ASSESSMENT OF THE SORPTION ENHANCED GASIFICATION IN A 30 kWth BFB REACTOR

Isabel Martínez*, Gemma Grasa, Maria S. Callén, Jose M. López, Ramón Murillo
Instituto de Carboquímica, Spanish National Research Council (CSIC), Zaragoza (SPAIN)
Assess the performance of the Sorption Enhanced Gasification (SEG) process in a 30 kWth bubbling fluidized bed reactor (BFB) placed at the Instituto de Carboquímica (CSIC) (Zaragoza, Spain)

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

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)
Description of the 30 kWth 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

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

<table>
<thead>
<tr>
<th>WOOD PELLETS</th>
<th>GRAPE SEEDS</th>
<th>MSW-pellets</th>
<th>MSW biomass</th>
<th>Straw pellets</th>
<th>Pine wood</th>
</tr>
</thead>
<tbody>
<tr>
<td>% moisture</td>
<td>5.55</td>
<td>6.30</td>
<td>5.90</td>
<td>6.56</td>
<td>6.51</td>
</tr>
<tr>
<td>% ash</td>
<td>0.36</td>
<td>4.30</td>
<td>32.20</td>
<td>32.47</td>
<td>4.87</td>
</tr>
<tr>
<td>% volatile matter</td>
<td>78.80</td>
<td>65.12</td>
<td>55.40</td>
<td>53.63</td>
<td>70.28</td>
</tr>
<tr>
<td>% fixed carbon</td>
<td>15.29</td>
<td>24.28</td>
<td>6.60</td>
<td>7.34</td>
<td>18.33</td>
</tr>
<tr>
<td>% S</td>
<td>0.02</td>
<td>0.12</td>
<td>0.66</td>
<td>0.21</td>
<td>0.13</td>
</tr>
<tr>
<td>% Cl</td>
<td>0.00</td>
<td>0.06</td>
<td>0.43</td>
<td>0.56</td>
<td>0.36</td>
</tr>
<tr>
<td>LHV (MJ/kg)</td>
<td>17.59</td>
<td>20.51</td>
<td>12.84</td>
<td>13.47</td>
<td>16.06</td>
</tr>
</tbody>
</table>

---

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\textsubscript{CO}_2/g calcined material)

Operating variables analyzed

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

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

Deliverable 2.1. “Characterisation of raw materials for sorption enhanced gasification”, June 2017, Public
(http://www.fledged.eu/download/deliverables/)
Effect of the steam excess used in the gasifier (S/C ratio)

- No influence on permanent gases composition (M-module constant)
- Light hydrocarbons content slightly affected (i.e. decreasing as S/C increases) due to reforming reactions
- Fixed carbon conversion favored with S/C ratio (constant T and solid residence time). For example, $X_{FC}=29\%$ (S/C=1.3) vs. 18\% (S/C=1.0)
- Syngas yield slightly improved with the increase in fixed carbon conversion (limited fixed carbon contents)

Results discussion

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>6.50</td>
<td>64.10</td>
<td>11.62</td>
<td>10.90</td>
<td>5.42</td>
<td>10.59</td>
<td>5.36</td>
</tr>
<tr>
<td>1.0</td>
<td>6.60</td>
<td>64.98</td>
<td>11.37</td>
<td>10.90</td>
<td>5.36</td>
<td>10.59</td>
<td>5.36</td>
</tr>
<tr>
<td>1.7</td>
<td>5.26</td>
<td>44.01</td>
<td>16.65</td>
<td>13.60</td>
<td>15.91</td>
<td>15.91</td>
<td>15.91</td>
</tr>
<tr>
<td>2.4</td>
<td>4.68</td>
<td>45.54</td>
<td>15.30</td>
<td>13.44</td>
<td>15.29</td>
<td>15.29</td>
<td>15.29</td>
</tr>
</tbody>
</table>

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

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

**Wood pellets**
- CaO/C ratio: 0.7-0.8
- Temperature: 642-646°C

M=3.3 \hspace{1cm} M=3.1
M=3.0 \hspace{1cm} M=1.1

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

Graphs showing gas yield and gas volume fraction vs. solid bed temperature.
Results discussion

Effect of the gasification temperature

- Tailored 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 CO₂ partial pressure limits carbonation (as T ↑, CO₂ 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 CO₂ 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
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 $\tau$ to be reduced.

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

**MSW derived feedstock**

**S/C ratio = 1.4**

**Temperature = 705-707°C**
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 C₂-C₄, CO, H₂…)

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 second 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 properly evaluated.

- Experimental results obtained at the 30 kW\textsubscript{th} BFB gasifier have been validated with those obtained in a dual CFB reactor system (high sorbent/biomass ratio needed at BFB).

- Operating conditions window suitable for producing a tailored syngas with the correct H\textsubscript{2}/CO/CO\textsubscript{2} proportion for the DME synthesis has been obtained for each of the biomass tested.
Public documents at FLEDGED website:


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


General information

www.fledged.eu/
Thanks for your attention!

Spanish National Research Council (CSIC)
Instituto de Carboquímica, Environmental Research Group
imartinez@icb.csic.es

Find out more about us: https://www.icb.csic.es/

This project has received funding from the European Union’s Horizon 2020 research and innovation Programme under grant agreement No 727600