Biofuels and Pyrolysis Technology Overview

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May 23, 2007 for the JSEM Conference
National Renewable Energy Laboratory

• Only national laboratory *dedicated* to renewable energy and energy efficiency R&D
  – Fundamental *science* to *technology* solutions
  – *Collaboration* with industry and university partners
  – Research programs *linked* to market opportunities

• Originally the Solar Energy Research Institute, July 1977
• Designated a U.S. Department of Energy National Lab, Sept. 1991
• Current staff of 1100 and budget of $200 million/yr

100 Quadrillion Btu’s

- Nuclear 8%
- Natural Gas 23%
- Petroleum 40%
- Coal 23%
- Renewable 6%
- Biomass 47%
- Wind 2%
- Hydroelectric 45%
- Solar <1%
- Geothermal 5%

Note: Total U.S. Energy Supply is 100.278 QBtu; Energy Information Administration, August 2005.
Biomass Strengths

Biomass is:

- Abundant
- Renewable
- Carbon-neutral
- The only sustainable source of hydrocarbons.

Biomass can:

- Fill the gap between demand and availability of petroleum in the near/mid term.
- Serve as a renewable source of hydrogen in the long term.
The President’s State of the Union Address

“Tonight, I ask Congress to join me in pursuing a great goal. Let us build on the work we've done and reduce gasoline usage in the United States by 20 percent in the next 10 years.”
20 in 10 Summary

Increase supply of renewable and alternative fuels

- Set Alternative Fuels Standards (AFS) at 35 billion gallons per year by 2017
  - 5X the current Renewable Fuels Standard for 2012
  - 15% of projected annual gasoline use in 2017

Increase vehicle efficiency

- Reform and modernize CAFÉ
  - 5% of projected annual gasoline use in 2017
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Corn Prices and Estimated Ethanol Production Costs for 2006

- Corn Prices
- Ethanol Production Cost (Nat Gas $4)
- Ethanol Production Cost (Nat Gas $7)
- Gasoline Rack Price
- Ethanol Contract Prices

Jan | Feb | March | April | May | June | July | Aug | Sept | Oct | Nov | Dec

($/gallon or $/bushel)

$0.00 | $0.50 | $1.00 | $1.50 | $2.00 | $2.50 | $3.00 | $3.50 | $4.00

Jan | Feb | March | April | May | June | July | Aug | Sept | Oct | Nov | Dec
We Must Transition to Cellulosic Biomass

Today & Near Term
Corn Ethanol

Existing Distribution Infrastructure

Biochemical Conversion

2012 and Beyond
Cellulosic Ethanol

Advanced Biochemical Conversion and Thermochemical Conversion

Expanded, Advanced Distribution Infrastructure

Agricultural residues, energy crops, natural oils, wood/forestry resources

Cellulosic ethanol will help meet future biofuels demand

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Edible Constituents of Biomass

**Sugar/Starch:** 70%–75% (corn)
- Basis for existing corn ethanol
- Readily fermented

**Triglycerides:** 4%–7% (corn), 18%–20% (soybeans)
- Basis for biodiesel
- Also, palm oil and algal oils

**Protein:** 20%–25% (corn), 80% (soybean meal)
- Essentially component of food
Non-Edible Constituents of Biomass

Lignin:
- Complex aromatic structure
- Very high energy content
- Resists biochemical conversion

Hemicellulose:
- Polymer of 5C and 6C sugars
- Difficult to ferment

Cellulose:
- Polymer of glucose
- Most abundant form of carbon in biosphere
- Huge potential source of ethanol
- Focus of DOE research on ethanol
Components of Cellulosic Biomass

Both can be broken down into sugars that can be further converted into ethanol.

- Cellulose (38-50%)
- Hemicellulose (23-32%)
- Lignin (15-25%)
- Other (5-13%)

Can be combusted to generate heat and power, or converted thermally to make additional biofuels.
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”

![Graph showing biomass resources](http://www.eere.energy.gov/biomass/pdfs/final_billionton_vision_report2.pdf)
Significance of the “Billion Ton” Scenario

Billion Barrel of Oil Equivalents

Yields Based on Mid-Term Conversion Technology

- 1.9 Billion tons of Biomass-Heating Value Equivalent

- 1.3 Billion tons of Biomass-Heating Value Equivalent

U.S. Petroleum Production Levels

- 2.0
- 3.5
- 4.4

2003 U.S. Petroleum Consumption

- 6.4
- 4.4
- 2.7 - Gasoline (3.0 Actual)
- 0.5 Jet Fuel
- 1.4 Distillate
- Other (Gasses, LPG, Asphalt, etc.)

Based on ORNL & USDA Resource Assessment Study by Perlach et al. (April 2005)
Reducing the Cost of Cellulosic Ethanol

State of Technology Estimates

- Feed $53/ton
- Yield 65 gal/ton

Previous Cost Targets
- President’s Initiative

Cost of Production ($/gal)

- 2000
- 2005
- 2020

Yield 90 gal/ton
- Feed $30/ton

Yield 94 gal/ton
- Feed $30/ton

All Costs in 2002 Dollars

Enzyme
Conversion
Feedstock

2005 Yield 65 gal/ton
2,000 TPD

Yield 90 gal/ton
10,000 TPD
$1.07 is equivalent to $30/bbl oil and $55/bbl without a subsidy

Ethanol prices corrected for 51¢/gal subsidy & energy content

- $2.25 per gallon ethanol (SOT)
- $1.07 per gallon ethanol
- $0.59 per gallon ethanol (Advanced Technology)
Energy Required to Produce Ethanol

Total Btu spent for 1 Btu available at fuel pump


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Relative Emissions Impacts

Biofuels can lower our production of greenhouse gases

Ethanol is the 1st of Many Possible Biofuels

**Near Term**
- Ethanol – from grain, sugar, or cellulosic material
- Biodiesel – transesterified vegetable oils, fats, and greases
- Green Diesel – vegetable oils, fats, and greases converted to diesel by hyd roprocessing
- Other Fermentation Products – includes: butanol, acetates, lactates, and other possibilities
- Pyrolysis Liquids – low quality liquid made by thermal processing (“thermal cracking”) of biomass
- Synthesis Gas – for conversion to F-T liquids, methanol, dimethyl ether, or mixed alcohols

**Long Term**
- Algae-derived Fuels – alternative source of triglycerides and carbohydrates
- Hydrocarbon Fuels – from hydrogenation of biomass constituents
Military Fuel Mix is Very Different from Commercial Fuel Mix

Source: Energy Security ITP, July 2006
Other Near-Term Biofuel Technologies

**Near Term**
- **Ethanol** – as a blending agent from either grain or cellulosic material from Ag and/or Forestry industry
- **Biodiesel** – Transesterified vegetable oils blended with diesel
- **Green Diesel** – fats, waste oils, or virgin oils converted to low-sulfur diesel in petroleum refinery
- **Other Fermentation Products** – examples include: butanol, acetates, lactates, and other possibilities
- **Pyrolysis Liquids** – alternative feedstock to petroleum refinery or gasification facility
- **Synthesis Gas** – for conversion to Fischer-Tropsch liquids, methanol, dimethyl ether, or mixed alcohols
- **Algae-derived Fuels** – alternative source of triglycerides for biodiesel or green diesel, and a carbohydrate source

**Long Term**
- **Hydrocarbon Fuels** – from hydrogenation of biomass constituents
Green Diesel

- Hydrotreating of biorenewable oils in existing refinery units
- Lower capital costs than biodiesel
- Excellent fuel properties

### Feed

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>% Oil or Grease</td>
<td>100</td>
</tr>
<tr>
<td>% H₂</td>
<td>1.5-3.8</td>
</tr>
</tbody>
</table>

### Products

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>% water, CO₂</td>
<td>12-16</td>
</tr>
<tr>
<td>% Lt HC</td>
<td>2-5</td>
</tr>
<tr>
<td>% Diesel</td>
<td>83-89</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>80-100</td>
</tr>
<tr>
<td>ppm S</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

Source: U.O.P. Corp.
1st International Biorefinery Conference, August 2005
Mid-Term Biofuel Technologies

**Near Term**

- **Ethanol** – as a blending agent from either grain or cellulosic material from Ag and/or Forestry industry
- **Biodiesel** – Transesterified vegetable oils blended with diesel
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**Long Term**

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- **Algae-derived Fuels** – alternative source of triglycerides for biodiesel or green diesel, and a carbohydrate source
- **Hydrocarbon Fuels** – from hydrogenation of biomass constituents
Fast Pyrolysis Bio-oil

Bio-oil is water miscible and is comprised of many oxygenated organic chemicals.

- Dark brown mobile liquid
- Combustible
- Not 100% miscible with hydrocarbons
- Heating value ~ 17 MJ/kg
- Density ~ 1.2 kg/l
- Acid, pH ~ 2.5
- Pungent odour
- “Ages” - viscosity increases with time
Refinery Upgrading Proof of Concept Project

Preliminary upgrading tests by UOP/PNNL using pyrolysis oils provided by NREL

Estimated Yields (gal EtOH eq/ton biomass)
- Gasoline – 33
- Diesel - 8

Table 8. Performance estimates for the production of gasoline and diesel from pyrolysis oil

<table>
<thead>
<tr>
<th>Feed</th>
<th>$40/bbl Crude</th>
<th>$50/bbl Cru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolytic Lignin</td>
<td>2,250</td>
<td>40,500</td>
</tr>
<tr>
<td>H2</td>
<td>21.4 T</td>
<td>25,680</td>
</tr>
<tr>
<td>Products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lt Hydrocarbons</td>
<td>64T/D</td>
<td>19,303</td>
</tr>
<tr>
<td>Naphtha</td>
<td>1,010</td>
<td>52,520</td>
</tr>
<tr>
<td>Diesel</td>
<td>250</td>
<td>12,000</td>
</tr>
<tr>
<td>Other</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Utilities</td>
<td>-4,800</td>
<td>-5,760</td>
</tr>
<tr>
<td>Net</td>
<td>12,843</td>
<td>28,734</td>
</tr>
<tr>
<td>Annual Value</td>
<td>$4.2MM</td>
<td>$9.5MM</td>
</tr>
</tbody>
</table>

Figure 6. Years to payback for conversion of pyrolytic lignin to gasoline.

Biomass Gasification Integrates with Fossil Fuels

Primary Energy Source
- Natural Gas
- Coal
- Biomass
- Extra Heavy Oil

Syngas Step
- Syngas (CO + H₂)

Conversion Technology
- Fischer Tropsch (FT)
- Upgrading

Products
- Diesel
- Naphtha
- Lubes

Syngas to Liquids (GTL) Process

Syngas to Chemicals Technologies
- Acetic Acid
- Methanol
- Hydrogen
- Mixed Alcohols (e.g. ethanol, propanol)
- Others (e.g. Triptane, DME, etc)

Slide courtesy of BP Corporation
Longer Term Biofuel Technologies

**Near Term**

- **Ethanol** – as a blending agent from either grain or cellulosic material from Ag and/or Forestry industry
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**Long Term**

- **Algae-derived Fuels** – alternative source of triglycerides for biodiesel or green diesel, and a carbohydrate source
- **Hydrocarbon Fuels** – from hydrogenation of biomass constituents
Microalgae as a Source of Biofuels

DOE’s Aquatic Species Program at NREL (1978-96) provided the technical foundation for producing biodiesel from algae.

The concept involves producing biofuels from:
- Sunlight
- CO2 in fuel gases and/or vent gases
- Unproductive land
- Brackish or saline water

- Productivity per acre potential (~10,000 gal/acre/yr) far exceeds terrestrial plants – *R&D is needed to reach this potential!*
- NREL partnerships with petroleum refiners revealed an approach that converts algal oils in existing refineries
- Algal carbohydrates can be integrated into ethanol production
Jet Fuel From Algae

Productivity
SOT: 10gm/m²/day
Target: 50gm/m²/day

- Food
- Other Fuels (Ethanol)
- Power
Technology Maturity

<table>
<thead>
<tr>
<th>Low</th>
<th>High</th>
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<tr>
<td>Ethanol</td>
<td>New market for grain and</td>
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<td>agriculture products. Large</td>
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<td>supply of lignocellulose.</td>
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<tr>
<td>Biodiesel</td>
<td>New market for excess oils,</td>
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<td>fats, and greases.</td>
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<tr>
<td>Green Diesel</td>
<td>Lower cost and higher product</td>
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<td>quality than FAME.</td>
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<tr>
<td>Butanol</td>
<td>New market for grain and</td>
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<td>agriculture products. Large</td>
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<td>supply of lignocellulose.</td>
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<tr>
<td>Syngas Liquids</td>
<td>Integration of biomass with</td>
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<td>Coal, Coke, Shale, or Heavy</td>
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<td>Oils.</td>
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<td>Bio-oil Derivative</td>
<td>Technical fit with woody</td>
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<td>biomass and liquid bio-crude.</td>
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<tr>
<td>H2 from Biomass</td>
<td>Potential transportation fuel</td>
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<tr>
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<td>from any fuel/power source.</td>
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<tr>
<td>Diesel from Algae</td>
<td>Potential to integrate into</td>
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<td>existing large scale refinery</td>
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<td>and pipeline infrastructure.</td>
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<td>Hydrocarbons from Carbohydrates</td>
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<td>fossil).</td>
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Key Drivers

- High octane gasoline blend stock from carbohydrates.
- Petroleum compatible and biodegradable.
- Utilize existing assets. High quality jet fuel or diesel.
- Better gasoline blending properties than ethanol.
- High quality jet fuel or diesel. Reduced criteria for sequestration, and economy of scale (in combination with fossil).
- Potential to integrate into existing large scale refinery and pipeline infrastructure.
- Ideal feed for fuel cells, and lowest tail pipe emissions.
- High quality jet fuel or diesel yield per acre, with both off-shore and on-shore potential.
- Potential for higher reaction rates than fermentation, and potential as H2 carrier.

Value Added

Organizations Leading the R&D

- Grain/Agriculture
- Coal
- Chemical
- Petroleum
- Forestry
- Academia & Startups

Renewable Fuels & Low GHG Emissions

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Summary & Conclusions

- Biofuels are the only renewable option for liquid transportation fuels
- Resource is sufficient to supply a large portion of demand today, with potential to expand in the future
- Ethanol and biodiesel are the best near-term options for deployment – must transition to cellulosic biomass
- On-going R&D may create other biofuel options in the future
- Different biofuel options offer a mix of pro’s and con’s