

# Tailored Syngas Production from the Gasification of Biogenic Waste in the Presence of a CO<sub>2</sub> Sorbent

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Syngas production via steam gasification is one of the thermochemical processes with the greatest potential for obtaining synthetic fuels from a solid fuel, especially indirect gasification in a dual fluidised bed system where the energy needed for gasification is provided by the circulating material from a high temperature secondary reactor. When the circulating material is a CO<sub>2</sub> sorbent, a sorption enhanced gasification (SEG) system results where the circulating solid, in addition to the energy provided by sensible heat, supplies additional heat by means of the exothermic carbonation reaction with the CO<sub>2</sub> generated from biomass gasification. In the presented work, the SEG process was studied for a biogenic waste material (consisting of the organic fraction of municipal solid waste) in a 30 kW<sub>th</sub> bubbling fluidised bed reactor using lime as CO<sub>2</sub> sorbent. The effect of the main operating variables (temperature, steam-to-carbon (S/C) ratio and sorbent-to-biomass ratio (Ca/C)) on gas quality was assessed. M-modules ( $M=(H_2-CO_2)/(CO+CO_2)$ ) between 1.2 to almost 4 have been obtained acting on the variables that mostly affect the permanent gas composition, i.e. gasification temperature and/or sorbent-to-biomass ratio.

## 1. Introduction

Sorption enhanced gasification (SEG) is an indirect gasification process performed in a dual fluidized bed (DFB) system using steam as gasifying agent and a CaO-based material as heat and CO<sub>2</sub> carrier. In this gasification concept, the energy required in the gasifier for biomass gasification is provided by the sensible heat of the circulating solids and by the reaction heat of the exothermic carbonation reaction  $CaO+CO_2 \rightarrow CaCO_3$ . This energy is indirectly provided in the combustor-calciner reactor by the combustion of unconverted char from the gasifier and of additional biomass (if needed), which heats the circulating solids while providing the heat for the CaCO<sub>3</sub> decomposition (calcination) into CaO and CO<sub>2</sub>. The use of CaO as bed material allows removing CO<sub>2</sub> from the syngas generated in the gasifier. In this way, a H<sub>2</sub>-rich and N<sub>2</sub>-free syngas can be produced with no need of high purity oxygen (See Figure 1 for scheme). An intrinsic characteristic of the process is the lower temperature in the gasifier reactor compared to typical indirect gasification systems, as it is in the range 650 °C to 750 °C, to favour the carbonation reaction of CaO [Florin and Harris, 2008; Heidenreich and Foscolo, 2015; Martínez et al. 2020]. Also, the presence of CaO has a proven effect on tar cracking, presenting the reported values in literature a relatively low tar content [Pfeifer et al. 2009]. As a consequence of the CO<sub>2</sub> retired from the produced gas, char gasification reactions are enhanced and the H<sub>2</sub> content in a syngas produced by SEG of biomass, can be up to 70-75 % vol. (in dry basis) [Pfeifer et al. 2009]. However, one of the main benefits of the process is that it is possible to produce a tailored syngas by acting on the operating variables those affect the amount of CO<sub>2</sub> removed from the gas phase (i.e. temperature, CaO/C ratio in the reactor). It is therefore possible to produce a syngas with selected gas composition (in terms of H<sub>2</sub>, CO, CO<sub>2</sub> content) for a subsequent synthetic fuel synthesis process. Typically, the M-module (defined as  $(H_2-CO_2)/(CO+CO_2)$  ratio) or the H<sub>2</sub>/CO molar ratio are key parameters to assess the suitability of a syngas for a downstream synthesis process. As an example, typical M-modules between 0.1-0.8 are obtained through conventional indirect biomass gasification while M-modules around 2 are preferred for the production of DME, methanol or Fischer-Tropsch biodiesel [Isaksson et al. 2013]. M-modules wide above this value can be obtained from the conventional SEG process. In this way it has been

recently proposed the idea of a flexible SEG process that allows regulating the CO<sub>2</sub> removed from the gas phase through the modification of some of the plant operation conditions [Martínez and Romano, 2016].

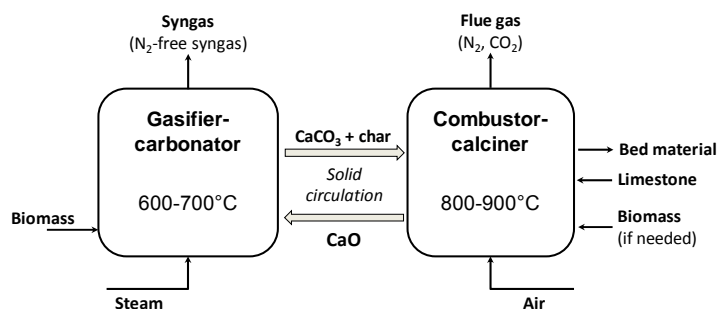


Figure 1: Sorption Enhanced Gasification (SEG) concept scheme.

This process is being developed within the framework of the EU H2020 project FLEDGED whose main objective is the demonstration at TRL-5 of an intensified and flexible DME production process based on the SEG process of biomass [Fledged eu]. Fledged project aims for the production of advanced biofuels, produced from feedstock that do not compete directly with food and feed crops. In this way, a biogenic waste material (produced from municipal solid waste) has been one of the biomasses tested along the project, and the presented work aims at analysing the influence of the main operating parameters in a SEG process on the composition of the syngas obtained. In this way, the effect of the gasification temperature, the steam-to-carbon (S/C) molar ratio and the sorbent to biomass (CaO/C) molar ratio on gas yield and gas quality (as well as for tar formation) has been assessed.

## 2. Materials and methods

The biomass used in the gasification experiments was a biogenic waste produced from a pre-treated municipal solid waste (MSW). This pre-treatment allowed the separation of metal, paper and plastic fractions of the waste and stabilised the organic fraction of the residue, which constituted the biomass used in this work. The material has been dried and pelletized (5x10 mm). Table 1 compiles the composition of the biomass (proximate and ultimate analysis) as well as its calorific value. Ultimate analysis was determined in a Thermo Flash 111 (UNE-EN-5104) to the stabilised sample, and moisture, volatile matter and ash contents were determined according to standards UNE-EN 18134-3, UNE-EN 14775 and UNE-EN 15148 respectively. Ash composition was determined by ICP-OES being Si and Ca the most abundant elements (65222 and 52214 ppm respectively) followed by Na, K and Al (13393, 9515 and 9984 ppm respectively).

Table 1: Proximate, ultimate analysis and calorific value of the biomass tested in the 30 kW<sub>th</sub> BFB gasifier

Proximate Analysis		Ultimate Analysis	
% wt. moisture	5.90	% wt. C	34.80
% wt. ash	32.20	% wt. H*	4.40
% volatile matter	55.40	% wt. N	1.70
% fixed carbon	6.60	% wt. S**	0.66
		% wt. O	30.9
		% wt. Cl**	0.43
HHV (MJ/kg)	13.80		
LHV (MJ/kg)	12.84		

\*Includes H in the moisture

\*\* this number was determined by ionic chromatography

Sorption enhanced gasification (SEG) tests were carried out in a 30 kW<sub>th</sub> (referred to the thermal input of biomass in LHV-basis) bubbling fluidized bed reactor (BFBR) shown in Figure 2. It consisted of a 3 m height stainless steel reactor comprising two zones: a bottom dense zone of 1 m height (0.15 m of internal diameter) and a freeboard zone of 2 m height (0.20 m of ID). The reactor was externally heated through electrical resistances and insulated with glass wool as shown in the plant scheme. CO<sub>2</sub> sorbent and biomass were fed separately into the reactor from two independent closed hoppers. As indicated in the figure, these hoppers were placed over two screw feeders those introduced the solids at the bottom of the reactor (right above the

gas distribution plate). Both feeders were provided with a regulation system that changed the rotation speed of the electric motor for regulating the mass flow rate. Biomass screw feeder was externally cooled with water in order to prevent its excessive heating due to conduction and so the prompt decomposition of the biomass in the screw. Solids ( $\text{CaO}/\text{CaCO}_3$ , unconverted char and ashes) left the reactor through a lateral overflow (shown schematically on the left-hand side of the reactor in Figure 2), and were collected in a hopper that was periodically discharged during operation. This overflow regulated the solid bed inventory in the bottom dense zone of the reactor, which resulted around 5-7 kg depending on the fluidization conditions. For the experimental campaign presented, a high purity limestone (that was previously calcined in the BFB) with an average  $\text{CO}_2$  carrying capacity of  $0.35 \text{ g CO}_2/\text{g}$  calcined sorbent was introduced in the gasifier. The experimental routine followed during the SEG experiments comprised a first stage where the reactor was heated up by the electric resistances while fluidising in air ( $0.1 \text{ Nm}^3/\text{min}$ ) until reaching the desired temperature, then there was a short period in which biomass was fed to the gasifier at the desired input value for the test, and finally the fluidisation agent was set as steam (to reach the desired S/C molar ratio) and the flow of  $\text{CaO}$  was started (to reach the desired  $\text{CaO}/\text{C}$  molar ratio). The data presented corresponded to 1 hour periods of stationary operation, in which solid and gas samples were collected to proceed with their analysis. For the gas sampling, permanent gases concentration ( $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{CO}_2$ ) was measured online (SICK GMS810 analyser) and Tedlar sampling bags were collected every 15 min during the stationary period to quantify higher hydrocarbons (up to  $\text{C}_4$ ) present in the gas stream. A Hewlett Packard series II gas chromatograph (GC) coupled to a TCD detector was used for determining the concentration of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  using a HayeSep Q column. In addition,  $\text{C}_3$ - $\text{C}_4$  hydrocarbons ( $\text{C}_3\text{H}_6$ ,  $\text{C}_3\text{H}_8$  and  $\text{C}_4+$ ) were measured using a Varian 3400 GC through a capillary column coupled to a FID detector.

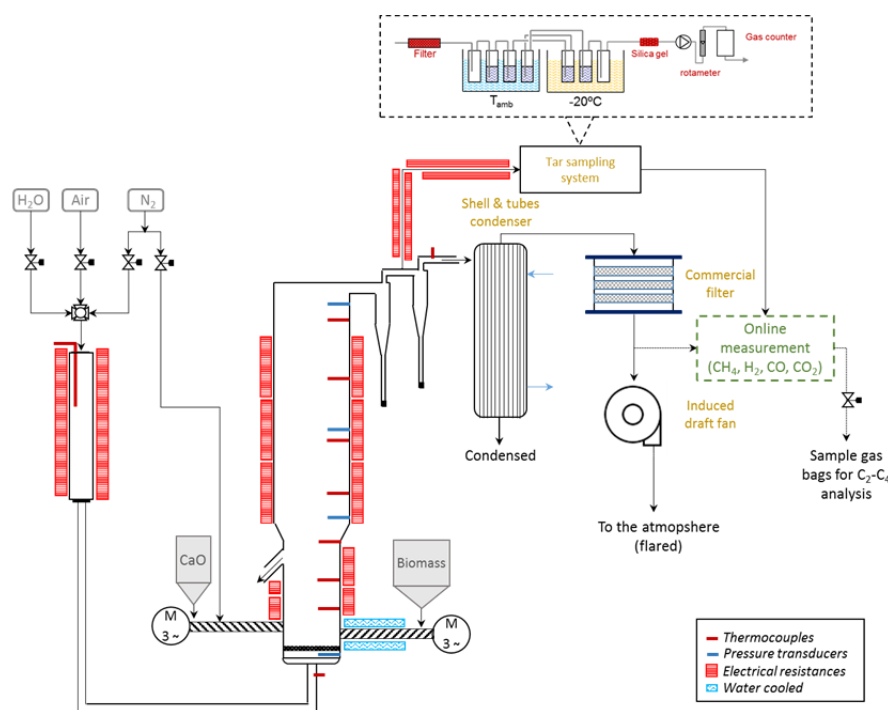


Figure 2: Scheme of the  $30 \text{ kW}_{th}$  gasification plant at ICB-CSIC (Horizontal red bars indicate the position of thermocouples throughout the main components of the plant)

An off-line method for tar sampling was used based on the specific protocol for biomass gasification units described in [Neef, 2005]. This tar sampling method was based on absorbing tars by flowing the gas through a series of 7 impinger bottles filled with isopropanol, which were placed in two different cooling baths: four impingers (1, 2, 3 and 5) at room temperature and three (4, 6 and 7) at  $-20 \text{ }^\circ\text{C}$ . All of them contained 100 ml of isopropanol with the exception of impingers 1 and 7, which were empty. Gas flow rate sampled through the tar system was regulated by a pump and the total volume passed was measured by a gas-meter before sending the gas to the online analyser. In general, the sampling time was around 20 minutes, collecting gas volumes those varied among  $0.06$  and  $0.147 \text{ Nm}^3$  of dry gas. Once finished the tar sampling test, the isopropanol from the impingers was collected, measuring its final volume. This was named as collected tar and the tar content

was determined by GC-MS. In addition, from each sample, it was also determined the gravimetric tar. An aliquot of 100 mL of collected tar was concentrated by rotary evaporator until dryness at controlled temperature and vacuum. In this way, the gravimetric tar was determined according to the gas volume that has passed through the sampling system and expressed as  $\text{g}/\text{Nm}^3$  dry gas.

The experimental campaign has paid special attention to study the influence of the main operating variables of this SEG process on the syngas yield and syngas composition and tar content, with the aim of determining the suitability of modifying each variable depending on the desired effect. Concretely, it has been studied the influence of the gasification temperature (between 630 and 740 °C), the steam-to-biomass ratio (calculated as the molar ratio of steam and C in the biomass and modified between 1 and 1.4) and the sorbent-to-biomass ratio (i.e. CaO/C molar ratios between 0.20 and 1.22) for biomass inputs ranging from 8.7  $\text{kW}_{\text{th}}$  to 18.4  $\text{kW}_{\text{th}}$ .

### 3. Results

As it is shown in Figure 3, gasification temperature had a great impact on gas yield. According to the figure, gas yield varied from 0.8  $\text{Nm}^3$  (dry gas)/ $\text{kg}_{\text{BSwaf}}$  at temperatures around 630 °C for a thermal input of 18.4  $\text{kW}_{\text{th}}$ , to 1.6  $\text{Nm}^3$  (dry gas)/ $\text{kg}_{\text{BSwaf}}$  obtained at 710 °C for a steam-to-carbon (S/C) ratio of 1 and 8.7  $\text{kW}_{\text{th}}$ . For a given biomass thermal input, syngas increased with increasing gasification temperature due to: increased gas production during the primary pyrolysis stage, steam cracking and reforming of heavier hydrocarbons and tars and enhanced char gasification reactions [Florin and Harris 20018, Schildhauer and Biollaz 2016]. Char gasification is influenced by operating parameters such as temperature, solid residence time or the steam to carbon ratio. From Figure 3, it can be also extracted the effect that solid residence time and S/C ratio had on solids conversion and therefore in the gas yield. For a given temperature, the syngas yield increased with the solid residence time of the particles in the gasifier (reduced biomass thermal input). For a similar thermal input, increasing the S/C increased the gas yield.

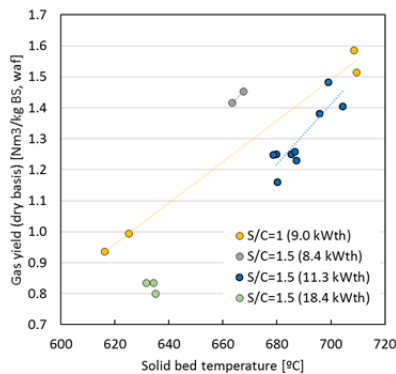


Figure 3: Gas yield ( $\text{Nm}^3$  dry gas/kg of biomass, water-ash-free basis) as function of solid bed temperature for experiments performed at different thermal input and S/C molar ratios.

Considering the effect of the temperature on syngas composition, Figure 4 a) represents the permanent gas composition ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ ) and M-module for two experiments performed at different temperature and very similar S/C (1.2 and 1.4 respectively) and CaO/C (0.28) ratios. As it can be observed, temperature had an important effect on M-module. An increase in the temperature favoured the endothermic water gas reactions of  $\text{C}_{(\text{s})}$  into  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2$ , as well as the Boudouard, water gas shift (WGS), and methane reforming reactions [Florin and Harris, 2008]. Consequently, considering these reactions, the content of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  should increase with the temperature whereas the  $\text{CH}_4$  content should diminish. However, the presence of the CaO carbonation reaction influenced such trend since CaO reacted with the  $\text{CO}_2$  from the gas phase. As temperature increased, the CaO/ $\text{CaCO}_3$  equilibrium limited the carbonation kinetics towards  $\text{CaCO}_3$  formation and the carbonation degree, which made the  $\text{CO}_2$  content in the gas phase to increase [Barker, 1973]. The CO content in gas was linked to the presence of  $\text{CO}_2$  via WGS reaction, and therefore the CO increased as it did the  $\text{CO}_2$ .  $\text{H}_2$  increased up to 53 %vol. ( $\text{H}_2\text{O}-\text{N}_2$  free basis) when decreasing the gasifier temperature down to 635 °C since the carbonation and water gas shift reactions were favoured under those conditions, which enhanced  $\text{H}_2$  formation. The combination of the behaviour explained for  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2$  contents in the syngas made the M-module reached at 635 °C to be 3.8 while it was 1.2 at 734 °C under the operating conditions represented in Figure 4.

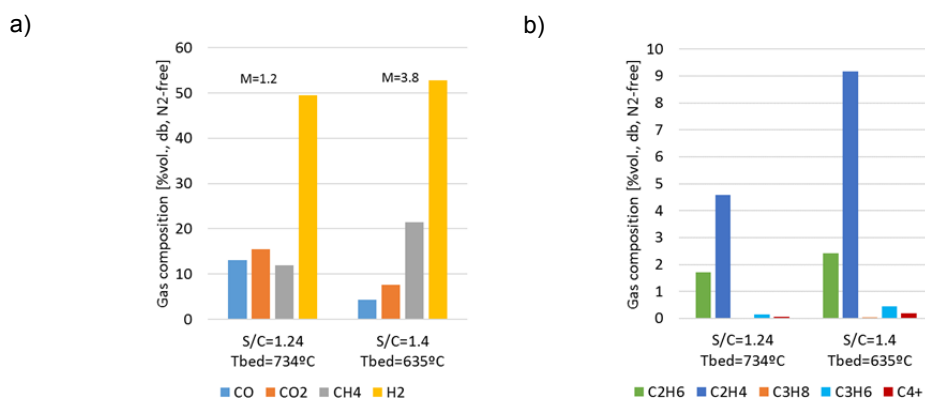


Figure 4: Gas concentration (dry and N<sub>2</sub> free basis) during steady state measured by GC for two experiments with similar CaO/C ratio (0.28) and biomass thermal inputs of 9 and 18.4 kW<sub>th</sub> (S/C=1.24 and 1.4, respectively).

Cracking and reforming reactions of light and heavy hydrocarbons were also favoured with the temperature, making the light hydrocarbons content (i.e. C<sub>2</sub>-C<sub>4</sub>) to be reduced with increasing this operating variable. As appreciated in Figure 4 a), CH<sub>4</sub> content was the compound being influenced the most by the temperature, around 21 %vol. (dry basis and N<sub>2</sub>-free syngas) at the lowest temperature (635 °C) and decreasing to 12 %vol. when increasing the gasification temperature to 734 °C. C<sub>2</sub>H<sub>4</sub> content was also noticeably reduced with the gasification temperature, being reduced to less than 5 %vol. at 734 °C. Tar content in the producer gas was also affected by bed temperature, as an example, 62.2 g/Nm<sup>3</sup> dry gas has been the collected tar for the experiment represented in Figure 4 (T<sub>bed</sub> 635 °C), while 23.9 g /Nm<sup>3</sup> dry gas were collected during the test at 734 °C. The same behaviour was observed for the gravimetric tar values, which resulted in 7.4 and 43.2 g/Nm<sup>3</sup> dry gas at 734 °C and 635 °C, respectively.

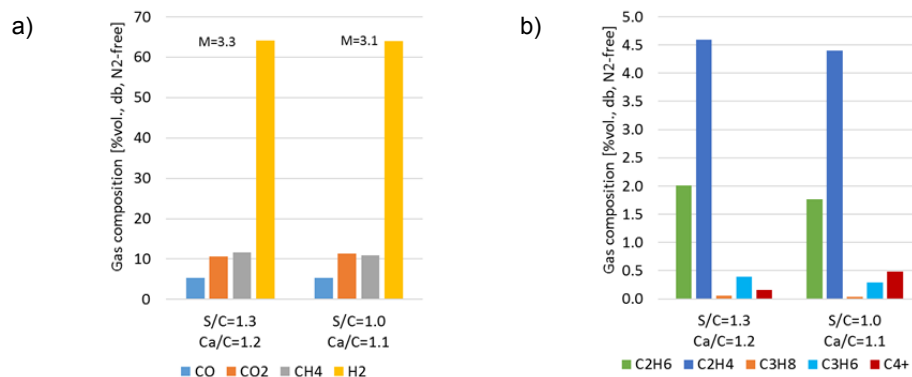


Figure 5: Gas concentration (dry and N<sub>2</sub> free basis) during steady state measured by GC for two different S/C ratios of 1.3 and 1.0 for a thermal input 9 kW<sub>th</sub>. Temperature of the solid bed 707-710 °C in both experiments.

In contrast to the gasification temperature, the steam-to-biomass (S/C) ratio did not influence significantly the permanent gas composition (i.e. the M-module) for the S/C ratios tested in this facility (i.e. 1 and 1.4) and a given CaO/C ratio, but affected the content of light hydrocarbons in the syngas (C<sub>2</sub>-C<sub>4</sub>) as well as tar yield (See Figure 5 as an example). As it can be observed in the figure, no influence was found in the permanent gas composition when modifying exclusively the S/C ratio. H<sub>2</sub> and CO contents resulted in 64 %vol. and 5.4 %vol., respectively, in both experiments, whereas CO<sub>2</sub> concentration slightly changed (i.e. 10.6 and 11.4 %vol. for S/C=1.3 and 1.0, respectively) due to the small differences in the CaO/C molar ratio reached in each case. As a result, the M-modules reached barely changed and resulted around 3 in both experiments. However, when increasing the S/C ratio, the content of C<sub>4</sub> hydrocarbons in the syngas diminished, increasing the content of C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. For the experiment at S/C=1.0, C<sub>4</sub> compounds corresponded to trans-2-butene, 1-butene, isobutene and cis-2 butene, and it was mainly isobutene at S/C=1.3. The cracking of the C<sub>4</sub> hydrocarbons into C<sub>2</sub> and C<sub>3</sub> compounds could be favoured when increasing the S/C ratio aided by

the presence of K, Al, Si, in biomass ashes, which would explain the increase of C<sub>3</sub> and C<sub>2</sub> olefins as well as C<sub>2</sub>H<sub>6</sub> when increasing the S/C ratio at a constant gasification temperature. Finally, with respect to the CaO/C molar ratio, this variable had not an important impact on the content of permanent gases whenever there is sufficient active CaO in bed and the rest of operating variables remained constant (gasification temperature and S/C molar ratio). This has been observed as an example for two experiments performed at similar S/C and gasification temperature (S/C 1.3-1.4 and gasification temperature 705-707 °C) with different CaO/C ratio (1.2 and 0.4). During these tests the M-modules were 3.1 and 3.3 respectively and the most relevant differences were observed on the C<sub>2</sub>-C<sub>4</sub> content of the producer gas, being higher for the test performed with CaO/C of 1.2 (2.65 % vol. compared with 2.57 % vol. for the CaO/C ratio of 0.4). The presence of C<sub>3</sub>-C<sub>4</sub> was more abundant for the test with the highest CaO/C (0.22 % vol. compared to 0.06 % vol.) and it could be related with the CaO tar cracking property that resulted in a reduced presence of collected tar in the gas (21 g / Nm<sup>3</sup> for the test at CaO/C 1.2, vs. 28 g / Nm<sup>3</sup> for the test with lower CaO/C).

#### 4. Conclusions

The flexibility of the SEG process has been assessed with a biogenic waste material (produced from municipal solid waste). M-modules between 1 and 4 have been obtained by acting on the operating variables of the system. Gasification temperature is the variable affecting most the concentration of permanent gases on the producer gas (whenever there is enough active CaO in bed, i.e. CaO/C 0.4 and higher) as it acts on the kinetics of the water gas reactions of C<sub>(s)</sub> into CO, CO<sub>2</sub> and H<sub>2</sub>, as well as the Boudouard, water gas shift, and methane reforming reactions. The presence of light hydrocarbons (C<sub>3</sub>-C<sub>4</sub> and unsaturated C<sub>2</sub>) is also highly affected by temperature being possible to reduce its content below 5 % vol. (dry gas free of N<sub>2</sub>) operating the gasifier at temperatures close to 735 °C. The presence of CaO acts on the CO<sub>2</sub> separated from the gas phase (affected by the gasification temperature) but also helps to reduce the collected tar thanks to its tar cracking properties (i.e 21 g /Nm<sup>3</sup> collected tar for a test performed with CaO/C of 1.22 vs. 28 g /Nm<sup>3</sup> for a test performed with CaO/C of 0.4, both at 705-707 °C and S/C 1.3-1.4).

#### Acknowledgments

This work has been carried out as part of the European Commission Horizon 2020 Framework Programme project FLEDGED (Grant agreement No. 727600) and the project WASYNG (No. RTI2018-095575-B-100) funded by the Spanish Ministry of Science, Innovation and Universities. Authors thank also the Regional Aragon Government (DGA) for the economic support under the research group's programme.

#### References

- Barker R., 1973, The reversibility of the reaction  $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ , *J. of Applied Chemistry Biotechnology* 23, 733–742.
- Fledged project [www.fledged.eu](http://www.fledged.eu) (Accessed November 26th, 2019)
- Florin N.H., Harris A.T., 2008, Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents, *Chemical Engineering Science*, 63, 287-316.
- Heidenreich S., Foscolo P.U., 2015, New concepts in biomass gasification, *Progress in Energy Combustion Science*, 46, 72-95.
- Isaksson J., Åsblad A., Berntsson T., 2013, Influence of Different Pretreatment Methods on Biomass Gasification and Production of Fischer-Tropsch Crude Integrated with a Pulp and Paper Mill, *Chemical Engineering Transactions*, 35, 559-564.
- Martínez I., Kulakova V., Grasa G., Murillo R., 2020, Experimental investigation on sorption enhanced gasification (SEG) of biomass in a fluidized bed reactor for producing a tailored syngas, *Fuel*, 259, 116252.
- Martínez I., Romano M.C., 2016, Flexible sorption enhanced gasification (SEG) of biomass for the production of synthetic natural gas (SNG) and liquid biofuels: Process assessment of stand-alone a power-to-gas plant schemes for SNG production, *Energy*, 113, 615-630.
- Neeft J.P.A., 2005, Rationale for setup of impinger train as used in the technical specification of sampling and analysis of tar and particles in the product gases of biomass gasification. Technical background document.
- Pfeifer C., Puchner B, Hofbauer H., 2009, Comparison of dual fluidized bed steam gasification of biomass with and without selective transport of CO<sub>2</sub>, *Chemical Engineering Science*, 64, 5073-5083.
- Schildhauer T.J, Biollaz S.M.A, editors. *Synthetic Natural Gas from Coal, Dry Biomass, and power-to-gas applications*. Wiley; 2016