The Promise of Thermochemical Conversion of Biomass to Biofuels

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Faculty Retreat: Energy Sciences Research
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Why thermochemical conversion?
Try this with enzymes.
Why is cellulose so difficult to enzymatically decompose?

- Starch is a storage polysaccharide designed by nature as a food reservoir
- Cellulose is structural polysaccharide designed by nature to resist degradation
Thermochemical conversion can produce more than just ethanol

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Specific Gravity</th>
<th>LHV (MJ/kg)</th>
<th>Octane Number</th>
<th>Cetane Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0.794</td>
<td>27</td>
<td>109</td>
<td>-</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>0.886</td>
<td>37</td>
<td>-</td>
<td>55</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.796</td>
<td>20.1</td>
<td>109</td>
<td>-</td>
</tr>
<tr>
<td>Butanol</td>
<td>0.81</td>
<td>36</td>
<td>96 - 105</td>
<td>-</td>
</tr>
<tr>
<td>Mixed Alcohols</td>
<td>~0.80</td>
<td>27-36</td>
<td>96-109</td>
<td>-</td>
</tr>
<tr>
<td>Fischer-Tropsch Diesel</td>
<td>0.770</td>
<td>43.9</td>
<td>-</td>
<td>74.6</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.07 (liq)</td>
<td>120</td>
<td>&gt;130</td>
<td>-</td>
</tr>
<tr>
<td>Methane</td>
<td>0.42 (liq)</td>
<td>49.5</td>
<td>&gt;120</td>
<td>-</td>
</tr>
<tr>
<td>Dimethyl Ether</td>
<td>0.66 (liq)</td>
<td>28.9</td>
<td>-</td>
<td>&gt;55</td>
</tr>
<tr>
<td>Gasoline</td>
<td>0.72-0.78</td>
<td>43.5</td>
<td>91-100</td>
<td>-</td>
</tr>
<tr>
<td>Diesel</td>
<td>0.85</td>
<td>45</td>
<td>-</td>
<td>37-56</td>
</tr>
</tbody>
</table>
Thermochemical Options

- Gasification
- Fast pyrolysis
- Hydrothermal processing
Gasification

• Gasification - high temperature (750 – 1800 °C) conversion of solid, carbonaceous fuels into flammable gas mixtures
  – Carbon monoxide (CO), hydrogen (H₂), methane (CH₄), nitrogen (N₂), carbon dioxide (CO₂), and smaller quantities of higher hydrocarbons
  – Gas mixture called producer gas or syngas
• Gas production is endothermic
  – Requires either the simultaneous burning of part of the fuel or the delivery of an external source of heat to drive the process
Why Gasification?

Biomass → GASIFICATION → CO + H₂ → COMBUSTION → CO₂ + H₂O → THERMAL POWER

Steam → WATER-GAS SHIFT → H₂ + CO₂ → FUEL CELLS

Air

CATALYSIS/BIOCATALSIS → Organic acids, Alcohols, Esters, Hydrocarbons → FUELS & CHEMICALS
Common Types of Gasifiers

**Updraft**
- Biomass
- Product gas
- Fixed bed of biomass
  - Oxidant
  - Ash
  - Grate

**Downdraft**
- Biomass
- Fixed bed of biomass
  - Oxidant
  - Product gas + ash
  - Throat

**Fluidized Bed**
- Biomass
- Product gas + fly ash
  - Oxidant
  - Freeboard
  - Fluid bed
  - Feeder
  - Distributor plate
  - Oxidant

**Entrained Flow**
- Biomass
- Steam and Oxygen
  - Slag
  - Product gas
Gasification Efficiency

• Thermal efficiency - conversion of chemical energy of solid fuel to chemical energy and sensible heat of gaseous product
  – High temperature, high-pressure gasifiers: >95%
  – Typical biomass gasifiers: 70 - 90%

• Cold gas efficiency – conversion of chemical energy of solid fuel to chemical energy of gaseous product
  – Typical biomass gasifiers: 50-75%
## Synthetic Fuels from Syngas

<table>
<thead>
<tr>
<th>Process</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Reforming</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>Methanol synthesis</td>
<td>Methanol, acetic acid, ethanol, diethyl ether, olefins</td>
</tr>
<tr>
<td>Fischer Tropsch Synthesis</td>
<td>Synthetic diesel and gasoline</td>
</tr>
<tr>
<td>Alcohol from Syngas</td>
<td>Ethanol, mixed alcohols</td>
</tr>
<tr>
<td>Syngas Fermentation</td>
<td>Ethanol, esters, and other metabolic products</td>
</tr>
</tbody>
</table>
### Biomass-to-Fuels Efficiencies
(current technology)

#### Fuel Production Efficiencies

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain Ethanol&lt;sup&gt;1&lt;/sup&gt;</td>
<td>38%</td>
</tr>
<tr>
<td>Lignocellulosic Ethanol&lt;sup&gt;2&lt;/sup&gt;</td>
<td>35%</td>
</tr>
<tr>
<td>Methanol&lt;sup&gt;3&lt;/sup&gt;</td>
<td>45%</td>
</tr>
<tr>
<td>Hydrogen&lt;sup&gt;3&lt;/sup&gt;</td>
<td>50%</td>
</tr>
<tr>
<td>Fischer-Tropsch&lt;sup&gt;4&lt;/sup&gt;</td>
<td>45%</td>
</tr>
</tbody>
</table>

*BPD – barrels per day  **MMGPy – million gallons per year (gasoline equivalent)

Note: Efficiencies do not account for byproduct value or power production although production costs do.

References:

### Comparing Costs

<table>
<thead>
<tr>
<th>150 MMGPY*</th>
<th>Capital</th>
<th>Operating</th>
<th>Feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity (2005 basis)</td>
<td>Cost ($/bpd)*</td>
<td>Cost ($/gal)</td>
<td>Cost ($)</td>
</tr>
<tr>
<td>Grain Ethanol$^1$</td>
<td>13,000</td>
<td>$1.74/gal</td>
<td>$3.00/bu</td>
</tr>
<tr>
<td>Lignocellulosic Ethanol$^2$</td>
<td>76,000</td>
<td>1.76</td>
<td>$50/ton</td>
</tr>
<tr>
<td>Methanol$^3$</td>
<td>66,000</td>
<td>1.19</td>
<td>$50/ton</td>
</tr>
<tr>
<td>Hydrogen$^3$</td>
<td>59,000</td>
<td>1.07</td>
<td>$50/ton</td>
</tr>
<tr>
<td>Fischer-Tropsch$^4$</td>
<td>86,000</td>
<td>1.87</td>
<td>$50/ton</td>
</tr>
</tbody>
</table>

*BPD – barrels per day  **MMGPY – million gallons per year (gasoline equivalent)

Note: Operating costs include credit for byproduct utilization.

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**References for Base Case Data:**

Fast Pyrolysis

- Rapid thermal decomposition of organic compounds in the absence of oxygen to produce liquids, char, and gas
  - Small particles: 1 - 3 mm
  - Short residence times: 0.5 - 2 s
  - Moderate temperatures (400-500 °C)
  - Rapid quenching at the end of the process

- Typical yields
  - Oil: 60 - 70%
  - Char: 12 - 15%
  - Gas: 13 - 25%
Bio-Oil

Pyrolysis liquid (bio-oil) from flash pyrolysis is a low viscosity, dark-brown fluid with up to 15 to 20% water.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content, wt%</td>
<td>7.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Particle size, μm (max)</td>
<td>1000</td>
<td>590</td>
</tr>
<tr>
<td>Temperature</td>
<td>500</td>
<td>497</td>
</tr>
<tr>
<td>Apparent residence time</td>
<td>0.65</td>
<td>0.48</td>
</tr>
<tr>
<td><strong>Product Yields, wt %, m.f.</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>11.6</td>
<td>12.2</td>
</tr>
<tr>
<td>Gas</td>
<td>7.8</td>
<td>10.8</td>
</tr>
<tr>
<td>Bio-char</td>
<td>12.2</td>
<td>7.7</td>
</tr>
<tr>
<td>Bio-oil</td>
<td>66.5</td>
<td>65.7</td>
</tr>
<tr>
<td><strong>Bio-oil composition, wt %, m.f.</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saccharides</td>
<td>3.3</td>
<td>2.4</td>
</tr>
<tr>
<td>Anhydrosugars</td>
<td>6.5</td>
<td>6.8</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>10.1</td>
<td>14.0</td>
</tr>
<tr>
<td>Furans</td>
<td>0.35</td>
<td>--</td>
</tr>
<tr>
<td>Ketones</td>
<td>1.24</td>
<td>1.4</td>
</tr>
<tr>
<td>Alcohols</td>
<td>2.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td>11.0</td>
<td>8.5</td>
</tr>
<tr>
<td>Water-Soluble – Total Above</td>
<td>34.5</td>
<td>34.3</td>
</tr>
<tr>
<td>Pyrolytic Lignin</td>
<td>20.6</td>
<td>16.2</td>
</tr>
<tr>
<td>Unaccounted fraction</td>
<td>11.4</td>
<td>15.2</td>
</tr>
</tbody>
</table>
Bio-Oil

- **Advantages include:**
  - Liquid fuel
  - Decoupled conversion processes
  - Easier to transport than biomass or syngas

- **Disadvantages**
  - High oxygen and water content makes bio-oil inferior to petroleum-derived fuels
  - Phase-separation and polymerization and corrosiveness make long-term storage difficult
Fundamentals of Fast Pyrolysis

- Multiple reaction pathways for pyrolysis of cellulose

Cellulose →

- Fast
  - Depolymerization → Levoglucosan
  - Alkali-catalyzed dehydration → Hydroxyacetaldehyde

- Slow
  → Char + water
Several kinds of pyrolysis technology

Adapted from PYNE IEA Bioenergy http://www.pyne.co.uk
Energy efficiency of bio-oil production

• Conversion to 75 wt-% bio-oil translates to energy efficiency of 70%

• If carbon used for energy source (process heat or slurried with liquid) then efficiency approaches 94%

Source:  http://www.ensyn.com/info/23102000.htm
Synfuels from bio-oil: Hydrocracking

- Directly converts biomass into liquid bio-oil (lignin, carbohydrate derivatives, and water) and char
- Bio-oil catalytically converted into hydrocarbon fuel (green diesel)
Synfuels from bio-oil: Gasification

- Bio-oil and char slurried together to recover 90% of the original biomass energy
- Slurry transported to central processing site where it is gasified in an entrained flow gasifier to syngas
- Syngas is catalytic processed into F-T liquids
Co-Products

• Gas (CO, H2, light hydrocarbons)
  – Can be used to heat pyrolysis reactor

• Char: Several potential applications
  – Process heat
  – Activated carbon
  – Soil amendment
  – Carbon sequestration
Agri-char: Soil amendment and carbon sequestration agent

Black is the new green

1978, he explored Herbert Smith, author of the classic The Discovery of Australia. His later works included The Discovery of America and The Discovery of Canada, providing a comprehensive overview of the European exploration of the Americas from the 15th to the 18th century. Smith was a prominent figure in the field of exploration and geography, and his works continue to be influential in the study of early European exploration.

The soil scientists, archaeologists, geographers, ecologists, and historians who study these sites now agree that the American Dream, as we cherish it today, was made possible by the efforts of early explorers and settlers. The American Dream is a concept that has evolved over time, but its roots can be traced back to the early explorations of the Americas.

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Greenhouse gases reduced by carbon storage in agricultural soils

Char from pyrolyzing one-half of corn stover
Hydrothermal Processing (HTP)

• Processing in hot, compressed liquid water or supercritical water

• Pressure and temperature determine products:
  – **Carbohydrate from HTP**: 200°C and 20 bar yields carbohydrate that can be hydrolyzed to fermentable sugars
  – **Biocrude from HTP**: 330°C and 150 bar yields hydrocarbons suitable for production of diesel fuel
  – **Syngas from HTP**: 600°C and 230 bar yields hydrogen, carbon monoxide, and methane
Carbohydrate from HTP

- **Feedstock:** Fibrous (cellulosic) biomass
- **Conditions:** 200°C; 20 bar in liquid water
- **Typical products:** Fractionated cellulose, lignin, and pentose (from hemicellulose)
- **Applications:** Pretreatment for more effective simultaneous saccharification and fermentation
Biocrude from HTP

Feedstock: A variety of wet biomass

Conditions: 300 - 350 C; 120 - 180 bar for 5 - 20 minutes in liquid water

Products: 45 Biocrude (%w on feedstock, DAF basis)
25 Gas (> 90% CO₂)
20 H₂O
10 dissolved organics (e.g., acetic acid, ethanol)

Properties: Biocrude is a heavy organic liquid, immiscible in water that solidifies at 80 °C; H/C = 1.1; oxygen content 10 - 18 %w; LHV 30 -35 MJ/kg

Efficiency: 70 - 90 %

Developers: Changing World Technologies (West Hampstead, NY), EnerTech Environmental Inc (Atlanta, GA), and Biofuel B.V. (Heemskerk, Netherlands), TNO (Netherlands).
Syngas from HTP

• Conditions: 600 - 650 °C; 300 bar for 0.5 - 2 minutes in supercritical water

• Theoretical: 2 C6H2O6 + 7 H2O => 9 CO2 + 2 CH4 + CO + 15 H2

• Typical products:
  – H2 56 v%
  – CO 4 v%
  – CO2 33 v%
  – CH4 7 v%

• Applications: Syngas for Fischer-Tropsch reaction or other catalytic synthesis reactions
Hybrid biochemical/thermochemical biorefinery

Lignin gasified to CO and H2

Syngas

Gas Cleaning

Catalytic Reactor

Heat

CO₂

Biobased fuels

Distillation

Ethanol & other fermentation products

water

Fibrous Crop

Pretreatment

Saccharification

Cellulose Enzymes

C5 & C6 Sugars

Fermenter

CO₂

Air

Gasifier

Lignin

Syngas

Gas Cleaning

Catalytic Reactor

Heat

CO₂

Biobased fuels

Distillation

Ethanol & other fermentation products

water
The trouble with having an open mind is that people keep coming along and sticking things in it.
Hybrid thermochemical/biochemical biorefinery – Syngas fermentation

Biomass → Gasifier → Syngas → Gas Cleaning → Bioreactor → CO₂ → Biobased fuels and chemicals

Air
Syngas fermentation: Advantages & challenges

• Advantages compared to cellulose hydrolysis
  – Both carbohydrate and lignin converted to syngas
  – Less finicky about composition of feedstock

• Advantages compared to Fischer-Tropsch
  – Robust to inorganic contaminants
  – Opportunity to diversify products

• Challenges
  – Gas-liquid transfer is bottleneck
  – Some tarry products are fermentation inhibitors
  – Limited development of suitable microorganisms
Hybrid thermochemical/biochemical biorefinery: *Bio-oil fermentation*

1. **Fiber**
   - Hot water extraction
   - Pentose

2. **Fermenter**
   - Bio-oil vapor
   - Bio-Oil Recovery
   - Char
   - Char Recovery
   - Phase Separation
   - Anhydrosugar & other carbohydrate
   - Detoxification
   - Fermenter

3. **Distillation**
   - Ethanol
   - Water

4. **Pyrolyzer**
   - Fiber byproduct

5. **Cyclone**
   - Char
Bio-oil fermentation: Advantages & challenges

• Advantages
  – Densifies biomass for transportation
  – Leap frogs the problem of carbohydrate depolymerization

• Challenges
  – Pyrolysis produces some fermentation inhibitors
  – Gas, charcoal, and lignin do not contribute to synfuels production
  – Limited development to date
Questions?