Hydrogen from Glycerol: A Feasibility Study

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Project Overview

Timeline
- Project Start: October 2009
- Project End: TBD

Barriers
- D. Feedstock Issues
- E. Greenhouse Gas Emissions

Budget
- FY10 - $100K + TBD

Partners
- TBD
Relevance - Technical Overview

Background
- The rapid growth in biodiesel production has led to an abundance of glycerol
- The crude glycerol, containing salts and methanol, has to be disposed as hazardous waste

Opportunity
- The alcohol and water content in crude glycerol is acceptable for reforming
- Secondary products from crude glycerol are attractive to biodiesel producers
Relevance - Glycerol can contribute to the mix of feedstock used in the $H_2$ refueling infrastructure

- Glycerol, a product of biomass and animal fats, is a renewable resource
- As a liquid, glycerol has high energy density (heating value) and is easy to transport
- Glycerol can be converted to $H_2$ to refuel fuel cell vehicles
  - Glycerol can also be used by reformate-based stationary fuel cell systems
- The hydrogen can be generated at or close to biodiesel production facilities
- Glycerol production capacity (2008) can yield 200,000 kg of $H_2$ per day
Objective

- Evaluate the economic feasibility of producing hydrogen from glycerol derived as a byproduct of the biodiesel industry
  - For the distributed production of hydrogen
  - Based on the steam reforming of glycerol, followed by purification using pressure swing adsorption
Approach

- Review the availability and price of glycerol
- Evaluate hydrogen-from-glycerol process at a distributed hydrogen production facility using systems analysis
- Estimate cost of hydrogen and its sensitivities
## Technical Accomplishments and Progress

**Glycerol supply and price**

<table>
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<tbody>
<tr>
<td><strong>Biodiesel</strong></td>
<td>19.0 $10^9$ lb/year</td>
<td>5.2 $10^9$ lb/year</td>
<td>3.8 $10^9$ lb/year</td>
<td>2.0 $10^9$ lb/year</td>
<td>3 – 10 cents/lb</td>
<td>40 – 50 cents/lb</td>
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<tr>
<td><strong>Glycerol</strong></td>
<td></td>
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Technical Accomplishments and Progress
Systems analysis was followed by cost estimation using H2A

Production Unit
- Crude Glycerol Feed
- Steam Reformer
- Water Gas Shift Reactor
- Pressure Swing Adsorption Unit for H₂ Purification

Refueling Station
- Compression, Storage, and Dispensing

Cost Analysis
- H2A
Base Case: Converting glycerol to hydrogen with an efficiency\(^{(a)}\) of 72% 

\[ \text{Efficiency} = \frac{H_2 - \text{LHV}}{(\text{Glycerol LHV} + \text{NG LHV} + \text{electricity})} \times 100 \]

\[ \text{Yield} = \left( \frac{\text{moles of } H_2}{7 \times \text{moles of Glycerol}} \right) \times 100 \]

\(^{(a)}\) H\(_2\)-yield = 69%
Technical Accomplishments and Progress
Base Case: Cost of H₂ from glycerol is estimated at $4.86/kg

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>H₂A (v2.1.3) Glycerol</th>
<th>H₂A (v2.1.3) Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production Unit Energy Efficiency</td>
<td>%</td>
<td>72.0</td>
<td>72.0</td>
</tr>
<tr>
<td>Operating Capacity Factor</td>
<td>%</td>
<td>85.2</td>
<td>85.2</td>
</tr>
<tr>
<td>Production Unit Capital Cost (Uninstalled)</td>
<td>$</td>
<td>1.0M</td>
<td>1.0M</td>
</tr>
<tr>
<td>Feedstock Cost</td>
<td>$/gal</td>
<td>1.07 (0.10 ¢/lb)</td>
<td>1.07</td>
</tr>
<tr>
<td><strong>Hydrogen Cost</strong></td>
<td>$/kg</td>
<td><strong>4.86</strong></td>
<td><strong>4.83</strong></td>
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</table>
Technical Accomplishments and Progress

Feedstock and capital costs are the main contributors to the cost of hydrogen.

- **Feedstock**: $2.12/kg (44%)
- **Production Unit (PU)**: $2.97/kg (61%)
- **Capital RS**: $1.26/kg (26%)
- **Refueling Station (RS)**: $1.88/kg (39%)
- **Variable + O&M**: $0.32/kg (7%)
- **Capital PU**: $0.53/kg (11%)
Technical Accomplishments and Progress

Glycerol price needs to be <5.2 cents/lb ($0.55/gal) to meet the hydrogen cost target of $3.80/kg
Technical Accomplishments and Progress
Changing the cost of H₂ by 5% would require
40% change in capital cost or,
11% change in feedstock price
Technical Accomplishments and Progress

Hydrogen yield improves with higher PSA recovery, but requires more natural gas to meet reforming energy needs.

![Graph showing PSA recovery vs H2-Yield and Efficiency](image_url)

- **H2-Yield** increases with higher PSA recovery.
- **Efficiency** also increases with higher PSA recovery.

![Graph showing PSA recovery vs Feedstock and Utility Usage](image_url)

- **Electrical (kWh/kg-H2)** decreases as PSA recovery increases.
- **Glycerol (gal/kg-H2)** decreases as PSA recovery increases.
- **NG Nm³/kg-H2** increases as PSA recovery increases.
Technical Accomplishments and Progress
A hydrogen cost of $3.80/kg may be achievable with process maturity

<table>
<thead>
<tr>
<th></th>
<th>“Better”</th>
<th>Base</th>
<th>“Worse”</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H₂ Cost</strong></td>
<td>$3.80/kg</td>
<td>$4.86/kg</td>
<td>$5.90/kg</td>
</tr>
<tr>
<td><strong>Feedstock Cost</strong></td>
<td>$0.74/gal</td>
<td>$1.07/gal</td>
<td>$1.58/gal</td>
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<tr>
<td></td>
<td>7 cents/lb</td>
<td>10.2 cents/lb</td>
<td>15 cents/lb</td>
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<tr>
<td><strong>Efficiency</strong></td>
<td>74%</td>
<td>72%</td>
<td>72%</td>
</tr>
<tr>
<td><strong>Capital (PU)</strong></td>
<td>$750K</td>
<td>$1M</td>
<td>$1M</td>
</tr>
<tr>
<td><strong>Plant Capacity Factor</strong></td>
<td>95%</td>
<td>85.2%</td>
<td>85.2%</td>
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</table>
### Technical Accomplishments and Progress

Some Projections

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
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<tbody>
<tr>
<td><strong>US Crude Glycerol Produced from Biodiesel (2008)</strong></td>
<td>0.52 $10^9$ lb/year</td>
</tr>
<tr>
<td><strong>H₂ from Glycerol (Base Case)</strong></td>
<td>0.505 kg-H₂/gal-glycerol</td>
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<tr>
<td><strong>H₂ from Crude Glycerol</strong></td>
<td>55 $10^3$ kg-H₂/day</td>
</tr>
<tr>
<td>Distributed H₂ Production Center Capacity (operating at 85% of capacity)</td>
<td>1275 kg/day</td>
</tr>
<tr>
<td><strong>No. of Distributed H₂ Production Centers</strong></td>
<td>43</td>
</tr>
<tr>
<td><strong>US Crude Glycerol Capacity from Biodiesel (2008)</strong></td>
<td>19.0 $10^9$ lb/year</td>
</tr>
<tr>
<td><strong>Capacity / Production Factor (2008)</strong></td>
<td>3.7</td>
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Collaborations

- The system diagram was modified from a similar system used by DTI for hydrogen-from-ethanol
- Collaboration plans will depend on future direction of this project
  - Catalysis, clean-up, etc.
Summary

- Glycerol supply is outpacing its demand as a result of the biodiesel industry
  - Biodiesel industry, researchers are seeking high value secondary products from glycerol

- Glycerol is renewable and can be efficiently converted to hydrogen (72% efficiency is feasible)
  - When the PSA recovery is 80% or more
  - When the steam-to-carbon molar ratio is ≈3

- With crude glycerol at $1.07/gal (10 ¢/lb) the estimated H₂ cost is $4.86/kg
  - Cost of H₂ produced from glycerol is similar to that from ethanol

- The cost of hydrogen is highly sensitive to the price of the feedstock

- To achieve the target H₂ cost of $3.80 /kg with a glycerol price of 7 ¢/lb, need a combination of
  - Process efficiency of 74%
  - Capital cost of $750 K
  - Plant operating capacity of 95%
Proposed Future Work

- Extend systems analysis to evaluate most promising production process and operating conditions
  - Define range of operating conditions (T, P, S/C, ...)
- Identify key challenges with glycerol reforming
  - Feed delivery, conversion, coke formation, crude glycerol cleanup, etc.
- Address technical barriers
  - Feed delivery, catalysis, reactor design, etc.)
Supplementary Slides
The new version of H2A increases the contribution of the Refueling Station costs.

Storage, Compression, Dispensing Capital Cost
- Storage, Compression, Dispensing
- Capital Cost

Variable O&M including Utilities
- Variable O&M including Utilities

Fixed O&M
- Fixed O&M

Feedstock Cost
- Feedstock Cost

Capital cost
- Capital cost

H2 Cost Contribution ($/kg)

2012 target
- Multi-Year Research, Development & Demonstration Plan (Ethanol case)
  - H2A (v2.1.3)
  - Production Unit (60%)
  - Refueling Station (40%)

Ethanol
- Production Unit (60%)
- Refueling Station (40%)
- Capital cost
- Variable O&M including Utilities
- Fixed O&M

Glycerol
- Production Unit (60%)
- Refueling Station (40%)
- Capital cost
- Variable O&M including Utilities
- Fixed O&M

*H2A (v2.1.3)