Biomass Chemical Looping Gasification for syngas/H_2 production without CO_2 emissions

Iván Samprón Alonso

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Supervisors: F. García-Labiano (Instituto de Carboquímica, ICB-CSIC, Spain) and L. F. de Diego (Instituto de Carboquímica, ICB-CSIC, Spain).

Objectives and novelty

Fuels and chemicals produced from renewable sources are expected to play a key role on the decarbonization of industry and transport. Through the gasification of lignocellulosic biomass, a wide range of bioproducts such as diesel, gasoline, methanol or even ammonia can be synthetized. Although there are several gasification processes already developed, Biomass Chemical Looping Gasification (BCLG) has emerged recently due to its advantages over conventional gasification. In the BCLG process, a solid oxygen carrier is used to transfer oxygen and heat from an oxidation reactor to a reduction reactor, avoiding the direct contact between air and fuel (Figure 1).

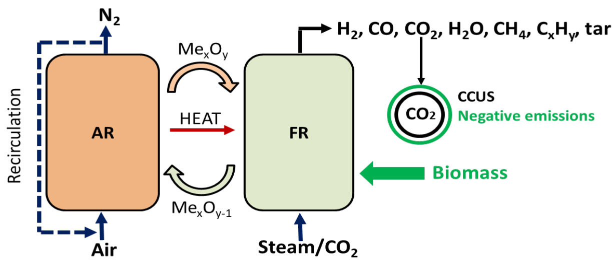

Figure 1. Main scheme of the BCLG process.

The oxygen carrier can also reduce tar generation, improving the syngas quality. Thus, BCLG enables de production of high purity and N_2-free syngas at autothermal conditions whereas pure oxygen needing is avoided. In addition, CO_2 generated is concentrated in a single reactor, permitting its capture for further use or storage. Therefore, it allows not only the production of high interest products, such as fuels, but also the removal of carbon from the atmosphere. In literature it can be found several works investigating different parameters of the BCLG process, but most of these studies have been carried out in discontinuous reactors, where unrealistic conditions take place. In spite of the high research about oxygen carriers, the increase of its lifetime still being a goal, and the obtention of an oxygen carrier suitable to resist a large number of redox cycles while preserving its chemical properties is required.

Present work investigates the BCLG process in a 1.5 kW_{th} continuous unit using four synthetic solids. It was investigated the whole process; from the selection and preparation of the oxygen carriers, to the testing the different variables affecting the operation. Also, a study to improve the quantity and quality of syngas was carried out. Finally, the process was optimized, determining the conditions that permit the operation of the system under autothermal state. An innovative method for better controlling of the oxygen transference between reactors was also proposed.

Results

Three synthetic oxygen carriers with different Fe_2O_3 contents (10, 20 and 25%) over Al_2O_3 were tested in the 1.5 kW_{th} unit during more than 150 h. The oxygen transferred between reactors was controlled by limiting the air fed in the oxidation reactor. The Fe-solids showed similar trends on the molar flows of gases generated and on the gasification parameters when oxygen-to-fuel ratio and temperature were varied. A high CH_4 generation was also found for the three solids (Figure 2a). A syngas yield about 0.9 Nm^3/Kg was obtained for a typical oxygen-to fuel ratio about 0.3. The increase of temperature improved the gasification rate, enhancing the CO_2 capture, which reached values >95 % and reduced tar formation as can be seen in Figure 2b.

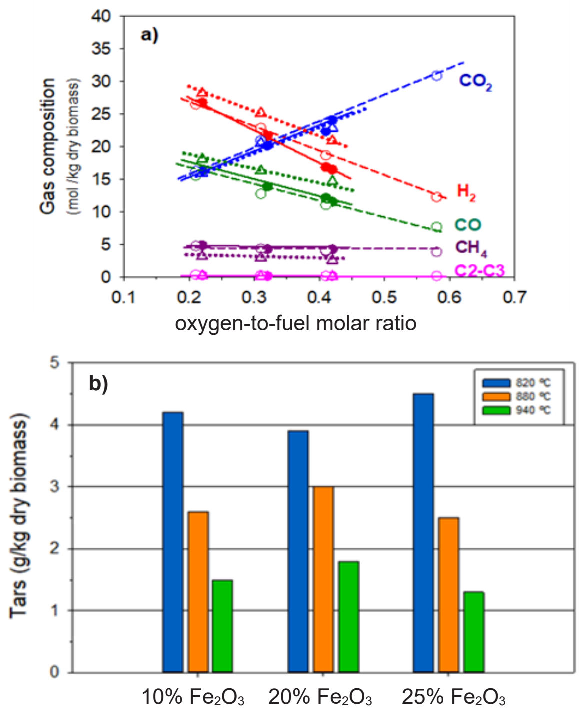

Figure 2. Syngas compositions (a) and tar generation (b) using Fe-based oxygen carriers.

The characterization of the Fe solids showed that lifetime increased from 100 to 900 h as Fe_2O_3 content in the oxygen carriers decreased from 25 to 10 %. This behaviour was studied in detail carrying out redox cycles in TGA. It was observed that a reducing atmosphere, the increase in temperature and high Fe_2O_3 contents promoted the weakening of oxygen carrier particles. In this sense, it was revealed that the oxygen carrier consisting in a 10 % of Fe_2O_3 over Al_2O_3 was suitable for the BCLG process since over Al_2O_3 was suitable for the BCLG process since it performed a high lifetime and kept its chemical properties.

In order to improve the syngas quantity, the catalytic activity of eight oxygen carriers over CH_4 reforming was studied in batch fluidized bed reactor. It was found that a new oxygen carrier based on a 14 % of CuO over Al_2O_3 was able to convert the 85 % of CH_4 fed at a temperature of 940 °C. In another work conducted to increase the syngas quality by the elimination of tars, this oxygen carrier removed >95 % of the ethylene fed whereas complete benzene conversion was achieved at 940 °C. Thus, the Cu-based solid was selected for its evaluation in the 1.5 kWth unit.

About 45 h of continuous operation were done in the 1.5 kWth unit using the Cu-based oxygen carrier. It was revealed that this solid reduced the CH_4 concentration in the produced gas whereas the syngas generation increased. A carbon capture >90 % and syngas yield reached about 1.14 Nm_3/kg at a typical oxygen-to-fuel ratio about 0.3 and 940 °C. Furthermore, tar generation was reduced until 0.3 g/kg bio, which is the lowest tar concentration found in literature. It was revealed an excellent behaviour of the solid particles, which showed an estimated lifetime about 8000 h. This is the highest lifetime found under gasification conditions as can be seen in Table 1.

	Syngas Yield (Nm^3/kg)	Tar (g/kg bio)	Lifetime (h)
Ilmenite	0.6	1.3	630
Mn-ore	0.8	5.1	130
Fe-ore	0.6	11.5	300
10 % Fe_2O_3	0.8	1.5	900
20 % Fe_2O_3	0.8	1.8	350
25 % Fe_2O_3	0.9	1.3	100
14 % CuO	1.14	0.3	8000

Table 1. Comparison of results obtained in BCLG continuous operation at similar conditions.

Finally, the BCLG process was optimized by solving mass and energy balances in order to determine the conditions that permit the autothermal operation. The oxygen controlling method consisting in limiting the oxygen fed in the oxidation reactor (proposed in this work) allows to obtain a higher amount of syngas and to operate in a wide range of oxygen carrier circulation flows. Using this method, a cold gas efficiency about 86% can be obtained operation under autothermal conditions. Also, it was found that it enables the generation of a nearly pure stream of N_2 in the outlet of air reactor, which can be considered a valuable product.

Conclusions

BCLG continuous operation was demonstrated during 200 h of operation in a 1.5 kW_{th} unit using Fe- and Cu-based oxygen carriers.

The Fe oxygen carriers showed almost similar values in gas compositions and gasification parameters, being its main difference on lifetime, which increased as Fe_2O_3 content decreased.

The oxygen carrier composed by a 14 % of CuO over Al_2O_3 is the optimal candidate for the BCLG process. This solid performed the highest lifetime found in literature, and the lowest tar concentration. A syngas yield about 1.14 Nm^3/kg was obtained.

An oxygen to fuel ratio about 0.3-0.35 is required to operate without external energy supply. The oxygen controlling method proposed permits to operate under autothermal conditions obtaining a higher syngas yield and producing a nearly pure stream of N_2.

Related Publications

[1] Samprón I, de Diego LF, García-Labiano F, Izquierdo MT, Abad A, Adánez J. Biomass Chemical Looping Gasification of pine wood using a synthetic Fe_2O_3/Al_2O_3 oxygen carrier in a continuous unit. Bioresource Technol 2020; 316: 123908. *Published JCR(FI) 2020: 9.642; (Energy & Fuels): 12/114 - Q1*

[2] Samprón I, de Diego LF, García-Labiano F, Izquierdo MT. Effect of the Fe content on the behavior of synthetic oxygen carriers in a 1.5 kW biomass chemical looping gasification unit. Fuel 2022; 309: 122193. *Published JCR(FI) 2022: 7.4; (Chemical Engineering): 19/142 - Q1*

[3] Samprón I, García-Labiano F, Izquierdo MT, de Diego LF. Understanding the structural changes on Fe_2O_3/Al_2O_3 oxygen carriers under chemical looping gasification conditions. Fuel 2024; 335; 129326. *Published JCR(FI) 2023: 6.7; (Chemical Engineering): 19/142 - Q1*

[4] Sampron I, de Diego LF, García-Labiano F, Izquierdo MT, Adánez J. Influence of an Oxygen Carrier on the CH_4 Reforming Reaction Linked to the Biomass Chemical Looping Gasification Process. Energy Fuels 2022; 36(17): 9460-9469. *Published JCR(FI) 2022: 5.3; (Chemical Engineering): 28/142 - Q1*

[5] Sampron I, Purnomo V, Mattisson T, Leion H, de Diego LF, García-Labiano F. Catalytic activity of oxygen carriers on the removal of tar byproducts for Biomass Chemical Looping Gasification application. Energy Fuels 2023; 37(21): 16629–16638. *Published JCR(FI) 2023: 5.2; (Chemical Engineering): 28/142 - Q1*

[6] Sampron I, Cabello A, García-Labiano F, Izquierdo MT, de Diego LF. An innovative Cu-Al oxygen carrier for the biomass chemical looping gasification process. Chem Eng J 2023; 465: 142919. *Published JCR(FI) 2023: 13.3; (Chemical Engineering): 5/142 - Q1*

[7] Sampron I, de Diego LF, García-Labiano F, Izquierdo MT. Optimization of synthesis gas production in the biomass chemical looping gasification process operating under auto-thermal conditions. Energy 2021; 226: 120317. Publicada JCR(FI) 2021: 8.857; *Published (Energy & Fuels): 24/119 - Q1; (Thermodynamics): 3/63 - Q1*

Full thesis can be downloaded from *https://digital.csic.es/handle/10261/355908*