HYDROGEN FROM BIOMASS FOR URBAN TRANSPORTATION

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Collaborating Project Team

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D. McGee (Enviro-Tech Enterprises Inc., Matthews, NC)
M. Realff (Georgia Institute of Technology, Atlanta, GA)
OBJECTIVES

• Undertake the engineering research and pilot scale process development studies relating to:
  - Production of hydrogen from biomass (e.g., agricultural residues) for $2.90/kg H₂ by 2010; $2.30 by 2015
  - Separation, safe storage and utilization of the hydrogen
  - Production and identification of uses of the co-products

• Increase diversity of the Nation’s workforce and the broader impact of the project through the education and training of underrepresented minorities.
Relevance to DOE, FreedomCAR, and Hydrogen Initiative

• **Project was to develop technology (pyrolysis-reformer process) that will:**
  - Produce hydrogen from biomass (e.g., peanut shells)
  - Utilize the biomass hydrogen for transportation and/or stationary power generation
  - Reduce cost, and develop improved technologies

• **Project addressed national and global issues related to:**
  - Improvement in America’s energy security by reducing the need for imported oil
  - Improving air quality and reducing greenhouse gas emissions
  - Revitalization of rural economy (e.g., Georgia)
  - The four E’s: Energy, Environment, Economy, and Education
Technical Barriers: Hydrogen from biomass via pyrolysis and steam reforming

• Feedstock cost and availability
• Efficiency of pyrolysis and reforming technologies
• Durable, efficient and impurity tolerant catalysts
• Hydrogen separation, purification and storage
• Market and delivery
Technical Targets: hydrogen from biomass via pyrolysis and steam reforming

<table>
<thead>
<tr>
<th></th>
<th>Units</th>
<th>2003</th>
<th>2005</th>
<th>2010</th>
<th>2015</th>
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<tbody>
<tr>
<td><strong>Biomass Feed</strong></td>
<td>Cost</td>
<td>$/kg H₂</td>
<td>0.80</td>
<td>0.80</td>
<td>0.70</td>
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<tr>
<td><strong>Operations through</strong></td>
<td>Cost</td>
<td>$/kg H₂</td>
<td>1.90</td>
<td>1.90</td>
<td>1.50</td>
</tr>
<tr>
<td>pyrolysis</td>
<td></td>
<td>Energy Efficiency % (LHV)</td>
<td>65</td>
<td>66</td>
<td>72</td>
</tr>
<tr>
<td><strong>Reforming</strong></td>
<td>Cost</td>
<td>$/kg H₂</td>
<td>0.70</td>
<td>0.60</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Energy Efficiency % (LHV)</td>
<td>83</td>
<td>84</td>
<td>87</td>
</tr>
<tr>
<td><strong>Purification</strong></td>
<td>Cost</td>
<td>$/kg H₂</td>
<td>0.40</td>
<td>0.40</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Energy Efficiency % (LHV)</td>
<td>74</td>
<td>74</td>
<td>77</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>Cost</td>
<td>$/kg H₂</td>
<td>3.80</td>
<td>3.70</td>
<td>2.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Net Energy Ratio</td>
<td>26</td>
<td>27</td>
<td>32</td>
</tr>
</tbody>
</table>
Reforming Reactions

- \( \text{C}_n\text{H}_m + n\text{H}_2\text{O} = n\text{CO} + (n + m/2)\text{H}_2 \) 
  \((-\Delta H^\circ_{298} < 0)\)

- \( \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \) 
  \((-\Delta H^\circ_{298} = 9.48\text{kcal/mol})\)

- \( \text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} \) 
  \((-\Delta H^\circ_{298} = 49.27\text{kcal/mol})\)
APPROACH

• Develop process based on biomass pyrolysis and steam reforming of pyrolysis vapors (bio-oils and gases).

• Perform catalytic steam reforming in a fluidized-bed (25-250 kg/day H₂ production)

• Conduct pyrolysis at: T: 500°C; P: 10 psig; Feed Rate: 50-500 kg/hr pelletized peanut shells. Gas and charcoal exit at 425 °C

• Study reforming at: T: 850°C; P: 6 psig; H₂O/C = 5, Catalyst: nickel-based (300-500 microns)
PROJECT TASKS

• Task 1: Feedstock supply, process economics and deployment strategies (modeling, extraction, and property estimation)
• Task 2: Process modifications, integration, and shakedown
• Task 3: Long term (1,000 hours) catalyst and process testing
• Task 4: Hydrogen separation, storage, and utilization
• Task 5: Environmental and technical evaluation
• Task 6: Partnership building and outreach
Schematic Flow Diagram of the Biomass Refinery for Hydrogen, Char and Chemicals

Biomass

Preparation e.g., Densifier <0.2 SG

Superheater

Steam From Boiler

Pyrolysis

Filter

Vapor Heater

Catalytic Reformer 850 C

Baghouse

Solids

Cooling Tower

Condenser

Condensed Water

Dryer

Engine

Off Gas

Sampling For Emissions

Accumulator

H2

PSA System

CH4

CO2

Flare

Compressor Or Blower

Phenolics

Adhesives or Biofuel additives

Superheated Steam Or Preheat fuel Gas

Char For Fertilizer etc
PICTURES OF PILOT PLANT
Blakely, Georgia Site
PICTURES OF PILOT PLANT BEING MOVED TO UGA, ATHENS
PICTURES OF UNLOADING AND REINSTALLATION OF PILOT PLANT AT UGA, ATHENS
2004 Bio-refinery Conversion Project at University of Georgia


DOE estimates that hydrogen production from biomass is one of the most cost competitive
**Typical Analysis of Peanut Shell Feedstock**

- **Component**
  - Lignin: 34.8%
  - Glucan: 21.1%
  - Extractives: 14.2%
  - Protein: 11.1%
  - Xylan: 7.9%
  - Ash: 3.4%
  - Arabinan: 0.7%
  - Galactan: 0.2%
  - Mannan: 0.1%
  - Others (e.g., free carbohydrates): 6.5%
### RESULTS: TYPICAL PRODUCT COMPOSITION/ YIELDS

<table>
<thead>
<tr>
<th>Pyrolyzer (Yields)</th>
<th>Reformer (Gas product composition, on dry N\textsubscript{2}-free basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char</td>
<td>32% Hydrogen 57%</td>
</tr>
<tr>
<td>Water</td>
<td>32% Carbon Dioxide 26%</td>
</tr>
<tr>
<td>Bio-Oils</td>
<td>31% Carbon Monoxide 12%</td>
</tr>
<tr>
<td>Gases</td>
<td>5% Methane 5%</td>
</tr>
</tbody>
</table>
Pyrolysis Bio-Oil Product

- **Empirical Formula:** \( \text{CH}_{1.9}\text{O}_{0.7} \)
- **Water:** 15 – 25%
- **Organics:** 75 – 85%
  - Aldehydes, alcohols and acids from carbohydrate fraction
  - Phenolics from lignin fraction

- **Representative Compounds**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Ethanol</td>
<td>Methanol</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>Formic Acid</td>
<td>Acetic Acid</td>
</tr>
<tr>
<td>Glucose</td>
<td>Phenol</td>
<td>O-cresol</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>Dodecanoic acid</td>
<td>Tannin</td>
</tr>
</tbody>
</table>
Selectivity / Distribution Plot

Distribution coefficients

\[ K = \frac{(X_{\text{phe}})_{\text{sol}}}{(X_{\text{phe}})_{\text{wat}}} \]

Selectivity

\[ \ln(\mathbb{G}) = \ln \left\{ \frac{(X_{\text{phe}})_{\text{sol}}/(X_{\text{phe}})_{\text{wat}}}{(X_{\text{phe}})_{\text{wat}}/(X_{\text{phe}})_{\text{sol}}} \right\} \]

- MIBK
- IPA
- Benzene
Biocarbon-Based Fertilizers

Formation of Ammonium Bicarbonate
Inside the 15 min Char Interior

Courtesy
D. Day, Eprida Scientific Carbons Inc.
Bark Charcoal and Fertilizer

Effect of bark charcoal and fertilizer on the plant growth and soil properties in south Sumatra (Yamato 2004 unpublished)
Charcoal provides a preferred habitat for soil microorganisms

The germination rate of G. margarita was higher than that on soil (Ogawa 1991)

Bacterial populations show marked increase with charcoal addition (Beijerinckia, Ogawa 1992)

Note the 3 fold increase
Formation of ABC in Fractures

Interior Formations

Exterior Buildup as Expected

Volcano like Structures around pores

Sizable Interior Cavities
Crushed Interior 2000x SEM

The residual cell structure of the original biomass is clearly visible.

The ABC fibrous buildup has started inside the carbon structure.

After complete processing, interior is full.

Trace minerals are returned to the soil along with essential nitrogen.
Proposed Peanut Shell to Hydrogen Cycle

Stationary fuel cell power generation
CONCLUSIONS

• Demonstrated successfully pyrolysis-reformer concept for 1000 hours operation
• Discovered agricultural uses and carbon sequestration strategy: Novel carbon slow release sequestered fertilizer.
• Identified economical co-product options for bio-oils: Adhesives.
• Run successfully the product gas in an engine with significant reduction of $\text{NO}_x$
• Further R & D over 1,000 hours operation and higher hydrogen production rate could lead to economically competitive hydrogen and a viable integrated bioconversion process.
INTERACTIONS AND COLLABORATIONS

• The project resulted in significant interactions and collaborations between the following organizations:

- Clark Atlanta University, Atlanta, GA
- EPRIDA Scientific Carbons Inc., Atlanta, GA
- Enviro-Tech Enterprises Inc., Matthews, NC
- Georgia Institute of Technology, Atlanta, GA
- National Renewable Energy Lab, Golden, CO
- Oak Ridge National Lab, Oak Ridge, TN
- Southern Company, Atlanta, GA
- The University of Georgia, Athens, GA
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  - Doug Hooker, James Alkire, Beth Dwyer
  - Chris Bordeaux, Sigmund Gronich, Neil Rossmeissl

• **Support of the Partner Institutions**
  - Clark Atlanta University
  - EPRIDA Scientific Carbons Inc.
  - Enviro-Tech Enterprises Inc.
  - Georgia Institute of Technology
  - National Renewable Energy Laboratory
  - The University of Georgia, Athens