II.A.3 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 Company, Decatur, IL

Project Start Date: September 1, 2005
Project End Date: September 29, 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 a 10 kg H_2/day demonstration system.
- Develop initial process flow diagram (PFD) and catalytic reactor design for a 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/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:
  - Identified detailed catalytic activity metrics.

  - Developed detailed kinetic model.
- Techno-Economic Analysis
  - Development pathways identified to reach 2012 and 2017 goals.
  - Identified most cost sensitive aspects of the APR process.
- Catalytic Fundamentals
  - Developed detail chemical pathways of APR process.
  - Identified preferred chemical route for high efficiency production of H_2 from glucose.
  - Completed detailed review of thermodynamics.
  - Optimized operating conditions for improving H_2 yield and conversion to gas.
  - Developed method to analyze catalyst and support chemistry.
- Reactor Scale-Up
  - Scaled up APR reactor to reactor development scale.
  - Maintained H_2 yield and performance.

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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 the feedstock. This project will result in development of a catalyst system and an initial reactor design and associated PFD for the design of a 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 feedstocks.

Approach

This project combines the expertise of Virent Energy Systems (Virent), 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. Additionally, detailed activity and kinetic modeling has been completed for the hydrogenation reaction. The main focus of catalytic research is focused on the use of sorbitol in the APR process to produce a hydrogen rich reformate stream.

- Detailed techno-economic analysis for the production of hydrogen from glucose via the APR process has been completed. The economic analysis identified the most cost sensitive aspects of the APR process. The largest cost component for the production of hydrogen from the APR process is

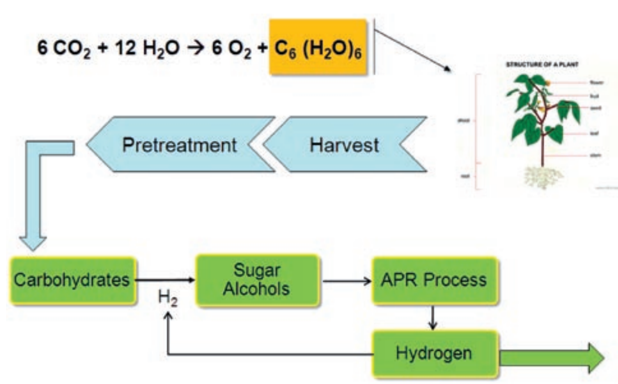

FIGURE 1. Biomass to Hydrogen via the APR Process

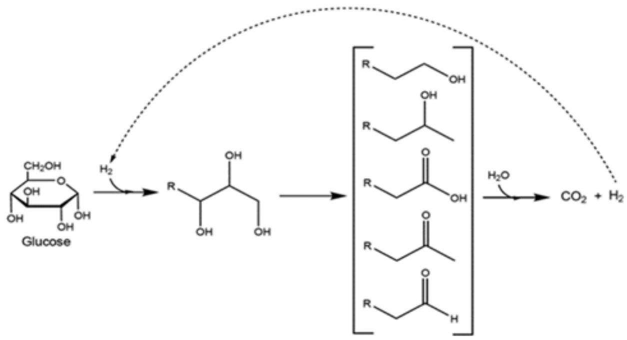

FIGURE 2. Intermediate Products of the APR Process

the cost of feedstock, followed by capital costs and operations and maintenance. The sensitivity of the cost of H_2 is greatest in regards to the effect of increasing the overall H_2 yield of the system. The second and tertiary cost 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 MYPP goal for cellulosic sugars cost in 2020, and continued development of the APR process. The analysis identified development pathways for the APR technology towards the 2012 and 2017 targets.

Economic-driven research continued focus on increasing H_2 yield. Fundamental reviews were completed in order to develop a detailed chemistry pathway, detailed catalyst metal and support chemistry and thermodynamic relationships. The chemistry pathway, simplified in Figure 2, details the intermediate compounds that may be produced such as alcohols, acids, ketones and aldehydes. The pathways also identified which of these intermediate components are favorable for H_2 generation and those that are undesirable. The chemistry pathways, in conjunction with the corresponding thermodynamic relationships, led to the exploration of new operating conditions. The new operating conditions led to an increase in H_2 yield and conversion to gas as detailed in Figure 3. The improvement in performance translates to a 10% decrease in H_2 cost over the past year. Overall, the cost of H_2 has been reduced by a factor of 10 over the course of the project.

Reactor scale-up activities were completed in the reactor development unit (RDU). The RDU has the capability of an active heating media, increased instrumentation for determination of heat transfer coefficients and a larger active

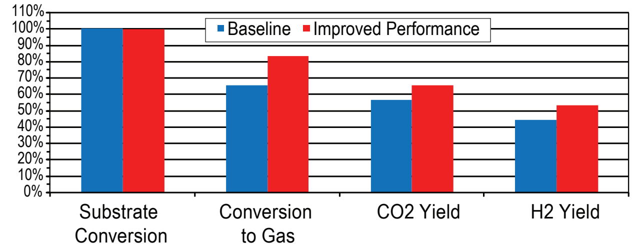

FIGURE 3. Improvement in Catalytic Performance

reactor section, in both diameter and length. The RDU demonstrated similar H_2 and CO_2 yield performance as the catalyst development unit along with an increase in conversion to gas as shown in Figure 4. The successful scaled up RDU will be numbered up for the design of a 10 kg/day H_2 demonstration system.

Conclusions and Future Directions

The APR technology is a promising and cost-competitive technology for the production of renewable H_2. However, technology development is still required to reach the DOE 2012 and 2017 cost targets. Virent's detailed model of the process 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.
- Complete initial reactor design and associated PFD for a 10 kg H_2/day demonstration system.
- Review techno-economic performance of the APR system utilizing the updated H2A platform.
- Re-evaluate the thermal efficiency and economics of the APR system with respect to Hydrogen Program goals utilizing H2A.
- Final project reporting and close-out.

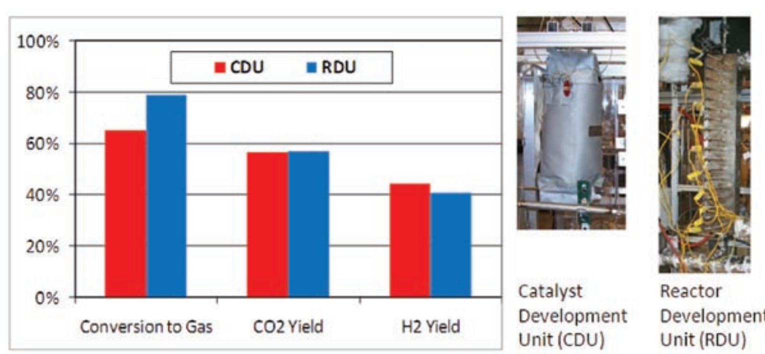

FIGURE 4. Reactor Scale-Up and Performance

FY 2009 Publications/Presentations

1. Presentation – NHA Hydrogen from Renewables Conference – September 23, 2008.

2. Presentation – DOE Hydrogen Program Annual Merit Review Meeting – May 19, 2009.