

II.B.2 A Novel Slurry-Based Biomass Reforming Process

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Technical Targets

This project consists of three key elements: plant and system design, catalyst research, and a proof-of-concept demonstration. The information obtained from all three efforts will be used to demonstrate that the proposed H₂ production system will meet the DOE's 2012 Biomass Gasification/Pyrolysis Hydrogen Production energy efficiency and total hydrogen cost targets of 43% (based on feedstock LHV) and \$1.60/kg H₂. The current progress toward achieving the DOE's technical targets based on the preliminary plant and system design is shown in Table 1.

TABLE 1. Technical progress for the project as measured against the DOE's technical targets for biomass gasification/pyrolysis hydrogen production.

Characteristics	Units	2012 Target	Current Status	2008 Status
Hydrogen Cost (Plant Gate)	\$/gge	1.60	1.27 (0.95–1.85)	1.58–2.16
Total Capital Investment	\$M	150	177 (71–365)	203–291
Energy Efficiency	%	43	53.9 (53.9–58)	46.6

Objectives

- Develop an initial reactor and system design, with cost projections, for a biomass slurry hydrolysis and reforming process for H₂ production.
- Develop a cost-effective catalyst for liquid phase reforming of biomass hydrolysis-derived oxygenates.
- Perform a proof-of-concept demonstration of a micro-scale pilot system based on liquid-phase reforming of biomass hydrolysis-derived oxygenates.
- Demonstrate that the proposed H₂ production system will meet the 2012 efficiency and cost targets of 43% lower heating value (LHV) and \$1.60/kg H₂.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

- (T) Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology

Accomplishments

- A baseline 2,000 ton/day biomass to hydrogen plant has been designed using the process simulator HYSYS which has a plant hydrogen efficiency of 53.9%.
- The preliminary economic analysis of the baseline plant design shows that a hydrogen production cost of \$1.27/kg H₂ could be attainable.
- Simultaneous base hydrolysis in the presence of a Pt-Re/CeZrO₂ catalyst results in the complete conversion of yellow poplar sawdust to H₂, CH₄, and C₂H₆ with trace C₃H₈ as well as CO₂.
- The resulting clear, colorless aqueous solutions apparently contained potassium carbonates and possibly trace potassium acetate.



Introduction

This project is focused on developing a catalytic means of producing hydrogen from raw, ground biomass, such as fast growing poplar trees, willow trees, or switch grass. The use of a renewable, biomass feedstock with minimal processing can enable a carbon

neutral means of producing hydrogen in that the carbon dioxide produced from the process can be used in the environment to produce additional biomass. For economically viable production of hydrogen, the biomass is hydrolyzed and then reformed without any additional purification steps. Any unreacted biomass and other byproduct streams are burned to provide process energy. Thus, the development of a catalyst that can operate in the demanding pH, high pressures, and presence of potential poisons is vital to this approach.

Approach

The concept for this project is shown in Figure 1. The initial feed is assumed to be a >5 wt% slurry of ground poplar wood in dilute base. Potassium carbonate, derived from wood ash, is an effective base. Base hydrolysis of the wood is carried out at high but sub-critical pressures and temperatures in the presence of a high surface area, high metal dispersion, large pore, base stable Pt-Re/Ce_(1-x)Zr_xO₂ catalyst. A palladium alloy membrane allows the continuous removal of pure hydrogen, thus limiting methane formation, while the retentate is used as fuel in the proposed plant.

Results

Task 1: Reactor and H₂ Production System Modeling, Energy, and Economic Analysis

The baseline techno-economic analysis was updated to reflect the use of base instead of acid for the hydrolysis process. The model feedstock representing the wood was adjusted to be 72.6% cellulose, 27% lignin surrogate (C₈H₈O₃) and 0.4% ash. The hydrolysis was reduced to a single step process where the alkali is derived from potassium in the wood and where the lignin is completely hydrolyzed. The sulfur removal process was eliminated from the system. The burner system was also adjusted to reflect the combustion of process derived gases, such as methane, rather than unconverted lignin as the experimental work has shown that essentially 100% of the wood can be converted into gas products. The reformer size was also reduced based on the kinetic results from ethanol experiments described later in this report.

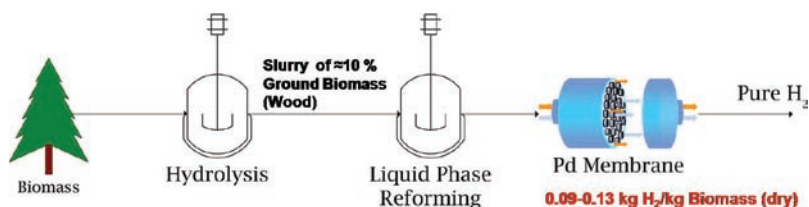


FIGURE 1. The UTRC Approach to Biomass Slurry Reforming



FIGURE 2. Reaction product liquor from hydrolysis and liquid phase reforming of 1 wt% yellow poplar at 310°C in 0.1M K₂CO₃ with a 0.5 L/min N₂ sweep gas. White sediment is potassium titanate, a titanium corrosion product.

Task 2: Catalyst Development and Testing

Nearly 100% conversion of 1 wt% yellow poplar was achieved with a Pt-Re/Ce_(1-x)Zr_xO₂ based catalyst in a custom built titanium reactor. Approximately 75% selectivity towards H₂ was achieved with an energy recovery of 75% based on the LHV of yellow poplar. The reaction product liquor is shown in Figure 2. Unfortunately, some corrosion products were evident in the reactor in the form of potassium titanate. The probable major source of this was caustic attack on the titanium screen used to hold the catalyst.

To avoid reactor corrosion and to simplify kinetic studies, it was decided to move to a corrosion resistant flow reactor. A flow reactor was constructed of zirconium. A high pressure Isco syringe pump (500D) is used to pump high pressure reactants. In addition to the liquid reactants, the system is also set up to allow for inlet flows of H₂ and N₂. A high pressure N₂ sweep gas is introduced after the reactor to minimize residence time in the exit piping and act as a diluent for gas production calculation. Upon depressurization to atmospheric pressure, the effluent passes through a gas-liquid separator, followed by a

flow meter and gas chromatographs for analysis. The powdered catalyst is set in the hottest portion of the heated zone, mixed with yttria-stabilized ZrO_2 beads which act as a diluent. The remainder of the reactor is filled with the inert beads.

The initial test of the reactor consisted of using 1 g Pt-Re/Ce_(1-x)Zr_xO₂ with 1 wt% ethanol as the feedstock. The reactor was operated at temperatures of 250°C, 280°C, and 310°C at a pressure of 1,640 psi with a reactant liquid flow rate of 1 mL/min and a N₂ sweep gas flow rate of 0.3 L/min. At each temperature, the effluent molar flow rates were stable, and increased with increasing temperature. The conversion increased with increasing temperature, with a calculated activation energy for the net formation of H₂ of 54 kJ/mol. The reaction selectivity towards H₂ was 48%, 46%, and 48% at each subsequent temperature step, with CH₄, and to a lesser degree C₂H₆, being the main byproducts of the reaction.

Subsequent experiments in the flow reactor were performed with 1.7 wt% ethanol in 0.1M K₂CO₃ to determine how the system behaves in the presence of base. The reactor was run at 250°C, 280°C, and 310°C with a liquid feed flow rate of 2 mL/min, and 3 mL/min, given in Figure 3. For both flow rates, the reaction gas production increased with increasing temperature. Both flow rates produced H₂ as the main product with CH₄ being the major byproduct. CO₂ was only noted at higher temperatures due to the CO₂ scrubbing effect K₂CO₃ will have on the system. More than a saturation level of CO₂ must be generated before any CO₂ will be observed in the gas phase. The H₂ selectivity of the system varied depending on the temperature. The selectivities were 46%, 48%, and 65% at 2 mL/min and 41%, 51%, and 71% at 3 mL/min for 250°C, 280°C, and 310°C, respectively. At 3 mL/min, the reactor was allowed to run for over 200 minutes at

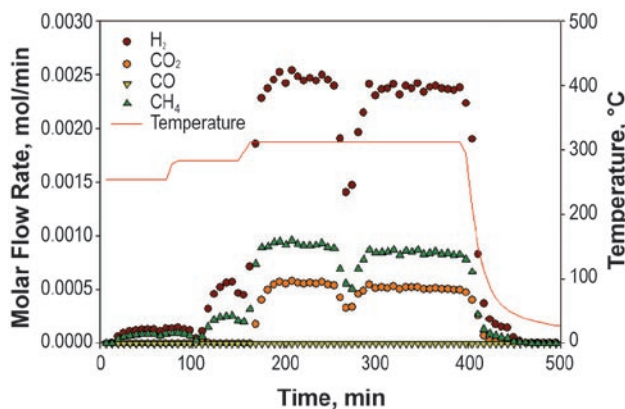


FIGURE 3. Effluent molar flow rate of gas during the liquid phase reforming of 1.7 wt% ethanol in 0.1 M K₂CO₃ with 1 g 1.5% Pt-1.2% Re/Ce_{0.65}Zr_{0.35}O₂, at a feed flow rate of 3 mL/min and a sweep gas flow rate of 0.3 L/min at 1,640 psi.

310°C to determine the effect of time on stream. Little degradation in H₂ production was noted during the experiment (the large dip in H₂ production was due to the reactor being taken off line for refilling of the syringe pump). Upon dissecting the reactor after the reactions, it was found that the inert packing had lost its structural integrity and became a powder. More importantly, the beads used as a diluent for the catalyst also lost their integrity, encapsulating the catalyst particles as if in a cement plug. This may have been detrimental to the reaction kinetics of the system and prevented high conversions.

With the data obtained from the liquid phase reforming of ethanol in the presence of base, a network of reactions to describe the system was derived. In addition to the main reaction products of H₂ and CO₂, only CH₄, C₂H₆, and C₃H₈ byproducts were detected in any appreciable quantities. This reaction network led to the development of rate equations and a kinetic model for a plug flow reactor used to estimate the rate constants. Parameter estimation techniques were used to fit the ethanol data to the model. Figure 4 shows the model prediction and experimental data points for the liquid phase reforming of ethanol in 0.1M K₂CO₃ at 310°C. It is evident that the reaction network adequately described the reforming of ethanol at the conditions studied. It is thus possible to use this network to determine optimal conditions and required bed length for high conversion. The approach should also be applicable to more complicated systems, including the liquid phase reforming of raw biomass.

Attempts to run hydrolyzed biomass proved much more difficult than ethanol. Two factors thwarted our efforts: (1) the instability and apparent oligomerization of base-hydrolyzed wood suspensions and (2) the degradation of the inert packing confounding the reactor

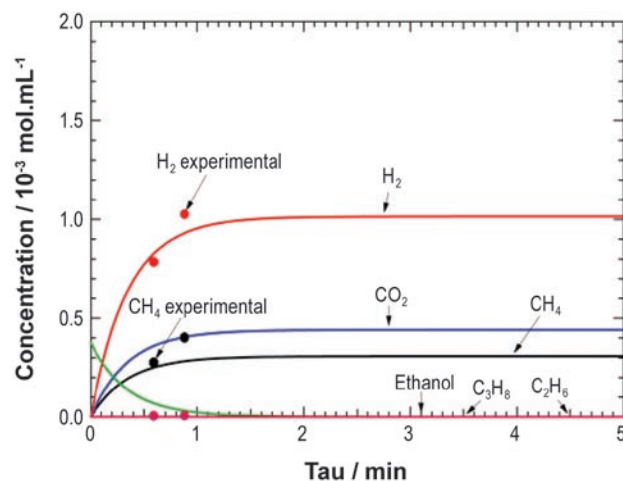


FIGURE 4. Model prediction and experimental data for the liquid phase reforming of ethanol at 310°C in 0.1M K₂CO₃ as a function of residence time (tau) in the flow reactor.

liquid flow and catalyst contacting. Support stability studies were conducted at 310°C for 12 hours carried out in a batch high pressure bomb to determine whether acceptable inert materials could be identified. Rutile TiO₂, Ce stabilized ZrO₂, and SiC showed promise.

Rutile TiO₂ was used as the next inert packing due to its availability. Yellow poplar (1 wt%) was hydrolyzed in the zirconium autoclave in 0.2 M KOH at 310°C for 10 hours. The hydrolyzed solution was filtered to remove residual solids (approximately 1.2% solids recovered from the original solid loading). After hydrolysis and filtration, it was noted that a solution left out at ambient conditions or in a refrigerator continued to precipitate solids. This discovery may be extremely important in the process, as these tar-like solids may be much more difficult to deal with than the precursors which led to their formation. These precursors are likely highly active lignin fragments that may be best reformed immediately following their production. The solution of hydrolyzed yellow poplar was flowed over a 2 g bed of Pt-Re/Ce_(1-x)Zr_xO₂ chunks (≈4 mm square) mixed with crushed rutile TiO₂ pellets. The total bed volume was 4 cm³. The flow of yellow poplar slurry was set at 1 mL/min and the reactions carried out at 310°C. Unfortunately, significant chromatography issues arose, due to plugging of downstream valves and lines. Data could not be gathered and extensive system repair and redesign has been required.

Work at the University of North Dakota Energy & Environmental Research Center (UND-EERC) has begun. The main emphasis of their work has been on analysis of reaction liquors. Significant learning was necessary in how to properly prepare reaction samples for analysis to quantify production of organic and aqueous phase hydrolysis products. Initial hydrolysis has shown similar results to those performed at UTRC, with complete liquefaction of 1 wt% DM Poplar. Initial analytical results have led to identification of several organic acids in the aqueous phase. However, non-aqueous products have yet to be identified.

Conclusions and Future Directions

Based on the results from this last year, the best path for success is to produce hydrogen using base hydrolysis of wood, probably in the presence of a catalyst that reacts away the hydrolysis products as they are formed. The focus of the project will move toward: (1) the identification of plausible model compound from base hydrolysis studies; (2) model compound reforming studies in a flow reactor to enable the capture of fundamental reaction engineering information; and (3) system design of a coupled wood hydrolysis/reforming system based on this information. Once this is tested and refined work can proceed toward a hydrogen separation membrane enabled demonstration unit.

FY 2009 Publications/Presentations

1. Vanderspurt, T.H.; Emerson, S.C.; Davis, T.D.; MacLeod, J.; Marigliani, G.; Peles, A.; Seiser, S.; She, Y.; Willigan, R. A Novel Slurry-Based Biomass Reforming Process, presentation at the 2009 DOE Annual Merit Review, Arlington, VA, 20 May 2009.
2. Davis, T.D.; Emerson, S.C.; MacLeod, J.; Marigliani, G.; Peles, A.; Seiser, S.; She, Y.; Willigan, R.; Vanderspurt, T.H. Aqueous Phase Reforming of Yellow Poplar to Hydrogen, presentation at the 21st North American Catalysis Society Meeting, San Francisco, California, 8 June 2009.

References

1. DOE Office of Energy Efficiency and Renewable Energy. Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, U.S. Department of Energy: Washington, D.C., 27 April 2007.