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## 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, Wisconsin  
Archer Daniels Midland Company, Decatur, IL

Start Date: September 1, 2005

Projected End Date: August 30, 2008

- Install and operate the APR hydrogen generator system at a sugar facility owned by ADM.
- Assess APR hydrogen generator system performance with respect to Hydrogen Program goals.

### Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Fuel Processor Capital Costs

### 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 2010 cost target for distributed production from renewable liquid fuels of \$3.60/gge delivered.

### 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:

- Develop the detail design of the demonstration APR hydrogen generator system (50 kg/day).
- Fabrication of the integrated hydrogen generator system.

### 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.
- Reported a preliminary cost model using DOE's H2A spreadsheet.

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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 50 kg H<sub>2</sub>/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. 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 1 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 than 10% to greater than 80% at a 100% conversion of glucose. In this analysis it 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 1 shows that it is desired to operate at feed concentrations of 30 wt% or greater to achieve the desired thermal efficiency for the system.

Virent has investigated a variety of catalyst and reactor configurations. Table 1 shows a summary of operations of the different reactor configurations tested to date. The baseline utilized in Table 1 is the conversion of 30 wt% sorbitol, fed at 240°C and 500 psig over a proprietary catalyst under basic conditions. Under these conditions, a sorbitol conversion of 100% was observed

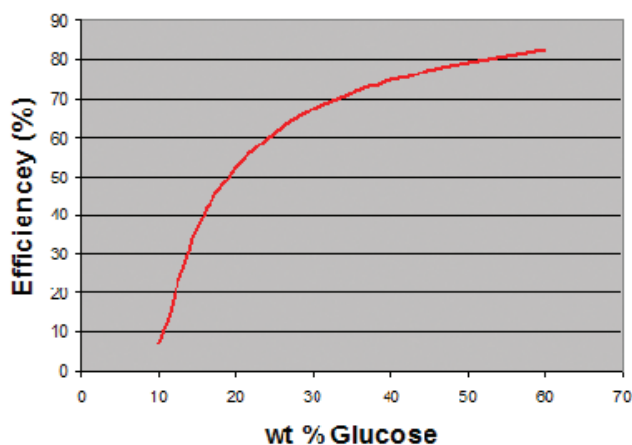


FIGURE 1. Efficiency of APR with Increasing Feed Concentration of Glucose

across the reactor with selectivity to hydrogen of 72%. The activities in Table 1 are given in terms of watt-equivalent of the product gas utilizing the lower heating value of hydrogen and the gas-phase alkanes.

Table 1 shows that with a standard reactor configuration and catalyst that it was not possible to completely convert a 3 wt% solution of glucose. However, Virent has demonstrated that it is possible to completely convert 30 wt% glucose in the feed.

Day-to-day performance of this improved reactor system is shown in Figure 2. This figure shows that the system was stable with some variability (for example, power output on D10 was high and on D13 it was low).

TABLE 1. Summary of Operations for the Conversion of Glucose

| Date                       | Apr-04       | Sep-05     | Jan-06      |             |
|----------------------------|--------------|------------|-------------|-------------|
| Feedstock                  | 30% Sorbitol | 3% Glucose | 30% Glucose | 30% Glucose |
| WHSV                       | 2.0/h        | 0.897/h    | 0.996/h     | 2.1/h       |
| Reactor                    |              |            |             |             |
| Temperature                | 240°C        | 230°C      | 240°C       | 240°C       |
| Pressure                   | 500 psig     | 430 psig   | 500 psig    | 600 psig    |
| Conversion                 | 100%         | 73%        | 100%        | 100%        |
| Conversion to Gas          | 75%          | 14%        | 58%         | 36%         |
| H <sub>2</sub> Selectivity | 72%          | 33%        | 23%         | 58%         |
| Watt H <sub>2</sub> /gram  | 4.2          | 0.12       | 0.39        | 0.91        |
| Watt Alkane/Gram           | 2.1          | 0.03       | 1.26        | 0.73        |

WHSV = Weight hourly space velocity (grams of oxygenated compound per gram of catalyst per hour).

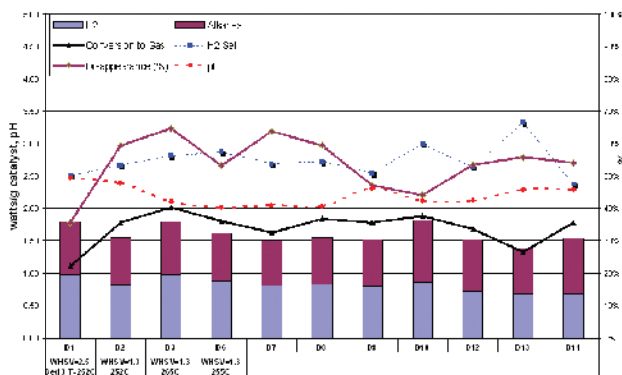


FIGURE 2. Stability of System with 30 wt% Glucose

Power output has been about 1.5 Watts/g with half of that coming from hydrogen, selectivity to hydrogen has averaged 55±6%. Conversion to gas has averaged 34±4% and disappearance 54±6%.

A cost analysis was performed for the process flow shown in Figure 3 for the generation of hydrogen from glucose using the APR process. In this schematic, water/glucose syrup is mixed with water and the resulting aqueous solution is fed to the APR process where hydrogen is generated in a single reactor. The effluent gas from the APR process is purified to produce high purity hydrogen.

A 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<sub>2</sub> per day. This analysis includes the capital cost of the reformer, PSA separator, compressor, storage, and dispensing equipment. Figure 4 shows the results of this analysis utilizing the the following assumptions:

- Capital cost of reformer, APR, compression, storage, and dispensing: \$1,960,000
- Conversion of low purity sorbitol (15 cents/kg 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

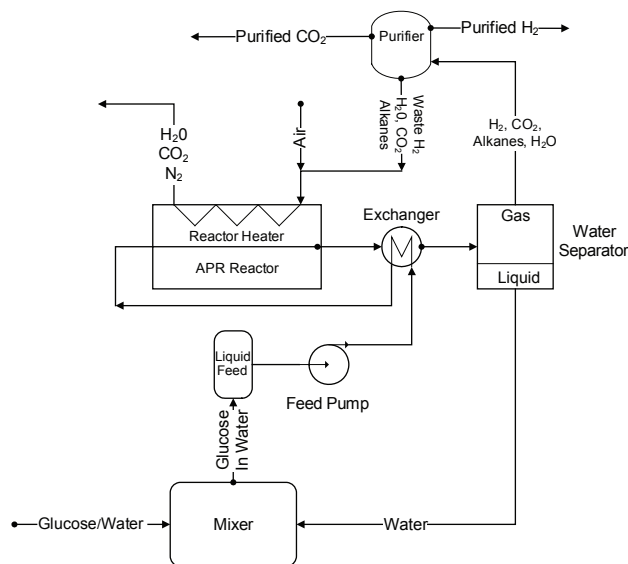


FIGURE 3. Process Flow for the Generation of Hydrogen from Glucose

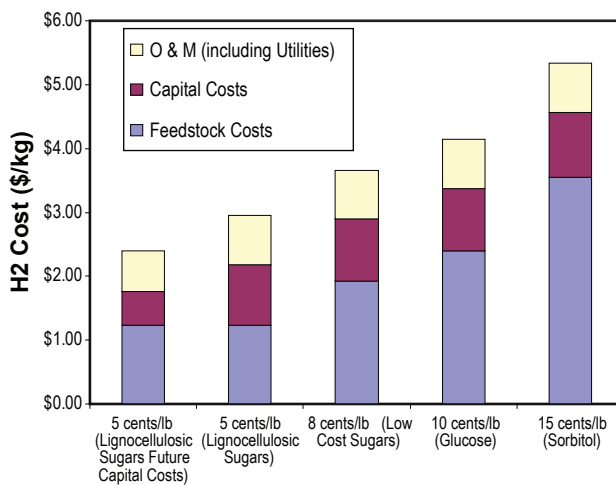


FIGURE 4. Preliminary Cost Analysis Utilizing H2A

- 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 2010 DOE Target of \$3.60/gge could be achieved utilizing low-cost sugars (less than 8 cents/lb). The 2015 DOE Target of \$2.50/gge could be achieved with sugars derived from lignocellulosic biomass and lower capital costs for the system.

### Conclusions and Future Directions

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

### FY 2006 Publications/Presentations

1. Presentation – Hydrogen Program Review Meeting - May 16–19, 2006.
2. Presentation - World Hydrogen Energy Congress - June 12–16, 2006, Lyon, France.