Introduction

In this Phase I Small Business Innovation research project Virent Energy Systems (Virent) attempted to demonstrate the feasibility of generating high yields of hydrogen by developing the appropriate reactor system for the novel liquid-phase reforming of aqueous-phase carbohydrate streams derived from biomass. The problem with the standard biomass gasification technologies to generate hydrogen is that these methods are not currently economically viable and require the coupling with the production of higher-value fuels or chemicals. Virent will utilize novel liquid-phase reforming process that allows the generation of hydrogen by reactions of carbohydrates (glycerol, sugars, and sugar alcohols) derived from bio-mass with liquid water at low temperatures. This novel process provides routes to generate hydrogen as a value-added chemical from aqueous-phase carbohydrates found in waste water from biomass processing (e.g. cheese whey, beer brewery waste water, sugar processing), from aqueous-phase carbohydrates extracted from agricultural products such as corn and sugar beets, and from aqueous-phase carbohydrates extracted by steam-aqueous fractionation of lower-valued hemicellulose from biomass. The resulting hydrogen can be easily purified and utilized as:

- a chemical feedstock for production of ammonia and fertilizers,
- a chemical reagent for the future hydrogenation of carbohydrates to produce glycols,
- a hydrogen-rich gas stream that augments the gas stream from biomass gasification unit utilized for the production of liquid fuel via the Fischer-Tropsch process,
- a future renewable fuel source for PEM fuel cells.

The competing technology for generating hydrogen from biomass involves the catalytic vapor-phase steam reforming of either liquid or gas fractions from biomass thermoconversion processes. The thermodynamic properties of the vapor-phase process dictate that two widely different process regimes are required to react the fractions from the different biomass thermoconversion processes with water to generate H₂ and CO₂ with low concentrations of CO. Accordingly, the generation of hydrogen via vapor-phase steam reforming requires several reaction steps such as: (i) high temperature (e.g.,
1000 K) steam reforming that reacts water with the hydrocarbon to form H₂ and CO; (ii)
high-temperature (e.g., 700 K) water-gas shift reaction; (iii) a low-temperature (e.g.,
500 K) water-gas shift reaction to react water with CO to generate H₂ and CO₂; and (iii)
preferential oxidation of CO impurities (PROX). Such reforming requires a series of
reactors that are thermally interconnected to reduce the amount of energy utilized to
convert the hydrocarbons to hydrogen and carbon dioxide.

Virent’s newly discovered aqueous-phase carbohydrate reforming (ACR) process
reacts water with carbohydrate-type compounds (glycerol, sugars, and sugar alcohols) 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.

Laboratory proof-of-concept measurements have shown it is possible to generate
hydrogen in high yields via the conversion of glucose in the aqueous-phase [1]. Reaction
kinetics data have been collected for the aqueous-phase reforming of glucose over a 3
wt% Pt catalyst supported on γ-alumina (500 m²/g, Argonide Corporation). Figure 1
shows that it is possible to generate hydrogen in high yields via the liquid-phase
reforming of oxygenated compounds. Figure 1 shows the effect of feedstock on H₂ and
alkane selectivities over the alumina-supported Pt catalyst at different temperatures.
These data were collected at high conversion utilizing aqueous solutions containing 1
wt% of the oxygenated compound. Figure 1 shows that the reaction selectivity for
aqueous-phase reforming is dependent on the nature of the reactant. In particular, the
selectivity for H₂ production decreased in the order: Ethylene glycol > Glycerol >
Sorbitol > Glucose. At the reaction temperatures of this investigation, the CO
concentrations were below detection limits of the GC. These detection limits would
 correspond to CO levels of 300 ppm. Accordingly, the gas generated from aqueous-phase
reforming of these oxygenated compounds would require minimal CO clean-up for low
temperature fuel cell applications.
Figure 1 shows that improvements can be achieved for the hydrogen selectivity for the aqueous-phase reforming of glucose. As will be discussed in more detail below, the hydrogen selectivity for the liquid-phase reforming of glucose is at least partially influenced by homogeneous reactions of glucose in the aqueous-phase. It is expected that improved selectivity for hydrogen production from concentrated sugar solutions can be achieved over the correct combination of catalysts and reactor configurations that minimize homogeneous decomposition reactions. Furthermore, since this is a two-phase system, it is necessary to develop a reactor system that minimizes limitations attributed to heat transfer, mass transfer, and to pressure drop across the reactor system. Accordingly, the development of commercially viable processes based on this new technology requires the development of effective and selective reactor systems. Virent Energy Systems LLC (Virent) therefore proposes to conduct studies and develop an integrated reactor system. It has been found that platinum-based catalysts are reasonably selective for the generation of hydrogen [1, 6]. Virent Energy Systems is working in collaboration with the University of Wisconsin in the investigations and development of other less expensive catalytic materials. This collaborative catalysis investigation is a NSF STTR funded project. Accordingly, in this project platinum-based catalysts will initially be utilized to establish the technical feasibility of reactor design for reforming carbohydrates found in biomass to hydrogen. Virent will address the following technical objectives in this proposed project:

1. Identification of the necessary catalytic reactor configuration.
2. Identification of the necessary structure of the catalyst substrate.
3. Identification of reaction conditions necessary for conversion of carbohydrates to hydrogen.
   a. Effect of temperature
   b. Effect of carbohydrate concentration in the reactor feed.
   c. Effect of liquid feed rate to the reactor.

**Results of studies**

Glucose is the most common biomass derived carbohydrate that could be used as a feedstock for Aqueous Phase Reforming (APR) to produce Hydrogen or fuel gas. Compared to other, less complex, substrates Glucose, and other sugars, are challenging potential feedstocks for APR due to their thermal instability under the necessary reaction conditions. Finding solutions to these challenges is important for Virent’s efforts to develop APR into an economically viable renewable energy technology.

**Glucose Reforming**

A detailed study of the effects of concentration and space velocity during reforming of Glucose has been performed. This study used a 1% Pt on granular carbon catalyst, reforming was performed at 230°C. Results from this study are summarized in Figure 2.
Conversion of Glucose was determined by measuring concentrations by GC. For 1% Glucose, all the substrate had disappeared except for the test at a space velocity of ~15/h where 10% of the glucose remained. Most of the glucose was converted to other materials in the 3% trials also; the space velocity of ~15/h again gave the minimum conversion, 58% in this case. Yields for hydrogen were always low, <10%, indicating that most of the glucose conversion was following other pathways. Hydrocarbon formation was not the primary pathway; the largest total hydrocarbon (Methane through Hexane) yield obtained was 5.4% for 3% Glucose at a space velocity of 4.4/h. Attempts to collect data for 5% glucose were not successful due to burning of the glucose at the inlet to the reactor.

Competition from other reaction pathways for Glucose and other sugars is likely due to the presence of aldehyde and ketone groups. These groups cause the predominate structure of the sugars to be cyclic forms which may be less easily reformed to CO₂ and H₂. Aldehydes and ketones also have reactivity not available to polyalcohols, for example aldol condensation reactions. Reactivity of this type may explain the competing reaction pathways.

Glucose versus Sorbitol

One option for reducing the competition from other reaction pathways for sugars like Glucose is to hydrogenate the aldehyde and ketone groups converting them to sugar alcohols. This eliminates interference from cyclic structures and aldehyde and ketone group reactivity. The sugar alcohol produced by hydrogenating glucose is Sorbitol. Results from a comparison of the reactivity of Glucose versus Sorbitol is summarized in Figure 3.
The total power available from reforming Sorbitol was almost 3 times that from glucose even though the extent of conversion was less than half. Approximately two thirds of the potential power from Sorbitol was hydrogen while less than half that from Glucose was hydrogen.

**Sorbitol Reforming**

Based on these results, the reactivity of Sorbitol over a more active APR catalyst. Figure 3 shows the potential power produced from 10% Sorbitol over this catalyst. Total power produced increased as feed rate increased, while conversion of the Sorbitol decreased. In all cases alkanes were the major energy containing products; the fraction of total power from hydrogen increased with feed rate. At 2mL/minute hydrogen production was 17.5% of the total potential power produced while at 12 mL/min it was 32.8%. A higher yield of hydrogen at lower feedstock conversion is a general trend for Aqueous Phase Reforming.
Hydrogen production is improved by increasing the pH of the feedstock. Figure 4 shows the potential power produced from 10% Sorbitol fed at 12mL/min for three concentrations of potassium hydroxide (KOH). Total power was not appreciably affected but the fraction of power from hydrogen increased to 59% with feedstock containing 0.5M KOH. It is not clear why conversion, and total power, were slightly lower at 0.1M KOH where 52% of the power was hydrogen. Attempts to use KOH to increase hydrogen production from Glucose have been unsuccessful because KOH increases burning of the glucose.
Conclusion

The above results show that initial attempts to reform aqueous solutions of glucose were hampered by liquid-phase side reactions. The above results suggest that functionalizing the mono-saccharide to its appropriate sugar alcohol may be an effective strategy to generate hydrogen from biomass derived compounds.