Maximizing value from biomass: Developing pathways for the production of fuels and products

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Outline

• Overview of NREL
• Techno-economic Analysis and Life Cycle Assessment
• Hydrocarbon Biofuel Pathways

• Analysis considerations
  • Market Pull
  • Job Development
  • Resource Assessment
Snapshot of NREL

Only National Laboratory Dedicated Solely to Energy Efficiency and Renewable Energy

- Leading clean-energy innovation for 37 years
- 1500 employees with world-class facilities
- Campus is a living model of sustainable energy
- Owned by the Department of Energy (DOE)
- Biofuel/Bioproduct Partner Facilities (IBRF and TCUF)
NREL’s Mission Covers

**Energy Efficiency**
- Residential Buildings
- Commercial Buildings
- Personal and Commercial Vehicles

**Renewable Energy**
- Solar
- Wind and Water
- Biomass
- Hydrogen
- Geothermal

**Systems Integration**
- Grid
- Infrastructure
- Distributed Energy
- Interconnection
- Battery and Thermal Storage
- Transportation

**Market Focus**
- Private Industry
- Federal Agencies
- Defense Dept.
- State/Local Govt.
- International
Thermochemical Process Development Unit (TCPDU)

Pilot scale system for scaling-up and testing technologies and catalysts developed at the lab scale.

- Flexible system design - configurable unit operations
  - Three reformer configuration options for gasification
    - Full stream fluidized bed reformer
    - Full stream FBR + full stream packed bed reformer
    - Circulating fluidized reforming system (R-cubed)
  - Equipment can be used for gasification and pyrolysis with minimal changes
    - R-cubed could be used as vapor-phase upgrading of pyrolysis vapors OR as a catalytic fast pyrolysis system
    - Davison Circulating Reactor (DCR) for upgrading of pyrolysis vapors to fuels and chemicals
Integrated Biorefinery Facility

Pilot scale equipment for integrated biomass processing

- Feed milling and handling
- Three continuous pretreatment process trains
- Two enzymatic hydrolysis process trains
- Fermentation systems (30-L to 9000-L vessels)
- Fermentation labs
- Separation equipment
- Small batch and continuous pretreatment reactors
- Techno-economic and lifecycle modeling
- Compositional analysis laboratories

Horizontal-Tube Pretreatment Reactor

Enzymatic Hydrolysis Reactors

Centrifuge

Fermentors
NREL is co-developing biofuel and chemical technologies with a large mix of leading bio-ethanol, -butanol, -gasoline, -diesel, -jet and -chemical producers.

Technology development ranges from individual pieces of the process to fully integrated biomass to biofuel demonstrations and from bench to pilot scale.

Collaborations range from a few weeks to multiple years in duration.

NREL engages in dozens of collaborative pilot scale research projects with industrial partners annually.
Biorefinery Analysis

TEA: Assess technical & economic feasibility of biofuels conversion processes
- Detailed process analysis with mass and energy balances
- Impact of major cost drivers (sensitivity studies)
- Set research targets & use them as measure of research progress

LCA: Overall environmental impacts of the technology (supporting ANL)
- Quantification of impacts and areas of improvement (focus on CONVERSION)
- Track research progress (economic & sustainability criteria)

- Land Use Change
- Feedstock Logistics
- Biomass Conversion
- Product Distribution
- Fuel Utilization

- GHG Emissions
- Water Use
- Net Energy Use
- Criteria Air Emissions
2011 Biochem Design Report for Cellulosic Ethanol

- 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

Process and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol

D. Humbird, R. Davis, L. Tao, C. Konche, D. Hsu, and A. Aden
National Renewable Energy Laboratory
Golden, Colorado

P. Scholze, J. Lukas, B. Olhoff, M. Wonesy, D. Sexton, and D. Dadson
March Group Inc.
Seattle, Washington and Atlanta, Georgia

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Technical Report
NREL/PR-5500-48077
May 2011

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Historic State of Technology

Minimum Ethanol Selling Price (2007$ per gallon)

- Conversion
- Feedstock

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

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
Target: $2.15

Historic State of Technology
<table>
<thead>
<tr>
<th>Technical Target Table</th>
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<tbody>
<tr>
<td></td>
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<tr>
<td>Feedstock Contribution ($/gal)</td>
</tr>
<tr>
<td>Conversion Contribution ($/gal)</td>
</tr>
<tr>
<td>Yield (Gallon/dry ton)</td>
</tr>
<tr>
<td>Feedstock Cost ($/dry ton)</td>
</tr>
<tr>
<td>Pretreatment</td>
</tr>
<tr>
<td>Solids Loading (wt%)</td>
</tr>
<tr>
<td>Xylan to Xylose (including enzymatic)</td>
</tr>
<tr>
<td>Xylan to Degradation Products</td>
</tr>
<tr>
<td>Conditioning</td>
</tr>
<tr>
<td>Ammonia Loading (mL per L Hydrolyzate)</td>
</tr>
<tr>
<td>Hydrolyzate solid-liquid separation</td>
</tr>
<tr>
<td>Xylose Sugar Loss</td>
</tr>
<tr>
<td>Glucose Sugar Loss</td>
</tr>
<tr>
<td>Enzymes</td>
</tr>
<tr>
<td>Enzyme Contribution ($/gal EtOH)</td>
</tr>
<tr>
<td>Enzymatic Hydrolysis &amp; Fermentation</td>
</tr>
<tr>
<td>Total Solids Loading (wt%)</td>
</tr>
<tr>
<td>Combined Saccharification &amp; Fermentation Time (d)</td>
</tr>
<tr>
<td>Corn Steep Liquor Loading (wt%)</td>
</tr>
<tr>
<td>Overall Cellulose to Ethanol</td>
</tr>
<tr>
<td>Xylose to Ethanol</td>
</tr>
<tr>
<td>Arabinose to Ethanol</td>
</tr>
</tbody>
</table>
Design reports of 8 representative pathways for the conversion of biomass to hydrocarbon fuels and products.
Thermochemical Conversion: Pyrolysis
Hydrocarbon Biofuels Technology Pathways

**Fast Pyrolysis With Upgrading**

1. Woody Biomass → Feed Handling & Preparation
2. Woody Biomass → Uncatalyzed Fast Pyrolysis
3. Condense → Non-condensable Gas → Catalytic Hydrotreating and Fractionation
4. Condense → Hydrogen
5. Condense → Hydrocarbon Biofuels (i.e. Gasoline, Diesel, Jet)
6. Condense → solids

**In-Situ Catalytic Pyrolysis With Upgrading**

1. Woody Biomass → Feed Handling & Preparation
2. Woody Biomass → Catalyzed Fast Pyrolysis
3. Condense → Non-condensable Gas → Catalytic Hydrotreating and Fractionation
4. Condense → Hydrogen
5. Condense → Hydrocarbon Biofuels (i.e. Gasoline, Diesel, Jet)
6. Condense → Water
7. Condense → solids

**Ex-Situ Catalytic Pyrolysis With Upgrading**

1. Woody Biomass → Feed Handling & Preparation
2. Woody Biomass → Uncatalyzed Fast Pyrolysis
3. Condense → Non-condensable Gas → Catalytic Hydrotreating and Fractionation
4. Condense → Hydrogen
5. Condense → Hydrocarbon Biofuels (i.e. Gasoline, Diesel, Jet)
6. Condense → Water
7. Condense → solids
Char as biomass-derived soil amendment

Biomass $\rightarrow$ 400$^\circ$C $\rightarrow$ Char

C-storing, designed soil amendment

Figure 1: Corn plant roots 35 days post germination in potting soil (PS), PS and NPK addition, PS and 5% char 1.
Harvested Corn after 35 Days

- PS + 10% Char
- PS + 5% Char
- Potting soil (PS)

• 5 and 10% char improved plant mass and root growth similarly
Valorizing Aqueous Pyrolysis Waste Streams

Robust reforming catalysts for H\textsubscript{2} production
Oxygenate upgrading catalyst to hydrocarbons
Biological upgrading to chemical products
Comprehensive fraction analysis

**Catalyst Targets**
- Coking < 10%
- Hydrogen > 90%

**Project rationale:**
Waste water management from a pyrolysis plant likely a significant cost
Work on valorization instead of loss of carbon in the aqueous phase.

*In Situ* 2022 cost target from NREL/TP-5100-62455, 2015.
Assumes thermal oxidation of aqueous carbon.
The first catalyst had high initial H<sub>2</sub> production which decreased to a lower steady level. Not all of the COD could be accounted for, suggesting the formation of char, coke or heavy tars.

The second catalyst had a lower initial H<sub>2</sub> yield but was more stable and all of the COD could be accounted for, suggesting that this material is resistant to coking.

Future work will 1) combine the two formulations to achieve higher stable H<sub>2</sub> conversion and 2) add a downstream WGS catalyst to shift to maximize H<sub>2</sub> yield (approach used for naphtha reforming to H<sub>2</sub>).
Waste stream valorization

Develop approaches for waste valorization in pyrolysis processes

- Focus on products with sufficient market size and growth potential to aid bioenergy industry
- Develop biological strategies for valorization of TC waste streams to fuels and chemicals

Growth on HMF

Enhanced Furfural Utilization

Work from Gregg Beckham’s Team
Thermochemical Conversion: Gasification
Primary focus for R&D and engineering optimization.

INL R&D

Leveraging gasification & syngas cleanup technologies.

Flue Gas

Gasification (Indirect Circulating Dual Fluidized Beds)

Gas Cleanup (Tar Reforming, Syngas Scrubbing, Compression)

Heat Integration & Power Generation

Methanol Synthesis (Acid Gas Removal, PSA, Methanol Synthesis)

Methanol Recovery (Syngas/Methanol Separation, Degassing)

Fuel Gas

Product Recovery

DME to High-Octane Gasoline

Methanol to Dimethyl Ether (DME)

DME + C4 Recycle

Cooling Water & Wastewater Treatment

High-Octane Gasoline Blendstock

Woody Biomass

H2

H2

Methanol Intermediate

Commercially available technologies.

Note: Syngas to DME (single-step) RD&D is funded through BETO (HT TIGAS).
Algae Pathways
Hydrocarbon Biofuels Technology Pathways

**Algal Lipid Extraction and Upgrading to Hydrocarbons (ALU)**

- **CO₂** → Algae Growth → Water & Nutrients → Evaporation → Floculant → Solvent → Hydrogen → Hydrocarbon Biofuels (i.e. Gasoline, Diesel, Jet)
- **CO₂ + Nutrient Recycle** → Residual Biomass for Anaerobic digestion

**Whole Algae Hydrothermal Liquefaction and Upgrading to Hydrocarbons (Algae HTL)**

- **CO₂** → Algae Growth → Water & Nutrients → Evaporation → Floculant → Solvent → Hydrogen → Hydrocarbon Biofuels (i.e. Gasoline, Diesel, Jet)
- **CO₂ + Nutrient Recycle** → Residual Biomass for Anaerobic digestion
Background: Prior TEA Focus – Lipid-Only Extraction (Benchmark as of 2013 Peer Review)

- Historical focus in public domain on traditional lipid extraction pathways; challenged by:
  a) No definition of “traditional”: majority of TEA assumed a black-box lipid extraction process, but data largely lacking on high yield/wet extraction methods → increased uncertainty
  b) Asymptotic limits to cost reductions, dictated by achievable yields (≤50% lipids = ≥50% unutilized biomass)

[Diagram of lipid extraction process]

http://www.nrel.gov/docs/fy12osti/55431.pdf
Alternative approach: biochemical processing for selective conversion of multiple biomass components to multiple fuel products/coproducts

- Potential for similar fuel yields as HTL, but non-destructive conversion of biomass allows high selectivity towards numerous product options
- “Plug and play” flexibility for conversion of carbohydrate, lipid, and protein fractions
- Experimentally demonstrated high lipid extraction yield on wet biomass
Chemicals and Materials from Algae

- **Fractionation**
  - Lipids upgraded to a renewable diesel or surfactants
  - Carbohydrates converted to ethanol or chemicals
  - Protein to higher value products
Biological Conversion: Sugar Pathways
Sugar Conversion to Hydrocarbons

Corn Stover → Feed Handling & Preparation → Pretreatment & Conditioning → Enzymatic Hydrolysis → Biological Conversion → Catalytic Conversion → Product Upgrading/Recovery → Hydrocarbon Biofuels (i.e. Gasoline, Diesel, Jet)
Key to meeting cost target will be maximizing biomass utilization

Investigating routes for chemicals production and lignin conversion
Deacetylation and Mechanical Refining Process (DMR)

3/4" Milled Corn Stover → Atmosphere Deacetylation Tank

Belt Conveyor → Deacetylation

Press → Disc Refining (Atmospheric) → Paddle Reactor

Mechanical Refiner (Atmospheric)

Fermenter → Fuels and Chemicals

Lignin for Upgrading to Fuels and Chemicals

Boiler fuel

HDO

Super Capacitors

Alkaline Spent Liquor for Recycling or Waste Water Treatment

Published in:

ChemSusChem

Work from Melvin Tucker and Xiaowen Chen

NREL, WSU

PNNL, NREL, WSU
Lignin Deconstruction via Alkaline Pulping

Alkaline Pretreatment

Biomass → NaOH → in situ Lignin Deconstruction → Lignin Upgrading → Lignin-derived fuels and chemicals

Solid carbohydrates → Carbohydrate Deconstruction → Upgrading → Carbohydrate-derived fuels

Work from Gregg Beckham’s Team

Karp et al., ACS. Sust. Chem. Eng., 2014
Biological Funneling enables conversion of lignin-derived aromatics into value-added compounds

- Significant versatility in lignin stream, organism, and target product
- Demonstrated mcl-PHA production in *Pseudomonas putida* KT2440 on alkaline pretreated liquor
- Higher-solids pretreatment will enable more efficient biological conversion step
- Examining mcl-PHA separation and cleanup strategies

Linger, Vardon, Guarnieri, Karp *et al.*, *PNAS*, 2014
Adipic acid production from lignin

Adipic acid identified as a primary target from lignin from a TEA and LCA perspective

- Combined metabolic engineering, fermentation, separations, and catalysis
- Demonstrated muconic acid production in engineered *P. putida* KT2440 on alkaline pretreated liquor
- Purity is a key cost driver; examining separations options and downstream polymer properties

Work from Gregg Beckham’s Team

• We selected a small subset of chemical coproducts among many more possibilities
• Some coproducts show the potential to achieve $3/GGE target, others do not
• Critical to consider market volume capacity for coproducts from a high-volume industry such as biofuels

<table>
<thead>
<tr>
<th>Product</th>
<th>World Production (thousand tons/year)</th>
<th>Price ($/ton)</th>
<th>Projected growth rate</th>
<th>Primary Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3 Butadiene</td>
<td>&gt;12,000</td>
<td>3200</td>
<td>5%</td>
<td>Synthetic rubber</td>
</tr>
<tr>
<td>1,4 Butanediol</td>
<td>&gt;1,000</td>
<td>3170</td>
<td>5%</td>
<td>Tetrahydrofuran, specialty chemicals</td>
</tr>
<tr>
<td>Adipic Acid</td>
<td>&gt;3,000</td>
<td>1700</td>
<td>4-4.5%</td>
<td>Nylon-6,6</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>&gt;5,700</td>
<td>1000</td>
<td>2.5%</td>
<td>Nylon-6,6 precursors</td>
</tr>
</tbody>
</table>

Addition of lignin deconstruction/conversion process equipment increases MFSP

*Plot is based on % lignin conversion, of the 80% solubilized upstream in deconstruction*
High-level GHG estimate for lignin coproduct pathways

- High-level analysis shows that oxygenated products can improve MFSP and GHGs
  - Adipic acid and 1,4 butanediol provide increased GHG offset credit vs lignin combustion to power coproduct
  - Conventional adipic acid production is very carbon-intensive, note x0.1 multiplier on plot (large GHG credit)
  - Minimization and eventual loss of power coproduct, replaced by increasing offsets from chemical coproduct as more lignin diverted away from the boiler
Chemicals Market Analysis

Market analysis report for the production of bio-derived chemicals

- Focus of the report is on products that will have near-term market impact
- Understand the key drivers and challenges to move biomass-derived chemicals to market
  - Low-cost natural gas has allowed for opportunities for C3/C4 products
  - Push by large companies to utilize renewable materials
  - Growth in the functional replacements market
- Assess ways in which chemicals production can be leveraged to accelerate the growth of biofuels
- Planned publication in FY16
Jobs estimates using JEDI

Development of a suite of Jobs and Economic Development Impact (JEDI) models

- Publically available tools found at http://www.nrel.gov/analysis/jedi/

The model represents the entire economy as a system of linkages between subsectors of the economy

- The linkages are represented by multipliers (derived from IMPLAN, 2014) that determine the impact of construction and operation of a new project on employment, earnings, and output in other sectors
- Uses input-output analysis to capture the impacts throughout the supply chain
Overview of JEDI Models

- Publicly available Excel-based, user friendly models
- JEDI tools include
  - Biopower
  - Starch and cellulosic ethanol
  - Hydrocarbons from fast pyrolysis
- Each JEDI model has a user guide that summarizes input requirements, interpretation of results and limitations of the tool
BioEnergy Atlas

BioEnergy Atlas

Built into Google Maps, BioEnergy Atlas includes two interactive maps, BioPower and BioFuels. These maps allow you to compare and analyze biomass feedstocks, biopower and biofuels data from the U.S. Department of Energy (DOE), U.S. Environmental Protection Agency (EPA), and the U.S. Department of Agriculture.

BioFuels

BioFuels Atlas is an interactive map for comparing biomass feedstocks and biofuels by location. This tool helps users select from and apply biomass data layers to a map as well as query and download biofuels and feedstock data. The state zoom function summarizes state energy use and infrastructure for traditional and bioenergy power, fuels, and resources. The tool also calculates the biofuels potential for a given area.

BioFuels Atlas was developed by the National Renewable Energy Laboratory with funding from the DOE Biomass Program.

BioPower

BioPower is an interactive map for comparing biomass feedstocks and biopower by location. This tool helps users select from and apply biomass data layers to a map as well as query and download biopower and feedstock data. The analysis function offers common conversion factors that allow users to determine the potential biopower production for a selected feedstock in a specific area.

BioPower was developed by the National Renewable Energy Laboratory with funding from the EPA Blue Skyways Collaborative.

About ORNL's Knowledge Discovery Framework and NREL's BioEnergy Atlas

Oak Ridge National Laboratory's (ORNL) Knowledge Discovery Framework (KDF) is an online collaboration toolkit for information sharing. It serves as a central repository for biomass energy information. KDF provides comprehensive datasets, publications, analysis and query capabilities, models, mapping functionality, and collaboration between users. The National Renewable Energy Laboratory's (NREL) BioEnergy Atlas, is one of many tools and datasets available through KDF. The BioEnergy Atlas includes the BioPower and BioFuels Atlas, the two interactive mapping tools described above.

https://maps.nrel.gov/bioenergyatlas/
Biomass Resources Assessment – United States

Crop residues
- Harvesting residues
- Processing residues

Wood residues
- Forest residues
- Primary mill residues
- Secondary mill residues
- Urban wood waste

Lipid-based feedstock
- Vegetable oils
- Animal fats
- Greases
- Algae

Biogas/Biomethane
- Landfills
- Animal manure
- Wastewater treatment
- Industrial, institutional, and commercial organic waste (e.g. food waste).

BioFuels Atlas (3)

Bioenergy Resource Analysis
Run an analysis on the amount of yield that can be produced in a specific area.

Results
These data show the amount of yield from each feedstock in the area you selected.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Dry Amt (tonnes)</th>
<th>Gallons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagasse</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>Molasses</td>
<td>1,914.41</td>
<td>79,361</td>
</tr>
<tr>
<td>Forest Residues</td>
<td>459,937.20</td>
<td>14,468,025</td>
</tr>
<tr>
<td>Lignin Wood</td>
<td>249,107.30</td>
<td>10,285,310</td>
</tr>
<tr>
<td>and Sac. Mill Residues</td>
<td>716,900.00</td>
<td>29,463,412</td>
</tr>
<tr>
<td>Corn Stover</td>
<td>36,987.59</td>
<td>3,788,722</td>
</tr>
<tr>
<td>Rice Straw</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>Sugar Beets</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>Sugarcane</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>Wheat Straw</td>
<td>65,395.50</td>
<td>2,432,854</td>
</tr>
<tr>
<td>Totals</td>
<td>1,580,783.96</td>
<td>60,469,484</td>
</tr>
</tbody>
</table>
Acknowledgements

• Thank you to...

  o Bioenergy Technologies Office:
    • Alicia Lindauer, Kristen Johnson, Zia Haq (Strategic Analysis and Sustainability Platform)
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  o National Laboratory Partners (PNNL, INL, ORNL)

  o Industrial and Academic Partners
Back up slides
Questions?

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Abhijit Dutta
  – abhijit.dutta@nrel.gov
  – 303-384-7782 (office)


Link to NREL public TEA models: http://www.nrel.gov/extranet/biorefinery/aspen_models/
Biochemical Pathways

Catalytic Conversion of Sugars -- 2015

Biological Conversion of Sugars -- 2013
http://www.nrel.gov/docs/fy14osti/60223.pdf
Thermochemical Pathways

Indirect Liquefaction -- 2015
http://www.nrel.gov/docs/fy15osti/62402.pdf

In Situ and Ex Situ Pyrolysis -- 2015
http://www.nrel.gov/docs/fy15osti/62455.pdf

Updated Fast Pyrolysis Design -- 2013
Design Report Publications

Algae Pathways
Algal Lipid Upgrading – 2014
http://www.nrel.gov/docs/fy14osti/62368.pdf

Whole Algal Hydrothermal Liquefaction and Upgrading – 2014
Technical Memo Publications


http://www.nrel.gov/docs/fy13osti/58051.pdf

http://www.nrel.gov/docs/fy13osti/58056.pdf

http://www.nrel.gov/docs/fy13osti/58055.pdf
Technical Memo Publications

http://www.nrel.gov/docs/fy13osti/58049.pdf


Feedstock cost is primary driver at $430/ton (70% of total MFSP)

Additional drivers = PT + Extraction CAPEX