2007 DOE Hydrogen Program

Hydrogen Generation from Biomass-Derived Carbohydrates via Aqueous-Phase Reforming Process

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This presentation does not contain any proprietary or confidential information
Overview

Timeline

• Start – Sept 2005
• Finish – Aug 2008 (Tentative)
• 20 % complete

Budget

• Total project funding
  – DOE share - 1,942 K
  – Contractor share - 679 K
• Funding received to date
  – 369 K DOE
• Funding Reduction in FY06 resulted in limiting work to catalyst development

Barriers

– Feedstock Cost, Reformer Capital Cost, Operations Cost, and GHG emissions
– Feedstock Cost Reduction
  • 2012 Feedstock Cost Contribution $2.10/gge
  • 2017 Feedstock Cost Contribution $1.55/gge
– By 2012, reduce H₂ costs to $3.80/gge
  • Overall Efficiency 72%
– By 2017, reduce H₂ cost to <$3.00/gge

Partners

• ADM
• University of Wisconsin
## Objectives

| Overall | • Design a generating system that uses low cost sugars or sugar alcohols that can meet the DOE H₂ cost target of $2 to 3/gge for 2017.  
• Fabricate and operate an integrated 10 kg of H₂/day generating system. |
| 2006 | • Limited scope of work for 2006 due to funding cutbacks.  
• Develop APR catalyst, reaction conditions, and reactor suitable for converting glucose to hydrogen. |
Objectives (cont)

<table>
<thead>
<tr>
<th>Year</th>
<th>Objectives</th>
</tr>
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</table>
| 2007 | • Virent will continue to investigate catalyst, reaction conditions, and reactor suitable for converting low cost sugars to hydrogen  
   • Calculate the thermal efficiency and economics of the APR system utilizing different feedstocks (low cost sugars, glucose, sugar alcohols)  
   • Compare results of techno-economic analysis with DOE Hydrogen Programs Goals  
   • Make a Go No-Go decision on moving forward to the design and construction of a 10 kg H2/day demonstration system with the preferred feedstock.  
   • Design of 10 kg H₂/day demonstration system |
| 2008 | • Fabrication of 10 kg H₂/day system  
   • Startup and operation of 10 kg H₂/day system  
   • Analysis of 10 kg H₂/day system |
Hydrogen Production using the APR Process

- Simple Catalytic Process
  - No Water Gas Shift
  - No Steam System
  - No Gas Compressor
  - No Desulphurizer
- Energy Efficient
- Scalable
- Feedstock Flexible
Approach

Corn
Corn Stover
Sugar Cane
Bagasse

Hydrolysis
C\textsubscript{6}H\textsubscript{12}O\textsubscript{6} \rightarrow \text{Glucose} (C\textsubscript{6}H\textsubscript{12}O\textsubscript{6})
6 to 11 cents/lb

Sugar Alcohols

Sorption (C\textsubscript{6}H\textsubscript{14}O\textsubscript{6})
10 to 15 cents/lb

Hydrogenation
C\textsubscript{6}H\textsubscript{12}O\textsubscript{6} + H\textsubscript{2} \rightarrow C\textsubscript{6}H\textsubscript{14}O\textsubscript{6}

APR
Demonstrated

APR
Under Development
Biomass to Hydrogen via the APR Process

- **Biomass**
  - Pretreat
  - Cooking
    - Acids / Enzymes
      - Starch / Cellulosic
  - Hydrolysis
  - Filtration
    - Virent APR
  - Sugar Syrup
    - Hydrogen
Technical Accomplishments/Progress/Results

- Initiated project in September 2005
- ADM provided glucose samples for processing.
- Investigating catalyst and conditions for operations with high concentrations of sorbitol
- Investigating catalyst and conditions for operation with high concentrations of glucose
- Virent funded project to convert glycerol to hydrogen
  - Proved Catalyst Lifetime of greater than a year
  - Tested First Generation Reactor System
  - Designed and Constructed Second Generation Reactor System
Effects of Feed Concentration

- System Efficiency
  - Combustion of Hydrogen for Process Energy Required
  - Higher Feedstock Concentrations Reduce Heating Requirements
# Reforming of Glucose

<table>
<thead>
<tr>
<th>Date</th>
<th>Apr-04</th>
<th>Sep-05</th>
<th>Jan-06</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
<td>30% Sorbitol</td>
<td>3% Glucose</td>
<td>30% Glucose</td>
</tr>
<tr>
<td>WHSV</td>
<td>2.0 /h</td>
<td>0.897 /h</td>
<td>0.996 /h</td>
</tr>
<tr>
<td>Reactor</td>
<td>240 °C</td>
<td>230 °C</td>
<td>240 °C</td>
</tr>
<tr>
<td>Temperature</td>
<td>500 psig</td>
<td>430 psig</td>
<td>500 psig</td>
</tr>
<tr>
<td>Pressure</td>
<td>240 °C</td>
<td>230 °C</td>
<td>240 °C</td>
</tr>
<tr>
<td>Conversion</td>
<td>100%</td>
<td>73%</td>
<td>100%</td>
</tr>
<tr>
<td>Conversion to Gas</td>
<td>75%</td>
<td>14%</td>
<td>58%</td>
</tr>
<tr>
<td>H2 Selectivity</td>
<td>72%</td>
<td>33%</td>
<td>23%</td>
</tr>
<tr>
<td>Watt H2/gram</td>
<td>4.2</td>
<td>0.12</td>
<td>0.39</td>
</tr>
<tr>
<td>Watt Alkane/Gram</td>
<td>2.1</td>
<td>0.03</td>
<td>1.26</td>
</tr>
</tbody>
</table>

WHSV – gram of oxygenated compound per gram of catalyst per h
Green Energy Machine (GEM)
APR Reactor Performance

Single Pass Conversion

1.8 WHSV based on Glycerol

Reactor Thermal Efficiency

\[
100 \times \left( 1.0 - \frac{\text{Process Energy}}{\text{Generated Energy}} \right)
\]

Process Thermal Efficiency
78.5 % of LHV of Feed
GEM Catalyst Lifetime Testing
13 months of Continuous operation

- 50 wt% Glycerol in water
- First Generation Catalyst
- One pass operation
- Very stable H₂ production
- Temperature can be raised to keep conversion high
## APR Outlet Gas Composition

### Glycerol Feedstock

<table>
<thead>
<tr>
<th></th>
<th>SNG Catalyst Vol. %, Dry</th>
<th>H2 Catalyst Vol. %, Dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>35%</td>
<td>60%</td>
</tr>
<tr>
<td>Methane</td>
<td>8%</td>
<td>7.5%</td>
</tr>
<tr>
<td>Ethane</td>
<td>12%</td>
<td>1.5%</td>
</tr>
<tr>
<td>Propane</td>
<td>5%</td>
<td>0.5%</td>
</tr>
<tr>
<td>CO2</td>
<td>40%</td>
<td>30.5%</td>
</tr>
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</table>
Hydrogen Pilot Plant
Projected Cost of Hydrogen Using the BioForming Process

1500 Kg/day H₂, 10% ROI, 10 Year Project Life, Glycerol Feed

*LHV Eff: LHV of hydrogen exit PSA / LHV of Feed Glycerol
Future Work

- Worked Planned for 2007
  - Develop APR catalyst and reactor that converts glucose to hydrogen.
  - Develop APR catalyst and reactor that effectively converts sugar alcohols to hydrogen.
  - Investigate hydrogenation technologies that convert both monosaccharides and polysaccharides to sugar alcohols.
  - Investigate the integration of the hydrogenation technology with the APR technology.
  - Calculate the thermal efficiency and economics of the baseline APR system utilizing sugars or sugar alcohols as the feedstock.
  - Evaluate the baseline APR system against US Hydrogen program goals and determine whether to proceed to development of the demonstration system.
Future Work beyond 2007

• Develop the detail design of the demonstration APR hydrogen generation system (10 kg/day).

• Fabrication of the integrated hydrogen generation system.

• Evaluate APR hydrogen generation system performance against US Hydrogen program goals.
Summary

• Initiated Project in September 2005 with limited funding.

• Initial work with higher concentrations of glucose shows promise.

• Virent has already built and operate a 6 NM³/h Alpha Unit utilizing glycerol as a feedstock.

• Virent will soon be starting up a second generation reactor system for generation of hydrogen from glycerol

• Will continue work with sugars as funding is available.