II.A.3 Hydrogen from Glycerol: A Feasibility Study

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Objectives

Evaluate the economic feasibility of distributed hydrogen production from glycerol derived as a byproduct of the biodiesel industry.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) Feedstock Issues
(E) Greenhouse Gas Emissions

Technical Targets

TABLE 1. Technical Targets: Distributed Production of Hydrogen from Bio-Derived Renewable Liquids

Characteristics	Units	2012 Target
Production Unit Energy Efficiency	%	72.0
Total Hydrogen Cost	$/gge	3.80

The project is conducting the analysis to determine the feasibility of meeting the efficiency and cost targets for producing hydrogen from glycerol at distributed production centers with a capacity of 1,500 kg of hydrogen per day and operating at 85% of capacity.

Accomplishments

- Completed the study using systems analysis followed by H2A to estimate the cost of hydrogen.
- Defined the process conditions needed to produce hydrogen from glycerol with an efficiency of 72%.
- The cost of hydrogen for a base case set of conditions was estimated at $4.86 per kg, where the price of glycerol was assumed to be $1.07/gal (10 cents/lb). The current price of crude glycerol ranges between 3-10 cents per pound.
- The cost of feedstock (crude glycerol) represents 44% of the cost of hydrogen.

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Introduction

Gycerol is a biomass-derived liquid that is being generated by the biodiesel industry as a byproduct (waste stream) in quantities that exceed current demands. As a byproduct of the biodiesel industry the crude glycerol (80–88% pure) contains methanol, water, and salts (soaps). The presence of methanol requires that the crude glycerol be treated as a hazardous waste, which adds to the cost of biodiesel production. A preferred alternative is to convert the waste glycerol to secondary products within the bio-refinery (which has a very limited potential at this time), or to sell the glycerol, either as the crude glycerol as is, or after refining it to commodity grade. Table 2 summarizes some information on the supply, demand, and the price of glycerol.

TABLE 2. Production Rates and Prices

Characteristics	Value	Units
Biodiesel Production Capacity in U.S. (2008) [1]	2.6×10^9 19.0×10^9	gal/year lb/year
Biodiesel Production in U.S. (2008) [1]	0.7×10^9 5.2×10^9	gal/year lb/year
Crude Glycerol from Biodiesel Production in U.S. (2008)[a)]	5.2×10^8	lb/year
World Demand for Glycerol (2005) [2]	19.8×10^8 9.0×10^8	lb/year kg/year
World Production of Glycerol (2008) [3]	3.8×10^9 1.7×10^9	lb/year kg/year
Price of Crude Glycerol [4-8]	3.5 – 10	cents/lb
Price of Refined Glycerol (2009) [3]	40 – 50	cents/lb

a) Each pound of biodiesel produced generates approximately 0.1 pound of crude glycerol byproduct

The burgeoning demand for hydrogen, preferably produced from renewable sources, and the growing availability of glycerol has attracted attention as a potential pathway for the distributed production of hydrogen from glycerol. A distributed hydrogen refueling infrastructure can potentially use this surplus renewable resource to produce hydrogen. This approach would simultaneously help manage a waste/surplus stream (to reduce the cost of biodiesel production costs) and produce hydrogen from a renewable resource. The economic viability of this pathway will be determined, in part, by the availability and cost of glycerol, and the cost of producing hydrogen from it.

Approach

The project reviewed the availability of glycerol which was then used to estimate the amount of hydrogen that can be produced annually in the U.S.

The process was based on the steam reforming of glycerol followed by purification using pressure swing adsorption. The model was set up, along with a set of assumptions, to determine the process conditions that would be needed to meet DOE's efficiency target. The inputs and results from the base case were used to estimate the cost of hydrogen and the cost contributors.

Results

Glycerol can be steam reformed to produce up to 7 mol of hydrogen per mol of glycerol, according to the reaction,

$$C_3H_8O_3 + 3H_2O = 3CO_2 + 7H_2, \qquad \Delta H_1 = +347 \text{ kJ} \qquad (1)$$

The reaction is strongly endothermic and requires a combination of catalysts, excess steam, and temperatures greater than 500°C to achieve high conversions of glycerol to hydrogen and carbon oxides. The actual reaction mechanism is complex, beginning with the decomposition of glycerol to intermediates including CO and H_2, followed by steam reforming of the intermediate carbonaceous species (Eqn.(2)) and water-gas shift (WGS) reaction (Eqn.(3)).

$$C_nH_mO_p + H_2O \rightarrow CO + H_2, \qquad \Delta H_2 > 0 \qquad (2)$$

$$CO + H_2O = CO_2 + H_2, \qquad \Delta H_3 = -41 \text{ kJ} \qquad (3)$$

Figure 1 shows the process schematic where hydrogen is produced at 72%[1] efficiency in the base case scenario for the production of 1,500 kg of H_2/day. The reforming process is based on 20 atm (~300 psi) steam-reforming/WGS reaction followed by a pressure-swing adsorption (PSA) unit for hydrogen purification. The steam reformer is operated with a molar steam-to-carbon ratio (S/C) of 3. The product stream leaving the reformer (reformate at chemical equilibrium at 800°C) is cooled and then processed in a high-temperature WGS reactor at 400°C. The reformate, composition is shown

[1] Energy efficiency is defined as the energy of the hydrogen (lower heating value, LHV) out of the production unit divided by the sum of energy inputs into the process, i.e., Σ (Feedstock (LHV) + Natural Gas (LHV) + electricity). Electrical energy utilized does not include efficiency losses from the production and the transmission of electricity.

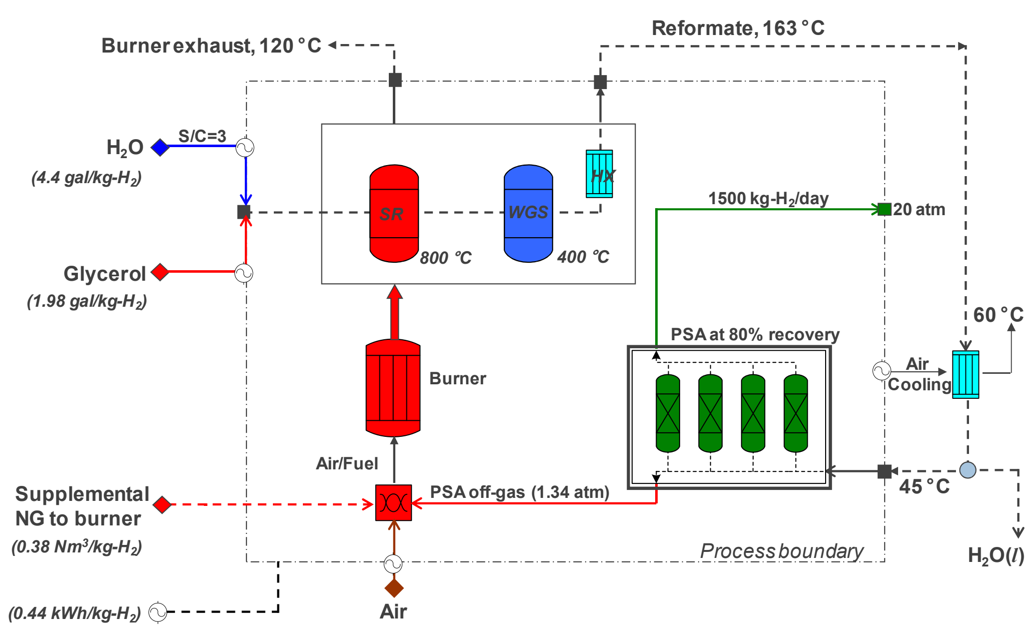

FIGURE 1. Schematic of the process for distributed hydrogen production by steam-reforming of glycerol at 20 atm and 72% efficiency. The maximum hydrogen production capacity is 1,500 kg/day.

in Table 3, then enters the PSA unit where high purity hydrogen is extracted with 80% recovery, exiting the production unit at 20 atm.

The PSA off-gas containing the carbon oxides and methane, along with the un-recovered hydrogen is combusted in the burner to generate heat for the reforming process. Additional fuel (natural gas) is used in the burner, if needed.

TABLE 3. Reformate Composition to PSA

Reformate	Composition (mol-%)
H_2	65.52
CO_2	28.76
CO	2.17
CH_4	2.08
H_2O	0.47
Hydrocarbons	trace

For the base case, the cost of hydrogen (untaxed) from the steam-reforming of glycerol was calculated to be $4.86/kg-$H_2$. For this set of (base case) conditions, the estimated cost is 27% higher than the 2012 DOE target of 3.8/kg-H_2 from bio-derived liquids. The contributions of various elements to the cost of hydrogen are shown in Figure 2. The production unit accounts for ~60% ($2.97/kg) of the hydrogen cost, with feedstock being the main cost contributor. The refueling station part accounts for almost 40% ($1.88/kg) of the delivered hydrogen cost, where the majority of that cost is due to the required capital investment. Overall, the highest cost contributors for the delivered hydrogen are the feedstock costs (44%) and the combined capital investment costs for the production unit and refueling station (37%).

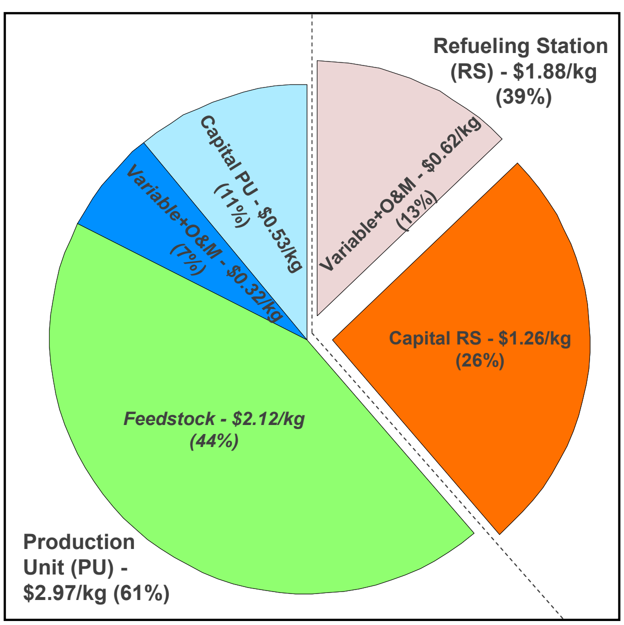

FIGURE 2. Cost breakdown for the delivered hydrogen cost of $4.86/kg H_2 from the steam-reforming of glycerol for the base case.

The production unit efficiency, affecting feedstock utilization, influences the cost of the delivered hydrogen. Figure 3 shows the cost of hydrogen as a function of production efficiency for four different feedstock prices. When the price of glycerol is high (>10 cents/lb), efficiency has a significant impact on hydrogen cost. At such a high feedstock price, however, the cost of delivered hydrogen exceeds the target by over 50%, even at 72% efficiency. The targeted cost of hydrogen for 2012 ($3.80) can be met with the glycerol price at 5 cents/lb. At this price, the efficiency has only a marginal impact on the hydrogen cost. At the low feedstock prices (2.4 cents/lb), efficiencies above 68% actually increase the cost of the delivered hydrogen, since the cost of the natural gas which is assumed to provide supplemental heat to the reformer is more expensive (LHV basis) than the glycerol feedstock.

Hydrogen that can be Produced from Glycerol in the U.S.: The U.S. produced 0.52 billion pounds of crude (80% purity) glycerol in 2008. If this glycerol were to be converted into hydrogen, in plants such as in Figure 1, it would yield approximately 55,000 kg of hydrogen per day. The hydrogen output would be 3.7 times higher, or ~200,000 kg of hydrogen per day, if the U.S. biodiesel plants in 2008 operated at full capacity and the byproduct crude was then converted to hydrogen.

Conclusions

- Glycerol supply is outpacing its demand as a result of the biodiesel industry.

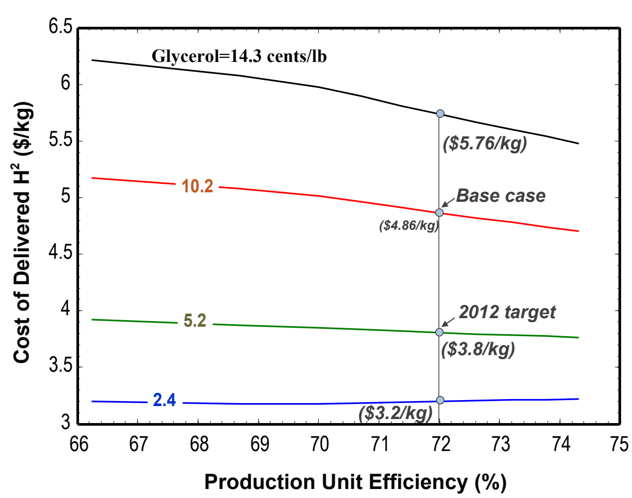

FIGURE 3. Effect of production unit efficiency and price of glycerol on the cost of delivered hydrogen.

- Glycerol is renewable and can be efficiently converted to hydrogen.
- With glycerol at $1.07/gal (10¢/lb) the estimated cost of H_2 is $4.86/kg.
- The cost of hydrogen is highly sensitive to the price of the feedstock.
- The U.S. biodiesel plants (capacity in 2008) can produce sufficient crude glycerol to enable 200,000 kg/day of hydrogen.

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