Technical Barriers in Converting Lignocellulose to ethanol

Samson Hailemichael
Introduction to Green Chemistry (CHEM 0671)
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Outline

• Introduction
• Benefits
• Drawbacks
• Conventional process
• Pretreatment methods
• Cellulolytic processes
• Conclusion
Background History

- First attempt was done in Germany in 1898
- It involved dilute acid hydrolysis of cellulose to glucose
- Were able to produce 18 gallon per ton of wood waste
- Improved to 50 gallons per ton of biomass
- USA were able to produce 25 gallons per ton
- During World War II, USA improved its production to 50 gallons per ton
- Still wasn’t profitable
- Gradually this process is replaced by enzyme hydrolysis
- Still some form of pretreatment is necessary
Implication to Green Chemistry

• Excess availability (agricultural and forest residues, Solid Municipal Waste)
• Reduction of GHG emission
• Renewability
• In the case of perennial plants
  – Increase nutrient capture,
  – improve soil quality,
  – sequester organic carbon, and reduce erosion.
### National Resources For Biofuel Production

#### Fig. A. Potential Biomass Resources: A Total of More than 1.3 Billion Dry Tons a Year from Agricultural and Forest Resources.

#### Table A. Potential Biomass Resources

<table>
<thead>
<tr>
<th>Biomass Resources</th>
<th>Million Dry Tons per Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest Biomass</td>
<td></td>
</tr>
<tr>
<td>Forest products industry residues</td>
<td>145</td>
</tr>
<tr>
<td>Logging and site-clearing residues</td>
<td>64</td>
</tr>
<tr>
<td>Forest thinning</td>
<td>60</td>
</tr>
<tr>
<td>Fuelwood</td>
<td>52</td>
</tr>
<tr>
<td>Urban wood residues</td>
<td>47</td>
</tr>
<tr>
<td><strong>Subtotal for Forest Resources</strong></td>
<td><strong>368</strong></td>
</tr>
<tr>
<td>Agricultural Biomass</td>
<td></td>
</tr>
<tr>
<td>Annual crop residues</td>
<td>428</td>
</tr>
<tr>
<td>Perennial crops</td>
<td>377</td>
</tr>
<tr>
<td>Miscellaneous process residues, manure</td>
<td>106</td>
</tr>
<tr>
<td>Grains</td>
<td>87</td>
</tr>
<tr>
<td><strong>Subtotal for Agricultural Resources</strong></td>
<td><strong>998</strong></td>
</tr>
<tr>
<td><strong>Total Biomass Resource Potential</strong></td>
<td><strong>1366</strong></td>
</tr>
</tbody>
</table>
Figure 5. Total MSW Generation (by material), 2008
250 Million Tons (before recycling)

- Paper: 31.0%
- Other: 3.3%
- Food scraps: 12.7%
- Metals: 8.4%
- Glass: 4.9%
- Plastics: 12.0%
- Rubber, leather and textiles: 7.9%
- Wood: 6.6%
- Yard trimmings: 13.2%
Land area of crops planting and annual production in Malaysia for year 2007 (DOA, 2009a).

<table>
<thead>
<tr>
<th></th>
<th>Area of planting (Ha)</th>
<th>Production (MT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil palm(^a)</td>
<td>4,304,914</td>
<td>26,120,754</td>
</tr>
</tbody>
</table>

Estimated quantity of lignocellulosic biomass produced in Malaysia in the year 2007.

<table>
<thead>
<tr>
<th>Types</th>
<th>Quantity (ktons)</th>
<th>Ratio</th>
<th>Source</th>
<th>Source (ktons)</th>
<th>MC (% wt)</th>
<th>DW (ktons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agriculture waste</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil palm fronds</td>
<td>46,837(^a)</td>
<td>0.572</td>
<td>Oil palm FFB</td>
<td>81,920(^c)</td>
<td>60.0(^d)</td>
<td>18,735</td>
</tr>
<tr>
<td>EPFB</td>
<td>18,022</td>
<td>0.220 (^b)</td>
<td></td>
<td></td>
<td>65.0(^b)</td>
<td>6308</td>
</tr>
<tr>
<td>Oil palm fibers</td>
<td>11,059</td>
<td>0.135 (^b)</td>
<td></td>
<td></td>
<td>42.0(^b)</td>
<td>6414</td>
</tr>
<tr>
<td>Oil palm shells</td>
<td>4506</td>
<td>0.055 (^b)</td>
<td></td>
<td></td>
<td>7.0(^b)</td>
<td>4190</td>
</tr>
<tr>
<td>Oil palm trunks(^a)</td>
<td>10,827</td>
<td>–</td>
<td>Replanting</td>
<td>–</td>
<td>75.9(^e)</td>
<td>2609</td>
</tr>
</tbody>
</table>
Draw backs in converting lignocellulose to ethanol

• Fermentable sugars are protected

• Lack of available substrate’s surface area

• Slow conversion rate

• Co-production of inhibitor

• Creating technical barriers
Structure of Lignocellulose

• **Lignocellulose** has three major components
  1. Cellulose (38-50%)
  2. Hemicellulose (17-32%)
  3. Lignin (15-30%)
<table>
<thead>
<tr>
<th>Lignocellulosic Material</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardwood stems</td>
<td>40–55</td>
<td>24–40</td>
<td>18–25</td>
</tr>
<tr>
<td>Corn cobs</td>
<td>45</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>Grasses</td>
<td>25–40</td>
<td>35–50</td>
<td>10–30</td>
</tr>
<tr>
<td>Paper</td>
<td>85–99</td>
<td>0</td>
<td>0–15</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>30</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
<td>Sorted refuse</td>
<td>60</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Leaves</td>
<td>15–20</td>
<td>80–85</td>
<td>0</td>
</tr>
<tr>
<td>Cotton seed hairs</td>
<td>80–95</td>
<td>5–20</td>
<td>0</td>
</tr>
<tr>
<td>Newspaper</td>
<td>40–55</td>
<td>25–40</td>
<td>18–30</td>
</tr>
<tr>
<td>Waste papers from chemical pulps</td>
<td>60–70</td>
<td>10–20</td>
<td>5–10</td>
</tr>
<tr>
<td>Primary wastewater solids</td>
<td>8–15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid cattle manure</td>
<td>1.6–4.7</td>
<td>1.4–3.3</td>
<td>2.7–5.7</td>
</tr>
<tr>
<td>Coastal bermudagrass</td>
<td>25</td>
<td>35.7</td>
<td>6.4</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>45</td>
<td>31.4</td>
<td>12</td>
</tr>
<tr>
<td>Swine waste</td>
<td>6.0</td>
<td>28</td>
<td>na</td>
</tr>
</tbody>
</table>

Traditional Process

• It includes four main steps
  – Pretreatment
  – Hydrolysis
  – Fermentation
  – Purification
• Ethanol concentration should be over 99.5%
• Pretreatment remains the main obstacle
Traditional Process

How Cellulosic Ethanol is Made

1. **Biomass is harvested and delivered to the biorefinery.**
2. **Biomass is cut into shreds and pretreated with heat and chemicals to make cellulose accessible to enzymes.**
3. **Enzymes break down cellulose chains into sugars.**
4. **Microbes ferment sugars into ethanol.**
5. **Ethanol is purified through distillation and prepared for distribution.**
Disadvantage of Traditional process

• In this conventional process, the enzyme hydrolytic reaction rate decreases
  – End product inhibition
• Increased amount of enzyme to reach the maximum concentration of end product (which is glucose)
• Larger cost in building different reactor
1. Size reduction
2. Pretreatment
3. Detoxification and neutralization
4. Solid and liquid separation
5. Enzymatic hydrolysis
6. Fermentation of cellulosic sugars
7. Product recovery
8. Residue processing
9. Fermentation of hemicellulosic sugars
10. Coproducts
11. Ethanol
Pretreatment

• To break the lignin seal and to disrupt the crystalline structure of cellulose
• Expensive processing step
• Effective pretreatment is characterized by several factors
  – Production of reactive cellulosic fiber for enzymatic attack
  – it avoids the size reduction process
  – Minimizes the presence of inhibitor byproduct
  – Avoid the destruction of hemicellulose and cellulose
  – Minimize energy demands and limits cost
  – Less residue
The Importance of Pretreatment

Fig. 1. Scanning Electron Microscopy. 
(a) A corn stover particle shows a smooth surface with a few micron-sized pores after enzyme hydrolysis converted 11% of cellulose to glucose in 3 h.  
(b) This corn stover particle has many more pores. It was pretreated in water at 190°C for 15 min and hydrolyzed by enzymes at 50°C for 3 h, resulting in 40% cellulose conversion to glucose.
<table>
<thead>
<tr>
<th>Pretreatment Process</th>
<th>Advantages</th>
<th>Limitations and Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical comminution</td>
<td>Reduces cellulose crystallinity</td>
<td>Power consumption usually higher than inherent biomass energy</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>Causes hemicellulose degradation and lignin transformation; cost-effective</td>
<td>Destruction of a portion of the xylan fraction; incomplete disruption of the lignin–carbohydrate matrix; generation of compounds inhibitory to microorganisms</td>
</tr>
<tr>
<td>AFEX</td>
<td>Increases accessible surface area, removes lignin and hemicellulose to an extent; does not produce inhibitors for downstream processes</td>
<td>Not efficient for biomass with high lignin content</td>
</tr>
<tr>
<td>CO₂ explosion</td>
<td>Increases accessible surface area; cost-effective; does not cause formation of inhibitory compounds</td>
<td>Does not modify lignin or hemicelluloses</td>
</tr>
<tr>
<td>Ozonolysis</td>
<td>Reduces lignin content; does not produce toxic residues</td>
<td>Large amount of ozone required; expensive</td>
</tr>
<tr>
<td>Acid hydrolysis</td>
<td>Hydrolyzes hemicellulose to xylose and other sugars; alters lignin structure</td>
<td>High cost; equipment corrosion; formation of toxic substances</td>
</tr>
<tr>
<td>Alkaline hydrolysis</td>
<td>Removes hemicelluloses and lignin; increases accessible surface area</td>
<td>Long residence times required; irrecoverable salts formed and incorporated into biomass</td>
</tr>
<tr>
<td>Organosolv</td>
<td>Hydrolyzes lignin and hemicelluloses</td>
<td>Solvents need to be drained from the reactor, evaporated, condensed, and recycled; high cost</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>Produces gas and liquid products</td>
<td>High temperature; ash production process needs more research</td>
</tr>
<tr>
<td>Pulsed electrical field</td>
<td>Ambient conditions; disrupts plant cells; simple equipment</td>
<td>Rate of hydrolysis is very low</td>
</tr>
<tr>
<td>Biological</td>
<td>Degradates lignin and hemicelluloses; low energy requirements</td>
<td></td>
</tr>
</tbody>
</table>

Acid Pretreatment

Size reduction

Pretreatment

Detoxification and neutralization

Solid and liquid separation

Ammonia Fiber Explosion (AFEX)

The SunOpta BioProcess Group developed the first continuous process in the world to pretreat cellulosic materials with high pressure anhydrous ammonia.
Trifluoroacetic Acid to pretreat Lignocellulose

Diagram showing the process:
- Straw is cut and dissolved with TFA.
- The mixture undergoes fractional distillation.
- The residue is separated from the supernatant and precipitate.

Dong D, et al.
Enzyme Hydrolysis

Cellulose (crystalline) → Endo-1,4-β-glucanase → Cellulose (non-crystalline)

Exo-cellobiohydrolase → Celllobiose

Endo-1,4-β-glucanase → Cellobiase → D-glucose

Exo-1,4-β-glucosidase
Size reduction

Pretreatment

- Increase biomass yield per acre
- Improve biomass characteristics

Direct conversion of cellulose and hemicellulosic sugars

Product recovery

Ethanol

Residue processing

Coproducts

- Exploit biological catalysts
- Reduce severity and wastes
- Raise sugar yields

- Eliminate separation
- Combine enzyme production, hydrolysis, and fermentation into one reactor
- Integrate total process

Conclusion

• To meet our current energy demand, we need to diversify our energy source
• There is a huge amount of biomass available as a waste every year that can be potential converted into bio-fuel
• One of the key barriers in lignocellulosic ethanol production is the pretreatment step
• To address this problem intensive research has to be done to find one efficient pretreatment method which can apply for all available biomass resources
References


• Dexian Dong, Jie Sun, Feiyun Huang, Qian Gao, Yi Wang, Rongxiu Li. Using Trifluoroacetic Acid to Pretreat Lignocellulosic Biomass. biomass and bioenergy xxx (2009 ) 1–5.


• WWW.Wikipedia.org
Thank you for your patience!!!