Experimental investigation on sorption enhanced gasification (SEG) of biomass in a fluidized bed reactor for producing a tailored syngas

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OBJECTIVE FLEDGED project: Develop a highly intensified and flexible process for DME production from biomass and validate it under industrially relevant environments (i.e. Technology Readiness Level 5 (TRL))

- Indirect gasification in a dual fluidized bed system using CaO as bed material
- Energy needed for gasification supplied by CaO carbonation (→ CaCO₃) and by circulating solids
- Unconverted char leaving the gasifier supplies the energy needed in the combustor
- The presence of CaO simplifies the syngas cleaning and purification section

More info: http://www.fledged.eu/
Objectives

FUNDAMENTAL RESEARCH ON GASIFICATION OF DIFFERENT BIOMASSES AND DIFFERENT NATURAL SORBENTS

✔ Assessment of the enhanced gasification process in a bubbling fluidized bed reactor

- Test the different biomasses under different conditions of temperature, sorbent/fuel ratio and steam/carbon ratio.
- Influence of type of sorbent and the activity of the limestone (number of cycles)

Sorption enhanced gasification tests using grape seeds as biomass have been performed, analyzing the effect of the S/C ratio, the sorbent-to-biomass ratio and the activity of the sorbent on the syngas composition.
Sorption enhanced gasification (SEG) tests

Materials used

- **Biomass: Grape seeds**
  - 4.5-6.8 mm
  - Ultimate analysis [%wt.]
    - C: 53.92
    - H: 6.58
    - N: 2.20
    - S: 0.12
    - O: 32.35
  - Proximate analysis [%wt.]
    - Moisture: 6.30
    - Volatile matter: 65.12
    - Ash: 4.30
    - Fixed carbon: 24.28
    - LHV [MJ/kg]: 20.51
  - Homogenous biomass
  - High LHV (compared with PW or A1 pellets)
  - Relatively low Ash and S contents (residual biomass)

- **CO2 sorbent: Calcined limestone**
  - CaO [%wt]: 98.25
  - Al₂O₃ [%wt]: 0.145
  - Fe₂O₃ [%wt]: 0.002
  - K₂O [%wt]: <0.001
  - MgO [%wt]: 0.183
  - Na₂O [%wt]: <0.001
  - SiO₂ [%wt]: 0.132
  - Porosity [-]: 0.52
  - Surface area [m²/g]: 8.8
  - Solid density [kg/m³]: 3139
  - High purity limestone
  - Mean particle diameter: 450 microns
  - Typical CO₂ sorption decay of natural Ca-based sorbents
Sorption enhanced gasification (SEG) tests

Experimental facility

- Bubbling Fluidized Bed (BFB) reactor
- 3 m height (Bottom part: 0.15 m x 1 m)
- Independent screw feeders
- Externally heated
- Bed inventory ≈ 5-6 kg (lateral overflow)
- N2 flow rate fed to the evaporator (heater) and to the CaO screw feeder
Sorption enhanced gasification (SEG) tests
Experimental routine

Electric heating in air up to ≈ 700ºC (flow rate of 0.10 Nm³/min)- 2h

Feed of biomass for speeding the heating up to 820-850ºC while feeding CaO to fill the bed

Steady state reached for the gas and bed temperature (BEGINNING OF GAS AND SOLID SAMPLING)

Stabilization of temperature and gases
Sorption enhanced gasification (SEG) tests

Experimental conditions

<table>
<thead>
<tr>
<th>Ca/C ratio</th>
<th>S/C ratio</th>
<th>1</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55</td>
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<tr>
<td>0.5</td>
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<tr>
<td>0.45</td>
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<tr>
<td>0.4</td>
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<tr>
<td>0.3</td>
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</tbody>
</table>

- Different Ca/C ratios (0.3-0.55) and S/C ratios (1 and 1.5) tested
- Stabilization temperature between 707 and 755ºC
- Effect of CO₂ carrying capacity of the sorbent used tested

Char conversion in the BFB gasifier:

\[ X_{\text{CHAR}} = 1 - \frac{m_{C,s \, \text{overflow}}}{m_{FC, \text{biomass}}} \]

Char particles residence time:

\[ \tau_{\text{CHAR}} = \frac{m_{\text{char,SS}}}{\dot{m}_{\text{biomass}} \cdot (y_{FC} + y_{ash})} \]
Effect of S/C ratio (Ca/C ratio constant)

- Amount of C3+ and unsaturated C2 reduced <0.53% vol. with S/C ratio of 1.5 (≈2.4% vol. for S/C=1)
- C3+ and C2H4 cracked into C2H6 and CH4, resulting into a larger gas yield
- Solid residence time for char particles has not changed, differences in conversion due to temperature

\[ M = \frac{H_2 - CO_2}{CO + CO_2} \]
Sorption enhanced gasification (SEG) tests
Results discussion

✓ **Effect of Ca/C ratio (S/C ratio constant)**

<table>
<thead>
<tr>
<th>Ca/C</th>
<th>Gas yield (db) [Nm³/min]</th>
<th>X_{CHAR} [%]</th>
<th>τ_{CHAR} [min]</th>
<th>X_{CaO} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.065</td>
<td>41</td>
<td>50</td>
<td>22-23</td>
</tr>
<tr>
<td>0.55</td>
<td>0.055</td>
<td>37</td>
<td>35</td>
<td>27</td>
</tr>
</tbody>
</table>

\[
M = \frac{H_2 - CO_2}{CO + CO_2}
\]

- No effect on C₃+ and unsaturated C₂ (<0.59%vol.) since S/C ratio is high
- CH₄ (and C₂H₆) is **slightly higher for Ca/C=0.55** due to the **lower stabilization temperature** when Ca/C increases
- Larger M module for Ca/C=0.5 (lower temperature): linked to the amount of CO₂ separated
- Lower temperature and larger excess of CaO improve CO₂ separation and reduce CO₂ in the syngas (less CO content since WGS reaction is pushed)
Sorption enhanced gasification (SEG) tests
Results discussion

✓ **Effect of CO$_2$ sorbent activity (S/C and Ca/C ratios constant)**

<table>
<thead>
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<th>S/C ratio</th>
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<tr>
<td>Ca/C ratio</td>
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- Less CO$_2$ is separated from the gas phase (less activity of the CaO) → lower amount of H$_2$ and higher CO
- CH$_4$ concentration is kept constant at 8.5%vol. (db) (stabilization temperature is the same)
- Amount of C$_3$+ and unsaturated C$_2$ increased for deactivated CaO (4.4%vol. vs 0.7%vol.) → less H$_2$ produced (less cracking into saturated C$_2$ and CH$_4$)
- Increased gas yield for more active CO$_2$ sorbent since the amount of lighter C+ and H$_2$ is raised

<table>
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<tr>
<th>g$<em>{CO_2}$/g$</em>{CaO}$</th>
<th>Gas yield (db) [Nm³/min]</th>
<th>X$_{CHAR}$ [%]</th>
<th>τ$_{CHAR}$ [min]</th>
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</tr>
<tr>
<td>0.1</td>
<td>0.056</td>
<td>40</td>
<td>48</td>
<td>15</td>
</tr>
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</table>
Factors influencing the efficiency of the biomass-to-biofuel process

- Important to reduce the CH₄ and C₂+ concentrations (inerts $\rightarrow$ reduce yield and decrease the global efficiency)

- Dependence of HCs content on temperature $\rightarrow$ higher temperature decreases HCs concentration (except for C₂+ and S/C=1.5, not depicted in figure)

- Limit on HCs reduction $\rightarrow$ need of conditioning steps before the synthetic fuel production process (i.e. reforming stage)

Char conversion in the gasifier influenced by the temperature (CaO excess and $\tau$ barely affect)

Efficiency of the SEG has an optimum: increasing char conversion boosts the efficiency but if there is not enough unconverted char in the combustor/calciner, additional biomass is needed (↓ efficiency)
Conclusions and future work

✓ The **effect of the steam-to-carbon, CO₂ sorbent-to-biomass and the sorbent CO₂ carrying capacity have been assessed** for the sorption enhanced gasification of grape seeds

✓ **S/C** ratios of 1.5 needed for reducing C₂H₄ and C₃+ concentrations below 0.6%vol. (db), which will impact the downstream fuel production process

✓ CH₄ and C₂H₆ concentrations have shown dependence with temperature (i.e. decreases with increasing temperature). CH₄ contents as low as 4.5 %vol. (db) at around 755°C have been obtained

✓ A wide range of M modules has been obtained (M=1.7-2.7), suitable for producing different types of biofuels (i.e., M=2 for DME or M=3 for SNG)

**FUTURE WORK**

✓ Tar and S- compounds analysis to be tuned-up (analysis under different operating conditions in the next campaign)

✓ Higher S/C and wider range of temperatures to be tested

✓ Other biomasses to be studied
Thanks for your attention

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