Overview

- Techno-Economic Analysis Approach
- biochemical conversion to Ethanol
- Biochemical conversion to Advanced Hydrocarbons
Techno-Economic Analysis Approach

- Collaborate with engineering & construction firm to enhance credibility, quality
- Conceptual design reports are transparent, highly peer reviewed
- Iteration with researchers and experimentalists is crucial
Techno-Economic Analysis Approach

- Modeling is rigorous and detailed with transparent assumptions
- Assumes $n^{th}$-plant equipment costs
- Discounted cash-flow ROR calculation includes return on investment, equity payback, and taxes
- Determines the minimum selling price required for zero NPV
State of Technology Background

2006 State of the Union

“America is addicted to oil…the best way to break this addiction is through technology.”

“Our goal is to make cellulosic ethanol practical and cost competitive within 6 years.”

2007 State of the Union

“Reduce U.S. gasoline usage by 20% in 10 years – 75% from new fuels and 25% from vehicle efficiency”

“Mandatory fuel standard to require 35B gallons of renewable and alternative fuels by 2022.”
State of Technology Background

Cost Targets Developed

- Original Design Reports updated to ~$2.00/gal target (2011 timeframe)
  - Total bottoms up approach with no end cost target in mind
  - Incorporation of state of the art knowledge on capital costs, financing assumptions, process design
  - Roughly equivalent to gasoline production at $110/BBL crude

<table>
<thead>
<tr>
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<tr>
<td>EIA, AEO2009, High Oil Price Case</td>
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<td>EIA, AEO2009, Reference Case</td>
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<td>EIA, AEO2009, Low Oil Price Case</td>
<td>51</td>
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Hybrid Saccharification & Fermentation - HSF

- Conceptual design of a 2,000 tonnes/day commercial plant – one possible tech package, not optimized
- NREL pilot plant based on this process
- Basis for connecting R&D targets to cost targets
- Has undergone rigorous peer review
- Basis for comparison against other technology options
Energy Efficiency & Renewable Energy

BC Conversion to Cellulosic Ethanol
Historic State of Technology

Minimum Ethanol Selling Price (2007$ per gallon)

- Bench Scale - Enzymes
- Scale Up Pretreatment
- Saccharification Improvement
- Fermentation Improvement

Conversion | Feedstock
--- | ---
2001 | $9.16
2002 | $6.90
2003 | $5.33
2004 | $4.27
2005 | $3.85
2006 | $3.64
2007 | $3.57
2008 | $3.18
2009 | $2.77
2010 | $2.56
2011 | $2.15
2012 Target | $2.15

Energy Efficiency & Renewable Energy
### BC Conversion to Cellulosic Ethanol

#### Technical Target Table

<table>
<thead>
<tr>
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<tbody>
<tr>
<td><strong>Minimum Ethanol Selling Price ($/gal)</strong></td>
<td>$3.64</td>
<td>$3.56</td>
<td>$3.19</td>
<td>$2.77</td>
<td>$2.62</td>
<td>$2.56</td>
<td>$2.37</td>
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<td>Feedstock Contribution ($/gal)</td>
<td>$1.12</td>
<td>$1.04</td>
<td>$0.95</td>
<td>$0.82</td>
<td>$0.76</td>
<td>$0.76</td>
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<td>Conversion Contribution ($/gal)</td>
<td>$2.52</td>
<td>$2.52</td>
<td>$2.24</td>
<td>$1.95</td>
<td>$1.86</td>
<td>$1.80</td>
<td>$1.55</td>
<td>$1.41</td>
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<tr>
<td>Yield (Gallon/dry ton)</td>
<td>69</td>
<td>70</td>
<td>73</td>
<td>75</td>
<td>78</td>
<td>78</td>
<td>71</td>
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<tr>
<td><strong>Feedstock</strong></td>
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<td>Feedstock Cost ($/dry ton)</td>
<td>$77.20</td>
<td>$72.90</td>
<td>$69.65</td>
<td>$61.30</td>
<td>$59.60</td>
<td>$59.60</td>
<td>$59.60</td>
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<td><strong>Pretreatment</strong></td>
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</tr>
<tr>
<td>Solids Loading (wt%)</td>
<td>30%</td>
<td>30%</td>
<td>30%</td>
<td>30%</td>
<td>30%</td>
<td>30%</td>
<td>30%</td>
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<tr>
<td>Xylan to Xylose (including enzymatic)</td>
<td>75%</td>
<td>75%</td>
<td>84%</td>
<td>85%</td>
<td>88%</td>
<td>88%</td>
<td>78%</td>
<td>90%</td>
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<tr>
<td>Xylan to Degradation Products</td>
<td>13%</td>
<td>11%</td>
<td>6%</td>
<td>8%</td>
<td>5%</td>
<td>5%</td>
<td>6%</td>
<td>5%</td>
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<tr>
<td><strong>Conditioning</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Ammonia Loading (mL per L Hydrolyzate)</td>
<td>50</td>
<td>50</td>
<td>38</td>
<td>23</td>
<td>25</td>
<td>25</td>
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<tr>
<td>Hydrolyzate solid-liquid separation</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
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<tr>
<td>Xylose Sugar Loss</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
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<tr>
<td>Glucose Sugar Loss</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>0%</td>
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<tr>
<td><strong>Enzymes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Enzyme Contribution ($/gal EtOH)</td>
<td>$0.39</td>
<td>$0.38</td>
<td>$0.36</td>
<td>$0.36</td>
<td>$0.36</td>
<td>$0.34</td>
<td>$0.34</td>
<td>$0.34</td>
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<tr>
<td><strong>Enzymatic Hydrolysis &amp; Fermentation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Solids Loading (wt%)</td>
<td>20%</td>
<td>20%</td>
<td>20%</td>
<td>17.5%</td>
<td>20%</td>
<td>17.5%</td>
<td>17.5%</td>
<td>20%</td>
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<tr>
<td>Combined Saccharification &amp; Fermentation Time (d)</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
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<tr>
<td>Corn Steep Liquor Loading (wt%)</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>0.60%</td>
<td>0.25%</td>
<td>0.25%</td>
<td>0.25%</td>
</tr>
<tr>
<td>Overall Cellulose to Ethanol</td>
<td>86%</td>
<td>86%</td>
<td>84%</td>
<td>86%</td>
<td>86%</td>
<td>89%</td>
<td>80%</td>
<td>86%</td>
</tr>
<tr>
<td>Xylose to Ethanol</td>
<td>76%</td>
<td>80%</td>
<td>82%</td>
<td>79%</td>
<td>85%</td>
<td>85%</td>
<td>85%</td>
<td>85%</td>
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<tr>
<td>Arabinose to Ethanol</td>
<td>0%</td>
<td>0%</td>
<td>51%</td>
<td>68%</td>
<td>80%</td>
<td>47%</td>
<td>47%</td>
<td>85%</td>
</tr>
</tbody>
</table>
BC Conversion to Cellulosic Ethanol
Hemicellulose to Sugars ($C_5$)

Xylan

\[ \text{Oligomeric Xylose} \]

\[ \text{Monomeric Xylose} \]

\[ \text{Degradation Products} \]

Experimental Results from High-Solids Pretreatment
Physical/Biochemistry (physical experimentation)
- Protein purification
- Physical/Chemical analyses
- MS and spectro. analyses
- Special and HTP activity testing

Numerical Models (empirical experimentation)
- Molecular dynamics
- Multi-scale modeling (e.g. atomistic)
- Detailed Sub-sets to the system
- Force field determinations

Molecular Structure (experimentally verified)
- X-ray crystallography
- Structure diversity (genomics)
- Homology modeling

Mechanistic Model (systematic kinetics/thermodynamics)
- F*
- Surface binding
- Recognition
- Initial processivity
- Decrystallization
- Processivity
- Hydrolysis
- Processivity
- Hydrolysis
- { ... }
- Hydrolysis + Processivity

Cellulose
- Linker Peptide
- Catalytic Domain
- CBM
- Cellulose
**BC Conversion to Cellulosic Ethanol**

**Enzymatic Saccharification**

---

### Cellulose Conversion (%)

- **2010:**
  - Commercial Enzyme Package 1 (40 mg/g)
    - ~90% Cellulose to Glucose (Washed Solids)
    - ~70% Cellulose to Glucose (Whole Slurry)

- **2011:**
  - Commercial Enzyme Package 2 (40 mg/g)
    - >90% Cellulose to Glucose (Washed Solids)
    - >80% Cellulose to Glucose (Whole Slurry)
  
  - Commercial Enzyme Package 2 (20 mg/g)
    - ~75% Cellulose to Glucose (Whole Slurry)

- **2012:**
  - De-acetylation + Commercial Enzyme Package 2 (20 mg/g)
    - ~78% Cellulose to Glucose (Whole Slurry)

---

**Energy Efficiency & Renewable Energy**

**eere.energy.gov**
Microbial conversion of sugars to products

- Introduced Xylose Utilization - 1994
- Introduced Arabinose Utilization - 1995
- Combined pentose utilization - 1997
- Stabilization by integration - 1999
- Further Development in CRADA with DuPont 2002-2007

Development of *Zymomonas*

DOE Grants to Further Strain Development (2007-2011)

- Cargill
- Mascoma
- Purdue / ADM
- DuPont
- Verenium
BC Conversion to Cellulosic Ethanol
Fermentation - End Product Inhibition

Fermentation vs. Solids Loading
Zymomonas mobilis 8b

2010:
Zymomonas mobilis 8b (NREL)
- ~95% Glucose to Ethanol
- ~79% Xylose to Ethanol
- No arabinose conversion demonstrated at NREL
- Ethanol titer ~50 g/L

2011:
Industrial Organism
- 95% Glucose to Ethanol
- 85% Xylose to Ethanol
- 47% Arabinose to Ethanol
- Ethanol titer ~ 55 g/L

2012:
De-Acetylation / Industrial Organism
- Decrease acetic acid and furfural dramatically
- 96-97% Glucose to Ethanol
- 93% Xylose to Ethanol
- 54% Arabinose to Ethanol
- Ethanol titer ~72 g/L
# BC Conversion to Cellullosic Ethanol

## Technical Target Table

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<td>$1.55</td>
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<td>78</td>
<td>78</td>
<td>71</td>
<td>79</td>
</tr>
</tbody>
</table>

### Feedstock
- **Feedstock Cost ($/dry ton):**
  - 2011 Washed Solids: $59.60
  - 2011 Whole Slurry: $59.60
  - 2012 Targets: $58.50

### Pretreatment
- **Solids Loading (wt%):**
  - 2011 Washed Solids: 30%
  - 2011 Whole Slurry: 30%
  - 2012 Targets: 30%

### Conditioning
- **Ammonia Loading (mL per L Hydrolyzate):**
  - 2011 Washed Solids: 25
  - 2011 Whole Slurry: 25
  - 2012 Targets: 25

### Enzymes
- **Enzyme Contribution ($/gal EtOH):**
  - 2011 Washed Solids: $0.36
  - 2011 Whole Slurry: $0.38
  - 2012 Targets: $0.34

### Enzymatic Hydrolysis & Fermentation
- **Total Solids Loading (wt%):**
  - 2011 Washed Solids: 20%
  - 2011 Whole Slurry: 17.5%
  - 2012 Targets: 17.5%

### Keys to Hitting 2012 Targets

- **Pilot scale integrated testing was in place and ready**
- **Whole slurry mode was necessary**
  - Solid/Liquid separation and washing too costly
- **Incorporation of de-acetylation**
  - Better fermentation (ethanol tolerance)
  - Better digestibility (glucose yield) at lower enzyme loadings
  - OPEX savings outweigh CAPEX costs
    - Lower acid usage
    - Lower ammonia usage
    - Lower wastewater treatment costs
**2012 Cellulosic Ethanol Successful Demonstration**

- Developed pretreatment/conditioning strategy (bench and pilot scale) capable of releasing >80% of the hemicellulosic sugars in whole slurry mode
- Reduced Enzyme Costs >20x and developed strategy for further reductions
- Developed Industrially Relevant Strains Capable of Converting C$_5$ and C$_6$ Cellulosic Sugars at total conversion yields >95% and tolerant of ethanol titers of ~72 g/L
- Built/adapted fully integrated pilot scale capability for 2012 demonstration
- Developed peer reviewed model for extrapolation to commercial scale
- Commercial demonstrations of similar design coming online (Poet, Abengoa)

**Leveragability to Hydrocarbons**

- Pretreatment and enzymatic saccharification technologies can make cellulosic sugars
- Compositional analysis techniques fully applicable
- Pilot/bench scale P/T, Saccharification and Fermentation equipment easily re-purposed
- Need some minor, relatively easy modifications for different downstream needs (e.g. separations, purification, hybrid techniques)
Hydrocarbon Pathways
Fermentation of Sugars to Advanced Fuels

• Key research needs:
  – Maximize sugar production
  – Optimize process integration
  – Understand the need for hydrolyzate conditioning and effect of inhibitors
  – Maximize overall conversion yield to final products
  – Investigate routes to cost-effectively utilize entire biomass; Understand sustainability trade-offs
Hydrocarbon Pathways

Catalytic Conversion of Sugars to Advanced Fuels

- Key research needs:
  - Maximize sugar production
  - Optimize process integration
  - Understand the need for hydrolyzate conditioning and effect of inhibitors
  - Maximize overall conversion yield to final products
  - Investigate routes to cost-effectively utilize entire biomass; Understand sustainability trade-offs
EERE is sponsoring research on producing jet-range hydrocarbons from minimally processed alcohols produced by fermentation or catalysis.

The example on this slide used a mixed alcohol feedstock (see table) which was fed into a catalytic reactor.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Feed Concentration (wt%)</th>
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<tbody>
<tr>
<td>Methanol</td>
<td>0 to 2.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>8 to 28</td>
</tr>
<tr>
<td>C3+ Alcohols</td>
<td>1 to 3</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>4 to 14</td>
</tr>
<tr>
<td>C2+ Aldehydes</td>
<td>6 to 17</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>1 to 18</td>
</tr>
<tr>
<td>Water</td>
<td>41 to 60</td>
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</tbody>
</table>
Pathways to Jet Fuel
Direct from Ethanol

• PNNL prepared samples for fuel property evaluation
• Off-site specification testing conducted by AFRL

<table>
<thead>
<tr>
<th>Specification Test</th>
<th>MIL-DTL-83133H Spec Requirement</th>
<th>PNNL-1</th>
<th>PNNL-2</th>
<th>FT-SPK</th>
<th>JP-8</th>
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<tbody>
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<td>Aromatics, vol %</td>
<td>≤25</td>
<td>1.9</td>
<td>2.2</td>
<td>0.0</td>
<td>18.8</td>
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<td>Olefins, vol %</td>
<td>1.2</td>
<td>1.1</td>
<td>0.0</td>
<td>0.8</td>
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<tr>
<td>Heat of Combustion (measured), MJ/Kg</td>
<td>≥42.8</td>
<td>43.1</td>
<td>43.1</td>
<td>44.3</td>
<td>43.3</td>
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</table>

Distillation:

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<td>IBP, °C</td>
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<tr>
<td>10% recovered, °C</td>
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<tr>
<td>20% recovered, °C</td>
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<tr>
<td>50% recovered, °C</td>
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<tr>
<td>90% recovered, °C</td>
<td></td>
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<td>EP, °C</td>
<td>≤300</td>
<td>214</td>
<td>243</td>
<td>275</td>
<td>265</td>
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<td>T90-T10, °C</td>
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<td>25</td>
<td>49</td>
<td>89</td>
<td>62</td>
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<td>Residue, % vol</td>
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<td>1.1</td>
<td>1.1</td>
<td>1.5</td>
<td>1.3</td>
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<td>Loss, % vol</td>
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<td>0.8</td>
<td>0.9</td>
<td>0.8</td>
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<td>Flash point, °C</td>
<td>≥38</td>
<td>44</td>
<td>48</td>
<td>45</td>
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<td>Freeze Point, °C</td>
<td>≤-47</td>
<td>-60</td>
<td>-60</td>
<td>-51</td>
<td>-50</td>
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<td>Density @ 15°C, kg/L</td>
<td>0.775 - 0.840 (0.751 - 0.770)</td>
<td>0.803</td>
<td>0.814</td>
<td>0.756</td>
<td>0.804</td>
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</tbody>
</table>

• Possible jet fuel blend stock
• Large volume samples required for fit-for purpose testing