Experimental activities in the 30 kWth Bubbling Fluidized Bed gasifier at ICB-CSIC

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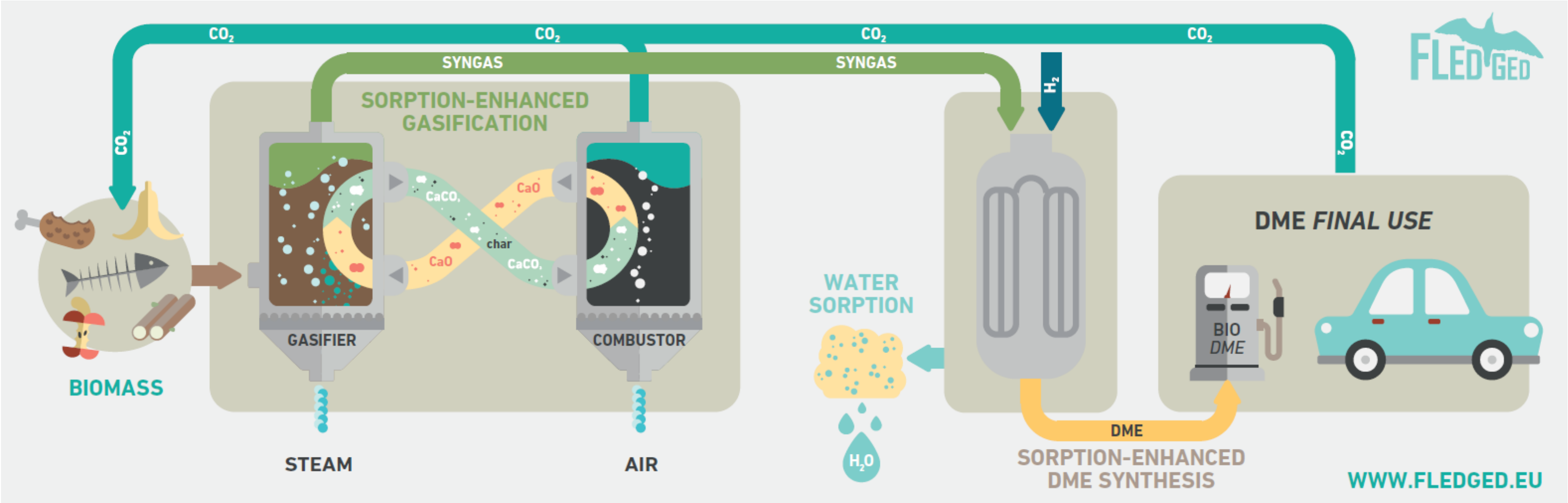
Summary of the activities performed at the 30 kWth BFB plant (TRL-4)

Assess the performance of the Sorption Enhanced Gasification process in a 30 kW_{th} bubbling fluidized bed reactor (BFB) placed at the Instituto de Carboquímica (CSIC) (Zaragoza, Spain)



Main operating variables

- **Steam/biomass ratio**
- **Sorbent/biomass ratio**
- **Gasifier temperature**

- **Syngas yield and composition** (H_2/CO/CO_2 and light hydrocarbons up to C_4)
- **Char conversion in the gasifier**
- **Tar formation (yield and composition)**

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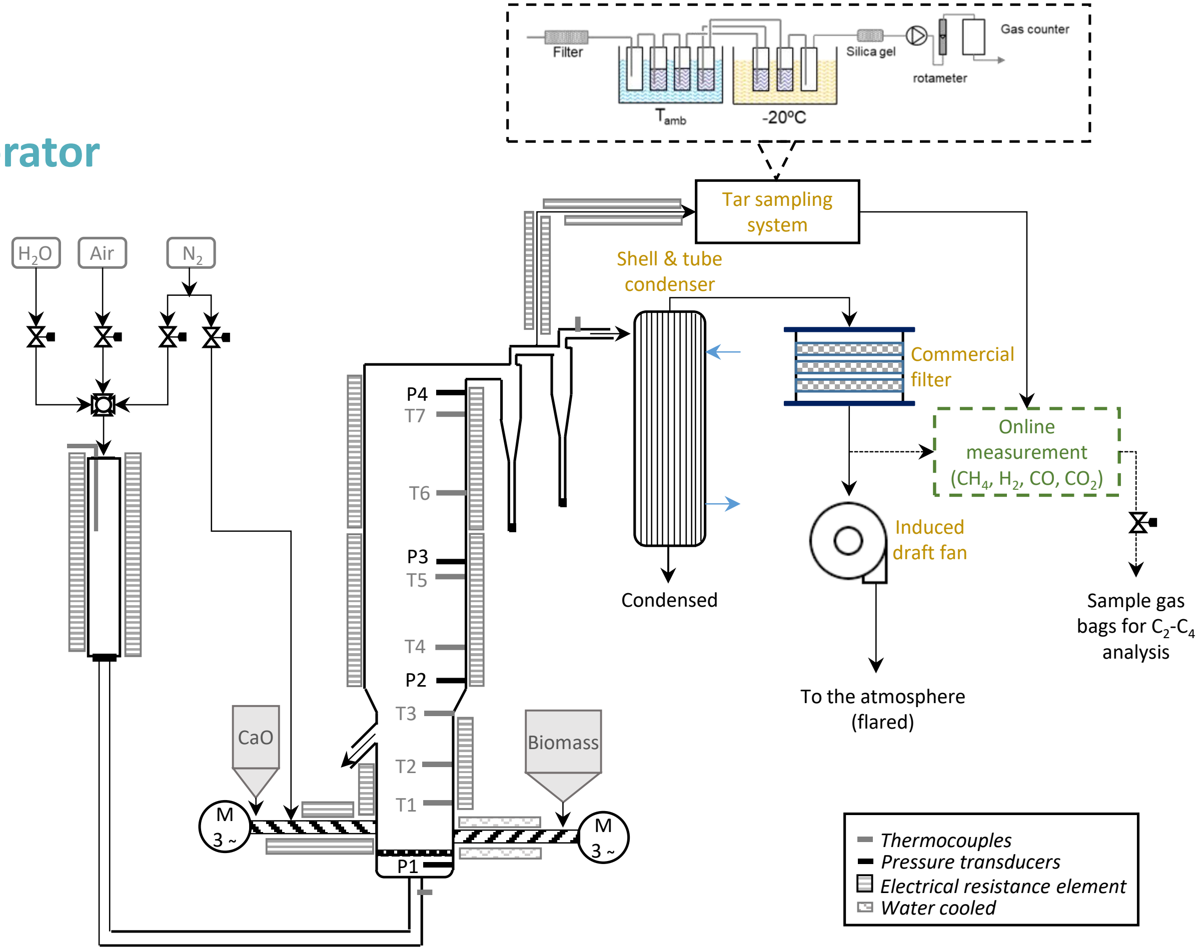
Description of the 30 kW$_{th}$ BFB gasification plant



BFB reactor

- Two zones with different ID
  - 1 m with 0.15 m
  - 2 m with 0.2 m
- Bottom dense zone of 0.54 m
- Two independent screw feeders at the bottom
- Lateral solid exit overflow
- Temperature and pressure monitored along the reactor

Tar sampling system with isopropanol (GC-MS analysis)

On-line **gas analyser** (CH_4, H_2, CO, CO_2) and gas sampling bags analysis through GC (up to C_4)

Biomass feedstocks characterization

<u>6 biomass feedstocks have been tested </u>(lignocellulosic biomass from agriculture and forestry activities (3), organic fraction of municipal solid waste (2) and residue from wine industry (1))

	WOOD PELLETS 	**GRAPE SEEDS** 	**MSW-pellets** 	**MSW biomass** 	**Straw pellets** 	**Pine wood** 
%wt.	**Proximate analysis**					
% moisture	5.55	6.30	5.90	6.56	6.51	8.09
% ash	0.36	4.30	**32.20**	**32.47**	4.87	1.30
% volatile matter	78.80	65.12	55.40	53.63	70.28	72.94
% fixed carbon	15.29	24.28	6.60	7.34	18.33	17.67
% S	0.02	0.12	**0.66**	**0.21**	0.13	0.05
% Cl	0.00	**0.06**	**0.43**	**0.56**	**0.36**	0.01
LHV (MJ/kg)	**17.59**	**20.51**	**12.84**	**13.47**	**16.06**	**16.69**

☞ *Deliverable 2.1. "Characterisation of raw materials for sorption enhanced gasification"*, **June 2017**, Public (http://www.fledged.eu/download/deliverables/)

Additional information

Sorbent used

☑ **High purity limestone** used (> **92 %wt. CaO** in calcined material)

☑ Material calcined in the BFB reactor using a low-S fuel (0.55 g_{CO2}/g calcined material)

Operating variables analyzed

Steam-to-Carbon ratio (**S/C**) = $\frac{kmol/_h\ steam\ fed\ into\ the\ gasifier\ (excl.\ biomass\ moisture)}{kmol/_h\ C\ in\ the\ biomass\ fed\ into\ the\ gasifier}$

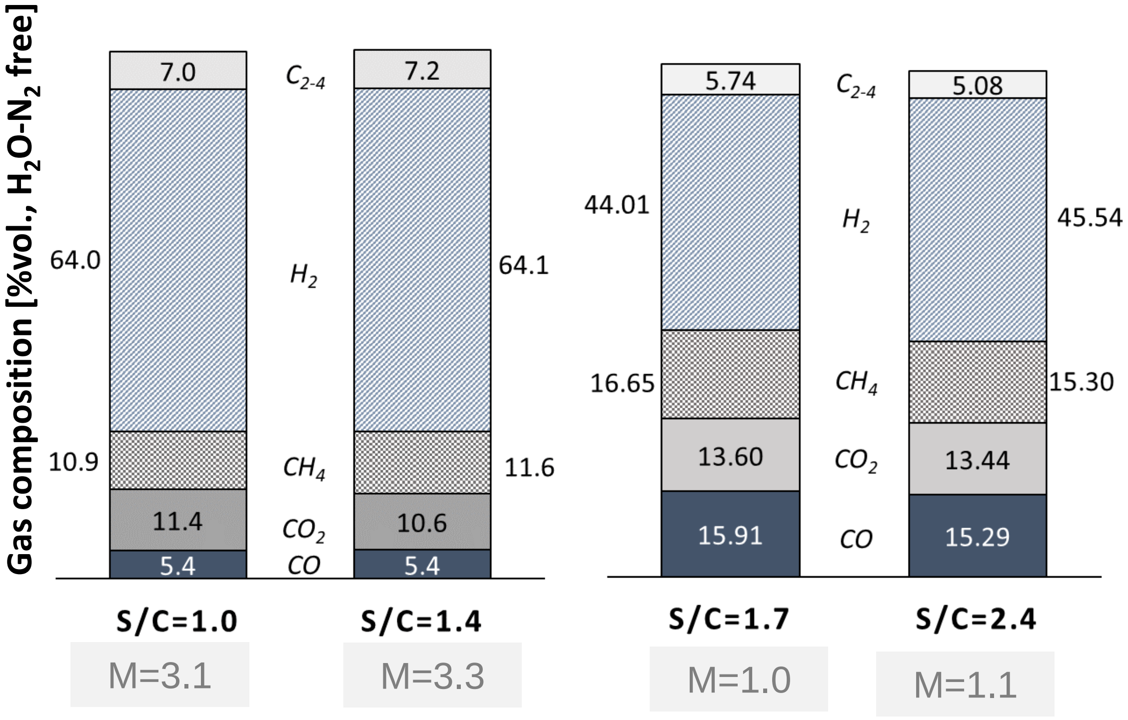
Calcium-to-Carbon ratio (**CaO/C**) = $\frac{kmol/_h\ CaO\ fed\ into\ the\ gasifier\ with\ the\ sorbent}{kmol/_h\ C\ in\ the\ biomass\ fed\ into\ the\ gasifier}$

M-module (**M**) = $\frac{(N_{H2}-N_{CO2})}{(N_{CO}+N_{CO2})}$

☞ *Deliverable 2.1. "Characterisation of raw materials for sorption enhanced gasification"*, **June 2017**, Public (http://www.fledged.eu/download/deliverables/)

Results discussion

Effect of the steam excess used in the gasifier (S/C ratio)



MSW-derived feedstock
CaO/C ratio= 1.1-1.2
Temperature= 707-710°C

Wood pellets
CaO/C ratio= 0.7-0.8
Temperature= 640°C

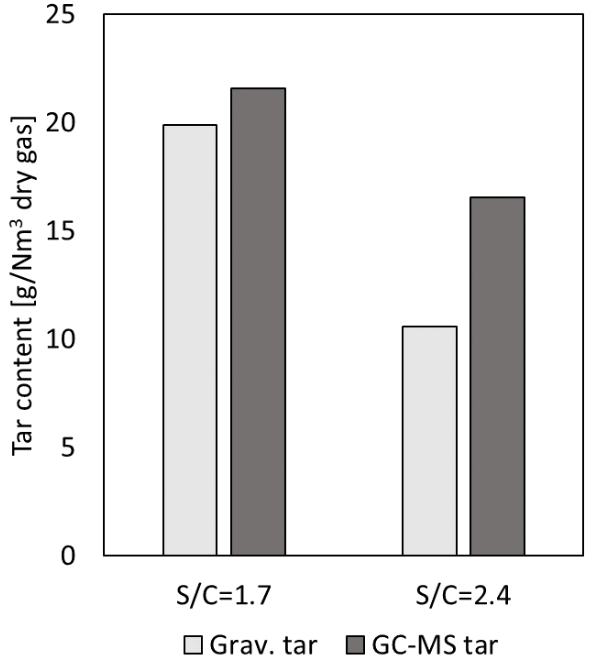
- ✓ **No significant influence on permanent gases** (M-module constant) **and light hydrocarbons content**.

  In dual fluidized bed systems, variations in M-modules are observed since S/C ratio effect cannot be isolated (Ca/C is adjusted)

- ✓ **Fixed carbon conversion favored** with S/C ratio (constant T and solid residence time). For example, X_{FC}=29 % (S/C=1.4) vs. 18 % (S/C=1.0)

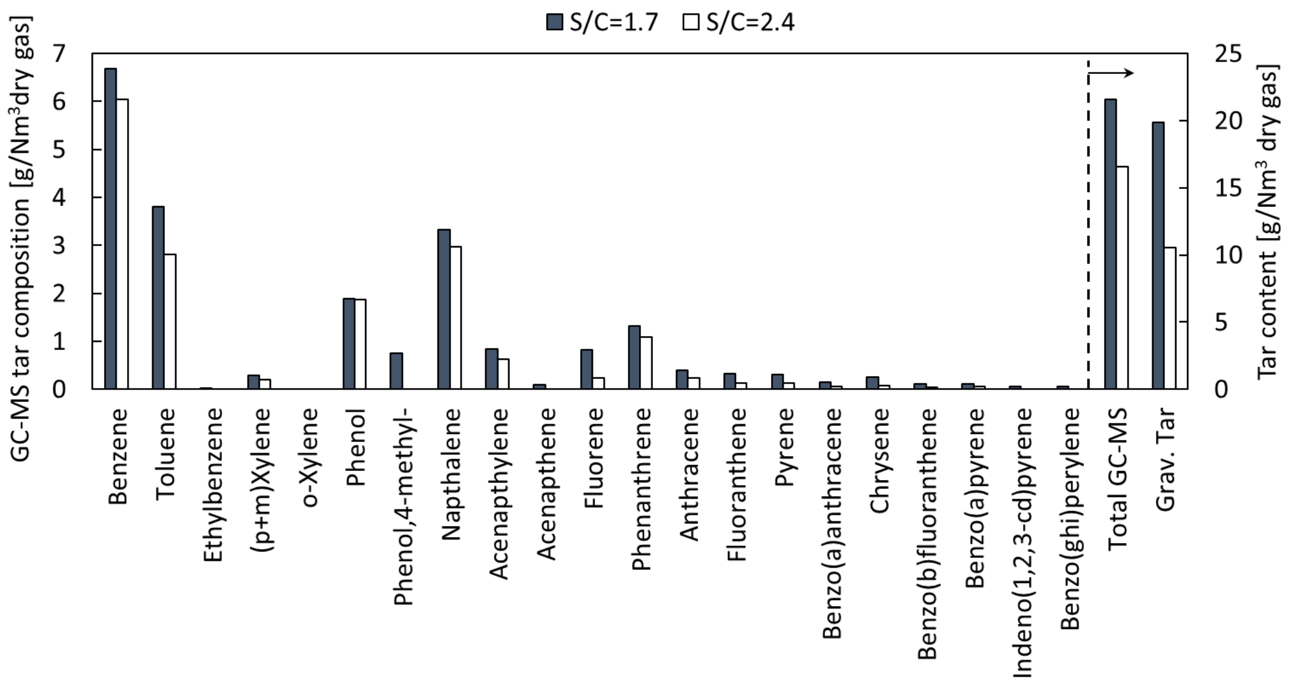
- ✓ **Syngas yield slightly improved** with the increase in fixed carbon conversion (limited fixed carbon contents)

Effect of the steam excess used in the gasifier (S/C ratio)



Wood pellets
CaO/C ratio= 0.7-0.8
Temperature= 640°C

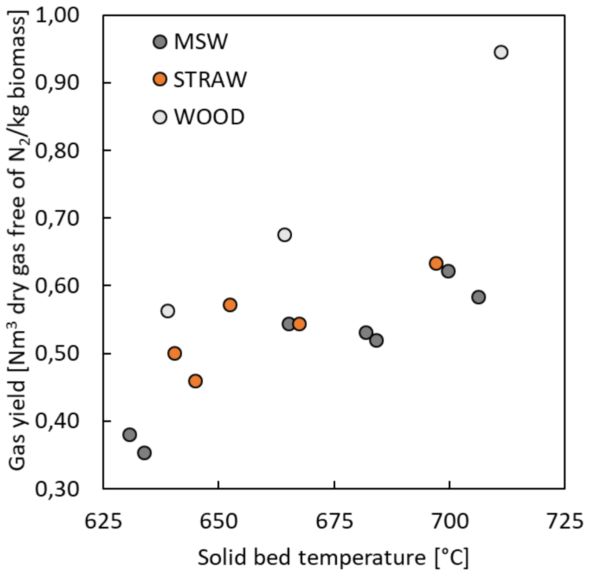
- ✓ Tar yield is influenced by the steam excess used, **decreasing the amount of tar as the S/C ratio is raised** (steam cracking and reforming reactions)



Results discussion

Effect of the gasification temperature

- **Operating variable influencing most the syngas quality** (yield, composition, tars) **and solids conversion**
- Regardless of the biomass, **syngas yield is significantly raised with the gasification temperature**



S/C ratio: 1.4 (mol/mol)
Variable CaO/C ratio

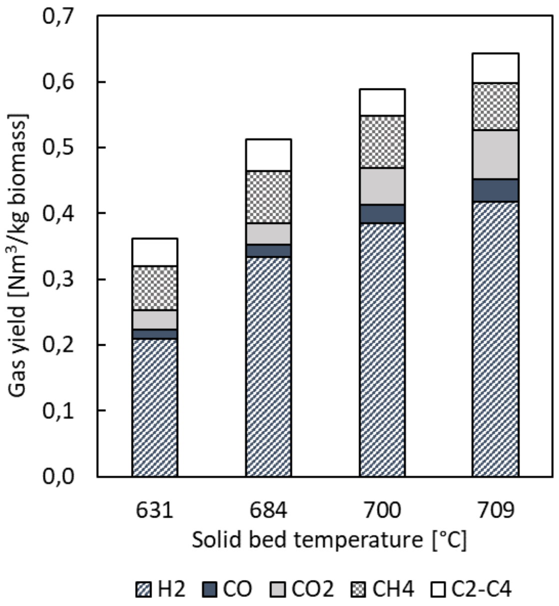
Devolatilization

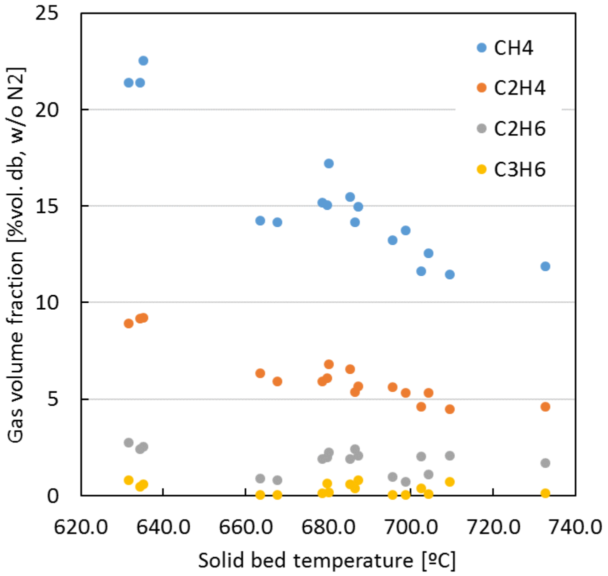
Steam cracking and reforming reactions of hydrocarbons and tars

Char gasification

$C_{(s)} \rightarrow CO, CO_2, H_2, CH_4$

Composition (VM and FC) of the biomass and gasification kinetics

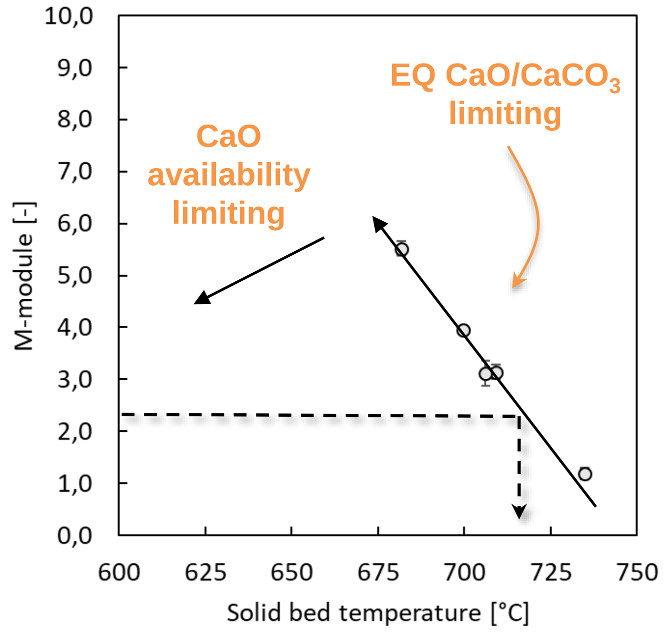


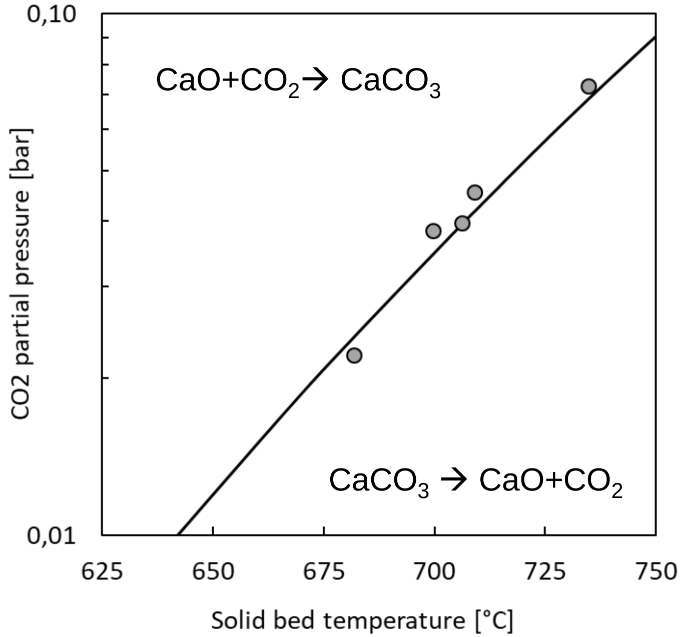


Results discussion

Effect of the gasification temperature

- **M-module in the syngas varies with the temperature. Two regions can be identified** *(specific of BFB compared to dual CFB, i.e. lower sorbent/biomass proportions and higher CaO residence times in the gasifier)*





- ☑ For high temperatures, the M-module is limited by the CaO carbonation reaction equilibrium.

  There is enough CaO but **equilibrium CO_2 partial pressure limits carbonation** (as T↑, CO_2 content in the gas ↑ and so M ↓)

- ☑ For low temperatures, M-module limited by the active CaO available in the solid bed

  Equilibrium allows reaching very low CO_2 contents, but **there is not enough CaO**

M-module:

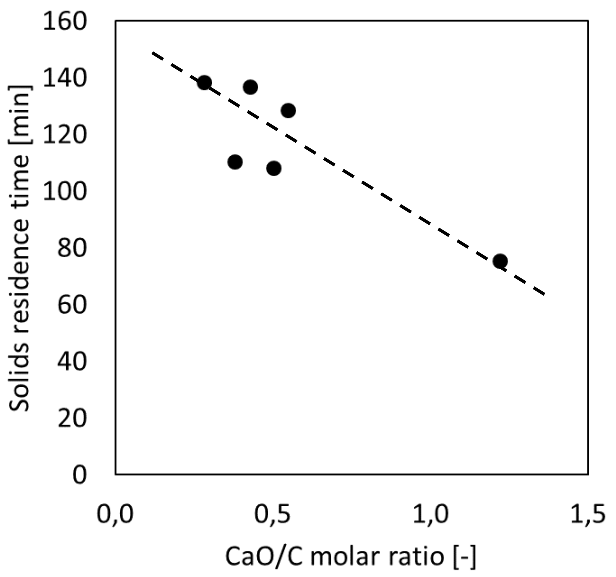
$$M = \frac{N_{H2} - N_{CO2}}{N_{CO2} + N_{CO}}$$

For DME production, **M module slightly higher than 2 is needed** (small composition adjustments along the syngas cleaning path).
Temperature and sorbent/biomass proportion needed can be elucidated for each biomass

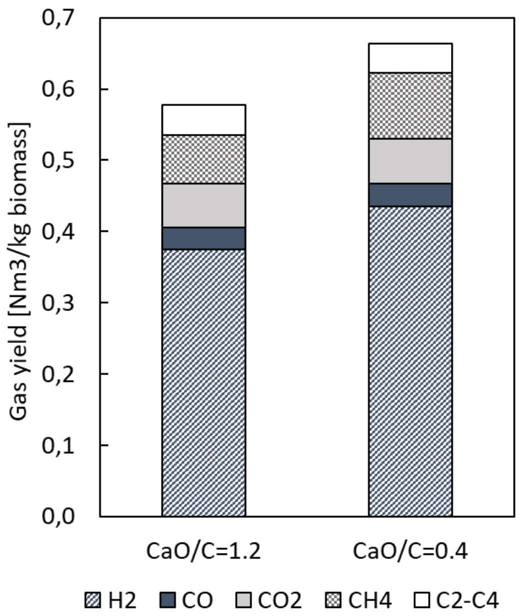
Results discussion

Effect of the sorbent/biomass proportion in the gasifier

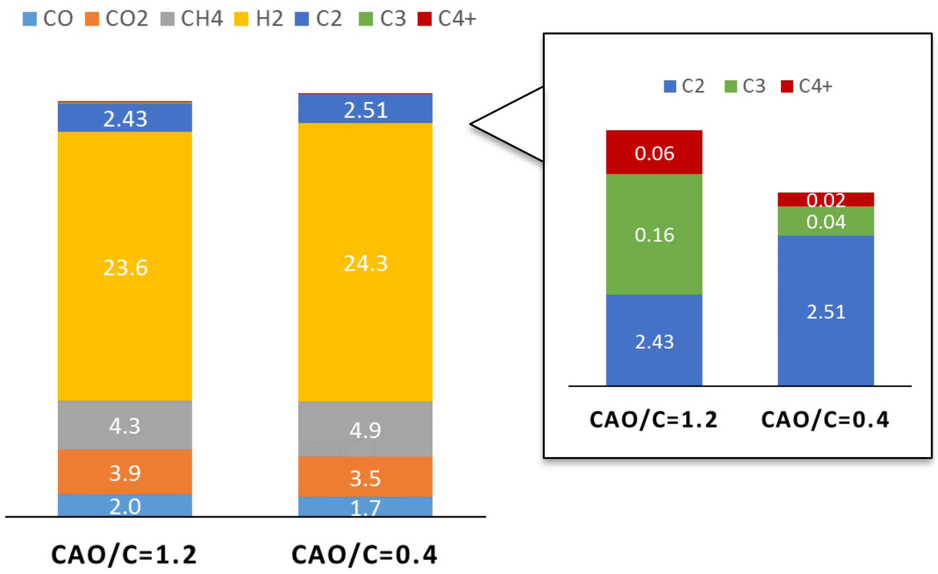
- **Main influence** of the sorbent excess used is found in **tar formation**
- Sorbent excess used influences solid residence time in the gasifier and so char conversion



Increasing the amount of calcined CaO into the gasifier (CaO/C) makes τ to be reduced



MSW derived feedstock
S/C ratio= 1.4
Temperature= 705-707ºC



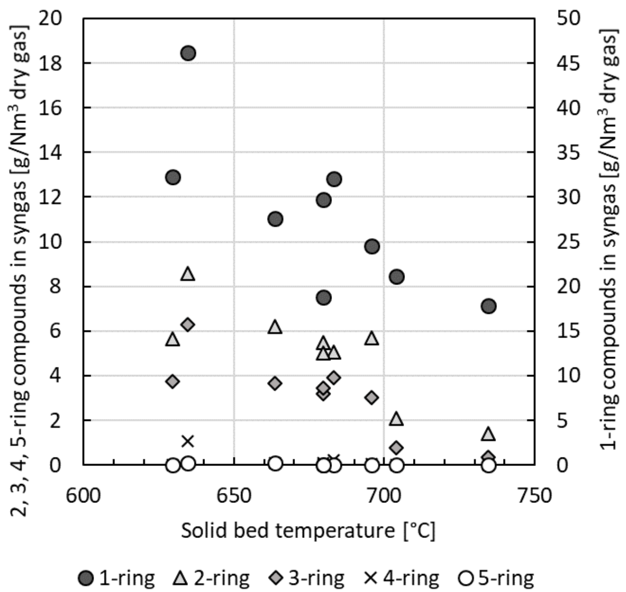
M=3.3 M=4.0

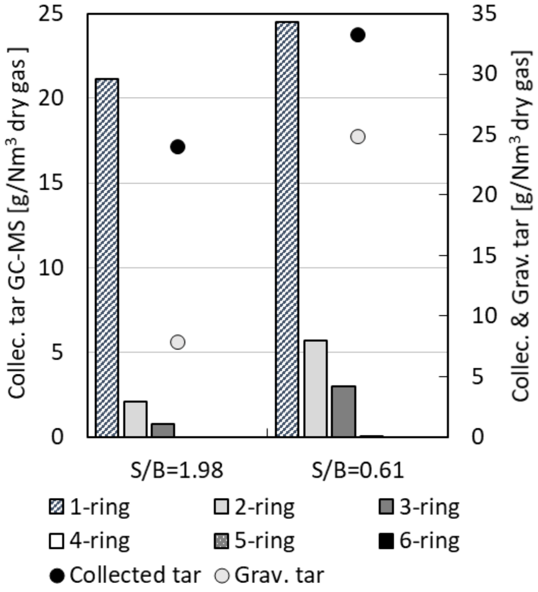
Slightly higher H_2 contents as τ is increased (lower CaO/C) and so M-modules

Results discussion

Influence of operating conditions on tar yield and composition

- **Tar content in the syngas can be reduced by increasing temperature, as well as sorbent and steam excess** (cracking and reforming reactions favored)
- Heavier tar compounds result into lighter tars and linear hydrocarbons (usually 1-, 2- and 3-ring tars →linear olefins and non saturated C_2-C_4, CO, H_2…)





MSW feedstock (S/C ratio: 1.4)

1-, 2- and 3-ring compounds are quite sensitive to temperature and sorbent excess

Catalytic tar cracking effect of CaO confirmed

Benzene is the major 1-ring tar determined by GC-MS for all the feedstocks studied (followed by toluene)

Naphthalene (MSW) and phenols (lignocellulosic) are the third most common tars

Conclusions

- The **performance of the flexible Sorption Enhanced Gasification** process has been **successfully studied for 6 different biomass feedstocks**
- The individual effect of the main operating variables of the SEG process (steam excess, temperature and sorbent/biomass proportion) has been evaluated
- Experimental results obtained at the 30 kW_{th} BFB gasifier have been validated with those obtained in a dual FB reactor system (high sorbent/biomass ratio needed at BFB)
- Operating conditions window suitable for producing a tailored syngas with the correct $H_2/CO/CO_2$ proportion for the DME synthesis has been obtained for those feedstocks tested under wider operating conditions

Detailed information

- *Public documents at FLEDGED website*:

  Deliverable 2.1. “Characterisation of raw materials for sorption enhanced gasification”, ***June 2017***, Public (http://www.fledged.eu/download/deliverables/)

  Deliverable 2.5. “Results of the sorption enhanced gasification in CSIC and USTUTT lab-scale testing”, **July 2019** (revised version by September 2019), Public (http://www.fledged.eu/download/deliverables/)

- *Open Access scientific publications*:

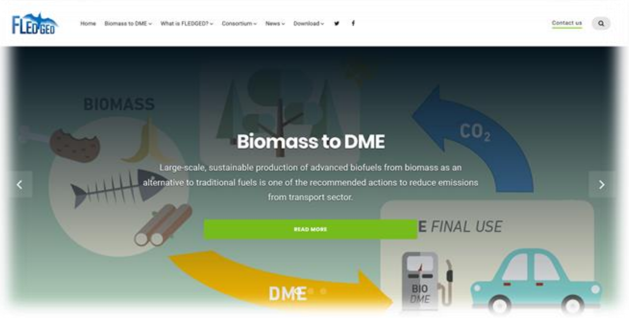
  Martínez, I., Kulakova, V., Grasa, G., Murillo, R. *Experimental investigation on sorption enhanced gasification (SEG) of biomass in a fluidized bed reactor for producing a tailored syngas*, **Fuel**, 259 (**2020**) 116252

  Martínez, I., Grasa, G., Callén, M.S., López, J.M., Murillo, R. *Optimised production of tailored syngas from municipal solid waste (MSW) by sorption-enhanced gasification*, **Chemical Engineering Journal**, accepted June **2020**, DOI: 10.1016/j.cej.2020.126067

  Callén, M.S., Martínez, I., Grasa, G., López, J.M., Murillo, R. *Principal Component Analysis and Partial Least Square Regression Models to under-stand sorption enhanced biomass gasification*, **to be submitted**

- *General information*

  www.fledged.eu/



Thanks for your attention!

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