

## II.D.3 A Novel Slurry-Based Biomass Reforming Process

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### Objectives

- Develop an initial reactor and system design, with cost projections, for a biomass slurry hydrolysis and reforming process for H<sub>2</sub> 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 through modeling that the proposed H<sub>2</sub> production system will meet the 2012 efficiency and cost targets of 43% (based on lower heating value, LHV) and \$1.60/kg H<sub>2</sub>.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

- (S) Feedstock Cost and Availability
- (T) Capital Cost 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 through validated models that the proposed H<sub>2</sub> 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 H<sub>2</sub>. 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 Targets for Biomass Gasification/Pyrolysis Hydrogen Production

Characteristics	Units	2012 Target	2008 Current Progress
Hydrogen Cost (Plant Gate)	\$/gge	1.60	1.58
Total Capital Investment	\$M	150	203
Energy Efficiency	%	43	46.6

### 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 46.6%.
- The preliminary economic analysis of the baseline plant design shows that a hydrogen production cost of \$1.58/kg H<sub>2</sub> is attainable.
- Addition of acid and sulfur in the form of KHSO<sub>4</sub> to liquid phase reforming shuts down H<sub>2</sub> production while increasing ethane production.
- Use of a water-gas shift (WGS) catalyst, such as Pt/CeZrO<sub>x</sub>, can promote H<sub>2</sub> production at temperatures <190°C in liquid phase reforming.
- Use of a base, such as K<sub>2</sub>CO<sub>3</sub>, instead of an acid increases liquid phase reforming activity by a factor of three while minimizing char formation.
- Demonstrated production of hydrogen from wood chips in the presence of a catalyst and base.



### 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 basic concept for this project is shown in Figure 1. The initial feed is assumed to be a 10 wt% slurry of ground poplar wood in dilute acid. The acid will hydrolyze the cellulose and hemicellulose in the wood to produce a reformable mixture for the catalyst to be developed during this project. To avoid char formation and to reach hydrogen production goals, an optional hydrogenation step may be needed in conjunction with the hydrolysis step. The reformable mixture will be reacted in the liquid phase over a catalyst to convert the hydrolyzed biomass to hydrogen. A palladium alloy membrane will be used to remove the pure hydrogen, thus limiting methane formation, while the retentate is used as fuel in the proposed plant.

The catalyst development approach is based on an approach used successfully in the past at UTRC to produce a high activity precious metal-based WGS catalyst that had a very low alkane (methane) production rate. This approach, shown in Figure 2, combines catalyst conceptual design, quantum mechanical atomistic modeling, and advanced catalyst synthesis techniques, to determine the best catalyst formulations to focus the synthesis effort on prior to experimentation. Initially, a theoretical catalyst design is proposed to maximize high catalytic activity and selectivity and minimize less desired attributes such as diffusion limitations. Using atomistic modeling tools such as VASP, variations in catalyst formulations can be explored to define the best compositions and structures

on which to focus the synthesis effort. Then, special synthesis techniques can be employed to make only the materials that will show the greatest promise. These materials are then characterized and tested under reaction conditions to feed back information to the design and modeling efforts in an iterative effort that will produce the optimal catalyst for a given process.

## Results

During the last year, the project switched focus from system and economic modeling to catalyst development. The modeling work indicated that reforming conversion could be as low as 75% and still achieve the DOE's 2012 efficiency targets. Also, it was found that the production of alkanes, such as methane, was not detrimental to system efficiency because the alkanes can be burned to produce energy to operate the process. Thus, the techno-economic modeling established boundaries for catalyst performance.

As part of the catalyst development effort, significant atomistic and chemical reaction modeling was performed to identify the best candidate oxide supports for platinum. In parallel, experiments were performed in autoclaves to identify conditions (temperature and acid concentration) where model sugars and sugar alcohols would not form significant amounts of char. Based on these char experiments, glycerol was selected as the first model compound to be used for catalyst activity screening.

Many experiments were performed in a semi-batch, high pressure, liquid phase reactor to establish the activity of different catalyst candidates. As part of this catalyst screening activity, a 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> benchmark catalyst from Alfa/Aesar was also tested. Lack of reproducibility of the reactor results for the 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst resulted in a root cause investigation of both the catalyst and the reactor setup. It was determined that part of the reproducibility issue was due to the benchmark catalyst itself, which lost platinum to the reaction solution, and was mitigated by recalcining the as received material; and part was due to reactor design issue. The reactor design used a nitrogen sweep

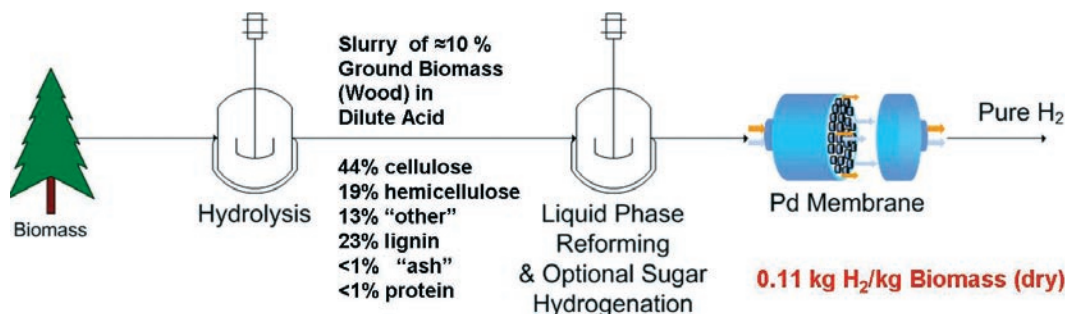


FIGURE 1. The UTRC Approach to Biomass Slurry Reforming

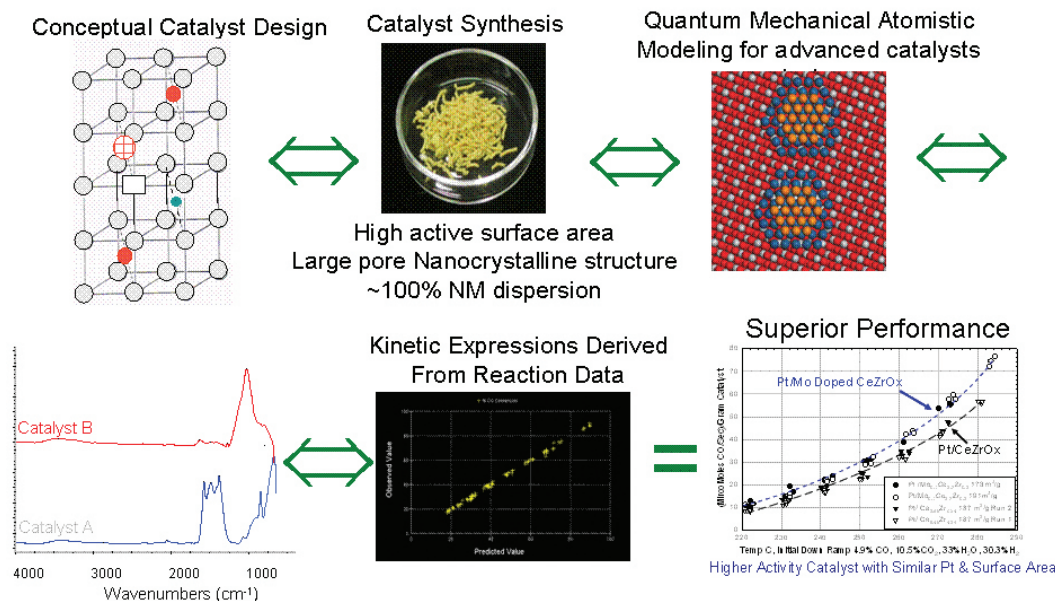


FIGURE 2. The UTRC Catalyst Discovery Approach

gas to remove gas products and impart some mixing, but the low diffusivity of glycerol and small variations in catalyst pellet placement within the reactor contributed to test reproduction issues.

As a result of the root cause investigation, the catalyst screening work was moved to a larger scale, stirred, zirconium autoclave. Proper pretreatment of the 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, combined with increased agitation from the autoclave impeller, resulted in very reproducible activity measurements. The relative activity of many of the catalysts investigated during this project were comparable to that of the 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, but the use of a good WGS catalyst, such as Pt on ceria-zirconia, enables hydrogen production at temperatures <190°C while the baseline alumina catalyst has no hydrogen production below 210°C. Figure 3 shows the main gas concentrations in the nitrogen sweep gas as the temperature is increased in the autoclave using a vendor scaled-up 2% Pt/Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> WGS catalyst. The selectivity toward hydrogen production from glycerol was 93% throughout the temperature range.

In the previous reactor design, the presence of sulfur and acid in the form of KHSO<sub>4</sub> has a small effect on catalyst performance. However, with the larger autoclave and increased agitation, addition of KHSO<sub>4</sub> terminates hydrogen production and increases the production of higher hydrocarbons such as ethane. Figure 4 shows typical gas concentration results in the nitrogen sweep gas for an autoclave run at 240°C with the 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in a 2.5 wt% glycerol solution (0.283 mol/L). After 400 minutes of operation, 0.1 mol/L of KHSO<sub>4</sub> was injected into the autoclave

resulting in a rapid deactivation of the hydrogen production.

At the end of the year, the use of base instead of acid for hydrolysis was investigated. The use of a base, such as K<sub>2</sub>CO<sub>3</sub>, resulted in an increase in hydrogen production rates for the baseline 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst by a factor of three while also minimizing char formation of the glycerol. In addition to the first base experiments, some initial experiments were performed on wood chips in the presence of a catalyst and base resulting in the first direct production from wood in the aqueous phase.

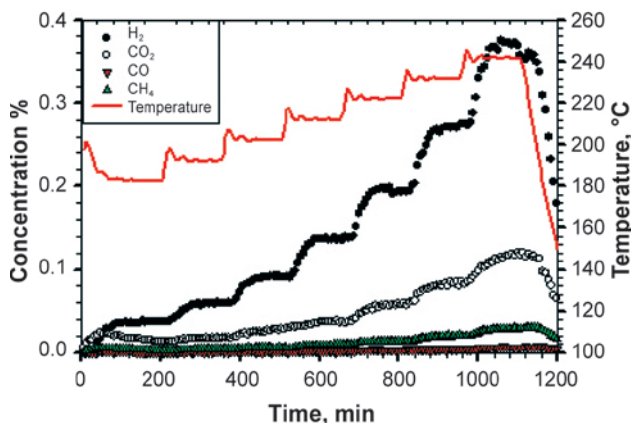
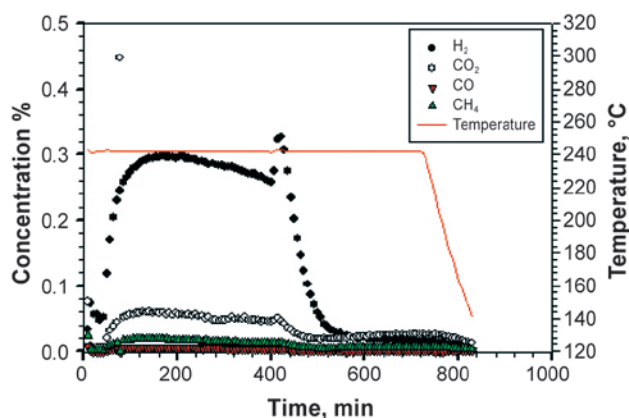


FIGURE 3. Gas concentrations in nitrogen sweep gas as a function of increasing temperature and reaction time produced from liquid phase reforming of 2.5 wt% glycerol (0.283 mol/L) in the presence of a vendor scaled-up 2% Pt/Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> WGS catalyst.



**FIGURE 4.** Gas concentrations in nitrogen sweep gas for an autoclave test at 240°C with a 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in a 2.5 wt% glycerol solution (0.283 mol/L). After 400 minutes of operation, 0.1 mol/L of KHSO<sub>4</sub> was injected into the autoclave resulting in a rapid deactivation of the hydrogen production.

## Conclusions and Future Directions

Based on the results from this last year, the best path for success is to produce hydrogen using base instead of acid hydrolyzed wood. The focus of the project will also move toward the optimization of UTRC's WGS catalysts based on supported noble metals for further catalyst optimization. This type of catalyst has been scaled up commercially and thus can be produced in large-scale for a hydrogen production facility. Catalyst testing on simple compounds like glycerol will transition to the use of more complicated feedstocks, such as cellulose, hemicellulose, and lignin, as well as wood chips. The University of North Dakota will also begin wood hydrolysis studies to provide information for further techno-economic analysis of hydrogen production from biomass.

## FY 2008 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 2007.
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 2007.
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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 2008.
5. Vanderspurt, T. H.; Emerson, S. C.; Willigan, R.; Davis, T.; Peles, A.; She, Y.; Arsenault, S.; Hebert, R.; MacLeod, J.; Marigliani, G.; Seiser, S. A Novel Slurry-Based Biomass Reforming Process, presentation at 2008 DOE Annual Merit Review, Arlington, VA, June 12, 2008.

## 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.