

## II.D.2 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 that the proposed H<sub>2</sub> production system will meet the 2010 efficiency and cost targets of 50% lower heating value (LHV) and \$1.75/kg H<sub>2</sub>.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4.2.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (V) Feedstock Cost and Availability
- (W) 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 that the proposed H<sub>2</sub> production system will meet the DOE's 2010 biomass gasification/pyrolysis hydrogen production energy efficiency and total hydrogen cost targets of 50% (based on feedstock LHV) and \$1.75/kg H<sub>2</sub>.

### Approach

The concept for this project is shown in Figure 1. The initial feed is assumed to be 10% slurry ground poplar wood in dilute acid. This slurry will be hydrolyzed to produce a reformable mixture. Acid and sulfur tolerant catalysts will be developed to reform this mixture. If the aldehyde functionalities of the sugars in the hydrolyzate prevent the advanced catalysts from achieving the required H<sub>2</sub> selectivity and thus the H<sub>2</sub> production goals, hydrogenation of the sugars, lignins, and cellulose fragments mix in the hydrolyzate should increase net H<sub>2</sub> production. Both paths use a Pt-based mixed metal (Pt-MM), mixed metal oxide supported catalyst to convert the hydrolyzed biomass to hydrogen through aqueous liquid phase reforming. A Pd alloy membrane will remove the pure H<sub>2</sub> from the reformer while the retentate will be fuel gas for the proposed plant.

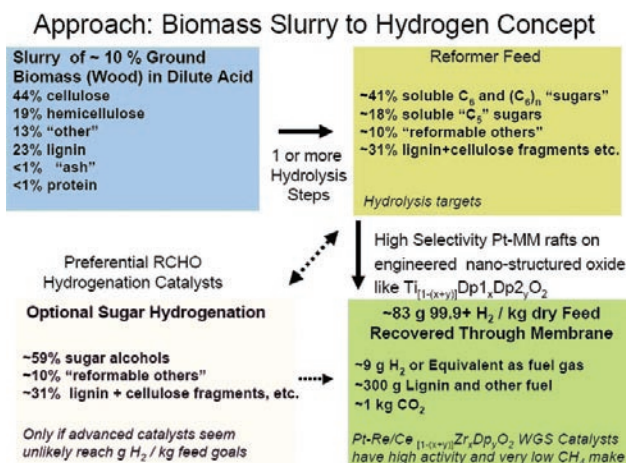


FIGURE 1. The UTRC Approach to Biomass Slurry Reforming

A HYSYS-based model of the proposed plant will be used to determine how active and selective the new catalysts have to be to meet the DOE's 50% LHV efficiency and related cost targets.

The catalyst development approach is based on a paradigm used successfully in the past at United Technologies Research Center (UTRC) to produce a high-activity precious metal-based water-gas-shift (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 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 the Vienna Ab Initio Simulation Package (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 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.

**UTRC Catalyst Discovery Approach**

Atomistic catalyst design, synthesis, characterization, reaction studies & kinetic analysis

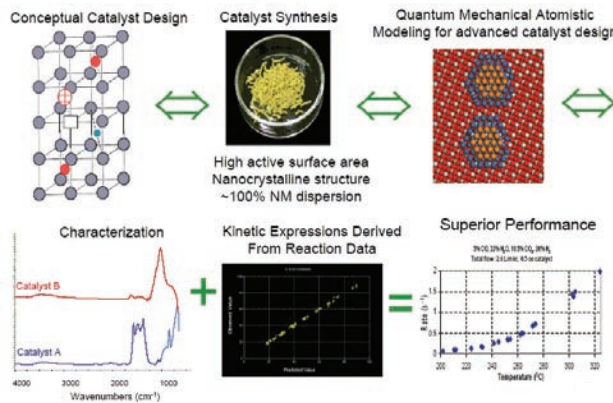


FIGURE 2. The UTRC Catalyst Discovery Approach

**FY 2006 Progress**

This project did not receive funding in FY 2006. DOE plans to restart project funding in FY 2007.

**Conclusions and Future Directions**

The FY 2005 HYSYS model of the proposed plant (Figure 3) that identified the key plant metrics (Table 1) shows that the DOE's 50% LHV efficiency targets (LHV High Purity H<sub>2</sub> Out/LHV Raw Biomass In) can be met if the reformable biomass is converted to H<sub>2</sub> at 94% selectivity and >95% of the hydrogen produced is recovered. As soon as funding is received: 1) the economic phase of this model will be completed to support a go/no go decision, 2) assuming a "go"

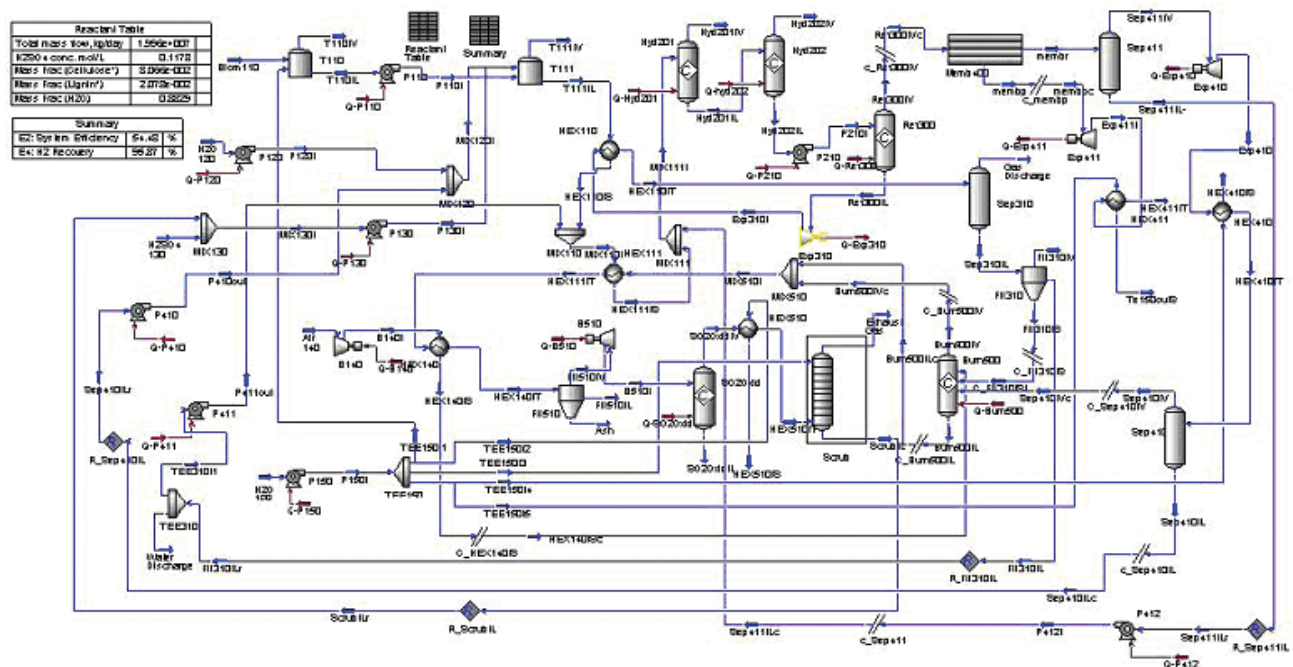


FIGURE 3. Simulation Flowsheet Diagram of the Proposed Biomass Reforming Plant from HYSYS

**TABLE 1.** Key Results Summary from HYSYS Modeled Baseline Biomass Reforming Plant Design

Key plant metric	Value
System efficiency	54.5%
Hydrogen recovery	95.9%
Mass flow rate of hydrogen exiting plant	$2.22 \times 10^5$ kg/day
Hydrogen produced per dry mass of biomass	0.111 kg H <sub>2</sub> /kg biomass (dry)
Mass flow of biomass (dry)	$2 \times 10^6$ kg/day
Percent water in biomass feed	50%
Percent reformable biomass (e.g., cellulose) in biomass feed (dry basis)	75%
Percent lignin in biomass feed (dry basis)	25%

decision, the remaining project will be replanned based on available funding and time. The replan may include: a) catalyst modeling and model validation, b) preparing and evaluating with model compounds the initial family of hot acid insoluble Pt alloy/mixed metal oxide supported catalysts, and c) wood hydrolysis tests to prepare FY 2008 reformer feed for lab and future larger scale tests.

### FY 2006 Publications/Presentations

1. Y. She, S. C. Emerson, and T. H. Vanderspurt, Modeling and Simulation of Hydrogen Production from Biomass through Hydrolysis and Liquid-Phase Reforming Processes, 231<sup>st</sup> ACS Meeting, Atlanta, Georgia, March 26–30, 2006.