R&D Needs for Integrated Biorefineries
The 30 x 30 Vision
(30% of 2004 Motor Gasoline Supplied by Biofuels by 2030)

David C. Dayton
Thermochemical Area Leader
National Renewable Energy Laboratory

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The President’s Biofuels Initiative: The 30x30 Vision

Transformation through Intermediates (sugars)

"Biochemical conversion"

main difference is in the primary catalysis system

Reduction to building blocks (CO, H₂)

"Thermochemical conversion"

Actual Volumes (Billion gal/yr)

Existing & Unexploited Resources
High Yield Growth But No Energy Crops
High Yield Growth With Energy Crops
2004 Motor Gasoline

0 50 100 150 200 250 300 350 400 450 500

Million Tons Annually

Thermochemically Derived
Biochemically Derived
Grain Derived

30% 2004 Gasoline Energy Equivalent from Ethanol

High Yield Growth With Energy Crops
High Yield Growth Without Energy Crops
Existing & Unexploited Resources

Forest Resources Total
Grains & Manure Sub-Total
Ag Residues (non Energy Crops)
Perennial (Energy) Crops
30 X 30 Plan Development in Support of OBP

Authors

Thomas Foust – National Renewable Energy Laboratory
John Ashworth – National Renewable Energy Laboratory
Paul Bergeron – National Renewable Energy Laboratory
David Dayton – National Renewable Energy Laboratory
Richard Hess – Idaho National Laboratory
Michael Himmel – National Renewable Energy Laboratory
Kelly Ibsen – National Renewable Energy Laboratory
John Jechura – National Renewable Energy Laboratory
Jonathan Mielenz – Oak Ridge National Laboratory
Margo Melendez – National Renewable Energy Laboratory
Seth Snyder – Argonne National Laboratory
John Sheehan – National Renewable Energy Laboratory
Michael Wang – Argonne National Laboratory
Robert Wallace – National Renewable Energy Laboratory
Todd Werpy – Pacific Northwest Laboratory
Robert Wooley – National Renewable Energy Laboratory

U.S. Department of Energy
Energy Efficiency and Renewable Energy
Biomass

30 x 30 A Scenario for Supplying 30% of 2004 Motor Gasoline with Ethanol by 2030

National Renewable Energy Laboratory
30 X 30 Scenario Model-Developed

• System dynamics model
• Dynamic implications of how the marketplace behaves in response to new technology
• Models behaviors of:
  • Investors
  • Farmers
  • Policymakers
• Can test different strategies to see whether or not they lead to successful achievement of the 30 x 30 goal
• Drivers can be either technology price targets or policy incentives
Five Critical Aspects to Achieving the 30 x 30 Scenario

1. Continue rapid deployment of starch based ethanol technology in the next decade
2. Achieve “$1.07/gallon” production cost target in 2012
3. Cost share deployment with industry to reduce risk hurdle
4. Achieve the advanced technology target to reduce the conversion cost component of the ethanol production cost by addressing identified barriers in 2025 – 2030
5. Continue tax incentive of $0.50/gallon and raise Renewable Fuels Standard ceiling to 20 billion gallons or develop more dynamic market driven incentive
Historic Fuel Ethanol Prices

- Fuel Alcohol
- Ethyl Alcohol
- Specially Denatured Alcohol

¢ per gallon

Achieving the $1.07 Production Cost Target by 2012
Technical Barrier Areas for $1.07 Biochemical Ethanol

*Hybrid Saccharification & Fermentation - HSF*
Summary: Biomass Recalcitrance

Impacts at many length scales (mm to nm)
Pretreatment

- Converts hemicellulose to fermentable sugars
- Makes cellulose susceptible to enzymatic hydrolysis
How Do Chemicals Penetrate Biomass?

Pretreatment chemicals and enzymes penetrate corn tissue through vessels and pits.

Source: Himmel et al. in collaboration with the CSM EM Facility (2004)
Saccharification

- Enzymatic hydrolysis of cellulose or starch to glucose

Buffer treated corn stover

Enzyme treated corn stover

Note: zone around vascular bundle is eroded compared to native (suggests enzymes leak through pores in bundle)
Enzyme Costs Have Fallen Sharply

- DOE Subcontracts to Genencor and Novozymes (cost-shared)
  Focus: lower production cost, increase enzyme system efficacy
  - Enzyme cost ($/gallon EtOH) = Prod. Cost ($/kg) x Usage Req. (kg/gallon EtOH)
  ➢ Cellulase cost reduced 20-30X reduction (by subcontract metric)
Cofermentation Pathway in Engineered *Zymomonas mobilis* (putative)

**Pentose Metabolism Pathway**

- **D-Xylose**
  - Xylose isomerase
  - Xylose kinase
  - ATP
  - ADP
  - Transketolase
  - Transaldolase
  - Erythrose-4-P
  - Fructose-6-P
  - Phosphoenolpyruvate
  - Acetaldehyde + CO₂
  - Ethanol

**Entner Doudoroff Pathway**

- **D-Glucose**
  - Glucose-6-P
  - Gluconolactone-6-P
  - 6-P-Gluconate
  - 2-Keto-3-deoxy-6-P-Gluconate
  - 2-P-Glycerate
  - 3-P-Glycerate
  - 1,3-P-Glycerate
  - Pyruvate
  - Ethanol

**Xylose Utilization Enzymes**

- Xylose isomerase
- Xylose kinase
- ATP
- ADP
- Transketolase

**Pentose Phosphate Pathway Enzymes**

- Transketolase
- Transaldolase
- Erythrose-4-P
- Fructose-6-P
- Phosphoenolpyruvate
- Acetaldehyde + CO₂
- Ethanol

**XYL Transport**

**GLUC Transport**

**ETOH Transport**

**XYL Transport GLUC Transport**

**ETOH Transport**

**XYL Transport GLUC Transport**

**ETOH Transport**
Technical Barrier Areas for $1.07 Thermochemical Ethanol

- Feedstock Interface
  - Size Reduction
  - Storage & Handling
  - De-watering
  - Drying

- Gasification
  - Thermal Efficiency
  - Carbon Conversion
  - Ash Chemistry
  - Pressure
  - Steam/oxygen

- Gas Cleanup & Conditioning
  - Particulate removal
  - Catalytic Reforming
  - S, N, Cl mitigation
  - CO₂ removal
  - H₂/CO adjustment

- Fuel Synthesis
  - By-products:
    - Methanol
    - n-Propanol
    - n-Butanol
    - n-Pentanol
  - Separations
  - Recycle
  - Selectivity

- Products
  - Ethanol
  - Heat & Power

- Storage & Handling
  - Drying
  - Size Reduction
  - De-watering
  - Drying

- By-products:
  - Methanol
  - n-Propanol
  - n-Butanol
  - n-Pentanol

- Thermal Efficiency
Thermochemical Route to Ethanol

Overall Stoichiometry:

\[ nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O \]

Optimal H2/CO ratio \( \sim 1 \rightarrow 1.2 \) due to water-gas shift (WGS) activity of catalysts

Reactions largely kinetically controlled
Gasification R&D for “$1.07” Thermochemical Ethanol Target

- Gas Cleanup and Conditioning – Tar Reforming Catalyst Development
  - Consolidated tar and light hydrocarbon reforming to reduce capital and operating costs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Current</th>
<th>Goal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (CH₄)</td>
<td>20%</td>
<td>80%</td>
</tr>
<tr>
<td>Ethane (C₂H₆)</td>
<td>90%</td>
<td>99%</td>
</tr>
<tr>
<td>Ethene (C₂H₄)</td>
<td>50%</td>
<td>99%</td>
</tr>
<tr>
<td>Tars (C₁₀+)</td>
<td>95%</td>
<td>99.9%</td>
</tr>
<tr>
<td>Benzene (C₆H₆)</td>
<td>70%</td>
<td>99%</td>
</tr>
<tr>
<td>Ammonia (NH₃)</td>
<td>70%</td>
<td>90%</td>
</tr>
</tbody>
</table>

- Advanced Catalysts and Process Improvements for Mixed Alcohol Synthesis
  - Increase single pass conversion efficiency (38.5% to 50%)
  - Improve selectivity (80% to 90%)
  - Improve yields at lower synthesis pressure

- Fundamental Gasification Studies
  - Technical validation of comparable syngas quality from biorefinery residues and wood residues
# Pros & Cons of Mixed Alcohol Catalysts

<table>
<thead>
<tr>
<th>Catalyst Class</th>
<th>Benefits</th>
<th>Negatives</th>
<th>Likely C2+ alcohol STY g/L/hr possible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std MeOH Cu-Zn-Al</td>
<td>Excellent performance &amp; commercial record</td>
<td>Highly sensitive to reduction, sintering, Cl- &amp; S</td>
<td>Very low</td>
</tr>
<tr>
<td>Modified Methanol (Cu/Zn/Al + X)</td>
<td>Easy to make &amp; retrofit into existing units</td>
<td>Low overall yields, same sensitivity as parent Cu-Zn-Al, branched prods may dominate.</td>
<td>&gt; 50, &lt; 500</td>
</tr>
<tr>
<td>Molybdenum Sulfide</td>
<td>Good linear alcohol selectivity is claimed</td>
<td>S required in feed, &amp; S is in product, highly sensitive to the activation process &amp; O2. HC yield possibly high</td>
<td>500-1000</td>
</tr>
<tr>
<td>Molybdenum Oxide + XYZ</td>
<td>No S required, good linear product yield</td>
<td>Composition not optimized, HC yield higher than desired</td>
<td>800-1200</td>
</tr>
<tr>
<td>Rhodium based +XYZ</td>
<td>Good ethanol selectivity</td>
<td>Composition not optimized, high costs for Rh, HC yields are too high</td>
<td>500-1000</td>
</tr>
<tr>
<td>Fischer-Tropsch + modifiers</td>
<td>Good activity &amp; many opportunities for improvement</td>
<td>Composition is not optimized, alcohol selectivity may be too low HC yields may be high?</td>
<td>400-1000</td>
</tr>
<tr>
<td>Mixed Composite Catalysts (Inui claims)</td>
<td>Good reported C2+ yields reported, many possible improvements &amp; refinements</td>
<td>Very complex system, optimization difficult., yields of HC, acids &amp; aldehydes are too high</td>
<td>600 - &gt;1000</td>
</tr>
</tbody>
</table>

X, Y, Z = various modifiers or promoters
ALTERNATE SYNGAS ROUTES
Using “Already Developed” Technology
(Syngas fermentations not considered)

<table>
<thead>
<tr>
<th>Catalytic Step 1</th>
<th>Catalytic Step 2</th>
<th>Catalytic Step 3</th>
<th>+</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syngas to DME + MEOH in one step over Cu-Zn-Al combined w/ dehydration cat</td>
<td>DME + MEOH to mixed C2-C4 Olefins over ZSM-5 MTO* catalyst</td>
<td>Olefins hydration to mixed C2-C4 alcohols over H2PO4 catalyst</td>
<td>DME defeats MeOH equilibrium limit, DME+MeOH is ideal feed for MTO</td>
<td>3 steps (but all are highly efficient)</td>
</tr>
<tr>
<td>Syngas to MeOH over std. Cu-Zn-Al</td>
<td>MeOH +CO to Acetic acid, w/homogeneous Rh, Ir &amp; Ru</td>
<td>Acetic acid hydrogenation to ethanol</td>
<td>All steps highly efficient, only EtOH produced</td>
<td>3 steps (possibly can combine #2 &amp; #3 with development)</td>
</tr>
<tr>
<td>Syngas to DME + MEOH in one step over Cu-Zn-Al combined w/ dehydration cat</td>
<td>DME + MEOH to gasoline hydrocarbons over a ZSM-5 MTG* catalyst</td>
<td>none</td>
<td>All steps Claimed highly efficient, gasoline produced</td>
<td>No Ethanol, possibly some olefin co-product, high aromaticity</td>
</tr>
</tbody>
</table>

*MTO = Methanol to Olefins  MTG = Methanol to Gasoline,
Catalysts are variants of modified ZSM-5
From DOE GTL Bioenergy Roadmap

Systems Biology to Overcome Barriers to Cellulosic Ethanol

More Available Polysaccharides
Reduced Lignin
In Planta Enzyme Digestion

Feedstock Engineering

Feedstock Cell-Wall Deconstruction

Fermentation Microbe (Ethanologen) Development

Optimal Plant Sugars
Reduced Toxins
Reduced Feedstock Costs

Biomass Analysis
Protein Engineering
Advanced Imaging
Protein Machines

Plant Science

High Sugar Yields
Low Capital Costs
Low Enzyme Costs

Soil Science

Community Modeling
Cellular Modeling
Biomolecular Modeling
Systems Biology
Microbial Science

Crosscutting Science

NREL National Renewable Energy Laboratory
2030 Target for a Large Cellulosic Biorefinery to Integrate BC & TC Paths

Lignocellulosic Feedstock
10,000 ton/day

Ethanol via Bioconversion

Steam & Power

Lignin-rich Residue
1,400 ton/day

Lignin-rich Residue
1,500 ton/day

Gasification

Losses

Lignin Plant

Syngas

Higher Alcohols
29,700 gpd

Ethanol Synthesis

Ethanol
133,500 gpd

Ethanol
1,168,000 gpd
409 MM gal/yr

Yield: 117 gal/ton

S. Phillips and J. Jechura
Questions?