II.B.4 Hydrogen Generation from Biomass-Derived Carbohydrates via the Aqueous-Phase Reforming (APR) Process

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Subcontractors:
- University of Wisconsin, Madison, WI
- Archer Daniels Midland (ADM) Company, Decatur, IL

Project Start Date: September 1, 2005
Project End Date: August 30, 2008

Objectives

The objectives of the first year of this project are as follows:

- Identify candidate sugar streams (glucose), document plant integration requirements and associated economic factors.
- Develop catalyst and reactor based on the aqueous phase reforming (APR) process suitable for converting candidate sugar streams to hydrogen.
- Design a baseline hydrogen generation system utilizing the APR process.
- Calculate the thermal efficiency and economics of the baseline APR system.
- Assess the baseline APR system with respect to Hydrogen Program goals and make a go/no-go decision to proceed with further development of a demonstration system.

The objectives of the second and third years of this project are as follows:

- 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 Program goals.
- Make a go/no-go decision on moving forward to the design and construction of a 10 kg H_2/day demonstration system with the preferred feedstock.
- Develop the detail design of the demonstration APR hydrogen generator system (10 kg/day).
- Fabrication of the integrated hydrogen generator system.
- Install and operate the APR hydrogen generator system.
- Assess APR hydrogen generator system performance with respect to Hydrogen Program goals.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Reformer Capital Costs

(C) Operation and Maintenance (O&M)

(D) Feedstock Issues

(E) Greenhouse Gas Emissions

Technical Targets

It is believed that using corn as a feedstock, converting this corn to glucose with cost-effective and established technologies and developing the APR process will provide a cost-effective and energy-efficient method to generate hydrogen from biomass. The project objective is to achieve the DOE 2012 cost target for distributed production of hydrogen from bio-derived renewable liquids of:

- H_2 Cost: $3.80/gge
- Feedstock Cost Contribution: $2.10/gge

Accomplishments

- Established baseline performance with sorbitol feed.
- Established operating conditions for conversion of glucose to hydrogen.

- Devised a reactor configuration that allows the conversion of high concentrations of glucose and sorbitol.
- Reported a preliminary cost model using DOE's H2A spreadsheet.
- 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.

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Introduction

The conversion of corn to glucose via either wet or dry milling is a well known and optimized technology. ADM is the leading producer of sweeteners from corn utilizing such processes. Virent's APR process reacts water with carbohydrate-type compounds (glycerol, sugars, and sugar alcohols) and has the following advantages over conventional vapor-phase steam reforming processes: (1) generates hydrogen and/or alkanes without the need to volatilize water, which represents a major energy saving; (2) occurs at temperatures and pressures where the water-gas shift reaction is favorable, making it possible to generate hydrogen with low amounts of CO in a single chemical reactor; and (3) takes place at low temperatures that minimize undesirable decomposition reactions typically encountered when carbohydrates are heated to elevated temperatures.

While proven in the laboratory, the APR technology must be shown viable on a larger scale. This project will result in the design, construction, and operation of a 10 kg H_2/day prototype reactor system. Such a system will provide the necessary scale-up information for the generation of hydrogen from glucose derived from corn.

Approach

This project combines the expertise of Virent Energy Systems (Virent), Archer Daniels Midland Company (ADM), and the University of Wisconsin (UW) to demonstrate the feasibility of generating high yields of hydrogen from corn-derived glucose. This proposed concept takes advantage of the fact that corn contains large amounts of starch which can be extracted and converted to glucose. The resulting aqueous solutions of glucose can be fed to the Virent's novel APR process that generates hydrogen in a single reactor. The effluent gas from the APR process can then be efficiently purified to produce high purity hydrogen utilizing pressure swing adsorption.

Results

Virent is investigating proprietary reactor configurations that allow the conversion of high concentrations of glucose derived from corn. The biomass to hydrogen route via the APR process is detailed in Figure 1. Energy balances on the APR system indicate that significant energy losses can occur because of vaporization of water in the reactor system to maintain the partial pressure of water in the hydrogen gas bubbles formed in the reactor. Figure 2 shows that the thermal efficiency of the system can be improved by operating it with higher concentrations of feedstock. This figure shows that as the feed concentration is increased from 10 wt% to 60 wt%, the efficiency of the system increases from less that 10% to greater than 80% at a 100% conversion of glucose. This analysis assumed that a portion of the product hydrogen will be combusted to provide the process heat for the generation of hydrogen via the APR process. Accordingly, Figure 2 shows that it is desirable to operate at feed concentrations of 30 wt% or greater to achieve the desired thermal efficiency for the system.

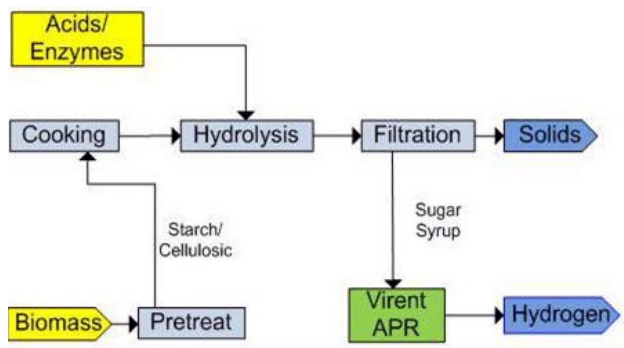

FIGURE 1. Biomass to Hydrogen via the APR Process

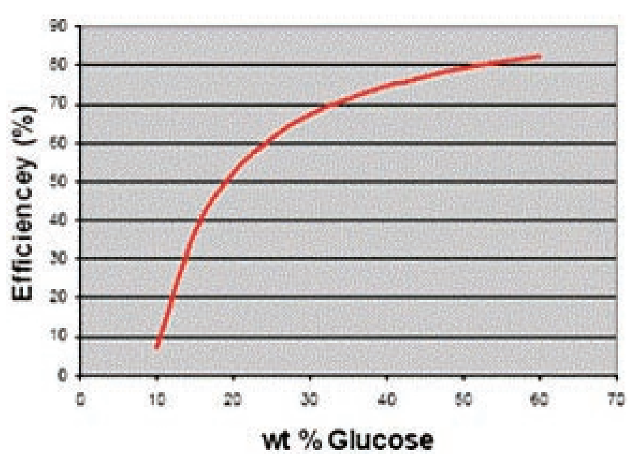

FIGURE 2. Efficiency of APR with Increasing Feed Concentration of Glucose

Catalyst lifetime at the desired feed concentration levels is a variable of importance in the overall economic feasibility of the APR process. Virent funded extended catalyst lifetime testing has been performed on glycerol feedstocks at 50 wt% concentration. Figure 3 details the extended lifetime run. The extended lifetime run was performed with a first generation catalyst. The reactor operates in a one pass system in which the reaction temperature can be raised to keep conversion high while exhibiting very stable H_2 production. The data gained from glycerol testing should correspond with future glucose catalyst information.

An initial cost estimate was made for the generation of hydrogen from glucose for fueling station applications which included the cost of feedstock, capital equipment (including catalyst costs), and operation and maintenance. DOE's H2A spreadsheet was used for this analysis. This cost estimate was for a reformer that generates 1,500 kg of H_2 per day. This analysis includes the capital cost of the reformer, pressure swing absorption (PSA) separator, compressor, storage, and dispensing equipment. Figure 4 shows the results of this analysis utilizing the following assumptions:

- Capital cost of reformer, APR, compression, storage, and dispensing: $1,960,000
- Conversion of low purity sorbitol (15 cents/lb of sorbitol)
- Conversion of high purity glucose (10 cents/lb of glucose)
- Conversion of lower grade glucose (8 cents/lb of glucose)
- Conversion of sugars derived from lignocellulosic biomass (5 cents/lb)
- Conversion of lignocellulosic biomass (5 cents/lb) at a capital cost of $980,000
- A 70% yield of hydrogen, the other 30% needs to be combusted to provide process heat

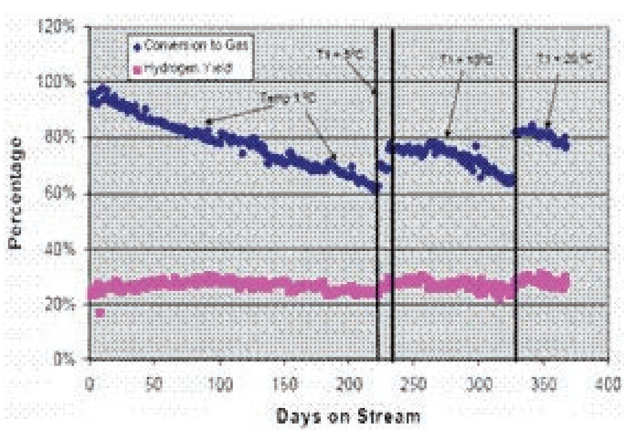

FIGURE 3. APR Catalyst Lifetime Testing

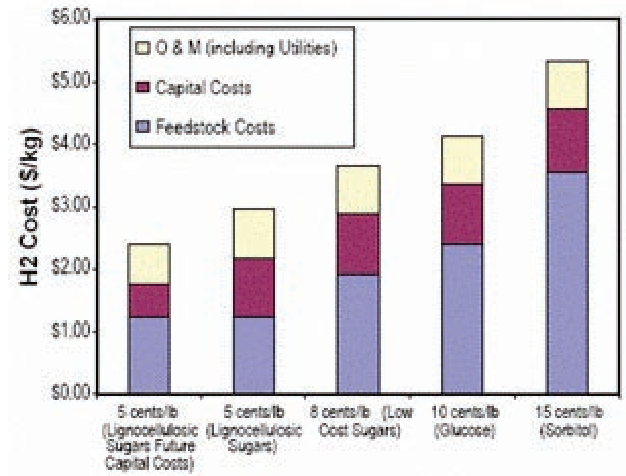

FIGURE 4. Preliminary Cost Analysis Utilizing H2A

- The above translates into a thermal efficiency of 81% based on the lower heating value (LHV) of glucose
- Catalyst contains precious metal (catalyst cost of $1,700 per kg of catalyst)
- Purification of the hydrogen with a PSA unit

Results from this cost analyses show that the 2012 DOE Target of $3.80/gge could be achieved utilizing low-cost sugars (less than 8 cents/lb). The 2017 DOE Target of <$3.00/gge could be achieved with sugars derived from lignocellulosic biomass and lower capital costs for the system. More extensive cost estimations will be performed to validate these initial model results.

Conclusions and Future Directions

Virent has identified a reactor system that allows the aqueous phase reforming of glucose. While initial results showed low selectivity to hydrogen, subsequent developments have shown improvement in generation of hydrogen with appropriate catalyst, reactor configuration, and reaction conditions.

Future Directions

- Continue development of APR catalyst and reactor that converts glucose and sugar alcohols to hydrogen.
- Investigate hydrogenation technologies that convert both monosaccharides and polysaccharides to sugar alcohols.
- Investigate the integrations 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 U.S. Hydrogen Program goals and determine whether to proceed to development of the demonstration system.

FY 2007 Publications/Presentations

1. Presentation – NHA Annual Hydrogen Conference, March 20–22, 2007.

2. Presentation – Gordon Research Conference, January 10, 2007.

3. Poster – Hydrogen Program Review Meeting, May 15, 2007.