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

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Virent Energy Systems, Inc  
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Project ID #  
PD6
Renewable Hydrogen Production Using Sugars and Sugar Alcohols

- **Problem:** Need to develop renewable hydrogen production technologies using diverse feedstocks

- **Description:** The BioForming™ process uses aqueous phase reforming to cost effectively produce hydrogen from a range of feedstocks, including sugar and sugar alcohols. The key breakthrough is a proprietary catalyst that operates in the aqueous phase and has high hydrogen selectivity at low temperature.

- **Impact:** Sugars and sugar alcohols are capable of producing hydrogen for $2 to $4/gge.

- **IP Position:** Exclusive worldwide licenses have been granted, multiple new patent applications placed, and solid trade secret position established.

- **Status:** A pilot plant for hydrogen production from glycerol is in operation and one using sugar is being developed as part of a DOE funded program.

10 kg/day Hydrogen Pilot Plant
Overview

Timeline
• Start – September 2005
• Finish – September 2009
• Percent complete ~ 65%

Barriers

<table>
<thead>
<tr>
<th>Barriers Addressed</th>
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</thead>
<tbody>
<tr>
<td>A) Reformer Capital Cost</td>
<td>C) O&amp;M</td>
</tr>
<tr>
<td>D) Feedstock Issues</td>
<td>E) Greenhouse Gas Emissions</td>
</tr>
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Targets

<table>
<thead>
<tr>
<th></th>
<th>2012</th>
<th>2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production Unit Capital Cost</td>
<td>$1 million</td>
<td>$600 k</td>
</tr>
<tr>
<td>Feedstock Cost Reduction</td>
<td>$2.10 / gge</td>
<td>$1.55 / gge</td>
</tr>
<tr>
<td>Total H₂ Cost</td>
<td>$3.80 / gge</td>
<td>&lt; $3.00 / gge</td>
</tr>
</tbody>
</table>

Budget

• Total project funding
  – DOE share – 1,942 K
  – Contractor share – 679 K
• Funding received to date
  • 1,215 K DOE

Partners

• Interactions/ collaborations
  • ADM
  • University of Wisconsin
**Objectives**

<table>
<thead>
<tr>
<th>Year</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Overall</td>
<td>Design a generating system that uses low cost sugars or sugar alcohols that can meet the DOE H$_2$ cost target of $2 to $3 / gge for 2017. Fabricate and operate an integrated 10 kg of H$_2$/day generating system.</td>
</tr>
<tr>
<td>2006</td>
<td>Development of APR catalyst, reaction conditions, and a reactor system suitable for converting glucose to hydrogen.</td>
</tr>
</tbody>
</table>
| 2007 | Virent continued to investigate catalyst, reaction conditions, and reactor suitable for converting low cost sugars to hydrogen.  
Calculated the thermal efficiency and economics of the APR system utilizing different feedstocks (low cost sugars, glucose, sugar alcohols)  
Compared results of techno-economic analysis with DOE Hydrogen Programs Goals  
Made a Go decision based on technical progress to date and the techno-economic feasibility from the H2A model results. |
| 2008 | Made an internal No decision on moving forward to the design and construction of a 10 kg H$_2$/day demonstration system  
Continue fundamental catalyst development to increase thermal efficiency of the APR system to meet 10 kg H$_2$/day demonstration metrics  
Re-evaluate the thermal efficiency and techno-economics of the APR catalyst system |
Milestones

• **Go/no-go Metrics for FY07 (10/2007)**

  ✓ Utilized H2A model to revalidate the potential to meet the 2012 and 2017 DOE cost targets.

  ✓ Validated 2nd generation reactor design.

  ✓ Demonstrated Catalyst Lifetime >= 1 year under aqueous phase reforming conditions.

  ✓ Specific Catalyst Performance Metrics:
    – WHSV >= 1
    – Feed Concentration >= 30%
    – Feed Conversion: 100%
    – Hydrogen Yield: 45%
Accomplishments

• Catalyst Development
  – Technology Progress to Date
    • 10 X reduction in hydrogen cost
    • 700 X scale-up reactor demonstrated
    • Demonstrated catalyst lifetime > 1 year under APR conditions

• Techno-Economic Analysis
  – Development pathways identified to reach 2012 and 2017 goals
  – Identified most cost sensitive aspects
    • H₂ Yield
    • Feed stock concentration
    • Reactor productivity
**Technical Approach**

**Biomass Derived Liquids**

\[ 6 \text{ CO}_2 + 12 \text{ H}_2\text{O} \rightarrow 6 \text{ O}_2 + \text{C}_6(\text{H}_2\text{O})_6 \]

- **Pretreatment**
- **Harvest**

**Carbohydrates**
- Glucose
- Mannose
- Fructose
- Sucrose

**Enzyme**

**Sugar Alcohols**
- Sorbitol
- Mannitol
- Glycerol
- Ethylene Glycol

**H\textsubscript{2}**

**Alcohols**
- Methanol
- Ethanol
- Butanol
Hydrogen Production using the BioForming Process

- Simple Catalytic Process
  - No Water Gas Shift
  - No Steam System
  - No Gas Compressor
  - No Desulphurizer
- Energy Efficient
- Scalable
- Feedstock Flexible
Technical Approach – Glucose
Catalyst Development: Hydrogenation

- Hydrogenation of glucose
  - Conditions
  - Integration with APR
  - Sorbitol Yield and Selectivity
  - Industrial process
  - Feedstock H₂ Carrier
Testing Summary

– 75 different catalyst compositions/preparation methods
– 90 different conditions
Catalyst Performance: APR

- **Sorbitol Feed Modification**
  - Increase
    - H₂ Yield
    - Conversion to Gas
  - Decrease
    - Conversion to organics
Catalyst Performance: APR

- Increasing WHSV
  - Stable H₂ Yield
  - Decreasing Conversion
  - Potential for decreased capital
Measure of Productivity: Space Time Yield

(*moles reactant per second per cc of reaction volume*)

- 2002: Biochemical Processes
- 2004: Current
- 2007: Industrial Catalysts
Bio-Derived Liquid Metrics

<table>
<thead>
<tr>
<th></th>
<th>Current Status</th>
<th>2017 Metrics</th>
</tr>
</thead>
<tbody>
<tr>
<td>WHSV</td>
<td>1 - 2</td>
<td>5 - 10</td>
</tr>
<tr>
<td>Feed Concentration</td>
<td>30%</td>
<td>50%</td>
</tr>
<tr>
<td>Feed Conversion</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Hydrogen Yield</td>
<td>&gt; 50%</td>
<td>&gt; 80%</td>
</tr>
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• 2017 Metrics represents one set of catalyst characteristics that enables the Virent APR process to meet the DOE Hydrogen Cost Target
Equipment Costing (PFD Level)

- Aspen Simulations
  - Current Data
  - Sensitivity Analysis on Process Efficiency
- Initial Sizing Estimates
  - ~3 Line specs
  - Equipment Sizing
  - Utility Utilization
- Costing based on standard graphs/charts with appropriate materials of construction and pressure considerations
- Equipment costing cross-checked utilizing price quotes for current equipment and vendor quotes
- Multiple Third Party Verification
H2A Inputs-Capital Equipment

- Uninstalled APR Reforming Equipment (Capital Investment)
  - Purchased Equipment
  - Skid Fabrication
    - Equipment Delivery and Skid Mounting
    - Instruments and Controls
    - Piping
      - Learning Curve factor (@ 5000 Units)
        - Forecourt Specific Assumptions 2005 (DTI Study)
  - Installation Factor = 1.1 (H2A)
<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production Unit H2 Efficiency</td>
<td>70.4%</td>
<td>Aspen Model</td>
</tr>
<tr>
<td>Virent Package</td>
<td>$791,000</td>
<td>Installed Cost</td>
</tr>
<tr>
<td>Product Handling Package</td>
<td>$833,000</td>
<td>H2A</td>
</tr>
<tr>
<td>Indirect Depreciable</td>
<td>$297,000</td>
<td>H2A</td>
</tr>
<tr>
<td>Feedstock (LHV 14.1 MJ/Kg)</td>
<td>12.2 kg / kg H2</td>
<td>Aspen Model</td>
</tr>
<tr>
<td>Other Raw Materials</td>
<td>~ $0.011 / kg H2</td>
<td>Aspen Model / H2A</td>
</tr>
<tr>
<td>Utilities</td>
<td>$13,400 / yr</td>
<td>Aspen Model / H2A</td>
</tr>
</tbody>
</table>
## 2017 Cost Breakdown

### Specific Item Cost Calculation

<table>
<thead>
<tr>
<th>Cost Component</th>
<th>Cost Contribution ($/kg)</th>
<th>Percentage of H2 Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital Costs</td>
<td>$0.727</td>
<td>24.0%</td>
</tr>
<tr>
<td>Decommissioning Costs</td>
<td>$0.000</td>
<td>0.0%</td>
</tr>
<tr>
<td>Fixed O&amp;M</td>
<td>$0.415</td>
<td>13.7%</td>
</tr>
<tr>
<td>Feedstock Costs</td>
<td>$1.834</td>
<td>60.6%</td>
</tr>
<tr>
<td>Other Raw Material Costs</td>
<td>$0.011</td>
<td>0.3%</td>
</tr>
<tr>
<td>Byproduct Credits</td>
<td>$0.000</td>
<td>0.0%</td>
</tr>
<tr>
<td>Other Variable Costs</td>
<td>$0.040</td>
<td>1.3%</td>
</tr>
</tbody>
</table>

### Pie Chart

- **Capital Costs**
- **Fixed O&M**
- **Feedstock Costs**
- **Other Raw Material Costs**
- **Other Variable Costs (including utilities)**
Cost Breakdown from H2A modeling of the APR Process
1500kg/day H2 Production with $0.064/lb glucose
Future Work Plan

• Continue development of the APR catalyst and reactor system that converts glucose to hydrogen.
  • Primary Focus: H₂ Yield
  • Secondary: Reactor Productivity & Feedstock Concentration
• Continue fundamental catalyst development and analysis to increase thermal efficiency of the APR system to meet 10 kg H₂/day demonstration metrics
• Review techno-economic performance of the APR system
• Investigate fundamental catalysis science (UW)
• Interaction with PNNL on data exchange and fundamental surface science study
Summary

• APR
  – A promising and cost competitive technology for the production of renewable $H_2$
  – Technology development still required to reach DOE cost targets

• Techno-Economic Analysis
  – Development pathways identified to reach 2012 and 2017 goals
  – Identified most cost sensitive aspects
    • $H_2$ Yield
    • Feed stock concentration
    • Reactor productivity

• Catalyst Development
  – Technology Progress to Date
    • 10 X reduction in hydrogen cost
    • 700 X scale-up reactor demonstrated