

## II.A.2 Distributed Bio-Oil Reforming

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## Technical Targets

**TABLE 1.** Progress toward Meeting DOE Distributed Hydrogen Production Targets

Distributed Production of Hydrogen from Bio-Derived Renewable Liquids			
Process Characteristics	Units	2012 DOE Targets	2012 NREL Status
Production Energy Efficiency	%	72	62
Total Hydrogen Production Costs	\$/gge	3.80	4.80–6.60*

\*Based on hydrogen production cost of \$2.80–4.60/gasoline gallon equivalent (gge) assuming bio-oil cost ranges from \$100–\$236/ton. Allowance for compression, storage, and distribution is \$2.00/gge.

## FY 2012 Accomplishments

- Demonstrated hydrogen production by auto-thermal reforming using an integrated bench-scale system including WGS and electrochemical separation.
- Produced hydrogen at 100 L/h on the integrated bench-scale system and obtained a yield of 9.1 g H<sub>2</sub>/100 g bio-oil.
- Demonstrated >30 h of hydrogen production on the integrated bench-scale system.



## Introduction

Renewable biomass is an attractive near-term alternative to fossil resources because it has near zero life-cycle carbon dioxide (CO<sub>2</sub>) impact. The most recent assessment says that more than 1 billion tons of biomass could be available in the United States each year at less than \$60/ton [1]. This cost may increase to \$72/ton when transportation, drying, and grinding are included. This biomass could be converted to 100 million tons of hydrogen, enough to supply the light-duty transportation needs of the United States. This work addresses the challenge of distributed hydrogen production with a targeted total dispensed hydrogen cost of \$3.80/kg by 2012 [2]. Pyrolysis is used to convert biomass to a liquid that can be transported more efficiently and has the potential to be used in automated operation conversion systems [3,4]. “Bio-oil” can then be converted to hydrogen and CO<sub>2</sub> in a distributed manner at fueling stations.

The thermally reactive compounds in bio-oil tend to decompose thermally and may form carbonaceous deposits and/or aromatic hydrocarbons, which are more difficult to convert to hydrogen. Thus, conventional fixed-bed reformers

## Fiscal Year (FY) 2012 Objectives

- By 2012, develop and demonstrate distributed reforming technology for producing hydrogen from bio-oil at \$4.10/kilogram (kg) purified hydrogen.
- Demonstrate integrated performance at bench scale including bio-oil vaporization, partial-oxidation (POX) reforming, water-gas shift (WGS), and hydrogen separation.
- Demonstrate production of hydrogen at a rate of 100 liters per hour (L/h) for 100 hours.

## 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:

- (A) Fuel Processor Capital
- (C) Operation & Maintenance
- (D) Feedstock Issues

have not been proven efficient for this highly reactive feedstock. Reactors that fluidize or circulate the catalyst are much more suited for this application [5] but are not the optimal choice for small-scale and unattended operation. The objective of this project is to develop a system that will provide distributed production of hydrogen from bio-oil at filling stations. To accomplish this we are developing a simple fixed-bed reactor suitable for unsupervised automated operation.

## Approach

This research project is focused on developing a compact, low-capital-cost, low/no maintenance reforming system that will enable achievement of the cost and energy efficiency targets for distributed reforming of renewable liquids. In this project, we are evaluating the following steps in the process:

- **Bio-oil volatilization** using ultrasonic atomization. Blending with alcohol is being used to control the physical and chemical properties of the liquid, primarily to achieve an acceptable viscosity.
- **Heterogeneous auto-thermal reforming of bio-oil derived gas and vapor.** Nickel and precious-metal reforming catalysts have been tested. Platinum has proven to be the most effective.

Earlier experiments were carried out using a micro-scale continuous flow tubular reactor coupled with a molecular-beam mass-spectrometer gas analyzer or a bench-scale quartz-tubular reactor with full mass balances and chromatographic gas analysis. This year, a series of tests was conducted using an integrated bench-scale reactor system that included evaporation, vapor filtration, partial-oxidation reforming, WGS, and hydrogen separation to provide a more complete and realistic assessment of the performance of the process.

## Results

Integrated bench-scale auto-thermal reforming tests were carried out in the system shown in Figure 1. Poplar pyrolysis bio-oil diluted with 10 wt% methanol was fed at 60–120 g/h using a high-pressure syringe pump (Isco) and 60 kHz ultrasonic nozzle (Sono-Tek) to the top of a 37 mm internal diameter (ID), 150 mm long tubular stainless steel evaporation chamber where it was mixed with air and nitrogen. This was placed on top of a 40 mm ID, 250 mm long 2  $\mu$ m stainless-steel mesh filter vessel. Both vessels operated at 400°–600°C. The resulting vapors passed with additional steam into an Incolloy 800 vessel containing a 40 mm by 300 mm bed containing 0.5% platinum-on-alumina reforming catalyst (200 g, BASF) operating at 800°–900°C. The product gas was further processed in a 22-mm

ID by 30-cm fixed bed of high-temperature (350°C) WGS catalyst (190 g, iron/chrome, Sud Chemie), and then on to an electrochemical separator (H<sub>2</sub> Pump), which separated a pure hydrogen stream from the wet, mixed product gas. Water was removed from the remaining product gas in the condenser. The outlet gas flow rate was measured by a dry test meter. The concentrations of CO<sub>2</sub>, CO, and CH<sub>4</sub> in the product gas were monitored by a non-dispersive infra-red analyzer (Model 300 from California Analytical Instruments); the hydrogen concentration was tracked by a TCM4 thermal conductivity monitor. In addition, the gas was analyzed every four minutes by an on-line Varian (Model 4900) micro gas chromatograph, which provided concentrations of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub>. The temperatures in the system, as well as the flows, were recorded and controlled by an OPTO 22 data acquisition and control system. Based on the flows and compositions of the process streams, mass balances as well as the yields of hydrogen generated from the feed were calculated.

Some integrated testing was achieved in which it was found that the WGS reactor reduced the CO concentration in

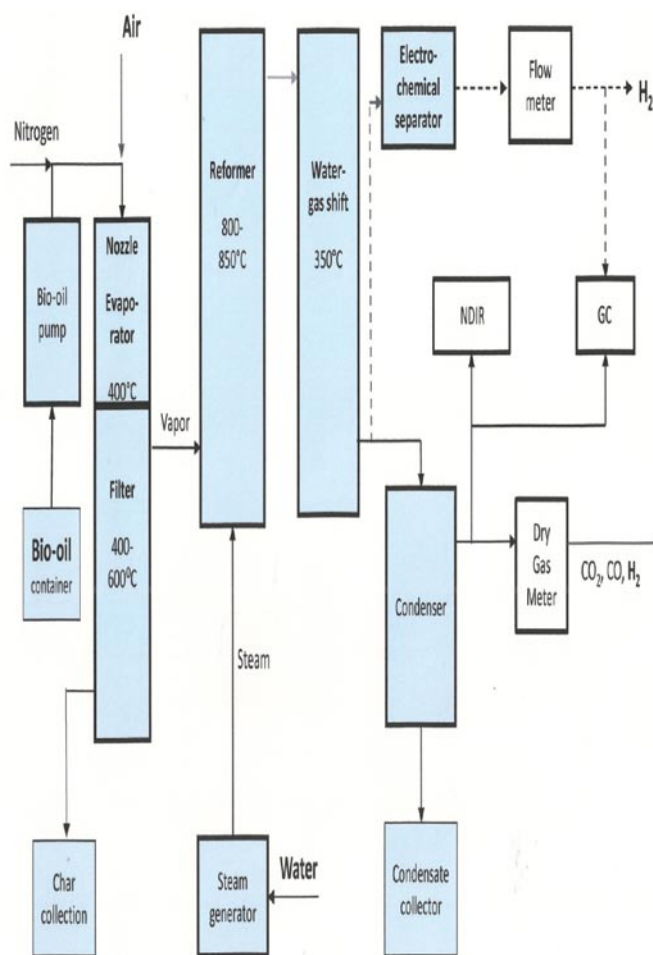


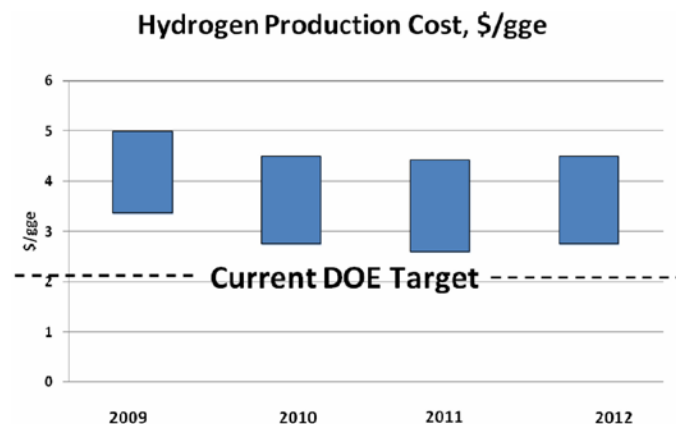
FIGURE 1. Schematic of integrated bio-oil to hydrogen system

the product by about a factor of 4 for at least a short period of time. Also, the hydrogen separator did initially produce a pure hydrogen stream. However, after achieving initially promising yields at the end of FY 2011, it was necessary to start using a new batch of oil. This oil proved more difficult to vaporize, tending to form deposits in the top of the evaporator, leaving more char cenospheres in the filter, and giving more re-deposition of vapor on the filter. It eventually proved possible to get more reliable performance from this oil by raising the evaporator and filter temperatures to about 600°C, and carefully controlling the oil flow rate and the nozzle power and temperature. However, the char yield from this oil was still high, so the best yield obtained from this oil was 9.1 g H<sub>2</sub>/100 g oil versus 10.1 g H<sub>2</sub>/100 g oil for the previous batch. Some data are shown in Figure 2. This experiment was performed at 850°C with an O/C of 1.5 and an S/C of 3.0 at a gas hourly space velocity of 1,950 h<sup>-1</sup>. These data show effective CO reduction by the WGS catalyst.

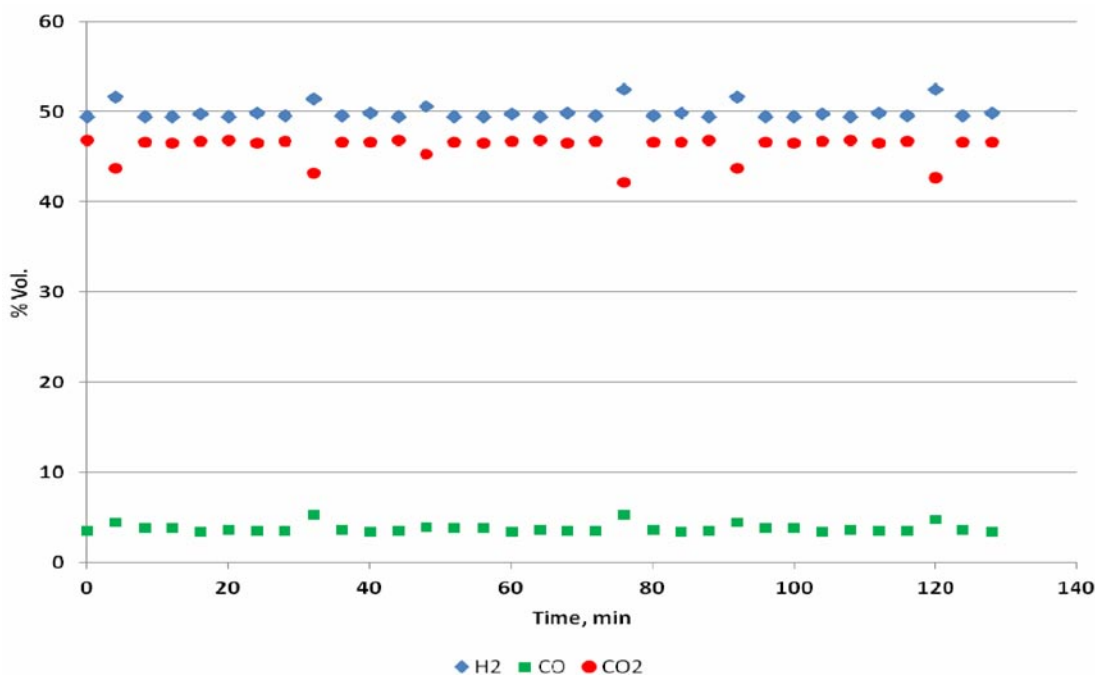
Recent changes in estimated biomass costs have had a large effect on the estimated cost of this process. Previous economic assessments were based on a biomass cost of \$30/ton. Figure 3 shows recent cost estimates for this project; the range of costs is based on different costs for biomass pyrolysis oil (\$100–\$236/ton) from different costs of biomass (\$30–\$72/ton) and different-sized plants (500–2,000 dry tons per day). This shows that although the lower yield from the lower-quality oil used in 2012 had some effect on cost, the largest effect on the cost is the cost of the bio-oil which is about 59% of the hydrogen production cost. In practice, biomass will be available at a range of costs, from about

\$30–\$72/ton, and eventual commercial plant sizes are still uncertain. To meet the DOE targets it would be necessary to have low-cost biomass, a very cost-efficient pyrolysis process and continued progress in development of the POX reforming technology.

In the near future, tests will continue to demonstrate 100 hours of operation on the integrated system. This will



**FIGURE 3.** Hydrogen production cost estimates from 2009–2012 for distributed bio-oil reforming. The hydrogen cost values correspond to bio-oil prices in a range of \$100–\$236/ton. Increase in cost from 2011 to 2012 is due to a lower yield of hydrogen produced from a new batch of bio-oil (contains higher fraction of non-volatile compounds). For a 1,500 kg/day hydrogen plant with \$236/ton oil, the total production cost was estimated to be \$4.60/gge. Compression, storage, and dispensing are assumed to add \$2.00/gge to the total cost of hydrogen.



**FIGURE 2.** Product gas composition from auto-thermal reforming with WGS of poplar bio-oil using BASF 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst

demonstrate the performance of the reforming and WGS catalysts and the hydrogen separator over a longer time period, revealing any effects of organic and inorganic poisons on the components of the integrated system.

Since this work has shown the importance of bio-oil properties to the hydrogen yield, any continuing funding for FY 2013 will be used to explore the dependence of system performance on bio-oil composition, measured as the hydrogen yield and carbon-to-gas conversion. Two different bio-oils and a lignin-free bio-oil will be analyzed to determine elemental and proximate composition as well as average molecular weight (related to volatility). These three liquids will be processed in the bench-scale integrated reforming system to determine process performance data (mass balances, hydrogen yields). Based on those tests, the relationship between the amount of non-volatile fraction and the hydrogen yield will be established. If further additional funding is available, a pressurized system will be constructed to assess how much improvement in reforming kinetics can be achieved at a pressure of about 200 psig (14 bar)—a pressure that is typically used for methane steam reforming. This could reduce reactor size and catalyst use, thus reducing hydrogen production costs.

## Conclusions and Future Directions

- Operation of the integrated bench-scale reactor using 90 wt% bio-oil/10 wt% methanol mixtures produced a hydrogen yield of 9.1 gH<sub>2</sub>/100 g bio-oil, demonstrated hydrogen production at 100 L/h, and demonstrated the initial effectiveness of water-gas shift and electrochemical separation. Except for the gas compression, this system includes all the same basic unit operations as the design for the 1,500 kg/day hydrogen plant.
- For the new batch of bio-oil, the hydrogen yield achieved so far was 9.1 g/100 g bio-oil and the bio-oil carbon-to-gas conversion was >85%.
- It was demonstrated that the composition of the bio-oil can have a substantial impact on the hydrogen yield.
- Tests will continue to obtain 100 hours of operation at 100 L/h hydrogen production.
- If funded, integrated bench-scale tests of pyrolysis oils with different compositions will be carried out in order to determine the effect of bio-oil composition on hydrogen yield.
- If funded, a pressurized bench-scale auto-thermal bio-oil reformer will be constructed and the effect of pressure on bio-oil reforming will be tested.

## FY 2012 Publications/Presentations

1. Czernik, S., “Distributed Bio-Oil Reforming,” 2012 DOE Fuel Cell Technologies Program Annual Merit Review, May 17, 2012, Washington, D.C.

## References

1. Perlack, R.; Stokes, B. (Leads). U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry, U.S. Department of Energy, ORNL/TM 2011/224, August 2011.
2. U.S. Department of Energy. *Fuel Cell Technologies Program, Multi-Year Research, Development and Demonstration Plan*, Section 3.1 Hydrogen Production, 2011 Interim Update. U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy: Washington, D.C.
3. Czernik, S., Elam, C., Evans, R., Milne, T. “Thermochemical Routes to Hydrogen from Biomass—A Review.” In *Science in Thermal and Chemical Biomass Conversion*, Bridgwater AV, Boocock DGB, eds., CPL Press: Newbury, UK, 2006, pp.1752–1761.
4. Evans, R.J., Czernik, S., French, R., Marda, J. “Distributed Bio-Oil Reforming,” *DOE Hydrogen Program FY2007 Annual Progress Report*, 2007.
5. Czernik, S., French, R., Feik, C., Chornet, E. “Hydrogen by Catalytic Steam Reforming of Liquid Byproducts from Biomass Thermoconversion Processes.” *Industrial & Engineering Chemistry Research*. 2002, 41(17), 4209–4215.