or molecular mass of i elements or compound (kg/mol)
$\dot{m}_{SF}$	Mass flow rate of biomass fed into the fuel reactor (kg/h)
m_{FR}^*	Specific solids inventory (kg/MW _{th})
$\dot{m}_s$	Solids circulation rate (kg/h)

r_{Char}	Char conversion rate (s^{-1})
R_{OC}	Oxygen transport capability (kg oxygen per kg oxygen carrier)
X_{char}	Char conversion (-)

Greek letters

ϕ	Oxygen carrier-to-fuel ratio (-)
η_{CC}	CO_2 capture efficiency (-)
$\eta_{\text{comb,FR}}$	Combustion efficiency in the fuel reactor (-)
λ	Air excess ratio (-)
τ_{char}	Mean residence time of char particles in the fuel reactor (s)
τ_{FR}	Mean residence time of solids in the fuel reactor (s)
Ω_{SF}	Stoichiometric mass of O_2 to convert 1 kg of biomass (kg/kg)

Subscripts

inAR	Inlet stream to the air reactor
inFR	Inlet stream to the fuel reactor
outAR	Outlet stream from air reactor
outFR	Outlet stream from fuel reactor

Bibliography

- [1] N. United, United Nations Framework Convention for Climate Change. The Paris Agreement, (2015).
- [2] IEA, Energy technology perspectives 2016, International Energy Agency, Paris, France, (2016).
- [3] R. Global CCS Institute, Global CCS Institute, (2017).
- [4] IPCC, Special Report on Renewable Energy Sources and Climate Change, Mitigation Technical Support Unit Working Group III, Potsdam Institute for Climate Impact Research (PIK), (2012).
- [5] N.R. McGlashan, M.H.W. Workman, B. Caldecott, N. Shah, Negative Emissions Technologies, Imperial College London Grantham Institute for Climate Change, (2012).
- [6] J. Adánez, A. Abad, T. Mendiara, P. Gayán, L. De Diego, F. García-Labiano, Chemical Looping Combustion of solid fuels, *Prog. Energy Combust. Sci.* (2017), <http://dx.doi.org/10.1016/j.pecs.2017.07.005>
- [7] A. Lyngfelt, B. Leckner, A 1000MW_{th} boiler for chemical-looping combustion of solid fuels – Discussion of design and costs, *Applied Energy*, 157 (2015) 475-487.
- [8] T. Mendiara, A. Pérez-Astray, M.T. Izquierdo, A. Abad, L.F. de Diego, F. García-Labiano, P. Gayán, J. Adánez, Chemical Looping Combustion of different types of biomass in a 0.5 kW_{th} unit, *Fuel*, Submitted (2017).
- [9] T. Mendiara, A. Abad, L.F. de Diego, F. García-Labiano, P. Gayán, J. Adánez, Biomass combustion in a CLC system using an iron ore as an oxygen carrier, *International Journal of Greenhouse Gas Control*, 19 (2013) 322-330.
- [10] T. Berdugo Vilches, F. Lind, M. Rydén, H. Thunman, Experience of more than 1000 h of operation with oxygen carriers and solid biomass at large scale, *Applied Energy*, 190 (2017) 1174-1183.

- [11] A. Abad, I. Adánez-Rubio, P. Gayán, F. García-Labiano, L. de Diego, J. Adánez, Demonstration of chemical-looping with oxygen uncoupling (CLOU) process in a 1.5 kW_{th} continuously operating unit using a Cu-based oxygen-carrier, *International Journal of Greenhouse Gas Control*, 6 (2012) 189-200.
- [12] T. Mattisson, A. Lyngfelt, H. Leion, Chemical-looping with oxygen uncoupling for combustion of solid fuels, *International Journal of Greenhouse Gas Control*, 3 (2009) 11-19.
- [13] A. Shulman, E. Cleverstam, T. Mattisson, A. Lyngfelt, Manganese/Iron, Manganese/Nickel, and Manganese/Silicon Oxides Used in Chemical-Looping With Oxygen Uncoupling (CLOU) for Combustion of Methane, *Energy Fuels*, 23 (2009) 5269-5275.
- [14] A. Shulman, E. Cleverstam, T. Mattisson, A. Lyngfelt, Chemical – Looping with oxygen uncoupling using Mn/Mg-based oxygen carriers – Oxygen release and reactivity with methane, *Fuel*, 90 (2011) 941-950.
- [15] N. Pour, H. Leion, M. Rydén, T. Mattisson, Combined Cu/Mn oxides as an oxygen carrier in chemical looping with oxygen uncoupling (CLOU), *Energy Fuels*, 27 (2013) 6031-6039.
- [16] H. Leion, Y. Larring, E. Bakken, R. Bredesen, T. Mattisson, A. Lyngfelt, Use of CaMn_{0.875}Ti_{0.125}O₃ as oxygen carrier in chemical-looping with oxygen uncoupling, *Energy Fuel*, 23 (2009) 76-83.
- [17] I. Adánez-Rubio, A. Abad, P. Gayán, I. Adánez, L.F. De Diego, F. García-Labiano, J. Adánez, Use of Hopcalite-Derived Cu-Mn Mixed Oxide as Oxygen Carrier for Chemical Looping with Oxygen Uncoupling Process, *Energy Fuels*, 30 (2016) 5953-5963.
- [18] D. Hosseini, Q. Imtiaz, P.M. Abdala, S. Yoon, A.M. Kierzkowska, A. Weidenkaff, C.R. Müller, CuO promoted Mn₂O₃-based materials for solid fuel combustion with inherent CO₂ capture, *Journal of Materials Chemistry A*, 3 (2015) 10545-10550.
- [19] M. Rydén, H. Leion, T. Mattisson, A. Lyngfelt, Combined oxides as oxygen-carrier material for chemical-looping with oxygen uncoupling, *Applied Energy*, 113 (2014) 1924-1932.

- [20] A.-M. Azad, A. Hedayati, M. Rydén, H. Leion, T. Mattisson, Examining the Cu–Mn–O Spinel System as an Oxygen Carrier in Chemical Looping Combustion, *Energy Technology*, 1 (2013) 59-69.
- [21] S. Sajen, S.K. Singh, P. Mungse, S. Rayalu, K. Watanabe, G. Saravanan, N. Labhasetwar, Mechanically stable mixed metal oxide of Cu and Mn as oxygen carrier for chemical looping syngas combustion, *Energy Fuels*, 30 (2016) 7596-7603.
- [22] I. Adánez-Rubio, M.T. Izquierdo, A. Abad, P. Gayan, L.F. De Diego, J. Adánez, Spray granulated Cu-Mn oxygen carrier for chemical looping with oxygen uncoupling (CLOU) process, *International Journal of Greenhouse Gas Control*, 65 (2017) 76-85.
- [23] I. Adánez-Rubio, P. Gayan, A. Abad, L.F. De Diego, F. García-Labiano, J. Adánez, Coal combustion by a spray granulated Cu-Mn mixed oxide for CLOU process, *Applied Energy*, 208 (2017) 561-570.
- [24] I. Adánez-Rubio, A. Abad, P. Gayan, L.F. De Diego, J. Adánez, CLOU process performance with a Cu-Mn oxygen carrier in the combustion of different types of coal with CO₂ capture, *Fuel*, 212 (2018) 605-612.
- [25] I. Adánez-Rubio, A. Abad, P. Gayán, L.F. de Diego, F. García-Labiano, J. Adánez, Biomass combustion with CO₂ capture by chemical looping with oxygen uncoupling (CLOU), *Fuel Processing Technology*, 124 (2014) 104-114.
- [26] M. Schmitz, C.J. Linderholm, Performance of calcium manganate as oxygen carrier in chemical looping combustion of biochar in a 10 kW pilot, *Applied Energy*, 169 (2016) 729-737.
- [27] X. Wang, T. Xu, X. Jin, Z. Hu, S. Liu, B. Xiao, Z. Chen, M. Hu, CuO supported on olivine as an oxygen carrier in chemical looping processes with pine sawdust used as fuel, *Chemical Engineering Journal*, 330 (2017) 480-490.
- [28] M. Hanning, V. Frick, T. Mattisson, M. Rydén, A. Lyngfelt, Performance of Combined Manganese-Silicon Oxygen Carriers and Effects of Including Titanium, *Energy and Fuels*, 30 (2016) 1171-1182.
- [29] I.O.O. Council, <http://www.internationaloliveoil.org>, (2017).

- [30] I.N.D. Fruit, <http://www.nutfruit.org>, (2017).
- [31] P. Gayán, I. Adánez-Rubio, A. Abad, L.F. de Diego, F. García Labiano, J. Adánez, Development of Cu-based oxygen carriers for Chemical-Looping with Oxygen Uncoupling (CLOU) process, *Fuel*, 96 (2012) 226-238.
- [32] I. Adánez-Rubio, P. Gayán, A. Abad, L.F. de Diego, F. García Labiano, J. Adánez, Evaluation of a Spray-Dried CuO/MgAl₂O₄Oxygen Carrier for the Chemical Looping with Oxygen Uncoupling Process, *Energy Fuels*, 26 (2012) 3069-3081.