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Effect of the Fe content on the behavior of synthetic oxygen carriers in a 1.5 kW biomass chemical looping gasification unit

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ABSTRACT

Biomass Chemical Looping Gasification (BCLG) is a promising technology that enables the production of high-purity and N<sub>2</sub>-free renewable syngas under autothermal operating conditions. In this work, the effect of the Fe-content (10, 20, and 25 wt% as Fe<sub>2</sub>O<sub>3</sub>) of three synthetic oxygen carriers supported on alumina was studied in a 1.5 kW<sub>th</sub> BCLG continuous unit. Similar syngas compositions and gasification parameters, biomass conversion, syngas yield, cold gas efficiency, etc., were obtained for the three oxygen carriers when analyzing the effect of oxygen-to-fuel ratio (λ) and fuel reactor (FR) temperature. Tars were also unaffected by the Fe-content, the increase in the FR temperature being the only parameter that allowed their reduction. A deep characterization of the oxygen carriers showed that the increase of Fe-content in the oxygen carrier promoted the migration of iron to the outer layer of particles, being detached of them. Lifetimes of 900, 350 and 100 h (corresponding to approximately 4500, 1750 and 500 cycles) were found for the oxygen carriers with 10 wt%, 20 wt% and 25 wt% of iron oxide, respectively. Therefore, among the three oxygen carrier tested, the one composed by a 10% of Fe<sub>2</sub>O<sub>3</sub> was shown to be the most suitable for BCLG, providing the longest lifetime whereas the same syngas composition and tar removal could be obtained regardless of the Fe-content.

1. Introduction

Almost a quarter of the total carbon dioxide in the European Union in 2019 was emitted by transport sector [1]. Therefore, the decarbonization in this sector is a priority in order to achieve the Agreement of the COP21, where the limitation of a maximum increase in global temperature of 2 °C for the end of the century was established [2]. Syngas obtained from renewable biomass is an interesting product which could be transformed into a wide variety of liquid biofuels such as DME, MTBE, gasoline, diesel, etc. In fact, liquid biofuels are identified as promising substitutes of fossil fuels both for terrestrial and aviation transport in the near future. Biofuel consumption will increase three times by 2030 in the Sustainable Development Scenario [3], and it is expected to reach a 30% of share in the total consumption by 2060 [4]. There are several routes toward these products being one well-known option the performance of Fischer-Tropsch (FT) processes [5]. Among the different options for syngas production, Biomass Chemical Looping Gasification (BCLG) has emerged in recent years as an innovative route due to its advantages over conventional gasification. BCLG enables to produce high-purity and N<sub>2</sub>-free syngas (mainly CO and H<sub>2</sub>) at autothermal conditions, avoiding the need of external power supply and cryogenic air separation units. Additionally, low tar generation and inherent carbon capture are achieved with respect to conventional gasification [6-7]. As shown in Fig. 1, BCLG follows the same principles as Chemical Looping Combustion (CLC) but partial conversion of biomass to CO and H<sub>2</sub> occurs instead of complete combustion to CO<sub>2</sub> and H<sub>2</sub>O. These processes are usually based on the use of interconnected fluidized beds, a technology well developed and existing at commercial scale.

In BCLG, a solid oxygen carrier is used to transport both oxygen and heat between two interconnected reactors, Air Reactor (AR) and Fuel Reactor (FR). The oxygen carrier circulates between reactors, being reduced and oxidized during many repeated cycles. In the FR, biomass is converted into H<sub>2</sub>O, CO, CO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and CH<sub>4</sub> by the effect of a gasification agent (steam or CO<sub>2</sub>) and the oxygen carrier is reduced by partial combustion of gases generated from biomass devolatilization and gasification. The reduced oxygen carrier passes to AR, where it is regenerated with oxygen from air. Oxidation reaction is exothermic (ΔH > 0) and hot solids transport heat to FR, supplying the energy required by endothermic gasification reactions happening in this reactor. Thus, a N<sub>2</sub>-
Free renewable syngas stream is obtained without the need for an external energy input [8].

Oxygen carrier is one of the keys to the development of BCLG processes. In a chemical looping process, oxygen carriers require having high integrity and mechanical strength during repeated redox cycles at high temperature and, at the same time, it is desirable to be a low-cost and environmentally friendly material. In addition, it must have good fluidization properties and avoid agglomeration or sintering. Several and environmentally friendly material. In addition, it must have good high temperature and, at the same time, it is desirable to be a low-cost high integrity and mechanical strength during repeated redox cycles at external energy input [8].

However, the use of these materials in the gasification introduces new challenges due to the highly reducing atmosphere present in this process [10].

Natural iron ores, such as hematite and ilmenite, have low prices and can be found in abundance. Hematite, mixed with silica sand, has been tested in continuous CLG units [11] showing good results although agglomeration was found in some cases [12]. Ilmenite, a natural ore composed mainly of iron and titanium, has been used in a continuous unit showing high lifetimes and no agglomeration [6]. Another low-cost oxygen carrier would be LD slag, a by-product from the steel production [13], which had been tested for combustion [14] and more recently in BCLG, generating high syngas yields, albeit with a high attrition rate [15].

In spite of the higher costs, synthetic materials have been proposed to improve oxygen carrier properties, such as particle lifetime and tar cracking/reforming [16–19]. Most of these materials are based on the mixture of different metallic oxides, one of which is usually based on Fe. These materials have only been tested in thermogravimetric analyzers (TGA) or in fixed bed and batch fluidized bed reactors at laboratory scale. The exception is a bimetallic Fe-Ni based oxygen carrier tested by Wei et al. 2015 in a continuous BCLG prototype [20]. They obtained excellent results, but the use of Ni could be a handicap due to their high cost and toxicity.

Regarding monometallic oxygen carriers, iron on alumina is one of the preferred synthetic materials. The research group at the Guangzhou Energy Conversion Institute [21–22] performed BCLG tests in a 10 kWth pilot plant using a Fe₂O₃–Al₂O₃ (7:3) oxygen carrier to analyze the effect of operating conditions in the flue gas composition, gasification efficiency, and carbon conversion rate. The oxygen carrier did not suffer sintering, crushing phenomenon or decrease in performance, indicating good stability of this type of synthetic oxygen carriers. In these tests, the oxygen transferred from AR to FR was controlled by varying the oxygen carrier circulation flow per fuel unit. Therefore, fully oxidized oxygen carrier was present at the outlet of the AR.

However, a previous study of our research group demonstrated the advantages of using the control of the oxygen transported from AR to FR by limiting its feeding in the air reactor instead of using the control of the solid circulation rates [8]. Under this control method, the oxygen carrier could be completely reduced at the outlet of FR and partially oxidized at the outlet of AR, which could affect its physical stability. It must be considered that the variation of the oxygen carrier conversion in a redox cycle depends mainly on oxygen-to-fuel ratio (λ), solid circulation rate, and metal oxide content in the oxygen carrier [8,23].

Using this oxygen control method, the behavior of a synthetic FeO₃–Al₂O₃ (2:8) oxygen carrier was recently evaluated in the BCLG 1.5 kWth unit located at Instituto de Carboquímica (ICB-CSIC) using pine wood as fuel [7]. Good oxygen carrier performance was observed, although some iron loss was found after 50 h of continuous operation. In addition, it was also observed a significant reduction in particle lifetime, 350 h in BCLG compared to 1100 h under CLC conditions [24]. This was a consequence of the more fragile internal structure derived from the highly reduced conditions in which the oxygen carrier operates in BCLG. However, several studies have demonstrated that the amount of metal oxide in the oxygen carrier could affect its stability during operation in CLC [16]. As far as authors’ knowledge, there are no previous studies on the effect of metal oxide content on the behavior of synthetic materials in BCLG.

This work aimed to evaluate the effect of the Fe-content on the behavior of a synthetic oxygen carrier in gasification conditions. Three Fe-Al materials with FeO₃ content of 10 wt%, 20 wt% and 25 wt% were used as oxygen carriers in a 1.5 kWth BCLG continuous unit. The effect of the main operating conditions (oxygen-to-fuel ratio and FR temperature) on the main process parameters (syngas composition, syngas yield, cold gas efficiency, and tar formation) was analyzed. Finally, a deep characterization of the oxygen carriers was conducted to optimize the amount of active phase in the particles that maximizes its lifetime.

2. Experimental

2.1. Materials

5 kg batches of each of the three Fe-based synthetic oxygen carriers were prepared by the hot incipient wetness impregnation method. Commercial γ-alumina particles (Puralox NWa-155, Sasol Germany GmbH) of 0.1–0.3 mm, with a density of 1.3 g/cm³ and a porosity of 55.4%, were used as support. Oxygen carriers were prepared in a planetary mixer by impregnating the support, which was heated at 80 °C, with a saturated hot solution of iron nitrate (3.8 M) from Panreac. Successive impregnations were done depending on the final

![Fig. 1. Route for syngas production via BCLG and final use.](image-url)
concentration of iron required as active phase. They were designated as Fe10Al, Fe20Al and Fe25Al according to the Fe content in the oxygen carriers was determined by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) using a Xpertextrobue-EOP-TI FTM26 (Spectro) spectrophotometer. The crystallographic analysis carried out in each carrier was determined using a Bruker D8 Advance A25 polycrystalline powder X-ray diffractometer (XRD). A Hitachi S-3400N with energy-dispersive X-ray NTE-5 polycrystalline powder X-ray diffractometer (XRD). A Hitachi S-3400N with energy-dispersive X-ray line analyzer (SEM-EDX) was used for microstructural analysis of entire oxygen carrier particles and for the determination of the dispersion of different components (Fe, Al, O) and internal view of particles after being embedded in epoxy resin, polished and cut. Skeletal density was measured with a Micromeritics Accucpve II 1340 helium pycnometer. The crushing strength was taken as the average value of at least 20 measurements. Porosity was measured by Hg intrusion in a Quantachrome PoreMaster 133. A thermodiffusometric analyzer (TGA), CI Electronics type, was used to determine oxygen transport capacity of fresh and used oxygen carriers. For this, redox cycles were carried out using a gas composed of 15 vol% CO, 20 vol% CO2 (N2 balance) for reduction and air for oxidation. CO was used instead of H2 as a reducing agent because previous studies showed that CO is capable of reducing Fe2O3-Al2O3 to FeAl2O4 since H2 reduces Fe2O3 to metallic Fe, which is never formed in continuous operation in pilot plants [25]. It should be noted that oxygen transport capacity obtained in the TGA coincided with the theoretical oxygen transport capacity corresponding to the Fe content determined by ICP-OES for the three materials and assuming the redox pair Fe2O3-Al2O3/FeAl2O4.

Table 1 shows the physical and chemical properties of the fresh oxygen carrier particles during the preparation process. Subsequently, the air flow was replaced by steam in the FR and by N2 in the loop-seal, at the same time biomass was fed (CLC operation). Later, the operating conditions corresponding to CLG were set by replacing the air flow by a mixture of N2 and air in the AR. As it can be seen in Fig. 3a, initially there was complete combustion of the biomass to CO2 and H2O, due to the excess of lattice oxygen supplied by the oxygen carrier, and then the concentration of these gases began to decrease while the concentrations of CO and H2 increased. Fig. 3b shows the oxygen reacted in the FR and AR during the operation change from CLG to CLC. It can be observed that during non-steady state operation the oxygen reacted in the FR was higher than the reacted in the AR due to the oxygen released by the oxygen carrier during its reduction. The concentrations of the different gases stabilized after approximately 1 h of operation. One additional hour was spent to be sure that the oxygen carrier had reached steady state and the facility was ready to analyze the gasification process. At the end of each day of operation and the following days, the BCLG unit was cooled and heated under N2 atmosphere to prevent re-oxidation of the oxygen carrier.

2.2. Biomass chemical looping gasification unit

The experiments were carried out in the ICB-CSIC 1.5 kWth unit, whose scheme is shown in Fig. 2. It consists of two bubbling fluidized beds, Air Reactor (0.08 m id) and Fuel Reactor (0.05 m id), interconnected through a Loop Seal (0.03 m id) which prevented gas mixing between reactors. The reactors were electrically heated for a better temperature control. A gas mixture of 2100 Nl/h of N2 and air was fed to the AR to control the oxygen-to-fuel ratio maintaining a constant solid circulation flow (~12 kg/h). Although the FR could be fed with steam, CO2, N2 or a mixture of them, 130 Nl/h of pure steam was used for fluidization of this reactor in all tests. A stream of 90 Nl/h of N2 was introduced into the Loop Seal. An additional description of the unit can be found elsewhere [26].

Table 1  
Table 2

<table>
<thead>
<tr>
<th>Physical and chemical properties of fresh oxygen carriers.</th>
<th>Fe10AI</th>
<th>Fe20AI</th>
<th>Fe25AI</th>
</tr>
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<tbody>
<tr>
<td>Number of impregnations</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Fe2O3 content (wt%)</td>
<td>10 ± 0.1</td>
<td>20 ± 0.2</td>
<td>25 ± 0.2</td>
</tr>
<tr>
<td>Particle size (μm)</td>
<td>100–300</td>
<td>100–300</td>
<td>100–300</td>
</tr>
<tr>
<td>Skeletal density (kg/m³)</td>
<td>3744 ± 55</td>
<td>3950 ± 60</td>
<td>4105 ± 61</td>
</tr>
<tr>
<td>Crushing strength (N)</td>
<td>1.8 ± 0.5</td>
<td>1.5 ± 0.4</td>
<td>1.6 ± 0.5</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>50.2 ± 0.4</td>
<td>45.6 ± 0.4</td>
<td>44.4 ± 0.4</td>
</tr>
<tr>
<td>Oxygen transport capacity, Rox</td>
<td>0.010</td>
<td>0.020</td>
<td>0.025</td>
</tr>
<tr>
<td>Main XRD phases</td>
<td>Fe3O4, α-Al2O3, θ-Al2O3</td>
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<td></td>
</tr>
</tbody>
</table>

* Metal content determined by ICP-OES.

Table 2  
Table 2

<table>
<thead>
<tr>
<th>Proximate analysis (wt%, as received)</th>
<th>Moisture (EN 14774-3)</th>
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<tbody>
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<td>Ash (EN 14775)</td>
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<tr>
<td>Volatile matter (EN 15148)</td>
<td>79.9</td>
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<tr>
<td>Fixed carbon (by difference)</td>
<td>14.8</td>
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<tr>
<td>Ultimate analysis (wt%, dry basis)</td>
<td>C</td>
<td>53.7</td>
</tr>
<tr>
<td>H</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>O (by difference)</td>
<td>39.8</td>
<td></td>
</tr>
<tr>
<td>LHV (kJ/kg dry biomass) (EN 14918)</td>
<td>19,309</td>
<td></td>
</tr>
<tr>
<td>Ω (mol O/kg dry biomass)</td>
<td>95.3</td>
<td></td>
</tr>
</tbody>
</table>

* Determined in a Thermo Flash 1112 analyzer.

CO2, CO, and O2 concentrations were measured in the gas outlet stream of the AR with a Siemens Ultramat/Oxymat 6 analyzer. The gas leaving FR was divided into two streams. One of them was sent to the tar collection system. Tars were recovered following the European tar protocol [27] and analyzed in a Gas Chromatograph (GC-2010 Plus) coupled to a Mass Spectrometer (QP2020i) Shimadzu, calibrated using naphthalene and EPA 525 PAH MIX-A standards. After tar cleaning, CO2, CH4, and CO concentrations were measured by a non-dispersive infrared analyzer (Siemens Ultramat 23) and H2 concentration by a thermal conductivity analyzer (Siemens Calomat 6). In addition, an offline determination of C1-C4 hydrocarbons was done in gas chromatograph (Perkin Elmer CLARUS 580). The other stream leaving the FR was burnt with O2 in a supplementary reactor in order to measure oxygen consumption for a better check of the mass balances. CO2, CO and O2 concentrations were measured at the exit of this combustor with a Siemens Ultramat/Oxymat 6 analyzer.

To start the experiments with each oxygen carrier, the CLG unit was loaded with 2.5 kg of oxygen carrier, which was circulated for 6 h at 850 °C in an air atmosphere to elutriate the fine particles attached to the oxygen carrier particles during the preparation process. Subsequently, the air flow was replaced by steam in the FR and by N2 in the loop-seal, at the same time biomass was fed (CLC operation). Later, the operating conditions corresponding to CLG were set by replacing the air flow by a mixture of N2 and air in the AR. As it can be seen in Fig. 3a, initially there was complete combustion of the biomass to CO2 and H2O, due to the excess of lattice oxygen supplied by the oxygen carrier, and then the concentration of these gases began to decrease while the concentrations of CO and H2 increased. Fig. 3b shows the oxygen reacted in the FR and AR during the operation change from CLG to CLC. It can be observed that during non-steady state operation the oxygen reacted in the FR was higher than the reacted in the AR due to the oxygen released by the oxygen carrier during its reduction. The concentrations of the different gases stabilized after approximately 1 h of operation. One additional hour was spent to be sure that the oxygen carrier had reached steady state and the facility was ready to analyze the gasification process. At the end of each day of operation and the following days, the BCLG unit was cooled and heated under N2 atmosphere to prevent re-oxidation of the oxygen carrier.

2.3. Oxygen control method

In CLG, the solid oxygen carrier is used to transport heat and oxygen between AR and FR. The oxygen transported from AR to FR is closely related to the amount of synthesis gas obtained, being necessary to operate below stoichiometric conditions for full combustion (λ < 1). In the literature, different methods have been used to control the oxygen transported between reactors in CLG prototypes under continuous operation. The most commonly used method to regulate the oxygen-to-fuel ratio was to change the amount of biomass fed, while the solids circulation rate was kept constant [12,20]. However, significant changes...
in the power and in the specific solids inventory occur, which could
difficult the control of the temperature in the system. In some cases, the
dilution of the oxygen carrier with an inert, such as silica sand, has been
carried out to solve this problem [11].

In previous studies performed by our research group, the oxygen-to-
fuel ratio was controlled by limiting the oxygen fed to the AR [6–7,15].
This method allowed a smooth operation, maintaining constant lattice
oxygen transference between reactors, regardless of the solids circula-
tion flow rate in the system. Therefore, the oxygen-to-biomass ratio was
varied without modifying the amount of biomass fed, i.e., the power and
the specific solids inventory were maintained constant. Thus, this
method offered the opportunity to modify and analyze the effect of each
operating parameter maintaining constant the rest of the variables.

Considering all the operational advantages mentioned above, this
method was also used in this work.

2.4. Reactions

When biomass is fed into the CLG system multiple reactions occur. A
summary of them is showed in Table 3. In FR, biomass is decomposed
into three phases: char, tar, and gases (R1). Depending on the gasifying
agent used, char is converted into CO and $\text{H}_2$ by effect of steam (R2) or
into CO if $\text{CO}_2$ is used (R3). Gases generated by biomass devolatilization
($\text{CH}_4$, $\text{H}_2$, CO and hydrocarbons) and by gasification of char react with
lattice oxygen of the oxygen carrier, becoming $\text{CO}_2$ and $\text{H}_2\text{O}$ (R4–R7). At
the same time, methane and light hydrocarbons could also be trans-
formed into CO and $\text{H}_2$ by reforming reactions (R8–R9) and heavy hy-
drocarbons (tar) could be decomposed into other lighter hydrocarbons
(R11), gasified (R12) or be burned with the lattice oxygen of the carrier
(R13). It should be noted that the redox pair of the oxygen carrier is
always Fe$_3$O$_4$Al$_2$O$_3$/FeAl$_2$O$_4$ since metallic Fe is never formed in mentioned conditions and no intermediate phases were found by XRD in any experiment. In AR, two reactions can occur. The oxidation of the oxygen carrier (R14) and the combustion of non-gasified char that passes from FR to AR through the loop seal (R15).

2.5. Data evaluation

It is well known that BCLG operation is affected by temperature and the amount of oxygen transferred to fuel, named as oxygen-to-biomass ratio, $\lambda$.

- Oxygen-to-biomass ratio, $\lambda$, 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$_2$O,

$$\lambda = \frac{2F_{O_2,AR,in}}{F_{S} \Delta \Omega_s}$$  \hspace{1cm} (1)

where $F_{O_2,AR,in}$ was the flow of O$_2$ fed into the AR (mol/h), $F_S$ was the biomass (dry basis) fed into the system (kg/h), and $\Delta \Omega_s$ (mol O/kg dry biomass) was the stoichiometric oxygen necessary for complete combustion of biomass fed. This last parameter was calculated as:

$$\Delta \Omega_s = \left( \frac{32}{x_F} + \frac{16}{2} + \frac{32}{32} - x_O \right) \frac{1000}{16}$$  \hspace{1cm} (2)

where $x_F$ was the fraction of each component present in the biomass.

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

$$X_b = \frac{F_{C,FR,OUT} + F_{C,AR,OUT}}{F_{C,b}}$$  \hspace{1cm} (3)

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

- Carbon conversion efficiency, $\eta_{CC}$, represents the fraction of carbon converted to gas in the FR relative to the total carbon converted in the unit.

$$\eta_{CC} = \frac{F_{C,FR,OUT}}{F_{C,FR,OUT} + F_{C,AR,OUT}}$$  \hspace{1cm} (4)

- Syngas Yield, $Y$, evaluates the amount of H$_2$ and CO (Nm$^3$/kg dry biomass) produced in the FR with respect to the biomass (d.b.) fed into the system (kg/h):

$$Y = \frac{Y_{H_2} + Y_{CO}}{F_{b}^s} = \frac{G_{H_2}}{F_{b}^s} + \frac{G_{CO}}{F_{b}^s}$$  \hspace{1cm} (5)

where $G_{H_2}$ and $G_{CO}$ are the flowrates of H$_2$ and CO generated in the FR (Nm$^3$/h).

- Cold gas efficiency, $\eta_c$, represents the fraction of chemical energy contained in the gases leaving the FR with respect to the total energy contained in biomass:

$$\eta_c = \frac{F_{g,FR,OUT} \cdot \text{LHV}_g}{F_b \cdot \text{LHV}_b}$$  \hspace{1cm} (6)

where $F_{g,FR,OUT}$ is the molar flowrate of gas leaving the FR (mol/h), $\text{LHV}_g$ is the low heating value of gas produced (kJ/mol) and $\text{LHV}_b$ is the low heating value of dry biomass (kJ/kg).

3. Results and discussion

More than 150 h of hot operation, around 100 of which corresponded to the gasification mode, was performed in the 1.5 kW$_b$ BCLG continuous unit with the three oxygen carriers, Fe10Al, Fe20Al, and Fe25Al, to analyze the effect of different operating conditions, such as FR temperature and oxygen-to-biomass ratio (See S-Table 1 in Supplementary Information). During the operation, oxygen carrier samples were extracted from the experimental unit and a deep characterization of the fresh and used oxygen carrier particles was carried out to determine the optimal amount of active phase required by the oxygen carrier in the BCLG process.

3.1. Effect of operating conditions

3.1.1. Effect of oxygen-to-fuel ratio

One of the most important parameters affecting to BCLG process is the oxygen-to-fuel ratio, $\lambda$. As previously commented, this parameter was controlled by limiting the air fed to the AR.

Fig. 4 shows the effect of the oxygen-to-fuel ratio on the syngas composition and gasification performance, at 940 °C, S/B ~ 0.6 and solids circulation rate, $F_s$, of ~ 12 kg/h, working with the three oxygen carriers. As it can be seen in Fig. 4a, the same tendencies in the gas composition were observed with the three oxygen carriers. The CO$_2$ concentration increased and the CO and H$_2$ concentrations decreased as the $\lambda$ value increased. In contrast, the CH$_4$ and C$\_2$C$\_3$ hydrocarbons (light hydrocarbons) concentrations were hardly affected by the $\lambda$ value. It must be remarked that the CH$_4$ concentration was lower working with the Fe25Al oxygen carrier than with the other materials. As a consequence of the higher CH$_4$ conversion, the CO and H$_2$ concentrations were slightly higher for this oxygen carrier. No significant differences were observed between the oxygen carriers Fe10Al and Fe20Al.

In Fig. 4b, it can be seen that the carbon conversion efficiencies were very high (>95%) in all cases and were unaffected by the value of $\lambda$. In contrast, biomass conversion increased as the value of $\lambda$ increased, reaching values higher than 90% for $\lambda$ values above 0.3. These parameters were not affected by the Fe content in the oxygen carrier. Obviously, the decrease in CO and H$_2$ concentrations with increasing $\lambda$ values promoted a significant reduction in the syngas yield, from ~ 1.0 Nm$^3$/kg to ~ 0.7 Nm$^3$/kg for Fe10Al and Fe20Al oxygen carriers and from ~ 1.0 Nm$^3$/kg to ~ 0.8 Nm$^3$/kg for Fe25Al oxygen carrier when $\lambda$ value
increased from 0.2 to 0.4. In the same λ interval, the cold gas efficiency decreased from ~ 80% to ~ 60%, which means that less energy was harnessed from the biomass when more oxygen was transported to FR. Nevertheless, the cold gas efficiency value will be given by the λ value necessary to achieve the energy balance and get the process to operate under autothermal conditions [8].

Although similar gas compositions and operating parameter values were obtained using the three oxygen carriers at the same operating conditions, the conversion variations of the oxygen carriers were different due to their different Fe content. Fig. 5 shows the theoretical conversion variation of the oxygen carriers as a function of λ value, assuming the redox pair FeOx-Al2O3/FeAl2O4. Obviously, conversion variation increased as λ value increased and the Fe content of oxygen carrier decreased.

Working with Fe10Al and a solids circulation rate of 12 kg/h, a maximum λ of 0.42 could be reached and no more oxygen could be transported. This occurs because at that value the entire oxygen transport capacity of the oxygen carrier is reached, i.e., conversion = 1. In spite of this, the operation at λ > 0.42 it is not necessary because autothermic state is achieved at lower values of λ [8]. It should also be noted that although the conversion variation of the oxygen carrier hardly influences the syngas composition and process performance, it implies that different proportion of Fe compounds (FeOx-Al2O3/FeAl2O4) are present in the gasification process. In addition, the internal structure changes of particles in every redox cycle are also different depending on the Fe content, and this could affect to the lifetime of the materials.

3.1.2. Effect of gasification temperature

The FR temperature is a parameter analyzed in most of the BCLG studies due to its effect on gasification rates [6-7,15,20-22]. In this work, the effect of temperature in the FR has been analyzed in a common range covered in gasification studies (820 °C-940 °C) with the three oxygen carriers. The gas concentrations measured at the outlet of the FR (dry basis and free of N2) are shown in Fig. 6a. It can be seen that with increasing FR temperature, the CO concentration slightly increased, while H2 and CO2 concentrations slightly decreased, mainly due to the effect of the water gas shift reaction (R10). Moreover, increasing the temperature slightly decreased the concentrations of CH4 and C2-C3 due to the increased influence of the reforming reactions (R8, R9 and R13), being the effect similar for the three oxygen carriers regardless the Fe content.

FR temperature also affected slightly to the gasification parameters. As shown in Fig. 6b, an increase in carbon conversion efficiency was observed with increasing FR temperature, reaching values close to 100% at 940 °C with the three oxygen carriers. High temperatures in FR improved gasification rate, allowing more char to be converted to syngas rather than passing to the AR where it is burned with air. The fuel conversion increased slightly with the temperature, indicating that char elutriation was hardly affected by the char gasification rate. Finally, a slight increase in the syngas yield and cold gas efficiency was found when temperature increased as a result of the improvement in the above-mentioned parameters. However, it should be remarked that no significant differences were observed among the three oxygen carriers.

3.2. Tar content in syngas

Tars are large molecular compounds produced during the pyrolysis/devolatilization of biomass in FR. Tar removal is necessary due to its corrosive nature, which causes damage to the gasification reactors [28-29], and because it poisons the catalysts used in downstream processes, for example in the Fischer-Tropsch process if biofuel production is the end use of syngas [29].

Virginie et al. [30] demonstrated the possibility to reduce tar generation in conventional pine wood gasification, from 17 g/Nm^3 to values of 5.1–8.3 g/Nm^3, using olivine instead of silica sand as fluidizing material. A further reduction was achieved, up to 2.6–4.2 g/Nm^3, with the addition of Fe to the olivine during the indirect gasification process. There are many works, performed in discontinuous units, corroborating the catalytic activity of metals used as oxygen carriers [18,31] and analyzing the oxidation state of the metal oxides on tar reforming and decomposition [32]. Data about tar removal in a continuous BCLG unit are reported by our group. Condori et al. [6] observed a reduction in the...
tar concentration until reaching values about 2.0 g/kg dry biomass using ilmenite as an oxygen carrier during pine wood gasification. Higher values, 3–4 g/kg dry biomass, were obtained using LD slag as oxygen carrier [15].

Nevertheless, the effect of active metal oxide content in the oxygen carrier on tar removal has never been analyzed before in a BCLG continuous unit. In this study, tars were collected following the European Tar Protocol [27] for its subsequent quantification by GC–MS. A total of 14 tests, each lasting one hour under steady state conditions, were carried out with the three oxygen carriers (Fe10Al, Fe20Al, and Fe25Al) covering different operating conditions. In each trial, 20 tar compounds were identified and quantified. Fig. 7 shows the complete report of tars collected in all experiments.

Despite the differences shown in the amount of each compound, which strongly depended on the operating conditions, naphthalene was the major compound in all tests. Its values ranged between 1.2 and 3.1 g/kg dry biomass, which represented 60%-90% of the total tars generated in each test. Other compounds such as phenanthrene, anthracene, biphenyl, acenaphthylene or 2-ethenyl naphthalene also appeared in significant quantities. In some tests, a small amount of benzene, a highly toxic compound, was generated although in any case exceeded 0.15 g/kg dry biomass.

The operating condition most affecting the generation of tars was the fuel reactor temperature (see Fig. 8), reducing the total amount of tars in gas from ~ 4.0–4.5 g/kg dry biomass at 820 °C to ~ 1.2–1.8 g/kg dry biomass at 940 °C. Tar compounds were cracked with increasing temperature, leading to the major compounds, such as naphthalene, phenanthrene and anthracene, being reduced by more than 50%. However, it...
was observed that the Fe content in the oxygen carrier did not have a relevant effect on tar removal at any temperature or operating condition.

3.3. Characterization of oxygen carriers.

The behavior of the oxygen carriers is a key factor in the BCLG process as, in addition to the syngas quality produced, it also affects operating costs, especially when synthetic oxygen carriers are used. To reduce operating costs, long-lifetime oxygen carriers are desirable. In fact, the oxygen carrier should maintain its structural and mechanical properties over time to avoid fluidization problems or agglomeration. In addition, it should also keep high reactivity during repeated redox cycles and avoid the loss of oxygen transport capacity.

One of the most useful parameters to determine the lifetime of an oxygen carrier is the measurement of its attrition rate. In this work, the attrition rates of the three oxygen carriers were analyzed during the operation in the continuous unit. Fine particles (<40 µm) elutriated from the FR and collected by the cyclone and those recovered in the filters located downstream of AR were weighed throughout the operating time. As shown in Fig. 9, similar attrition rates, ~0.1 wt%/h, were found for the three oxygen carriers during the first 10~15 h of operation. After that, the attrition rate of the Fe10Al oxygen carrier remained constant during the next ~35 h of operation, whereas the attrition rates of the Fe20Al and Fe25Al oxygen carriers increased. With the Fe20Al oxygen carrier, the attrition rate increased slightly with operating time, reaching a value of ~0.3 wt%/h after 50 h of operation. However, the attrition rate of the Fe25Al oxygen carrier increased almost linearly until ~40 h of operation and then it experienced an exponential increase, reaching an attrition rate value of ~0.9 wt%/h in 45 h of operation.

The inferred lifetimes were around 900, 350, and 100 h for the Fe10Al, Fe20Al, and Fe25Al oxygen carriers, respectively. Thus, taking into account the experimental conditions used (a solids inventory of 2.5 kg and a solids circulation of 12 kg/h), these lifetimes correspond approximately to 4500, 1750 and 500 redox cycles, respectively. Comparing these values with those found in other BCLG works, it was concluded that the estimated lifetime of the Fe10Al oxygen carrier was higher than those obtained for natural ores as ilmenite (630 h) [6] and was also higher than that obtained using the waste product LD slag (300 h) [15].

Of the three oxygen carriers analyzed in this work, only Fe20Al had been previously tested in CLC using methane as fuel [24]. Comparing the lifetime obtained in the aforementioned study with the lifetime obtained in this work, a remarkable decrease of lifetime is observed, from 1100 h in CLC to 350 h in BCLG. However, it is noteworthy that decreasing the amount of FeO in the oxygen carrier increases its lifetime, in such a way that the Fe10Al oxygen carrier used in BCLG has a similar lifetime (900 h) to that obtained with Fe20Al in CLC. Therefore, it can be concluded that although a decrease in lifetime occurs in BCLG with respect to CLC, similar lifetimes could be achieved, but it is necessary to reduce the amount of FeO3 in the oxygen carrier. This is possible because the amount of oxygen that needs to be transported from AR to FR is notably less in CLG than in CLC.

To determine the cause of the different lifetime of the three oxygen carriers, microstructural analyses of fresh and used particles were carried out by SEM. Furthermore, the dispersion of the different components (Fe, Al, O) throughout a cut of the particles was also determined by EDX analysis. Fig. 10 shows SEM photographs of the entire particles, both fresh and used, and additionally the internal view of the particles after being embedded in epoxy resin, polished and cut. The entire fresh particles of the three oxygen carriers exhibited similar structure with irregular rounded shapes and smooth outer surfaces. The cross-sectional view of the fresh particles showed a thin outer layer concentrated on Fe due to the impregnation method used in the preparation. However, strong differences were observed in the particles after BCLG operation depending on the Fe content. Used particles of Fe10Al oxygen carrier showed a structure similar to the fresh material, indicating that these particles were hardly affected by the operating time in the continuous unit, which agrees well with the attrition rate measured using this oxygen carrier. In contrast, the used particles of Fe20Al and Fe25Al oxygen carriers exhibited cracks and material loss in the outer surface, which matches with the highest attrition rates measured using these oxygen carriers. However, the cut particles of these used oxygen carriers showed an internal core without cracks.

EDX line-scans done along the cross-section of fresh and used particles of the three oxygen carriers showed iron migration from the core to the external layer (see S-Fig. 1 in Supplementary information). In fresh samples, most iron appeared uniformly distributed throughout the particle and a small amount concentrated on a thin outer layer. In used samples, the iron also appeared uniformly distributed throughout the particle, but the amount of iron accumulated in the outer layer was greater. It can be seen that the thickness of the outer Fe layer followed the order Fe25Al > Fe20Al > Fe10Al. Therefore, it was deduced that there was a migration of iron from the inner to the outer zone of the particles, which was accumulated in an external layer. This outer layer is detached from the particles due to attrition and thermal stress and decreases the Fe content of the particles and therefore their oxygen transport capacity, as it will be commented later. The higher concentration of Fe in the detached outer layer was confirmed by SEM-EDX (See S-Fig. 2 in Supplementary Information).

Iron loss was corroborated and quantified by ICP-OES analyses. The amount of iron loss after ~50 h of operation showed a big difference depending on the Fe content of the oxygen carrier. The Fe loss percentages were 6%, 13%, and 22% for the oxygen carriers Fe10Al, Fe20Al, and Fe25Al, respectively. Fines collected in the cyclone and filters located downstream of the reactors were concentrated in Fe, verifying the loss of this metal outside the pilot plant.

The decrease in iron content during operation implies a loss in the oxygen transport capacity, R OC, which was confirmed by TGA tests. The samples were reduced with a gaseous mixture of 15 vol% CO and 20 vol% CO2 (N2 balance) and oxidized using air. Results obtained in TGA agreed with those determined in ICP-OES, since the oxygen transport capacities of Fe20Al and Fe25Al decreased from 2 to 1.74 and from 2.5 to 1.75, respectively. In contrast, Fe10Al hardly lost oxygen transport capacity after ~50 h of operation.

In summary, the Fe10Al oxygen carrier maintained its structural properties over time, with a high lifetime, and kept its oxygen transport capacity through cycles, while Fe20Al and Fe25Al suffered higher attrition rates and loss of oxygen transport capacity, being especially significant for the Fe25Al oxygen carrier.

The differences observed among the three oxygen carriers lead to the...
conclusion that an increase in the amount of iron present in the oxygen carrier has negative consequences on the evolution of its properties throughout the operating time. Increasing the Fe content increased the attrition rate and decreased the lifetime of the particles. This effect seems to be related to the degree of conversion of the oxygen carrier. It has to be considered that the oxygen carriers are highly reduced during operation in CLG. This oxygen carrier reduction was even more pronounced in this work due to the method used for oxygen control. In fact, XRD analyses showed that the samples extracted from FR were fully reduced at all operating conditions, reaching FeAl$_2$O$_4$ (see Fig. 11), which is the maximum-reduced state thermodynamically possible considering the gas composition in the FR. As a result (Fig. 10), samples leaving the AR were partially oxidized (Fe$_2$O$_3$ and FeAl$_2$O$_4$), and the oxidation conversion depended on the $\lambda$ value and on the Fe content of the oxygen carrier.

For the same operating conditions ($\lambda$, S/B ratio and FR temperature),
oxygen carrier conversion was proportional to its Fe content. At higher Fe content, lower oxygen carrier conversion occurs (see Fig. 4), increasing the amount of Fe in reduced state (FeAl\(_2\)O\(_4\)). This higher Fe concentration in a reduced state seems to be responsible for the increase in Fe migration and particle deterioration.

In any case, it can be concluded that the Fe10Al oxygen carrier has maintained excellent structural properties during the operating time in the pilot plant and it can be considered a suitable solid oxygen carrier for the BCLG process where, in contrast with CLC, high oxygen transport capacities are not necessary because low amounts of oxygen should be transported (operation below stoichiometric point, \(\lambda < 1\)) from AR to FR.


The effect of the Fe-content (10, 20, and 25 wt\% as Fe\(_2\)O\(_3\)) of three synthetic oxygen carriers supported on alumina on the BCLG process was studied in a 1.5 kW\(_{th}\) BCLG continuous unit. The main conclusions found have been the following:

- Similar syngas composition and gasification parameters, such as biomass conversion, syngas yield, cold gas efficiency, etc., were obtained using the three oxygen carriers.
- Tar generation/destruction was not affected by the Fe-content, the increase in the FR temperature being the only parameter which allowed their reduction.
- Iron migration to the outer layer of particles, being detached of them, was promoted with the increase of Fe-content in the oxygen carrier.
- Lifetimes of 900, 350, and 100 h were found for the oxygen carriers with 10 wt\%, 20 wt\%, and 25 wt\% of iron oxide, respectively.
- Among the three oxygen carriers tested, the composed by a 10% of Fe\(_2\)O\(_3\) maintained excellent structural properties during the operating time and was shown to be the most suitable for BCLG.

CRediT authorship contribution statement

Iván Samprón: Conceptualization, Methodology, Validation, Investigation, Resources, Writing – original draft, Visualization. Luis F. de Diego: Conceptualization, Methodology, Validation, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. Francisco García-Labiano: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. María T. Izquierdo: Conceptualization, Methodology, Investigation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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