

II.E.1 Distributed Bio-Oil Reforming

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Project Start Date: October 1, 2004
Project End Date: September 30, 2013

Technical Targets

Table 1 presents the technical targets for this project.

TABLE 1. Progress towards Meeting DOE Distributed Hydrogen Production Targets

Distributed Production of Hydrogen from Bio-Derived Renewable Liquids			
Process Characteristics	Units	2015 DOE Targets	2013 NREL Status
Production Energy Efficiency	%	70	70
Total Hydrogen Production Costs	\$/gge	5.90	4.26+2.00*

*It was assumed that the allowance for compression, storage, and distribution will be \$2.00/gge.

gge – gasoline gallon equivalent

Overall Objectives

- Develop the necessary understanding of process chemistry, catalyst deactivation and regeneration, and bio-oil compositional effects as a basis to define the process for distributed reforming.
- Demonstrate the technical feasibility for the process of producing hydrogen from biomass pyrolysis oils.

Fiscal Year (FY) 2013 Objectives

- Provide mass balances for auto-thermal reforming of three pyrolysis liquids.
- Show the relation between hydrogen yield and bio-oil composition and identify bio-oil that can deliver 10 g of hydrogen per 100 g of bio-oil.
- Update the H₂A analysis based on the validated process performance results to assess the process energy efficiency and the cost of hydrogen.

Technical Barriers

This project addresses the following technical barriers from the production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (A) Reformer Capital Costs and Efficiency
- (B) Operations and Maintenance
- (C) Biomass Feedstock Issues

FY 2013 Accomplishments

- Demonstrated hydrogen production by auto-thermal reforming of bio-oils generated from three feedstocks.
- Produced hydrogen from two bio-oils at a yield >10 g H₂/100 g bio-oil.
- Calculated a process energy efficiency of 70% and estimated the cost of production at \$4.26/gge.



INTRODUCTION

Renewable biomass is an attractive near-term alternative to fossil resources because it has near zero life-cycle carbon dioxide (CO₂) 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 \$2-\$4/kg H₂ (produced, delivered and dispensed, but untaxed) [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 CO₂ in a distributed manner at or near fueling stations.

The objective of this project is to develop a system that will provide distributed production of hydrogen from bio-oil.

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.

This year, a series of tests was conducted using an integrated bench-scale reactor system that was constructed in the previous year. As shown schematically in Figure 1, the system included the following operations: bio-oil atomization and evaporation, hot vapor filtration, partial-oxidation/steam

reforming, water-gas shift, and hydrogen separation. Such a unit provided more complete and reliable assessment of the process performance results necessary for techno-economic evaluation. The operation of the unit was described in the FY 2012 annual progress report.

RESULTS

In FY 2012 we produced hydrogen from bio-oils produced by fast pyrolysis of oak and poplar wood. This year, in order to evaluate the relation between the hydrogen yield and the feed properties we prepared two more biomass-derived liquids—pine fast pyrolysis bio-oil and the lignin-free fraction of oak pyrolysis bio-oil—and used them in a similar series of reforming tests. We also characterized the physical and chemical properties that can affect hydrogen production for all of those liquids. The four biomass-derived liquids were analyzed to determine the following properties:

- Elemental composition (performed by Huffman Laboratories)
- Water content (Karl-Fischer titration)
- Lignin content (calculated from water content measurements for the whole oil and for the aqueous fraction produced by the water separation process)

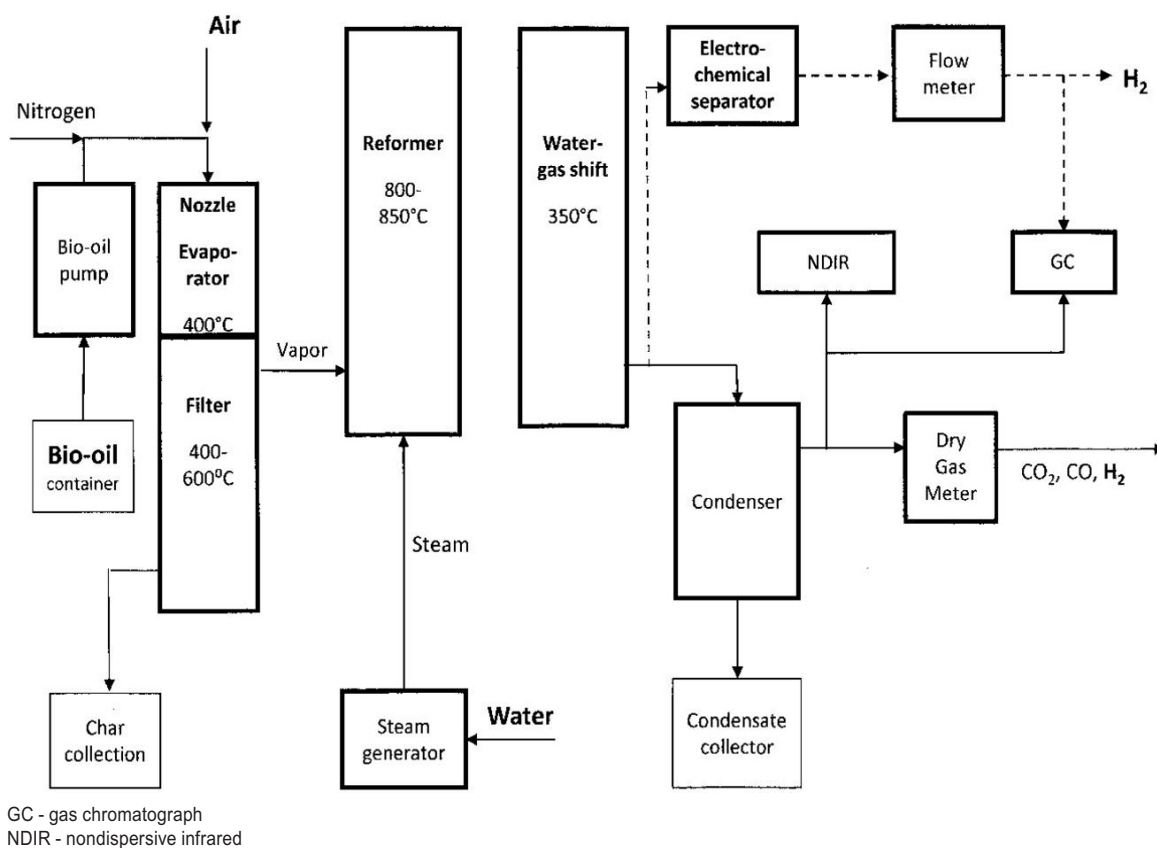


FIGURE 1. Schematic of the Integrated Bio-Oil to Hydrogen System

- Viscosity (rotary viscometer)
- Molecular weight distribution (size exclusion chromatography)
- Surface tension (performed by Kibron/PM Scientific)

Elemental composition of the feedstock sets a limit for a theoretical maximum yield of hydrogen (based on stoichiometric conversion). This yield will be greater for the materials with high carbon and hydrogen content and low oxygen content. Water content mostly affects (reduces) the viscosity of bio-oil and makes it easier to pump and atomize. Lignin, though it has theoretically higher potential for the production of hydrogen, is non-volatile and tends to form carbon deposits in the reactor. The average molecular weight is a measure of the amount of a high-molecular-weight fraction that is difficult to evaporate and, consequently, to convert to hydrogen. The high molecular weight of bio-oils indicates the presence of oligomeric lignin and possibly oligomeric carbohydrates originating from incomplete degradation during fast pyrolysis. Finally, surface tension affects the size of the droplets formed during liquid atomization; the average volume of a droplet is proportional to the surface tension of the liquid. Therefore, a high surface tension reduces the efficiency of liquid evaporation, which is an important stage of our process. Bio-oil characteristics are shown in Table 2.

TABLE 2. Bio-Oil Characteristics

	Oak Bio-Oil	Poplar Bio-Oil	Pine Bio-Oil	Lignin-Free Oak Bio-Oil
Elemental comp.				
C, wt%	44.9	47.4	48.2	12.5
H, wt%	7.2	7.5	7.4	10.0
O, wt%	47.8	45.1	44.3	77.5
Water, wt%	25.3	19.6	22.4	74.6
Lignin, wt%	32.9	38.0	31.2	0
Molecular weight,^a Da	860	670	710	290
Viscosity, cP (25°C)	150	350	200	3.1
Surface tension, mN*m	43	20	30	37
Theoretical hydrogen yield, g/100 g feed	12.6	13.8	13.5	3.8 (15.2)^b

^aWeight average molecular weight

^bPotential hydrogen yield on water-free basis

A series of experiments was carried out in the bench-scale reforming system using two biomass-derived liquids: pine pyrolysis bio-oil and a lignin-free fraction of oak pyrolysis bio-oil. Similar to the previously performed tests with oak and poplar bio-oils, the pine bio-oil was mixed with methanol at a 9:1 ratio, which stabilized the feed and reduced its viscosity. The lignin-free bio-oil fraction was used as is, without the addition of methanol. During these tests the bio-oil/methanol mixture was fed at a rate of 90 g/h and the

lignin-free fraction was fed at 120 g/h. The reformer operated at a temperature of 850°C and the water-gas shift reactor at 350°C, with the atomic oxygen-to-carbon ratio (O/C) in the range of 0.85 to 1.0 and a steam-to-carbon molar ratio (S/C) of 3 to 4. The packed-bed reformer contained 200 g of 0.5% Pt/Al₂O₃ catalyst (BASF) and the water-gas shift reactor was packed with 200 g of a commercial Fe/Cr catalyst (Süd-Chemie). With a pine bio-oil feed rate of 90 g/h the system produced 107 L/h of hydrogen mixed with CO and CO₂ at the composition shown in Figure 2.

The process parameters and the yields of hydrogen produced from the two previously tested bio-oils and the two biomass-derived liquids processed in FY 2013 are summarized in Table 3.

These results show that reforming of poplar and pine bio-oils delivered >10 g H₂ per 100 g bio-oil, while reforming of oak bio-oil and of its lignin-free fraction produced less hydrogen. The lower hydrogen yield obtained from oak

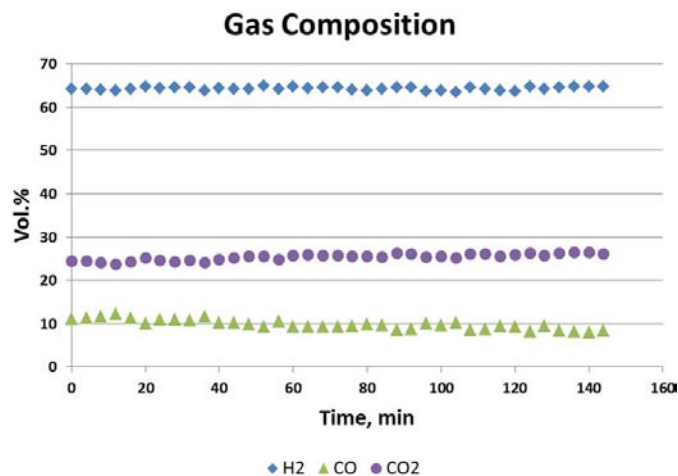


FIGURE 2. Product Gas Composition from Auto-Thermal Reforming with Water-Gas Shift of Pine Bio-Oil using BASF 0.5% Pt/Al₂O₃ Catalyst

TABLE 3. Process Parameters and Hydrogen Yields Produced by Reforming Bio-Oils

Feedstock	VHSV, h ⁻¹	S/C	O/C	C conv, %	H ₂ yield, g/100 g bio-oil
Oak bio-oil	2,100	3.5	1.0	84	9.1
Poplar bio-oil	2,100	3.0	0.9	89	11.0
Pine bio-oil	2,100	2.8	0.85	86	10.5
Oak lignin-free	1,100	4.0	1.5	89	3.0 (12)^a

VHSV – methane-equivalent volumetric hourly space velocity

S/C – molar steam-to-carbon ratio

O/C – atomic oxygen-to-carbon ratio

C conv. – carbon conversion from bio-oil to gas

^aHydrogen yield on water-free basis (lignin-free oak bio-oil fraction contained only 25.6% organic compounds and 74.6% water)

bio-oil, compared to those from poplar and pine bio-oils, resulted from its lower carbon and higher oxygen content, which determined the maximum potential yield as shown in Table 2. In addition, the amount of carbon residue retained in the evaporator was greater for oak bio-oil than for the other liquids tested. This may have resulted from its higher molecular weight, which indicates higher non-volatile material content. Consequently, the carbon-to-gas conversion for the oak bio-oil was less than for the other liquids, which also negatively impacted the yield of hydrogen. The incomplete carbon-to-gas conversion—ranging from 84% to 89% for the different bio-oils—was due to the incomplete evaporation of non-volatile compounds (oligomeric lignin and carbohydrates) in the bio-oils, resulting in the solid residue in the evaporator. Because comparable amounts of the non-volatile material were found in all four bio-oils, the less-effective evaporation of oak bio-oil was most likely caused by its higher surface tension resulting in larger-sized bio-oil droplets generated by the ultrasonic nozzle.

Energy efficiency of the process is defined according to the following equation:

$$\text{Energy efficiency} = \frac{\text{LHV Hydrogen} \times 100\%}{\text{LHVbio-oil} + \text{external process energy}}$$

where LHV is the lower heating value for hydrogen and for bio-oil used in the process. Because our bio-oil reforming process is auto-thermal, the only external energy needed is electricity to operate pumps and compressors; this is estimated at 2.92 kWh/kg H₂ or 10.5 MJ/kg H₂ (H₂A analysis). For the lignin-free bio-oil fraction, external energy is needed to evaporate water added in the separation process; this is estimated at 10.0 MJ/kg H₂.

For the process energy efficiency calculation we assumed that the hydrogen yields in the full-scale system would be the same as those achieved in our bench-scale unit. With the LHV equal to 120.2 MJ/kg for hydrogen and 17.5 MJ/kg for the bio-oil/methanol feed (13.0 MJ/kg for the lignin-free fraction), the energy efficiency for the production of hydrogen from the bio-oils will range from 59% to 70% as shown in Table 4.

Costs of hydrogen production in a 1,500 kg/day plant were calculated for an nth plant in 2007 \$ using the H2A v3 spreadsheet. According to the analysis performed by the NREL/Pacific Northwest National Laboratory techno-economic analysis group for DOE's Biomass Program, the cost of bio-oil was estimated at \$236/ton. In our calculations we used that price for each bio-oil. The results are provided in Table 4.

The energy efficiency and production cost are strongly dependent on hydrogen yield and consequently are the most favorable for the poplar bio-oil and the least favorable for the lignin-free fraction. However, the production of the lignin-free fraction also delivers 6.6 kg of pyrolytic lignin per

TABLE 4. Energy Efficiency and Costs of Hydrogen Production from Different Bio-Oils

Feedstock	Energy Efficiency, %	Hydrogen Production Cost, \$/kg
Oak bio-oil	59.0	4.75
Poplar bio-oil	70.8	4.26
Pine bio-oil	67.8	4.37
Lignin-free oak bio-oil	62.0	5.06 3.74 ^a

^aThis value was calculated assuming a \$200/ton credit for the co-produced lignin fraction.

1 kg of hydrogen. The market price of lignin from pulping processes is in the range of \$200–\$1,000/ton, thus the hydrogen production cost from the lignin-free fraction would be reduced by \$1.32/kg to \$3.74/kg. The pyrolytic lignin fraction potentially can have a much higher value, especially if it is applied as a phenol replacement for adhesive resin formulation—if it sells for half the price of phenol (\$1.4/kg) it could bring a credit of up to \$4.6/kg hydrogen. Considering this, we believe that the integrated production of hydrogen and co-products from bio-oil presents the most attractive scenario and should be thoroughly studied.

CONCLUSIONS AND FUTURE DIRECTIONS

- We identified optimum process parameters for the bio-oil auto-thermal reforming process: temperature 800–850°C, steam-to-carbon ratio 2.5–3.5, oxygen-to-carbon ratio 0.9–1.1, 0.5% Pt/Al₂O₃ catalyst, methane-equivalent space velocity about 2,000 h⁻¹.
- The hydrogen yields depended on both chemical composition and physical properties of bio-oils that were produced from different biomass feedstocks. The lower hydrogen yield obtained from oak bio-oil, compared to those from poplar and pine bio-oils, resulted from its lower carbon and higher oxygen content as well as the lower carbon-to-gas conversion.
- The incomplete carbon-to-gas conversion that ranged from 84% to 89% for the different bio-oils was due to the incomplete evaporation of non-volatile bio-oil compounds (oligomeric lignin and carbohydrates) that formed solid residue in the evaporator. The less-effective evaporation of oak bio-oil was most likely caused by its higher surface tension that resulted in larger-sized bio-oil droplets generated by the ultrasonic nozzle.
- Production of hydrogen from the lignin-free bio-oil fraction may be the most economically favorable process, but that strongly depends on the credit that can be obtained for the lignin fraction of bio-oil, which could be used for the production of adhesives or liquid fuels (by hydroprocessing).

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Czernik, S. “Distributed Bio-Oil Reforming,” 2013 DOE Hydrogen and Fuel Cells Program Annual Merit Review, May 15, 2013, Washington, DC.

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4. Evans, R.J.; Czernik, S.; French, R.; Marda, J. “Distributed Bio-Oil Reforming,” *DOE Hydrogen Program FY2007 Annual Progress Report*, 2007.