1 Comparative study of fuel-N and tar evolution in chemical 2 looping combustion of biomass under both *i*G-CLC and 3 CLOU modes

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15 Abstract

16 Chemical looping combustion (CLC) processes combined with CO₂ sequestration and
17 sustainable management of biomass represent a promising BioEnergy with Carbon
18 Capture and Storage (BECCS) technology. One of the aspects to be considered in the
19 combustion of biomass is the formation of NO_x and the possible existence of tar in the
20 gaseous product stream. The advantage of the CLC technology compared to other CO₂
21 capture technologies is that only fuel-N contributes to nitrogen oxide formation.
22 Moreover, scarce information is available about tar formation in CLC. Thus, this work
23 focuses on these two aspects and compares the results obtained when two different

chemical looping combustion modes are used, namely *In Situ* Gasification Chemical Looping Combustion (*iG-CLC*) and Chemical Looping with Oxygen Uncoupling (CLOU). Important differences were observed depending on the combustion mode. In both cases most of the fuel-N appeared as N_2 in the fuel reactor. However, in *iG-CLC* more than 94% of the nitrogen measured in the fuel reactor was N_2 independently of the biomass used. These percentages under the CLOU mode were lower. In this case, low amounts of N_2O were also detected, although it decreased to almost zero at 850°C. In the air reactor, NO was found and its concentration remained below the legal limit for NO_x emissions in power installations with all the types of biomass and operating modes. Tar species and concentrations found at the fuel reactor outlet stream were different under the two combustion modes. About 2.5- 3.7 g/Nm³ total tar could be found at 980°C burning under *iG-CLC* mode, mostly naphthalene. On the contrary, insignificant tar amounts were found in CLOU.

Keywords: BECCS technologies; biomass; *iG-CLC*; CLOU; NO_x ; tar

1. Introduction

The last report from the Intergovernmental Panel on Climate Change (IPCC) outlined the average increase of the global temperature that could be expected depending on the CO_2 emission trends in the present century [1]. Considering this report and in order to restrict the impact of climate change, the Paris Agreement established a commitment to limit the global temperature increase to 2 °C or less [2]. To reach this milestone it becomes necessary to decrease CO_2 emissions to the atmosphere and even to reach negative CO_2 emissions at the end of this century. If a safe CO_2 storage is guaranteed, Biomass Energy with Carbon Capture and Storage (BECCS) can be considered as Negative Emission Technologies (NETs) [3]. Some studies anticipate that BECCS technologies could contribute to about 12% of the global CO_2 emission reduction

needed in 2060 to mitigate the climate change [1]. Excluding emission from biomass transport and pretreatment, biomass combustion emits the same quantity of CO_2 as that previously removed from the atmosphere (neutral CO_2 emitter). Moreover, CCS technologies have reached an important level of development in recent years [4, 5]. CCS technologies allow generating a concentrated CO_2 stream from stationary combustion sources and storing it, mainly in geological formations.

Among CCS technologies, Chemical Looping Combustion (CLC) is one of the most promising due to its low energy penalty associated to CO_2 capture [6]. In CLC, combustion takes place in two separate reactors so that there is no mixture between fuels and air (see Fig. 1). In one of the reactors, noted as fuel reactor in the figure, the fuel is burned with the oxygen supplied by a solid oxygen carrier (M_xO_y), which circulates between the fuel reactor and the air reactor. CO_2 and steam are obtained in the combustion and once the steam is condensed, a highly-concentrated CO_2 stream is obtained, which can be easily transported and stored. In the fuel reactor, the oxygen carrier is reduced. Afterwards, it is regenerated in air once it reaches the air reactor. Then it is ready for a new redox cycle and continuous combustion of the fuel is maintained.

Fig. 1. Scheme of the CLC process.

When solid fuels such as biomass are considered, CLC has developed two possible combustion processes [7]. One of them is the *In Situ* Gasification Chemical Looping

Combustion (*iG-CLC*). In this process, steam or carbon dioxide should be fed to the fuel reactor as fluidizing/gasifying agents. Once the solid fuel is introduced in the fuel reactor, the volatiles are released and the char is gasified. Then, volatiles and char gasification products (H_2/CO) react with the oxygen carrier forming CO_2 and H_2O . The other option for solid fuel CLC is known as Chemical Looping with Oxygen Uncoupling (CLOU). In this case, the oxygen carrier is capable of releasing gaseous oxygen (O_2) that reacts with volatiles and char as in conventional combustion. Both processes have advantages and disadvantages. In the *iG-CLC* process, the main limiting step is the slow gasification rate of the char generated but cheap oxygen carriers can be used in the process [7]. In order to enhance char gasification, the use of a carbon stripper between fuel and air reactors has been proposed [8, 9]. In the carbon stripper, unconverted char is separated and returned to the fuel reactor for further gasification. Another drawback in the *iG-CLC* process, is the existence of unburnt compounds (both volatile and char gasification products) at the fuel reactor outlet [7]. This makes the incorporation of an oxygen polishing step downstream the fuel reactor necessary to complete the combustion. The CLOU process facilitates volatile and char combustion compared to the *iG-CLC* mode, as the gaseous oxygen released by the oxygen carrier is able to react directly with the char produced. The oxygen carrier must have adequate oxygen equilibrium partial pressure at temperatures of interest for combustion (800-1200°C) and also withstands long periods of continuous redox cycles. Up to date, only few materials have demonstrated their adequacy for the CLOU process [10-12], mostly based on copper oxides or perovskites. Thus, they are also expensive oxygen carriers when compared to those for *iG-CLC*.

Although most of the works on CLC of solid fuels have been performed using different types of coal as fuel, in the recent years, some experience has also been gained in

biomass combustion, named Bio-CLC [13]. Many of those works correspond to operation in continuous units under *i*G-CLC mode in the range of 0.5 kW_{th} to 4 MW_{th}. These works used different oxygen carriers, mainly based on iron oxides and manganese oxides [14-21]. They demonstrated that working under optimized conditions it is possible to reach almost 100% CO₂ capture [15, 22]. Some tar was detected in the gas stream at the fuel reactor outlet and no problems related with the ash present in biomass have been found. However, high values of unburnt compounds at the fuel reactor outlet have been reported, which requires the incorporation of an oxygen polishing step after the fuel reactor. Only few works addressed biomass combustion under CLOU mode in continuous units ranging from 1.5 to 10 kW_{th} [23-26]. However, the challenge of finding CLOU materials with longer lifetime still remains.

One of the advantages of CLC over conventional combustion is the reduction in NO_x [27] and tar formation [14]. In CLC there is no mixing between fuel and air and combustion temperatures are lower, therefore, the contribution to NO_x formation of thermal NO is avoided and the main source for NO_x formation is the nitrogen contained in the biomass. There is some information in literature about the fate of fuel-N in CLC processes, mainly referred to coal as fuel [7]. The majority of the *i*G-CLC studies carried out conclude that most of fuel-N is released in the fuel reactor as N₂ and only low amounts of NO_x can be found [28-30]. In the air reactor, the fuel-N in the unconverted char that may reach the air reactor is released as NO. The oxidizing atmosphere existing in the fuel reactor in the CLOU process influences NO_x formation compared to what occurs in *i*G-CLC. Although most of the fuel-N is again released in the fuel reactor as N₂, there are larger amounts of NO_x [31]. Besides, tar formation in the fuel reactor in *i*G-CLC can be reduced since tar can be either burned by the oxygen carrier particles or even reformed with steam/CO₂ aided by the oxygen carrier that

would then act as a catalyst. Regarding tar formation, previous *iG*-CLC studies with different types of biomass showed tar contents of about 2.5-4.5 g/Nm³ at temperatures between 950-980°C with the major contribution of naphthalene. This would represent an increase of about 1% in the total oxygen demand from unburnt compounds at the fuel reactor outlet [15]. On the other hand, no tar was detected in any of the experiments performed under CLOU mode with a Cu-based oxygen carrier operating in the 900-950°C range [23, 32]. Considering that the information about both NO_x and tar formation in CLC is still scarce if biomass is considered as fuel, the aim of the present paper is to further contribute to the understanding of these aspects and therefore contribute to the advance of the Bio-CLC as a BECCS technology. Experiments both under *iG*-CLC and CLOU modes will be performed using different types of biomass as fuel and later compared.

2. Experimental

2.1 Oxygen carrier and biomass

Fe-based minerals are commonly used as cheap materials in CLC processes [14, 15, 18, 21, 22, 33]. In the present work, a Fe-based ore obtained in a hematite mine from Tierga (Zaragoza, Spain) was used as oxygen carrier for *iG*-CLC. A Cu-Mn mixed oxide, named as Cu₃₄Mn₆₆-GR, was used as oxygen carrier under CLOU operation. In both cases, the oxygen carrier was sieved to a particle size of 100-300 µm. Table 1 shows the main properties of both oxygen carriers. Further information about properties of both materials can be found elsewhere [15, 24]. In this work, three Spanish biomass wastes were used as fuels. Pine sawdust (*Pinus sylvestris*) was chosen as the reference material because of its wide use and distribution. Also two different types of biomass wastes used for energetic purposes were chosen, namely, olive stone (*Olea europaea*) and almond shell (*Prunus dulcis*). Raw biomass was dried and sieved to 0.5 - 2 mm. Table 2

comprises proximate and ultimate analyses of each biomass including the low heating value and the value of the oxygen demand of the solid fuel (Ω_{SF}), which represents the amount of oxygen needed to burn the biomass.

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

	Tierga ore	Cu ₃₄ Mn ₆₆ -GR
Composition	Fe ₂ O ₃ , SiO ₂ , Al ₂ O ₃ , CaO, MgO	Cu _{1.5} Mn _{1.5} O ₄ , Mn ₃ O ₄
XRD active phases, Me _x O _y (wt.%)	76.5 (Fe ₂ O ₃)	72.0 (Cu _{1.5} Mn _{1.5} O ₄)
Crushing strength (N)	5.8	1.9
Oxygen transport capacity, R_{OC} (wt.%)	2.5	4.0
Porosity (%)	26.3	12.1
Skeletal density of particles ^d (kg/m ³)	4216	4100
Specific surface area, BET (m ² /g)	1.4	< 0.5

Table 2. Proximate and ultimate analyses of the types of biomass

	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

Fig. 2 shows the experimental unit at ICB-CSIC-s1 used in the experiments both under *i*G-CLC and CLOU modes. Detailed information about the design and operation of the unit can be found elsewhere [10] and only its main features will be mentioned here. The

ICB-CSIC-s1 unit consists of two interconnected fluidized bed reactors, acting as fuel and air reactors, respectively. To prevent the mixing of atmospheres, a third fluidized bed reactor is placed as a loop seal between the fuel and the air reactors. The biomass is fed into the fuel reactor at the bottom of the bubbling fluidized bed with a series of two screw feeders. The ICB-CSIC-s1 unit allows operation between 0.5 (iG-CLC) and 1.5 kW_{th} (CLOU) nominal power. There is no carbon stripper between fuel and air reactors and an important feature of this unit is the possibility of measuring and controlling the solids flow circulating between the fuel and the air reactors.

Fig. 2. Experimental unit ICB-CSIC-s1

During this experimental campaign where nitrogen emissions were evaluated, CO₂ was used to fluidize the fuel reactor and the loop seal. It was also introduced in the screw feeder in order to avoid N₂ in the gases fed to the system. However, tar measurements

were performed using steam as gasifying agent in the *iG*-CLC experiments and nitrogen as fluidizing agent in CLOU.

CO, CO₂, H₂, CH₄ and O₂ concentrations in the fuel reactor exit as well as CO, CO₂ and O₂ concentrations at the exit of the air reactor were measured and recorded. For CH₄, CO and CO₂ a nondispersive infrared (NDIR) analyzer (Siemens Ultramat 23) was used; a paramagnetic analyzer (Siemens Ultramat 23 and Oxymat 6) was used for O₂ concentration measurement and a thermal conductivity detector (Siemens Calomat 6) was used for H₂.

NH₃, HCN, N₂, NO, N₂O and NO₂ were measured with a quadrupole mass spectrometer from Pfeiffer. NO in fuel and air reactor was also measured using a nondispersive infrared (NDIR) analyzer (Siemens Ultramat 23). The collection of tar at the fuel reactor outlet was done according to the standard tar protocol [34]. The concentrations of the different tar compounds in the samples was measured 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 [35]. A standard solution with several lineal hydrocarbons was used in the external calibration in some of the compounds detected under CLOU mode.

The total oxygen carrier inventory in the ICB-CSIC-s1 unit was about 3.5 kg in the *iG*-CLC experiments and about 3 kg during CLOU operation. In *iG*-CLC, a total of 60 h of hot operation were accomplished, 40 h of which with biomass combustion. In CLOU, 45 h were reached in hot operation with 25 h of those with biomass combustion. Tables 3 and 4 shows the experimental conditions of the experiments performed (PN=pine

sawdust; OS=olive stone; AS=almond shell) [15, 24]. In the tables, the value of the parameter oxygen carrier to fuel ratio (ϕ) was included. This parameter compares the available oxygen in the circulating oxygen carrier with the oxygen needed for the complete combustion of the fed fuel.

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

Table 3. Operating conditions of the *i*G-CLC tests with the different types of biomass

Biomass	PN_1	PN_2	PN_3	OS_1	OS_2	OS_3	AS_1	AS_2	AS_3
Time of combustion (h)	5.7	2.6	2.2	8.1	3.0	2.3	3.7	3.3	3.8
Time hot fluidization (h)	8.2	4.1	3.1	9.4	4.5	3.0	6.3	9.3	6.4
Temperatures (°C)									
Fuel reactor	910	950	985	905	955	980	905	955	985
Air reactor	950	950	950	950	950	950	950	950	950
Operating conditions									
Biomass flow (g/h)	113	98	98	164	141	141	190	102	88
OC circulation rate (kg/h)	9.2	6.7	6.7	8.8	7.6	7.6	13	7	5.9
Oxygen carrier to fuel ratio, ϕ	1.3	1.1	1.1	1.0	1.0	1.0	1.2	1.2	1.2
Specific solids inventory in fuel reactor (kg/MW _{th})	750	785	780	600	600	590	370	550	890

Table 4. Operating of the CLOU tests with the different types of biomass

Biomass	PN_4	PN_5	PN_6	PN_7	OS_4	OS_5	OS_6	OS_7	AS_4	AS_5	AS_6	AS_7
Time of combustion (h)	2.2	2	2.1	1.9	1.9	2	1.8	2.1	2.3	2.1	2.2	2.1
Time hot fluidization (h)	3.4	3.2	3.3	3.5	3.7	3.6	3.2	3.6	3.3	4	3.9	3.8
Temperatures (°C)												
Fuel reactor	775	800	825	850	775	800	825	850	775	800	825	850
Air reactor	800	800	800	800	800	800	800	800	800	800	800	800
Operating conditions												
Biomass flow (g/h)	140	140	140	140	225	225	225	225	173	173	173	173
OC circulation rate (kg/h)	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	20.3	20.3	20.3	20.3
Oxygen carrier to fuel ratio, ϕ	3.9	3.9	3.9	3.9	3.3	3.3	3.3	3.3	3.0	3.0	3.0	3.0
Specific solids inventory in fuel reactor(kg/MW _{th})	1200	1200	1200	1200	760	760	760	760	1150	1150	1150	1150

3. Results and discussion

3.1 Analysis of the performance of the CLC unit

Before analyzing NO_x and tar formation in the biomass experiments under both *i*G-CLC and CLOU modes, the performance of the system should be evaluated. First of all, the carbon conversion efficiency was checked and an average value about 95% was found. In order to analyze the performance of the CLC system three parameters were considered, i.e. the combustion efficiency in the fuel reactor, the CO₂ capture efficiency and the char conversion in the fuel reactor. The combustion efficiency in the fuel reactor ($\eta_{comb,FR}$) is a measure of the gas conversion in the fuel reactor. It is defined as the fraction of oxygen demanded by the volatile matter and gasification products supplied by the oxygen carrier in the fuel reactor [7].

$$\eta_{comb,FR} = \frac{\text{oxygen transferred in fuel reactor}}{\text{oxygen demanded by solid fuel converted in fuel reactor}} \quad (2)$$

The CO₂ capture efficiency (η_{CC}) specifies how much of the carbon introduced with the solid fuel is captured in gaseous form at the fuel reactor outlet [7]

$$\eta_{CC} = \frac{\text{carbon in gases from fuel reactor}}{\text{carbon in gases from fuel reactor and air reactor}} \quad (3)$$

Carbon in gases exiting the fuel reactor comes from carbon contained in the volatiles and the carbon in the gasified char. As a result, all this carbon will be converted to captured CO₂. The CO₂ capture efficiency depends on the fraction of char gasified in the fuel reactor, which is noted as char conversion in the fuel reactor ($X_{char,FR}$). This char conversion can be also considered as an indicator of the gasification efficiency.

$$X_{char,FR} = \frac{\text{fixed carbon converted in fuel reactor}}{\text{fixed carbon in solid fuel - carbon in elutriated char}} \quad (4)$$

Performance results from the experiments under both *i*G-CLC and CLOU modes were discussed in detail in Fig.3 in order to be afterwards correlated to the results obtained in the analysis of pollutant emissions. Note that although all the experiments in this work

were done using CO₂ as gasifying agent in the fuel reactor, Fig.3 shows performance results obtained in similar operating conditions using steam/nitrogen as gasifying agents [15, 24] as they could be calculated more accurately.

Figure 3. Combustion ($\eta_{comb,FR}$) and CO₂ capture efficiencies (η_{CC}) for *iG-CLC* (filled symbols) and CLOU (open symbols) burning pine sawdust, almond shell and olive stone

The first consideration about *iG-CLC* and CLOU results is the different temperature range in the fuel reactor within which they were obtained. The experiments with the two oxygen carriers were done under previously optimized operating conditions for each of them. The different temperature interval is justified by the reactivity of the material used as oxygen carrier [36]. The experiments under *iG-CLC* mode operated between 900-980°C while in the CLOU mode lower temperatures were used (775-850°C). In the case of *iG-CLC*, it was observed that the reactivity of the Tierga ore notably increases at temperatures above 950°C [37]. However, in the case of CLOU experiments, the suitable operating conditions are found at those lower temperatures [36, 38]. Previous studies indicated that it was possible to reach adequate O₂ equilibrium concentrations (up to 2% at 850°C) to achieve complete combustion of the fuel with the Cu-Mn oxygen

carrier used in this work [38]. The different temperature interval considered for each operating mode is important as it can affect the nitrogen chemistry and tar formation occurring in the fuel reactor. As it can be seen in Fig.3, under the *i*G-CLC mode high values of CO₂ capture efficiencies were obtained with all the types of biomass. The values increase with the fuel reactor temperature reaching almost 100% at 980°C. These values for CO₂ capture efficiencies are correlated to those calculated for the char conversion in the fuel reactor, which also increase with the fuel reactor temperature from 70-80 to almost 100%. In *i*G-CLC, low combustion efficiencies (about 70%) were found for all the types of biomass tested mainly due to the fraction of volatiles released by the biomass that are not burnt by the oxygen carrier. In the CLOU experiments also shown in Fig.3, the CO₂ capture efficiencies increased with temperature because more char was converted at higher temperatures in the fuel reactor and therefore, less unconverted char reached the air reactor. With this Cu-Mn based oxygen carrier values of CO₂ capture efficiencies about 95% at 850°C were obtained. In order to increase the values of these CO₂ capture efficiencies a carbon stripper would be needed. The combustion efficiencies for CLOU experiments in Fig.3 were always close to 100% even at the lowest temperature (775°C), due to the release of gaseous oxygen in the fuel reactor.

3.2 Fate of fuel-N

3.2.1 Fuel-N distribution between fuel and air reactors

As it was mentioned before, one of the advantages of CLC is that the contribution of thermal NO_x to the NO_x formation in combustion is avoided [27]. Therefore, the main contribution to NO_x formation comes from fuel-N. According to the composition of the different types of biomass in Table 2, the highest nitrogen content is observed for pine sawdust (0.3 wt.%), while olive stone and almond shell are reported 0.2 wt.%. Fuel-N in

biomass is released during biomass devolatilization. The dominant nitrogenous volatile species are NH_3 and HCN [39]. Both can evolve to either N_2 or NO , depending on the combustion conditions. On the other hand, char-bound nitrogen can evolve to NO , N_2O or N_2 . However, at temperatures higher than 900°C N_2O decomposes to N_2 [40]. In the experiments performed under both *iG*-CLC and CLOU modes, different atmospheres can be found in the fuel reactor when biomass devolatilization takes place. In the experiments CO_2 was supplied to the fuel reactor as gasifying/fluidizing agent. Therefore, in *iG*-CLC a reducing environment is generated due to the presence of gasification products, i.e. H_2 and CO . However, oxygen is present in the reacting atmosphere under CLOU operation. In both processes, N_2 from air is not present, which is an important difference compared to the conventional combustion in air.

Fig.4 presents fuel-N distribution between fuel and air reactors in the experiments under *iG*-CLC and CLOU modes summarized in Tables 3 and 4. Results from three types of biomass tested are shown. As a general conclusion shown in Fig.4, it can be said that for both operating modes, the most of the nitrogen in the fuel is released in the fuel reactor, in line with the results previously reported in literature for CLC using coal as fuel [7]. This is a consequence of the high CO_2 capture efficiencies reached and shown in Fig.3. The percentage of fuel-N released in the fuel reactor slightly increases with temperature. The fuel-N released in the air reactor comes from the little amounts of unconverted char that reaches this reactor and is burned there. The trend in the percentage of fuel- N released in the air reactor is the opposite of that observed for char conversion in the fuel reactor in Fig.3. Larger values of char conversion imply little bypass of unconverted char to the air reactor and therefore, less fuel-N reaching the air reactor.

289

290 **Figure 4.** Fuel-N distribution between fuel and air reactors for *iG-CLC* and CLOU processes burning the
 291 three different types of biomass: (a) pine sawdust, (b) olive stone and (c) almond shell at different fuel
 292 reactor temperatures

293 However, there are differences between both operating modes that can be observed in
 294 Figs. 3 and 4, especially in the case of the experiments with pine sawdust. In Fig. 3
 295 similar CO₂ capture efficiencies were observed at 850 °C under CLOU mode and 900
 296 °C under *iG-CLC* conditions. However, lower amounts of fuel-N were found in the fuel
 297 reactor in Fig. 4 under the CLOU mode despite the high char conversions reached in
 298 both CLC modes. This reveals the different nitrogen chemistry behind the two
 299 processes. Under similar operating conditions, fuel-N conversion in the fuel reactor
 300 seems to be favoured under *iG-CLC* mode.

3.2.2 Evolution of nitrogen species in the fuel reactor

Neither under *i*G-CLC nor under CLOU mode the presence of NH₃ or HCN was detected at the fuel reactor outlet. As it is shown in Table 5, only N₂, NO_x and N₂O were identified depending on the conditions. This indicated that all the nitrogen released as NH₃ or HCN in the devolatilization was converted via homogenous or heterogeneous reactions.

Table 5. Nitrogen species found at the fuel reactor outlet in the *i*G-CLC and CLOU experiments

iG-CLC	N ₂ , NO _x
CLOU	N ₂ , NO _x , N ₂ O

Both in *i*G-CLC and CLOU, the major nitrogen species found in the fuel reactor was N₂, followed by NO_x and by certain amounts of N₂O, the later only in the case of CLOU experiments. The presence of N₂O can be attributed to the temperature range of operation (775-850°C) and the release of molecular oxygen in the fuel reactor atmosphere [40]. In *i*G-CLC, 97.2, 96.7 and 94.6% of the nitrogen measured in the fuel reactor was N₂ in the experiments at 980°C with pine sawdust, olive stone and almond shell, respectively. The corresponding percentages under the CLOU mode operating at 850°C were 97.3, 92.0 and 81.5%.

Fig. 5(A) shows the different trends in the evolution of the molar ratio NO_x/C (expressed in ppm) with the fuel reactor temperature for both *i*G-CLC and CLOU, i.e. the NO_x/C ratio increased with temperature in CLOU since more oxygen was released by the oxygen carrier with the increase of the fuel reactor temperature [38]. However, this molar ratio slightly varied with the fuel reactor temperature under *i*G-CLC. Besides higher values of the NO_x/C ratio were found in CLOU. This was expected since the presence of gaseous oxygen in the fuel reactor atmosphere favours fuel-N oxidation to

NO [41]. Focusing on the CLOU experiments for the three types of biomass, higher values of NO_x/C ratio were obtained for almond shell followed by olive stone and pine sawdust. This order was the opposite of that found for the corresponding char conversion in Fig. 3, where the higher char conversion values were obtained for pine sawdust then followed by olive stone and almond shell. Therefore, although pine char was converted in a larger extent, the conversion of fuel-N to NO was less favoured than in the rest of the biomass types considered. This effect becomes clearly shown at the highest temperature tested in CLOU (850°C). Once formed, NO can react with biomass char to be reduced to N₂ following reaction (R1) [40]:

The differences in char reactivity to NO could contribute to the different NO_x/C molar ratios obtained in Fig. 5(A) with the different types of biomass. If the pine sawdust char were more reactive to NO than the rest of the chars in the temperature interval considered (775-850 °C), it could react with the NO in the atmosphere to produce N₂, therefore decreasing the NO_x/C molar ratio. Different results were found for the *i*G-CLC experiments, where no significant differences in NO_x/C ratio were found in the fuel reactor temperature range studied. In this case, the fuel reactor temperature is higher than in CLOU and it would notably enhance the heterogeneous reaction between char and NO (R1). Thus, the possible differences in char reactivity would be hindered or softened.

Figure 5. (A) Molar ratio NO_x/C and (B) NO_x concentration per MJ at the fuel reactor outlet for CLOU (open symbols) and iG-CLC (filled symbols) processes at different fuel reactor temperatures

The quality of the CO_2 to be captured can be affected by the presence of different compounds in the outlet stream from the fuel reactor. Steam, N_2 , O_2 , CO, H_2 , CH_4 and other hydrocarbons, SO_2 , particles and also NO_x levels should be controlled in order to ensure that the captured CO_2 stream can be transported and safely stored. To date, no legal requirements exist and only recommendations have been outlined for the quality of CO_2 [42]. The limit marked by this recommendations regarding NO_x content in the CO_2 stream is indicated in Fig. 5(A). The experiments under iG-CLC would fulfil the requirements, as well as almost all of those performed under CLOU mode. Fig. 5(B) normalizes the emissions registered per MJ of fuel fed. According to Fig. 5(B), the trends previously observed in Fig. 5(A) are mostly maintained.

N_2O is a greenhouse gas with a long atmospheric lifetime and important radiative forcing compared to CO_2 . Moreover, N_2O also plays an important role in the depletion of the ozone layer. The temperatures used in conventional fluidized bed combustion (800-900°C) facilitate N_2O appearance [40]. Thus, its presence in CLC was assessed. Fig.6(A) presents the evolution of N_2O concentration (expressed in mg/Nm^3) with the fuel reactor temperature for both iG-CLC and CLOU.

Figure 6. N₂O concentrations (A) in mg/Nm³ and (B) in mg/MJ at the fuel reactor outlet for CLOU (open symbols) and *i*G-CLC (filled symbols) processes at different fuel reactor temperatures.

As it can be seen in Fig. 6(A), only in the experiments under CLOU mode N₂O was observed. The concentration of N₂O in the fuel reactor outlet stream decreased with temperature to values close to zero at 850°C. This was observed for the three types of biomass tested. The maximum concentration reached at the lowest temperature did not exceed 20 mg/Nm³; see Fig. 6(A). The reduction of N₂O with the increase in temperature has already been reported in literature in the case of conventional combustion in fluidized bed [43]. Under *i*G-CLC mode, no N₂O was detected at the outlet of the fuel reactor, since temperatures were always higher than 900°C. Fig. 6(B) shows the same results normalized per MJ of fuel fed.

3.2.3 Evolution of nitrogen species in the air reactor

Both during *i*G-CLC and CLOU operation, the main nitrogen species besides N₂ found at the air reactor outlet was NO. In this case, no N₂O was detected. This NO is originated in the oxidation of the fuel-N present in the unconverted char that reaches the air reactor. Fig. 7(A) and (B) shows the evolution of the NO concentration (both in mg/Nm³ and mg/MJ) with the fuel reactor temperature, respectively. The NO concentrations have been normalized to 6% O₂ in the stream, as it is indicated in the legal emission limit. In Fig. 7(A), the trends for both operating modes, *i*G-CLC and

CLOU, are the same for all the types of biomass tested. The NO emissions decrease when the fuel reactor temperature increases. The reason for this trend is that an increase in the fuel reactor temperature enhances char gasification. If more char is converted, less unconverted char is transferred to the air reactor. Thus, the fuel-N released in the air reactor is decreased. Some differences can be appreciated between types of biomass. In all cases, higher NO concentrations in the air reactor were found in the experiments with olive stone and almond shell. It should be taken into account that the NO present in the outlet stream of the air reactor can be considered an emission to the atmosphere and therefore, the levels should fulfil those specified in the current legislation [44]. The Directive 2010/75/EU on industrial emissions (integrated pollution prevention and control) sets the NO_x emission limit to 150 mg/Nm³ (normalized to 6% O₂) for new installations in the EU and for the highest power (>300 MW). According to the values shown in Fig. 7(A), the NO_x level at the air reactor outlet was in the range 10-120 mg/Nm³ for the CLOU experiments and in the range 0-50 mg/Nm³ for *i*G-CLC experiments. Thus, no emission problems could be anticipated when biomass is used as fuel in a CLC system. Moreover, these values were obtained in the absence of a carbon stripper, which would decrease the unconverted char bypassed to the air reactor and hence the NO_x formed in the air reactor.

Figure 7. NO_x concentrations (A) in mg/Nm³(6% O₂) and (B) in mg/MJ at the air reactor outlet for CLOU (open symbols) and *i*G-CLC (filled symbols) processes at different fuel reactor temperatures burning the three different types of biomass: pine sawdust, olive stone and almond shell

3.3 Tar formation under *i*G-CLC and CLOU

Tar formation control during gasification represents one of the main challenges in the use of biomass. Tar has been reported to cause fouling problems downstream of the gasification chamber and strict limits have been imposed for its presence when the syngas produced is intended to be used for energy generation or chemicals production [45]. In the case of the CLC process, scarce information about tar formation can be found. The presence of tar is limited to the fuel reactor outlet and it is therefore affecting the quality of the CO₂ stream there generated and the further operations prior to CO₂ storage (compression and transport). In the recommendations summarized by de Visser about CO₂ quality [42], there is no clear reference to tar. Nevertheless, in order to set a range of values for safe operation, the limit given by Reed et al. [46] for compressing and piping any distance a biomass gasification gas can be used. According to these authors, the tar content should be lower than 0.5 g/Nm³.

In the experiments under *i*G-CLC and CLOU modes, the tar compounds at the fuel reactor outlet were detected and quantified. In these experiments, steam was used in the fuel reactor as fluidizing agent in *i*G-CLC and nitrogen in CLOU. Most of the results from *i*G-CLC experiments were previously presented [15] and are included here to facilitate comparison with those obtained under CLOU mode. Fig. 8 plotted the tar compounds grouped as primary, secondary and tertiary tars [47, 48] and also includes lineal hydrocarbons. The figure shows the concentration values for each group in the experiments with the different types of biomass.

Figure 8. Tar concentration for the three types of biomass tested at different fuel reactor temperatures operating under (A) CLOU mode and (B) *iG-CLC* mode

In *iG-CLC*, the amount of tar found decreased when the fuel reactor temperature was increased. The two most significant results when both operating *CLC* modes are compared are summarized next. First of all, the different levels of tar found. While in the *iG-CLC* operation, the total tar values oscillated between 2.5-3.7 g/Nm³ at the highest temperature (980°C), the values determined for CLOU were about two orders of magnitude lower (<0.02 g/Nm³) in a lower fuel reactor temperature interval (775-850°C). Therefore, in the case of *iG-CLC* additional measures should be considered in order to reduce the amount of tar present and to make it compatible with the <0.5 g/Nm³ limit proposed by Reed et al. [46]. One of the possibilities is the combustion of tar in an oxygen polishing step after the fuel reactor together with the rest of unburnt compounds from the combustion process (CO, H₂ and CH₄) [15]. The tar levels found in the CLOU experiments are so low that it should not represent a problem in the CO₂ transport-storage chain. In any case, the combustion of biomass using both of any combustion modes results in lower tar content in the product gas stream than that expected in conventional processes such as biomass air-fired gasification. Note that for an air-blown

circulating fluidized bed (CFB) gasifier a typical tar content of about 10 g/Nm³ has been reported [49].

The second relevant result is the tar composition found in the experiments. In the *iG*-CLC process the composition is similar for the three types of biomass tested and not clearly influenced by temperature (see [15]). The major compound is naphthalene accompanied by some other tertiary tars such as acenaphthylene and phenantrene. No benzene was detected, although the standard tar protocol followed to collect tar samples allows its collection as it was shown in previous works from the authors [35]. However, tar composition obtained in CLOU experiments showed some differences with respect to that obtained in *iG*-CLC. Table 6 shows the compounds identified in the CLOU experiments for different fuel reactor temperatures.

Table 6. Tar composition for the CLOU tests with the three types of biomass

Biomass	PN_5	PN_6	PN_7	OS_4	OS_5	OS_6	AS_4	AS_5	AS_6
Temperatures (°C)									
Fuel reactor	775	800	825	775	800	825	775	800	825
Air reactor	800	800	800	800	800	800	800	800	800
Tar composition (g/Nm³ dry)									
Benzene, 1 propenyl	-	1·10 ⁻⁴	-	1.7·10 ⁻³	-	1.9·10 ⁻³	1·10 ⁻⁴	-	5·10 ⁻⁴
Dodecane	4·10 ⁻⁴	1·10 ⁻³	6·10 ⁻³	1.8·10 ⁻³	-	-	9·10 ⁻⁴	2·10 ⁻⁴	7·10 ⁻⁴
Indene	-	-	-	6·10 ⁻⁴	1.1·10 ⁻³	1.4·10 ⁻³	-	-	3·10 ⁻⁴
Tetradecane	4·10 ⁻⁴	5·10 ⁻⁴	3.2·10 ⁻³	-	-	-	7·10 ⁻⁴	2·10 ⁻⁴	5·10 ⁻⁴
Naphthalene	2·10 ⁻⁴	3·10 ⁻⁴	7·10 ⁻⁴	10.5·10 ⁻³	19.4·10 ⁻³	11.9·10 ⁻³	1·10 ⁻⁴	0.0000	1.7·10 ⁻³
2,6,10 trimethyltridecane	2·10 ⁻⁴	3·10 ⁻⁴	2.5·10 ⁻³	-	-	-	5·10 ⁻⁴	1·10 ⁻⁴	-
Naphthalene 2-methyl	-	-	-	1.1·10 ⁻³	1.6·10 ⁻³	1.6·10 ⁻³	-	-	-
Naphthalene 1-methyl	-	-	-	7·10 ⁻⁴	1.1·10 ⁻³	1.1·10 ⁻³	-	-	-
Biphenil	-	-	-	9·10 ⁻⁴	1.4·10 ⁻³	1.0·10 ⁻³	-	-	-
Benzophenone	-	-	-	-	-	--	4·10 ⁻⁴	-	-
Acenaphthylene	0.0000	-	-	4·10 ⁻⁴	-	9·10 ⁻⁴	-	-	-
Fluoranthene	-	-	-	-	-	-	-	-	-
Phenantrene	-	-	9·10 ⁻⁴	1.4·10 ⁻³	-	-	-	-	-
Total tar (g/Nm³ dry)	0.004	0.01	0.04	0.04	0.05	0.04	0.01	0.01	0.01

As it can be seen, low amounts of naphthalene are found but certain quantities of linear or branched hydrocarbons are detected, such as dodecane or tetradecane. This may

indicate a different mechanism for the consumption/reforming of the tar under CLOU environment when compared to *iG*-CLC.

4. Conclusions

The two operating modes currently available to burn biomass using the Chemical Looping Combustion technology, namely *iG*-CLC and CLOU, were compared regarding two aspects in biomass combustion: NO_x and tar formation. Three different biomass residues were tested as fuels: pine sawdust, olive stone and almond shell.

Under similar operating conditions, fuel-N conversion seems to be favoured under *iG*-CLC mode. Although the combustion took place in different fuel reactor temperature ranges, in both combustion modes most the fuel-N appeared as N₂ at the fuel reactor outlet with only little presence of NO. The ratio N₂/NO_x in the fuel reactor was higher in the case of *iG*-CLC experiments due to the absence of molecular oxygen that favours NO formation. Some differences between biomasses were observed regarding the amount of NO formed in the fuel reactor under CLOU mode and were attributed to the different char reactivity of the three types of biomass. Little amounts of N₂O were detected under CLOU mode at lower temperatures, but it disappeared at 850 °C. In the air reactor and for both combustion modes NO was detected and its concentration decreased when the fuel reactor temperature increased. However, its concentration never exceeded the current legal limits for power plants.

Regarding tar formation, total tar values between 2.5-3.7 g/Nm³ were encountered under *iG*-CLC mode at the highest temperature (980°C) at the fuel reactor outlet, mostly naphthalene. This makes a further oxygen polishing step necessary in order to condition the stream for subsequent transport and storage. Under CLOU, insignificant amounts were found although in this case also linear or branched hydrocarbons were detected.

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