Valorisation of char residues from biomass gasification in adsorption applications

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Background

Biomass gasification

- Gas
- Tar (liquid)
- Char (solid)

South Tyrol: about 1300 tons/year of char disposed of as industrial waste with a high cost for disposal (140 - 150 €/ton)

Valorization
Char valorization at UNIBZ

- Catalysis
- Adsorption
- Agriculture
- Tar removal

Symbols:
- CO$_2$
- H$_2$S
Char collection and characterization

CO₂ adsorption

H₂S adsorption

Other applications
### Gasification technologies

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Technology</th>
<th>Electric power $kW_{el}$</th>
<th>Thermal power $kW_{th}$</th>
<th>$T$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Wood chips</td>
<td>Dual-stage</td>
<td>50</td>
<td>110</td>
<td>~900</td>
</tr>
<tr>
<td>2 Wood chips</td>
<td>Dual-stage</td>
<td>280</td>
<td>540</td>
<td>~850</td>
</tr>
<tr>
<td>3 Pellets</td>
<td>Rising co-current</td>
<td>180</td>
<td>270</td>
<td>~700</td>
</tr>
<tr>
<td>4 Wood chips</td>
<td>Downdraft</td>
<td>150</td>
<td>260</td>
<td>~650</td>
</tr>
<tr>
<td>5 Wood chips</td>
<td>Downdraft</td>
<td>296</td>
<td>550</td>
<td>~800</td>
</tr>
<tr>
<td>6 Wood chips</td>
<td>Downdraft</td>
<td>45</td>
<td>120</td>
<td>~650</td>
</tr>
</tbody>
</table>

- Scanning electron microscopy
- Small angle X-ray scattering
- Thermogravimetric analysis

Differences among chars

SEM

XRD

Q: quartz (SiO$_2$), P: portlandite (Ca(OH)$_2$), C: calcite (CaCO$_3$), L: lime (CaO)
### Elemental analysis (% wt<sub>dry</sub>)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C %wt&lt;sub&gt;dry&lt;/sub&gt;</th>
<th>H %wt&lt;sub&gt;dry&lt;/sub&gt;</th>
<th>N %wt&lt;sub&gt;dry&lt;/sub&gt;</th>
<th>S %wt&lt;sub&gt;dry&lt;/sub&gt;</th>
<th>O %wt&lt;sub&gt;dry&lt;/sub&gt;</th>
<th>Ash %wt&lt;sub&gt;dry&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHAR1</td>
<td>81.1</td>
<td>0.23</td>
<td>0.28</td>
<td>0.35</td>
<td>3.74</td>
<td>14.6</td>
</tr>
<tr>
<td>CHAR2</td>
<td>91.3</td>
<td>0.72</td>
<td>0.26</td>
<td>0.57</td>
<td>3.43</td>
<td>4.20</td>
</tr>
<tr>
<td>CHAR3</td>
<td>81.1</td>
<td>0.25</td>
<td>0.61</td>
<td>0.27</td>
<td>1.89</td>
<td>16.0</td>
</tr>
<tr>
<td>CHAR4</td>
<td>48.1</td>
<td>0.49</td>
<td>0.23</td>
<td>0.32</td>
<td>1.64</td>
<td>49.5</td>
</tr>
<tr>
<td>CHAR5</td>
<td>80.6</td>
<td>0.55</td>
<td>0.27</td>
<td>0.20</td>
<td>2.79</td>
<td>15.8</td>
</tr>
<tr>
<td>CHAR6</td>
<td>68.6</td>
<td>0.33</td>
<td>0.83</td>
<td>0.32</td>
<td>2.05</td>
<td>27.8</td>
</tr>
</tbody>
</table>

### Surface area

<table>
<thead>
<tr>
<th>Sample</th>
<th>S&lt;sub&gt;BET&lt;/sub&gt;</th>
<th>Pore size</th>
<th>Pore volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHAR1</td>
<td>603</td>
<td>3.88</td>
<td>0.30</td>
</tr>
<tr>
<td>CHAR2</td>
<td>297</td>
<td>4.50</td>
<td>0.26</td>
</tr>
<tr>
<td>CHAR3</td>
<td>403</td>
<td>4.70</td>
<td>0.50</td>
</tr>
<tr>
<td>CHAR4</td>
<td>183</td>
<td>4.90</td>
<td>0.25</td>
</tr>
<tr>
<td>CHAR5</td>
<td>427</td>
<td>4.40</td>
<td>0.39</td>
</tr>
<tr>
<td>CHAR6</td>
<td>352</td>
<td>4.54</td>
<td>0.24</td>
</tr>
</tbody>
</table>

1. Highest surface area
2. Lowest amount of ash
3. High surface area
4. Low amount of ash

**ADSORPTION**

**CATALYSIS**
Outline

Char collection and characterization

H$_2$S adsorption

CO$_2$ adsorption

Other applications
Materials and methods

Adsorptive:
CO₂

Adsorbent:
5 pure chars
2 activated chars
2 AC

Thermo-gravimetric tests run in a Jupiter STA449-F3 (Netzsch)

- \( T_{\text{ads}} = 50 - 75 - 100 \, ^\circ\text{C} \)
- \( \text{CO}_2:\text{N}_2 = 1:1 - 1:4 \)
- KOH - \( \text{ZnCl}_2 \)
- \( \text{N}_2 \)
- 600 °C
- 1 hour
Results

V. Benedetti et al., CO\textsubscript{2} adsorption study on pure and chemically activated chars derived from commercial biomass gasifiers, J. CO\textsubscript{2} util., 33 (2019) 46-54.

Adsorption curves

![Graph showing adsorption curves for AC1, CHAR3, and Temperature over time.]

SEM images

![Images of SEM analysis showing chars with various compositions: AC1, AC2, 1_KOH, 1_ZnCl\textsubscript{2}.]
Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Uptake, %</th>
<th>N$_2$ uptake, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHAR1</td>
<td>3.49</td>
<td>0.20</td>
</tr>
<tr>
<td>CHAR2</td>
<td>3.04</td>
<td>0.14</td>
</tr>
<tr>
<td>CHAR3</td>
<td>2.09</td>
<td>0.08</td>
</tr>
<tr>
<td>CHAR4</td>
<td>1.69</td>
<td>0.65</td>
</tr>
<tr>
<td>CHAR5</td>
<td>2.75</td>
<td>0.17</td>
</tr>
<tr>
<td>AC1</td>
<td>3.01</td>
<td>0.10</td>
</tr>
<tr>
<td>AC2</td>
<td>2.13</td>
<td>0.07</td>
</tr>
<tr>
<td>CHAR1_KOH</td>
<td>3.73</td>
<td>0.35</td>
</tr>
<tr>
<td>CHAR1_ZnCl2</td>
<td>3.03</td>
<td>0.13</td>
</tr>
</tbody>
</table>

\[
\text{Uptake} = \frac{(W_{\text{end}} - W_0) \cdot 100}{W_0}
\]

Effect of T and gas composition

Literature: 2.50 - 10.70
Results - physisorption

![Graph showing physisorption results](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>$S_{\text{BET}}$ m$^2$/g</th>
<th>Pore size nm</th>
<th>Pore volume cm$^3$/g</th>
<th>μ-pore volume cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHAR1</td>
<td>603</td>
<td>3.88</td>
<td>0.30</td>
<td>0.05</td>
</tr>
<tr>
<td>CHAR2</td>
<td>297</td>
<td>4.50</td>
<td>0.26</td>
<td>0.02</td>
</tr>
<tr>
<td>CHAR3</td>
<td>403</td>
<td>4.70</td>
<td>0.50</td>
<td>0.02</td>
</tr>
<tr>
<td>CHAR4</td>
<td>183</td>
<td>4.90</td>
<td>0.25</td>
<td>n.a.</td>
</tr>
<tr>
<td>CHAR5</td>
<td>427</td>
<td>4.40</td>
<td>0.39</td>
<td>0.06</td>
</tr>
<tr>
<td>AC1</td>
<td>1002</td>
<td>6.10</td>
<td>0.51</td>
<td>0.22</td>
</tr>
<tr>
<td>AC2</td>
<td>984</td>
<td>2.90</td>
<td>0.25</td>
<td>0.14</td>
</tr>
<tr>
<td>CHAR1_KOH</td>
<td>774</td>
<td>4.57</td>
<td>0.41</td>
<td>0.11</td>
</tr>
<tr>
<td>CHAR1_ZnCl2</td>
<td>739</td>
<td>4.85</td>
<td>0.37</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Results - physisorption

Amount adsorbed, cm$^3$/g

Relative pressure, $p/p_0$

Uptake, %

SBET, m$^2$/g
Results

**CHAR1_KOH** → **Adsorption/desorption cycles** to test loss of char adsorption capacity

- High selectivity
- High adsorption capacity
- Good adsorption/desorption kinetics
- Stable adsorption capacity after repeated cycles

**Effective CO₂ adsorbent**
Char collection and characterization

CO₂ adsorption

H₂S adsorption

Other applications
Materials and methods

Adsorptive: \( \text{H}_2\text{S} \)

Adsorbent:
- 5 pure chars
- 2 AC

1 - Adsorption capacity

- Fixed bed reactor - quartz
- Char bed height: 2.5 cm (150 - 200 mg)
- \( \text{H}_2\text{S} + \text{N}_2 \): 100 NmL/min
- \( \text{H}_2\text{S} \): 250 ppm
- \( T_{\text{amb}} \)
- Micro-GC for gas analysis at the outlet

\[
m_{\text{ads}} = f \frac{MPQ}{RTm_{\text{char}}} \int_{0}^{t_{\text{fin}}} (y_{\text{in}} - y_{\text{out}}) \, dt
\]
Materials and methods

2 - Effect of inlet concentration

- Fixed bed reactor - quartz
- Char bed height: 2.5 cm (150 - 200 mg)
- $\text{H}_2\text{S} + \text{N}_2$: 100 NmL/min
- $\text{H}_2\text{S}$: 250 - 550 - 1000 ppm
- $T_{\text{amb}}$
- Micro-GC for gas analysis at the outlet

$$m_{\text{ads}} = \frac{M P Q}{R T m_{\text{char}}} \int_{0}^{t_{\text{fin}}} (y_{\text{in}} - y_{\text{out}}) \, dt$$
Results

H2S adsorption capacity [mg/g]

Char-A 6.88
Char-B 5.41
Char-C 5.38
Char-D 1.61
Char-E 2.77
AC-1 2.35
AC-2 2.61

Effect of surface area

H2S adsorption capacity [mg/g] vs. Char surface area [m²/g]

Literature

1.71 - 65 mg/g AC
0.04 - 0.22 mg/g char from pyrolysis

Results

Effect of ash

Metal content

H2S adsorption capacity [mg/g]
Results

Effects of:

- Oxygen content
- Metals mass fraction
- Surface area
Results - Effect of concentration

Low concentrations slow down the process, but do not affect the adsorption capacity.
Outline

Char collection and characterization

CO$_2$ adsorption

H$_2$S adsorption

Other applications
Char as catalyst support for Fischer-Tropsch synthesis

V. Benedetti et al., Investigating the feasibility of valorizing residual char from biomass gasification as catalyst support in Fischer-Tropsch synthesis, under review.

<table>
<thead>
<tr>
<th>Products distribution</th>
<th>CO conv., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char, 10% Co</td>
<td>8</td>
</tr>
<tr>
<td>Char, 10% Fe</td>
<td>26</td>
</tr>
</tbody>
</table>

Literature 15 - 80
Char as catalyst support for Dry Reforming of Methane (DRM)

Tar removal by thermal and catalytic cracking

Evaluation of tar removal efficiency and analysis of converted products (both condensables and gaseous)

Changing operating conditions

- Effect of temperature 800-1000 °C
- Effect of space velocity
- Effect of tar concentration

Model tar compounds:
- Toluene
- Naphthalene
- Phenol

First stage

Second stage

Other gas mixtures/real tar from lab-scale gasifier
Thank you for your attention

Valorisation of char residues from biomass gasification in adsorption applications

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Website: https://bnb.groups.unibz.it/