Session 1
Biochar and Torrefied Biomass Short Course
Penn State Bioenergy Short Course Series

Principles of Pyrolysis

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Biomass Conversion Pathways

<table>
<thead>
<tr>
<th>Thermochemical Conversion</th>
<th>Biochemical Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass molecules broken down by heat (and sometimes pressure).</td>
<td>Biomass molecules broken down by bacteria or enzymes.</td>
</tr>
</tbody>
</table>

**Example Processes:**
- Combustion (Excess air)
- Gasification (Partial air)
- Pyrolysis (No air)
- Hydrothermal Carbonization
- Hydrothermal Liquefaction

**Example Processes:**
- Acid Hydrolysis
- Aerobic Digestion
- Anaerobic Digestion
- Enzymatic Hydrolysis
- Fermentation

Rapidly produce solid, liquid and gas fuels and/or materials in batch or continuous processes.

Slower than thermochemical conversions, batch processes, but require less energy than thermochemical conversions.
Biomass Valorization: A Balancing Act

Biochar: carbon-rich product obtained by heating biomass with no oxygen (air)

Potential Production Volume

Adapted from: Budzianowski, Wojciech M. "High-value low-volume bioproducts coupled to bioenergies with potential to enhance business development of sustainable biorefineries." Renewable and Sustainable Energy Reviews (2016).

Why Biochar? The Carbon Cycle

The Global Carbon Cycle

Interrupting the Carbon Cycle with Biochar

**Terra preta (Amazonian dark earth)**

![Diagram of the Carbon Cycle](https://www.biochar.org/joomla/index.php?option=com_content&task=view&id=67&Itemid=7&limit=1&limitstart=4)

![Image of biochar and soil samples](https://agreport.bz/2017/08/biochar-implementation-agricultural-systems-of-belize/)

**Fig. 3** Photographs showing, from left to right, 10 g biochar from pyrolysis of cornstover, 10 g soil, and 10 g mixture of biochar (10% W) and soil (90% W). The soil sample shown here is a surface soil from 0 to 15 cm deep at the University of Tennessee’s Research and Education Center, Milan, Tennessee, USA (35.8560 N latitude, 88.410 W longitude), which is also known as the Carbon Sequestration in Terrestrial Ecosystems site (CSiTE) supported by the US Department of Energy (reproduced from ref. [5]).

Motivations for Biochar Applications

- **Biochar as a soil amendment**
  - Improve soil fertility and nutrient-use efficiency
  - Efficiently use existing resources
  - Decrease environmental impact on soil and water

- **Biochar as a waste management strategy**
  - Mitigate burden of animal and crop wastes
  - Reduce industrial and municipal solid waste footprint
  - Decrease methane emissions from landfill/decomposition

- **Biochar to produce energy**
  - Capture energy while producing biochar
  - Use biochar to generate energy
  - Offset fossil fuel contributions to climate change

What is Pyrolysis?

- Air Diffusion of Plume
- Luminous Burning Gases (from soot)
- Combustion Products
- Pyrolysis Gas
- Char
Pyrolysis at Scale

Heat (T>400°C) Inert Atmosphere

Solid Moisture Evaporates
- (100-120°C)

Unstable Biomass Polymers Degrade
- (180-220°C)

Stable Components Decompose, Release Gas
- (300 – 500°C)

Char Carbon Structure Condenses
- (500 – 700°C)

H₂, CH₄, C₂H₆, CO, CO₂, H₂O

Pyrolysis Process Operating Parameters

<table>
<thead>
<tr>
<th>Operating Parameter</th>
<th>Slow Pyrolysis</th>
<th>Fast Pyrolysis</th>
<th>Flash Pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>300 – 700</td>
<td>600 – 1000</td>
<td>800 – 1000</td>
</tr>
<tr>
<td>Heating Rate (°C/sec)</td>
<td>0.1 – 1</td>
<td>10 – 200</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>Particle Size (mm)</td>
<td>5 – 50</td>
<td>&lt; 1</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Residence Time (sec)</td>
<td>300 – 550</td>
<td>0.5 – 10</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>

Slow Pyrolysis - “Conventional Pyrolysis”
Gas phase products continuously react with solid and tar, forming char (better bio-char)

Fast and Flash - “Rapid Pyrolysis”
The reaction rates and transport of gases limit secondary reactions, favoring liquid production (better bio-oil)

Adapted from: http://cngl.org/agr/600/HFS662/lec16.pdf
Pyrolysis Process: Describing Yield

- Yields are usually expressed on a per mass basis as a function of dry starting material.
- Biochar yield on a total dry solid basis:
  \[
  \eta_{\text{biochar}} = \frac{M_{\text{biochar}}}{M_{\text{dry biomass}}}
  \]
- Biochar yield on a dry, ash-free basis:
  \[
  \eta_{\text{biochar}} = \frac{M_{\text{biochar}} - M_{\text{ash in char}}}{M_{\text{dry biomass}} - M_{\text{ash in biomass}}}
  \]

Pyrolysis is a Chemical Reaction: Reactants

<table>
<thead>
<tr>
<th>Cellulose</th>
<th>Hemicellulose</th>
<th>Lignin</th>
<th>Extractive</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood biomass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ponderosa Pine</td>
<td>48.4</td>
<td>17.6</td>
<td>24.1</td>
<td>9.5</td>
</tr>
<tr>
<td>Fir</td>
<td>46.9</td>
<td>20.3</td>
<td>27.3</td>
<td>5.1</td>
</tr>
<tr>
<td>Spruce</td>
<td>45.6</td>
<td>20.5</td>
<td>28.2</td>
<td>5.9</td>
</tr>
<tr>
<td>Beech</td>
<td>43.0</td>
<td>29.4</td>
<td>27.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Alc</td>
<td>45</td>
<td>22</td>
<td>30</td>
<td>1.6</td>
</tr>
<tr>
<td>Japanese cedar</td>
<td>38.6</td>
<td>21.3</td>
<td>33.8</td>
<td>4</td>
</tr>
<tr>
<td>Eastern Red cedar</td>
<td>40.3</td>
<td>17.9</td>
<td>35.9</td>
<td>5.8</td>
</tr>
<tr>
<td>Hardwood biomass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alder</td>
<td>45.5</td>
<td>20.6</td>
<td>23.3</td>
<td>9.8</td>
</tr>
<tr>
<td>Aspen</td>
<td>45.7</td>
<td>21.7</td>
<td>19.5</td>
<td>5.7</td>
</tr>
<tr>
<td>Willow</td>
<td>42.7</td>
<td>18.7</td>
<td>28.3</td>
<td>9.7</td>
</tr>
<tr>
<td>Poplar</td>
<td>49</td>
<td>26</td>
<td>29</td>
<td>5.9</td>
</tr>
<tr>
<td>Cherry wood</td>
<td>46</td>
<td>29</td>
<td>18</td>
<td>6.3</td>
</tr>
<tr>
<td>Beech</td>
<td>45</td>
<td>33</td>
<td>26</td>
<td>2</td>
</tr>
<tr>
<td>Beech</td>
<td>44.2</td>
<td>33.5</td>
<td>21.8</td>
<td>2.6</td>
</tr>
<tr>
<td>Japanese beech</td>
<td>43.9</td>
<td>28.4</td>
<td>24.3</td>
<td>3</td>
</tr>
<tr>
<td>Herbaceous and agricultural biomass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice straw</td>
<td>37</td>
<td>16.5</td>
<td>13.8</td>
<td>12.1</td>
</tr>
<tr>
<td>Rice husk</td>
<td>37.00</td>
<td>23.43</td>
<td>24.77</td>
<td>3.19</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>37.55</td>
<td>19.22</td>
<td>25.24</td>
<td>4.95</td>
</tr>
<tr>
<td>Corn straw</td>
<td>42.7</td>
<td>23.2</td>
<td>17.5</td>
<td>9.8</td>
</tr>
<tr>
<td>Corn leaf</td>
<td>26.93</td>
<td>13.27</td>
<td>15.18</td>
<td>12.0</td>
</tr>
<tr>
<td>Corn cob</td>
<td>34.61</td>
<td>15.24</td>
<td>18.16</td>
<td>10.6</td>
</tr>
<tr>
<td>Bamboo</td>
<td>34.4</td>
<td>25.6</td>
<td>22.8</td>
<td>11.8</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>40–45</td>
<td>31–35</td>
<td>6–12</td>
<td>5–13</td>
</tr>
<tr>
<td>Hazelnut shell</td>
<td>25.2</td>
<td>28.2</td>
<td>42.1</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Pyrolysis is a Chemical Reaction: In The Weeds

Char Formation

Depolymerization

Fragmentation

Pathways involved in the primary mechanisms of the conversion of biomass constituents (M: monomer; MW: molecular weight).

Pyrolysis is a Chemical Reaction: In The Weeds

Fig. 6. Cellulosic pyrolysis: (A) Typical TGA analysis (2) (a) mass loss: conversion and evolution of the chemical structure of the reng (within the residue and the evolved products) throughout the temperature increase; ISAA: hydroxyacetone, IRA: hydroxyacetone, and AA: acetaldehyde.

Fig. 6. Cellulosic pyrolysis: (A) Typical TGA analysis (2) (a) mass loss: conversion and evolution of the chemical structure of the reng (within the residue and the evolved products) throughout the temperature increase; ISAA: hydroxyacetone, IRA: hydroxyacetone, and AA: acetaldehyde.
Pyrolysis is a Chemical Reaction: Simplified

Cellulose
- Gas
- Tar
- Char

Lignin
- Gas
- Tar
- Char

Increasing Temperature

Line thickness indicates relative proportion of products formed


Reactions are a Function of Feedstock

Main volatiles products obtained by primary mechanisms during the conversion of biomass constituents.

<table>
<thead>
<tr>
<th></th>
<th>Char formation</th>
<th>Depolymerisation</th>
<th>Fragmentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 &lt; 400 °C</td>
<td>7 &gt; 500 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignin</td>
<td>-</td>
<td>CO, CH₄, H₂</td>
<td>Guaiacol, calcite, cresol, phenol</td>
</tr>
<tr>
<td>Cellulose</td>
<td>H₂O, CO₂</td>
<td>CO, CH₄, H₂</td>
<td>LG, S,HMF, furfural</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>H₂O, CO₂</td>
<td>CO, CH₄, H₂</td>
<td>Paraldehyde</td>
</tr>
<tr>
<td>Hylan</td>
<td>H₂O, CO₂</td>
<td>CO, CH₄, H₂</td>
<td>LG, levulinic acid, furfural</td>
</tr>
</tbody>
</table>


Impact of Feedstock on Char Yield

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hemicelluloses</th>
<th>Cellulose</th>
<th>Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olive husk</td>
<td>24.2</td>
<td>25.2</td>
<td>50.6</td>
</tr>
<tr>
<td>Corncob</td>
<td>32.5</td>
<td>52.0</td>
<td>15.5</td>
</tr>
<tr>
<td>Tea waste</td>
<td>23.3</td>
<td>33.2</td>
<td>43.5</td>
</tr>
</tbody>
</table>

Fig. 1. Effect of temperature on bio-char yield. Particle size: 1.5–2.2 mm.

Fig. 6. Effect of lignin content on yield of bio-char at 950 K final temperature. Particle size: 1.5–2.2 mm.

Pyrolysis is a Chemical Reaction: Big Picture

Biomass

1. tar
2. char
3. tar

Primary devolatilization
Secondary char devolatilization
Secondary tar cracking
Char devolatilization

Increasing Temperature

Line thickness indicates relative proportion of products formed


Impact of Temperature on Product Distribution

Pyrolysis: “Accepted” Reaction Knowledge

- Lower temperatures + longer residence times favor char production
- Moderate temperatures + shorter residence times favor liquid production
- Higher temperatures + longer residence times increase decomposition of primary products, favor gas production
- Faster heating rates + moderate temperatures favor liquid production
- Smaller particle sizes increase conversion rate, favor liquid + gas production
Pyrolysis Gases: Noncondensable

Table 2: Deconvoluted pyrolysis gases from 488 and 500°C pyrolysis, determined by integrating mass spectra of each compound, normalized to sample mass and nitrogen error.

<table>
<thead>
<tr>
<th>Species</th>
<th>Integrated MS Peak Area (E/E₀)</th>
<th>% Increase in Heating to 500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>3.02664</td>
<td>3.125-03</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.23885</td>
<td>9.540-03</td>
</tr>
<tr>
<td>CO</td>
<td>0.3065</td>
<td>1.180-04</td>
</tr>
<tr>
<td>H₂O</td>
<td>3.245-04</td>
<td>5.580-04</td>
</tr>
<tr>
<td>CH₄</td>
<td>3.63668</td>
<td>5.460-05</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>2.786-04</td>
<td>4.850-04</td>
</tr>
</tbody>
</table>

Pyrolysis Gases: Condensable (Bio-oil)

Bio-oil = water miscible, comprised of (oxygenated) organic chemicals (it is NOT “oil” like a petroleum fuel)!

- Dark brown/black liquid with pungent odor
- Not miscible with hydrocarbons
- Heating value ~ 17 MJ/kg
- Dense and Viscous ~ 1.2 kg/l,
- Acidic, pH ~ 2.5 - 4
- Bio-oil ages over time
  - Viscosity increases
  - Volatility decreases
  - Phase separation, deposits, gums

https://news.engineering.iastate.edu/2011/08/10/me-graduate-student-launches-new-company/?
Heterogeniety of Pyrolysis Bio-oils

Pyrolysis Bio-oil from Avocado Pits, 600°C:
- Wide product distribution
- Oxygenated, acidic components
- Plasticizers and thermosets
- Polycyclic aromatic hydrocarbons

Char Formation, Destruction, Formation

Biomass $\rightarrow$ Water + (Volatile + Gases)$_1$ + (Char)$_1$
(Char)$_1$ $\rightarrow$ (Volatile + Gases)$_2$ + (Char)$_2$

https://jooinn.com/burned-logs.html
Degree of Carbonization

\[ \text{C}_n\text{H}_m\text{O}_p(\text{biomass}) \rightarrow \sum_{\text{liquid}} \text{C}_x\text{H}_y\text{O}_z + \sum_{\text{gas}} \text{C}_x\text{H}_y\text{O}_z + \text{H}_2\text{O} + \text{C}(\text{char}) \]

“Complete carbonization”

Impact of Feedstock on Carbonization

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Moisture (wt%)</th>
<th>Volatile Matter (wt%)</th>
<th>Fixed Carbon (wt%)</th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>O (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagasse (raw)</td>
<td>13.2</td>
<td>71.0</td>
<td>13.8</td>
<td>51.7</td>
<td>5.3</td>
<td>42.6</td>
</tr>
<tr>
<td>Bagasse (char)</td>
<td>1.3</td>
<td>9.2</td>
<td>81.0</td>
<td>85.6</td>
<td>2.8</td>
<td>10.5</td>
</tr>
<tr>
<td>Cocopeat (raw)</td>
<td>21.0</td>
<td>49.1</td>
<td>25.4</td>
<td>61.6</td>
<td>4.4</td>
<td>33.0</td>
</tr>
<tr>
<td>Cocopeat (char)</td>
<td>2.6</td>
<td>14.3</td>
<td>84.4</td>
<td>86.3</td>
<td>87.6</td>
<td></td>
</tr>
<tr>
<td>Paddy Straw (raw)</td>
<td>7.3</td>
<td>56.4</td>
<td>15.4</td>
<td>48.8</td>
<td>6.0</td>
<td>43.3</td>
</tr>
<tr>
<td>Paddy Straw (char)</td>
<td>2.1</td>
<td>6.5</td>
<td>39.1</td>
<td>86.3</td>
<td>3.1</td>
<td>7.4</td>
</tr>
</tbody>
</table>

Changes in Proximate and Ultimate Analysis Upon Carbonization to 550°C
Impact of Temperature on Carbonization

Implications of Carbonization Degree

- Persistence and stability of biochar depends on its chemistry and physical structure
  -Chars with retained phenols, quinones, pyrroles, and furans and small (poly)aromatic units are less stable, may pose risk of leaching
  -Chars with lower surface areas (collapsed pores) – less carbonized – may result in low pore water, limited water transport
  -Highly carbonized biochar is more stable, less reactive

Torrefaction: Low-temperature Pyrolysis

Basic Torrefaction Principle

Slow heating in non-oxidative atmosphere, 200-300°C
Torrefied Biomass as Solid Fuel

- Decreased moisture content, increased hydrophobicity
- Increased brittleness compared to raw biomass
- Increased energy density than raw biomass
- Homogeneous solid (and combustion properties)
- Eliminates pathogenic microorganisms and most odors
- Increases storage stability
- Decreases transportation costs

Classification of Torrefaction Processes

<table>
<thead>
<tr>
<th>Classification</th>
<th>Light</th>
<th>Mild</th>
<th>Severe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>200–235</td>
<td>235–275</td>
<td>275–300</td>
</tr>
<tr>
<td>Consumption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>Mild</td>
<td>Mild to severe</td>
<td>Severe</td>
</tr>
<tr>
<td>Cellulose</td>
<td>Slight</td>
<td>Slight to mild</td>
<td>Mild to severe</td>
</tr>
<tr>
<td>Lignin</td>
<td>Slight</td>
<td>Slight</td>
<td>Slight</td>
</tr>
<tr>
<td>Liquid color</td>
<td>Brown</td>
<td>Brown dark</td>
<td>Black</td>
</tr>
<tr>
<td>Product</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>H₂, CO, CO₂, CH₄, toluene, benzene and C₆H₆</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td>H₂O, acetic acids, alcohols, aldehydes and ketones</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid</td>
<td>Char and ash</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reaction akin to primary pyrolysis, without secondary char formation
Impact of Torrefaction on Biomass

Summary: Pyrolytic Processes

- Pyrolysis and Torrefaction: Thermochemical biomass conversion processes in an inert (no air/oxygen) atmosphere

- Yields of solid biochar (and liquid/gas biofuels) depend on the processing conditions (temperature, heating rate, hold time)
  - Solid yield maximized at lower temperatures, slow heating rate, longer residence times
  - Highly carbonized char maximized at higher temperature, slow heating rate, moderate residence times
Opportunities for Biochar Use

- Soil amendment – improve soil fertility and stability
- Upgraded to activated carbons to use as electrodes for advanced batteries
- Use as-is or upgraded as adsorbents for water treatment
- Combusted or co-fired as solid fuel with enhanced energy density
- Use depends strongly on degree of carbonization

Upcoming...

- How do we characterize biochars?
  - Techniques
  - Data analysis
  - Comparing properties
- How do characteristics translate to possible uses?
  - Soil amendments
  - Solid fuels
  - “Upgraded” carbon applications
Further Readings: Biomass Pyrolysis