13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

Chemical looping combustion of biomass: an approach to BECCS

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Abstract

The climate change challenge demands a commitment of combined strategies between global institutions, governments, companies and citizens. In order to reach 2015 Paris Agreement, greenhouse gas emissions need to be reduced. Any single technology is currently able to achieve atmospheric greenhouse concentration values for the purpose of climate change mitigation. Also carbon sinks will be needed to further this cause as well as Carbon Capture and Storage (CCS) technologies. In this sense, biomass represents an interesting alternative fuel for heat and power production as a carbon dioxide-neutral fuel. Moreover, if the CO_2 generated during biomass combustion process was captured then negative-CO_2 emissions would be reached. In this way, Bio-Energy with Carbon Capture and Storage (BECCS) technologies enable energy generation while CO_2 is being removed from the atmosphere.

Among the different options, Chemical Looping Combustion (CLC) is considered one of the most promising second generation CCS technologies due to its negligible energy and cost penalty for CO_2 capture. In this work, three types of biomass were evaluated under CLC conditions: pine sawdust, olive stone and almond shell. Combustion experiments were performed in a continuous 500 W_{th} CLC unit at Instituto de Carboquímica (ICB-CSIC, Spain) using a highly-reactive low-cost iron ore as oxygen carrier (Tierga ore). During the experimental campaign, the effect of fuel reactor temperature (900-980 ºC) on the combustion performance was analyzed. At the highest temperature tested (980 ºC) a CO_2 capture efficiency of 100% was reached with all the biomasses. However, the total oxygen demand followed no clear trend with temperature and the average value was close to 25%. The high volatile content of biomass compared to coal contributed to this effect. For a correct operation with biomass, further design measures should be taken to reduce the amount of unburned compounds at the outlet of the fuel reactor. In addition, tar and NOx measurements were done. No relevant drawbacks by the use of biomass in CLC were found related with other pollutants present in the system such as tar production or NOx emissions.

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1. Introduction

World energy systems need to be decarbonized in the near future in order to control the levels of CO_2 in the atmosphere. This was one of the main conclusions drawn in the 5th Assessment Report of the International Panel on Climate Change (IPCC) published in 2014 [1].

In this way, the Paris Agreement in 2015 [2], the new United Nations Framework Convention on Climate Change (UNFCC) treaty that will substitute the Kyoto Protocol, describes three main points: to hold the increase in the global average temperature to well below 2 ℃ above preindustrial levels, to increase the ability to adapt to the adverse climate impacts, and to make finance flows consistent with a pathway towards low greenhouse gases (GHG) emissions. The agreement will enter into force when at least 55 countries accounting for at least 55 per cent of the GHG emissions have ratified it. On April 2016 both China and USA, which represent around 40 % of GHG emissions, confirmed they will sign the Agreement.

According to the IPPC, to limit the temperature increase to 2 ℃, CO_2 emissions should start to decrease by 2020 and even should be negative by the end of the century [1]. Negative Emission Technologies (NETs) denote those technologies actually able to remove CO_2 from the atmosphere. Some of these technologies, actually fall into this category, are those that use biomass with Carbon Capture and Storage (also denoted as BECCS, Bio-Energy with Carbon Capture and Storage) [3]. Biomass is a CO_2-neutral fuel which means that the carbon dioxide released during biomass combustion has been previously removed from the atmosphere during biomass growth. If this CO_2 is captured then negative CO_2 emissions are reached.

Different technological alternatives have been proposed for CO_2 capture during the last years. One of them is the Chemical Looping Combustion (CLC) process. In CLC the oxygen needed for combustion is provided by a solid oxygen carrier. Thus, the direct contact between fuel and air is avoided. For solid fuels CLC processes, the use of low cost materials (mineral or industrial residues) as oxygen carrier is preferred as they minimize the cost associated to possible losses of material together with the drainage of the ashes in the CLC system. The solid oxygen carrier circulates between two reactors identified as fuel and air reactors, respectively. In the fuel reactor, the oxygen carrier is reduced and the biomass oxidized to CO_2 and H_2O. After reduction, the oxygen carrier is transported to the air reactor and oxidized to its original form before a new cycle is started. CO_2 capture is inherent to the process and the energy penalty associated to it is quite low compared to other CCS technologies.

Chemical Looping Combustion of solid fuels has experienced a significant development in the last decade, especially with coal as fuel [4 - 7]. One the most advanced CLC processes using solid fuels is the *In Situ* Gasification Chemical Looping Combustion (*i*G-CLC), where steam or carbon dioxide is introduced as fluidizing/gasifying agents to the fuel reactor and gasification products reacts with the oxygen carrier carrying out the combustion. However, the use of biomass in the CLC process introduces new challenges as a consequence of its specific characteristics with respect to coal, such as the larger volatile content, the more reactive char, the favored tar formation, the lower ash content, the higher alkaline content, and the biomasses heterogeneity. Few studies addressed the use of biomass in CLC can be found in literature [8 - 11].

The aim of the present work is to assess the feasibility of CLC of biomass and reinforce its potential as BECCS technology. Experiments were conducted in a CLC continuous unit consisting in two interconnected bubbling fluidized beds. A low-cost material (Tierga iron ore, Spain) was used as oxygen carrier. In the present work different types of biomass were used: pine sawdust, olive stone and almond shell. The study considered the influence of the operation temperature (between 900 and 980 ℃) on the product gas composition. Based on these results, the performance of the process regarding carbon capture efficiency and oxygen demand can be evaluated. In addition, the study of other pollutants formation, such as tar and NOx, was carried out for the different biomasses.

2. Experimental

2.1. Oxygen-carrier

The iron ore used in the iG-CLC experiments was provided by PROMINDSA from a hematite mine in Tierga (Zaragoza, Spain). Tierga ore was first crushed and sieved to the desired size (+100-300 µm). XRD diffraction identified hematite (Fe_2O_3), dolomite, and SiO_2 as main solid phases. Prior to be used, the Tierga ore was calcined at 950 ºC during 12 hours, so that the dolomite decomposes to CaO and MgO. The calcination step also increased the mechanical strength of the material. Table 1 shows the main properties of this oxygen carrier.

Table 1. Characterization of Tierga ore oxygen carrier for iG-CLC tests.

Fe_2O_3 (wt.%)	75
Crushing strength (N)	4.7
Oxygen transport capacity, R_{OC} (%)	2.5
Porosity (%)	26.2
Skeletal density (kg/m^3)	4400
Specific surface area, BET (m^2/g)	1.7
XRD main phases	Fe_2O_3, SiO_2, Al_2O_3,CaO, MgO

2.2. Fuels

Three copious Spanish biomasses were chosen. Pine sawdust (Pinus Sylvestris) was chosen as reference biomass. Olive stones (Olea Europaea) and almond shell (Prunus Dulcis) are two large secondary products with biological origin as well as susceptible to energetic valorization. Spanish production of olive oil represents the 50 % of the world production (3252 kton in 2014) [12] while 5 % of total almond production (1077 kton in 2014) [13] corresponds to Spain. All biomasses were sieved to 0.5 - 2 mm particle size. Table 2 shows the proximate and ultimate analyses of each biomass.

Table 2. Proximate and ultimate analyses of each biomass (wt.%).

	Pine sawdust	Olive stone	Almond shell
Proximate analysis			
Moisture	4.2	9.4	2.3
Ash	0.4	0.8	1.1
Volatile matter	81.0	72.5	76.6
Fixed carbon	14.4	17.3	20.0
Ultimate analysis			
Carbon	51.35	46.17	49.78
Hydrogen	6.01	4.69	5.62
Nitrogen	0.28	0.18	0.16
Sulfur	0.00	0.00	0.00
Oxygen	37.78	38.00	40.35

2.3. Experimental facility, ICB-CSIC-s1

The biomass combustion experiments were performed at the ICB-CSIC-s1 unit (Fig. 1). This experimental unit comprised two interconnected fluidized bed reactors, (1) and (3) in Fig. 1, heated by electric furnaces (11). The fuel reactor (1) and the air reactor (3) were connected by a fluidized bed acting as loop seal (2). A riser (4) transported solids from the air to the fuel reactor. A cyclone recovered the entrained solids (5) and sent them to a deposit. A solids valve controlled the solids flow fed from this deposit to the fuel reactor (8). The flow controlling system was recently upgraded so that a better control of the solid flow was achieved. The fuel reactor consisted of a bubbling fluidized bed (50 mm ID). Biomass was fed with a screw feeder (9) at the bottom of this bed and just above the fuel reactor distributor plate. The fuel reactor was fluidized with steam which also acted as gasifying agent. The reduced oxygen carrier particles overflowed to the air reactor through a U-shaped fluidized bed loop seal that was fluidized using nitrogen (50 mm ID), thus preventing the mixing of gaseous atmospheres between the fuel and air reactors. Preliminary results showed that between 40 – 65 % of the fluidizing gas in the loop seal reached the fuel reactor and the rest the air reactor. The reduced oxygen carrier from the fuel reactor is oxidized in the air reactor (80 mm ID). Secondary air was introduced at the top of the bubbling bed to help particle entrainment. The outlet stream from the air reactor was sent up the riser to the stack through a high efficiency cyclone and filter. A diverting solid valve (6) enabled the measurement of the solid flow rates at any time.

Unconverted char particles could be transported together with the oxygen carrier to the air reactor. To prevent this loss of carbon, a carbon stripper located after the fuel reactor is considered one of the best options to maximize carbon capture in CLC of solid fuels [14]. However, the absence of a carbon stripper in this unit facilitated interpretation of the effect of different operating conditions on the results obtained.
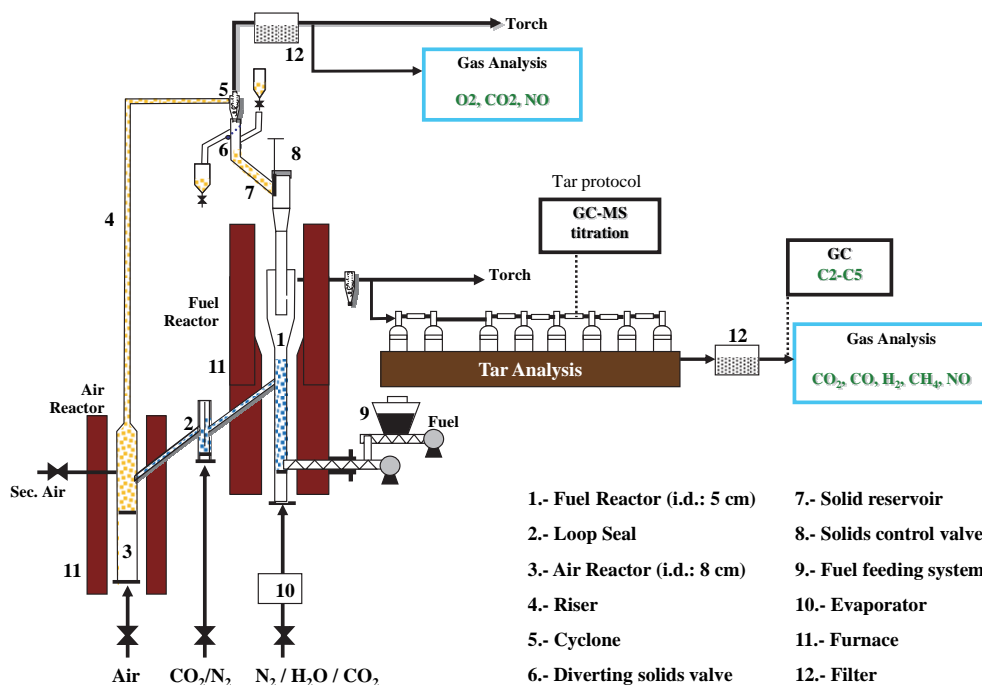

1.- Fuel Reactor (i.d.: 5 cm)	7.- Solid reservoir
2.- Loop Seal	8.- Solids control valve
3.- Air Reactor (i.d.: 8 cm)	9.- Fuel feeding system
4.- Riser	10.- Evaporator
5.- Cyclone	11.- Furnace
6.- Diverting solids valve	12.- Filter

Fig. 1. Scheme of the ICB_CSIC-s1 prototype.

On-line analyzers were used to know both air and fuel reactor outlet gases composition. CO, CO_2, H_2, CH_4, and NO concentrations in the fuel reactor outlet stream together with CO_2, NO, and O_2 from the air reactor were recorded. Sampling bags were also used to detect heavy hydrocarbons at the fuel reactor outlet with an HP 5890 gas chromatograph (GC) equipped with a TCD detector. Nitrogen compounds (NO, N_2O and N_2) concentration were also measured at the outlet of both fuel and air reactors in a mass spectrometer. Tar protocol [15] was used for tar sampling and determination. Therefore, the gas outlet stream from the FR was flowed through two empty impingers at 0 ºC and then another six containing isopropanol at -18 ºC. The quantitative determination of the different tar compounds was determined by a Gas Chromatograph (Agilent 7890A) fitted with a capillary column (HP-5) and a FID detector. Furthermore, the GC was coupled with a mass spectrometer (Agilent 5975C).

2.4. Operational Conditions

The oxygen carrier to fuel ratio (ϕ) defined the conditions under which the experiments were performed. The oxygen carrier to fuel ratio is a measure of how much oxygen can be supplied by the circulating oxygen carrier compared to the oxygen needed to burn the fuel fed into the system. Stoichiometric conditions are represented by an oxygen carrier to fuel ratio equal to one.

$$\phi = \frac{F_{OC} \cdot R_{OC}}{\dot{m}_{SF} \cdot \Omega_{SF}} \tag{1}$$

where F_{OC} is the solid circulation rate (kg/h), $\dot{m}_{SF}$ is the biomass mass flow (kg/h), R_{OC} is the oxygen transport capacity of the oxygen carrier, and Ω_{SF} is the amount of oxygen necessary to burn the solid fuel introduced to the fuel reactor (kg oxygen/kg biomass). In the experiments, values of parameter ϕ close to one were used.

The steam flow to the fuel reactor corresponded to a velocity of 0.08 m/s at 900 °C. In the air reactor the total air flow, corresponded to a velocity of 0.5 m/s at 900 °C. The circulation flow rate was maintained about 8 kg/h and the solids inventory varied between 580 and 880 kg/MW$_{th}$.

Different experiments were carried out varying the fuel reactor temperature from 900°C to 980°C. The temperature in the air reactor was maintained at about 950°C. Measurements were done when stable conditions were reached and each experimental data corresponds to at least 1 hour of steady state operation. A total of 70 hours of continuous operation feeding fuel and 200 hours of continuous fluidization were accumulated during this experimental campaign.

2.5. Data evaluation

To evaluate the performance of the iG-CLC process with biomass, two main parameters were considered. The CO_2 capture efficiency (η_{CC}) is defined as the fraction of the carbon introduced which is converted to gas in the fuel reactor. This parameter considers the CH_4, CO, and CO_2 exiting the fuel reactor, as the amount of hydrocarbons heavier than CH_4 were negligible or very low compared the rest of the carbonaceous components.

$$\eta_{CC} = \frac{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR}]_{out}}{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} + F_{CO_2,AR}]_{out}} \tag{2}$$

where $F_{i,FR}$ is the i species molar flow in the fuel reactor outlet stream and $F_{CO2,AR}$ represents the CO_2 molar flow resulting from the combustion of unconverted char entering the air reactor.

The total oxygen demand (Ω_T) is calculated as the quotient between the oxygen required to reach the complete combustion of the unconverted gases (CH_4, CO, and H_2) in the fuel reactor and the oxygen needed for complete combustion of the biomass fed.

$$\Omega_T = \frac{F_{CO,FR} + 4 \cdot F_{CH_4,FR} + F_{H2,FR}}{\dfrac{1}{M_O} \cdot \dot{m}_{SF} \cdot \Omega_{SF}}$$

(3)

where M_O is the oxygen atomic weight.

3. Results and discussion

The biomass Chemical Looping Combustion experiments were performed at the ICB-CSIC-s1 unit using comparable solid inventories in the fuel reactor for the different types of biomass (pine sawdust: 770 kg/MW$_{th}$; olive stone: 580 kg/MW$_{th}$; almond shell: 880 kg/MW$_{th}$). As mentioned before, in all cases, operating conditions close to stoichiometric were maintained ($\phi \approx 1$).

Fig. 2 shows the main results obtained during a standard experiment. Smooth operations were observed for all biomasses and no differences were found among different fuels. Measurements were done when stable conditions were reached and each experimental data corresponds to at least 1 hour of steady state operation. Concentrations (dry N_2 free) of the main gaseous products at the fuel reactor outlet are presented as a function of time using pine sawdust as fuel. The major compound was always CO_2 (about 70%). Unburned volatiles and biomass gasification products were also detected (CH_4, CO and H_2), higher hydrocarbons were negligible. Oxygen was maintained at values $\approx$ 17 vol.% although in an industrial CLC plant lower values will be reached. CO_2 concentration in the air reactor, representing the carbon capture efficiency loss, was negligible in this test.
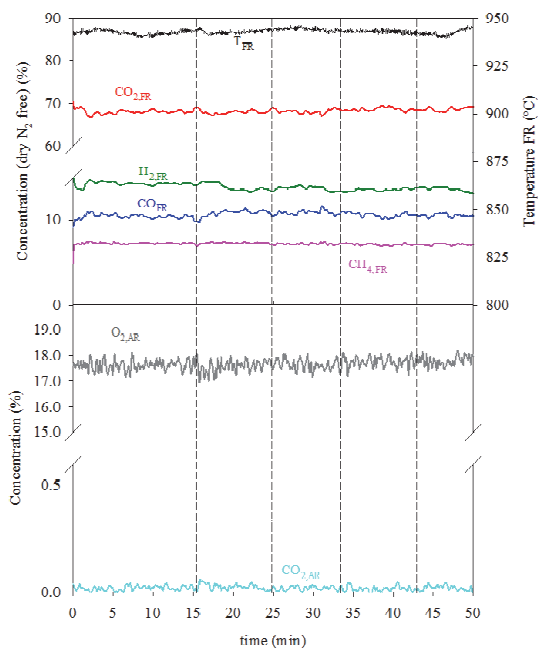

Fig. 2. Fuel reactor temperature, concentrations (dry N_2 free) of the main gaseous products at the fuel reactor outlet and oxygen concentration at the air reactor outlet in a typical test. Biomass=pine sawdust. ϕ=1.1. T_{AR}=950 ºC.

3.1. Carbon capture efficiency and oxygen demand

In order to evaluate the CLC process with biomass different chemical looping parameters were calculated. Fig. 3 and 4 present the carbon capture efficiency and total oxygen demand as a function of fuel reactor temperature for each biomass. As it is shown, CO_2 capture efficiency increased with the fuel reactor temperature in all cases. The values obtained for pine sawdust were always higher than those obtained at similar temperatures for the other biomasses. This could be consequence of the higher volatile content of this biomass, as shown in Table 2. In any case, it is interesting to highlight that 100% CO_2 capture was reached with the three biomasses at 980 ºC without the presence of a carbon stripper in the CLC unit.

Also total oxygen demand is shown on Fig. 4 as a function of the fuel reactor temperature. The values of total oxygen demand for all biomasses were high, reaching values up to 30 %, and no clear trend was observed with the fuel reactor temperature. These values were higher than those previously reported by Mendiara et al. [8] in experiments using Tierga ore and pine sawdust. However, those values were obtained using higher solids inventory in the fuel reactor ($\approx$1400 kg/MW$_{th}$). It must be considered that higher solids inventory represents more oxygen availability to oxidize the volatiles and char gasification products generated in the fuel reactor. Nevertheless, solids inventories higher than 1000 kg/MW$_{th}$ are not recommended as it could result in high pressure drop in the fuel reactor [16, 17]. Thus, the total oxygen demand values obtained in the present work can be considered as more representative of what could be expected in iG-CLC of biomass.

For biomass CLC processes, efforts should then be conducted to reduce the amount of unburned compounds at the outlet of the fuel reactor. The most common option to decrease the total oxygen demand is to implement an oxygen polishing unit at the fuel reactor outlet although the energy penalty associated to the production of pure oxygen is high. Alternative options aiming at lower energy penalty where recently presented by Gayán et al. [18]. The technological options evaluated include measures to increase the gas–solid contact in the fuel reactor, the incorporation of a secondary fuel reactor, re-circulation of exhaust gases to the fuel reactor or the carbon stripper, or the feed of the fuel to the carbon stripper instead of the fuel reactor. Another modification to the fuel reactor design called "volatile distributor" was recently proposed by Lyngfelt and Leckner [19] consisting in a new design for the fuel injection to avoid the formation of local plume of volatiles. In any case, further experimental work will be necessary to assess the viability of these alternatives in the iG-CLC process with biomass.
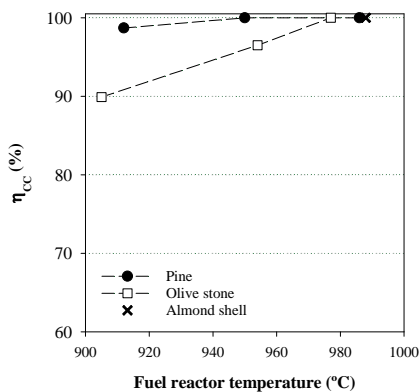

Fig. 3. Carbon capture efficiency (η_{CC}) as a function of the fuel reactor temperature for all the biomasses. $\phi\approx$1. T_{AR}=950 ºC.
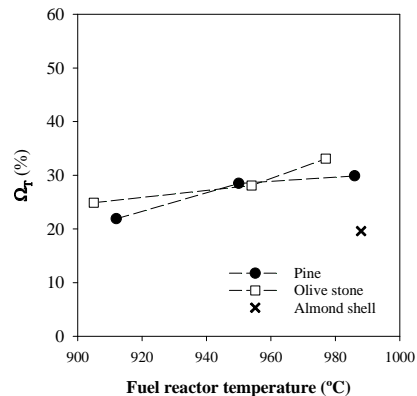
Fig. 4. Total oxygen demand in the fuel reactor (Ω_T) as a function of the fuel reactor temperature for all the biomasses. $\phi\approx$1. T_{AR}=950 ºC.

3.2. Tar production

As it was mentioned, tar compounds were collected in impingers following the standard tar protocol [15]. Fig 4 shows the tar composition obtained during the biomass processing at the same temperature, T_{FR}=950 ℃. No major differences were found among the three biomasses: pine sawdust, olive stone, and almond shell. In all cases naphthalene appeared as the major tar compound. However, Tar generation would not represent a cornerstone in the use of biomass CLC process since these pollutants would be majorly converted in the downstream oxygen polishing step.
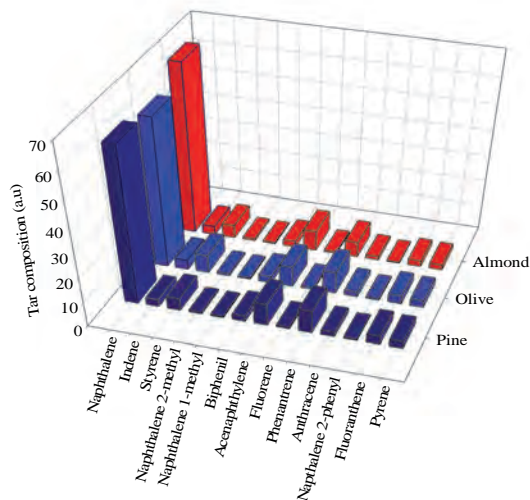

Fig. 4. Tar composition for the different biomasses. T_{FR}=950 ℃.

3.3. NOx emissions

CLC processes avoid air entering into the fuel reactor. In this way, high temperature enhanced reactions of thermal NOx formation were not relevant during this tests because of low temperatures and reducing and oxidizing separate atmospheres. In this work it was found that most of the fuel-N was emitted as N_2 in the fuel reactor, meanwhile the NO varied between 4-14 wt.%. NO emissions decreased with increasing the fuel reactor temperature as a consequence of the enhanced reduction reaction of NO by the presence of biomass char. Despite of the fact of different fuel-N concentrations between biomasses (Table 2), no clear differences in NO emissions were observed.

4. Conclusions

Biomass combustion combined with CO_2 capture would lead to negative CO_2 emissions. In order to reach this objective, a study of the performance of the iG-CLC process for pine sawdust, olive stone and almond shell was herein presented. An iron ore oxygen carrier (Tierga ore) was used due to its low-cost and good reactivity. Pine sawdust, olive stone and almond shell were used as renewable fuels. The experimental campaign included 70 h of combustion.

The study analyzed the influence of the fuel reactor temperature (900-980 ℃) on the CO_2 capture efficiency and total oxygen demand. It should be highlighted that it was possible to reach 100% of CO_2 capture efficiency with all the biomasses tested at 980 ℃ without the presence of a carbon stripper. However, the high values of oxygen demand obtained in the combustion tests would made necessary the implementation of additional design measures

to decrease the amount of unburned compounds obtained at the outlet of the fuel reactor. In addition, tar and NOx studies showed that no special drawbacks would be expected by the use of biomass in CLC.

Acknowledgements

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