VIII.E Renewable Energy

VIII.E.1 Hydrogen from Biomass for Urban Transportation

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Objectives

- Undertake the engineering research and pilot scale process development studies to economically produce hydrogen from biomass such as peanut shells.

Technical Barriers

This project addresses the following technical barriers from the Biomass Gasification/Pyrolysis Hydrogen Production (3.1.4.2.4) and Separations and Other Cross-Cutting Hydrogen Production (3.1.4.2.3) sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- V. Feedstock Cost and Availability
- W. Efficiency of Gasification, Pyrolysis, and Reforming Technologies
- L. Durability
- M. Impurities
- O. Selectivity

Introduction

Biomass can be converted to hydrogen by two distinct strategies: 1) gasification followed by shift conversion, and 2) pyrolysis of biomass to form a bio-oil that can be subsequently converted to hydrogen via catalytic steam reforming and shift conversion. This project uses the latter approach, which has the potential to be cost competitive with current commercial processes for hydrogen production [1]. The process was demonstrated at the bench scale at the National Renewable Energy Laboratory (NREL) using model compounds and the carbohydrate-derived fraction of bio-oil [2, 3]. This approach has several advantages over the traditional gasification technology. Bio-oil is transportable, so the second step (steam reforming) can be carried out at a different location, close to the existing infrastructure for hydrogen use or distribution. The second advantage is the potential for production and recovery of higher-value co-products from bio-oil that could significantly impact the economics of the entire process.

The project has focused on the use of agricultural residues such as peanut shells to produce hydrogen for urban transportation using the pyrolysis-reforming technology. Specifically, a pilot-scale reactor at Eprida Scientific Carbons Inc., a small company in Georgia, that produces activated carbon by pyrolysis of densified peanut shells, was initially used to test the concept. The primary focus of Phases 1 and 2 of the project was to undertake the process development studies in the use of the large quantities of peanut shells produced in Georgia as feedstock for the proposed pyrolysis-steam reforming process. In Phase 1, the reformer unit was designed, constructed and tested. In Phase 2, the pilot-scale pyrolyzer, which had a feed rate of 50 kg/hour, was integrated with the Phase 1 reformer and used to perform a demonstration of the process to convert the off-gas of the peanut-shell carbonization process to hydrogen. The integrated pilot process was successfully tested for 100 hours. In Phase 3 further modifications were made to allow a 1,000-hour long-term performance testing of the catalyst and pilot system. The process could be modified and expanded to run a variety of other agricultural feedstocks and to make a range of alternative products.

Approach

The approach used to conduct the study is based on six main tasks:

- Develop feedstock supply, process economics, and deployment strategies (modeling, extraction and property estimation): Literature data and thermodynamic models were employed to evaluate a large number of organic solvents for the extraction of phenol from aqueous bio-oils. Several good solvents were identified and extractions were carried out on bio-oil samples provided by NREL. Process models for feedstock supply and deployment strategies were developed.
- Design, construct, integrate and test pyrolysis-reformer pilot reaction unit including reactor modifications and shakedown: Modifications in the pyrolyzer and reformer were made and the entire system, including the pyrolyzer, reformer, and analytical instruments were integrated and tested. The pyrolyzer unit achieves its heat requirements through the use of a rich burning natural gas burner. A computer is used to track the temperature and pressure drops across the reactors. Pyrolysis conditions were T at 500°C; P at 10 psig; and feed rate at 50-500 kg/hr pelletized peanut shells. Gas and charcoal exited at about 425°C.
- Long-term catalyst testing: The pilot unit was operated in Phase 2 for 100 hours for the long-term catalyst testing and is being operated for 1,000 hours in Phase 3. Reforming conditions were T at 850°C; P at 6 psig; $H_2O/C = 5$, using a nickel-based (300-500 microns) catalyst. The long-term (1,000 hours) testing of the performance of the catalytic steam reforming in a fluidized-bed (25-250 kg/day H_2 production) is being undertaken.
- Hydrogen separation, storage and utilization: The effort in hydrogen separation initially focused on the use of pressure swing adsorption (PSA) for the separation of the hydrogen from carbon dioxide. After the baghouse and condenser, the reformer gas was to be dried and compressed before being sent to the PSA system. The current design sends the reformer gases directly into an engine for performance testing.

- Environmental and technical evaluation: Develop an environmental and technical evaluation method based on engine tests and analytical monitoring of the process streams. A hydrogen analyzer and a gas chromatograph were set up to continuously monitor online the reformer gas composition and the performance of the reformer bed and the engine run.
- Develop partnerships, collaborations and education and training programs through partnership building and outreach: The project team completed discussions with the University of Georgia (UGA) and moved the pilot unit from Blakely, Georgia to the UGA Bioconversion Center in Athens. The Phase 3 experiments were conducted at the new facility in Athens, Georgia.

Results

This project combined two stages: pyrolysis of biomass to generate bio-oil and catalytic steam reforming of the bio-oil to hydrogen and carbon dioxide. Figure 1 shows the schematic flow diagram of the process, which leads to the production of hydrogen and co-product charcoal.

The flow procedure of the process is: feeder accepts biomass; the pyrolysis unit pyrolyzes the biomass into pyrolysis gas, bio-oil, and char with a temperature around 450°C; char is let out at this stage; before the gas and bio-oil are introduced into catalytic reformer, they are heated to 680°C; in the reformer at 850°C, most of pyrolysis gas is converted to hydrogen, carbon dioxide and water; after

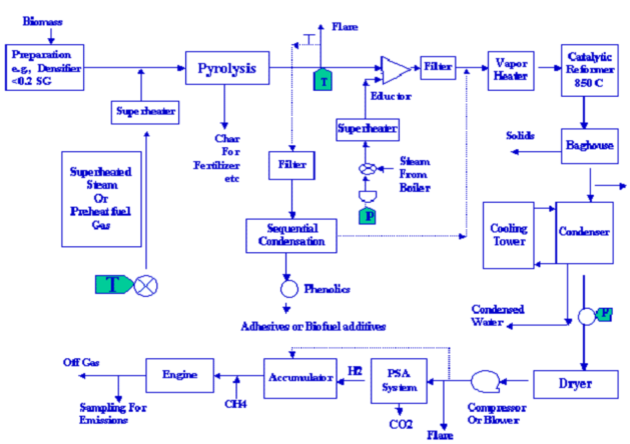

Figure 1. Schematic Flow Diagram of the Biomass Pyrolysis-Reformer Process

condensation and cooling down the water vapor, a mixture of hydrogen and carbon dioxide, along with nitrogen and other gases at normal temperature is produced. Hydrogen can be purified from this mixture by PSA system, then stored and used for engines or other applications. In our experiments, hydrogen was burned at the exit.

The major components of the pilot scale plant include the feeder, superheater, pyrolyzer, filter, vapor heater, catalytic reformer, baghouse, condenser and dryer. The feeder accepts the feedstock (pelletized peanut shell) at a rate of 25-35 kg/hour. The superheater supplies water steam to the pyrolyzer at a rate of 15-25 kg/hour. The temperature and pressure inside the pyrolyzer are maintained at 450°C and 7 psi, respectively. In the pyrolyzer, the biomass was pyrolyzed into charcoal and pyrolysis gas. The baghouse acted as a filter. The vapor heater heats up the pyrolysis gas from 450°C to 680°C to prepare the gas to get into the reformer.

A photograph of the pilot scale hydrogen production plant from biomass via integrated pyrolysis and fluidized catalytic reforming is shown in Figure 2.

Results and Discussion

Pelletized peanut shell was used as the biomasss feedstock. Its composition is listed in Table 1.

Figure 2. Photo of Pilot Scale Hydrogen Production Plant from Biomass

Table 1. Typical Analysis of Peanut Shell Feedstock

Compounds	Component Percentage
Lignin	34.8%
Glucan	21.1%
Extractives	14.2%
Protein	11.1%
Xylan	7.9%
Ash	3.4%
Arabinan	0.7%
Galactan	0.2%
Mannan	0.1%
Others (e.g., free carbohydrates)	0.5%

More than 100 hours operation has been run for this plant. Figure 3 is the temperature and pressure graph of the catalytic reformer during a 100 hour period of operation. At the normal operation, the reformer differential pressure was about 9 in. H_2O and the temperature of reformer bed stayed constant at around 850°C.

The outcome of the pyrolysis process is shown in the Table 2. It includes 32 wt% activated carbon, 32 wt% water, 31 wt% bio-oil and 5 wt% gases. Bio-oil and gases can subsequently be converted into hydrogen

.Figure 4 is the plot of N_2-free basis gas composition vs. time during 100 hours continuous run experiment and Figure 5 is the gas composition obtained during a 20 hours continuous stable run

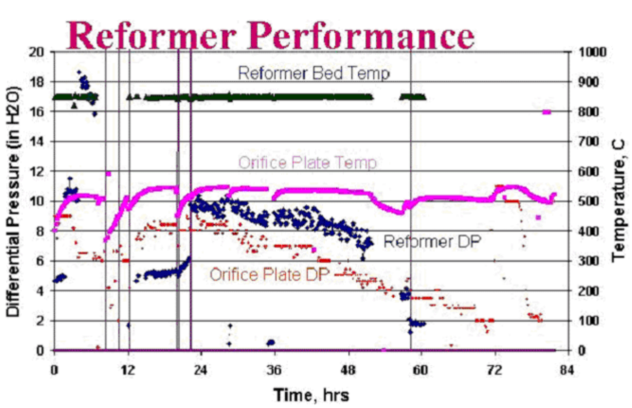

Figure 3. Reformer Performance

Table 2. Typical Product Composition/Yields

Pyrolyzer (Yields)	Percentage
Char	32%
Water	32%
Bio-Oils	31%
Gases	5%

period. The nitrogen was input from outside to form the reforming fluidized bed. Most of the water steam was used to reform the bio-oil and gases into hydrogen; the remainder of the water is the reactant of the process. These figures show that 57% (at dry N_2-free basis) of hydrogen was obtained from the integrated system. Meanwhile, the exit gas still included 31% carbon dioxide, 5% methane and 7% carbon monoxide. Thus, using peanut shells as feedstock, the overall yield from this system is up to 7 wt% hydrogen and 32 wt% charcoal/activated carbon.

An assessment of the technical and economic potential of producing hydrogen from biomass has been made: first, the economics of different scales of feedstock and hydrogen production systems by examining the different options for producing intermediates at different scales and shipping them for further processing; second, modeling the separation of the different fractions of the bio-oil for enhancing their value; and third, modeling the mass and energy balances to enable an overall efficiency of the system to be calculated and to perform heat integration studies.

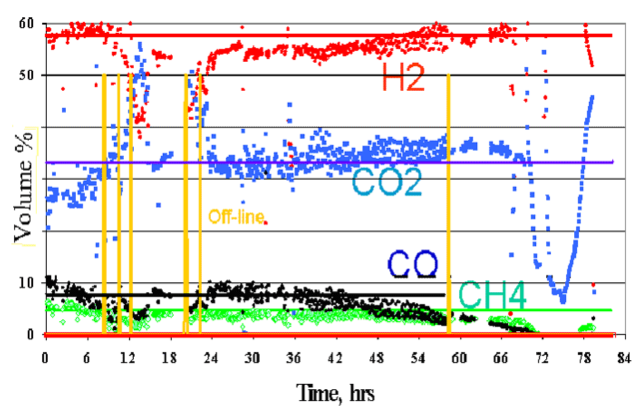

Figure 4. N_2-Free Basis Gas Composition During 100 Hours Continuous Run Experiment

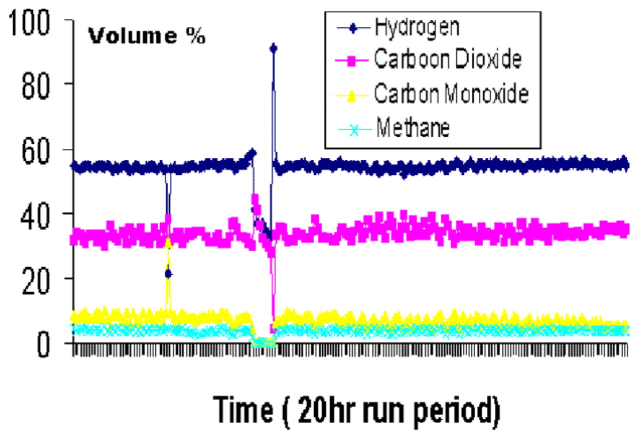

Figure 5. Dry N_2-Free Basis Gas Composition During a Stable Run Period

Capital costs were scaled from Mann's report using 0.84 exponents[1]. This exponent was derived from the three cases presented in the Mann report. Fixed operating costs and working capital were also based on the report. Variable operating costs were estimated from the material balance. For a small facility of daily production rate of 50 tons hydrogen, the total capital investment is $24 million. The feedstock cost $16.5/T and operating cost is $5.9/GJ. The overall yield from this process is 7 wt% hydrogen and 32 wt% charcoal/activated carbon of feedstock (peanut shell). The value of co-product activated carbon is $1.1/GJ and this co-product reduced the selling price of hydrogen. Thus the selling price of hydrogen is estimated to be $6.95/GJ.

Summary of Accomplishments

During the 100 hours of operation, 57% (at dry N_2-free basis) of the hydrogen was obtained from the integrated process, with the pyrolysis of biomass at 450°C and the reforming temperature of pyrolysis gas at 850°C, respectively. Using peanut shells as feedstock, the overall yield from this process is up to 7 wt% hydrogen and 32 wt% charcoal/activated carbon. The preliminary techno-economic analysis indicates that this developed integrated process has the potential of producing hydrogen at the cost of about $7/GJ with an assumed facility of a daily hydrogen production rate of 50 tons.

We have successfully developed an integrated process of pyrolysis of biomass and reforming of the pyrolysis gas for hydrogen production at the pilot scale. The pilot scale plant we built for this process has increased the hydrogen production rate by orders of magnitude, while the yields of hydrogen at the pilot scale and the bench scale are comparable. The developed process shows the potential of being cost-competitive with the conventional means of hydrogen production.

In summary, this project has:

- Continued developing a model of network of process steps to account for feedstock, location, process, and the uncertainties in these factors.
- Completed integration and 100 hours of successful operation of pyrolysis-reformer pilot unit (Phase 2).
- Completed analysis of the data for the 100 hour long-term catalyst testing.
- Developed plans and completed modifications for the 1,000 hour long-term testing of the catalyst and process for Phase 3.
- Currently coonducting the 1,000 hour run pilot operation of the pilot unit.
- Identified potential co-products options including agricultural uses of the carbon product from the pyrolysis.
- Conducted an analysis of the economic potential of producing hydrogen from biomass.
- Developed partnerships and collaborations with potential companies and organizations including the UGA. This resulted in the move of the pyrolysis-reformer pilot unit to UGA's Bioconversion Center.

Future Directions

- Complete and analyze the 1,000-hour long-term study.
- Complete the engine tests for stationary application.

References

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