

II.B.3 Distributed Bio-Oil Reforming

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

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 DOE targets.
- In fiscal year (FY) 2007, demonstrate bio-oil performance consistent with distributed reforming system concepts including volatilization, carbon management, partial oxidation, and catalytic auto-thermal reforming.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan:

(A) Reformer Capital Cost

(C) Operation and Maintenance (O&M)

(D) Feedstock Issues

(F) Control and Safety

Technical Targets

Distributed Production of Hydrogen from Bio-Derived Renewable Liquids

	2012	2017	NREL Status
Production Unit Energy Efficiency, %(LHV)	72.0	65-75	50
Production Unit Capital Cost (Un-installed)	1.0M	600K	1.5M
Total Hydrogen Cost \$/gge	3.80	<3.00	4.50

Accomplishments

- Improved bio-oil volatilization by enhancing the ultrasonic nozzle and reducing the methanol content to 10%.
- Demonstrated model development for methanol under oxidative-cracking process conditions (under subcontract to CSM).
- Validated oxidative cracking of bio-oil at temperatures less than 650°C and with high CO/CO₂ ratio.
- Introduced catalysts to the process and demonstrated equilibrium syn-gas composition over a 0.5% rhodium-supported on alumina catalyst.



Introduction

More than 500 million tons of biomass could be available in the United States at less than \$50/ton. This biomass can be converted to over 50 million tons of hydrogen (H₂) [1]. The challenges for the variety of feedstocks include handling and drying, regional and seasonal availability and variability, and the impurities inherent in biomass or/and generated in the process. Such impurities could impact conversion technology and hydrogen purity. Processes must be feedstock-flexible and minimize costs for feedstock collection, transport, and processing. Given the near-term technical barriers to hydrogen storage and delivery, technologies that can be distributed at or near the point of use are attractive.

This work addresses the challenge of distributed hydrogen production with a targeted 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]. “Bio-oil” can then be converted to hydrogen and carbon dioxide (CO_2) in a distributed manner at fueling stations. The thermally reactive compounds (e.g., anhydro-sugars, phenolics) in bio-oil do not evaporate cleanly. They tend to decompose and react, and may form carbonaceous deposits or be converted to aromatic hydrocarbons, which are thermally stable and 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, but have not been proven for small-scale and unattended operation.

Approach

A system has been developed for volatilizing bio-oil with manageable carbon deposits. It uses ultrasonic atomization to control physical properties and modifies bio-oil properties, such as viscosity, by blending or reacting bio-oil with alcohol. Homogeneous partial oxidation of bio-oil is then used to achieve significant conversion to carbon monoxide (CO) with minimal aromatic hydrocarbon formation by keeping the temperature at 650°C or lower and the oxygen (O_2) at a low and steady level. Model compounds are used to establish the underlying chemical understanding of the process and identify optimized conditions. The product gas is converted via heterogeneous auto-thermal reforming with precious metal catalysts to complete the conversion to hydrogen [4].

The reactor is shown in Figure 1. The reactor system is based on ultrasonic nebulization. A fine mist of oil is generated at ambient conditions and heated to the target temperature, typically 650°C , at which point a bio-oil vapor residence time of 300 ms is achieved. A catalyst bed is located at the bottom of the tube. The initial testing of homogeneous cracking used a bed of quartz particles to capture any deposits that formed in the volatilization and cracking zones. Performance of the bio-oil injection system was tested with a 50% bio-oil solution in methanol. The system allowed steady-state operation.

Molecular Beam Mass Spectrometry (MBMS).

The study of pyrolysis by MBMS has been described previously [5]. The gases exiting the reactor are expanded through an orifice on the apex of a sampling cone into the stage 1 vacuum at 40 mtorr. The free-jet expansion quenches the products and allows light gases, high-molecular-weight compounds, and reactive products to be sampled. A molecular beam, collimated through a second expansion, enters an ion source, where 25- to 50-eV electron-impact ionization is used to form ions that are analyzed by a quadrupole mass filter.

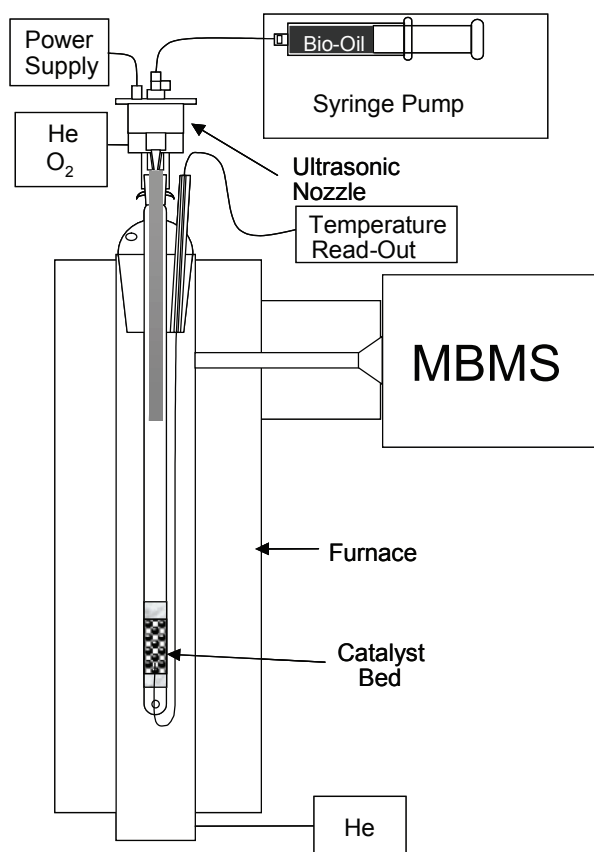


FIGURE 1. Auto-Thermal Bio-Oil Reforming Reactor

Results and Discussion

Experiments were performed in FY 2006 and FY 2007 without catalysts to determine the extent of low-temperature oxidation of the volatilized bio-oil. Variables were temperature and O_2 level. The objective was to break carbon-carbon bonds and avoid oxidation to CO_2 and water (H_2O) as well as aromatic hydrocarbon formation. The temperature was varied from 500 to 650°C . The oxygen level was varied from that of the methanol/bio-oil feed (no oxygen added) to the maximum level that could be added in the gas phase without the onset of flaming combustion.

The effects of the oxygen-to-carbon ratio (O/C) and temperature on CO and CO_2 yields are shown in Figures 2 and 3. Bio-oil was converted to CO at a greater than 50% yield on a carbon basis, with only 10% CO_2 yield. The most important variable in the range between 550 and 650°C is the O/C, with experiments at different temperatures following the same trend line. Runs below 550°C are affected by both O/C and temperature. The most significant conclusion here is that the oxidative cracking effect is observed at temperatures as low as 550°C . The lower temperatures allow higher O_2 levels to be introduced before the

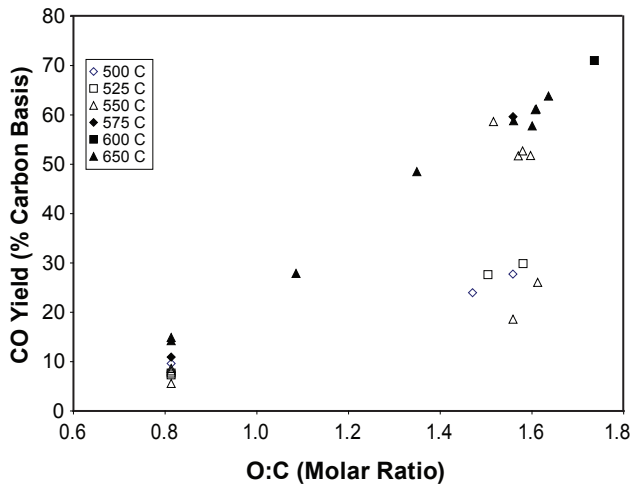


FIGURE 2. The Effect of O/C, Varied by the Introduction of O_2 , and Temperature on the Gas-Phase CO Yield at Different Temperatures for a 50% Bio-Oil in Methanol Solution

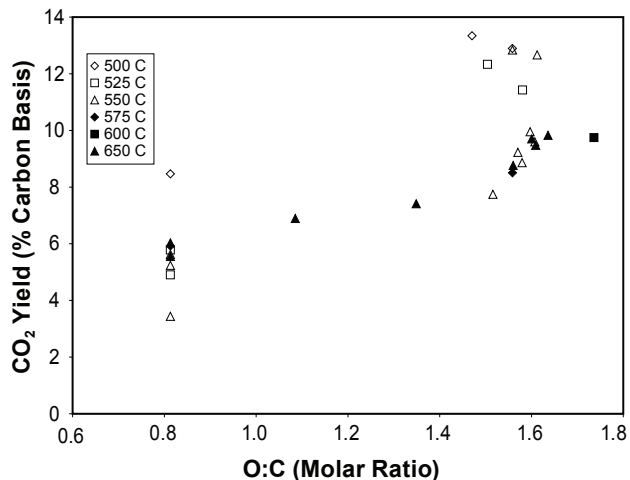


FIGURE 3. The Effect of O/C, Varied by the Introduction of O_2 , and Temperature on the Gas-Phase CO_2 Yield at Different Temperatures for a 50% Bio-Oil in Methanol Solution

onset of flaming combustion. The 600°C experiment was at the highest O/C and resulted in a CO yield of 70%. In the best case at 600°C, the conversion of bio-oil carbon to CO and CO_2 was comparable to the rate of conversion of methanol, which was around 80%. However, there was aromatic hydrocarbon formation and carbon deposited in the reactor approximately equal to 15% of the bio-oil, which was subsequently oxidized by the O_2 no longer consumed in the gas phase after feeding was suspended.

Catalytic Auto-Thermal Reforming. The products from oxidative cracking include some residual oxygenates and low-molecular-weight hydrocarbons, such as benzene. The oxidation and reforming of these

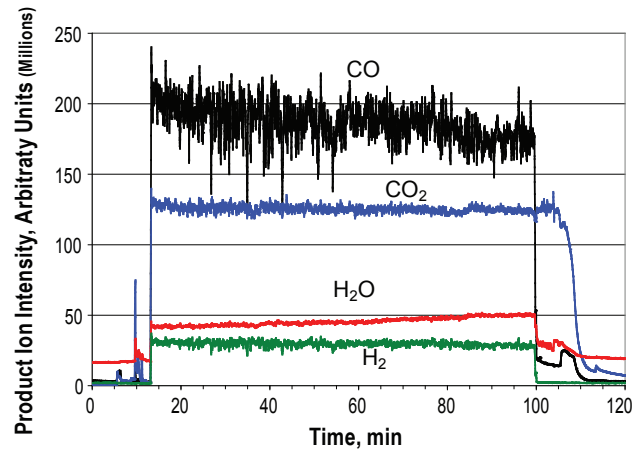


FIGURE 4. A typical catalyst experiment using 0.5% Rh on an alumina-packed bed showing the major product gases for 50:50 methanol/bio-oil fed at 6.7 g/hr with a gas-phase residence time of 300 ms at 650°C prior to the catalyst bed. Oxygen is added to give an O/C of 1.33. The bio-oil is fed from 13 to 100 minutes. The CO_2 , water, and CO signals continue after the feed is stopped due to the residual material that is oxidized by the available oxygen. These traces are considered the raw data and are not corrected for differences in response factors.

products followed by the water-gas shift reactions will be accomplished by low-temperature auto-thermal catalysis. Commercially available catalysts have been used to initiate catalyst testing experiments. A comparison of packed beds of 0.5% rhodium, palladium, platinum, and ruthenium catalysts on alumina was performed as a benchmark to establish the competitive reaction pathways for syngas reactions, such as oxidation, water-gas shift, and steam reforming. The major product traces are shown in Figure 4 for a typical catalyst experiment using 0.5% Rh on an alumina-packed bed for 50:50 methanol/bio-oil fed at 6.7 g/hr with a gas-phase residence time of 300 ms at 650°C prior to the catalyst bed. Oxygen is added to give an O/C of 1.33. The bio-oil is fed from 13 to 100 minutes. The CO_2 , water, and CO signals continue after the feed is stopped due to the residual material that is oxidized by the available oxygen. These traces are considered the raw data and are not corrected for differences in response factors. The results for different catalysts and conditions are shown in Tables 1 and 2. The equilibrium values and gas-phase-only results are shown for comparison. The amount of oxygen and water in the systems was the same as for the gas-phase reaction, which means that only steam was available as a reactant gas on the catalyst since all O_2 was completely used in the gas-phase section. The reaction with residual hydrocarbons on the catalyst was complete, although conversion to carbon is a likely reaction pathway. As with the gas-phase studies, the solid carbon was quantified when the feed was turned off and the oxygen became available for carbon burn off. To date, no attempt has been made to characterize

TABLE 1. Results of Catalyst Experiments with O/C = 1.3

	Equil.	Gas	Alumina	Rh	Pd	Pt	Ru
CH ₃ OH conversion	100.0	49.1	38.7	99.6	82.1	88.2	75.4
CO	68.7	38.6	36.0	61.1	50.9	45.5	48.4
CO ₂	23.8	7.2	7.5	23.2	9.6	11.6	9.3
H ₂	80.3	13.1	9.2	83.7	34.1	31.2	27.6
H ₂ O	13.5	38.5	38.0	17.8	40.6	45.3	40.7
CH ₄	3.9	5.2	5.3	5.9	7.7	8.2	9.5
Carbon deposition	3.6	1.0	1.6	4.4	7.7	10.4	6.9
Benzene	0.0	1.3	1.0	1.4	4.4	2.3	2.0

TABLE 2. Results of Catalyst Experiments with O/C = 1.7

	Equil.	Gas	Rh
CH ₃ OH conversion	100.0	87.5	100.0
CO	57.0	60.3	52.9
CO ₂	41.8	11.3	37.6
H ₂	72.3	27.7	74.1
H ₂ O	25.8	54.3	31.7
CH ₄	1.2	6.5	5.0
Carbon deposition	0.0	0.9	1.4
Benzene	0.0	2.7	0.5

the carbon that accumulates on the catalyst. The conversion on Rh catalyst was the closest to equilibrium conditions. The challenge for the integrated system will be to selectively reform the residual hydrocarbons and catalyze the water-gas shift reaction without catalyzing methanation and CO oxidation. The goal will be to attain equilibrium levels of hydrogen, CO, H₂O, and CO₂ at the exit of the catalyst bed and to maintain steady-state conditions, which requires adequate carbon conversion in the first phase of the catalyst bed.

Conclusions and Future Directions

These results show that a low-temperature oxidative cracking stage will reduce the required catalyst load in the reforming of bio-oil and that a clean syngas can be produced without high gasification severity conditions, namely temperatures higher than 650°C and excessive H₂O to drive the carbon reforming reactions to completion. Only trace amounts of methane and benzene are detected in the product gas when the catalyst is in place. Ongoing developments in the project are examining the parametric effects of variation in process variables (temperature, oxygen, and steam), the removal of CO₂ from the system by adsorption within the catalyst bed, and the impact of variations in the composition of the bio-oil. Model compounds are being studied to develop mechanisms of homogeneous oxidative cracking, which will add insight to the chemistry of the gas-phase reactions. Catalysis studies will be expanded to determine optimum materials to minimize costs and the formation of aromatics and other syngas contaminants.

FY 2007 Publications/Presentations

1. Marda, J, Czernik, S., Evans, R., French, R., and Dean A. *Hydrogen from Biomass; Distributed Production by Steam Reforming of Biomass Pyrolysis Oil*, 4th Annual World Congress on Industrial Biotechnology and Bioprocessing, March 21-24, 2007, Orlando, Florida.

References

1. Milbrandt A. A Geographic Perspective on the Current Biomass Resource Availability in the United States, National Renewable Energy Laboratory: Golden, CO, TP-560-39181, 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, 2007. 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 FY 2006 Annual Progress Report, 2006.
5. Evans, R. J., Milne, T. A. Energy & Fuel, 1987, 1,123.