

II.A.6 Distributed Bio-Oil Reforming

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Subcontractors:

- Colorado School of Mines, Golden, CO
- University of Minnesota, Minneapolis, MN

Project Start Date: October 1, 2004

Project End Date: September 30, 2012

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: high-pressure bio-oil injection, homogeneous partial oxidation, and catalytic autothermal reforming.
- 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 2009, produce process performance data, including yields of hydrogen and mass balances as a function of process conditions (temperature, catalyst, oxygen-to-carbon ratio, and steam-to-carbon ratio).
- 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 Hydrogen, Fuel Cells

and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

TABLE 1. Distributed Production of Hydrogen from Bio-Derived Renewable Liquids

Characteristics	Units	2012 Target	2015 Target
Total Energy Efficiency	%	66	70
Production Energy Efficiency	%	72	
Storage, Compression, Dispensing Efficiency	%	94	
Total Hydrogen Costs	\$/gge	3.80	2.50

Accomplishments

- Generated hydrogen by non-catalytic and catalytic partial oxidation of bio-oil using the bench-scale reactor.
- Successfully operated the bench-scale unit using a 90:10 wt% bio-oil/methanol mixture injected to the reactor using an ultrasonic nozzle.
- Achieved 95% bio-oil to gas conversion by auto-thermal catalytic reforming (1% Rh and 1% Ce on Al₂O₃) at oxygen-to-carbon ratio (O/C) of 1.4 and steam-to-carbon ratio (S/C) of 1.7.
- Demonstrated Rh catalyst regenerability by oxidation of carbon deposits.



Introduction

Renewable biomass is an attractive near-term alternative to fossil resources because it has near zero life-cycle carbon dioxide (CO₂) 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 CO₂ 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.
- Homogeneous partial oxidation of bio-oil. We demonstrated previously that we can achieve significant conversion of revolatilized bio-oil to CO with minimal aromatic hydrocarbon formation if we keep the temperature at 650°C and oxygen concentration at a low and steady level. This stage will allow the use of an immobilized catalyst system, reduce the required catalyst load, reduce coking tendencies, and also provide some of the required heat for the process.
- 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. Some promising target catalysts that can be used to complete the conversion of the bio-oil partial oxidation gases and vapors to hydrogen using a supported fixed bed have been identified by University of Minnesota, which works with NREL on this activity to develop less expensive catalysts that will be effective for the conversion of bio-oil-derived gas.

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 micro-scale non-catalytic partial oxidation experiments were completed. In most of the tests, a 1:1 (weight) bio-oil:methanol solution was used as the feedstock, the process temperatures varied between 625 and 850°C, and a gas residence time was about 0.3 s. The effective O:C ratio was varied from pyrolysis conditions (0.7 for the 1:1 mixture) to a maximum of ~1.6. The effective O:C ratio includes oxygen present in organic molecules of bio-oil and methanol as well as that introduced as O₂, but not oxygen in water because it was not reactive under these conditions. The maximum hydrogen yields (~25%) were obtained at effective O:C ratios between 1.4 and 1.6. Similarly, the maximum yields of carbon monoxide (75-80%) were produced over nearly the same range of effective O:C ratios (1.5 to 1.6). Both hydrogen and CO were nearly constant with temperature in the studied range as shown in Figures 1 and 2. Mass balance calculations showed that for O:C of 1.4, 7-10% of bio-oil carbon was converted to carbon dioxide, 8-10% to methane, 1.5-2.5% to benzene, and 4-6% formed solid residues. It confirmed that non-catalytic partial oxidation is an effective first step for producing hydrogen from bio-oil but needs to be followed by the catalytic reforming and water-gas shift to optimize the process yield.

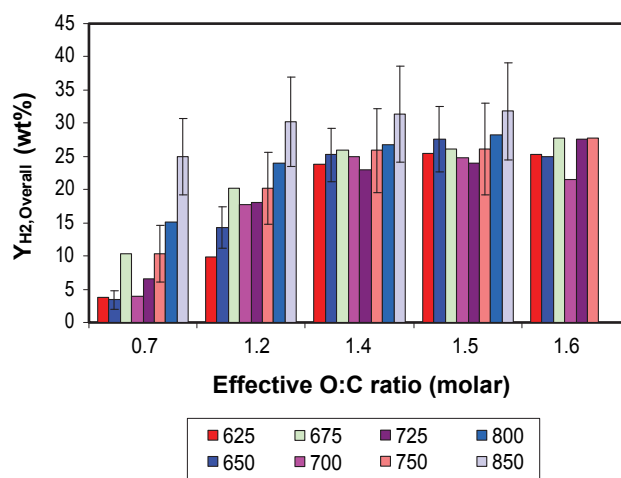


FIGURE 1. Yields of Hydrogen Produced by Non-Catalytic Partial Oxidation of Bio-Oil

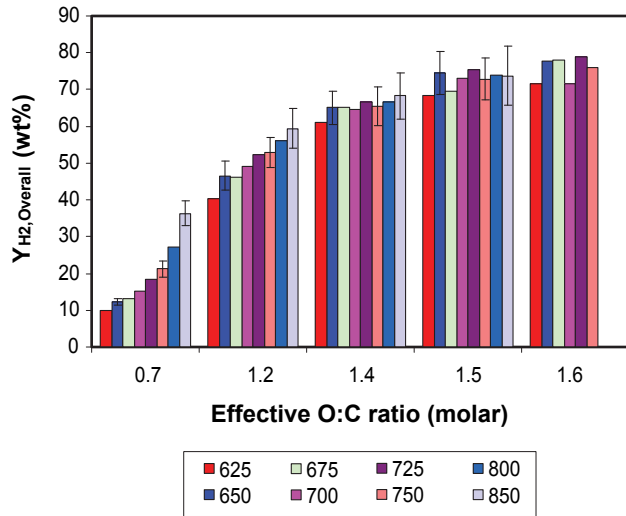


FIGURE 2. Yields of Carbon Monoxide Produced by Non-Catalytic Partial Oxidation of Bio-Oil

The micro-scale tests of partial oxidation followed by catalytic steam reforming using a rhodium catalyst provided by University of Minnesota were carried out for bio-oils produced from different biomass feedstocks. This work was also supported by Chevron. Catalytic partial oxidation (POX)/steam reforming produced in most cases 7-10 g hydrogen per 100 g bio-oil. Bio-oils

from herbaceous feedstock were more difficult to process and left more deposits than wood bio-oils.

The bench-scale partial oxidation and steam reforming tests were carried out in the systems shown in Figure 3. The experiments used 90% bio-oil solution in methanol as the feedstock. Both partial oxidation and POX/steam reforming tests were performed using the rhodium catalyst from University of Minnesota. The bio-oil was fed to the reactor at 60 g/h, and the methane-equivalent volumetric space velocity was 30,000 h⁻¹ (compared to 2,000 h⁻¹ used for industrial steam-methane reforming). Process performances were determined at varied temperature, O/C and S/C. Gas composition at different process conditions is shown in Figure 4.

Bio-oil to gas conversion for catalytic POX/steam reforming approached 95%. Though some carbon deposits formed and slowly deactivated the catalyst, regeneration by air oxidation restored its full activity.

Conclusions and Future Directions

- The results presented in this work show that a significant amount of bio-oil conversion can be achieved in a non-catalytic partial oxidation step. The products of this step can then be catalytically converted to produce high yields of hydrogen.

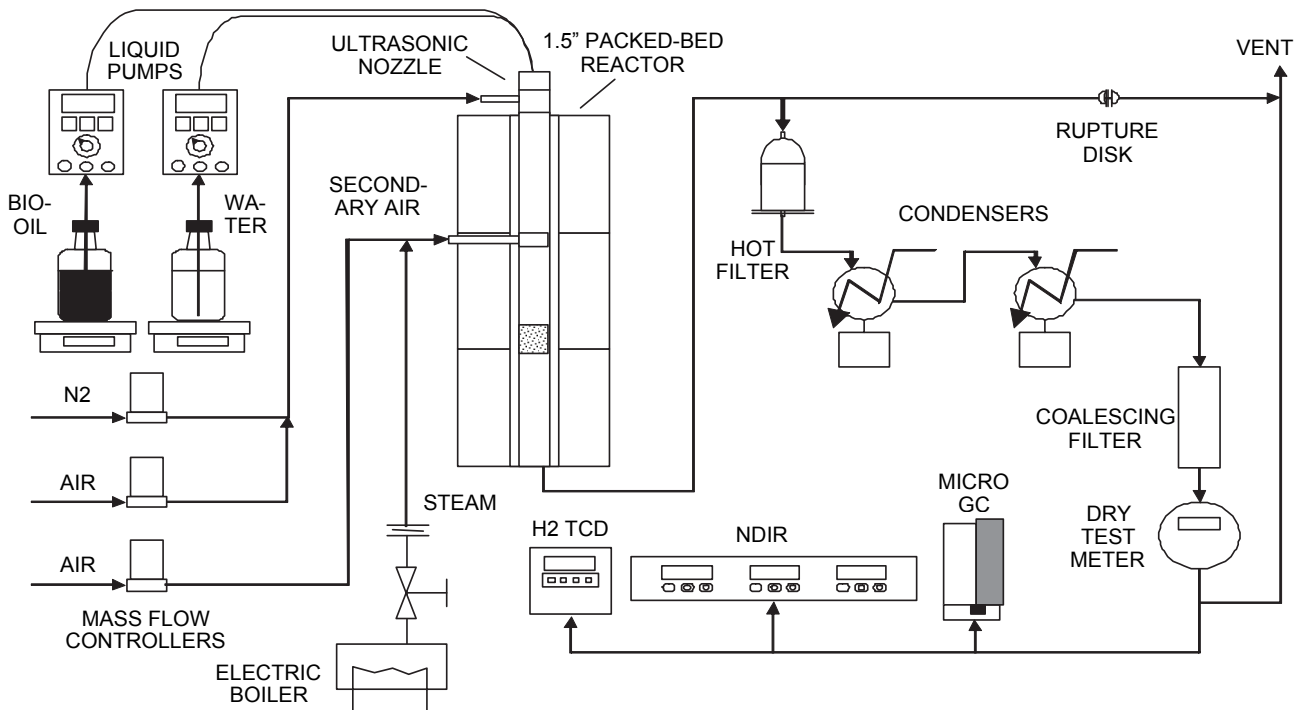


FIGURE 3. Schematic of the Bench-Scale Auto-Thermal Reforming System

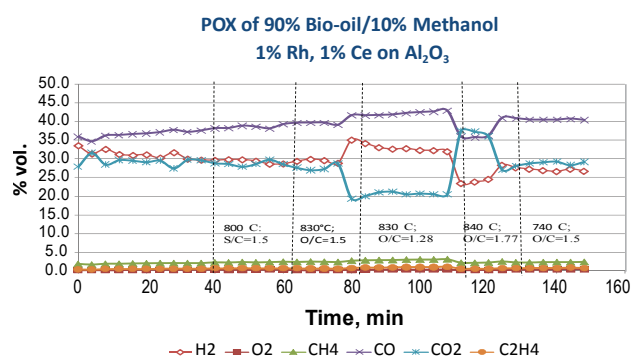


FIGURE 4. Gas Composition from POX of Bio-Oil at Different Process Conditions

- Bio-oils from herbaceous feedstock were more difficult to process and left more deposits than wood bio-oils.
- Initial results from bench-scale catalytic partial oxidation and steam reforming of bio-oil are very encouraging. A rhodium catalyst in a fixed-bed reactor showed a very good performance and full regenerability by air oxidation.
- Long-duration tests continue to demonstrate catalyst long-term performances.
- We initiated tests with lower-cost (nickel-based) catalysts that reduce the capital cost of the process.

FY 2009 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 of Hydrogen Energy* (accepted for publication).
2. Marda, J., Conversion of Bio Oil and Representative Model Compounds to Synthesis Gas for Distributed Hydrogen Production, Ph.D. Thesis, Colorado School of Mines, May 2009.
3. Czernik, S., French, R., Penev, M., Marda, J., Dean, A., 2009 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review, May 2009.

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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.