

## Hydrogen from Biomass - Catalytic Reforming of Pyrolysis Vapors

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### Objectives

- Demonstrate the production of hydrogen from biomass pyrolysis integrated with catalytic steam reforming and prepare for scale-up of the system to greater than 500 kg H<sub>2</sub>/day by 2009.
- Improve the efficiency of the system, including the reformer, and the use of appropriate catalysts to reduce the cost to below \$2.90/kg H<sub>2</sub> by 2009.
- Demonstrate the use of a variety of feedstocks so that significant quantities of hydrogen can be made from biomass.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- E. Control and Safety
- F. Feedstock Cost and Availability
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology
- Z. Catalysts
- AD. Market and Delivery

### Approach

- Support DOE funded partners to demonstrate the integrated pyrolysis/reforming process using agricultural residues (peanut shells) as feedstock; document mass balance and catalyst performance in a long-duration test.
- Validate the yields and throughputs obtained in the bench-scale system so that information can be used for techno-economic analysis of the process and for the design of the future scale-up of the process, which will begin in FY 2004 at a scale of 250 kg H<sub>2</sub> produced/day.
- Facilitate the addition of unit operations for use in a demonstration that will use H<sub>2</sub> to produce electricity and fuel vehicles such as buses.
- Work with interested parties to extend the applicability of the work to other geographical locations.
- Contribute state-of-the-art chemical analysis and process control so that the small-scale systems can be run with high confidence of safety and reliability.

## Accomplishments

- Developed gas filtration unit operation that solved the problem of plugging the distribution plate with entrained char.
- Provided technical support of the reformer installation in Blakely, Georgia, where the system was run for 100 hours.
- Filed a provisional patent that incorporates biomass conversion to hydrogen with a co-product of carbon-based soil amendment system.
- Supported partnership development in other areas of the country so that the results can be deployed when ready.

## Future Directions

- Develop the Phase 3 system design that will include better heat management in the pyrolyzer and reformer and will add a condenser, compressor, and pressure swing adsorption (PSA) system to the gas conditioning system.
- Initiate tests necessary to develop a circulating fluidized bed reforming process.
- Develop process control systems that will facilitate the cost-effective development of safety engineering for small-scale biomass-to-hydrogen systems.

## Introduction

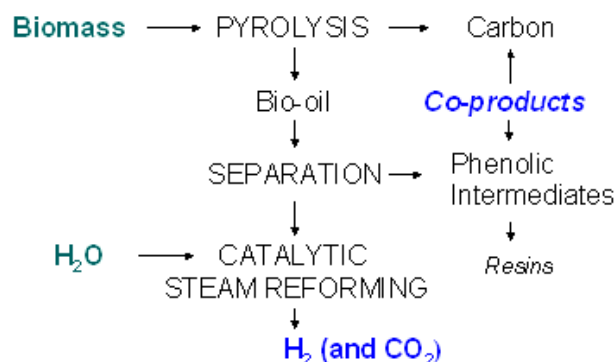
The goal of this work is the production of renewable hydrogen from agricultural residues at a comparable cost to existing methane-reforming technologies by 2015. Near-term production of renewable hydrogen from biomass requires a co-product strategy to compete with conventional production of hydrogen from the steam reforming of natural gas. The processing of pyrolysis co-products from the production of activated carbon is one possible path to demonstrate such a strategy.

The original concept was that the pyrolysis oil could be separated into two fractions based on water solubility. The water-soluble fraction would be used for hydrogen production, and the water insoluble fraction could be used in adhesive formulations. The bio-oil can be stored and shipped to a centralized facility for conversion to hydrogen via catalytic steam reforming and shift conversion. Although the adhesive byproduct option remains viable, commercial deployment opportunities are still not near-term. Hence, other opportunities had to be developed based on the co-product strategy. The conversion of biomass to activated carbon is an alternative route to hydrogen with a valuable co-

product, as outlined in Figure 1. A third option is converting the charcoal into carbon-based fertilizers. In those two options, the volatiles produced in the pyrolysis step can be converted to hydrogen. This is a near-term possibility for deployment. Slow pyrolysis is used in the first step of the activated carbon process to optimize the yield of charcoal and organic vapors.

## Approach

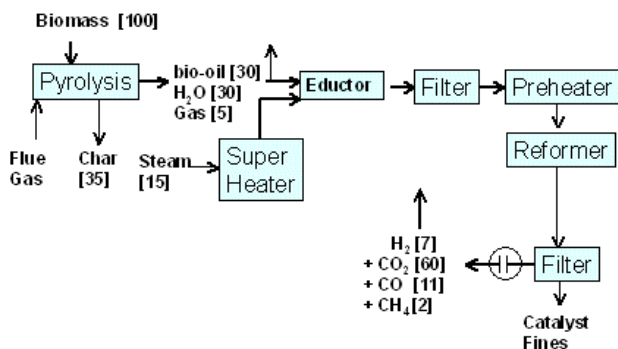
A schematic of the system is shown in Figure 2. Pelletized peanut shells were fed to a cross-draft,



**Figure 1.** Biomass to Hydrogen Based on Pyrolysis with a Co-Products Strategy

moving-bed pyrolysis reactor heated by propane combustion gases. Superheated steam was used to reduce a fraction of the vapors through a bag-house filter to remove char fines and then to a preheater before the reformer. Pelletized peanut shells were fed at a rate of 50 kg/hr to the pyrolysis reactor, which was controlled so the exit gas temperature was 500°C. Using a helium tracer, it was determined that 20% of the total gaseous products from the pyrolyzer were reduced in the steam flow to the reformer. Before reforming, the steam/vapor stream entered a preheater that raised the gas stream temperature to 650°-700°C.

The catalytic fluid bed reformer was fed with up to 5 kg/h of pyrolysis vapor. The maximum allowable operating temperature and pressure are 900°C and 140 kPa, respectively. The reformer is equipped with internal and external cyclones for disengaging catalyst particles, instrumentation, data acquisition, and safety features (alarms). Commercial nickel-based catalyst ground to particle sizes of 300-500  $\mu\text{m}$  was used in the reactor. The catalyst is fluidized using superheated steam, which is also a reactant in the reforming process. The cyclones capture both fine catalyst particles and solid carbon generated by gas-phase pyrolysis of the vapors that may occur in competition with the catalytic steam reforming. The Inconel reactor with a perforated distribution plate is placed inside a three-zone electric furnace to maintain the reactor at the desired temperature during the endothermic steam reforming operation. The reformed products flow through the spray scrubbers and a cold wall condenser before passing through a coalescing filter to remove aerosols.

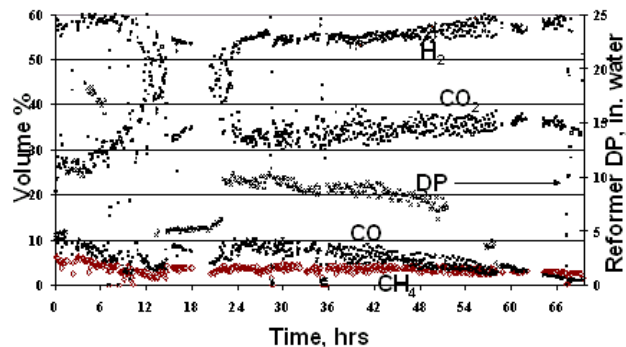


**Figure 2.** Diagram of Process as Performed for the 100-hour Duration Run

## Results

The purpose of the 100-hour run was to reform the whole pyrolysis vapors in the 30-cm catalytic steam reforming fluid bed reactor. The more chemically stable, lignin-derived phenolics are more likely to coke on the nickel catalyst. Prior runs in the 5-cm reformer have used only the aqueous carbohydrate-derived fraction of pyrolysis oil.

Figure 3 shows the product gas composition ( $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{CH}_4$ ) and the differential pressure (DP) across the reformer bed over the first 70 hours of the 86 hours that the reformer was on line. Periods where the reformer was taken off line, a total of 16 hours, are not included in the figure. The final 16 hours are not shown in Figure 3, since the plugging of the filter before the eductor made the system unstable. The build-up of char across the filter also caused the gradual decrease in DP across the reformer bed, as shown in Figure 3. The composition of the gas indicates that the yield of hydrogen from this agricultural residue feedstock is approximately 90% of maximum. Additional optimization of process conditions should result in somewhat higher yields (note that, in a commercial operation, the remaining  $\text{CO}$  could be converted to  $\text{CO}_2$  and additional hydrogen using conventional water-gas shift processing). In these tests, the gas product stream was flared. No breakthrough of pyrolysis products was noted, and the methane level, which is a sensitive indicator of catalyst activity, did not increase. The significant finding here is that the lignin-derived pyrolysis products were reformed completely. The changes in product gases were due



**Figure 3.** Product Gas Composition ( $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{CH}_4$ ) and Differential Pressure (DP) Across the Reformer Bed

to a systematic decrease in mass flow to the bed due to an increase in pressure drop across the hot gas filter. This build-up of particulate matter was unexpected, but the change in product gas composition indicates better performance. The increase in hydrogen yield and decrease in relative yield of both CO and CH<sub>4</sub> were the results of effectively decreasing the weight hourly space velocity and increasing the steam-to-carbon ratio. We achieved a higher rate of conversion most likely by allowing more time for carbon gasification from the catalyst surface.

### **Conclusions**

- The steam reforming of biomass pyrolysis vapors and liquids, when integrated with the production of high value products, is a promising near-term approach to the production of renewable hydrogen. This approach will be applied in Georgia at a plant that makes activated carbon from peanut shells and has pyrolysis by-products available for conversion. The key technical goal for the run is to obtain preliminary performance data on the catalyst, especially physical attrition and deactivation.

- In the next phase, the reactor will be run for 1000 hours with additional gas stream processing included. The hydrogen that is produced will be separated from CO and CO<sub>2</sub> using pressure swing adsorption. The purified hydrogen will be mixed with natural gas and used in engine demonstrations. Other agricultural residues and deployment logistics are being evaluated for cost and co-product potential.

### **FY 2003 Publications/Presentations**

"Renewable hydrogen production by catalytic steam reforming of peanut shells pyrolysis products." Robert J. Evans, Esteban Chornet, Stefan Czernik, Calvin Feik, Richard French, Steven Phillips, Yaw D. Yeboah, Danny Day, Shivayam Ellis, Dennis McGee, and Matthew J. Realf. Preprints, ACS Fuel Chemistry Symposium, Boston MA, 2002.

### **Special Recognitions & Awards/Patents Issued**

Provisional Patent, Danny Day and Robert J. Evans, "A process for the combined production of hydrogen, sequestered carbon and a slow release fertilizer from biomass."