Types of Carbon in Biochars from Slow Pyrolysis, Fast Pyrolysis and Gasification

Catherine Brewer, Klaus Schmidt-Rohr, Robert Brown

Center for Sustainable Environmental Technologies (CSET) & Department of Chemistry

Iowa State University

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Outline

- Biochar for soils & carbon sequestration
- Initial characterization: methodology
- Extent of pyrolysis
- Conclusions & future work
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• Biochar for soils & carbon sequestration
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• Conclusions & future work
Uses for Char

**Fuel**
- Combustion
- Heat
- Power
- Gasification

**Activated Carbon/Sorbent**
- Water Purification
- Gas Purification
- Site Remediation

**Biochar**
- Soil Amendment
- Carbon Sequestration
### Thermochemical Processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Temperature Range (°C)</th>
<th>Heating Rate</th>
<th>Pressure</th>
<th>Residence Time</th>
<th>Primary Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow Pyrolysis</td>
<td>350-800</td>
<td>Slow (&lt;10°C/min)</td>
<td>Atmospheric</td>
<td>Hours-Days</td>
<td>Char</td>
</tr>
<tr>
<td>Torrefaction</td>
<td>200-300</td>
<td>Slow (&lt;10°C/min)</td>
<td>Atmospheric</td>
<td>Minutes-Hours</td>
<td>Stabilized, friable biomass</td>
</tr>
<tr>
<td>Fast Pyrolysis</td>
<td>400-600</td>
<td>Very Fast (~1000°C/s)</td>
<td>Vacuum-Atmospheric</td>
<td>Seconds</td>
<td>Bio-oil</td>
</tr>
<tr>
<td>Flash Pyrolysis</td>
<td>300-800</td>
<td>Fast</td>
<td>Elevated</td>
<td>Minutes</td>
<td>Biocarbon/Char</td>
</tr>
<tr>
<td>Gasification</td>
<td>700-1500</td>
<td>Moderate-Very Fast</td>
<td>Atmospheric-Elevated</td>
<td>Seconds-Minutes</td>
<td>Syngas/Producer gas</td>
</tr>
<tr>
<td>Combustion</td>
<td>&gt;350</td>
<td>Varies</td>
<td>Atmospheric</td>
<td>Varies</td>
<td>Energy</td>
</tr>
</tbody>
</table>
Terra Preta Soils

Examples of Amazonian Dark Earths in comparison to a typical jungle soil profile.

Top left: Hatahara site.
Top right: deep terra preta.
Middle: Laranjal Coast.
Bottom left: Açutuba Coast.
Bottom right: typical jungle Oxisol soil profile.

(Source: Newton Falcão, Instituto Nacional de Pesquisas da Amazônia, Manaus, Brazil.)
Terra Preta & Terra Mulata

*Terra preta, terra mulata* and the adjacent Latassol soil from a site in the central Amazon. All three soils have similar soil texture.

Biochar Effects on Soils

Increases:
- Nutrient Availability
- Microbial Activity
- Soil Organic Matter
- Water Retention & Quality
- Crop Yields

Decreases:
- Fertilizer Needs
- Greenhouse Gas Emissions
- Nutrient Leaching
- Soil Bulk Density
Carbon Continuum

Carbon Sequestration


Graphic design by Christine Hobbs.
Carbon Residence Time


Graphic design by Christine Hobbs.
Biochar Engineering

Characterization: What kind of char did we make?

Production: How do we make good biochar?

Soil Testing: How well does our char work?

Formulation: What is good biochar?
Outline

• Biochar for soils & carbon sequestration
• Initial characterization: methodology
• Extent of pyrolysis
• Conclusions & future work
Initial Characterization Study

Used seven chars to develop characterization methods:

• Switchgrass slow pyrolysis (S.P.), fast pyrolysis (F.P.) & gasification
• Corn stover slow pyrolysis, fast pyrolysis & gasification
• Commercial hardwood slow pyrolysis
## Proximate Analysis

<table>
<thead>
<tr>
<th>Char</th>
<th>Moisture</th>
<th>Volatiles</th>
<th>Fixed C</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char Moisture Volatiles Fixed C Ash wt%--</td>
<td>----------</td>
<td>-----------</td>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>Switchgrass slow pyrolysis</td>
<td>0.9</td>
<td>7.1</td>
<td>39.5</td>
<td>52.5</td>
</tr>
<tr>
<td>Switchgrass fast pyrolysis</td>
<td>2.7</td>
<td>16.4</td>
<td>26.4</td>
<td>54.6</td>
</tr>
<tr>
<td>Switchgrass gasification</td>
<td>2.5</td>
<td>10.3</td>
<td>34.3</td>
<td>53.0</td>
</tr>
<tr>
<td>Corn stover fast pyrolysis</td>
<td>1.8</td>
<td>11.1</td>
<td>54.7</td>
<td>32.4</td>
</tr>
<tr>
<td>Corn stover gasification</td>
<td>1.0</td>
<td>14.9</td>
<td>34.4</td>
<td>49.7</td>
</tr>
<tr>
<td>Hardwood charcoal</td>
<td>2.6</td>
<td>19.7</td>
<td>63.8</td>
<td>13.9</td>
</tr>
</tbody>
</table>

### Inorganic Composition by XRD

<table>
<thead>
<tr>
<th>Element</th>
<th>Switchgrass Fast Pyrolysis Char</th>
<th>Corn Stover Fast Pyrolysis Char</th>
<th>Hardwood Charcoal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>0.49</td>
<td>2.33</td>
<td>0.60</td>
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<tr>
<td>CaO</td>
<td>3.65</td>
<td>3.80</td>
<td>22.37</td>
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<tr>
<td>Cl</td>
<td>0.47</td>
<td>0.59</td>
<td>0.03</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.76</td>
<td>1.87</td>
<td>2.36</td>
</tr>
<tr>
<td>K₂O</td>
<td>6.00</td>
<td>4.03</td>
<td>1.35</td>
</tr>
<tr>
<td>MgO</td>
<td>1.55</td>
<td>2.02</td>
<td>0.48</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>3.86</td>
<td>1.19</td>
<td>0.20</td>
</tr>
<tr>
<td>SiO₂</td>
<td>43.62</td>
<td>29.98</td>
<td>5.67</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.99</td>
<td>0.28</td>
<td>0.27</td>
</tr>
<tr>
<td>Other</td>
<td>0.47</td>
<td>0.97</td>
<td>1.40</td>
</tr>
</tbody>
</table>
### Elemental Analysis

<table>
<thead>
<tr>
<th>Char</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>--wt%--</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Switchgrass slow pyrolysis</td>
<td>65</td>
<td>2.8</td>
<td>1.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Switchgrass fast pyrolysis</td>
<td>39</td>
<td>1.7</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Switchgrass gasification</td>
<td>44</td>
<td>0.9</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Corn stover fast pyrolysis</td>
<td>37</td>
<td>2.0</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Corn stover gasification</td>
<td>38</td>
<td>1.0</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Hardwood charcoal</td>
<td>66</td>
<td>2.6</td>
<td>0.7</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

Photoacoustic FTIR

Solid-State $^{13}$C Nuclear Magnetic Resonance Spectroscopy (NMR)

- **Qualitative** $^1$H-$^{13}$C cross polarization magic angle spinning (CP/MAS) with total suppression of spinning sidebands (TOSS)

- **Quantitative** $^{13}$C direct polarization (DP/MAS), a.k.a. Bloch Decay

- DP/MAS with dipolar dephasing, a.k.a. “gated decoupling” (GADE)

- DP/MAS with recoupled dipolar dephasing, a.k.a. “gated re-coupling” (GARE)
CP/TOSS Spectra

DP/MAS & DP/GADE Spectra

(a) Slow pyrolysis (500°C)

- All C: 130 ppm
- Cq
- C=O
- CH$_3$
- OCH
- SSB

(b) Fast pyrolysis (500°C)

- 35% aromatic C-H: 131 ppm
- C-O
- CH$_3$
- SSB

(c) Gasification (760°C)

- 24% aromatic C-H: 127 ppm
- C=O
- OCH
- CH$_3$
- Alkyl

## Carbon Composition

<table>
<thead>
<tr>
<th>Moieties: ppm:</th>
<th>Carbonyls</th>
<th>Aromatics</th>
<th>Alkyls</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C=O 210-183</td>
<td>COO 183-165</td>
<td>C-O$<em>{0.75}$H$</em>{0.5}$ 165-145</td>
</tr>
<tr>
<td>Switchgrass S. P.</td>
<td>0.8%</td>
<td>1.4%</td>
<td>6.7%</td>
</tr>
<tr>
<td>Switchgrass F. P.</td>
<td>3.3%</td>
<td>3.2%</td>
<td>10.3%</td>
</tr>
<tr>
<td>Switchgrass Gasification</td>
<td>2.0%</td>
<td>2.2%</td>
<td>6.4%</td>
</tr>
<tr>
<td>Corn Stover F. P.</td>
<td>3.5%</td>
<td>4.2%</td>
<td>11.7%</td>
</tr>
<tr>
<td>Corn Stover Gasification</td>
<td>2.5%</td>
<td>2.8%</td>
<td>8.2%</td>
</tr>
</tbody>
</table>

## Aromatic Condensation

<table>
<thead>
<tr>
<th>Char</th>
<th>Aromaticity</th>
<th>$\chi_{\text{CH}}$</th>
<th>$\chi_{\text{edge,min}}$</th>
<th>$\chi_{\text{edge,max}}$</th>
<th>$n_{\text{C,min}}$</th>
<th>$H_{\text{arom}}/H_{\text{alk}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Switchgrass S. P.</td>
<td>94%</td>
<td>0.37</td>
<td>0.44</td>
<td>0.51</td>
<td>$&gt;23$ C</td>
<td>4.5</td>
</tr>
<tr>
<td>Switchgrass F. P.</td>
<td>83%</td>
<td>0.29</td>
<td>0.41</td>
<td>0.61</td>
<td>$&gt;16$ C</td>
<td>1.2</td>
</tr>
<tr>
<td>Switchgrass Gasification</td>
<td>86%</td>
<td>0.17</td>
<td>0.25</td>
<td>0.40</td>
<td>$&gt;37$ C</td>
<td>1.4</td>
</tr>
<tr>
<td>Corn Stover F. P.</td>
<td>81%</td>
<td>0.33</td>
<td>0.48</td>
<td>0.72</td>
<td>$&gt;12$ C</td>
<td>1.2</td>
</tr>
<tr>
<td>Corn Stover Gasification</td>
<td>87%</td>
<td>0.21</td>
<td>0.30</td>
<td>0.44</td>
<td>$&gt;31$ C</td>
<td>2</td>
</tr>
</tbody>
</table>

Biochar Models

*Sustainable Energy 2009, 28, 386-396*
Outline

• Biochar for soils & carbon sequestration
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• Conclusions & future work
Motivation

When characterizing corn stover fast pyrolysis chars by qualitative NMR, a very distinct pattern was noticed between biomass and biochar.

Want to identify what effects **extent of fast pyrolysis** has on char characteristics and soil properties.
## Amendment Properties

<table>
<thead>
<tr>
<th></th>
<th>Corn stover</th>
<th>Biochar 1</th>
<th>Biochar 2</th>
<th>Biochar 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (%)</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Volatiles (%)</td>
<td>73</td>
<td>26</td>
<td>17</td>
<td>14</td>
</tr>
<tr>
<td>Fixed carbon (%)</td>
<td>10</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>14</td>
<td>46</td>
<td>56</td>
<td>59</td>
</tr>
<tr>
<td>C (%)</td>
<td>41</td>
<td>35</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>H (%)</td>
<td>6</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>N (%)</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>S (%)</td>
<td></td>
<td>0.06</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>O (% by difference)</td>
<td>39</td>
<td>14</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>H/C molar ratio</td>
<td>1.81</td>
<td>0.99</td>
<td>0.77</td>
<td>0.63</td>
</tr>
<tr>
<td>O/C molar ratio</td>
<td>0.72</td>
<td>0.30</td>
<td>0.22</td>
<td>0.20</td>
</tr>
<tr>
<td>C/N molar ratio</td>
<td>68</td>
<td>51</td>
<td>54</td>
<td>46</td>
</tr>
<tr>
<td>Fixed carbon/volatiles</td>
<td>0.14</td>
<td>0.95</td>
<td>1.49</td>
<td>1.83</td>
</tr>
<tr>
<td>NMR Aromaticity (%^{13}C)</td>
<td>62</td>
<td>75</td>
<td>81</td>
<td></td>
</tr>
</tbody>
</table>
Van Krevelen Plot

- Keiluweit, et al. wood
- Keiluweit, et al. grass
- Bridgeman, et al. wood
- Bridgeman, et al. grass
- Bridgeman, et al. straw
- Baldock & Smernik red pine
- Stover
- Biochar 1
- Biochar 2
- Biochar 3
Quantitative $^{13}$C NMR

<table>
<thead>
<tr>
<th>Moiety:</th>
<th>Carbonyl</th>
<th>Aromatic</th>
<th>Alkyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range (ppm):</td>
<td>C=O</td>
<td>COO</td>
<td>CO$<em>{0.75}$H$</em>{0.5}$</td>
</tr>
<tr>
<td>210-183</td>
<td>4.0</td>
<td>11.2</td>
<td>165-145</td>
</tr>
<tr>
<td>Biochar 1</td>
<td>4.0</td>
<td>11.2</td>
<td>165-145</td>
</tr>
<tr>
<td>Biochar 2</td>
<td>4.1</td>
<td>11.4</td>
<td>165-145</td>
</tr>
<tr>
<td>Biochar 3</td>
<td>3.4</td>
<td>11.6</td>
<td>165-145</td>
</tr>
</tbody>
</table>

Note: The values represent the percentage of the respective moieties in each Biochar sample.
Incubation Study

- Sparta loamy fine sand (87% sand, 4 % clay)
- 0.5 wt % Amendment
- N, P, S nutrient solution to 10% moisture
- Incubate in the dark at 23°C for 24 weeks
- Soil sampling at week 8
- 9 replicates
- CO₂ evolution measured by alkali trap
Soil Respiration Rates

Incubation time (days)

Rate of evolution (mg CO₂-C/100g soil * day)

- Stover
- Biochar 1
- Biochar 2
- Biochar 3
- Control
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Conclusions

• The types of carbon in biochars are most affected by the highest temperature reached.
• Heating rate and residence time also have effects:
  ▫ Fast pyrolysis chars have more O-containing functional groups.
  ▫ Slow pyrolysis chars have more H-containing surface groups.
• Extent of pyrolysis provides consistent patterns in types of carbon present.
Future Work

- Effects of temperature on carbon composition within a less kinetically-controlled regime
- Effects of oxygen in reaction atmosphere at various stages of pyrolysis
- Safety of fast pyrolysis biochars
References

- Bridgeman, T. G.; Jones, J. M.; Shield, I.; Williams, P. T. *Fuel* **2008**, *87*, 844-856.
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- Thomas Loynachan (soil study)
- John McClelland and Roger Jones (FTIR)
- Scott Schlorhotz (XRD)
Questions?