Setting the Stage

- Oil shortage
- Greenhouse Effect

M. King Hubbert (1903-89)
American geophysicist
Shell Oil research laboratory
Houston, TX

US Oil Production
Hubbert’s Prediction (1956)

Source: Deffeyes, Hubbert’s Peak (2001)

World Oil Production
Deffeyes Prediction (2001)

Source: Deffeyes, Hubbert’s Peak (2001)

Where will we get our energy?

Study by Shell Group Planning
Georges Dupont-Roc
Alexon Khor
Chris Anastasi
The Evolution of the World’s Energy Systems
1996
Setting the Stage

- Oil shortage
- Greenhouse Effect

Greenhouse Effect

Visible
Infrared

Greenhouse Gases

- CH₄
- CFC
- NOₓ
- CO₂

Recent CO₂ Concentration

Historical CO₂ Concentration

Temperature Change
**Combined**

- Carbon Dioxide Concentration (ppm)
- Temperature Change from Present (°C)

**Correlation**

<table>
<thead>
<tr>
<th>Hypothesis</th>
<th>Independent</th>
<th>Dependent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Temp</td>
<td>CO₂</td>
</tr>
<tr>
<td>2</td>
<td>CO₂</td>
<td>Temp</td>
</tr>
</tbody>
</table>

**Carbon Emissions**

- Developed World (US, Canada, Western Europe)
- Rest of World

**Recent Correlation**

- Average Global Temperature (°C)
- CO₂ Concentration (ppm)

**Conclusion**

<table>
<thead>
<tr>
<th>Hypothesis</th>
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</tbody>
</table>

**Princeton Model**

- Model Includes:
  - CO₂
  - Aerosols
  - Solar Radiation
Potential Negative Effects

- rapid extinctions
- tropical diseases moving north
- Grain Belt becomes Dust Belt
- more insects
- rising ocean levels
- increased heat-related deaths
- Gulf Stream shuts down, chilling Europe
- increased storms/floods/hurricanes
- droughts and floods more common
- more forest fires due to drought
- weakened coral reefs

Exacerbating Effects

- extended thaw in tundra
- polar ice caps melt
- methane clathrates melt

Sustainable Energy and Transportation

Researchers

<table>
<thead>
<tr>
<th>Faculty</th>
<th>Masters</th>
<th>PhD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mark Holtzapple</td>
<td>Mariluhur Nagwani</td>
<td>Nan Sheng Chang</td>
</tr>
<tr>
<td>Richard Davison</td>
<td>Chang Ming Lee</td>
<td>Stehven Chan</td>
</tr>
</tbody>
</table>
<pre><code>              | Champoon Lee                          | Milch Lutcher |
              | Seth Adams                           | Kyle Ross  |
              | Robert Ranger                        | Stalin Domke |
              | William Kue                          | Salvador Albalat-Lee |
              | David Gasko                          | Cateryna Astino-Manara |
              | Hiroshi Shiraige                     | Winning Chan |
              | Wilfredo Adriano-Gomez               | Priyami Thanakas |
              | Shelly Willmanstrom                  | Sai Li     |
              | Marc Almenante                       | Cesar Grandal |
              | Ramakrishna Narayyan                 | Giralidio Coward-Kelly |
              | Parvez Iqbal                         | Li Zhe     |
              | Hang Shin Yeh                        | St Shen Kiu |
              | Manishar Vedavanathapu               | Frank Agbegbe |
</code></pre>

<table>
<thead>
<tr>
<th>Post Docs</th>
<th>Praveen Vadlani</th>
<th>Seth Adleson</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vincent Chang</td>
<td>Robert Rapier</td>
</tr>
<tr>
<td></td>
<td>Xu Li</td>
<td>William Kaar</td>
</tr>
</tbody>
</table>

Research Statistics

- Year started = early 1991
- Time spent = 12 years
- Labor = ~107 person-years
- Total funding = $2.1 mill

You can’t have it all!

University Industry

Cheap Good Fast
Examples of Biomass

- trees
- grass
- agricultural residues
- energy crops

Most of these are “lignocellulose.”

What is lignocellulose?

- Cellulose - glucose polymer
- Hemicellulose - xylose polymer
- Lignin - aromatic polymer

U.S. Biodegradable Wastes

<table>
<thead>
<tr>
<th>Waste</th>
<th>Amount (million ton/year)</th>
<th>Alcohol Potential (billion gal/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Municipal Solid Waste</td>
<td>34</td>
<td>10</td>
</tr>
<tr>
<td>Sewage Sludge</td>
<td>10.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Industrial Biosolids</td>
<td>3</td>
<td>0.4</td>
</tr>
<tr>
<td>Recycled Paper Fines</td>
<td>4.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Agricultural Residues</td>
<td>400</td>
<td>52</td>
</tr>
<tr>
<td>Forestry Residues</td>
<td>330</td>
<td>43</td>
</tr>
<tr>
<td>Manure</td>
<td>220</td>
<td>28</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1,046</strong></td>
<td><strong>135</strong></td>
</tr>
</tbody>
</table>

U.S. Gasoline Consumption = 130 billion gal/year
U.S. Diesel Consumption = 40 billion gal/year

MixAlco Process

Patents

- 5,865,898
- 5,962,307
- 5,692,296
- 5,374,283
- 5,486,133
- 6,262,313
- 5,969,189
- 5,874,263
- 5,865,898
- 6,043,392
- 6,395,926
- 6,043,392
- 6,395,926
**Pretreatment**

- Pretreatment
- Carbohydrate
- Trucks
- Mead Alcohol
- Hydrogenated

**Lime Treatment**

- $T = 100^\circ C$
- $t = 1 \text{ h}$
- Lime loading = 0.1 g Ca(OH)$_2$/g biomass
- Water loading = 5 to 15 g H$_2$O/g biomass

**In situ Digestion**

- Weigh ~ 2 g of biomass
- Place biomass in “tea bag”
- Place “tea bags” in porous sack
- Place porous sacks in cattle rumen
- Incubate
- Remove porous sack
- Wash “tea bags”
- Dry
- Weigh residue

**In-Situ Digestion**

- 48h Digestion
- Sugar cane bagasse
- African mullet straw
- Sorghum straw
- Tobacco stalks
- Untreated
- Lime-treated

**Pretreatment Vessels**
**Advanced Lime Treatment**

- Biomass + Lime
- Gravel
- Air

**Lignin Removal**

- Graph showing Lignin Content in Treated Bagasse vs. Time (days)
- Comparison with and without Air

**Fermentation**

- Processes: Fermentation, Dewatering, Pretreatment, Thermal Conversion, Hydrogenation
- Environments: Animal rumen (cattle, sheep, deer, elephants), Anaerobic sewage digestors, Swamps, Termite gut

**Why are organic acids favored?**

- Example reactions:
  \[ C_6H_{12}O_6 \rightarrow 2 C_2H_5OH + 2 CO_2 \quad \Delta G = -48.56 \text{ kcal/mol} \]
  \[ C_6H_{12}O_6 \rightarrow 3 C_3H_6O \quad \Delta G = -61.8 \text{ kcal/mol} \]

- Typical Product Spectrum at Different Culture Temperatures:
  - **40°C**
    - C2 – Acetic: 41 wt %
    - C3 – Propionic: 15 wt %
    - C4 – Butyric: 21 wt %
    - C5 – Valeric: 8 wt %
    - C6 – Caproic: 12 wt %
    - C7 – Heptanoic: 3 wt %
  - **55°C**
    - C2 – Acetic: 80 wt %
    - C3 – Propionic: 4 wt %
    - C4 – Butyric: 15 wt %
    - C5 – Valeric: <1 wt %
    - C6 – Caproic: <1 wt %
    - C7 – Heptanoic: 100 wt %

**Environments where organic acids naturally form**

- Animal rumen
  - Cattle, sheep, deer, elephants
- Anaerobic sewage digestors
- Swamps
- Termite gut

---

The actual stoichiometry is more complex.
Jet Ejector Dewatering

Heat Requirements

<table>
<thead>
<tr>
<th>Effect Type</th>
<th>Btu</th>
<th>lb water removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-effect evaporator</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Triple-effect evaporator</td>
<td>333</td>
<td></td>
</tr>
<tr>
<td>Jet ejector dewatering</td>
<td>10-effect</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>20-effect</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>30-effect</td>
<td>33</td>
</tr>
</tbody>
</table>

Thermal Conversion

Thermal Conversion Stoichiometry

\[
\text{H}_3\text{COCOCOCH}_3 \rightarrow \text{H}_3\text{CCCH}_3 + \text{CaCO}_3
\]

Calcium Acetate  
Acetone

\[
\text{H}_3\text{COCOCOCH}_3 \rightarrow \text{H}_3\text{CCCH}_3 + \text{CaCO}_3
\]

Calcium Propionate  
Dipropyl Ketone

Thermal Conversion Kinetics

Conversion (%) vs. T (°C)
Hydrogenation

Ketone Hydrogenation Stoichiometry

\[ \text{Acetone} + \text{H}_2 \rightarrow \text{Isopropyl alcohol} \]
\[ \text{Methyl Ethyl Ketone} + \text{H}_2 \rightarrow \text{2-Butanol} \]
\[ \text{Diethyl Ketone} + \text{H}_2 \rightarrow \text{3-Pentanol} \]

Hydrogenation

Advantages of MixAlco Approach

- nonsterile fermentation
- no spoiled batches
- inexpensive tanks
- robust plant operation
- adaptable microorganisms
- stable microorganisms
- microorganisms self-generate
- no enzyme addition

Catalyst = 200 g/L Raney nickel
Temperature = 130°C
Time = 35 min (at P = 15 atm)
### Economics

**Plant Capacity**

<table>
<thead>
<tr>
<th>Plant Capacity (tonne/h)</th>
<th>City Population</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>40,000</td>
</tr>
<tr>
<td>10</td>
<td>200,000</td>
</tr>
<tr>
<td>Base Case</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>800,000</td>
</tr>
<tr>
<td>160</td>
<td>3,200,000</td>
</tr>
<tr>
<td>800</td>
<td>16,000,000</td>
</tr>
</tbody>
</table>

### Capital Cost of Each Section (mill $)

<table>
<thead>
<tr>
<th>Section</th>
<th>$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreat/Ferment</td>
<td>10.6</td>
</tr>
<tr>
<td>Dewater</td>
<td>4.0</td>
</tr>
<tr>
<td>Thermal Conv</td>
<td>4.1</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>$20</strong></td>
</tr>
</tbody>
</table>

**Effect of Feedstock Cost**

-40                -20                  0                    20                 40

Biomass Cost ($/tonne)

-0.00 -0.20 -0.40 -0.60 -0.80 -1.00

Alcohol Selling Price ($/gal)

-30 g/L, 10-effect
-50 g/L, 20-effect
-70 g/L, 30-effect

### Fuels and Sugar from Energy Cane

**Productivity in Puerto Rico**

| Source: Alex Alexander, The Energy Cane Alternative, Sugar Series 6, Elsevier |
|--------------------------------|------------------|------------------|------------------|
| Energy Cane                   | 5.8              | 8.8              | 14.6             |
| Biomass                       |                  |                  |                  |
| Fiber                         |                  |                  |                  |
| Sugar                         |                  |                  |                  |
| Conventional Sugarcane        | 5.6              |                  |                  |
| Energy Cane                   | 30               | 21               |                  |

60% 40% 30% 30%
**Energy Cane Processing**

- Energy Cane → Extract → Sugar Mill → Sugar
- Extract → MixAlco Process → Alcohol Fuel
- Biomass → Fiber → Residue (Boiler Fuel)

**Fuels from Energy Cane (no sugar credit)**

**Required Area**

Scale = 800 tonne/h
Feedstock yield = 30 ton/(acre·yr)

\[
\text{Area} = \frac{800 \text{ tonne}}{h} \times \frac{8000 \text{ h}}{\text{yr}} \times \frac{1.1 \text{ ton}}{\text{acre} \cdot \text{yr}} \times \frac{30 \text{ acre}}{1000 \text{ acre}} = 235000 \text{ acre}
\]

\[
= 366 \text{ mi}^2
\]

**Centralized Processing**

15.3 mi
50% of area planted

**Supply US Gasoline Consumption**

Plants = \(\frac{130 \times 10^9 \text{ gal gas}}{\text{yr}} \times \frac{1.2 \text{ gal alc}}{\text{gal gas}} \times \frac{\text{plant-yr}}{629 \times 10^6 \text{ gal alc}} = 248 \text{ plants}\)

Area = \(248 \text{ plants} \times \frac{366 \text{ mi}^2}{\text{plant}} = 90,900 \text{ mi}^2\)

100% planted = 302 mi

**Effect of Automotive Efficiency**

1× better (Current) | 302 mi
2× better | 213 mi
3× better | 174 mi
Land required in Brazil

Sweet Sorghum
Grows in ~35 US states
Yield = 20–25 dry ton/(acre·yr)

Land Area in United States