Pyrolysis Characteristics of White Pine and Norway Spruce Needles and Properties of Resulting Biochars

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Presented at the USBI Biochar 2018, Wilmington, Delaware
11:40 AM - 12:05 PM, Wednesday, August 22 2018
Acknowledgements

Funding
1. United States Department of Agriculture McStennis Grant Program (Accession No. 1007044)
2. WV Energy Institute O’Brian Research Award
3. United State Department of Agriculture through Northeast SunGrant Initiative

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Biochar/Activated Carbons/Porous Carbons

Can any feedstock processed through any technology produce porous carbons suitable for all applications?

- Wood
- Forest Residues
- Crop Residues
- Manure
- Municipal Solid Waste
- Poultry Litter
- Undefined Organic Matter

Technology:
- Pyrolysis
- Gasification

Applications:
- BioChars
  - For combustion
  - As an absorbent
  - Soil amendment
  - Catalyst development
  - Agriculture/Horticulture
  - Waste water treatment
  - Electrochemical Devices

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### Characteristics of Porous Carbons as an absorbent

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Densities</strong></td>
<td>• Material density</td>
</tr>
<tr>
<td></td>
<td>• Bed density</td>
</tr>
<tr>
<td></td>
<td>• Particle density</td>
</tr>
<tr>
<td><strong>Porosity</strong></td>
<td>• Particle Porosity</td>
</tr>
<tr>
<td></td>
<td>• Bulk Porosity</td>
</tr>
<tr>
<td><strong>Surface Area</strong></td>
<td>• Internal</td>
</tr>
<tr>
<td></td>
<td>• External</td>
</tr>
<tr>
<td><strong>Pore Size Distribution</strong></td>
<td>• Macropore &gt; 25 nm</td>
</tr>
<tr>
<td></td>
<td>• Mesopore 1nm to 25 nm</td>
</tr>
<tr>
<td></td>
<td>• Micropores &lt; 1 nm</td>
</tr>
<tr>
<td><strong>Surface Chemistry</strong></td>
<td>• Surface functionalities</td>
</tr>
<tr>
<td></td>
<td>• Acidic</td>
</tr>
<tr>
<td></td>
<td>• Basic</td>
</tr>
<tr>
<td></td>
<td>• Oxygenated groups</td>
</tr>
<tr>
<td><strong>Nature of Carbon Surface</strong></td>
<td>• Diamond</td>
</tr>
<tr>
<td></td>
<td>• Graphitic</td>
</tr>
<tr>
<td></td>
<td>• Amorphous</td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td>• Surface charge</td>
</tr>
<tr>
<td></td>
<td>• Surface energy</td>
</tr>
<tr>
<td><strong>Application</strong></td>
<td>Removal of Acetaminophen from wastewater</td>
</tr>
<tr>
<td></td>
<td>Molecule size of acetaminophen: 1.25 nm</td>
</tr>
<tr>
<td></td>
<td>Minimum Pore Size Needed: about 2.5 nm or larger</td>
</tr>
<tr>
<td></td>
<td>Surface: Partially Graphitic but more disordered carbon surface</td>
</tr>
</tbody>
</table>
Selection of Feedstock is Important

Because we cannot create pore structure totally, otherwise most commercial applications would have use graphite only.
Our Research on Porous Carbons- Since 2004- Ongoing

• Poultry Litter Biochars
• Forest Residue Biochars
• Herbaceous Biomass Biochars
• Woody Biomass Biochars
• Selected Forest Materials

Focused Applications
• As an absorbent for agricultural nutrients and pharmaceutical compounds
• As an electrode material for electrochemical devices

6 research project and 12 published journal articles
Our Search for Porous Carbons for Cost Effective Electrode Materials


## Recent Work: Herbaceous Biomass Crop for Porous Carbon Production

<table>
<thead>
<tr>
<th>Source</th>
<th>Biomass</th>
<th>Properties $S_{\text{BET}}$</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ducey et al. [5]</td>
<td>Switchgrass</td>
<td>218.7 m²/g</td>
<td>Steam Activation. Used for soil amendment</td>
</tr>
<tr>
<td>Shim et al. [6]</td>
<td>Miscanthus</td>
<td>322 m²/g</td>
<td>Cu Sorption</td>
</tr>
<tr>
<td>Kalyani et al. [7]</td>
<td>Turf grass</td>
<td>250 m²/g</td>
<td>Chemical activation (ZnCl₂) Used for electrolysis of water for hydrogen production</td>
</tr>
<tr>
<td>Our Ongoing Research</td>
<td>Switchgrass</td>
<td>1372 m²/g</td>
<td>Chemical activation (H₃PO₄) Used for electrode materials for energy storage devices</td>
</tr>
</tbody>
</table>

• KOH-activated biomass (KOH-K) showed higher capacitance even after 1000 cycles.
• KOH activation is found to be more effective than H$_3$PO$_4$ activation.
## Surface Area and Pore Characteristics of Tested Porous Carbons

<table>
<thead>
<tr>
<th></th>
<th>BET Surface area (m²/g)</th>
<th>Micropore volume a (cm³/g)</th>
<th>Cumulative volume b (cm³/g)</th>
<th>Pore diameter c (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>&lt; 5.0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>H₃PO₄-Biomass</td>
<td>1372.9</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KOH-Biomass</td>
<td>1271.7</td>
<td>0.22</td>
<td>0.10</td>
<td>1.69</td>
</tr>
<tr>
<td>KOH-Biochar</td>
<td>698.0</td>
<td>0.12</td>
<td>0.62</td>
<td>1.65</td>
</tr>
</tbody>
</table>

(a) t-Plot micropore volume | (b) BJH Desorption cumulative volume of pores between 0.70 nm and 50.0 nm diameter | (c) BJH Desorption average pore diameter (4V/A)

We concluded that we need porous carbon with more micropore volume. **Find New Feedstock!!!!**

- KOH impregnation produced porous carbons with about half of internal pore volume made-up of micropores, whereas, H₃PO₄ produced mostly mesoporous carbons.
Searching for Microporous Carbons

White Pine Needles
Needle Leaves Survive Harsh Winter (-22 to -40°F), Why?

• Possible Reasons:
  • Leaves have sap (mixture of chemicals) that prevent cells from freezing
  • Leaves have lot of micropores that act as safe heaven for sap/liquid and not allowing them to freeze
Needle Leaves Survive Harsh Winter (-22 to -40°F), Why?

Significant depression in the freezing point ($\Delta T_m$) of pure water in small pores may be predicted the Gibbs–Thomson equation $^1$. For a pure substance in a cylindrical pore of radius $R$ (nm):

$$\Delta T_m = \frac{51.9}{R}$$

<table>
<thead>
<tr>
<th>Pores</th>
<th>Freezing Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>macropores (&gt;50 nm)</td>
<td>-1.03 °C or 30.14 °F</td>
</tr>
<tr>
<td>mesopores (&gt;2 nm)</td>
<td>-25.95 °C or -14.71 °F</td>
</tr>
<tr>
<td>micropore (&lt;1 nm)</td>
<td>-51.9 °C or -61.42 °F</td>
</tr>
</tbody>
</table>
Objective

- To compare pyrolysis behavior of White Pine and Norway Spruce needles and investigate characteristics of resulting biochars.
Processing and Characterization of Biomass

- Sample harvesting
- Sample drying
- Sample size reduction <1 mm for Characterization

Characterization

- Proximate Analysis: Ash, Volatile and Fixed carbon
- Ultimate Analysis: Carbon, Hydrogen, Nitrogen, Sulfur, Oxygen
- Chemical Composition: Cellulose, Hemicellulose, Lignin, mineral analysis
Biochar Production

Biomass

Drying 103 °C, 24 h

Carbonization Temperature: 500, 700 & 900 °C
Duration: 30 min
Gas: N₂

Biochar

Characterizations: BET Surface Area, Pore Volumes, Scanning Electron Microscopy, pH, R₅₀, Electrical conductivity, Specific gravity

Testing: Adsorption Kinetics and Equilibrium
## Testing - Adsorption Kinetics and Equilibrium

![Slurry Batch Reactor](image.png)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Caffeine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular structure</td>
<td><img src="image.png" alt="Caffeine Molecular Structure" /></td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>194.2</td>
</tr>
<tr>
<td>Molecular size (nm)</td>
<td>0.98 x 0.87</td>
</tr>
<tr>
<td>Use/category</td>
<td>Stimulant</td>
</tr>
</tbody>
</table>

Image Sources:
- [is-acetaminophen-a-blood-thinner](http://www.thrombocyte.com/is-acetaminophen-a-blood-thinner/)
- [things-you-should-know-about-caffeine](https://www.cbsnews.com/media/things-you-should-know-about-caffeine/)
Pore Structure of BioChars

• consists of crystallites with a strongly disturbed graphite structure.

• randomly oriented and interconnected by carbon cross-links.

• The micropores are formed by the voids between the crystallites.

• Slit-like pores are found.
How Does BioChars Work?

- **Physical Adsorption**-
  - It is caused by weak interactions of van der Waals forces (induction forces, dipole-dipole interactions, dispersion forces).
  - \( H_{\text{ads}} < 50 \text{ kJ/mol} \)

- **Chemical Adsorption**-
  - It is caused by chemical reaction between adsorbate and surface sites.
  - \( H_{\text{ads}} > 50 \text{ kJ/mol} \)

Theoretical Thermodynamic Considerations


When adsorption takes place:

$$\sigma_{ws} - \sigma_{as} = \pi > 0$$

For adsorption to take place, change in free energy must be negative:

$$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} < 0$$

, since

$$\Delta S_{ads} < 0$$

$$\Delta H_{ads} < 0$$

Adsorption is a Exothermic process
Adsorption Mass Transport Theory

**Adsorbent Loading** \( (q) = \frac{\text{Adsorbed Amount}}{\text{Adsorbent Mass}} \)

**Adsorption Equilibrium**
\[ q = f(C, T) \]

**Adsorption Kinetics**
\[ q = f(t) \text{ or } C = f(t) \]

**Adsorption Dynamics**
\[ q = f(t, z) \text{ or } C = f(t, z) \]

**Sources:** Worch, E., *Adsorption technology in water treatment: fundamentals, processes, and modeling*. Walter de Gruyter: 2012
Adsorption Testing - Single Solute System

**Adsorption Kinetics**

\[ C = f(t) \]

- Solute Concentration = 40 ppm
- Solution pH = 6.21
- Durations = 0.25, 0.50, 1, 3, 5, 7, and 9 hours
- Temperature = 25 °C
- Adsorbent Loading = 10 mg
- Solution volume = 40 ml

**Adsorption Equilibrium**

\[ q = f(C, T); T = \text{Constant} \]

- Solute Concentrations (ppm) = 10, 20, 30, 40
- Solution pH = 6.21
- Duration = 5 hours
- Temperature = 25 °C
- Adsorbent Loading = 10 mg
- Solution volume = 40 ml

Adsorption Kinetics - The pseudo-second order kinetic model

\[ q_t = \frac{C_0 - C_t}{W} V \]

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t \]

- \( C_0 = \) initial concentration (ppm),
- \( C_t = \) concentration at time \( t \) (ppm),
- \( V = \) volume of the adsorbate solution (ml),
- \( W = \) weight of the activated carbon used (mg), and
- \( q_t = \) amounts of the adsorbate adsorbed at time \( t \) (mg/g)

- \( q_e = \) amounts of the adsorbate adsorbed at equilibrium (mg/g),
- \( t = \) time (min)
- \( k_2 = \) equilibrium rate constant (g/mg.min),
- \( k_2 \) and \( q_e \) can be estimated from the intercept and slope, respectively, of the plot of \( t/q_t \) versus \( t \),
- \( h = k_2q_e^2 \) = the initial adsorption rate (mg/g.min),
- \( t_{1/2} = \) the time required for the adsorbent to uptake half of the adsorbate amount=

\[ t_{1/2} = \frac{1}{k_2q_e} \]

Adsorption Equilibrium

Langmuir isotherm model

$$q_e = \frac{q_m \cdot b \cdot C_e}{1 + b \cdot C_e}$$

- $q_e$ = equilibrium quantity adsorbed (mg/g)
- $C_e$ = equilibrium concentration of adsorbate (ppm)
- $q_m$ = maximum adsorption capacity (mg/g)
- $b$ = Langmuir constant (1/ppm)
- $q_m$ and $b$ can be determined from the linear plot of $C_e/q_e$ versus $C_e$.

Freundlich Isotherm Model

$$lnq_e = lnK_f + \frac{1}{n} lnC_e$$

- $K_f$ = strength of adsorption
- $n$ = energetic heterogeneity of adsorbent surface
- The values of $n$ and $K_f$ can be obtained from the slope and intercept of the linear plot of $lnq_e$ versus $lnC_e$. 

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Results - Biomass Characterization

• Both biomass appears to be producing 25-26% biochars and lost 75% of their mass during heating.
• Heating faster or slower does not appear to have much effect on biochar yields or mass loss.
Results - Thermo-Chemical Decomposition Behavior

White Pine Needles

Results - Pyrolysis Biochar Yields

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>White Pine Yield (%)</th>
<th>Norway Spruce Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>29.96</td>
<td>33.36</td>
</tr>
<tr>
<td>700</td>
<td>28.73</td>
<td>29.78</td>
</tr>
<tr>
<td>900</td>
<td>23.48</td>
<td>22.87</td>
</tr>
</tbody>
</table>
• pH of the biochars showed that they are alkaline in nature. This is a good indicator that the biochars will be good for amending acidic soils.
Results - Biochar Characteristics

Proximate Composition of Biochars

- Fixed Carbon
- Volatile
- Ash
- Calorific Value (MJ/kg)

- WP 500
- WP 700
- WP 900
- NS 500
- NS 700
- NS 900
Results - Biochar Characteristics

Harvey classification of Biochar Thermal Recalcitrance

<table>
<thead>
<tr>
<th>Thermal Recalcitrance</th>
<th>Class C</th>
<th>Class B</th>
<th>Class A</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{50}$</td>
<td>Highly susceptibility to biodegradation</td>
<td>Some susceptibility to biodegradation</td>
<td>Minimal susceptibility to biodegradation</td>
</tr>
<tr>
<td>$&lt; 0.50$</td>
<td>$0.50 &lt; R_{50} &lt; 0.70$</td>
<td>$&gt; 0.70$</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Thermal Recalcitrance values ($R_{50}$) of Biochars

<table>
<thead>
<tr>
<th>Pyrolysis Temp (°C)</th>
<th>White Pine</th>
<th>Norway Spruce</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.50</td>
<td>0.47</td>
</tr>
<tr>
<td>700</td>
<td>0.53</td>
<td>0.49</td>
</tr>
<tr>
<td>900</td>
<td>0.64</td>
<td>0.51</td>
</tr>
</tbody>
</table>

97-99% pores were made-up of micropores
Switchgrass Biochar’s Pore Characteristics

For effective adsorption, the pore diameter of the activated carbon has to be 1.7 to 2 times bigger than the adsorbate dimension.

Micropores

Mesopores
Results - Ultrastructure of Biochars

White Pine Biochar 500
White Pine Biochar 900
Norway Spruce Biochar 500
Norway Spruce Biochar 900
Langmuir isotherm model provides the better fit for the adsorption of caffeine than the Freundlich model.

The Langmuir isotherm model assumes the surface of the activated carbon is energetically homogenous and that a monolayer surface coverage is formed with no interactions between the molecules adsorbed.
Switchgrass-Derived Biochars had caffeine absorption of 140.85 mg/g, 14 times higher.
Take Home Message:
Carefully select feedstock that is suitable to produce porous carbons for the intended application.
Thank you for your undivided attention!!!!!!

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