Bioenergy, Agriculture and the Chemical Industry

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Bioenergy and Agriculture

Bioenergy

Energy derived from renewable resources in the form of transportation fuels, electrical energy, heat and power. Broadly defined, bioenergy would includes solar, photovoltaic, wind energy, and biomass, including energy crops. Agriculture provides biomass.

Agriculture

“the science, art, and business of cultivating the soil, producing crops, and raising livestock; farming.”

The American Heritage Dictionary, 1982
Snapshot: Agriculture in Mexico and US

Mexico: 27.3 million hectares total

7.7 million corn

67 kg fertilizer / hectare

US: 179 million hectares

28.7 million in corn

103 kg fertilizer / hectare

Mexico’s population about 40% of that of US.

2.47 acres = 1 hectare
World Energy Use: 13% is Renewable

46% Renewable Energy Use in Brazil

Source: MINISTÉRIO DE MINAS E ENERGIA - Brasil, 2008
### 2007 US Land Use: 2.3 Billion Acres
18% is cropland

<table>
<thead>
<tr>
<th>Allocated Use</th>
<th>% of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest-use Land</td>
<td>30</td>
</tr>
<tr>
<td>Grassland</td>
<td>27</td>
</tr>
<tr>
<td>Cropland</td>
<td>18</td>
</tr>
<tr>
<td>Parks, National Defense Areas,</td>
<td>14</td>
</tr>
<tr>
<td>Transportation</td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>9</td>
</tr>
<tr>
<td>Urban Areas</td>
<td>3</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>101</strong></td>
</tr>
</tbody>
</table>

**Source:**
### Agricultural Productivity

<table>
<thead>
<tr>
<th>Year</th>
<th>Output</th>
<th>Input</th>
<th>Total Factor Productivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1948</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1978</td>
<td>2.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2008</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: USDA ERS

Indices 1948 = 1
US Input / Output Ratios since 1950: fertilizers and pesticides are important

Index (1 = 1975 Value)

Agricultural Inputs per Unit of Output

- Pesticides
- Fertilizer
- Energy
- Labor
- Durable Goods
- Land

Source: USDA ERS

Source: USDA ERS
Agriculture depends on Chemical Industry for Fertilizer: Ammonia Synthesis

$$\frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \overset{\Rightarrow}{\text{NH}_3} ; \quad \Delta H_{298K} = -45.7 \text{kJ/mol}$$

Feedstocks:
- N\textsubscript{2} from air,
- H\textsubscript{2} from natural gas, naptha or heavy oil

Energetics (high pressure, temperatures, recycle require energy)
- Exothermic
- Rate favored by high temperature (1000 to 3000 C)
- Equilibrium favored by low temperature and high pressure

Role of Catalysis (Haber chemistry; process by Bosch; BASF)
- 1909 Os, reaction at 600 C, 175 atm (80 g NH\textsubscript{3})
- 1913 Fe / Al\textsubscript{2}O\textsubscript{3} / K catalyst, 400 – 700 C, 300 atm (30 tons NH\textsubscript{3})

Other catalysts / processes developed (plants at 1500 tons / day)

from Modak, Resonance, 2002
Ammonia Production (2010)
est. 80% used for fertilizing crops.

Global Total Produced: 131 million metric tons (32% from China)

US total consumed: 14.7 million metric tons

Produced in US: 8.3 million metric tons
Imported: 6.4
Price: $390 / ton

43% imported

Currently depends on natural gas, a non renewable resource.

1U.S. Geological Survey, Mineral Commodity Summaries, January 2011
## Companies and customer

### Seed Producers
- Dow Agrosciences
- Monsanto
- Dupont
- Syngenta
- Bayer

### GMO Crops
- Soybeans
- Maize
- Sugar Beet
- Potato
- Cotton

(Biotech) Chemical Enterprise

Agriculture

*Industry websites; GMO Compass, Genius GmbH, 2008*
Increase in Genetically Engineered Crops

US Percent of planted acres

HT = herbicide tolerance
Bt = insect resistance

Fernandez-Cornejo, USDA, ERS, July 1, 2011
## Energy consumed in Agriculture

### US Energy Consumed and CO2 emitted (snapshot, 2005)

<table>
<thead>
<tr>
<th>Sector</th>
<th>Energy, quads</th>
<th>CO₂, Tg emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agriculture</td>
<td>1+</td>
<td>69</td>
</tr>
<tr>
<td>All Sectors</td>
<td>95</td>
<td>5874</td>
</tr>
<tr>
<td>Total US</td>
<td>96</td>
<td>5943</td>
</tr>
</tbody>
</table>

*Does not include fertilizer, pesticide inputs*

**Fuel vs Food Debate?**

US agriculture and Forestry Greenhouse Gas Inventory, 1990-2005, USDA
Biomass (Cellulose) is Part of Agriculture

a. Agricultural residues
   Global, US Midwest

b. Wood
   Upper Midwest US, Canada (hardwoods)
   Southeast US (softwoods)
   Europe (softwoods, hardwoods)

c. Purposely grown energy crops
   Brazil
   US – still to be determined
   Africa?
Feedstocks for the Chemical Enterprise: Cornstalks

1 to 2 tons (dry basis) / acre

Residue left on ground

with permission, Shinners, 2009
Purposely Grown Switchgrass

- Warm-season perennial grass
- Low fertility requirement
- Tolerant of poor soils
- High yield (5-7 ton/acre)

Photos courtesy of Department of Agronomy, Purdue University
Biorefineries and the Chemical Enterprise

Bio(chemical) refinery:

1. Produce energy from renewable domestic raw materials (energy goal)
2. Establish robust biobased industry (economic goal)
3. Establish off-take contracts.

Biorefineries with diversified product portfolios could offer great potential for agriculture to capture added value, and a higher return on investment, while achieving energy and economic goals simultaneously.

Bozell and Petersen, 2010
Agriculture gives back:
Biochemical and 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
**Red Ocean / Blue Ocean**

**Red Ocean:** is where every industry is today: there is a defined market, defined competitors, and a typical way to run a business in any industry.

**Blue Ocean:** On the other hand, is where everyone would like to be. It is where you create uncontested markets and capture new demand, is where you break the value-cost trade-off and is where you make the competition irrelevant.

Agricultural Markets in the Americas

What can be done?

Red Ocean
- Grain
- Sugar
- Vegetable Oils
- Food (People)
- Feed (Animals)

Blue Ocean Strategy Thinking
- Cellulosic Biomass
  - Liquid Fuels
  - Ethanol Biofuel
  - Organic Molecules
  - Acids Aldehydes

- Chemicals
Mascoma’s CBP Process

Consolidated Bioprocessing ("CBP") Technology

Feedstock → CBP → Ethanol

Direct microbial conversion of cellulosic biomass to ethanol

Value Drivers
- Ethanol market & infrastructure in place
- Federal mandates for price and volume

Technology Advantages
- Little to no additional enzymes
- Single tank fermentation

Economic Advantages
- Low operating costs
- Low capital costs
Pretreatment Principles (step 2)

Pretreatment gives enzyme accessible substrate

Lignin

Amorphous Region

Crystalline Region

Cellulose

Hemicellulose

Mosier et al, 2005
Technology benefit of pretreatment:
enhanced hydrolysis yields

Corn Stover

Pretreatment

No Pretreatment

15 FPU/g glucan cellulase (Spezyme CP)
+40 IU/g glucan β-glucosidase (Novozyme 188)
Thermochemical Conversion of Cellulose: familiar to the Chemical Enterprise

1. Feedstock Preparation
2. Pretreatment
3. Cracking
4. Catalytic Conversion
5. Separations
6. Combustion or Gasification

- CO₂
- Residue
- Fuel, Chemicals
- Co-products
- Co-reactants
- Catalysts
- Feedstock
- Energy
- Catalysts

High temperatures / pressures, inorganic catalysts, requires low moisture feedstocks.
Potential Market Demand

Global Industrial Chemical Production
80 million tons of industrial chemicals / yr.
Utilizes 3 billion barrel-of-oil equivalents (crude oil, naphtha, and natural gas).

Petrochemical types:
Base chemical building blocks, intermediate chemicals, and polymers derived from building blocks

Look for oxygenated chemicals, derived from sugars with high margin in the future (“green” image, from renewable feedstocks)

Furans (precursor for levulinic acid, THF)

Sugar

Bozell and Petersen, 2010
Platform Chemicals from Sugars

Sugar derived platform chemicals include

- Hydroxymethylfurfural (HMF)
- Furfural
- Levulinic acid
- γ-valerolactone

Catalytic conversion to alkanes, and to precursor molecules for use in production of polymers, lubricants, and herbicides.

Bozell and Petersen, 2010
### Products from Levulinic Acid

**Potential Market Demand (small but significant)**

<table>
<thead>
<tr>
<th>Product</th>
<th>Use</th>
<th>Potential lactic acid market (million lb/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyltetrahydrofuran (MTHF)</td>
<td>Fuel extender</td>
<td>10,000-100,000</td>
</tr>
<tr>
<td>Delta-aminolevulinic acid (DALA)</td>
<td>Biodegradable herbicide</td>
<td>175-350</td>
</tr>
<tr>
<td>Diphenolic acid</td>
<td>Polymers</td>
<td>35</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>Solvent</td>
<td>200</td>
</tr>
<tr>
<td>Succinic Acid</td>
<td>Food additives, Pharmaceuticals</td>
<td>1,000</td>
</tr>
<tr>
<td>Butanediol</td>
<td>Monomers</td>
<td>200</td>
</tr>
</tbody>
</table>

Bozell et al., 2000, Hayes et al., 2008
Economic Synergies between Agriculture and the Chemical Enterprise

Agriculture is market for:
- Seeds
- Fertilizers
- Pesticides / herbicides

Agriculture provides hedge for some feedstocks needed by chemical enterprise
- Oil
- Carbohydrates
- Cellulosics
- Fermentation substrates

Translation of science from discovery to commercial scale is critical: requires sustained research and development
Partnerships (Agriculture and Chemical)

Chemical enterprise (exports of $86.9 billion, 2011).
Possible partnerships based on
1. discovery of new processes based on sugars
2. research on utilization of renewable resources
3. business models based on products from agricultural (particularly cellulosic) commodities

Agriculture (In U.S. net balance of trade of $43 billion, 2011; projected $24 billion in 2012)
1. design / grow crops for value-add chemicals
2. continue improvements in productivity
3. business models for year round supply
4. Industrial fermentation capacities
Conclusions

Chemical Enterprise and Agriculture are inter-dependent.

Resources are available to produce both food and chemicals.

1. Land  
2. Seeds.  
3. Productivity

The Chemical Enterprise will provide production tools to Agriculture, either in the field or in the plant.

Combined impact could be to reduce energy (feedstock) costs, and provide sources of biomass based bioenergy.