

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

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Projected End Date: Project continuation and direction determined annually by DOE

### Fiscal Year (FY) 2011 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.
- By 2010, demonstrate the process of auto-thermal reforming of bio-oil including a long-term catalyst performance, yields of hydrogen, and mass balances.
- Develop the necessary understanding of process chemistry, bio-oil compositional effects, catalyst chemistry, and deactivation and regeneration strategy to form a process definition basis for automated distributed reforming to meet the DOE targets.

### Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cell Technologies Program's 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	2012/2017 Targets	2011 NREL Status
Production Unit Energy Efficiency	%	72/65-75	62
Total Hydrogen Cost	\$/gge	3.80/<3.00	4.63
Hydrogen Production Cost	\$/gge		2.75

gge – gasoline gallon equivalent

### FY 2011 Accomplishments

- Demonstrated 60 hours of hydrogen production by auto-thermal reforming of bio-oil using a commercial (BASF) 0.5 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in the bench-scale reactor system.
- Demonstrated catalyst regenerability in several reforming/regeneration cycles.
- Optimized process conditions and achieved the hydrogen production of 10.1 g/100 g bio-oil with 90% bio-oil to gas conversion.
- Based on those results, the total production cost in a 1,500 kg/day hydrogen plant, was estimated at \$2.75/gge and the total delivered cost at \$4.63/gge.
- Constructed an integrated bench-scale system for producing 100 L/h of pure hydrogen by reforming bio-oil.



### 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. Recent assessments have shown that more than one 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<sub>2</sub> in a distributed manner at fueling stations.

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 (e.g., viscosity), so blending with alcohol may be necessary.
- Heterogeneous auto-thermal reforming of bio-oil derived gas and vapor. Precious metal catalysts appear to be the most effective in the application to bio-oil and its partial oxidation products.

Early in the project, experiments were carried out using a micro-scale, continuous flow, tubular reactor coupled with a molecular beam mass spectrometer (MBMS) for analyzing

the product gas composition. In the last two years, 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. In the bench-scale auto-thermal reforming tests carried out in 2011 we used two types of commercial (BASF) platinum catalyst: alumina-supported pellets and a monolith, both with 0.5% Pt. The experiments 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 100 g of pelletized catalyst or 55 g of the monolith. In the freeboard, the liquid in the form of a very fine mist produced by a 60 kHz ultrasonic nozzle contacted air and steam; steam was produced by a home-made micro-generator. The excess steam and some liquid organics were collected in two condensers. The outlet gas flow rate was measured by a dry test meter. The concentrations of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  in the product gas were monitored by a non-dispersive infrared analyzer (NDIR Model 300 from California Analytical Instruments); the hydrogen concentration was tracked by a thermal conductivity detector (TCD) TCM4. In addition, the gas was analyzed every four minutes by an on-line Varian (Model 4900) micro

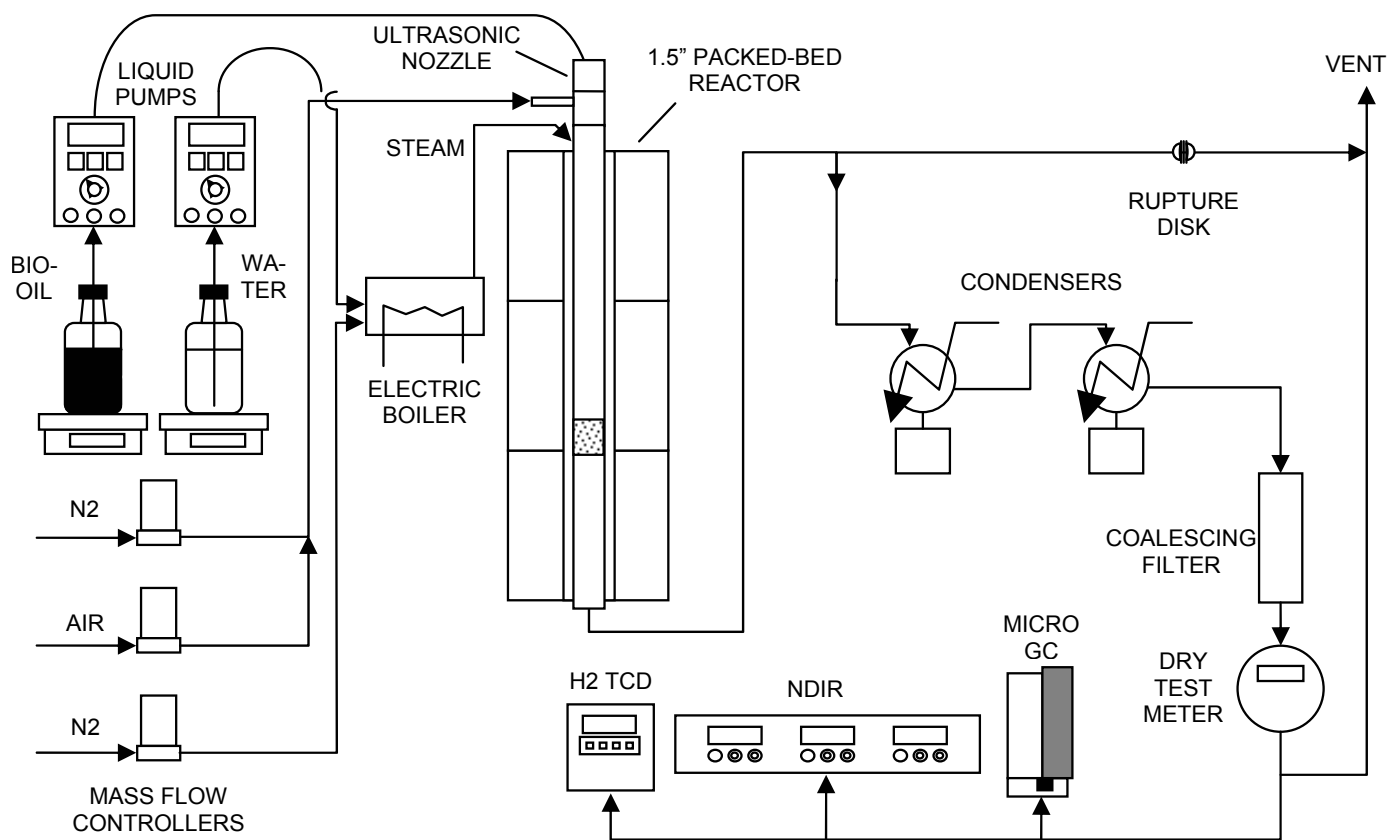


FIGURE 1. Schematic of the Bench-Scale Auto-Thermal Reforming System

gas chromatograph (GC), 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.

Last year, we applied the conditions that assured the optimal system operation in the micro-scale tests: 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 space velocity equal to 5,200 h<sup>-1</sup>. This year, using the 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst from BASF, we varied O/C and steam to carbon ratio (S/C) to find the optimal conditions for maximizing the hydrogen yield while still operating in the auto-thermal range.

### Results

A series of auto-thermal reforming tests included 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. Figure 2 shows the product gas composition as a function of time for one of the experiments. The results of the tests are summarized in Table 2.

Despite a lower carbon-to-gas conversion, the increase in S/C and the decrease in O/C resulted in higher hydrogen yields because a larger part of bio-oil reacted by steam reforming that forms more hydrogen than partial oxidation. The increase in space velocity had a negative impact on both carbon-to-gas conversion and hydrogen yield. Based on those tests, the optimum process conditions that will assure an autothermal operation and high hydrogen yields are temperature 850°C, O/C of 0.9-1, S/C=3, and weight hourly space velocity (WHSV)=0.6. Assuming those reactor conditions and performances, the hydrogen production cost estimated using H2A for a 1,500 kg H<sub>2</sub>/day plant is \$2.75/gge and the cost of delivered hydrogen is \$4.63/gge.

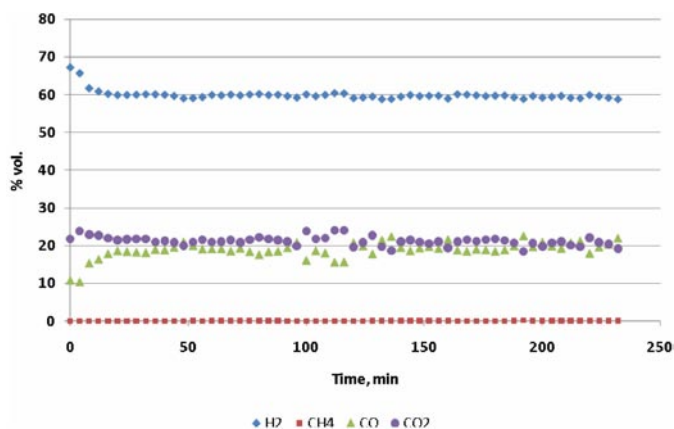


FIGURE 2. Product Gas Composition from Auto-Thermal Reforming of Poplar Bio-Oil Using BASF 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> Pelletized Catalyst

TABLE 2. Hydrogen Yields Produced at Different Process Conditions Using 0.5 Pt/Al<sub>2</sub>O<sub>3</sub> at 850°C

WHSV (g/h bio-oil/g cat)	O/C (mol/mol)	S/C (mol/mol)	Hydrogen yield (g H/100 g bio-oil)	C-to-gas Conversion, %
0.6	0.5	3	10.3	72
	0.89	3	10.1	86
	1.6	1.6	7.0	90
1.2	0.85	2.8	5.9	76
2.4	1.5	3	5.6	80
	0.9	3	4.1	60
4.8	1.3	2.8	4.7	80

The monolith platinum catalyst of nominally the same composition as the pellets did not perform as well as the packed bed. During all the tests, the product gas composition as a function of time (Figure 3) changed more than in the packed bed experiments. Especially, the water-gas shift activity decreased with time that was observed as the increase in the concentration of CO and the decrease of CO<sub>2</sub>. As before, the highest yields of hydrogen were obtained for lower values of WHSV, lower O/C, and higher S/C. However, these yields as well as carbon to gas conversion were lower than those achieved in the packed bed reactor at the same conditions. In the best case, for O/C=1, S/C=5, and G<sub>C1</sub>HSV=2,000 h<sup>-1</sup> the hydrogen yield was 8.5 g/100 g bio-oil and the carbon to gas conversion was 80% compared to respectively 10.1 g/100 g bio-oil and 90% carbon conversion for the packed bed reactor. The reason might be shorter residence time of the bio-oil vapors and especially of the carbon solids in the channels of the monolith than in the packed bed.

The construction of an integrated system for producing 100 L/h of hydrogen by auto-thermal reforming of bio-oil was completed. The main components of the system include

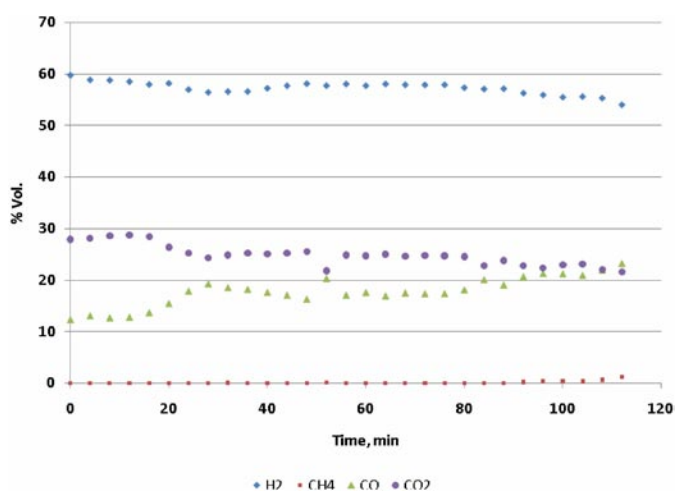


FIGURE 3. Product Gas Composition from Auto-Thermal Reforming of Poplar Bio-Oil Using BASF 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> Monolith Catalyst

a bio-oil evaporator, reforming reactor, water-gas shift convertor, and hydrogen separator.

### Conclusions and Future Direction

- Bench-scale reactor tests of catalytic auto-thermal reforming of bio-oil performed using 90 wt% bio-oil/10 wt% methanol mixtures produced hydrogen yields of 10 g/100 g bio-oil with 90% of carbon-to-gas conversion.
- The optimal process conditions for the bench-scale system are: temperature 850°C, O/C of 0.9-1, S/C=3, and WHSV=0.6 (BASF 0.5%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst).
- The construction of a prototype system including bio-oil evaporator/filter, catalytic reformer, water-gas shift reactor, and electrochemical hydrogen separator was completed. The system will produce 100 L/h of pure hydrogen. The performance of that prototype will be tested in FY 2012 and will help to make a go/no go decision on further process development.

### FY 2011 Publications/Presentations

1. Czernik, S., French, R., Penev, M., 2011 *DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review*, May 2011.

### References

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