II.A.4 Distributed Bio-Oil Reforming

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Objectives

- By 2012, develop and demonstrate distributed reforming technology for producing hydrogen from bio-oil at $3.80/kilogram (kg) purified hydrogen.
- By 2011, develop a prototype that incorporates the key operations: bio-oil injection, catalytic auto-thermal reforming, water-gas shift, and hydrogen isolation.
- Develop the necessary understanding of process chemistry, bio-oil compositional effects, catalyst chemistry, and deactivation and regeneration strategy to form a basis for process definition for automated distributed reforming to meet the DOE targets.
- In Fiscal Year (FY) 2010, demonstrate the process of auto-thermal reforming of bio-oil including a long-term catalyst performance, yields of hydrogen, and mass balances.
- Using a bench-scale reactor system, demonstrate catalytic conversion consistent with $3.80/kg hydrogen.

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

Technical Targets

TABLE 1. Progress toward Meeting DOE Distributed Hydrogen Production Targets

Distributed Production of Hydrogen from Bio-Derived Renewable Liquids			
Process Characteristics	**Units**	**2012/2015 Targets**	**2010 NREL Status**
Total Energy Efficiency	%	66/70	
Production Energy Efficiency	%	72	70
Storage, Compression, Dispensing Efficiency	%	94	
Total Hydrogen Costs Hydrogen Production Costs	$/gge	3.80/2.50	4.48
Hydrogen Production Costs	$/gge		2.59

gge = gasoline gallon equivalent

Accomplishments

- Demonstrated hydrogen production by auto-thermal reforming of bio-oil using the bench-scale reactor system.
- Achieved hydrogen production of 7.3 g/100 g bio-oil (potentially 9.6 g/100 g bio-oil after water-gas shift) with 93% bio-oil to gas conversion.
- Demonstrated 60 hours of steady performance of a research catalyst in several reforming/regeneration cycles.
- Achieved similar performance data for a commercial catalyst.

Introduction

Renewable biomass is an attractive near-term alternative to fossil resources because it has near-zero life-cycle CO_2 impact. Recent assessments have shown that more than 1 billion tons of biomass could be available in the United States each year at less than $50/ton [1]. 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 the target of 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 for automated operation of the conversion system [3,4]. "Bio-oil" can then be converted to hydrogen and CO_2 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 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

Research is focused on developing a compact, low capital cost, low/no maintenance reforming system to 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. We need to control physical and chemical properties of the liquid (viscosity), so blending with alcohol may be necessary.
- Heterogeneous auto-thermal reforming of bio-oil derived gas and vapor. Non-nickel reforming catalysts, including precious metal and potential cheaper oxides and other metals that remain active, need to be examined in application to bio-oil and its partial oxidation products.

Initial experiments were carried out using a micro-scale continuous flow tubular reactor coupled with a molecular-beam mass-spectrometer for analyzing the product gas composition. This year, we conducted a series of tests using a bench-scale reactor system that allowed for a longer-duration steady-state operation and provided more reliable data for mass balance calculations.

Results

The bench-scale auto-thermal reforming tests were carried out in the systems shown in Figure 1. Poplar pyrolysis bio-oil diluted with 10 wt% methanol was fed at 60 g/h using a membrane pump to the top of the 34 mm internal diameter, 45 cm long tubular quartz reactor. The bottom section of the reactor contained a fixed bed comprising 38 g of catalyst (1 wt% Rh, 1 wt% Ce on alumina) prepared at University of Minnesota mixed with 62 g of α-alumina. In the freeboard, the liquid in the form of a very fine mist produced by a 60 KHz ultrasonic nozzle (Sono-Tek) contacted air and steam; steam was produced by a home-made micro-generator. The non-catalytic oxidation was followed

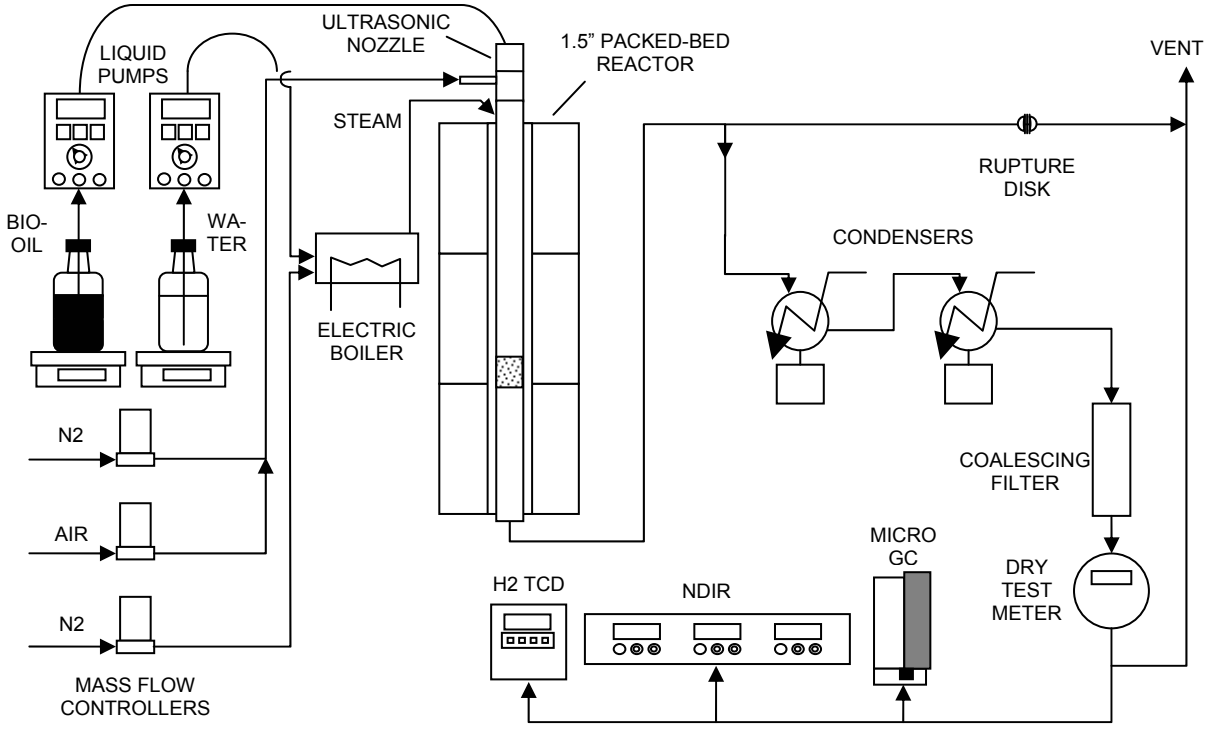

FIGURE 1. Schematic of the Bench-Scale Auto-Thermal Reforming System

by the reactions in the catalytic bed. The optimum conditions that assured a smooth operation, high hydrogen yields and high bio-oil to gas conversion were process temperature of 800-850°C, oxygen-to-carbon ratio O/C=1.5, molar steam-to-carbon ratio S/C=1.6, and methane-equivalent volumetric hourly space velocity equal to 5,200 h^{-1}. The steam excess and some organics were collected in two condensers. The outlet gas flow rate was measured by a dry test meter. The concentrations of CO_2, CO, and CH_4 in the product gas were monitored by a non-dispersive infra-red analyzer (NDIR Model 300 from California Analytical Instruments); the hydrogen concentration was tracked by a thermal conductivity monitor TCM4. In addition, the gas was analyzed every 4 minutes by an on-line Varian (Model 4900) micro gas chromatograph, which provided concentrations of H_2, CO, CO_2, CH_4, C_2H_4, O_2, and N_2. 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.

A series of auto-thermal reforming tests included several production and regeneration cycles. After each hydrogen production test, the catalyst was regenerated by air oxidation and reused in the subsequent tests carried out at the same process conditions. The catalyst performance gradually decreased during the reforming cycle but was restored after every regeneration cycle. Gas composition as a function of time is shown in Figure 2. The average hydrogen production during this time span was 7.3 g/100 g bio-oil. This yield could increase to 9.6 g/100 g bio-oil if CO in the gas were further converted by water-gas shift. The carbon-to-gas conversion was 91-93% with the remaining carbon recovered mostly in the form of solid cenospheres (very light weight hollow spheres). These carbon deposits caused pressure drop increase during the tests and had to be removed by burn-off.

The next step in our research on the process development was the application of a commercial catalyst similar to that prepared by University of Minnesota. Previously, noble metal catalysts provided by Engelhard showed significantly lower performance than the University catalyst in micro-scale tests. This year, we obtained new rhodium and platinum catalysts that are being developed by BASF for commercial applications. These were alumina-based catalysts with a noble metal content of only 0.5 wt% compared to 1 wt% for the University of Minnesota catalysts. The gas composition from reforming bio-oil using BASF rhodium catalyst is shown in Figure 3. This figure shows combined results of two reforming experiments separated by the catalyst regeneration after five hours on stream. Remarkably, the system operation was even more stable than during previous tests using the University of Minnesota catalyst. The catalyst did not show any deactivation during tests but similarly to the experiments described above, the pressure drop due to the carbon deposits was observed. The hydrogen production was 7.4 g/100 g bio-oil with the potential to increase to 10.3 g/100 g bio-oil after completing water-gas shift. The carbon-to-gas conversion was 93% with the remaining carbon forming cenospheres. Though the BASF catalyst was tested for only 11 hours compared to 60 hours for the University catalyst, the results allow us to expect that its performance will remain at the same level.

Conclusions and Future Directions

- Bench-scale reactor tests of catalytic auto-thermal reforming of bio-oil performed using 90 wt% bio-oil/10 wt% methanol mixtures produced hydrogen

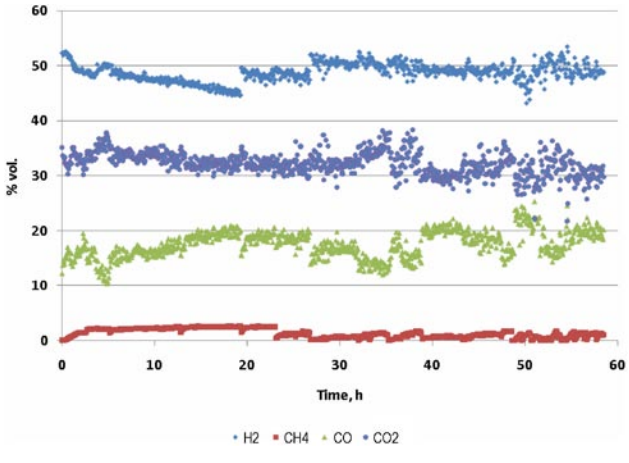

FIGURE 2. Product Gas Composition from Auto-Thermal Reforming of Poplar Bio-Oil using University of Minnesota 1% Rh, 1% Ce/Al_2O_3 Catalyst

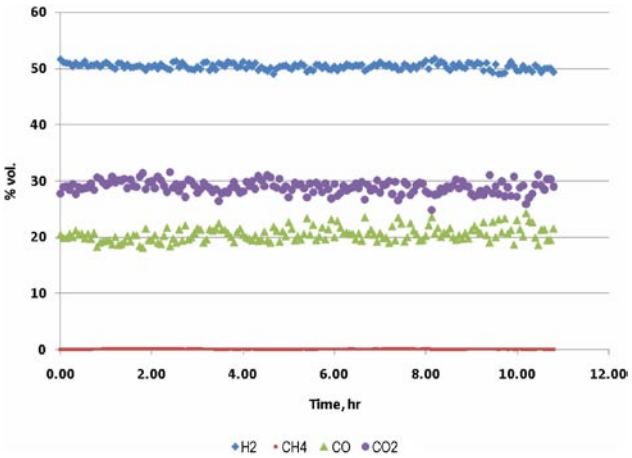

FIGURE 3. Product Gas Composition from Auto-Thermal Reforming of Poplar Bio-Oil using BASF 0.5% Rh/Al_2O_3 Catalyst

yields of 7.3-7.4 g/100 g bio-oil with 91-93% of carbon-to-gas conversion.

- Rh/Ce catalyst prepared at University of Minnesota performed satisfactorily during 60 hours of operation that included reforming and regeneration cycles. Noble metal catalysts produced by BASF also showed very promising performance and will be used extensively in further tests.
- Tests will continue with bio-oil containing more inorganic impurities to assess their impact on the catalyst performance.
- A prototype system including catalytic reformer, water-gas shift reactor, and electrochemical hydrogen separator will be constructed and operated to demonstrate the integrated process performance.

FY 2010 Publications/Presentations

1. Marda, J., DiBenedetto, J., McKibben, S., Evans, R., Czernik, S., French, R., and Dean, A., Non-Catalytic Partial Oxidation Of Bio-Oil To Synthesis Gas For Distributed Hydrogen Production, *International Journal for Hydrogen Energy*, 2009, 34, 8519-8534.

2. Rennard, D., French, R., Czernik, S., Josephson, T., Schmidt, L., Production of Synthesis Gas by Partial Oxidation and Steam Reforming of Biomass Pyrolysis Oils, *International Journal for Hydrogen Energy*, 2010, 35, 4048-4059.

3. Czernik, S. and French, R., Distributed Production of Hydrogen by Autothermal Reforming of Biomass Pyrolysis Oil, presented at ACS National Meeting, San Francisco, CA, March 21–25, 2010.

4. Czernik, S. and French, R., Production of Hydrogen by Partial Oxidation/Steam Reforming of Biomass Pyrolysis Oil, 18th European Biomass Conference and Exhibition, Lyon, France, May 3–7, 2010.

5. Czernik, S., French, R., Penev, M., 2010 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review, June 2010.

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1. Perlack, R., Wright, L., Turhollow, A., Graham, R., Stokes, B., Erbach, D. Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply: A joint U.S. Department of Energy and U.S. Department of Agriculture report DOE-GO-102995-2135 and ORNL/TM 2005-66, April 2005.

2. U.S. Department of Energy. *Hydrogen, Fuel Cells and Infrastructure Technologies Program, Multi-Year Research, Development and Demonstration Plan*, Section 3.1 Hydrogen Production, 2006. 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), 4209-15.