Activated biochar-based metal catalysts for steam reforming of pyrolysis bio-oil model compound

Christian Di Stasi 1*, Marta Cortese 2, Gianluca Greco 1, Belén González 1, Vincenzo Palma 2, Joan J. Manyà 1

1 Aragón Institute of Engineering Research (I3A), Technological College of Huesca, University of Zaragoza, crta. Cuarte s/n, Huesca, E-22071, Spain
2 Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy

Correspondence: christiandistasi@unizar.es
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Pyrolysis Conversion Routes for Dry Feedstocks

Hydrothermal Carbonization (HTC) Conversion Routes for Wet Feedstocks

Refining of Biochars and Advanced Applications

Sequential Biochar Systems
Outline

- Introduction
- Objective
- Methodology
- Results
- Conclusions and future work
Introduction

**Objective**

**Methodology**

**Results**

**Conclusions and future work**

**Introduction**

Nitrogen or nitrogen + carbon dioxide (N\textsubscript{2} or N\textsubscript{2}+ CO\textsubscript{2}) is pyrolyzed to produce pyrolysis vapors which include hydrogen (H\textsubscript{2}), methane (CH\textsubscript{4}), carbon monoxide (CO), carbon dioxide (CO\textsubscript{2}), C\textsubscript{2}H\textsubscript{x}, C\textsubscript{3}H\textsubscript{y} + H\textsubscript{2}O + organic condensable fraction.

**Pollutant removal**

**Catalyst/Catalyst support**

**Soil amendment**
Organic condensable fraction (i.e. Bio-oil)

- The high water content lowers the heating value of the products
- Heterogeneous composition depending on the feedstock
- Systems breakdown caused by the condensation in pipes and heat exchangers

- The solution could be represented by the steam reforming of the liquid products
  - Less condensation extent
  - No external water is needed
  - More valuable permanent gases
Introduction

Organic condensable fraction (i.e. Bio-oil)

Composition of bio-oil from slow pyrolysis of eastern redcedar woods\(^a\) (SW/HW450/550 = sapwood/heartwood pyrolyzed at 450/500 °C).

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Group</th>
<th>SW450</th>
<th>HW450</th>
<th>SW500</th>
<th>HW500</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Cellulose/hemicellulose derived compounds (area%)</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>Acid</td>
<td>18.18 ± 1.45</td>
<td>11.25 ± 1.52</td>
<td>18.15 ± 0.16</td>
<td>9.75 ± 1.84</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>Acid</td>
<td>2.42 ± 3.17</td>
<td>2.42 ± 0.36</td>
<td>3.42 ± 0.62</td>
<td>2.32 ± 0.85</td>
</tr>
<tr>
<td>1-Hydroxy-2-butanone</td>
<td>Ketone</td>
<td>2.54 ± 0.31</td>
<td>1.49 ± 0.28</td>
<td>2.09 ± 0.06</td>
<td>1.21 ± 0.26</td>
</tr>
<tr>
<td>Cyclopentanone</td>
<td>Ketone</td>
<td>2.92 ± 0.28</td>
<td>1.79</td>
<td>3.58</td>
<td>1.54 ± 0.13</td>
</tr>
<tr>
<td>2-Cyclopenten-1-one, 2-methyl-</td>
<td></td>
<td>4.42 ± 0.46</td>
<td>1.56 ± 0.56</td>
<td>2.58 ± 0.91</td>
<td>1.51 ± 0.25</td>
</tr>
<tr>
<td>Furfural</td>
<td>Furan</td>
<td>22.69 ± 0.40</td>
<td>26.29 ± 2.16</td>
<td>20.10 ± 3.39</td>
<td>21.80 ± 2.33</td>
</tr>
<tr>
<td>2-Furfuryl methyl</td>
<td>Furan</td>
<td>3.61 ± 1.54</td>
<td>--</td>
<td>1.47 ± 0.26</td>
<td>--</td>
</tr>
<tr>
<td>Ethanone, 1-(2-furanyl)-</td>
<td></td>
<td>0.99 ± 0.15</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2-Furancarboxaldehyde, 5-methyl-</td>
<td>Furan</td>
<td>3.16 ± 0.57</td>
<td>4.46 ± 0.97</td>
<td>2.94 ± 0.21</td>
<td>4.43 ± 0.38</td>
</tr>
<tr>
<td><em>Lignin derived compounds (area%)</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>Aromatic</td>
<td>1.97 ± 1.02</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>Aromatic</td>
<td>1.90 ± 0.14</td>
<td>1.65 ± 0.59</td>
<td>1.54 ± 0.51</td>
<td>1.77 ± 0.67</td>
</tr>
<tr>
<td>Phenol</td>
<td>Phenol</td>
<td>4.27 ± 2.08</td>
<td>3.04 ± 0.12</td>
<td>3.25 ± 1.24</td>
<td>3.55 ± 1.30</td>
</tr>
<tr>
<td>Phenol, 2-methyl-</td>
<td>Phenol</td>
<td>2.43 ± 0.79</td>
<td>2.54 ± 0.19</td>
<td>1.83 ± 0.30</td>
<td>2.71 ± 2.07</td>
</tr>
<tr>
<td>Phenol, 2-methoxy-</td>
<td>Guaiacyl</td>
<td>1.31 ± 0.68</td>
<td>1.67 ± 0.63</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Creosol</td>
<td>Guaiacyl</td>
<td>10.34 ± 1.63</td>
<td>7.98 ± 0.67</td>
<td>10.13 ± 1.82</td>
<td>5.22 ± 0.03</td>
</tr>
<tr>
<td>Cedar oil compounds (area%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(--) alpha-cede-</td>
<td>Olefin</td>
<td>8.39 ± 1.12</td>
<td>12.97 ± 1.08</td>
<td>8.65 ± 1.46</td>
<td>18.15 ± 0.74</td>
</tr>
<tr>
<td>(+) beta- cede-</td>
<td>Olefin</td>
<td>2.27 ± 0.32</td>
<td>1.93 ± 0.93</td>
<td>1.81 ± 0.10</td>
<td>2.89 ± 0.34</td>
</tr>
</tbody>
</table>

\(^{a}\) Values listed above are means ± standard deviation of two subsamples.

Due to the numerous compounds present in a real bio-oil, model compounds such as acetic acid (AcOH), ethanol, benzene, toluene and eugenol, are usually employed to study the reaction system.

\(^{b}\) means the relative peak area percentage of the detected compound is less than 0.5%.

1. Production of physically activated biochar with proper specific textural properties to be employed as catalyst support

2. Production of mono and bimetallic biochar-supported catalysts

3. Test of the produced catalysts for the steam reforming of acetic acid (AcOH) as bio-oil model compound
Biochar Activation (i.e. Catalysts Support Production)

\[ \text{CO}_2 + C \rightleftharpoons 2 \text{CO} \]

T=700°C; P= 1.0 MPa; CO\(_2\) = 100 vol.%; t= 2.5 h

<table>
<thead>
<tr>
<th>Material</th>
<th>Apparent specific surface area (m(^2) g(^{-1}))</th>
<th>Specific pore volume (cm(^3) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(S_{\text{BET}}^a)</td>
<td>(S_{\text{BET}}^b)</td>
</tr>
<tr>
<td>BC</td>
<td>1.68</td>
<td>72.4</td>
</tr>
<tr>
<td>ActBC</td>
<td>743</td>
<td>414</td>
</tr>
</tbody>
</table>

\(^a\) Determined from N\(_2\) adsorption data a –196 °C.

\(^b\) Determined from CO\(_2\) adsorption data a 0 °C.

*BC=wheat straw biochar produced at 500°C and 0.1 MPa
Catalyst synthesis

**Objective**

**Introduction**

**Methodology**

- Wet impregnation
- Calcination at 600°C in N₂

**Results**

**Monometallic**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Active phase</th>
<th>Load (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>BCFe</td>
<td>Fe</td>
<td>7</td>
</tr>
<tr>
<td>BCCo</td>
<td>Co</td>
<td>7</td>
</tr>
<tr>
<td>BCCe</td>
<td>Ce</td>
<td>7</td>
</tr>
<tr>
<td>BCK</td>
<td>K</td>
<td>7</td>
</tr>
<tr>
<td>BCNi7</td>
<td>Ni</td>
<td>7</td>
</tr>
<tr>
<td>BCNi4</td>
<td>Ni</td>
<td>4</td>
</tr>
<tr>
<td>BCNi10</td>
<td>Ni</td>
<td>10</td>
</tr>
</tbody>
</table>

**Bimetallic**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Active phase</th>
<th>Load (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCFeNi</td>
<td>Fe/Ni</td>
<td>7/10</td>
</tr>
<tr>
<td>BCCoNi</td>
<td>Co/Ni</td>
<td>7/10</td>
</tr>
<tr>
<td>BCCeNi</td>
<td>Ce/Ni</td>
<td>7/10</td>
</tr>
<tr>
<td>BCKNi</td>
<td>K/Ni</td>
<td>7/10</td>
</tr>
</tbody>
</table>
Steam reforming of AcOH

Acetic acid + water

\[ X_{\text{AcOH}} = \left( F_{\text{AcOH, in}} - F_{\text{AcOH, out}} \right) \frac{F_{\text{AcOH, in}}}{100} \]
\[ Y_{\text{H2}} = F_{\text{H2, out}} \left( 4 F_{\text{AcOH, in}} \right) \frac{F_{\text{AcOH, in}}}{100} \]
\[ Y_{\text{Ac}} = 2 F_{\text{Ac, out}} \frac{F_{\text{AcOH, in}}}{100} \]

T = 400 - 600°C
P = 0.1 MPa
\( t_r = 135 \text{ ms} \)
\( \text{molH}_2\text{O/molAcOH} = 4 \)

AcOH, Acetone, H\(_2\), CO\(_2\), CO, CH\(_4\)

Quadrupole mass spectrometer analyzer

Introduction Objective Methodology Results Conclusions and future work
Monometallic catalysts

Best performances with the Ni-based catalysts (no deactivation)

10% Ni loading represented the best tradeoff between conversion and stability (less coke deposition)

T=600°C

Introduction  Objective  Methodology  Results  Conclusions and future work
Bimetallic catalysts

*BCNi was very unstable. Therefore the results are not reported.*

- **BCFeNi**
  - Low conversions and hydrogen yields, even at high temperature

- **BCCeNi**
  - High conversions from 550 to 600°C.
  - Acetone yield not negligible.

- **BCCoNi**
  - Highest conversions, close to the equilibrium, even at 475°C.
  - No acetone production.
Cycling stability test of BCCoNi

- Constant AcOH conversion and pressure drop value from 600 to 475 °C.
- When the reactor was heated up again, the pressure drop increased again until the set temperature was reached.
- The final conversion was the same that that measured for the fresh catalyst, indicating negligible deactivation extent.
Conclusions and future work

• The physically activated biochar showed an excellent potential to be employed as support for metal active phases.

• Most of the tested metal catalysts showed rapid deactivation degree probably due to high coke deposition and/or sintering of the active phases.

• Among the monometallic catalysts, the Ni-based showed negligible deactivation rates. In particular a loading of 10 wt. % guaranteed a good tradeoff between performances and coke deposition.

• The Co-Ni bimetallic catalyst showed the best results obtained in this study, with high conversions even at low temperatures and almost no coke production.
Conclusions and future work

• Deep catalysts characterization (FT-IR, Raman, SEM, XRD).

• Add more model compounds to better simulate a real bio-oil composition.
Thank you for your attention

christiandistasi@unizar.es

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