Chemical Looping Combustion of different types of biomass in a 0.5 kW_{th} unit

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Abstract

Chemical Looping Combustion (CLC) using renewable solid fuels appears as an important option to reach negative carbon emissions. In this work, three types of forest and agricultural residues (pine sawdust, olive stone and almond shell) were tested between 900-980 °C in a 0.5 kW_{th} unit with an iron ore as oxygen carrier (Tierga ore) working under *In situ* Gasification-Chemical Looping Combustion (*iG*-CLC) mode. Specific solids inventories lower than 1000 kg/MW_{th} were tested as they were considered more representative of what can be used in a larger CLC unit. CO₂ represented about 70

% in the fuel reactor outlet gas stream, followed by unburnt compounds: H₂, CO and CH₄. Carbon capture efficiencies increased with the fuel reactor temperature achieving 100 % of carbon capture with the three biomasses at temperatures above 950 °C. In contrast, no clear trend with the fuel reactor temperature was observed for the total oxygen demand, achieving values about 25 %. The major contribution to this value comes from the unburned volatiles with a small contribution coming from tar (≈1%). Regarding tar, naphthalene was the major compound found at the different operating conditions. The present results support the consideration of the CLC process with biomass (bio-CLC) as a promising Bio-Energy with Carbon Capture (BECCS) technology.

Keywords; NETs, BECCS, Chemical Looping Combustion (CLC), biomass, low-cost oxygen carrier, tar

1. Introduction

Sustainability is becoming one of the most important challenges of present societies. One of the threats to the sustainability of our planet is climate change. In order to mitigate the effects of these changes in climate, different actions should be taken to restrict anthropogenic greenhouse gas (GHG) emissions. Based on the findings presented in the 5th Assessment Report of the International Panel on Climate Change (IPCC) [1], the Paris Agreement in 2015 set the objective of limiting the global average temperature increase to 2 °C by reducing the GHG emissions and within them, CO₂ emissions [2]. To reach this goal it becomes necessary to develop not only neutral but also negative carbon emission technologies (NETs) during the present century [3]. NETs comprise different types of technologies which actually reduce carbon concentration in the atmosphere, such as afforestation, agricultural land management,

bio-char soil sequestration, ocean liming, enhanced weathering, ocean fertilization and Bio-Energy with Carbon Capture and Storage (BECCS) [4].

BECCS technologies are drawing increasing attention in the last years. They match both biomass combustion and Carbon Capture and Storage (CCS) and this combination reinforces their potential to generate heat and/or power, while removing CO₂ from the atmosphere [4]. Biomass carbon emissions are considered neutral because of their short life cycle. Moreover, biomass accessibility, simply sustainable management as well as relatively homogeneous world distribution must be considered as important characteristics of biomass compared to other fuels. In this way, including biomass technologies, the energy mix self-sufficiency and environmental protection in energy supply would be ensured [5, 6]. The bio-energy concept associated with BECCS includes both biomass fuelled biochemical and thermochemical processes easily combinable with CCS [7]. An almost pure CO₂ stream should be produced during fuel conversion to make feasible its transportation and storage. Simply pre-treated biomass or even biomass derived liquid and gas fuels can be used.

CCS technologies allow CO₂ emission reduction from stationary point sources in energy production. In this context, chemical looping combustion (CLC) processes have demonstrated to be one of the most suitable alternatives for CCS because of the low cost of carbon capture and energy penalty [8]. This technology allows fuel combustion in nitrogen-free atmosphere. A solid oxygen carrier (OC) provides the oxygen needed for fuel oxidation via redox reaction while circulating between the so-called fuel and air reactors. CLC combustion of solid fuels has reached an important development in the last decade [9]. Most of the knowledge has been gained using coal as fuel in prototypes in the range 0.5 kW_{th} to 3 MW_{th}. The majority of the CLC units operated under the *In Situ* Gasification-Chemical Looping Combustion (*iG*-CLC) mode. Fig. 1 shows the scheme

of a typical *i*G-CLC unit for solid fuels. In this process, the solid fuel is gasified in the fuel reactor using steam as gasifying agent. Both the volatile compounds and the gasification products generated react with the oxygen carrier to produce CO_2 and H_2O . The possible unburnt compounds at the outlet of the fuel reactor would be further oxidised in an oxygen polishing step. This stream can be easily dried to obtain a CO_2 stream ready to be transported and stored. Finally, the oxygen carrier is re-oxidized in the air reactor.

Fig. 1. Scheme of the *i*G-CLC process.

Based on this experience, the biomass fuelled CLC became feasible as a BECCS technology. First results using biomass (pine sawdust) and iron ore as oxygen carrier were obtained by Shen et al. [10] in a $10 \text{ kW}_{\text{th}}$ unit. They evaluated the influence of the fuel reactor temperature on the gas products composition. Pine sawdust was also used in the experiments performed at Instituto de Carboquímica by Mendiara et al. [11] with a Fe-based iron ore (Tierga ore) as oxygen carrier. The influence of the fuel reactor temperature on the CO_2 capture and combustion efficiency was assessed. Tar measurements were also performed. Moreover, no interaction of biomass ashes with the oxygen carrier was observed after 78 h of continuous operation. Several manganese ores were used as oxygen carriers by Schmitz et al. [12] for wood char combustion in a continuous $10 \text{ kW}_{\text{th}}$ CLC unit at Chalmers University of Technology. Some of them

presented low oxygen demands and high carbon capture efficiencies. Wood char was also used by Linderholm et al. [13] in a 100 kW_{th} CLC plant also located at Chalmers University of Technology. In this case, Tierga ore was used as oxygen carrier. The highest combustion efficiency observed in these experiments was 93%. It should be mentioned that high specific solids inventories (>1000 kg/MW_{th}) were used in the previously described studies. According to the experience gained in experiments with coal in different continuous CLC units, the optimum value of this parameter would be lower to avoid high pressure drop in the fuel reactor [14]. This could affect the combustion efficiency reached. Recently, a new 10-50 kW_{th} scale CLC plant for biomass combustion was built at VTT Technical Research Centre in Finland and operated by Pikkarainen et al. [15]. They found high oxygen demands during the combustion of wood pellets due in this case to an insufficient bed temperature of the fuel reactor, as the unit was originally designed for gasification.

A big step in the scale-up of the biomass CLC process was recently presented by Berdugo-Vilches et al. [16]. Several experimental campaigns were carried out in a semi-commercial dual fluidized bed (DFB) unit at Chalmers University consisting of a 12 MW_{th} boiler coupled to a 2-4 MW_{th} bubbling bed gasifier. The gasifier can be assimilated to a fuel reactor of a conventional CLC unit and the boiler to the air reactor. More than 1000 hours of combustion were reported using commercial wood pellets as fuel and ilmenite and a manganese ore as oxygen carriers. Combustion efficiencies up to 60% were achieved although the temperature in the gasifier was not high, about 830 °C. Although this plant represents a non-optimized reactor design for CLC applications, these results highlight the strong potential of the CLC technology for biomass combustion and reinforce its possibilities as BECCS technology.

In this line, the present work aims at further contributing to the knowledge of biomass CLC. Commonly, pine or spruce tree pellets have been used as fuels. The objective of this work is to extend the study to other types of biomass (agricultural residues such as olive stones and almond shells) in order to identify possible differences during combustion. Besides, operation with specific solids inventories lower than 1000 kg/MW_{th} will be assessed. Experiments are performed in a continuous 0.5 kW_{th} unit operating under *i*G-CLC mode. The influence of the fuel reactor temperature on the results obtained is evaluated using specific solids inventories realistic for industrial CLC units.

2. Experimental

2.1 Oxygen carrier and biomass

Tierga ore was used as oxygen carrier in the present experiments. In a comparative study among Fe-based oxygen carriers, Tierga ore showed the highest reactivity in the combustion of coal [17, 18] as well as stability and durability combined with its low cost. Thus, it was also selected to perform biomass combustion experiments. After receiving it from an hematite mine in Tierga (Zaragoza, Spain), the ore was crushed to 100-300 µm size particle and calcined at 950 °C during 12 hours for increasing its mechanical strength. The main properties of Tierga ore are summarized in Table 1. A detailed description of the techniques used in the characterization of the sample can be found elsewhere [17].

Table 1. Main characteristics of the calcined Tierga ore used as oxygen carrier.

Fe₂O₃	wt %	76.5
XRD main phases	Fe ₂ O ₃ , SiO ₂ , Al ₂ O ₃ , CaO, MgO	
Crushing strength	N	5.8
Oxygen transport capacity, R_{OC}	%	2.5
Porosity	%	26.3
Skeletal density	kg/m ³	4216

Specific surface area, BET	(m ² /g)	1.4
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Three Spanish biomass residues were selected as fuels. One forest residue, pine sawdust (*Pinus sylvestris*) from Spain, was chosen as a reference material. Besides, olive stones (*Olea europaea*) and almond shell (*Prunus dulcis*) were selected as they are agricultural residues with high annual production. In 2014, world olive oil production reached 3.2 million tons and almond production 1.1 million tons [19, 20]. Raw materials were dried and sieved to adequate their size to a particle distribution between 0.5 - 2 mm. Proximate and ultimate analyses of each biomass are presented on Table 2. In this Table, the low heating value and the value of the oxygen demand of the solid fuel, Ω_{SF} , were also included. The latter parameter represents the stoichiometric amount of oxygen to burn the solid fuel.

Table 2. Analyses of the biomasses.

	Pine sawdust	Olive stone	Almond shell
Proximate analysis (wt%)			
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 (wt%)			
C	51.3	46.5	50.2
H	6.0	4.8	5.7
N	0.3	0.2	0.2
S	0.0	0.0	0.0
O	37.8	38.3	40.5
LHV (kJ/kg)	19158	16807	18071
Ω_{SF} (kg oxygen/kg fuel)	1.5	1.2	1.4

2.2 Experimental setup and procedure

The ICB-CSIC-s1 experimental unit showed in Fig. 2 consists of the fuel (1) and the air (3) reactors, both fluidized type. The biomass is fed into the fuel reactor (50 mm ID) at

the bottom of the bubbling fluidized bed with a series of two screw feeders. Steam used as gasifying agent was produced by heating up in an evaporator the corresponding water flow supplied by a peristaltic pump. There is no carbon stripper between fuel and air reactors. This facilitated the analysis of the influence on biomass combustion of different variables affecting the fuel reactor. The fuel reactor is connected to the air reactor by a U-shaped fluidized bed reactor (30 mm ID) placed as loop seal (2) to prevent the mixture of the gases between them. The loop seal was fluidized with nitrogen. Previous tests demonstrated that approximately 50% of the loop seal fluidizing agent reached the fuel reactor. The reduced oxygen carrier was transferred to the air reactor which is also a bubbling fluidized bed (80 mm ID). Once re-oxidized it was sent up the air reactor through a riser (4) helped by a secondary air entrance, collected by a cyclone (5) and sent to a deposit (7) that keeps both reactor atmospheres separated. A diverting solid valve (6) was used to measure the solid circulation rate during the experiment. The flow of oxygen carrier fed to the fuel reactor from this deposit was controlled by a solids valve (8).

Main combustion and gasification product concentrations at the fuel reactor outlet (CO, CO₂, H₂ and CH₄) and air reactor (CO, CO₂ and O₂) were recorded by on-line analyzers. Gas samples were taken in order to detect gaseous C₂-C₄ hydrocarbons at the fuel reactor outlet with an HP 5890 gas chromatograph (GC) coupled with a Thermal Conductivity Detector (TCD). Tar compounds at the fuel reactor outlet were collected in impingers following the standard tar protocol [21]. The quantitative determination of the concentrations of the different tar compounds in the samples was done by a GC (Agilent 7890A) fitted with a capillary column (HP-5) and a Flame Ionization Detector (FID). Furthermore, the GC was coupled with a mass spectrometer (Agilent 5975C). Naphthalene and phenanthrene were selected for the external calibration procedure. The

quantitative values were obtained assuming a similar response factor to naphthalene for tar compounds of 1–2 rings and similar to phenanthrene for 3-rings compounds [22].

Fig. 2. Experimental unit ICB-CSIC-s1.

Combustion conditions were maintained near to stoichiometric conditions during all the performed experiments. For this purpose, the oxygen carrier to fuel ratio (ϕ) compares the oxygen that could be supplied by the circulating oxygen carrier with the oxygen needed for the complete combustion of the fed fuel.

$$\phi = \frac{m_{OC} \cdot R_{OC}}{\dot{m}_{SF} \cdot \Omega_{SF}} \quad (1)$$

The oxygen carrier inventory in the unit was about 3.5 kg and the solids circulation rate of oxygen carrier was about 8 kg/h. The fuel reactor steam flow was set to achieve a velocity of 0.08 m/s at 900 °C. The velocity in the air reactor was 0.5 m/s at 900 °C. Table 3 shows the experimental conditions and results of the experiments performed. A

total of 60 hours of hot operation were accomplished, 40 of which corresponds to biomass combustion.

2.3 Data evaluation

In order to evaluate the performance of the *i*G-CLC process with biomass, three parameters were considered, i.e. CO₂ capture efficiency, char conversion and total oxygen demand. The CO₂ capture efficiency (η_{CC}) was defined as the fraction of the carbon introduced which was converted to gas in the fuel reactor. The carbon converted was calculated from the CH₄, CO and CO₂ concentrations exiting the fuel reactor. Considering the low amounts of C₂-C₄ detected in the tests, the amount of hydrocarbons heavier than CH₄ were considered negligible for the calculations.

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

Table 3. Operating conditions and experimental results of the tests with the biomasses (PN=pine sawdust, OS=olive stone, AS=almond shell).

Biomass	PN	PN	PN	PN	OS	OS	OS	AS	AS	AS
Time of combustion (h)	3.3	5.7	2.6	2.2	8.1	3.0	2.3	3.7	3.3	3.8
Time hot fluidization (h)	6.5	8.2	4.1	3.1	9.4	4.5	3.0	6.3	9.3	6.4
Temperatures (°C)										
Fuel reactor	895	910	950	985	905	955	980	905	955	985
Air reactor	950	950	950	950	950	950	950	950	950	950
Operating conditions										
Biomass flow (g/h)	152	113	98	98	164	141	141	190	102	88
OC circulation rate (kg/h)	10.1	9.2	6.7	6.7	8.8	7.6	7.6	13	7	5.9
Oxygen carrier to fuel ratio, ϕ	1.1	1.3	1.1	1.1	1.0	1.0	1.0	1.2	1.2	1.2
Specific solids inventory (kg/MW _{th})	475	750	785	780	600	600	590	370	550	890
Gas composition										
Fuel reactor (vol%, N ₂ free, dry basis)										
CO	11.0	9.5	10.1	11.7	10.3	12.7	12.5	10.4	10.6	9.8
CO ₂	69.2	71.1	72.1	65.2	70.0	66.2	65.0	70.8	65.0	72.9
H ₂	11.1	12.3	11.4	15.4	11.3	13.1	14.5	10.4	16.2	11.3
CH ₄	8.7	7.1	6.4	7.7	8.4	8.0	8.0	8.4	8.2	6.0
CH ₄ conversion (%)	-	73.5	-	-	65.1	-	-	71.0	-	-

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Air reactor (vol%)										
O ₂	17.5	18.4	19.4	19.3	17.8	18.6	19.2	17.2	19.4	19.3
CO ₂	0.2	0.1	0.0	0.0	0.5	0.1	0.0	0.5	0.0	0.0
Tar analysis										
H ₂ O content (vol%)	-	-	12.0	8.8	-	9.4	8.5	-	10.6	12.8
Total tar (g/Nm ³ dry)	-	-	4.30	2.48	-	3.59	3.72	-	2.98	2.64
Total tar (g/kg daf fuel)	-	-	2.76	1.59	-	1.70	1.77	-	1.82	1.84
Tar oxygen demand, Ω_{tar} (%)	-	-	1.4	0.9	-	1.2	1.3	-	1.0	1.0
Tar composition (g/Nm³ dry)										
Styrene	-	-	0.21	0.08	-	0.26	0.14	-	0.16	0.11
Indene	-	-	0.13	0.05	-	0.14	0.11	-	0.10	0.07
Naphthalene	-	-	2.64	1.77	-	2.11	2.47	-	1.98	1.73
Naphthalene 2-methyl	-	-	0.03	0.02	-	0.03	0.02	-	0.02	0.02
Naphthalene 1-methyl	-	-	0.02	0.01	-	0.02	0.01	-	0.02	0.01
Biphenil	-	-	0.09	0.05	-	0.09	0.07	-	0.07	0.07
Acenaphthylene	-	-	0.38	0.16	-	0.29	0.26	-	0.24	0.22
Fluorene	-	-	0.03	0.01	-	0.03	0.02	-	0.02	0.02
Phenantrene	-	-	0.39	0.16	-	0.32	0.28	-	0.18	0.19
Anthracene	-	-	0.08	0.04	-	0.07	0.06	-	0.04	0.04
Napthalene 2-phenyl	-	-	0.02	0.01	-	0.02	0.02	-	0.01	0.01
Fluoranthene	-	-	0.15	0.07	-	0.12	0.13	-	0.07	0.06
Pyrene	-	-	0.12	0.06	-	0.10	0.12	-	0.06	0.05
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The CO₂ capture efficiency calculated according equation (2) depended on the fraction of char that was gasified in the fuel reactor. The char conversion (X_{char}) was defined as the fraction of carbon in the char formed in the fuel reactor which was released to the fuel reactor exhaust gas stream:

$$X_{char} = \frac{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} - F_{C,vol}]_{out}}{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} + F_{CO_2,AR} - F_{C,vol}]_{out}} \quad (3)$$

$F_{C,vol}$ was calculated from the biomass analyses as the difference between the total carbon in the biomass and the fixed carbon.

The total oxygen demand (Ω_T) was calculated as the quotient between the oxygen required in order to reach complete combustion of the unconverted gases (CH₄, CO and H₂) and the oxygen needed for complete combustion of the biomass fed.

$$\Omega_T = \frac{4 \cdot F_{CH_4,FR} + F_{CO,FR} + F_{H_2,FR}}{\frac{1000}{M_O} \cdot \dot{m}_{SF} \cdot \Omega_{SF}} \quad (4)$$

Two more parameters were calculated in order to better understand the combustion of biomass in our CLC unit. The results were also included in Table 3. First, the volatile conversion was estimated. For its calculation, it was considered that methane is the compound at the fuel reactor outlet coming exclusively from volatile release. Both the CO and H₂ found could also come from char gasification. Therefore methane was used as volatile reference compound to calculate volatile conversion. Thus, the flow of methane at the fuel reactor outlet was compared to that predicted by an empirical model [23] at the corresponding fuel reactor temperature. Additionally, based on tar composition, the oxygen required to completely burn tar (C_nH_m) to CO₂ and H₂O was calculated and compared to the oxygen needed to completely burn the fuel. This ratio has been defined as the tar oxygen demand (Ω_{tar}).

$$\Omega_{tar} = \frac{(n+m/4) \cdot F_{C_nH_m,FR}}{\frac{1000}{M_O} \cdot \dot{m}_{SF} \cdot \Omega_{SF}} \quad (5)$$

3. Results and discussion

3.1 Gas composition at the fuel reactor outlet

Fig. 3 presents the temporal evolution of the main gaseous products obtained in both fuel and air reactors for a typical experiment. Data correspond to pine sawdust combustion although similar profiles were obtained for the other biomasses. Air and nitrogen were used as fluidizing agents during the heating period. After reaching the desired temperatures, the fluidizing agent in the fuel reactor was switched to steam and biomass was fed. After the stabilization period, steady state was reached and maintained for about 1 hour. The operation was generally smooth regarding fuel feeding and solids

circulation. The average concentrations so obtained both for the fuel and air reactors were considered as representative of those corresponding to the operating conditions.

Fig. 3. Example of data evolution in a typical test. Biomass: pine sawdust. $\phi=1.1$. $T_{FR}=950\text{ }^{\circ}\text{C}$.

Fig. 4 presents the concentration of the main gaseous products at the fuel reactor outlet obtained for the different temperatures and biomasses. No clear differences were detected among biomasses. CO_2 appeared as the major compound, with about 70 % in all cases, followed by unburnt compounds: H_2 (10-15 vol%), CO (10-12 vol%) and CH_4 (6-8 vol%). The amount of other light hydrocarbons, $\text{C}_2\text{-C}_4$, was negligible.

The high content of volatiles in biomass (between 72.5 and 81% according to Table 2) would explain these concentrations of unburnt products at the outlet of the fuel reactor. Previous works using coal as fuel performed in the same unit at ICB-CSIC already

indicated that the contact between volatiles and the oxygen carrier bed was not sufficient to ensure a good volatile conversion as volatiles were released in a plume [9].

Fig. 4. Effect of fuel reactor temperature on the gas product composition obtained with different biomasses. $\phi \approx 1.1$

3.2 Tar measurement

In the combustion experiments with the three biomasses, tar compounds from the fuel reactor were collected and further analysed using the tar protocol. Fig. 5 shows the tar compounds identified in experiments at 950 and 980 °C. In all cases, naphthalene was the major compound identified at any temperature followed by acenaphthylene and phenanthrene. These compounds account for approximately 80% of all the tar mass detected in any case.

No important differences in tar composition were observed for the different types of biomass. The high temperatures at which biomass gasification proceeds in the fuel reactor favours the formation of tertiary tars (mainly methyl derivatives of aromatics and PAHS without substituents) and this may soften possible differences in tar composition depending on the biomass used as fuel.

Recently, result data from operation in the boiler/gasifier loop (12 and 2-4 MW_{th}, respectively) at Chalmers University of Technology using low-cost oxygen carriers and biomass were reported by Berdugo-Vilches et al. [16]. Commercial wood pellets from

spruce trees were used as biomass fuel and the operating temperature in the gasifier was about 830 °C. Tar samples were collected using a high accuracy method based on Solid Phase Adsorption (SPA). Under these conditions, they also identified benzene, phenolic species and 1-ring compounds as tar compounds at the fuel reactor outlet. In our work, the experimental methodology used would allow detecting benzene in case it was present. Despite following the standard tar protocol, negligible amounts of benzene were detected.

Fig. 5. Tar composition for the three biomasses tested at different fuel reactor temperatures.

The results corresponding to pine sawdust in the present work can be compared to those previously obtained operating at lower temperatures (880-915°C) in the same experimental unit [11]. In that study, naphthalene was also detected as the major compound in tar, but only indene and styrene were detected at the same time. The fact that in the present experiments more 3-ring compounds were also present in the tar mixture can be attributed to the lower solids inventory present in the fuel reactor during the current tests (750-785 kg/MW_{th} compared to 1550 kg/MW_{th} in experiments in [11]).

According to Table 3, the increase of temperature in the fuel reactor produces a decrease in the tar concentration measured in the experiments with pine sawdust and almond shell. At the highest temperature tested (980°C), the total tar concentration was 2.48, 3.72 and 2.60 g/Nm³ for pine sawdust, olive stone and almond shell, respectively. In the experiments performed at Chalmers University [16], 21-22 g tar per kg dry-ash-free fuel was measured for ilmenite and a manganese ore as oxygen carriers. As it is shown in Table 3, the values in the present work are 8-13 times lower than those reported. Besides the different methodology employed in the tar collection and analysis, the differences can be also attributed to the higher temperatures used in the fuel reactor during gasification.

The tar concentration values found in the present work are higher than those considered adequate to avoid operational problems derived from tar condensation and subsequent polymerization leading to fouling. Reed et al. [24] limited to the range 0.05-0.5 g/Nm³ the tar content for compressing and piping any distance a biomass gasification gas. Nevertheless, no fouling problems downstream due to the tar presence can be anticipated in CLC. In an industrial CLC unit it would be expected that tar compounds were burned in the oxygen polishing step downstream the fuel reactor. From the tar composition showed in Table 3 for the three biomasses at 950 and 980 °C, the tar oxygen demand (Ω_{tar}) was calculated (see Table 3). According to the results obtained, the oxygen demanded by the tar would be about 1% of that needed to burn the fuel. Tar contribution to the oxygen demand should then be considered in the design of the oxygen polishing step. Nevertheless, it would not represent a problem since the oxygen demanded by the other gaseous unburned compounds (CO, H₂ and CH₄) would be significantly higher as it would be shown in the following sections.

3.3 Combustion parameters

The fuel and air reactor gas outlet concentrations were used to evaluate the combustion of the three different types of biomass in the *i*G-CLC process. Fig. 6 presents the obtained values for the CO₂ capture efficiency and the char conversion.

Fig. 6. Effect of fuel reactor temperature on the CO₂ capture efficiency (η_{CC}) and the char conversion (X_{char}) for the different biomasses.

Both parameters increased with the fuel reactor temperature reaching values of 100% from 950 °C in the case of pine sawdust and almond shell. This could be due to their higher volatile content compared to olive stone. It is interesting to highlight that 100% CO₂ capture was achieved with the three biomasses at 980 °C even in the absence of a carbon stripper between fuel and air reactors in this experimental unit. In fact, lower CO₂ capture efficiencies were reached in previous experiments with the same oxygen carrier and different types of coal. At temperatures in 900-930 °C range and specific solids inventories (1500-2000 kg/MW_{th}), Mendiara et al. [18] reported CO₂ capture efficiency values of 30-45% for anthracite, 50-57% for a bituminous Colombian coal and 85-94% for lignite. Therefore, it can be concluded that the higher volatile content of

biomass and higher reactivity of biomass char compared to coal makes that the use of a carbon stripper is not as decisive as in the combustion of coal.

Fig. 7 presents the total oxygen demand at different fuel reactor temperatures. No clear trend was observed with the fuel reactor temperature. In general, the total oxygen demand for the three biomasses was similar and about 20-30%. The high carbon capture efficiencies obtained in most cases indicates that char is completely gasified in the fuel reactor. Char gasification products are known to be almost completely consumed by the oxygen carrier in the fuel reactor in this continuous unit [9]. Therefore it is realistic to assume that most of the oxygen demand is generated by the volatiles that escape the fuel reactor bed without interacting with the oxygen carrier particles.

Fig. 7. Total oxygen demand (Ω_T) for the three biomasses at different fuel reactor temperatures.

In order to estimate how much is the volatile conversion in the present experiments, an empirical model by Neves et al. [23] for the prediction of biomass pyrolysis products was used. The amount of volatiles that could be released could be then calculated and afterwards compared to the results in the present experiments. The model does not consider the physical-chemical processes occurring within the biomass particles. It is based on mass balances to the overall pyrolysis processes and experimentally-based closing parameters obtained after the compilation of a significant amount of

experimental data for different types of biomass and pyrolysis conditions. It should be pointed out that only mass balances to carbon, hydrogen and oxygen are considered. Those corresponding to nitrogen, sulphur and chlorine were not included in the original model.

The input data required by the model used were the CHO composition of the parent fuel (dry-ash-free) and the temperature of pyrolysis in °C. As output, the model calculates the dry-ash-free composition of resulting tar, C_xH_y , CH_4 , CO , CO_2 , H_2O and H_2 . An extra assumption was herein made in order to adapt this composition to the reacting conditions existing in the CLC process. It must be remarked that steam is used as gasifying agent in the fuel reactor in order to convert the char produced during biomass pyrolysis to CO and H_2 . The presence of steam would facilitate the conversion of most of the tar and C_xH_y formed during biomass pyrolysis to CH_4 and carbon. Considering this, the amounts of the different species resulting from biomass pyrolysis predicted by the model were here recalculated.

Table 3 shows the volatile conversion in the 0.5 kW_{th} unit according to the assumptions detailed in section 2.3. Volatile conversion was estimated at 900 °C for the three biomasses tested. An average volatile conversion about 70% was estimated for the three biomasses. These values are in line with the oxygen demand about 25-30% showed in Fig. 7. It has to be remarked that the fuel reactor in this CLC unit is a bubbling fluidized bed. Previous studies in this unit indicated that under these conditions, all the gasification products are burned by the oxygen carrier [25]. Thus, the oxygen demand of the volatiles would correspond to the total oxygen demand. In order to improve volatile conversion, changes in both the design of the fuel reactor and in the reactivity of the oxygen carrier would be needed. In this respect, highly reactive carriers would

favour volatile conversion but more significant improvements in volatile conversion would be expected if a circulating fluidized bed was used as fuel reactor.

Results corresponding to pine sawdust experiments in the present work complement those previously published by Mendiara et al. [11] where higher specific solids inventories were used. Using higher but less realistic solids inventories in the fuel reactor allowed reaching lower values of oxygen demand in the temperature range 880-915 °C under similar experimental conditions. The influence of the solids inventory in the fuel reactor on the oxygen demand value is assessed in several experiments performed in this work with Tierga ore and pine sawdust and shown in Fig. 8.

Fig. 8. Effect of the specific solids inventory on the total oxygen demand (Ω_T). $T_{FR} = 900$ °C.

Biomass=pine sawdust, $\phi \approx 1.1$.

In fact, lower total oxygen demand values could be reached with higher solids inventories because of the increasing oxygen availability to oxidize the volatiles and char gasification products generated in the fuel reactor. However, in theoretical studies dedicated to CLC scale-up [14, 26], specific solids inventories larger than 1000 kg/MW_{th} are not recommended. These studies showed that higher inventories would only slightly improve combustion efficiency while the resulting high pressure drop in the fuel reactor would be too much increased. Nevertheless, a compromise should be reached between enlarging reactors to allow higher solids inventories and the reduction of the

oxygen demand. Additional actions for unburned compounds minimization should be also taken. Although an oxygen polishing step contributes to this point, different low energy penalty options were recently proposed. A system for a better volatile distribution in the fuel reactor bed has already been presented by Lyngfelt and Leckner [8]. The so-called “volatile distributor” is basically a downwards-opening box inserted at the bottom of the fuel reactor bed with holes in the sides. The design has been already patented but construction details are still not clear. This device is expected to be optimized using cold-flow or fluid-dynamic models. Gayán et al. [27] recently outlined several design solutions for reducing the total oxygen demand. Some of the most promising are the use of a secondary fuel reactor or the changes in the fuel feeding point to the CLC system. The incorporation of a secondary fuel reactor after the main fuel reactor would facilitate the combustion of unburned compounds with a low increase in the total specific solids inventory. This would not compromise the economics of the process, especially if a low-cost oxygen carrier is used. However, the operation of this second fluidized bed connected to the main fuel reactor should be also optimized in order to guarantee a correct solid flow. First operational results using two bubbling fluidized beds as fuel reactor were recently reported in experiments using coal as fuel [28]. On the other hand, feeding the solid fuel to the carbon stripper has also been proposed to minimize the unburned compounds generated. Under this configuration, the carbon stripper would act as the primary fuel reactor. In the carbon stripper, only a small fraction of the char generated would be gasified before being separated from the oxygen carrier particles and sent to the fuel reactor, which would then act as a secondary fuel reactor. In this second fuel reactor, char gasification would proceed in a higher extent and the volatiles already released in the carbon stripper would be better burned.

3.4 Effect of the biomass ashes on biomass combustion

It is already known that the presence of alkali (mainly Na and K) in biomass ashes can be the cause of different problems during biomass combustion (i.e ash melting, defluidization and corrosion). The major element in the biomasses tested in this work was potassium. The values of K_2O found were 8.9, 29.5 and 12.6 wt % for pine sawdust, olive stone and almond shell, respectively. Nevertheless, no operational problems (fluidization, melting) were observed during the present experiments which accumulated 40 h of biomass combustion. The reactivity of the oxygen carrier was also not affected. However, longer combustion times operating with the different biomasses would be needed in order to assess the effect of the alkali content of biomass ashes on biomass combustion in CLC. This would be the focus of future research.

4. Conclusions.

Three biomasses (pine sawdust, olive stone and almond shell) were tested under iG-CLC mode in a 0.5 kW_{th} unit. 40 hours of biomass combustion were achieved using a low-cost cost oxygen carrier (Tierga ore) at temperatures in the range 900-980 °C. Specific solids inventories lower than 1000 kg/MW_{th} were used as these were considered realistic to operate in a larger CLC unit.

No differences in the combustion behaviour were observed among the biomasses. CO₂ capture of 100 % can be achieved during biomass fuelled CLC without the use of any carbon stripper. However, the high volatile content of biomass led to high values of total oxygen demand, with values about 25-30 %. Using methane as volatile reference compound, the volatile conversion in these experiments was estimated to be about 70%. Naphthalene was the major compound detected in the tar for all biomasses and

temperatures. The presence of tar at the outlet of the fuel reactor increases about 1% of the value of the total oxygen demand.

Nomenclature

C_nH_m general formula for tar compounds

$F_{i,FR}$ i species molar flow in the fuel reactor outlet stream (mol/h)

$F_{CO_2,AR}$ CO_2 molar flow in the air reactor (mol/h)

$F_{C,vol}$ carbon flow coming from the volatile matter (mol/h)

M_O oxygen atomic weight (g/mol)

$\dot{m}_{OC}$ solid circulation rate (kg/h)

$\dot{m}_{SF}$ biomass mass flow (kg/h)

R_{OC} oxygen transport capacity

X_{char} char conversion (-)

Greek symbols:

η_{CC} CO_2 capture efficiency (%)

Ω_{SF} amount of oxygen to burn the solid fuel (kg oxygen/kg biomass)

ϕ oxygen carrier to fuel ratio

Ω_T total oxygen demand (%)

Ω_{tar} oxygen demanded by the tar at the fuel reactor outlet (%)

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