

II.B.1 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 H₂ cost targets of 43% (based on feedstock LHV) and \$1.60/kg H₂, respectively. 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
Hydrogen Cost (Plant Gate)	\$/gge	1.60	1.27 (0.95–2.13)
Total Capital Investment	\$M	150	177 (71–365)
Energy Efficiency	%	43	55 (55–58)

gge – gasoline gallon equivalent

Objectives

- Develop an initial reactor and system design, with cost projections, for a biomass slurry hydrolysis and reforming process for hydrogen (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.
- Demonstrate that the proposed H₂ production system will meet the 2012 efficiency and cost targets of 43% lowering heating value (LHV) and \$1.60/kg H₂.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

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

Accomplishments

- Demonstrated 100% conversion of wood using an inexpensive base metal catalyst.
- Examined the effect of base concentration on liquid phase reforming H₂ selectivity.
- Developed a promoted nickel (Ni) catalyst that maintains a high selectivity to H₂ with minimal base.
- Elucidated the liquid phase reforming reaction pathways for ethylene glycol via atomistic modeling.
- Demonstrated palladium (Pd) membrane integration with a liquid phase reforming flow reactor.



Introduction

This project is focused on developing a catalytic means of producing H₂ 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 H₂ in that the carbon dioxide produced from the process can be used in the environment to produce additional biomass. For economically viable production of H₂, 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 corrosive environment 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 solid catalyst. A Pd alloy membrane allows the continuous removal of pure H₂, while the retentate, including methane, is used as fuel in the proposed plant.

Results

Following the successful demonstration of the near 100% conversion of wood to hydrogen-containing gas using liquid-phase reforming (LPR), the project efforts were focused on further understanding the durability and kinetics of the process in a plug flow reactor system. Model compounds, such as ethanol, 1,4-butanediol, and ethylene glycol, were used to study a fixed bed reactor system using UTRC's Pt-Re based catalyst. Tests showed that the catalyst could reform the model compounds for periods greater than 250 hours without signs of degradation.

During the model compound study, the coupling of the flow reactor with a Pd alloy H₂ separation membrane was also demonstrated. A 10% ethanol in 0.1M K₂CO₃ solution was flowed through the reactor bed at 3 mL/min. The effluent gas stream from the reforming reactor was approximately 213 mL/min and composed of approximately 64% H₂. The effluent gas stream was fed to a palladium-copper alloy membrane held at 450°C at a pressure of 193 psig. The system was allowed to run for 45 minutes to stabilize and collect data. The data from the experiment is given in Figure 2. The system behaved as expected, with a 93% H₂ recovery, indicating maximum recovery of the H₂ from the reformat gas stream.

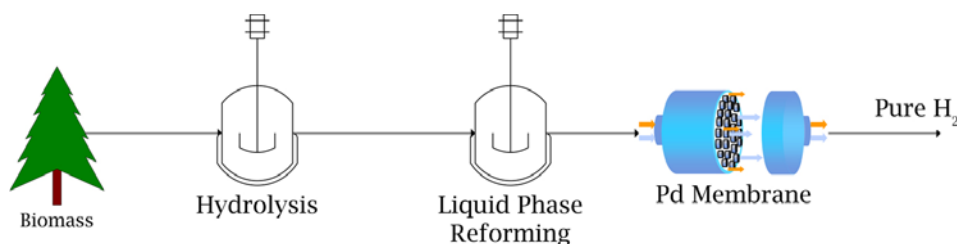


FIGURE 1. The UTRC Approach to Biomass Slurry Reforming

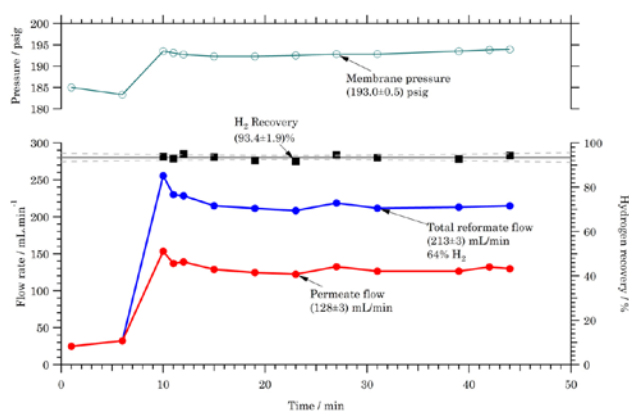


FIGURE 2. Experimental results for hydrogen separation with a Pd alloy membrane from liquid phase reformed ethanol over a PtRe/CeZrO₂ catalyst.

As part of the goal of reducing catalyst costs, and thus capital costs, the project focused on transitioning from a precious metal-based catalyst to one with base metal as the active component. At the same time, a study was performed to better understand the impact of base concentration on H₂ yield and selectivity. It was determined that for a commercially available Raney Ni catalyst, the selectivity toward H₂ could be adjusted by changing base concentration. By increasing base concentration, methane generation could be significantly suppressed, but at the expense of a reduced H₂ yield due to the formation of high levels of intractable organic acids. Figure 3 shows the impact of H₂ selectivity as a function of residence time and base concentration for a 5% ethylene glycol feed.

First principles atomistic modeling was used to gain an insight into the factors that control the activity and selectivity toward H₂ production by ethylene glycol reforming on Ni catalysts. The schematic diagram of reforming pathways is depicted in Figure 4. For ethylene glycol on a Ni surface, the first step after adsorption is hydroxyl bond breaking to form an ethylenedioxy intermediate. At the surface coverage considered, the activation of the C-O bond in ethylenedioxy and rearrangement to form the acetaldehyde intermediate and adsorbed oxygen are thermodynamically favorable. Subsequent dehydrogenation and C-C bond scission

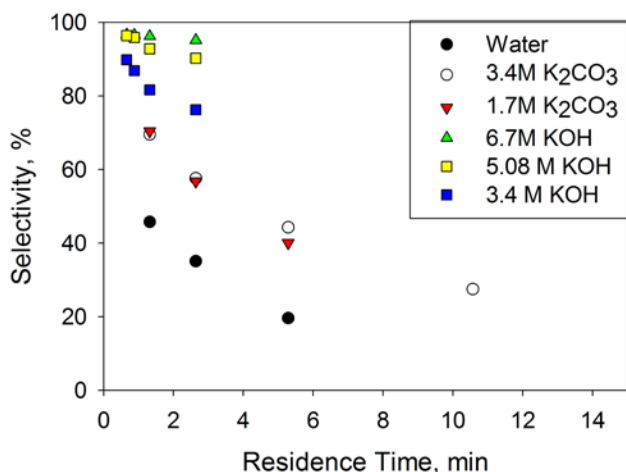


FIGURE 3. H₂ selectivity for LPR of 5 wt% ethylene glycol over a 4 g bed of Raney Ni at 1,780 psig and 310°C.

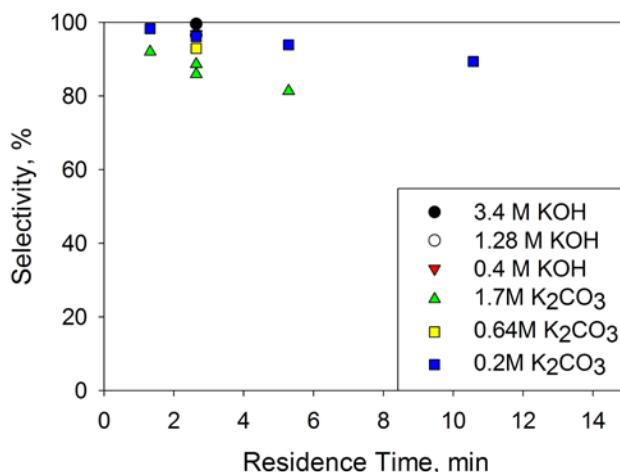


FIGURE 5. H₂ selectivity for LPR of 2.5 wt% ethylene glycol over an 8 g bed of modified Raney Ni at 1,780 psig and 310°C.

of acetaldehyde yields the CO and CH₃ as final decomposition intermediates. CO is shifted in water to CO₂ and H₂ while the methyl is hydrogenated into methane. In a basic environment, CO can also be converted to a formate ion in solution through hydrophilic attack, consistent with the experimental observation of formic acid in the spent liquor.

As the reaction pathway for LPR on Ni consists of three major paths toward either H₂, methane, or organic acid, modifications were performed to standard Raney Ni catalysts to adjust their selectivity. As a result, a modified Raney Ni catalyst was developed that enabled the use of dilute carbonate bases while still maintaining

high selectivity as well as high H₂ yield. Figure 5 shows the impact of H₂ selectivity as a function of residence time and base concentration for a 2.5% ethylene glycol feed. This performance was also reproduced using yellow poplar in a batch reactor.

Conclusions and Future Directions

Based on the successful work with base metal catalysts, the next step of the project is to construct a demonstration unit for H₂ production. The demonstrator shall integrate a liquid phase reformer with a Pd membrane separator and show the integration

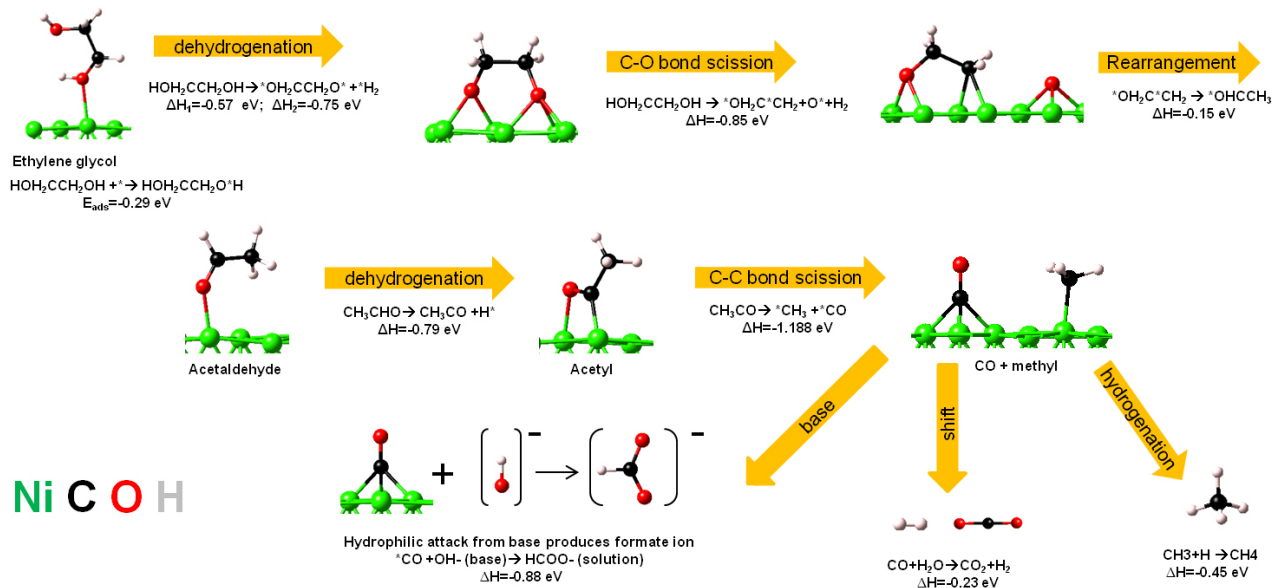


FIGURE 4. Atomistic modeling analysis of the reforming of ethylene glycol over Ni showing the intermediate reaction steps and the reaction enthalpies of their formation.

of the major process components in to a small system. Construction of a 12 L/min H₂ generation demonstrator fed by wood slurry has begun and shall be in operation later in 2010.

FY 2010 Publications/Presentations

1. Emerson, S.C.; Vanderspurt, T.H. Quarterly Progress Report: A Novel Slurry-Based Biomass Reforming Process, DOE Award Number DE-FG36-05GO15042, United Technologies Research Center: East Hartford, CT, July 2009.
2. Emerson, S.C.; Vanderspurt, T.H. Quarterly Progress Report: A Novel Slurry-Based Biomass Reforming Process, DOE Award Number DE-FG36-05GO15042, United Technologies Research Center: East Hartford, CT, October 2009.
3. Emerson, S.C.; Vanderspurt, T.H. Quarterly Progress Report: A Novel Slurry-Based Biomass Reforming Process, DOE Award Number DE-FG36-05GO15042, United Technologies Research Center: East Hartford, CT, January 2010.
4. Emerson, S.C.; Vanderspurt, T.H. Quarterly Progress Report: A Novel Slurry-Based Biomass Reforming Process, DOE Award Number DE-FG36-05GO15042, United Technologies Research Center: East Hartford, CT, April 2010.
5. Vanderspurt, T. H.; Emerson, S. C.; Davis, T.D.; Zhu, T.; Peles, A.; Saitta, S.; She, Y.; Willigan, R. A Novel Slurry-Based Biomass Reforming Process, presentation at the 2009 DOE Annual Merit Review, Arlington, VA, 20 June 2010.

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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, DC, 27 April 2007.