A Study of Slurries Produced from Pyrolysis Products from Alternative Lignocellulosic Biomass: Characterization and Use

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BECOOL is an ongoing research and innovation project to promote the cooperation between EU and Brazil in the development of advanced biofuels, from sustainable agricultural value chains, based on lignocellulosic biomass.

Objectives:
• Developing and validating integrated technology packages
• Introducing alternative sources of biomass
• Strengthen EU-Brazil cooperation
Thermochemical conversion routes

- Centralized solid biomass gasification
  - Gasification (low T, indirect, MILENA)
  - Biofuel (Fischer-Tropsch) synthesis

- Fast pyrolysis and gasification
  - Decentralized multiple pyrolysis plants
  - Centralized conversion to biofuel

- Slow & fast pyrolysis and gasification
  - Decentralized multiple and combined pyrolysis plants
  - Centralized conversion to biofuel

This work studies Char/bio-oil slurries as fuel for gasification: Preparation, characterization and gasification
Biomass densification – the slurry

Pyrolysis to intermediate bioenergy carriers (IBC)

- Product liquid >5x volumetric energy density increase
- Char-in-bio-oil increases density further
- Promising step to overcome logistic economics

Co-production of char is an interesting option to provide heat to dry biomass before thermochemical processing

Database for biomass and waste: https://phyllis.nl/
**Pyrolysis pathways**

BECOOL investigates all pyrolysis pathways to convert biomass.

- Focus is on fast (high liquid) and slow pyrolysis (high solid yield)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Conditions</th>
<th>Liquid %wt</th>
<th>Water %wt</th>
<th>Solid %wt</th>
<th>Gas %wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>fast</td>
<td>450-700 °C, short hot vapors residence time ≈1 s</td>
<td>65</td>
<td>5</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>intermediate</td>
<td>450-550 °C, hot vapors residence time 10-30 s</td>
<td>25</td>
<td>25</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>slow</td>
<td>400-500 °C, long vapors residence (hours up to days)</td>
<td>5</td>
<td>15</td>
<td>30</td>
<td>50</td>
</tr>
</tbody>
</table>

**Note:**
- **Fast (high liquid)**: Short residence time, high liquid yield.
- **Intermediate**: Moderate residence time, moderate yield.
- **Slow (carbonization)**: Long residence time, high solid yield.
Conversion technologies

- **Intermediate pyrolysis pilot unit** “PYRO”;
  - 1.5 kg/h feeding;
  - 400-600 °C reaction temperature.
  - Tests achieved low PO (≈14 wt.%) and high water fractions (≈26 wt.%) mixed together; fractional condensation is under testing to divide these fractions.

- **Oxidative carbonization pilot unit**, “CarbON”;
  - capacity of up to 50 kg/h of woody biomass;
  - 500 – 650 °C operating Temperature; 1.5 hr hot vapours residence time
  - equivalence ratio (ER), 0.1-0.2.
  - Tests with mixed wood chips produced a “high quality” char, used as solid fraction.
  - **BTG fast pyrolysis bio-oil** was selected as liquid fraction.
Slurries of **Char-In-Bio-Oil** combines different pyrolysis products. Characteristics depending on:

- Bio-oil quality, char quality, char particle size distribution, rheological properties, surfactant
- 0, 5, 10, 15 and 20 wt% char in bio-oil slurries prepared
### Slurry analysis

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Wood chips</th>
<th>Bio-oil</th>
<th>Char/bio-oil</th>
<th>Char</th>
</tr>
</thead>
<tbody>
<tr>
<td>%wt a.r.</td>
<td>100</td>
<td>100</td>
<td>10/90</td>
<td>20/80</td>
</tr>
<tr>
<td>Density at 15°C kg/m³</td>
<td>213</td>
<td>1200</td>
<td>1240</td>
<td></td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C mm²/s</td>
<td>27.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HHV MJ/kg</td>
<td>17.2</td>
<td>18.7</td>
<td>20.2</td>
<td>32.2</td>
</tr>
<tr>
<td>LHV MJ/kg</td>
<td>16.0</td>
<td>15.5</td>
<td><strong>17.1</strong></td>
<td><strong>18.7</strong></td>
</tr>
<tr>
<td>Carbon content (C) %wt d.b.</td>
<td>49.7</td>
<td>41.3</td>
<td>46.0</td>
<td>50.6</td>
</tr>
<tr>
<td>Hydrogen content (H) %wt d.b.</td>
<td>5.28</td>
<td>7.70</td>
<td>7.11</td>
<td>6.52</td>
</tr>
<tr>
<td>Nitrogen content (N) %wt d.b.</td>
<td>0.19</td>
<td>0.13</td>
<td>0.17</td>
<td>0.20</td>
</tr>
<tr>
<td>Sulphur content (S) %wt d.b.</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Oxygen (O) %wt d.b.</td>
<td>44.5</td>
<td>50.9</td>
<td>46.4</td>
<td>41.9</td>
</tr>
<tr>
<td>Ash %wt d.b.</td>
<td>0.7</td>
<td>0</td>
<td><strong>0.37</strong></td>
<td><strong>0.74</strong></td>
</tr>
<tr>
<td>Water content %wt a.r.</td>
<td>13.2</td>
<td>24</td>
<td>21.9</td>
<td>19.8</td>
</tr>
</tbody>
</table>

Char/Bio-oil slurry:
- Volumetric energy density >6x greater compared to wood chips
- Lower ash content
- Similar C,H,N and S content to solid biomass
- High H₂O content in bio-oil

Wood chips = Chestnut
Viscosity measurements at 15°C varying particle size and loading

- Bio-oil viscosity constant over shear rate (Newtonian)
- Slurries are non-Newtonian fluids
- Exponential viscosity increase at higher char loadings
- Application of 10/90 slurry at >60°C recommended
Thermogravimetric analysis

- Tests operated in Nitrogen atmosphere at approx. 10 LPM.
- Heating rate at 50 °C/min

At the plateau the mass loss is approx. proportional to char content.
Bio-oil gasification

Initial results in lab-scale fluidized bed reactor

• Bio-oil fed at r.t. using gas-assisted atomization probe
  (Feeding of the slurry at 50-70°C resulted in blockages)
• Bio-oil flow: 0.3 kg/h, Bed temperature: 770°C (1 kg silica sand).

• H₂O/C ratio varied via steam addition
  • More steam → less tar
  • No steam → poor conversion (higher temperature?)

<table>
<thead>
<tr>
<th>Entry</th>
<th>H₂O/C</th>
<th>Tar [g/Nm³]</th>
<th>CC [%]</th>
<th>CGE [%]</th>
<th>CO+H₂ [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9</td>
<td>18.3</td>
<td>82</td>
<td>81</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>1.6</td>
<td>14.0</td>
<td>77</td>
<td>74</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>16.3</td>
<td>74</td>
<td>68</td>
<td>68</td>
</tr>
</tbody>
</table>

No additional steam, poor conversion and probe blockage

On N₂-free and dry basis
Conditions: 0.3 kg/h feed, 0.88 NL/min O₂ (ER: 0.3), 37 NL/min N₂, 0.1, 0.3, 0 kg/h steam.
Product gas composition

Product gas for FT production

- 68 vol% syngas corresponding to 56-59 %$_{LHV}$
  - FB gasification of solid biomass, 50-60 vol% syngas*

- Ethylene and BTX contribute 21 %$_{LHV}$ to the energy, allows for value extraction

- Similar gas compositions expected for slurry gasification, small scale feeding challenging, char could be used separate for heat (indirect)

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Conclusions

- Char/bio-oil has a high potential as intermediate energy carrier (IBC)
  - Allows for decentralized biomass pretreatment
  - Optimal slurry: 10 wt% char in bio-oil
  - Heat value increases from 15.5 to 17.1 MJ/kg
  - Slurry >6x volumetric energy densification versus solid biomass
  - Char loading increases viscosity dramatically
  - Viscosity below 100 cP at 60°C

- Preliminary bio-oil gasification experiments
  - Addition of steam $\text{H}_2\text{O}/\text{C} >0.9$ or higher $T$ desired
  - High efficiency with CGE of $>80\%$
  - Ethylene and BTX contribute 21 %$_{\text{LHV}}$ to the energy, allows for value extraction
  - To overcome slurry feeding issues separate feeding, alternative slurry formulations and/or indirect gasification could be considered in lab-scale
Partners

Thank you for your attention!

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Questions?

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