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)
- 10 % complete

Budget

- Total project funding
  - DOE share - 1,942 K
  - Contractor share - 679 K
- Funding received in FY05
  - 100 K
- Funding received for FY06
  - 100 K
- Funding Reduction in FY06 resulted in limiting work to catalyst development

Barriers

- Feedstock Cost Reduction
  - 2005 Feedstock Cost Contribution $3.80/gge
  - 2010 Feedstock Cost Contribution $1.80/gge
- By 2010, reduce H₂ costs to $3.60/gge
  - Overall Efficiency 66%
- By 2015, reduce H₂ cost to $2.50/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 $H_2$ cost target of $2.50/gge for 2015.  
• Fabricate and operate an integrated 50 kg of $H_2$/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>
</thead>
</table>
| 2007 | - Development is funding dependent  
- Continued investigation of APR catalyst, reaction conditions, and reactor suitable for converting glucose to hydrogen  
- Calculate the thermal efficiency and economics of the APR system utilizing either glucose or sorbitol as a feedstock  
- Select preferred feedstock  
- Design of 50 kg H₂/day demonstration system |
| 2008 | - Fabrication of 50 kg H₂/day system  
- Startup and operation of 50 kg H₂/day system  
- Analysis of 50 kg H₂/day system |
Approach

Sorbitol \( (\text{C}_6\text{H}_{14}\text{O}_6) \)
10 to 15 cents/lb

Corn
Corn Stover
Sugar Cane
Bagasse

Hydrolysis
\( \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2 \rightarrow \text{C}_6\text{H}_{14}\text{O}_6 \)

Sugar Alcohols

Hydrogenation
\( \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2 \rightarrow \text{C}_6\text{H}_{14}\text{O}_6 \)

Sugars

6 to 11 cents/lb

Hydrogen

APR
Demonstrated

APR
Under Development
APR Processing of Sorbitol

Low Temperature Reforming and Water-Gas Shift
215 ºC over Platinum-Based Catalyst
Liquid-Phase System  Total Pressure 310 psia

\[ C_nH_{2y}O_n \leftrightarrow nCO + yH_2 \]
\[ CO + H_2O \leftrightarrow CO_2 + H_2 \]

Phase Separator

Aqueous Stream

- Utilizes a Single Reactor
- Generates High Pressure Hydrogen
- Low CO Concentrations

193 psi H₂
115 psi CO₂
1.4 psi Hydrocarbons
0.2 psi H₂O
Less than 100 ppm CO
H2A Projected Cost of Hydrogen Generation using the APR Process

- **O & M (including Utilities)**
- **Capital Costs**
- **Feedstock Costs**

<table>
<thead>
<tr>
<th>H2 Cost ($/kg)</th>
<th>5 cents/lb (Lignocellulosic Sugars Future Capital Costs)</th>
<th>5 cents/lb (Lignocellulosic Sugars)</th>
<th>8 cents/lb (Low Cost Sugars)</th>
<th>10 cents/lb (Glucose)</th>
<th>15 cents/lb (Sorbitol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500 kg H₂/day</td>
<td>15000 kg Feedstock/day</td>
<td>Capital Cost Includes APR PSA Compression Storage Dispensing</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- 7 cents/lb (Lignocellulosic Sugars Future Capital Costs)
- 8 cents/lb (Low Cost Sugars)
Technical Accomplishments/Progress/Results

• Initiated project in September 2005

• ADM provided glucose samples for processing.

• Established catalyst and conditions for operations with high concentrations of glucose.
Effects of Feed Concentration

- **System Efficiency**
  - Combustion of Hydrogen for Process Energy Required
  - Higher Feedstock Concentrations Reduce Heating Requirements
APR Improvements

(UW Results)

<table>
<thead>
<tr>
<th>Ethylene Glycol</th>
<th>Sorbitol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% EG</td>
<td>1% Sorbitol</td>
</tr>
<tr>
<td>(10 % LHV)</td>
<td>(50% LHV)</td>
</tr>
</tbody>
</table>

(Thermal Efficiency) Based on LHV

Theoretical
85 % LHV
## 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></td>
<td></td>
<td></td>
</tr>
<tr>
<td></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></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>240 °C</td>
<td>230 °C</td>
<td>240 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>500 psig</td>
<td>430 psig</td>
<td>500 psig</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
Related Technical Accomplishments

• Design, fabrication and operation of an integrated APR alpha unit for Madison Gas and Electric

• High Conversion of Biodiesel-Derived Glycerol

• Design of Effective Reactor System

• Integration of an APR Reactor System with ICEGenset
Approach
Aqueous Phase Reforming (APR)

- Glycerol
- Sorbitol
- Glucose
- Sucrose
- Five Carbon Sugars
- Alcohols
- Mixed Streams

Virent APR

Temperatures < 250°C
Pressures ~450 psi

- Polyols/Alcohols
- SuperNatural™ H₂/Alkane Mix
- Pure H₂
- LPG/Diesel
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
APR: ICE Integration
Madison Gas & Electric Project

APR >85% Efficient

SuperNatural Gas™

Ford 1.6 liter HCNGICE Genset
~30% Efficiency
By City Engine

Glycerol
Or Sorbitol
Water

H₂
Alkanes
CO₂

Heat

CO₂
Water
Heat

10 kWe
Green Energy Machine (GEM)
SuperNatural™ Gas Properties

Composition (by volume)

Hydrogen: ~35%
Methane: ~ 8%
Ethane: ~12%
Propane: ~ 5%
CO_2: ~40%

Heating Value: 510-600 BTU/ft^3
Pressure (exit of APR): 400-600 psig
10kWe GEM System

- Efficient, scalable, liquid phase reactor design.
- Generates > 6 NM³/h of Supernatural Gas
- Less than 260°C operating temperature.
- “Untethered” Operation
- Runs on glycerol or sorbitol.
Future Work

• **Worked Planned for 2007 (with restoration of funding)**

  – Develop APR catalyst and reactor that converts glucose to hydrogen.

  – Calculate the thermal efficiency and economics of the baseline APR system utilizing glucose as the feedstock.

  – Evaluate the baseline APR system against US Hydrogen program goals and determine whether to proceed with either glucose or sorbitol for further development the demonstration system.
Future Work beyond 2007

• Develop the detail design of the demonstration APR hydrogen generation system (50 kg/day).

• Fabrication of the integrated hydrogen generation system.

• Install and operate the APR hydrogen generation system at a sugar facility owned by ADM.

• 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.

• Will continue work with glucose as funding is available.
Back-up Slides

• The following slides are included for evaluation purposes.
Responses to Previous Year Reviewers’ Comments

Comment
Ultimately how much hydrogen could be expected from agriculture biomass in the U.S., without impacting food and industrial uses?

Response
An April 2005 report from DOE/USDA entitled “Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply” shows study results that indicate over 1 billion tons of biomass could be produced in the US above what is need for food and industrial use. Sugars extracted from this biomass could be converted using the APR process to generate over 45 billion kg of H2.
Responses to Previous Year Reviewers’ Comments

Comment
What about less clean feeds such as hydrolyzed lignocellulosics?

Response
Virent is currently investigating how to handle “dirty” feeds such as waste glycerol from biodiesel production.

In the future, it will be possible to handle hydrolyzed lignocellulosic feeds with either proper hydrolysis technology or implementation of low cost clean of the resulting sugar streams.
Critical Assumptions and Issues

• Conversion of high concentrations of sugars
  – As discussed previously, it is necessary to run at higher concentration of sugars to better thermal efficiency of the APR process.

• Development of lower cost catalyst
  – In this program, Virent will investigate catalyst formulation that will reduce the cost of the necessary catalyst.
Critical Assumptions and Issues

- **Catalyst lifetime issues**
  - Virent will conduct lifetime studies of the catalyst, identify deactivation modes, and either identify catalyst formulations that are resistant to deactivation or determine in-situ regeneration procedures.

- **Feedstock Purity Issues**
  - Initially Virent will utilize clean glucose or sorbitol samples provide by ADM.
  - In the future, less pure feedstocks will be investigated.