A Novel Slurry Based Biomass Reforming Process
(DE-FG36-05GO15042)

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Overview

Timeline
- Start: May 2005
- End: March 2011
- 75% Complete

Budget
- Total Project Funding
  - DOE share: $3M
  - Contractor share: $750k
- Funding Received in FY09
  - $600k
- Funding for FY10
  - $590k

Barriers
- T. Capital Costs and Efficiency of Biomass Gasification/Pyrolysis Technology

Partners
- University of North Dakota Environment Energy Research Center (UND-EERC)
  - Hydrolysis experimental studies
  - Slurry characterization
  - Wood reforming studies
Project Objectives & DOE Target Status

- Development of an initial reactor and system design, with cost projections, for a biomass slurry hydrolysis and reforming process for H₂ production
  - Efficiency & H₂ cost exceed gasification targets
  - Capital costs dependent on H₂ delivery pressure & H₂ separation membrane
- **Current costs assume a precious metal based catalyst**
- Development of cost effective catalysts for liquid phase reforming of biomass hydrolysis-derived oxygenates
  - **Switch to base metal catalyst decreases hydrogen cost by ≈$0.20/kg H₂**
- Proof-of-concept demonstration of a micro-scale pilot system based on liquid phase reforming of biomass hydrolysis-derived oxygenates
- **Phase II work now started**

<table>
<thead>
<tr>
<th></th>
<th>Target</th>
<th>2009 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Cost (Plant Gate)(^a)</td>
<td>1.60 $/gge</td>
<td>$1.27/kg H₂ ($0.95/kg – $2.13/kg)</td>
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<tr>
<td>Total Capital Investment</td>
<td>$150M</td>
<td>$177M ($71M – $365M)</td>
</tr>
<tr>
<td>Energy Efficiency(^b)</td>
<td>43%</td>
<td>55% (55% – 58%)</td>
</tr>
</tbody>
</table>

\(^a\) Gallon of gasoline equivalent (gge) ≈ kg H₂
\(^b\) Plant H₂ Efficiency

Plant H₂ Efficiency = \(\frac{\text{LHV of Product H}_2}{\text{LHV of Biomass Feed} + \text{Energy Consumed}}\)
**Approach: Biomass Slurry to Hydrogen Concept**

- Fuel flexible, using raw, ground biomass such as wood or switch grass
- Carbon neutral means to produce Hydrogen
- $H_2$ separation: Leverage experience with Advanced Pd membranes

$0.09-0.13 \text{ kg } H_2/\text{kg Biomass (dry)}$

**Alternative: Biomass Gasification to Hydrogen Concept**

- Fuel flexible, using raw, ground biomass such as wood or switch grass
- Gasification & PSA: Leverage existing technologies
- Process complexity
2009 Accomplishment: Total Reforming of Yellow Poplar

Demonstrated ≈100% conversion of yellow poplar to H₂ (75% LHV efficiency)

- Semi-batch conversion of yellow poplar to H₂, CH₄, C₂H₆, & C₃H₈
- H₂ selectivity of 74% (among H₂ containing gases)
- For LHV\textsubscript{wood} = 18 kJ/g; 75% of wood LHV is in hydrogen
- Complete conversion of wood, including lignin; trace organic acids left
- Burned alkanes could provide enough energy to run endothermic reformer

Effluent product profiles from the hydrolysis and liquid phase reforming of 1 wt% yellow poplar at 310 °C in 0.1M K₂CO₃ with a 0.5 L/min N₂ sweep gas.
Technical: Plug Flow Reactor for Kinetics/Durability Studies

- ½-in OD Inconel 625 Reactor.
- High Pressure syringe pump for pulseless liquid feed.
- Dual GCs for Permanent Gas and Hydrocarbon analysis.
Technical: Durability Testing with 1% Ethanol

A- 1% Ethanol
B- 1% Ethanol in 0.1M K₂CO₃
C- 1% 1,4-Butanediol in 0.1M K₂CO₃
D- 1% Ethanol in 0.1M K₂CO₃

<table>
<thead>
<tr>
<th>Time on Stream, hr</th>
<th>Product Flow Rate, mol/min x 10^-4</th>
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<tr>
<td>0</td>
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<tr>
<td>50</td>
<td>0.1</td>
</tr>
<tr>
<td>100</td>
<td>0.2</td>
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<tr>
<td>150</td>
<td>0.3</td>
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<tr>
<td>200</td>
<td>0.4</td>
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<tr>
<td>250</td>
<td>0.5</td>
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<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<tr>
<td>50</td>
<td>0.0</td>
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</table>

H₂, CO₂, CO, CH₄

Selectivity

Temperature, °C

Selectivity
- Liquid phase reforming of 5% ethanol in flow reactor
- Reformer product gas containing 64% H₂ fed to membrane rig at 193 psig
- Separated hydrogen with a recovery of 93%
Technical: High pH Increases \( \text{H}_2 \) & Decreases \( \text{CH}_4 \)

- **Moved to base metal catalyst to reduce cost (Raney Ni)**
- Methane generation with Raney nickel can be controlled by tailoring base concentrations.
- Increased base concentrations increased selectivity

Unpromoted Raney Ni 5% EG, 310 °C, 120 atm

\[
\text{H}_2 \text{ Selectivity} = \frac{2 \times \text{H}_2 \text{ in product gas stream}}{\text{Total H in product gas stream}} \times 100
\]
Technical: Reforming of Ethylene Glycol over Ni

Ethylene glycol

\[
\text{HOH}_2\text{CCH}_2\text{OH} \rightarrow \text{HOH}_2\text{CCH}_2\text{O}^* + \text{H}_2
\]
\[\Delta H_1 = -0.57 \text{ eV}; \Delta H_2 = -0.75 \text{ eV}\]
\[E_{\text{ads}} = -0.29 \text{ eV}\]

Dehydrogenation

\[
\text{HOH}_2\text{CCH}_2\text{OH} \rightarrow \text{HOH}_2\text{CCH}_2\text{OH}_{\text{ads}}
\]
\[\Delta H = -0.85 \text{ eV}\]

C-O bond scission

\[
\text{HOH}_2\text{CCH}_2\text{OH} \rightarrow \text{HOH}_2\text{CCH}_2\text{O}^* + \text{H}_2
\]
\[\Delta H = -0.85 \text{ eV}\]

Rearrangement

\[
\text{CO} + \text{H}_2 \rightarrow \text{CO}_2 + \text{H}_2
\]
\[\Delta H = -0.23 \text{ eV}\]

Hydrophilic attack from base produces formate ion

\[
\text{*CO} + \text{OH}^- \text{ (base)} \rightarrow \text{HCOO}^- \text{ (solution)}
\]
\[\Delta H = -0.88 \text{ eV}\]

Acetone

\[
\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO} + \text{H}^*
\]
\[\Delta H = -0.79 \text{ eV}\]

Acetyl

\[
\text{CH}_3\text{CO} \rightarrow \text{CH}_3^* + \text{*CO}
\]
\[\Delta H = -1.188 \text{ eV}\]

Hydrophilic attack from base produces formate ion

\[
\text{*CO} + \text{OH}^- \text{ (base)} \rightarrow \text{HCOO}^- \text{ (solution)}
\]
\[\Delta H = -0.88 \text{ eV}\]

Acetaldehyde

\[
\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO} + \text{H}^*
\]
\[\Delta H = -0.79 \text{ eV}\]

Acetyl

\[
\text{CH}_3\text{CO} \rightarrow \text{CH}_3^* + \text{*CO}
\]
\[\Delta H = -1.188 \text{ eV}\]

Hydrophilic attack from base produces formate ion

\[
\text{*CO} + \text{OH}^- \text{ (base)} \rightarrow \text{HCOO}^- \text{ (solution)}
\]
\[\Delta H = -0.88 \text{ eV}\]

With base

\[
\begin{align*}
\text{C}_2\text{H}_6\text{O}_2 + 4\text{KOH} & \leftrightarrow 2\text{K}_2\text{CO}_3 + 5\text{H}_2 \\
\Delta G_{300^\circ C} & = -423 \text{ kJ/mol} \\
\text{C}_2\text{H}_6\text{O}_2 + 2\text{KOH} & \leftrightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CH}_4 + \text{H}_2 \\
\Delta G_{300^\circ C} & = -315 \text{ kJ/mol}
\end{align*}
\]

Without base

\[
\begin{align*}
\text{C}_2\text{H}_6\text{O}_2 + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{CO}_3 + \text{CH}_4 + \text{H}_2 \\
\Delta G_{300^\circ C} & = -179 \text{ kJ/mol} \\
\text{C}_2\text{H}_6\text{O}_2 + 4\text{H}_2\text{O} & \leftrightarrow 2\text{H}_2\text{CO}_3 + 5\text{H}_2 \\
\Delta G_{300^\circ C} & = -111 \text{ kJ/mol}
\end{align*}
\]
Technical: Liquid Phase Reforming of Raw Biomass

Complete conversion of 5 wt% wood feed to gaseous species

- Liquid phase reforming of raw biomass over Ni

- Commercially available wood flour
  - Hardwood mixture, 100 mesh
- 5 wt% wood at 310 °C, 120 atm in:
  - 0.2 M KOH
  - 2.0 M KOH
- Raney nickel, ~1:1 mass wood
- Low flow of N₂ Sweep gas
Technical: Liquid Phase Reforming of Raw Biomass

Complete conversion of 5 wt% wood feed to gaseous species

\[ C_6H_{10}O_5 + 12\text{KOH} + H_2O \xleftrightarrow{} 6\text{K}_2\text{CO}_3 + 12\text{H}_2 \]

0.2 M = 0.05x Stoichiometric
2.0 M = 0.5x Stoichiometric

- Increased base increases selectivity
  - 0.2 M KOH - 15% selectivity to \( \text{H}_2 \)
  - Hydrogen Yield based on reforming \( \approx 100\% \)
  - C conversion into gas phase \( \approx 100\% \)

  - 2.0 M KOH - 60% selectivity to \( \text{H}_2 \)
  - Hydrogen Yield based on reforming \( \approx 75\% \)

- Issues with increased base
  - Increased base leads to high levels of intractable organic acids
  - Difficulty of recycling hydroxide base
Technical: Promoted Ni Removes Need for High Base Levels

- **High H₂ selectivity and conversion**
  - >90% conversion with >90% selectivity
- Enables use of dilute carbonate bases & low temperature CO₂ disengagement

Promoted Raney Ni 2.5% EG, 310 °C, 120 atm

\[
\text{H₂ Selectivity} = \frac{2 \times \text{H₂ in product gas stream}}{\text{Total H in product gas stream}} \times 100
\]
Technical: Construction of 12 L/min H$_2$ Demonstration System

Combine liquid phase reforming with advanced H$_2$ separation membrane

- High Pressure Inconel 625 Reactor
  - 310 °C, 120 atm

- Wood Slurry Pump
  - 10% Slurry
  - 100-200 mL/min

- Pd Membrane Separator
  - 99.9999% H$_2$

- Gas Liquid Separator

- Wood Slurry Mass Flow Meter
Collaborators

- University of North Dakota Energy and Environmental Research Center
  - 2010 objective to examine the effect of several variables (e.g., base concentration, temperature, and pressure) on batch LPR on base metal catalysts

- Membrane Technology Development on DE-FC26-07NT43055
  - Power+Energy (Industry)
    - Manufacture of hydrogen separators
    - UTRC alloy fabrication
  - Metal Hydride Technologies (Ted Flanagan from Univ. of Vermont)
    - Fundamental experiments on hydrogen solubility
    - Experimental measurements of alloy systems for thermodynamic phase modeling
Proposed Future Work

2010

- Begin testing of prototype demonstration system
- Evaluate caustic solution recycle
- Evaluate and down-select final catalyst for durability study
- Revise techno-economic analysis based on demonstration system
- Perform 500-h durability study with demonstration system
Summary

- Demonstrated 100% conversion of wood with base metal catalyst

Catalyst Development
- Substituted base metal catalyst for precious metal
- Promoted Ni catalyst maintaining high selectivity with dilute carbonate
- Performed atomistic modeling to elucidate ethylene glycol LPR pathway
- Catalyst durability >250 hours

Reactor Design
- Demonstrated Pd membrane integration with LPR flow reactor
- Examined the effect of base concentration on H₂ selectivity

Began construction of 12 L/min wood demonstration unit

Work performed under the DOE Grant DE-FG36-05GO15042 was authorized in part under a research license for the Aqueous Phase Reforming Process (Patent 6,699,457; 6,694,757; 6,694,758 [and all other licensed issued patents]) from Virent Energy Systems in Madison, Wisconsin.