Process Engineering of Renewable Resources for Ethanol Production

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Growth in US Population

Estimates and projections of US Population from 1950 to 2050

http://www.census.gov/population/www/pop-profile/natproj.html
US Petroleum Consumption

Source: Sandia National Laboratories and U.S. Dept. of Energy, Energy Information Administration

Oil Consumption

Projected Shortfall

Million Bbls / day

Oil Field Production at 1990-2000 Growth Rates

Source: Sandia National Laboratories and U.S. Dept. of Energy, Energy Information Administration
Green House Gases (GHG)

Amount generated in US: 20 tons / yr per person

According to Hill and Tilman, reduction in GHG varies according to feedstock:

- corn ethanol: - 12 %
- soy biodiesel: - 40 %
- cellulose ethanol: as much as - 275 % (depends on production process)

from Tyner, August, 2007
Trends

- More people
- Less Petroleum
- Growing Energy Needs
- Increasing CO$_2$
- Competing uses for Land
- Opportunities for Renewable Resources
Production: Biochemical vs. Chemical Conversion

Transformation through Intermediates (sugars)

"Biochemical conversion"

main difference is in the primary catalysis system

Reduction to building blocks (CO, H₂)

"Thermochemical conversion"

David Dayton, NREL, IEA, 2007
Alternate Biofuels

Cellulose Ethanol
Butanol
Isobutanol
Alkanes
Oils and lipids

Sommerville et al, Patrinos et al, 2007
Thermal Processing Derived Fuels

P-Series fuel
Synthetic bio Fischer-Tropsch diesel
Methanol
Dimethyl ether (DME)
Bio synthetic natural gas (Bio-SNG)
Green pyrolysis diesel

from the New York Times

“The fuel of the future is ethanol”

Henry Ford, 1925
Why ethanol?

1. Properties, use of fuel: known and accepted
2. Significant infrastructure exists due to corn ethanol
3. Cellulose ethanol uses non-food feedstocks
4. Larger volumes already produced; larger volumes are feasible
The 6 Steps: Conversion of Cellulose to Biofuels

1. Feedstock Preparation
2. Pretreatment
3. Hydrolysis
4. Fermentation
5. Separations
6. Combustion or Gasification

Microbes (Yeast, Bacteria)

Fuel

Co-products

Energy

CO₂

Feedstock

Catalysts

Residue

Ladisch, 2006
Feedstock: Corn Fiber
Corn Stover, 1 to 3 tons / acre
Switchgrass: 5 to 7 tons /acre

Elbersen, Wageningen, 2004
Feedstock: Trees, 5 to 10 tons /acre

Chapple and Meilan, 2006
Biomass Resources in Tons / sq km /year
Sets stage for Cellulose Ethanol

From NREL Website, 2005

This study estimates the technical biomass resources currently available in the United States by county. It includes the following feedstock categories:
- Agricultural residues (crops and animal manure);
- Wood residues (forest, primary mill, secondary mill, and urban wood);
- Municipal discards (methane emissions from landfills and domestic wastewater treatment);
- Dedicated energy crops (on Conservation Reserve Program and Abandoned Mine Lands).
Controlled pH Aqueous Pretreatment

Cook cellulose in liquid water at high temperatures and pressures

- Maximize solubilization to hemicellulose oligosaccharides
- Minimize hydrolysis to monomeric sugars (xylose)
- Minimize sugar degradation

Improves reactivity of cellulose
Pretreatment gives enzyme accessible substrate

Mosier et al, 2005

Amorphous Region

Crystalline Region

Hemicellulose
1. Pretreatment: (carry out at high temperature)

\[ \text{pretreatment (a physical change)} \]

\[ C \rightleftharpoons C^* \]

\[ C = \text{native cellulose} \]
\[ C^* = \text{hydrated cellulose} \]
2. Hydrolysis
(at low temperature, using enzymes)

\[ C \xrightarrow{k_1} C^* \xrightarrow{k_2} G_n \xrightarrow{k_3} G \xrightarrow{k_4} \text{Degradation Products} \]

- \( C \) = native cellulose
- \( C^* \) = hydrated cellulose
- \( G_n \) = glucans (oligosaccharides)
- \( G \) = glucose (monomer)
Example: Distillers Grains (contain cellulose)
Dry Mill (Grind) Process

Grain $\rightarrow$ Milling $\rightarrow$ Cooking $\rightarrow$ Ferment $\rightarrow$ Distillation / Dehydration $\rightarrow$ Ethanol

Water $\rightarrow$ Enzymes $\rightarrow$ CO₂ $\rightarrow$ Stillage $\rightarrow$ DG $\rightarrow$ DDGS $\rightarrow$ Backset

Mosier, et al., 2006
Dry Mill (Dry Grind) Process with Cellulose Conversion

Pretreatment Advances

Comparison of different pretreatments: cooperative effort between universities and industry (CAFI project)

1. Liquid hot water
2. Steam explosion
3. Ammonia freeze expansion
4. Dilute acid

All are viable, method depends on type of biomass
Without pretreatment, enzyme conversion < 5%
With pretreatment, enzyme conversion > 75%

Wyman et al. 2006, 2007
Components of plant cell walls give both 5 and 6 carbon sugars after pretreatment / enzyme hydrolysis. Cellulose conversion requires yeast or bacteria that ferment both 5 and 6 carbon sugars to ethanol.
Yeast Metabolism: pentose fermentation

**Glucose**
- Glucose-6-P
- Fructose-6-P
- 3-Phosphoglycerate
- Phosphoenolpyruvate
- Pyruvate
- Acetaldehyde
- Ethanol

**Xylose**
- NAD(P)H
- NAD(P)+
- NAD+
- NADH
- Xylulose
- Xylulose-5-P
- PPP
- Glyceraldehyde-3-P
- 3-Phosphoglycerate
- Phosphoenolpyruvate

Increased yield of ethanol by 40%

Ho, et al
# Cellulose Compositions of Feedstocks

<table>
<thead>
<tr>
<th></th>
<th>DDGS</th>
<th>DG</th>
<th>Corn Fiber</th>
<th>Corn Stover</th>
<th>Yellow Poplar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>16%</td>
<td>12%</td>
<td>14%</td>
<td>34%</td>
<td>46</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>13%</td>
<td>10%</td>
<td>24%</td>
<td>29%</td>
<td>24</td>
</tr>
<tr>
<td>Starch</td>
<td>5%</td>
<td>6%</td>
<td>20%</td>
<td>Neg.</td>
<td>-----</td>
</tr>
<tr>
<td>Protein</td>
<td>26%</td>
<td>34%</td>
<td>12%</td>
<td>2.3</td>
<td>-----</td>
</tr>
<tr>
<td>Lignin</td>
<td>2%</td>
<td>2%</td>
<td>8%</td>
<td>11</td>
<td>26</td>
</tr>
<tr>
<td>Est. Max. Ethanol gal / ton</td>
<td>58</td>
<td>48</td>
<td>100</td>
<td>106</td>
<td>115</td>
</tr>
</tbody>
</table>
Cellulose Conversion Plant

1. Production
   - Seed
   - Fertilizer
   - Water
   - Labor
   - Energy

2. Pre-processing + Storage
   - Water, Enzymes

3. Storage

4. Pretreatment
   - Water
   - Steam

5. Hydrolysis
   - Water
   - Stillage
   - Steam

6. Fermentation
   - Yeast

7. Filter, Centrifuge
   - Residue
   - Steam

8. Distillation/Drying
   - Ethanol
   - Stillage

9. Stillage
Hydrolysis / Fermentation / Consolidated Bioprocessing

**Hydrolysis:**
enzymes break down cellulose to sugars from pretreated biomass (Genencor, Novo)

**Fermentation:**
Engineered yeast or bacteria ferment both 5 and 6 carbon sugars to ethanol

**Consolidated Bioprocessing:**
Advanced microorganisms ferment cellulose directly to ethanol (Lynd et al)
Simpler Ethanol Production via Advanced Biotechnology

Current Approach

- Feedstock Supply
- Acid/Base Supply
- Neutralization Additive
- Enzyme Supply
- Harsh Pretreatment
- Conditioning
- Hydrolysis
- Cellulose Fermentation
- Xylose Fermentation
- Distillation & Storage

Mascomma Approach

- Feedstock Supply
- Simple Pretreatment
- Consolidated Bioprocessing (CBP)
- Distillation & Storage

Lynd, Flatt, South, Mascoma, 2007
Challenges and Opportunities

1. Implementing large scale systems
2. “De-risking” integrated technologies
3. Establishing test-beds
4. Reducing capital and operational costs
5. Maintaining investment environment
6. 10 year consistent policy (long term) sustained commitment
Plant Science Biofuel Research Targets Production

**Plant Science**

**Quantity**: Biomass productivity can be enhanced.

**Quality**: Biomass saccharification efficiency can be enhanced.

**Sustainability**: Low cost, environmentally sound production schemes will require optimized mineral and water-use efficiency.

**Durability**: For optimized yields biofuel crops must be resistant to pests and pathogens.

*These factors are intimately interconnected*
Bioprocess Engineering Targets Processing

Bioprocessing

**Yield at Plant Gate:** Biomass storage and utilization

**Pretreatment / Enzyme Hydrolysis:** Biomass saccharification efficiency

**Fermentation:** Substrate range. High rates at high concentrations.

**Recovery:** Bioproducts, biofuels, and coproducts from aqueous fermentation media at low cost using environmentally sound methods.

**Systems integration.** Process robustness, low(er) capital cost, energy efficiency. Sustainable. Reduced footprint.

*These factors are intimately interconnected with plant science*
Opportunities: Changing Landscapes

Designer crops for bio-energy production

Bioprocess Engineering built around advanced biocatalysts (yeasts, enzymes, fixed bed catalysts) that process designer crops

High energy corn that maximizes polysaccharides rather than oil or protein

Understand role of forages (switchgrass) and wood poplar grown for energy crops

Seeds for the same
A Global View

Sun → Heat → Net CO₂ → CO₂, H₂O → Renewable Carbon → O₂ → Non-Renewable Carbon → Waste → Fuels, Chemicals

Heat