

II.B.1 A Novel Slurry-Based Biomass Reforming Process

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Fiscal Year (FY) 2011 Objectives

- Develop an initial reactor and system design, with cost projections, for a biomass slurry hydrolysis and reforming process for hydrogen (H_2) production from woody biomass.
- 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 H_2 production system will meet the 2012 efficiency and cost targets of 43% lower heating value (LHV) and \$1.60/kg H_2 for a 2,000 ton/day (dry wood) plant.

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

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 H_2 production system will meet the DOE's 2012 Biomass Gasification/Pyrolysis Hydrogen Production energy efficiency and total H_2 cost targets of 43% (based on feedstock LHV) and \$1.60/kg H_2 , 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	1.54 (1.31–2.11)
Total Capital Investment	\$M	150	170 (117–304)
Energy Efficiency	%	43	51.1

FY 2011 Accomplishments

- Demonstrated 100% conversion of wood using an inexpensive base metal catalyst.
- Examined the effect of base concentration on liquid phase reforming H_2 selectivity and yield.
- Developed a promoted Ni catalyst that maintains a high selectivity to H_2 with minimal base.
- Elucidated the liquid phase reforming reaction pathways for ethylene glycol over Ni and Pt via atomistic modeling.
- Demonstrated a continuous flow H_2 production system for 1 wt% wood at 50 g min⁻¹.



Introduction

This project is focused on developing a catalytic means of producing H_2 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 H_2 in that the carbon dioxide produced from the process can be used in the environment to produce additional biomass. For economically viable production of H_2 , 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 (K_2CO_3), 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 H_2 , while the retentate, including methane is used as fuel in the proposed plant.

Results

The economics of the alkali hydrolysis-based plant design using Ni-based catalysts were updated using the latest version of the H2A tool from the DOE with input from HYSYS plant models. For all cases, a Pd membrane-based separator was used to produce >99.9999% H_2 from the process for fuel cell use. For the baseline economics, the H_2 was then compressed from atmospheric pressure up to a pipeline delivery pressure of 300 psia. The use of a H_2 compression system was a more economical investment compared to using a larger Pd membrane separator operating with a 300 psia back pressure. However, the electrical demands of the plant increase significantly due to the compression system.

There were several assumptions common to the HYSYS/H2A model analyses. The wood feedstock price was set at \$41/ton to keep with the DOE's cost target basis, although realistic feedstock prices will be higher. The cost of K_2CO_3 feed for the plant was set at \$900/ton and the design assumed that 95% of the K_2CO_3 will be recycled within the system. The reforming catalyst was assumed to be equivalent to Raney Ni at a cost of \$20/lb with catalyst replacement

occurring every three years. The reformer liquid residence time was fixed at 16 minutes with a catalyst to wood mass ratio set at a very conservative 20.

In general, the hypothetical 2,000 dry ton per day biomass plant can be run in three different modes. Table 2 shows the summary of the techno-economic modeling results compared to the DOE targets. The first of these modes would use an inexpensive fuel source, such as natural gas, to provide the heat required to operate the endothermic hydrolysis, reforming, and H_2 separation processes. The second mode of operation assumes that the plant is operated to achieve "carbon neutrality" in terms of CO_2 emissions, not counting the secondary emissions that come from electricity provided from the grid for H_2 compression. Instead of using inexpensive fossil fuels to provide the heat required for the plant, the retentate stream from the membrane separator, which contains H_2 , is burned to produce heat. This carbon neutrality comes at a cost both in terms of the H_2 cost, but the efficiency as well, as H_2 that could be delivered from the plant is diverted to heat production instead. The final mode of operation assumes that the plant is operated in a "carbon neutral; electric grid independent" mode. To achieve electric grid independence, the electrical demand from the H_2 compression system was reduced to the point that electricity generated from expanders in the plant could provide all the power needed. As a result, the delivery pressure of the H_2 was also reduced to 44.09 psia. The cost of H_2 in this scenario does not change relative to the "carbon neutral" mode, but the capital costs are lowered and the plant efficiency is reduced.

First principles atomistic modeling was previously used to gain an insight into the factors that control the activity and selectivity toward H_2 production by ethylene glycol reforming on Ni catalysts. Ethylene glycol was chosen as a model compound due to its oxygen bonding to adjacent carbons

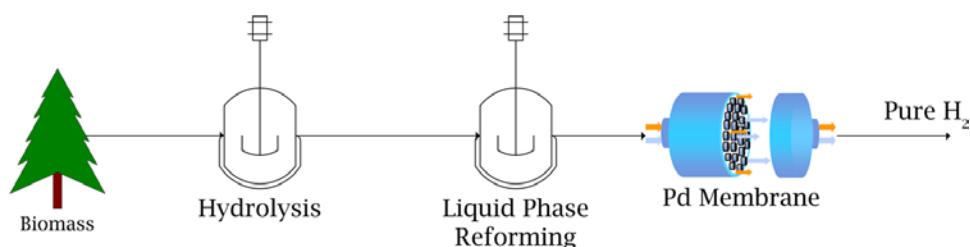


FIGURE 1. The UTRC Approach to Biomass Slurry Reforming

TABLE 2. Technoeconomic Modeling Results for Different Modes of Operation for a 2,000 Dry Tons of Wood per day Plant Compared to the DOE's Technical Targets for Biomass Gasification/Pyrolysis Hydrogen Production

Characteristics	Units	2012 Target	Natural gas fuel mode	Carbon neutral mode	Carbon neutral, electric grid independent mode
Hydrogen Cost (Plant Gate)	\$/gge	1.60	1.27 (1.05–1.84)	1.54 (1.31–2.11)	1.54 (1.31–2.11)
Total Capital Investment	\$M	150	188 (116–370)	170 (117–304)	164 (117–283)
Energy Efficiency	%	43	56.3	51.1	46.1

which represents some fragments of biomass. The schematic diagram of reforming pathways for ethylene glycol on Ni is depicted in Figure 2. 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 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 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.

To further investigate the impact of base to wood ratio on H₂ yield and selectivity, batch, single-step hydrolysis and reforming experiments were performed at EERC. The experiments were performed using a standard, unmodified

Raney nickel catalyst and potassium hydroxide base in EERC's 7.6-L autoclave system with a constant wood concentration of 8 wt%. The H₂ yield and H₂ selectivity results for the experiments are summarized in Figures 3 and 4, respectively. Consistent with previous predictions from atomistic and thermodynamic modeling for ethylene glycol, as well as batch wood reforming experiments performed at UTRC, increasing the base to wood ratio increased the selectivity of the process toward hydrogen production versus methane. However, the higher base levels decreased the H₂ yield, most likely favoring organic acid formation over gas production.

Earlier testing work used Pt-based catalysts before switching to less expensive Ni-based catalysts, and there is current interest for liquid phase reactions using precious metals. Thus, first principles atomistic modeling was used to understand the differences in reaction mechanisms. A schematic diagram of the reforming pathways for ethylene glycol on Pt is depicted in Figure 5. For ethylene glycol on the Pt surface, the first steps after adsorption are

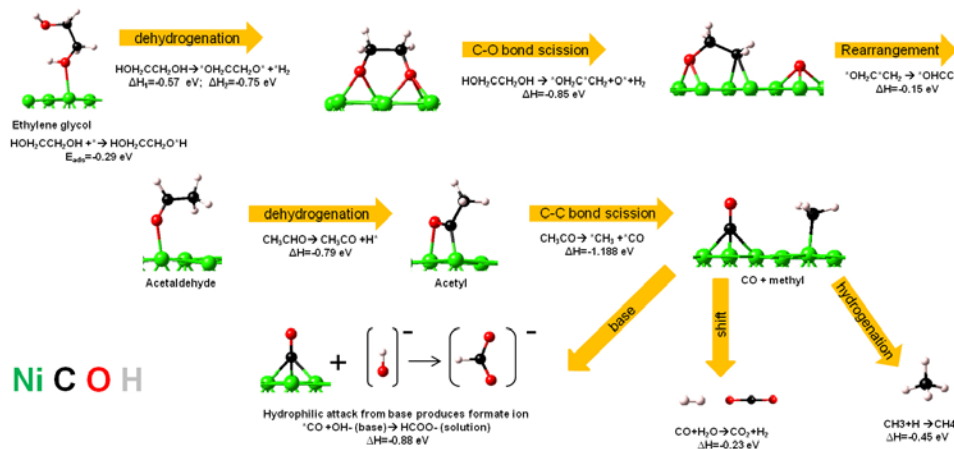


FIGURE 2. Atomistic modeling analysis of the reforming of ethylene glycol over Ni showing the intermediate reaction steps and the reaction enthalpies of their formation.

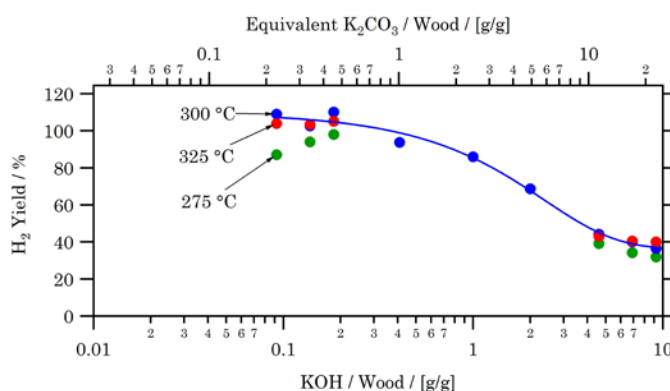


FIGURE 3. Impact of KOH to wood ratio on the H₂ yield with Raney Ni of 8 wt% hybrid poplar in a batch reactor. Also shown on the chart is the equivalent K₂CO₃ to wood ratio.

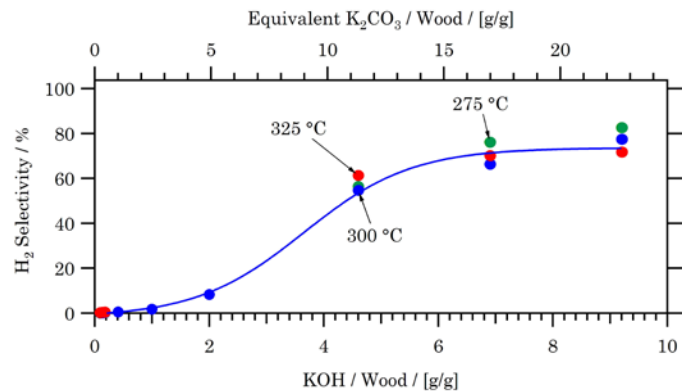


FIGURE 4. Impact of KOH to wood ratio on the H₂ selectivity with Raney Ni of 8 wt% hybrid poplar in a batch reactor. Also shown on the chart is the equivalent K₂CO₃ to wood ratio.

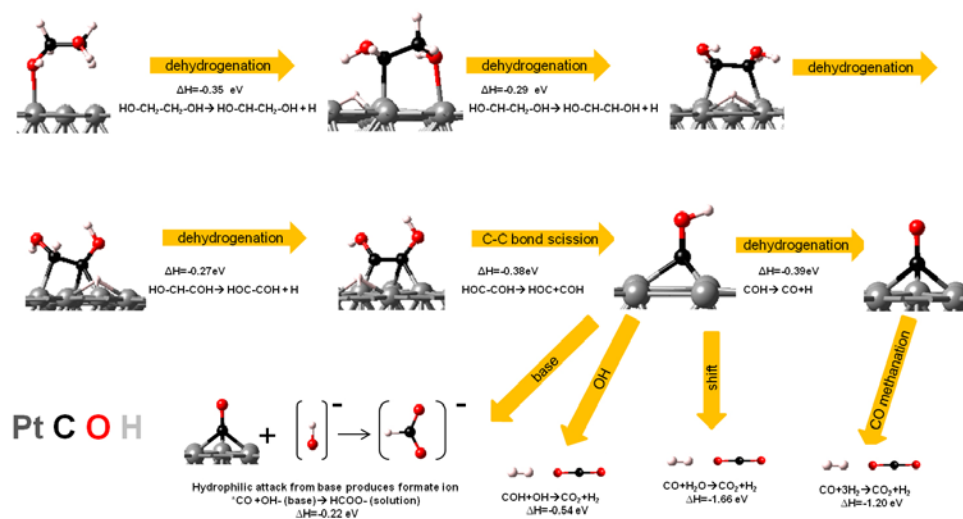


FIGURE 5. Atomistic modeling analysis of the reforming of ethylene glycol over Pt showing the intermediate reaction steps and the reaction enthalpies of their formation.

dehydrogenations. Unlike Ni catalysts, Pt appears to prefer C-C breaking rather than C-O breaking as the first step. As a result, the dehydrogenated species does not go through an ethylenedioxy intermediate as is the case with Ni, but rather undergoes a direct C-C bond scission which results in two COH species. The resulting COH groups can undergo a direct reaction with OH⁻ from the base to form CO₂ and H₂. Alternatively, the COH group can dehydrogenate further to a CO surface species which can react with hydrogen to form methane or be shifted in water to CO₂ and H₂ as happens with Ni. Also similar to the Ni case, the CO can be converted to a formate ion in solution through hydrophilic attack in a basic environment.

These modeling results offer an explanation as to why Pt-based catalysts favor reforming to H₂ while Ni prefers to form methane. Ni-based catalysts prefer to break C-O bonds, which result in both the formation of a methyl group and a CO. Pt-based catalysts prefer to break C-C bonds, resulting in only CO species. The increased preference toward CO species most likely leads to an increase in hydrogen production over methane.

Based on the successful work with base metal catalysts, the final step of the project was the construction and testing of a demonstration unit for H₂ production. This continuous flow demonstration unit consisted of wood slurry and potassium carbonate feed pump systems, two reactors for hydrolysis and reforming, and a gas-liquid separation system. The technical challenges associated with unreacted wood fines and Raney Ni catalyst retention limited the demonstration unit to using a fixed bed Raney Ni catalyst form. The lower activity of the larger particle Raney Ni in turn limited the residence time and thus the wood mass flow feed rate to 50 g min⁻¹ for a 1 wt% wood slurry. The project demonstrated continuous flow H₂ yields with unmodified, fixed bed Raney Ni, from 63% to 100% with corresponding

H₂ selectivities of 6% to 21%, for periods of several hours. The fixed bed form of the Raney Ni exhibited signs of deactivation which requires further study.

Conclusions and Future Directions

The project showed that it is possible to economically produce H₂ from woody biomass in a carbon neutral manner. However, further development work is required before this process can be commercialized. Some of the key technical areas for future projects are listed in the following.

- Further investigate catalyst kinetics for better reactor sizing.
- Demonstrate >90% base recycle in an integrated system.
- Investigate catalyst durability and higher activity base metal catalysts.
- Wood slurry pump development.
- Integration of a burner unit with the reformer.
- Demonstration of the system on a larger scale.
- Demonstration of the system with power generation (e.g., fuel cell, turbine, or internal combustion engine).

Acknowledgments

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FY 2011 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 2010.

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 2010.

3. Emerson, S.C. Quarterly Progress Report: A Novel Slurry-Based Biomass Reforming Process, DOE Award Number DE-FG36-05GO15042, United Technologies Research Center: East Hartford, CT, January 2011.

4. Emerson, S.C. Quarterly Progress Report: A Novel Slurry-Based Biomass Reforming Process, DOE Award Number DE-FG36-05GO15042, United Technologies Research Center: East Hartford, CT, April 2011.

5. Davis, T.D.; Emerson, S.C.; Zhu, T.; Willigan, R.R.; Peles, A.; She, Y.; Vanderspurt, T.H. Liquid Phase Reforming of Wood Flour to Hydrogen, Presented at the 2010 AIChE Annual Meeting, Salt Lake City, UT November 7–12, 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, D.C., 27 April 2007.