II.A.6 Hydrogen Generation from Biomass-Derived Carbohydrates via the Aqueous-Phase Reforming (APR) Process

Gregory Keenan (Primary Contact) and
Dr. Randy Cortright
Virent Energy Systems, Inc.
3571 Anderson Street
Madison, WI 53704
Phone: (608) 663-0228 Ext 203; Fax: (608) 663-1630
E-mail: Greg_Keenan@virent.com

DOE Technology Development Manager:
Sara Dillich
Phone: (202) 586-7925; Fax: (202) 586-2373
E-mail: sara.dillich@ee.doe.gov

DOE Project Officer: Jill Sims
Phone: (303) 275-4961; Fax: (303) 275-4788
E-mail: Jill.Sims@go.doe.gov

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Subcontractors:
University of Wisconsin, Madison, WI
Archer Daniels Midland Company, Decatur, IL

Project Start Date: September 1, 2005
Project End Date: August 30, 2009

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 feed stocks (low-cost sugars, glucose, sugar alcohols).
- Compare results of techno-economic analysis with DOE Hydrogen Program goals.
- Perform fundamental catalysis review.
- Review system performance with regards to demonstration performance goals.
- Continue catalyst development to enhance hydrogen production efficiency.
- Operate reactor development pilot plant to gain information required for the initial reactor design for the 5 to 10 kg H_2/day demonstration system.
- Develop initial process flow diagram (PFD) and catalytic reactor design for the 5 to 10 kg H_2/day demonstration system.
- Re-evaluate the thermal efficiency and economics of the APR system with respect to Hydrogen Program goals utilizing H2A.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1) 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 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/gasoline gallon equivalent (gge)
- Feedstock Cost Contribution: $2.10/gge

Accomplishments

- Demonstrated hydrogenation of glucose to sorbitol at conditions that allow for simple integration with the APR process.

- Go/no-go metrics for APR catalyst performance for the reformation of sorbitol demonstrated:
  - Weight hourly space velocity >= 1
  - Feed concentration >= 30%
  - Feed conversion: 100%
  - Hydrogen yield: 45%
- Techno-economic analysis:
  - Development pathways identified to reach 2012 and 2017 goals.
  - Identified most cost sensitive aspects of the APR process.
- Virent funded project to convert glycerol to hydrogen:
  - Proved catalyst lifetime of greater than a year.
  - Tested first generation reactor system.
  - Tested second generation reactor system.

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Introduction

The APR process allows the generation of hydrogen from biomass-derived compounds such as sugars, and sugar alcohols. This unique method generates hydrogen from aqueous solutions of these oxygenated compounds in a single step reactor process compared to the three or more reaction steps required for hydrogen generation via conventional processes that utilize non-renewable fossil fuels. The key breakthrough of the APR process is that the reforming is done in the liquid phase. The APR process occurs at temperatures (150°C to 270°C) where the water-gas shift reaction is favorable, making it possible to generate hydrogen with low amounts of CO in a single chemical reactor. Furthermore, the APR process occurs at pressures (typically 15 to 50 bar) where the hydrogen-rich effluent can be effectively purified.

While proven in the laboratory, the APR technology must be shown viable with low-cost sugars as feedstock. This project will result in development of a catalyst system and an initial reactor design and associated PFD for the design of a 5 to 10 kg H_2/day prototype reactor system. The catalyst, reactor design and PFD will provide information that will be necessary to scale-up the APR technology to a level that will allow for validation of system operation for generating hydrogen from low-cost sugar streams. The scaled demonstration system will provide the information required for scaling to commercial applications and will allow for techno-economic verification of the process. Glucose will be utilized as the model feedstock in this project. However, the process will be capable of processing mixed sugar streams, like those being produced from cellulosic feed stocks.

Approach

This project combines the expertise of Virent Energy Systems, Archer Daniels Midland Company, and the University of Wisconsin to demonstrate the feasibility of generating high yields of hydrogen from glucose. Aqueous solutions of glucose can be fed to the Virent's novel APR process to generate a high hydrogen content reformate stream. The effluent reformate stream from the APR process can then be efficiently purified to produce high purity hydrogen utilizing pressure swing adsorption.

Results

Virent is investigating a proprietary catalytic reactor configurations that allow the conversion of high concentrations of glucose to a hydrogen rich reformate. The biomass to hydrogen route via the APR process is detailed in Figure 1. The APR process utilizes biomass derived compounds such as glucose to produce hydrogen. The technical approach for processing glucose consists of a hydrogenation section followed by the APR process. The hydrogenation of glucose to sorbitol, at conditions that allow for simple integration with the APR process, has been demonstrated. The main focus of catalytic research is on the use of sorbitol in the APR process to produce a hydrogen rich reformate stream.

The go/no-go metrics from 2007 for specific catalyst performance metrics have been met. The metrics consisted of a catalyst operating at the following conditions:

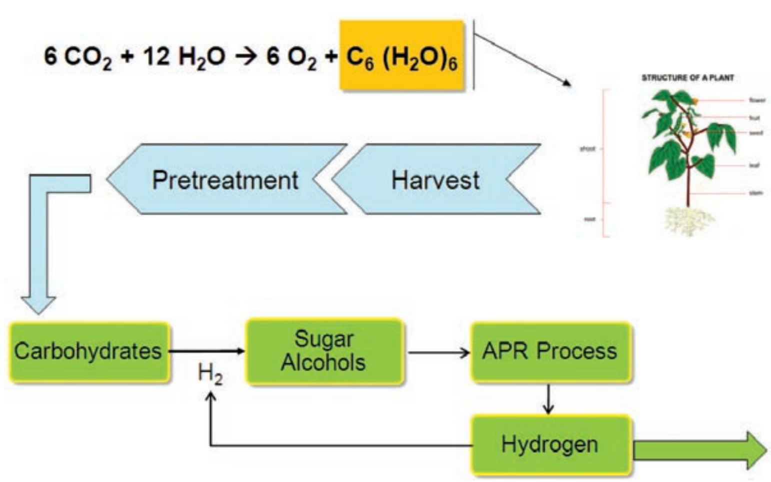

FIGURE 1. Biomass to Hydrogen via the APR Process

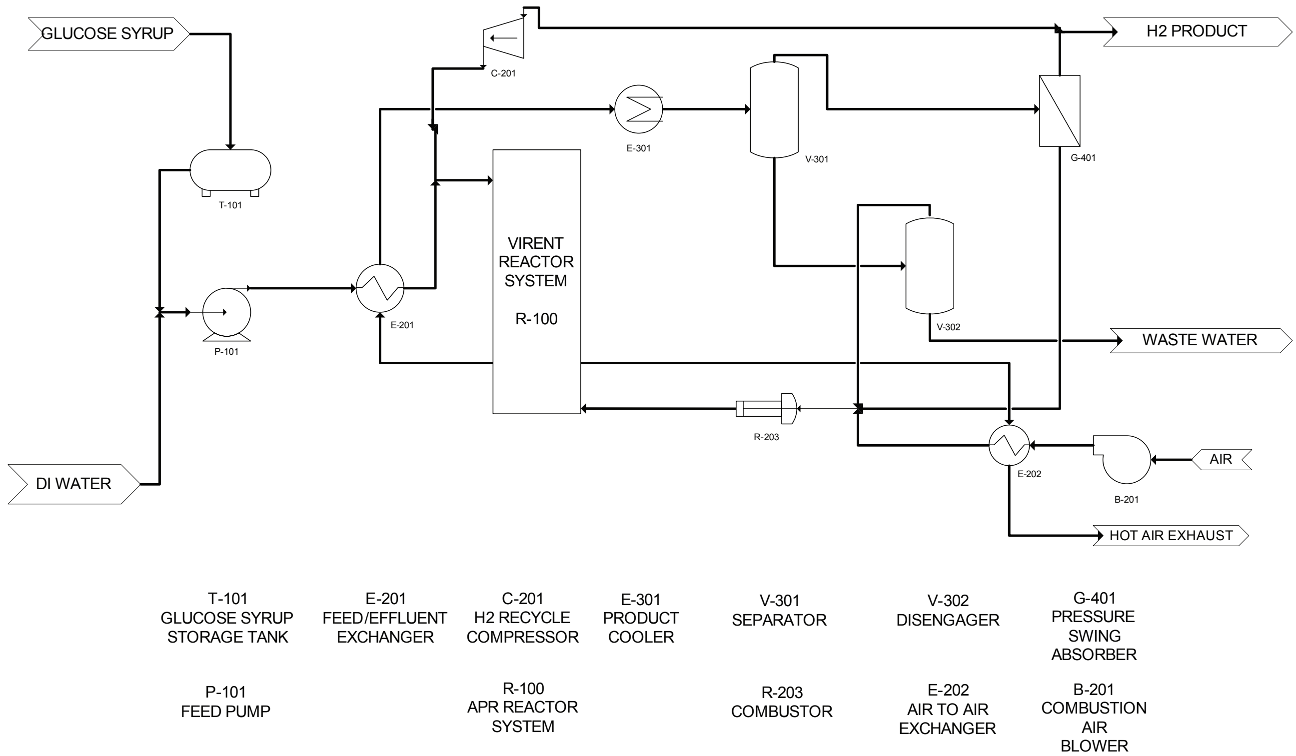

FIGURE 2. PFD of the APR Production Process

- Weight hourly space velocity >= 1
- Feed concentration >= 30%
- Feed conversion: 100%
- Hydrogen yield: 45%

A detailed techno-economic analysis for the production of hydrogen from glucose via the APR process has been completed. The economic analysis included the cost of feed stocks, capital equipment, Virent's process equipment as shown in Figure 2, along with compression, storage and dispensing equipment, catalyst, utilities, and operation and maintenance for a forecourt 1,500 kg H_2/day system. The economic analysis identified the most cost sensitive aspects of the APR process. Figure 3 details the H_2 cost components along with the sensitivity analysis of the varying performance cases. The largest cost component for the production of hydrogen from the APR process is the cost of feedstock, followed by capital costs and operations and maintenance. The sensitivity of the cost of hydrogen is greatest in regards to the effect of increasing the overall hydrogen yield of the system. The second and tertiary effects consist of the feed stock concentration and reactor productivity.

Results from this cost analyses show that the 2012 DOE target of $3.80/gge and the 2017 DOE target of <$3.00/gge could be achieved with sugars at 6.4 cents per lb, the Biomass Multi-Year Program Plan

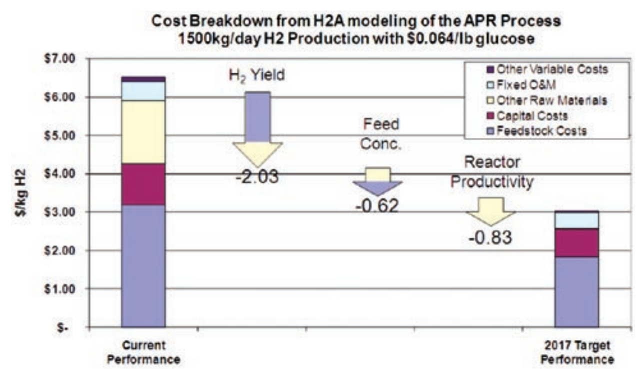

FIGURE 3. Cost Breakdown for H2A Analysis of the APR Process

goal for cellulosic sugars cost in 2020, and continued development of the APR process. The analysis has identified development pathways for the APR technology towards the 2012 and 2017 targets.

Conclusions and Future Directions

The APR technology is a promising and cost-competitive technology for the production of renewable hydrogen. However, technology development is still required to reach the DOE 2012 and 2017 cost targets. Virent has completed detailed modeling of the process and has identified development pathways intended to reach the 2012 and 2017 goals.

Future Directions

- Continue development of APR catalyst and reactor that converts glucose and sugar alcohols to hydrogen.
- Operate reactor development pilot plant to gain information required for the initial reactor design for the 5 to 10 kg H_2/day demonstration system.
- Develop initial PFD and catalytic reactor design for the 5 to 10 kg H_2/day demonstration system.
- Re-evaluate the thermal efficiency and economics of the APR system with respect to Hydrogen Program goals utilizing H2A.

FY 2008 Publications/Presentations

1. Presentation – NHA Annual Hydrogen Conference – March 31, 2008.

2. Presentation – 235th ACS National Meeting - April 7th, 2008.

3. Presentation – Hydrogen Program Review Meeting – June 10, 2008.