Production fuel from cellulosic biomass

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Motivation for biofuels

Climate Change

Global near-surface temperatures: Annual anomalies 1850-2006

Based on Brohan et al. (2006)
Biomass is renewable and can be carbon neutral
Corn ethanol

Cellulosic ethanol

Source: National Geographic
Motivation for biofuels

Economic utilization of waste biomass
Motivation for biofuels

Energy Independence
Motivation for biofuels

Expensive oil?

Running out of oil?

‘Peak Oil’ Is a Waste of Energy – NY Times 24 August 2009

BP Finds Giant Oil Field Deep in Gulf of Mexico
NY Times 2 Sept. 2009
Figure 4.4.2. Washington historic CO2e emissions by sector with fire emissions superimposed (adapted from Waterman-Hoey and Nothstein 2007, Wiedinmyer and Neff 2007).
Climate change mitigation: CO₂ emission goals relative to current emissions

WA GHG Reduction Goals

2020 to 1990
2035 to 75% 1990
2050 to 50% 1990

Current Market Overview

Current ethanol capacity = 10.6 billion gal/year

Current biodiesel capacity = 700 million gal/year

Source: http://www.ethanolrfa.org/industry/statistics.
Energy Independence and Security Act 2007
(Now they are talking about 60 billion gals/year!!!!)

Total US oil consumption = 320 billion gals/year  Total US oil imports = 220 billion gals/year
U.S. Biomass Resource Assessment

- Updated resource assessment - April 2005
- Jointly developed by U.S. DOE and USDA
- Referred to as the “Billion Ton Study”

- Current biomass production less than 500 million tons/year
The “Billion Ton” potential represents about 1/3 of our petroleum use when converted to liquid fuels.

The ORNL & USDA Resource Assessment Study by Perlach et al. (April 2005) estimated a potential of 1.3 billion tons of biomass at a heating value equivalent. This potential is represented in the graph as 1.9 billion barrels of oil equivalents.

Yields based on mid-term conversion technology:
- Thermochemically Convert Biochem Residues & Forest Resources (0.5)
- Biochemically Convert Non-Edible Carbohydrates (1.1)
- Near-Term Corn Without Affecting Food Prices (0.3)

U.S. Petroleum Production Levels:
- U.S. Oil Production - Max. 1970: 3.5 billion barrels of oil equivalents
- U.S. Oil Production - 2003: 4.4 billion barrels of oil equivalents

2003 U.S. Petroleum Consumption:
- Other (Gasses, LPG, Asphalt, etc.): 6.4 billion barrels of oil equivalents
- 0.5 Jet Fuel: 1.4 billion barrels of oil equivalents
- 2.7 - Gasoline (3.0 Actual)

Based on ORNL & USDA Resource Assessment Study by Perlach et al. (April 2005)
Washington State situation is different

Replace oil with biofuels in Washington State???

18 million tons of biomass available annually
Assume 90 gallons fuel/ton biomass
Total biofuel = 1,620,000,000 gallons/year

Total WA oil consumption = 6,500,000,000 gallons/year
Range of Biorefinery Concepts

Biomass Feedstock
- Trees
- Grasses
- Agricultural Crops
- Residues
- Animal Wastes
- Municipal Solid Waste

Conversion Processes
- Enzymatic Fermentation
- Gas/liquid Fermentation
- Acid Hydrolysis/Fermentation
- Gasification
- Pyrolysis
- Combustion
- Co-firing

Uses
- Fuels
  - Ethanol
  - Renewable Diesel
  - Mixed Alcohols
  - Dimethyl Ether
- Power
  - Electricity
  - Heat
- Chemicals
  - Plastics
  - Solvents
  - Chemical Intermediates
  - Phenolics
  - Adhesives
  - Furfural
  - Fatty Acids
  - Acetic Acid
  - Carbon Black
  - Etc.
- Food and Feed
Adapted from Holmgren et al (2008); Hydrocarbon Processing, Sep.
What is biomass made of?

Representation of Cell Wall Components

- Cellulose
- Hemicelluloses
- Lignin
Cellulose For Chemists

- Very long straight chain polymer of glucose: approximately 10,000 in a row in wood. Cotton is nearly pure cellulose.
- Cellulose molecules link up in bundles and bundles of bundles and bundles of bundles of bundles to make fibers.
- Cellulose forms tight bundles which are very resistant to chemical attack.

Cellulose

[Diagram of cellulose structure with cellobiose unit highlighted]
Hemicelluloses for Chemists

• Branched little uncolored sugar polymers (~ 50 to 300 sugar units)
  – Composition varies between wood species
    • 5 carbon sugars: xylose, arabinose
    • 6 carbon sugars: mannose, galactose, glucose
    • Uronic Acids: galacturonic acid, glucuronic acid
    • Acetyl and methoxyl groups (acetic acid & methanol)
Lignin for Chemists
## Chemical composition

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Glucan (cellulose) (%)</th>
<th>Xylan (hemicellulose) (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn stover</td>
<td>37.5</td>
<td>22.4</td>
<td>17.6</td>
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<tr>
<td>Corn fiber</td>
<td>14.3</td>
<td>16.8</td>
<td>8.4</td>
</tr>
<tr>
<td><strong>Pine wood</strong></td>
<td><strong>46.4</strong></td>
<td><strong>8.8</strong></td>
<td><strong>29.4</strong></td>
</tr>
<tr>
<td><strong>Poplar</strong></td>
<td><strong>49.9</strong></td>
<td><strong>17.4</strong></td>
<td><strong>18.1</strong></td>
</tr>
<tr>
<td>Wheat straw</td>
<td>38.2</td>
<td>21.2</td>
<td>23.4</td>
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<tr>
<td>Switchgrass</td>
<td>31.0</td>
<td>20.4</td>
<td>17.6</td>
</tr>
</tbody>
</table>

Chemical composition of biomass (adapted from Mosier et al., 2005).
Fig. 3. Current strategies for production of liquid fuels from biomass.

Bioconversion of biomass to ethanol (hydrolysis)

Biomass → Pretreatment

Pretreatment

Biomass → Liquid phase

Liquid phase → Sugars → Ethanol

Sugars → Fermentation

Ethanol

Ethanol

Recovery

Solid phase

Solid phase → Lignin

Lignin

Solid phase → Cellulose

Cellulose

Cellulose

Hydrolysis

Hydrolysis

Sugars

Sugars

Ethanol

Fermentation

Fermentation
Pretreatment

Schematic of goals of pretreatment on lignocellulosic material (adapted from Hsu et al., 1980).
Various pretreatment methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Increases accessible surface area</th>
<th>Decrystalizes cellulose</th>
<th>Removes hemicellulose</th>
<th>Removes lignin</th>
<th>Alters lignin structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncatalyzed steam explosion</td>
<td>■</td>
<td>■</td>
<td>■</td>
<td>■</td>
<td>■</td>
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<tr>
<td>Liquid hot water</td>
<td>■</td>
<td>ND</td>
<td>■</td>
<td>■</td>
<td>■</td>
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<tr>
<td>pH controlled hot water</td>
<td>■</td>
<td>ND</td>
<td>■</td>
<td>■</td>
<td>ND</td>
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<tr>
<td>Flow-through liquid hot water</td>
<td>■</td>
<td>ND</td>
<td>■</td>
<td>■</td>
<td>■</td>
</tr>
<tr>
<td>Dilute acid</td>
<td>■</td>
<td>■</td>
<td>■</td>
<td>■</td>
<td>■</td>
</tr>
<tr>
<td>Flow-through acid</td>
<td>■</td>
<td>■</td>
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<tr>
<td>AFEX</td>
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<td>ARP</td>
<td>■</td>
<td>■</td>
<td>■</td>
<td>■</td>
<td>■</td>
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<tr>
<td>Lime</td>
<td>■</td>
<td>ND</td>
<td>■</td>
<td>■</td>
<td>■</td>
</tr>
</tbody>
</table>

Minor effect ■ Major effect ■ Adapted from Mosier et al., 2005
Bioconversion of biomass to ethanol (hydrolysis)

Biomass → Pretreatment → Liquid phase → Sugars → Ethanol

Solid phase
- Lignin
- Cellulose

Hydrolysis → Fermentation → Sugars → Ethanol

Recovery
There are a large number of fungal enzymes responsible for the breakdown of each wood component. Each enzyme plays specific roles:

» **Endo-beta-1,4-glucanase** acts within the chain, breaking it into smaller units and providing more "ends" for CBH.

» **Cellobiohydrolase** (CBH), acts on the end of the molecule successively cleaving off the disaccharide cellobiose.

» **Beta-glucosidase** (or cellobiase) which cleaves cellobiose to two glucose units.
Cellulases

Endoglucanases (EG)
cutting the cellulose chains randomly

Celllobiohydrolyses (CBH)
cutting cellobiose units of the ends of the cellulose chains
Fermentation

- Defined as:
  Cellular metabolism under anaerobic conditions for the production of energy and metabolic intermediates
- Many organisms can “ferment” (i.e., grow anaerobically)
- Not all produce ethanol as an end-product of fermentation
  - Butanol
  - Acetic acid
  - Propionic acid
  - Lactic acid
Thermoconversion - Basic Definitions

Pyrolysis

- Thermal conversion (destruction) of organics in the absence of oxygen
- In the biomass community, this commonly refers to lower temperature thermal processes producing liquids as the primary product
- Possibility of chemical and food byproducts

Gasification

- Thermal conversion of organic materials at elevated temperature and reducing conditions to produce primarily permanent gases, with char, water, and condensibles as minor products
- Primary categories are partial oxidation and indirect steam
Biomass Conversion to Fuels –
Major *Biochemical* Conversion Steps

- **Feed Processing and Handling**
  - Size Reduction
  - Storage and Handling
  - De-watering
  - Drying

- **Gasification**
- **Pyrolysis**

- **Gas Cleanup**
  - Partial Oxidation
  - Air blown
  - Oxygen blown
  - Indirect
  - Flash pyrolysis
  - Steam pyrolysis
  - Vacuum pyrolysis

- **Gas Conditioning**
  - Methane reforming
  - CO₂ removal
  - H₂/CO adjustment
  - Sulfur polishing

- **Fuel Synthesis**
  - C1 chemistry
    - FT liquids
    - MTG
    - Mixed OH

- **Heat & Power**
  - Upgrading
  - Production Separation

**High T Separation**
- Particulate removal
- Tar reforming
- Benzene removal
- S, N, Cl mitigation
- High T Filtration
- Alkali removal

**Collection/Fractionation**
- Aerosol collection
- Microfiltration
- Chemical Stabilization
- Hydrotreating
- Dehydration

**Hydrotreating**

**Dehydration**

**Sulfur polishing**

**Aerosol collection**

**Microfiltration**

**Chemical Stabilization**

**Hydrotreating**

**Dehydration**

10/29/2009
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>FAST PYROLYSIS</td>
<td>75%</td>
<td>12%</td>
<td>13%</td>
</tr>
</tbody>
</table>
|                  | *moderate temperature*  
|                  | *short residence time*  
| GASIFICATION    | 5%     | 10%  | 85% |
|                  | *high temperature*  
|                  | *long residence time*  

Source: Bridgewater and Czernik
Primary Energy Source: Natural Gas, Coal, Biomass, Extra Heavy Oil

Syngas Step: Syngas (CO + H₂)

Conversion Technology: Fischer Tropsch (FT), Upgrading

Products:
- Syngas to Liquids (GTL) Process:
  - 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
Pyrolysis is usually performed at lower temperature to produce a liquid biocrude.

- Thermal decomposition occurring in the absence of oxygen
- Is also the first step in combustion and gasification processes
- Known as a technology for producing charcoal and chemicals for thousands of years
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
10/29/2009
There are a number of applications for biocrudes.
Potential for mobile unit

Upgrade biooil at refinery

Much cheaper to ship biooil than biomass because of higher energy density
### Yields & Carbon Utilization

<table>
<thead>
<tr>
<th></th>
<th>Cellulosic Ethanol (BC)</th>
<th>Cellulosic Ethanol (TC) Steam</th>
<th>Cellulosic Ethanol (TC) POX</th>
<th>Ethanol Corn Dry Mill</th>
<th>Ethanol Sugar Cane</th>
<th>Pyrolysis Fuel Oil Intermediate</th>
<th>Methanol Intermediate</th>
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<tbody>
<tr>
<td><strong>Yield</strong></td>
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<td></td>
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<tr>
<td>gal/tan biomass</td>
<td>90</td>
<td>80</td>
<td>77</td>
<td>102</td>
<td>12.3</td>
<td>137</td>
<td>149</td>
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<tr>
<td>gal Ethanol eq/ton biomass</td>
<td>90</td>
<td>80</td>
<td>77</td>
<td>102</td>
<td>12.3</td>
<td>135</td>
<td>115</td>
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<td><strong>By-Product</strong></td>
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<tr>
<td>gal Ethanol eq/ton biomass</td>
<td>--</td>
<td>C$_3$OH</td>
<td>C$_3$OH</td>
<td>DDGS</td>
<td>Sugar</td>
<td>--</td>
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<tr>
<td>Electricity, kWh/ton</td>
<td>196</td>
<td>14</td>
<td>15</td>
<td>33 wt%</td>
<td>5.7 wt%</td>
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<td><strong>External Fuel</strong></td>
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<td>Nat Gas, MMBtu/dry ton</td>
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<td>3.11</td>
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<td><strong>Process Efficency, HHV</strong></td>
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<tr>
<td>Overall (Prod + Byprod) %</td>
<td>48</td>
<td>47</td>
<td>46</td>
<td>74</td>
<td>68</td>
<td>55</td>
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<tr>
<td>Product %</td>
<td>44</td>
<td>40</td>
<td>37</td>
<td>44</td>
<td>67</td>
<td>55</td>
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<td><strong>Carbon Utilization (basis - feed carbon)</strong></td>
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<td>Product %</td>
<td>31</td>
<td>27</td>
<td>26</td>
<td>39</td>
<td>59</td>
<td>35</td>
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<tr>
<td>By-Product %</td>
<td>--</td>
<td>6</td>
<td>5</td>
<td>37</td>
<td>--</td>
<td>0</td>
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<tr>
<td>Acid Gas/Fermentation CO2 %</td>
<td>16</td>
<td>15</td>
<td>24</td>
<td>19</td>
<td>--</td>
<td>0.3</td>
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<tr>
<td>Combustion Flue Gas CO2 %</td>
<td>53</td>
<td>52</td>
<td>36</td>
<td>5</td>
<td>41</td>
<td>47</td>
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<tr>
<td>Other %</td>
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<td>%</td>
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<td>NG</td>
<td>Flue Gas</td>
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</table>
Major DOE Biofuels Project Locations
Geographic, Feedstock, and Technology Diversity

Nine Small-Scale Biorefinery Projects
Four Commercial-Scale Biorefinery Projects
Four Improved Enzyme Projects
Five Projects for Fermentation Organisms
Five Thermochemical Syngas Projects
Three Office of Science Bioenergy Centers
DOE Joint Solicitation Biomass Projects
Five Thermochemical Bio-Oil Projects
Six University Projects

Regional Partnerships
South Dakota State Univ., Brookings, SD
Cornell University, Ithaca, NY
Univ. of Tennessee, Knoxville, TN
Oklahoma State Univ., Stillwater, OK
Oregon State Univ., Corvallis, OR

Modified 10/1/2008