Thermochemical Technologies for Conversion of Biomass to Fuels and Chemicals

Presented by
Dr. Richard L. Bain,
Principal Research Supervisor,
Biorefinery Analysis and Exploratory Research Group
National Bioenergy Center

Biomass to Chemicals and Fuels: Science, Technology and Public Policy

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Presentation Outline

- Overview
- Biomass Properties
- Gasification Based Technologies
- Pyrolysis Based Technologies
- Other Technologies
Integrated biorefineries will involve both biochemical and thermochemical processes

- **Starch or Grain** → **Starch Hydrolysis** → **Fermentable Sugars**
  - **Fermentation of Sugars**
    - Glucose
    - C5/C6 Sugars
    - C5 Sugar(s)
  - **Product Recovery**
    - Food Products
    - Animal Feed
    - Ethanol
    - Chemicals

- **Lignocellulosic Biomass** → **Pretreatment** → **Cellulose Hydrolysis**

- **Thermochemical Conversion** → **Lignin Residue**
  - **Product Recovery**
    - Heat and Power
    - Fuels and Chemicals
      - Pyrolysis Oil
      - Synthesis Gas
The primary conversion routes give different types of products

- **Thermal Conversion**
  - **Excess air**
    - **Combustion**
      - Heat
  - **Partial air**
    - **Gasification**
      - Fuel Gases
        (\(CO + H_2\))
  - **No air**
    - **Pyrolysis & Hydrothermal**
      - Liquids
Fungible fuels & chemicals are major products. New classes of products (e.g., oxygenated oils) require market development.

* Examples: Hydrothermal Processing, Liquefaction, Wet Gasification
Thermal Conversion involves primary, secondary, and tertiary reactions

Primary Processes
- Vapor Phase: CO, CO₂, H₂O
- Primary Vapors
- Condensed Oils (phenols, aromatics)
- Pyrolysis Severity

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

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

Legend:
- Biomass
- Charcoal
- Coke
- Soot
- Low P
- High P
To understand thermochemical conversion we need to know the physical and thermal properties that influence thermal behavior.
The basic properties for the comparison of thermal behavior are proximate and ultimate analyses

<table>
<thead>
<tr>
<th></th>
<th>Poplar</th>
<th>Corn Stover</th>
<th>Chicken Litter</th>
<th>Black Liquor</th>
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<tbody>
<tr>
<td><strong>Proximate (wt% as received)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>1.16</td>
<td>4.75</td>
<td>18.65</td>
<td>52.01</td>
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<tr>
<td>Volatile Matter</td>
<td>81.99</td>
<td>75.96</td>
<td>58.21</td>
<td>35.26</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>13.05</td>
<td>13.23</td>
<td>11.53</td>
<td>6.11</td>
</tr>
<tr>
<td>Moisture</td>
<td>4.80</td>
<td>6.06</td>
<td>11.61</td>
<td>9.61</td>
</tr>
<tr>
<td>HHV, Dry (Btu/ib)</td>
<td>8382</td>
<td>7782</td>
<td>6310</td>
<td>4971</td>
</tr>
<tr>
<td><strong>Ultimate, wt% as received</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>47.05</td>
<td>43.98</td>
<td>32.00</td>
<td>32.12</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.71</td>
<td>5.39</td>
<td>5.48</td>
<td>2.85</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.22</td>
<td>0.62</td>
<td>6.64</td>
<td>0.24</td>
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<tr>
<td>Sulfur</td>
<td>0.05</td>
<td>0.10</td>
<td>0.96</td>
<td>4.79</td>
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<tr>
<td>Oxygen (by diff)</td>
<td>41.01</td>
<td>39.10</td>
<td>34.45</td>
<td>0.71</td>
</tr>
<tr>
<td>Chlorine</td>
<td>&lt;0.01</td>
<td>0.25</td>
<td>1.14</td>
<td>0.07</td>
</tr>
<tr>
<td>Ash</td>
<td>1.16</td>
<td>4.75</td>
<td>19.33</td>
<td>51.91</td>
</tr>
<tr>
<td><strong>Elemental Ash Analysis, wt% of fuel as received</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.05</td>
<td>1.20</td>
<td>0.82</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>---</td>
<td>---</td>
<td>0.25</td>
<td>0.05</td>
</tr>
<tr>
<td>Al</td>
<td>0.02</td>
<td>0.05</td>
<td>0.14</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Na</td>
<td>0.02</td>
<td>0.01</td>
<td>0.77</td>
<td>8.65</td>
</tr>
<tr>
<td>K</td>
<td>0.04</td>
<td>1.08</td>
<td>2.72</td>
<td>0.82</td>
</tr>
<tr>
<td>Ca</td>
<td>0.39</td>
<td>0.29</td>
<td>2.79</td>
<td>0.05</td>
</tr>
<tr>
<td>Mg</td>
<td>0.08</td>
<td>0.18</td>
<td>0.87</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>P</td>
<td>0.08</td>
<td>0.18</td>
<td>1.59</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>As (ppm)</td>
<td></td>
<td></td>
<td></td>
<td>14</td>
</tr>
</tbody>
</table>
Gasification has a long history of development and use

Murdoch (1792) coal distillation
London gas lights 1802
Blau gas – Fontana 1780
1900s Colonial power
MeOH 1913 BASF
Fischer Tropsch 1920s
Vehicle Gazogens WWII
SASOL 1955 - Present
GTL 1995 – Present
Hydrogen – Future?

Circa 1898
The world syngas market is approximately 6 EJ/yr

There are a number of gasification pathways.

- **Biomass**
  - Fast Pyrolysis
  - Slow Pyrolysis
  - Torrefaction
  - Dry-Ash Gasifier
    - Indirect
    - Direct

- **Primary Conversion**
  - Fast Entrained-Flow Gasifier
  - Slow High-Temp Thermal Gasifier

- **Tar Removal**
  - Catalytic Reforming
  - Slagging Tar Cracking
  - High-Temp Thermal Tar Cracking

- **Syngas Conditioning**
  - Filter
  - Quench
  - Sulfur Removal
  - Shift
  - Trace Removal

- **Biofuel Synthesis**
  - Ethanol
  - Mixed Alcohols
  - F-T Liquids
  - Methanol
  - DME
  - Other Hydrogen Ammonia SNG

Source: ECN (2006), ECN-C-06-001
A large number of companies are involved in biomass thermal conversion.
Small and medium size combined heat and power is a good opportunity for biomass

Credit: Community Power Corp

Credit: Carbona Corp
Producers are starting to use biomass gasifiers for CHP in corn ethanol facilities

- Central Minnesota Ethanol Cooperative (CMEC)
- 15 million gpy ethanol plant in Little Falls, MN
- Funding – USDA, XCEL Energy, Private
- E&C – Sebesta Blomberg
- Gasifier – Primenergy
- 280 tpd wood
- 50 k-lb/hr high pressure steam for electricity
- 35 MMBtu/hr thermal energy

http://www.primenergy.com/Projects_detail_LittleFalls.htm 8/28/06
Transportation fuels production will probably be at larger scale because of process complexity and capital intensive nature. There may be opportunities for smaller modular “skid mount” systems.
Hydrocarbon fungibility will be a key to success

Primary Energy Source
- Natural Gas
- Coal
- Biomass
- Extra Heavy Oil

Syngas Step
- Syngas (CO + H₂)

Conversion Technology
- Fischer Tropsch (FT)
- Upgrading

Products
- Diesel
- Naphtha
- Lubes

Syngas to Chemicals Technologies
- Acetic Acid
- Methanol
- Hydrogen
- Mixed Alcohols (e.g. ethanol, propanol)
- Others (e.g. Triptane, DME, etc)

Source: BP
A 30x30 advanced integrated biorefinery scenario, i.e., the E85 Refinery, includes both thermochemical and biochemical processing

Ethanol yield = 94 gal/dry ton stover
Gasoline yield = 90 gal/dry ton of lignin (13 gal/ton of stover)
(Plant total Ethanol equivalent yield = 118 gal/dry ton stover)

Ethanol via bioconversion
Corn Stover 10,000 dMT/day

Lignin via CHP Plant
Steam & Power
Lignin-rich Residue 1,432 dMT/day

Selective thermal processing
Lignin-rich Residue 1,500 dMT/day

Ethanol
1,035,000 gpd
36.2 MM gal/yr

Gasoline 148,011 gpd
Diesel 5,911 gpd

Minimum gasoline selling price = $0.51/gal gasoline
(Minimum Ethanol equivalent selling price = $0.35/galEtOH)
(Diesel is recycled to produce a lignin slurry feed)

Plant Minimum Ethanol equivalent selling price = $0.57/gal EtOH
Although ethanol and Fischer-Tropsch liquids are presently preferred products, previous work on methanol can help guide analysis.

**Methanol from Biomass**

**Comparison of Capital Investment (2002$)**

- Atmospheric O₂ slagging entrained flow
- Pressurized O₂ fluid bed
- Indirect steam
- Indirect steam with catalytic reforming
- Indirect Steam with hot particulate removal

*Wyman, et al., 1993 2000 tpd biomass*
*Hamelinck & Faaij, 2001 2000 tpd biomass*
*Katofsky, 1993 1815 tpd biomass*

*rlb, 08/25/06*
Analysis of ethanol from TC mixed alcohols shows the potential to reach the DOE goal of $1.07/gal in 2012.
Pyrolysis is usually performed at lower temperature to produce a liquid biocrude.

- Thermal decomposition occurring in the absence of oxygen
- Is always the first step in combustion and gasification processes
- Known as a technology for producing charcoal and chemicals for thousands of years
The distribution of products depends on temperature and residence time

<table>
<thead>
<tr>
<th>Process</th>
<th>Liquid</th>
<th>Char</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FAST PYROLYSIS</strong></td>
<td>75%</td>
<td>12%</td>
<td>13%</td>
</tr>
<tr>
<td><em>moderate</em> temperature</td>
<td><em>short</em> residence time</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CARBONIZATION</strong></td>
<td>30%</td>
<td>35%</td>
<td>35%</td>
</tr>
<tr>
<td><em>low</em> temperature</td>
<td><em>long</em> residence time</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>GASIFICATION</strong></td>
<td>5%</td>
<td>10%</td>
<td>85%</td>
</tr>
<tr>
<td><em>high</em> temperature</td>
<td><em>long</em> residence time</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Bridgewater and Czernik
There are a number of operating systems in North America and Europe

<table>
<thead>
<tr>
<th>System</th>
<th>Capacity</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid beds</td>
<td>400 kg/h</td>
<td>DynaMotive</td>
</tr>
<tr>
<td></td>
<td>20 kg/h</td>
<td>RTI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Many research units</td>
</tr>
<tr>
<td>CFBs</td>
<td>1000 kg/h</td>
<td>Red Arrow (Ensyn)</td>
</tr>
<tr>
<td></td>
<td>20 kg/h</td>
<td>VTT (Ensyn)</td>
</tr>
<tr>
<td></td>
<td>350 kg/h</td>
<td>Fortum, Finland</td>
</tr>
<tr>
<td>Rotating cone</td>
<td>200 kg/h</td>
<td>BTG (Netherlands)</td>
</tr>
<tr>
<td>Vacuum</td>
<td>3500 kg/h</td>
<td>Pyrovac</td>
</tr>
<tr>
<td>Auger</td>
<td>200 kg/h</td>
<td>ROI</td>
</tr>
</tbody>
</table>

Source: Bridgewater and Czernik
Biocrude is water miscible and is comprised of many oxygenated organic chemicals.

- Dark brown mobile liquid
- Combustible
- Not miscible with hydrocarbons
- Heating value ~ 17 MJ/kg
- Density ~ 1.2 kg/l
- Acid, pH ~ 2.5
- Pungent odour
- “Ages” - viscosity increases with time

Source: Bridgewater and Czernik
There are a number of applications for biocrudes

- Electricity
- Transport fuel
- Heat
- Bio-oil

Source: Bridgewater and Czernik
The biocrude can be upgraded in a petroleum refinery

- Must reduce acidity, improve stability and bio-oil miscibility with petroleum
- Deoxygenation may be required on either side of battery limits
- Fractionation could be beneficial, and may be performed outside the petroleum refinery
- Other processing options exist ISBL of the petroleum refinery

Based on UOP/NREL/PNNL R&D Project DOE-FG36-05GO15085 (2004 - 2005), and Colin Schaverien’s (Shell) Biorefining presentation at 1st International Biorefinery Workshop, July 20-21, 2005, Washington D.C.
A pyrolysis-based biorefinery can produce multiple products

Other Products of Interest:
- Heating oil
- PF resins
- FCC feed
- DDU feed

- Fast Pyrolysis Of Biomass
- Fractionation and/or Deoxygenation
- Carbohydrate Derivatives
- Fermentation or Hydrogenation of Aqueous Phase (Carbohydrates)

Lignin Derivatives

Aromatic Chemicals and/or Gasoline Blending
Oils, fats & greases can be used as bio-renewable petroleum refinery feedstocks

- Co-processing of oils and greases with petroleum fractions
- Utilize existing process capacity
- Potential for lower conversion costs (than FAME)
- Higher quality diesel blending component
- G/D flexibility

Based on Presentations at 1st International Biorefinery Workshop, Washington DC, July 20-21, 2005
- Future Energy for Mobility, James Simnick, BP
- From Bioblending to Biorefining, Veronique Hervouet, Total
- Opportunities for Biorenewables in Petroleum Refineries, Jennifer Holmgren, UOP
Green diesel has very attractive properties

<table>
<thead>
<tr>
<th></th>
<th>Biodiesel (FAME)</th>
<th>Green Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Oxygen</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>Density g/ml</td>
<td>.883</td>
<td>.78</td>
</tr>
<tr>
<td>Sulfur content</td>
<td>&lt;10ppm</td>
<td>&lt;10ppm</td>
</tr>
<tr>
<td>Heating Value (lower) MJ/kg</td>
<td>38</td>
<td>44</td>
</tr>
<tr>
<td>% change in NOx emission</td>
<td>0 to +10</td>
<td>0 to -10</td>
</tr>
<tr>
<td>Cloud Point °C</td>
<td>-5</td>
<td>-5 to -30</td>
</tr>
<tr>
<td>Distillation 10-90% pt</td>
<td>340-355</td>
<td>265-320</td>
</tr>
<tr>
<td>Cetane</td>
<td>50</td>
<td>80-90</td>
</tr>
</tbody>
</table>

Hydrothermal treatment can be used to produce liquid products, and is being developed by companies such as Changing World Technologies and Biofuel BV

- Water plus alkali at $T = 300-350°C$, $P$ high enough to keep water liquid. Use of CO is option
- Yield $> 95\%$
- Distillate ($-500°C$): 40 – 50%
- Distillate Composition: Hardwood (300°C) – $\text{CH}_{1.2}\text{O}_{0.2}$, Manure (350°C) – $\text{CH}_{1.4}\text{O}_{0.1}$
- Qualitative: long aliphatic chains, some cyclic compounds containing carbonyl groups, and a few hydroxy groups, ether linkages, and carboxylic acid groups
- HHV = 28 – 34 MBTU/ton