Thrust 1: Selective Thermal Processing of Cellulosic Biomass and Lignin

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Biomass Resources

2005 U.S. DOE and USDA “Billion Ton Study”

Corn (largest volume grain and source of EtOH in U.S.)

Soybeans, fats & greases (can make 6% of needed diesel fuel)

Lignocellulosic biomass (trees, grasses, agricultural residues); over 1 billion tons/year can be available in the U.S.

Food supplies

<20% of total biomass

Non food

80% of total biomass
Lignocellulosic Biomass

**Cellulose:** 38%–50%

Most abundant form of carbon in biosphere

Polymer of glucose

**Hemicellulose:** 23%–32%

Polymer of 5- and 6-carbon sugars

Xylose is the second most abundant sugar in the biosphere

**Lignin:** 15%–25%

Complex aromatic structure

p-hydroxyphenylpropene building blocks
Biomass Potential

Biomass is:

♣ Renewable
♣ Carbon-neutral
♣ Abundant
♣ The only sustainable source of hydrocarbons.

Biomass can:

♣ Be a source of fungible fuels
♣ Fill the gap between demand and availability of petroleum in the near/mid term.
♣ Serve as a renewable source of hydrogen in the long term.
Direct Production of Liquids from Biomass

**Fast Pyrolysis**
- 450-550 °C and 1 atm (maximize liquid)
- High heating rates and short residence time
- Rapid quench

\[
\text{CH}_{1.46}\text{O}_{0.67} \rightarrow 0.71\text{CH}_{1.98}\text{O}_{0.76} + 0.21\text{CH}_{0.1}\text{O}_{0.15} + 0.08\text{CH}_{0.44}\text{O}_{1.23}
\]

Biomass → Bio-oil + Char + Gas

**Liquefaction (Aqueous Solvent)**
- 120-200 atm
- 300-400 °C
- 5-20 min residence time

\[
\text{CH}_{1.46}\text{O}_{0.67} \rightarrow 0.63\text{CH}_{1.33}\text{O}_{0.16} + 0.23\text{CH}_{2.7}\text{O}_{1.22} + 0.13\text{CO}_2 + 0.01\text{CO}
\]

Biomass → Bio-oil + WSO + H_2O + Gas
Overall Product Distribution

- **Fast Pyrolysis**
  - 65% organics
  - 10% water (from rxn)
  - 12% char
  - 13% gases

- **Liquefaction**
  - 45% bio-oil
  - 25% gases (>90% CO2)
  - 30% aqueous phase
    - 20% water
    - 10% water soluble organics
Pyrolysis Pathways*

*(Observed at very high heating rates)*

Molten Biomass  
$T \sim 430^\circ C$

Biomass  
$H^+$, $M^+$  
Crosslinking

$H^+$, $M^+$  
Oligomers

Monomers/Isomers  
Low Mol. Wt Species  
Ring-opened Chains

Thermo-mechanical Ejection  
Vaporization

Aerosols  
High MW Species

Gases/Vapors

M$^+$: Catalyzed by Alkaline Cations  
$H^+$: Catalyzed by Acids  
TM$^+$: Catalyzed by Zero Valent Transition Metals

Reforming TM$^+$

Synthesis Gas

Volatile Products

CO + H$_2$

Char, CO$_2$, H$_2$O

Thermal Conversion Reactions

**Primary Processes**
- **Vapor Phase**
  - CO, CO₂, H₂O
- **Primary Liquids**
  - Condensed Oils (phenols, aromatics)
- **Solid Phase**
  - Biomass

**Secondary Processes**
- **Light HCs, Aromatics, & Oxygenates**
- **Olefins, Aromatics**
  - CO, H₂, CO₂, H₂O

**Tertiary Processes**
- **PNA’s, CO, H₂, CO₂, H₂O, CH₄**
- **CO, H₂, CO₂, H₂O**

**Pyrolysis Severity**
- Low P
- High P
## Composition: Fast Pyrolysis Bio-Oil*

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>20-30</td>
</tr>
<tr>
<td>Lignin fragments: insoluble pyrolytic lignin</td>
<td>15-30</td>
</tr>
<tr>
<td>Aldehydes: formaldehyde, acetaldehyde, hydroxyacetaldelyde, glyoxal</td>
<td>10-20</td>
</tr>
<tr>
<td>Carboxylic acids: formic, acetic, propionic, butyric, pentanoic, hexanoic</td>
<td>10-15</td>
</tr>
<tr>
<td>Carbohydrates: celllobiosan, levoglucosan, oligosaccharides</td>
<td>5-10</td>
</tr>
<tr>
<td>Phenols: phenol, cresol, guaiacols, syringols</td>
<td>2-5</td>
</tr>
<tr>
<td>Furfurals</td>
<td>1-4</td>
</tr>
<tr>
<td>Alcohols: methanol, ethanol</td>
<td>2-5</td>
</tr>
<tr>
<td>Ketones: acetol (1-hydroxy-2-propanone), cyclopentanone</td>
<td>1-5</td>
</tr>
</tbody>
</table>

## Liquefaction Events

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Technique</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrastructure Changes</td>
<td>Thermal stress</td>
<td>Hemicellulose $\rightarrow$</td>
</tr>
<tr>
<td></td>
<td>Mechanical stress</td>
<td>Solubles</td>
</tr>
<tr>
<td></td>
<td>Solvolytic action</td>
<td>Cellulose $\rightarrow$ Activated Lignin $\rightarrow$ Modified</td>
</tr>
<tr>
<td>Chemical degradation</td>
<td>1. Hydrolysis with catalysts $\text{H}^+$</td>
<td>Sugars, aldehydes</td>
</tr>
<tr>
<td></td>
<td>$\text{OH}^-$</td>
<td>Acids</td>
</tr>
<tr>
<td></td>
<td>2. Neutral aqueous</td>
<td>Solubilized sugars, acids, aldehydes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Swelling, dehydration in amorphous regions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>‘Acid’ lignin</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Partially soluble</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Attack by autohydrolysis products</td>
</tr>
<tr>
<td>Thermal decomposition 200-360 °C</td>
<td>1. $\text{Na}_2\text{CO}_3$, CO, $\text{OH}^-$ catalyzed high pressures</td>
<td>Mixture of oxygenates derived from above + thermal cracking</td>
</tr>
<tr>
<td></td>
<td>2. Autohydrolytic decomposition</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. $\text{H}^+$ transfer at high pressures</td>
<td></td>
</tr>
<tr>
<td>Hydrocracking 380–430 °C</td>
<td>$\text{H}_2$ + catalyst</td>
<td>Bio-oil</td>
</tr>
<tr>
<td></td>
<td>Catalytic cracking</td>
<td></td>
</tr>
<tr>
<td></td>
<td>De-oxygenation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogenolysis</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogenation</td>
<td></td>
</tr>
</tbody>
</table>

HC = hemicellulose; C = cellulose; L = lignin.

*Chornet and Overend; in Fundamentals of Thermochemical Biomass Conversion, Overend et al., ed. (1985) 967.*
Biomass Liquefaction

## Representative Bio-Oils*

<table>
<thead>
<tr>
<th>Property</th>
<th>Pyrolysis oil</th>
<th>Liquefaction oil</th>
<th>Heavy fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content, wt%</td>
<td>15-30</td>
<td>5.1</td>
<td>0.1</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.2</td>
<td>1.1</td>
<td>0.94</td>
</tr>
<tr>
<td>Elemental composition, wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>carbon</td>
<td>54-58</td>
<td>73</td>
<td>85</td>
</tr>
<tr>
<td>hydrogen</td>
<td>5.5-7.0</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>oxygen</td>
<td>35-40</td>
<td>16</td>
<td>1.0</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0-0.2</td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td>ash</td>
<td>0-0.2</td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Higher heating value, MJ/kg</td>
<td>16-19</td>
<td>34</td>
<td>40</td>
</tr>
<tr>
<td>Viscosity (50 °C), cP</td>
<td>40-100</td>
<td>15,000 (at 61°C)</td>
<td>180</td>
</tr>
<tr>
<td>Solids, wt%</td>
<td>0.2-1</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Distillation residue, wt%</td>
<td>Up to 50</td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

*Czernik and Bridgwater; Energy Fuels 18 (2004) 590.
Elliott and Schiefelbein; Preprints of Papers - American Chemical Society, Division of Fuel Chemistry 34 (1989) 1160.
Feedstocks That Can Be Processed

• Fast Pyrolysis
  – Broad range of lignocellulosics
  – Dry material generally preferred

• Liquefaction
  – Broad range of lignocellulosics
  – Wet material readily handled
Positive Features of Bio-Oils

• Flexible for different feedstocks
• Increased energy density and liquid product
• Relatively simple processes – potential for distributed production
• Removes some oxygen
  – Fast pyrolysis primarily dehydration
  – Liquefaction decarboxylation and dehydration
Bio-Oil Challenges

• Fast Pyrolysis
  – stability
  – acidity
  – high oxygen content
  – upgrading required for use as fuel
  – chemical complexity

• Liquefaction
  – high viscosity
  – elevated oxygen content
  – upgrading required for use as fuel
  – chemical complexity
  – (high pressure)
Fast Pyrolysis: Bio-Oil Stability*

- Reactions:
  - Esterification of acids with alcohols
  - Transesterification of esters
  - Homopolymerization of aldehydes
  - Hydration of aldehydes or ketones
  - Hemiacetal formation with aldehydes and alcohols
  - Acetalization of aldehydes and alcohols
  - Phenol/aldehyde reactions to form resins
  - Polymerization of furan derivatives
  - Dimerization of nitrogen compounds from proteins with aldehydes

Fast Pyrolysis Bio-oil Fuel Applications

Heat and power production:

Furnaces, Boilers, Diesel engines, Turbines – demonstrated using standard equipment *(modifications are necessary for a long-duration operation)*

Upgrading to transport fuel:

Emulsification with diesel fuel *(high wear of the valves)*
Hydrotreating, hydrocracking
Catalytic vapor cracking *(low yields, high aromatics, rapid deactivation of catalysts)*
## Economic Evaluation (1990)*

<table>
<thead>
<tr>
<th></th>
<th>Fast pyrolysis</th>
<th>Liquefaction in solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present</td>
<td>Potential</td>
</tr>
<tr>
<td></td>
<td>Present</td>
<td>Potential</td>
</tr>
<tr>
<td>Total capital requirement ($US millions)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>primary liquefaction</td>
<td>49.8</td>
<td>26.4</td>
</tr>
<tr>
<td>crude upgrading</td>
<td>46.6</td>
<td>34.3</td>
</tr>
<tr>
<td>product finishing</td>
<td>14.5</td>
<td>0.7</td>
</tr>
<tr>
<td>total</td>
<td>110.9</td>
<td>61.4</td>
</tr>
<tr>
<td>Production costs ($US million/year)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fixed operating costs</td>
<td>14.48</td>
<td>10.77</td>
</tr>
<tr>
<td>variable operating costs</td>
<td>25.74</td>
<td>23.67</td>
</tr>
<tr>
<td>(feedstock costs)</td>
<td>(20.00)</td>
<td>(20.00)</td>
</tr>
<tr>
<td>capital charges</td>
<td>12.96</td>
<td>7.17</td>
</tr>
<tr>
<td>total production cost</td>
<td>53.18</td>
<td>41.61</td>
</tr>
<tr>
<td>Minimum selling price ($US/GJ)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bio-oil</td>
<td>9.32</td>
<td>6.91</td>
</tr>
<tr>
<td>refined bio-oil</td>
<td>16.24</td>
<td>12.99</td>
</tr>
<tr>
<td>Process Thermal Efficiency</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(energy_{liquid products}/energy_{feed+inputs})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>primary product from liquefaction</td>
<td>0.61</td>
<td>0.68</td>
</tr>
<tr>
<td>finished product</td>
<td>0.52</td>
<td>0.53</td>
</tr>
</tbody>
</table>

---

Liquefaction Economics*

Limitations for Fast Pyrolysis Bio-Oil*

**Cost:** 10% – 100% more than fossil fuel

**Availability:** limited supplies for testing

**Standards:** lack of standards and inconsistent quality inhibits wider usage

**Compatibility:** not with conventional fuels, dedicated fuel handling needed

**User familiarity:** very low

**Image:** poor

*A.V. Bridgwater*
Fundamental Challenges

• Fast pyrolysis: reaction system understanding
  – Reactor design
  – Connection to downstream processing
  – Product capture
  – Non-empirical reactor systems

• Fast pyrolysis: catalyst incorporation

• Liquefaction: reaction system understanding
  – Reactor design
  – Connection to downstream processing
  – Non-empirical reactor systems
What is next?

• Upgrading existing biomass-derived liquids
  • hydrodeoxygenation
  • decarboxylation
  • reactions with other oxygenates

• Modifications of existing processes
  • catalysts
  • secondary reactions

• Alternative deconstruction strategies?