Comparison of low-cost and synthetic oxygen carriers for the Biomass Chemical Looping Gasification process

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ABSTRACT
Biomass Chemical Looping Gasification (BCLG) is a novel technology which permits the production of high purity, N_2-free renewable syngas. In this work, the behavior of seven oxygen carriers, 4 low-cost (3 ores, and 1 waste) and 3 synthetic materials, was compared during continuous operation in a 1.5 kW_{th} BCLG unit. For that, oxygen-to-fuel ratio (λ) and fuel reactor (FR) temperature were varied in a wide range of operating conditions. High carbon conversion, η_{cc} (> 95 %) and fuel conversion, X_b, (> 85%) were found for all the oxygen carriers. The same trends in the syngas composition were observed with low-cost and synthetic oxygen carriers when the λ and FR temperature were varied. However, the amount of syngas generated was higher for synthetic oxygen carriers due to their catalytic effect on CH_4 conversion. In addition, tar concentration in the generated syngas was lower using synthetic oxygen carriers than with low-cost materials and these concentrations decreased with increasing FR temperature. Finally, lifetime values between 100 h and 900 h were determined for all the oxygen carriers, being the best ilmenite (600 h) among the low-cost materials and Fe10Al (900) among the synthetic ones.

Keywords: biomass, chemical looping gasification, syngas, oxygen carriers.

1. Introduction.

The Paris Agreement set 2 °C as the maximum increase of global temperature by 2100 compared to preindustrial levels. Further efforts are recommended to limit the temperature increase below 1.5 °C [1]. The mitigation of Global Warming and the reduction of Greenhouse Gases (GHG) emissions are closely related to the decarbonization of economies, which must develop renewable sources to produce energy and materials.

In this sense, Biomass Chemical Looping Gasification (BCLG) is a promising technology that allows the production of high-concentrated renewable syngas from forestry residues or agro-industrial wastes, avoiding the use of alimentary crops. Syngas could be used as raw material to obtain chemicals (methanol, ethanol, ammonia…) or biofuels (FT-diesel, FT-gasoline) [2]. The Net Zero Emission (NZE) scenario of IEA forecasts the increase of almost three times the liquid biofuel consumption of 2020 to achieve climatic neutrality in 2050. In addition, advanced biofuels will contribute to about 90% of total biofuel consumption in the NZE scenario [3].

BCLG follows the same principles as Chemical Looping Combustion (CLC), but partial conversion of biomass to CO and H_2 occurs instead of complete combustion to CO_2 and H_2O. These processes are usually performed in interconnected fluidized beds, where a solid oxygen carrier is used to transport heat and oxygen between the reactors. In Fuel Reactor (FR), where the biomass is fed, the oxygen carrier is reduced by its contact with the volatile matter and gasification products (mainly H_2 and CO) coming from biomass decomposition and gasification. In Air Reactor (AR) the oxygen carrier is oxidized by oxygen from air, generating the heat needed by the endothermic gasification reactions happening in the FR. Thus, in FR a high purity and N_2-free syngas stream is obtained without the necessity of an external power supply whereas in AR pure N_2 is produced. BCLG has additional advantages regarding to other gasification technologies such as inherent carbon capture and low tar generation.

The oxygen carrier is one of the keys to the development of BCLG processes. Oxygen carriers for chemical looping processes are required to have high integrity and mechanical strength during repeated redox cycles at high temperature and, at the same time, a low-cost and environmentally friendly material is desirable. In addition, it must have good fluidization properties and avoid agglomeration or sintering. There are several experiences in Chemical Looping technologies accumulated from CLC [4], but it is necessary to study some specific issues for BCLG. Probably, the main challenge of the current stage of research is to develop an oxygen carrier capable of preserving its properties in the highly reducing atmosphere present in BCLG.

Several Fe and Mn-based low-cost ores have been tested in BCLG continuous units [5-6], but high attrition rates and low lifetimes were observed for most of them. In spite of higher costs, synthetic materials have been prepared through different techniques with the aim of increasing the lifetime [7-8], and achieving other benefits such as tar removal or methane reforming. Therefore, the suitability of the oxygen carrier is committed between its cost and the rest of the factors that affect the final product obtained.

The objective of this work is to compare the behavior of low-cost (natural ores and a waste) and synthetic oxygen carriers during their operation in a continuous BCLG unit. The comparison to determine the suitability of oxygen carriers for the BCLG process is based on the gas compositions and the main gasification parameters (biomass conversion, syngas yield, etc.) obtained under different operating conditions, the formation of tars and the lifetime of the oxygen carrier particles.

2. Experimental.

2.1. Materials.

2.1.1. Oxygen carriers.

Seven oxygen carriers were used in this work: 4 low-cost materials and 3 synthetic oxygen carrier materials. The low cost materials included a Norwegian ilmenite from Titania, a Spanish iron ore (Tierga), a manganese ore from Gabon (MnGB), and a waste obtained in the steel industry (LD slag) which was supplied by SSAB Merox (Sweden). The synthetic materials were prepared by the hot incipient wetness impregnation method using alumina of 0.1–0.3 mm as support (Puralox NWa-155, Sasol GermanyGmbH), with a density of 1.3 g/cm^3 and a porosity of 55.4%, and a hot solution of iron nitrate (3.8 M) from Panreac. These oxygen carriers were based on iron with different Fe_2O_3 weight contents: 10 wt%, 20 wt% and 25 wt% (Fe10Al, Fe20Al, Fe25Al). Table 1 shows the main properties of the oxygen carriers.

Table 1. Physical and chemical properties of the oxygen carriers.

	Ores			Waste	Synthetic		
	Ilmenite	Tierga	MnGB	LD Slag	Fe10Al	Fe20Al	Fe25Al
Particle size (μm)	100-300	100-300	100-300	100-300	100-300	100-300	100-300
Skeletal density (kg/m^3)	4100	4216	3997	2764	3744	3950	4105
Crushing strength (N)	2.2	5.8	1.8	3.7	1.8	1.5	1.6
Porosity (%)	1.2	26.3	35.7	14.1	50.2	45.6	44.4
Oxygen transport capacity, R_{oc}	0.043	0.077	0.056	0.018	0.01	0.02	0.025
Main XRD phases	Fe_2TiO_5 (54.7 wt%) Fe_2O_3 (11.2 wt%) TiO_2 (28.6 wt%)	Fe_2O_3 (76.5 wt%) SiO_2 Al_2O_3 CaO MgO	Fe_2O_3 (8.4 wt%) Mn_3O_4 (67.5 wt%) SiO_2	CaO Ca_2SiO_4 $Ca_2Fe_2O_5$ $Mg_2Fe_2Si_2O_5$ $CaMn_{14}SiO_{24}$ $Ca_2Mg(SiO_4)_2$ Mg_2SiO_4	Fe_2O_3 (10 wt%) α-Al_2O_3 θ-Al_2O_3	Fe_2O_3 (20 wt%) α-Al_2O_3 θ-Al_2O_3	Fe_2O_3 (25 wt%) α-Al_2O_3, θ-Al_2O_3

2.1.2 Biomass.
Pine sawdust from Ansó (Spain) with synthetic oxygen carriers and pine sawdust from Darmstadt (Germany) with low-cost materials were used in the experiments. The particle size in both cases was the same: 0.5–2.0 mm. Proximate and ultimate analyses are shown in Table 2.

Table 2. Proximate and ultimate analyses of the biomasses used.

	Ansó	Darmstadt
Proximate analysis (wt%, as received)		
Moisture (EN 14774–3)	5.0	5.6
Ash (EN 14775)	0.3	0.6
Volatile matter (EN 15148)	79.9	78.5
Fixed carbon (by difference)	14.8	15.3
Ultimate analysis (wt%, dry basis)		
C	53.7	52.6
H	6.1	6.0
N	0.1	0.1
S	0.0	0.0
O (by difference)	39.8	40.7
LHV (kJ/kg dry biomass) (EN 14918)	19309	18594
Ω_b (mol O/kg dry biomass)	95.3	92.5

2.2. BCLG unit.
The experiments were carried out in the ICB-CSIC 1.5 kW$_{th}$ unit, whose scheme is shown in Figure 1. It consists in two bubbling fluidized beds, Air Reactor (0.08 m id) and Fuel Reactor (0.05 m id), inter-connected through a Loop Seal which prevented gas mixing between reactors. The reactors were electrically heated for a better temperature control in the reactors. A gas mixture of 2100 Nl/h of N_2 and air was fed to the AR to control the oxygen-to-fuel ratio maintaining a constant solid circulation flow (~12 kg/h). The FR was fed with 120 Nl/h of steam and a flow of 90 Nl/h of N_2 was introduced in the Loop Seal. Further description of the unit could be found elsewhere [9].
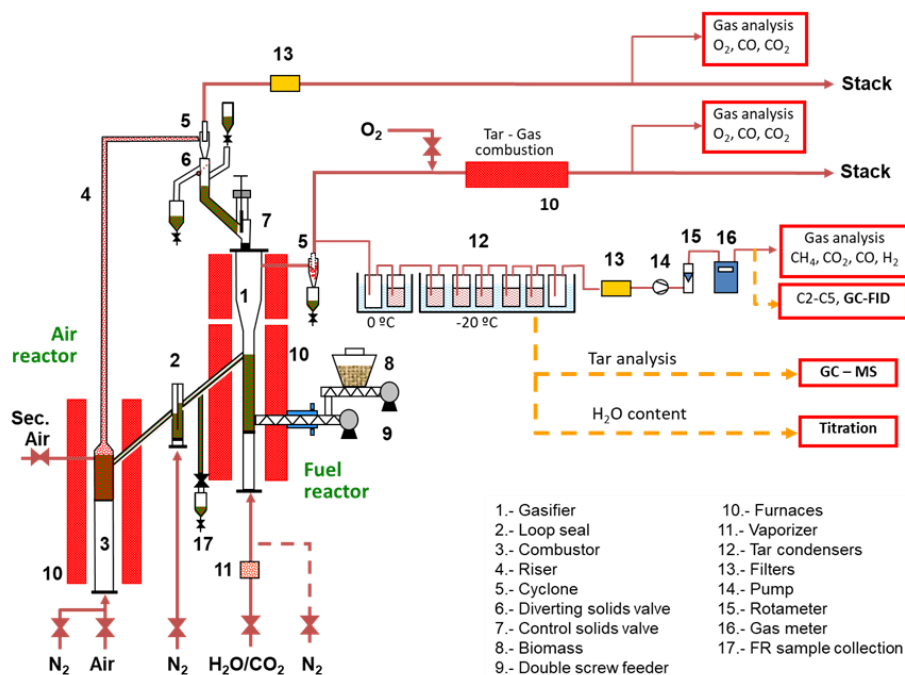

Figure 1. Scheme of the 1.5 KW$_{th}$ CLG unit at ICB-CSIC.

Gas concentrations were measured in the gas outlet stream of the FR and AR with on-line analyzers. Offline determination of C1-C4 hydrocarbons was done by gas chromatography (Perkin Elmer CLARUS 580). In addition, tars were recovered following the European tar protocol [10] and analyzed in a Gas Chromatograph (GC-2010 Plus) coupled to a Mass Spectrometer (QP2020) Shimadzu, calibrated using naphthalene and EPA 525 PAH MIX-A standards.

2.3. Oxygen control method.
In CLG, to avoid the full combustion of syngas to CO_2 and H_2O, it is necessary to operate below stoichiometric conditions ($\lambda < 1$). In this work, to control the transport of oxygen between reactors, the oxygen fed into the AR was limited. This method allowed a smooth operation, keeping constant the lattice oxygen transference between reactors, regardless of the flowrate of solids circulation in the system. To increase the gas velocity in the AR, which made it possible to maintain a constant and sufficiently high solids circulation flow with a low air flow, N_2 was fed together with the air into the AR, that is, a constant gas flow was maintained in all cases. The mixture of air and N_2 was varied to fit the oxygen-to-biomass ratio required in each experiment.

2.4. Data evaluation.
The main parameters used to evaluate the performance of the BCLG process were:

- Oxygen-to-biomass ratio, λ, which was defined as the amount of oxygen transported from the AR to the FR with respect to the stoichiometric oxygen necessary for the complete combustion of biomass to CO_2 and H_2O.

$$\lambda = \frac{2F_{O2,AR,in}}{F_b + \Omega_b}$$

where $F_{O2,AR,in}$ was the flow of O_2 fed into the AR (mol/h), F_b was the biomass (dry basis) fed into the system (kg/h), and Ω_b (mol O/kg dry biomass) was the stoichiometric oxygen necessary for complete combustion of biomass fed. This last parameter was calculated as:

$$\Omega_b = \left(x_C \frac{32}{12} + x_H \frac{16}{2} + x_S \frac{32}{32} - x_O \right) \frac{1000}{16}$$

being x_i the fraction of each component present in the biomass.

- Biomass conversion, X_b, which was defined as the amount of carbon contained in the biomass that was converted into gas, both in FR and AR.

$$X_b = \frac{F_{C,FR,out} + F_{C,AR,out}}{F_{C,b}} = \frac{\left[F_{CO_2} + F_{CO} + F_{CH_4} + xF_{C_xH_y} \right]_{FR,out} + \left[F_{CO_2} \right]_{AR,out}}{\frac{1000}{12} F_b x_C}$$

where F_i is the gas flowrate (mol/h) of component i.

- Carbon conversion efficiency, η_{cc}, which represented the fraction of carbon converted to gas in the FR relative to the total carbon converted in the unit.

$$\eta_{CC} = \frac{F_{C,FR,out}}{F_{C,FR,out} + F_{C,AR,out}}$$

- Syngas Yield, Y, which evaluated the amount of H_2 and CO (Nm³/kg dry biomass) produced in the FR with respect to the biomass (d.b.) fed into the system (kg/h).

$$Y = Y_{H2} + Y_{CO} = \frac{G_{H_2}}{F_b} + \frac{G_{CO}}{F_b}$$

where G_{H2} and G_{CO} were the flowrates of H_2 and CO generated in the FR (Nm³/h).

- Cold gas efficiency, η_g, represented the fraction of chemical energy contained in the gases leaving the FR with respect to the total energy contained in biomass:

$$\eta_g = \frac{F_{g,FR,out} \cdot LHV_g}{F_b \cdot LHV_b} \cdot 100$$

where $F_{g,FR,out}$ was the molar flowrate of gas leaving the FR (mol/h), LHV_g was the low heating value of the gas produced (kJ/mol) and LHV_b was the low heating value of the dry biomass (kJ/kg).

3. Results.

Each oxygen carrier was circulating in the 1.5 kW$_{th}$ continuous unit at high temperature for approximately 50 h, of which 35 h corresponded to biomass gasification. The oxygen-to-fuel ratio was varied between 0.2 and 0.6 and three temperatures were tested (820 °C, 880 °C, 930 °C). The steam to biomass ratio, S/B, was kept constant at ~0.6 kg of steam per kg of dry biomass. The lifetime of each oxygen carrier was determined by measuring the amount of fine particles collected in downstream cyclones and filters with a particle size below 40 μm.

3.1. Effect of the oxygen to-fuel-ratio

The amount of oxygen transported from the AR to the FR is one of the most relevant parameters affecting gasification, since it determines the composition of the outlet gas. Obviously, the increase in the oxygen-to-fuel ratio promotes the oxidation of syngas, decreasing the amount of CO and H_2 and increasing the CO_2 and H_2O concentrations. Therefore, the proper oxygen-to-fuel ratio must be determined to meet power requirements (autothermal process) while producing as much syngas as possible [11]. Figure 2 shows the effect of the oxygen-to-fuel ratio on the composition of the FR gas outlet stream using both synthetic oxygen carriers and low-cost materials.
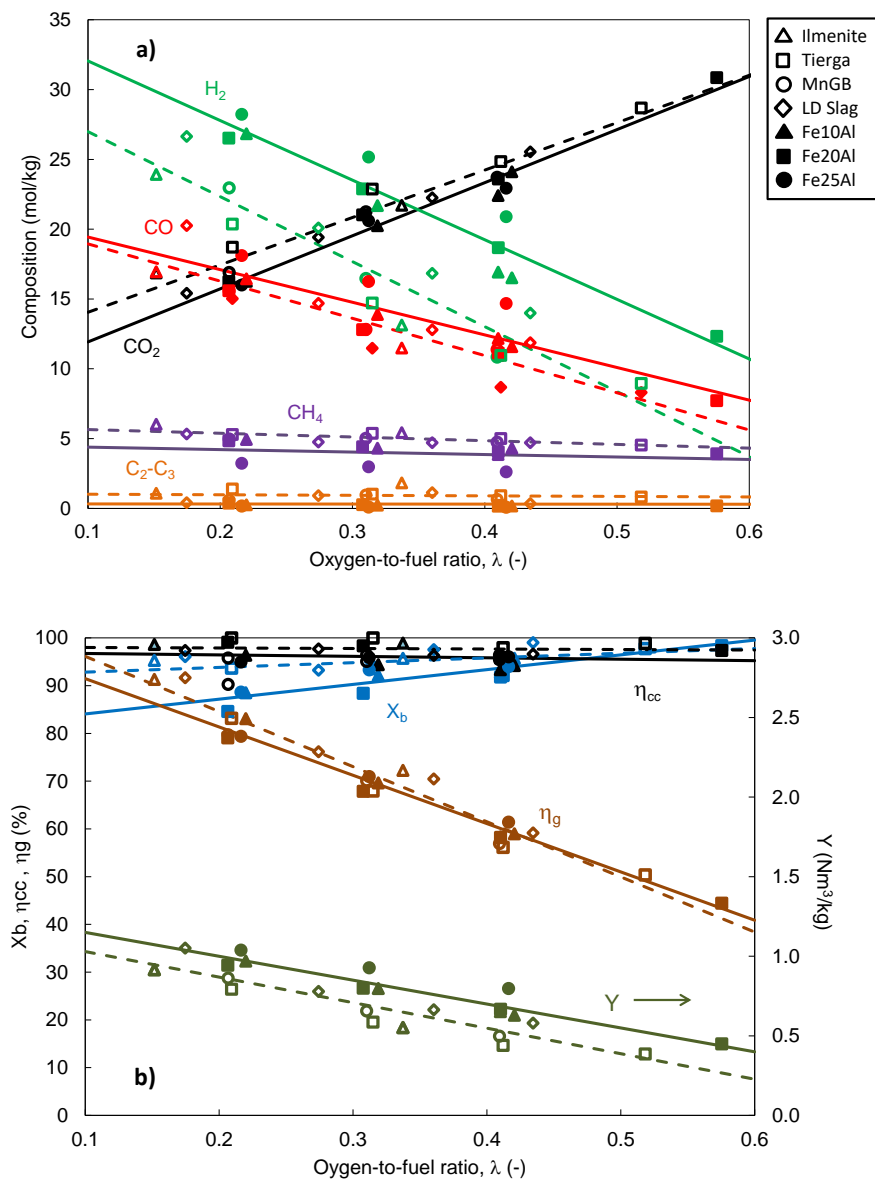

Figure 2. Effect of the oxygen-to-fuel ratio on (a) the syngas compositions, and (b) Carbon conversion, η_{CC}, Biomass conversion, X_b, Cold Gas Efficiency, η_g, and Syngas Yield, Y. T ~930 °C, S/B ~0.6.

As expected, the increase of λ led to a higher oxidation of the products generated in the FR, decreasing the generation of CO and H_2 and increasing that of CO_2 (and H_2O). In contrast, the amounts of methane and C_2-C_3 were hardly affected by the oxygen-to-fuel ratio, remaining practically stables at any λ. Although the same trends and similar compositions were obtained for both low-cost and synthetic oxygen carriers, since the same oxygen was transported with the same oxygen-to-fuel ratio, it is remarkable to indicate that higher amounts of CO and mainly of H_2 were generated with the synthetic oxygen carriers. This effect was attributed to the higher conversion of CH_4 (and light hydrocarbons) obtained using synthetic oxygen carriers, possibly due to the higher extent of the reforming reaction that seems to be more catalyzed by Fe-based synthetic oxygen carriers. It should be noted that 1 mol of CO and 3 mol of H_2 are generated for each mol of CH_4.

Obviously, the syngas yield decreased when λ increased (see Figure 2b), but it was also higher for synthetic oxygen carriers than for low-cost materials due to the higher CH_4 conversion discussed above. The gas composition obtained had also a significate effect over the cold gas efficiency, which decreased from ~85 % at λ ~0.2 to ~60 % at λ ~0.4. However, in this case, no differences in the cold gas efficiency were observed between the oxygen carriers because the additional syngas generated by synthetic oxygen carriers was partially offset by the converted CH_4.

Regarding the other gasification parameters, both the low-cost and synthetic oxygen carriers presented very high carbon conversion efficiencies (η_{cc}> 95%), being unaffected by the nature of the oxygen carrier or the oxygen-to-fuel ratio. The biomass conversion, X_b, increased from ~90% to ~95% when the oxygen-to-fuel ratio increased from 0.2 to 0.6, with no clear differences among the different oxygen carriers.

3.2. Effect of temperature.
Three temperatures in the range of 820 °C to 940 °C were tested with each oxygen carrier, keeping the S/B ratio at ~0.6 and λ ~0.3. The results obtained are shown in Figure 3. The main effect promoted by increasing the FR temperature was the improvement of char gasification in FR, decreasing the amount of char that passed through the loop-seal to be burned in the AR. As a consequence of improved biomass char gasification, the amount of CO and H_2 increased (Figure 3a). On the contrary, the amounts of methane and C_2-C_3 decreased slightly with increasing operating temperature in the FR. Once again, it can be seen that the amounts of CO and especially of H_2 generated were higher, and on the contrary, those of CH_4 and C_2-C_3 were lower with the synthetic oxygen carriers than with the low-cost ones.

The increase in char gasification in FR due to temperature was clearly reflected in the carbon capture, which increased for both synthetic and low-cost oxygen carriers, reaching close to 100 % of carbon capture at 930 ºC (see Figure 3b). Biomass conversion values greater than 85 %, Xb, were observed for all the oxygen carriers tested, and this conversion increased with increasing the FR temperature due to the increase in char gasification rate. As a consequence of the increase in char gasification by effect of the temperature, the syngas yield also increased, reaching values of ~0.8 Nm3/kg and ~0.7 Nm3/kg at 930 ºC with synthetic and low-cost oxygen carriers respectively. Cold gas efficiency also improved due to the effect of temperature, from 65-69 % to 69-76 %, but without significant differences between low-cost and synthetic oxygen carriers.
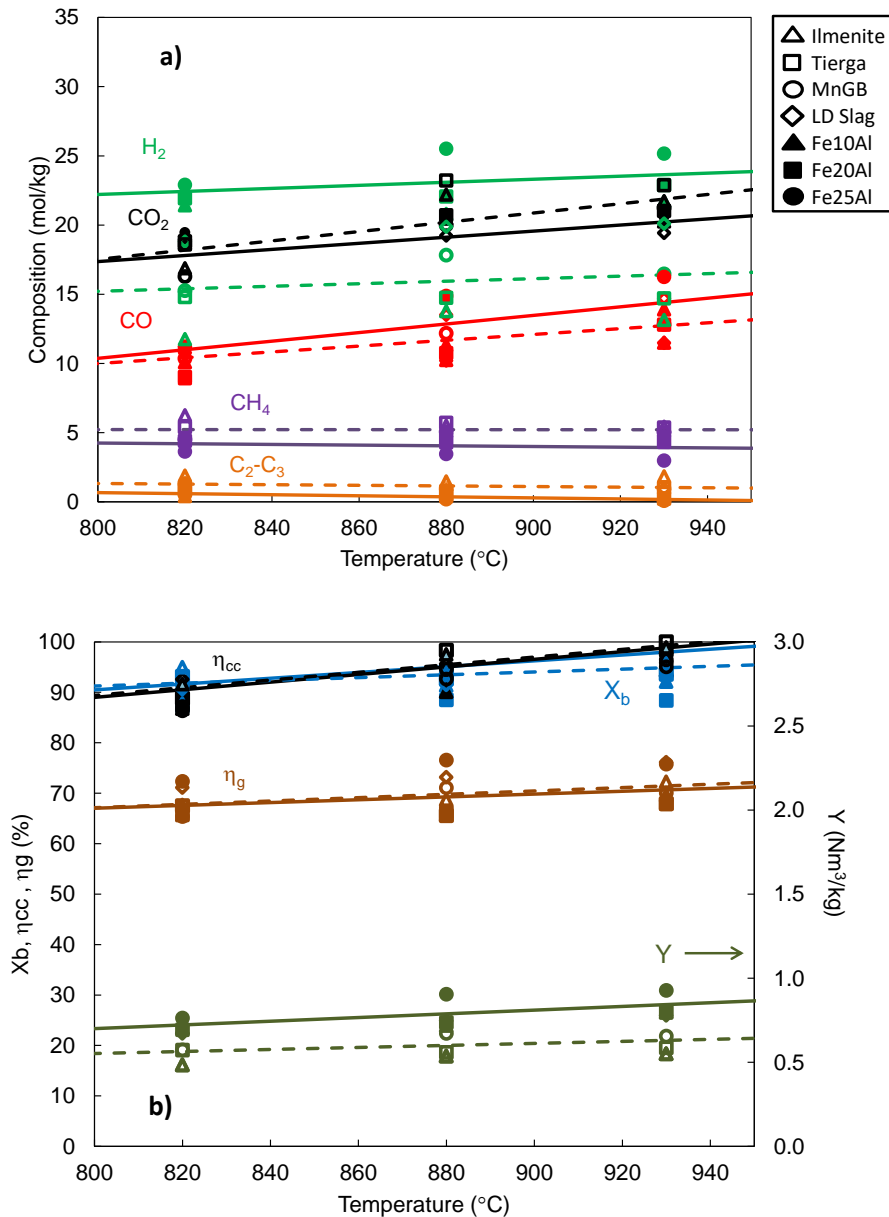
Figure 3. Effect of temperature on (a) the syngas compositions (in mol per kg of dry biomass), N_2-free and dry basis and (b) Carbon conversion, η_{cc}, Fuel conversion, X_b, Cold Gas Efficiency, η_g, and Syngas Yield, Y. λ ~0.3, S/B ~0.6.

3.3. Fate of tars.

Tars are compounds that cause damages to gasifiers and deactivate the catalysts used in the further processing of syngas [12-13]. Hence, their removal early in the process is a primary focus of BCLG. One of the advantages of BCLG over other biomass gasification processes is the lower tar generation, although few studies have been carried out in continuous BCLG units.

In this study, tars were recovered following the European Tar Protocol [10] and a total of 20 different tar-compounds were analyzed in a gas chromatograph coupled to a mass spectrometer. The amount of tar compounds was determined in tests at the three aforementioned temperatures.
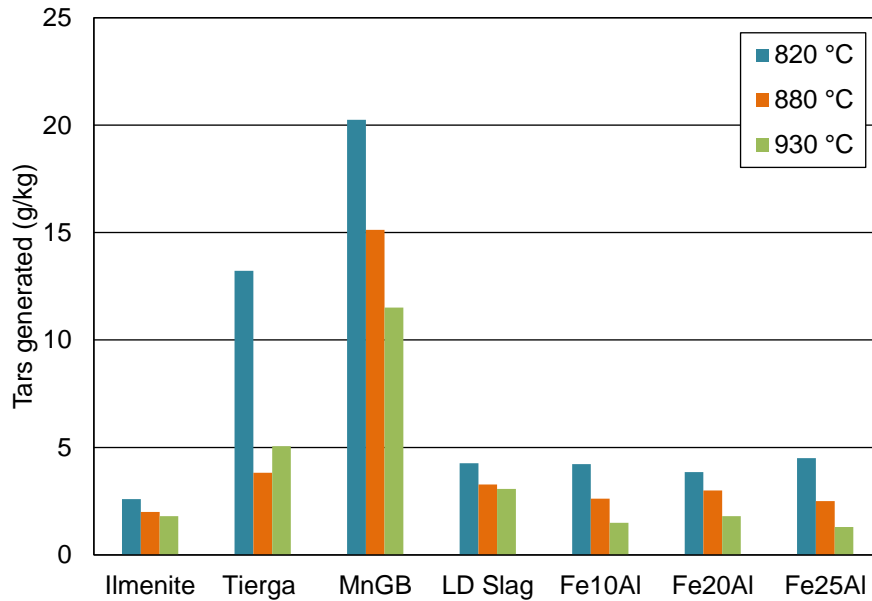
Figure 4. Effect of temperature on tar generation (g/kg of dry biomass) using low-cost and synthetic oxygen carriers. λ ~0.3, S/B ~0.6.

Figure 4 shows the total amount of tars obtained with all oxygen carriers at the three temperatures. The tar amounts are represented as grams of tars per kg of dry biomass fed.

Overall, it is can be seen that the tar compounds were cracked due to the effect of temperature, their content being strongly reduced with increasing temperature. In most cases, the tar content was halved by increasing the temperature from 820 °C to 930 °C.

Regarding the nature of the oxygen carrier, it is noteworthy that the synthetic oxygen carriers had the greatest catalytic effect on the tar compounds, reducing their content in the synthesis gas to values between 1.3 g/kg and 1.8 g/kg at the temperature of 930 ºC. The lowest values of tars measured corresponded to the Fe-based oxygen carriers at the highest temperature. Low tar contents were also obtained with ilmenite and LD slag (values of 1.8 g/kg and 3.1 g/kg at 930 ºC, respectively), but with these low-cost oxygen carriers the effect of operating temperature on the tar content of the syngas had a markedly lower effect than with the synthetic ones. Finally, it was observed that the Fe and Mn minerals (Tierga and MnGB) had the lowest capacity to reduce the tar concentration in the syngas (5.1 g/kg and 11.5 g/kg at 930 ºC, respectively).

Regardless of the oxygen carrier and the experimental operating conditions used, naphtalene was the main compound in all cases and represented about 50 % of the total tar content. Other compounds such as phenanthrene and acenaphthylene were found in significate quantities. The toxic product benzene appeared in low amounts (<0.1 g/kg) in most tests.

3.4 Lifetime.
The behavior of the oxygen carrier with respect to its fluidizing proprieties is one of the most important issues in processes that use fluidized bed reactors. In BGLG, in addition to the chemical looping operation taking place under high thermal stress, the oxygen carrier also undergoes chemical stress arising from changes in its structure during redox cycles in a highly reducing atmosphere. Therefore, the particles are more vulnerable in CLG than in CLC, increasing attrition as a result of their collision with the reactor wall and with each other. These fine particles released from the oxygen carrier are sometimes responsible for defluidization problems caused in the bed. In addition, the constant elutriation of fine particles makes it necessary to add new fresh carrier to the system, which increases the costs of the process. Thus, the resistance of the oxygen carrier to its breakage and attrition is one of the parameters that determine its lifetime.
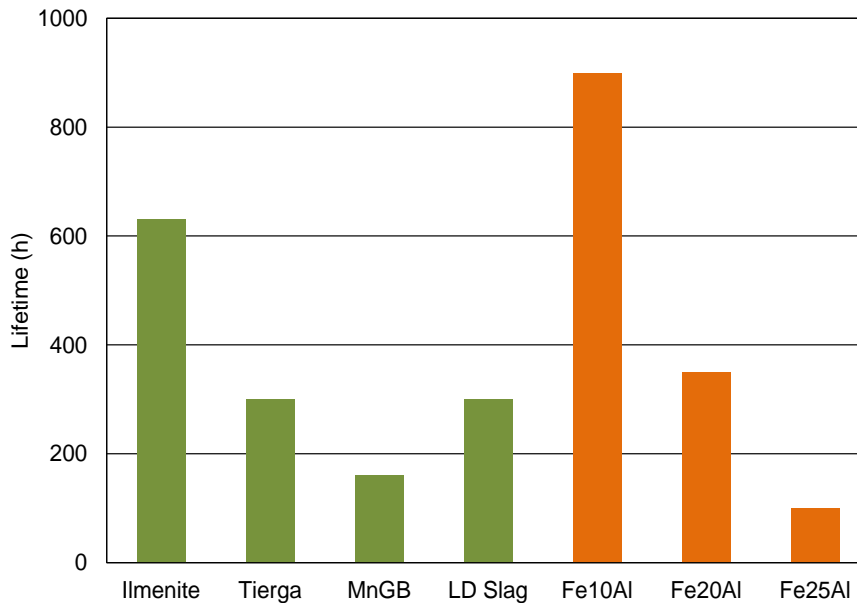
Figure 5. Lifetime (h) of each oxygen carrier.

In this work, fine particles (<40 μm) collected in the downstream cyclones and filters were measured to quantify the attrition (% of fines per hour) and determine its lifetime (h). Figure 5 shows the lifetime of each oxygen carrier tested in the BCLG experimental unit.

As can be seen in the figure, there were very important differences in the lifetime among the different oxygen carriers. Among the low-cost materials, Ilmenite had the highest lifetime, with a lifetime of 630 h, while LD Slag and Tierga had lifetimes of 300 h each one. The manganese ore, MnGB, showed the lowest lifetime of the low-cost oxygen carriers with 160 h. In the synthetic oxygen carriers, a clear dependence was observed between the amount of Fe in the carrier and its lifetime, with the lifetime being higher at low Fe contents. The lifetime of these oxygen carriers increased from 100 h with the Fe25Al oxygen carrier to 900 h with the Fe10Al oxygen carrier, being the highest value found for any CLG oxygen carrier in literature. It should be noted that during the experimental campaign no signs of agglomeration or sintering appeared in any of the oxygen carriers and the fluid dynamic behavior was good during continuous operation.

4. Conclusions.

The behaviour of 7 oxygen carriers, 4 low-cost materials (3 ores and 1 waste) and 3 synthetic Fe-based solids was analyzed in a 1.5 kW$_{th}$ BCLG unit. 50 h of solid circulation and 35 h of biomass gasification were accomplished with each oxygen carrier. The gas compositions and the main gasification parameters were compared by varying the oxygen-to-fuel ration, λ, and the FR temperature. The tar content in the syngas and lifetime of the oxygen carriers were also analyzed. It was found that:

- Increasing FR temperature enhanced the char gasification rate, which improved both the carbon conversion efficiency and the biomass conversion. High carbon conversions, η_{cc} (> 95 %) and fuel conversions, X_b, (> 85%) were obtained with all the oxygen carriers and operating conditions.

- The same trends in the syngas compositions were observed with both low-cost and synthetic oxygen carriers when the λ and the FR temperature varied. However, under the same operating conditions, the amount of syngas generated was higher for synthetic oxygen carriers due to its catalytic effect on CH$_4$ conversion. As a consequence, the syngas yield, Y, was always higher for the synthetic oxygen carriers.

- For all oxygen carriers the tar concentration in the syngas decreased with increasing FR temperature. The lowest tar values were produced working with synthetic oxygen carriers (1.3-1.8 g/kg at the FR temperature of 930 °C). Low values were also obtained with ilmenite ore and the LD Slag waste (2.6 g/kg and 3.1 g/kg at 930 °C, respectively) whereas high tar concentrations were obtained with the Mn-ore, MnGB, and Tierga Fe-ore.

- Lifetimes between 100 h and 900 h were determined by the selected oxygen carriers. Among the low-cost materials, ilmenite showed a lifetime of 630 h while MnGB, LD Slag and Tierga had higher attrition rates and hence lower lifetimes (160 h for MnGB and 300 h for LD Slag and Tierga). Nonetheless, the highest lifetime was determined for the synthetic oxygen carrier Fe10Al (900 h) and it was observed that the decrease in Fe content has a positive effect on the oxygen carrier lifetime.

5. Acknowledgements.

6. References.

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