II.A.12 Distributed Bio-Oil Reforming

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

Start Date: October 1, 2004
Projected 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 2008, improve bio-oil atomization with less methanol addition, continue the study of partial oxidation at 650°C, demonstrate catalytic conversion consistent with $3.80/kg hydrogen, and design, build and operate a bench-scale unit capable of long duration runs (8 hrs/cycle) with better material balances.

Technical Barriers

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

(A) Fuel Processor Capital
(C) Operation & Maintenance
(D) Feedstock Issues

Technical Targets

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

- Improved bio-oil volatilization by improvements in the ultrasonic nozzle so that no methanol will be used in the new bench-scale reactor.
- Demonstrated the effect of oxidative cracking of bio-oil at temperatures of less than 650°C prior to the rhodium catalyst bed.
- Designed bench-scale reactor to be built in FY 2008.
- Developed process flow sheets with preliminary engineering analysis.

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Introduction

This work addresses the challenge of distributed hydrogen production with the target of hydrogen cost of $3.80/kg by 2012 [1]. 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 [2,3]. "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 are not the optimal choice for small-scale and unattended operation.

A system has been developed for volatilizing bio-oil with manageable carbon deposits. It uses ultrasonic atomization of bio-oil or its blends with methanol (methanol addition allows us to control and modify bio-oil properties, such as viscosity). 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 or below 650 °C and 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 subsequently auto-thermally reformed using precious metal catalysts to complete the conversion to hydrogen and carbon oxides [3].

Approach

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 will have to implement unsupervised automated operation. Therefore, we have moved away from fluidized nickel catalysts and high temperatures. In this project we evaluate the following steps to produce the required hydrogen for proton exchange membrane fuel cell cars:

Bio-Oil Volatilization: NREL is developing low-maintenance systems for volatilizing bio-oil without carbon deposits using film volatilization or ultrasonic atomization. The near-term concern is carbon deposit management. A long-term concern is corrosion. We may need to control physical and chemical properties such as viscosity, so blending or reaction with alcohol may be necessary.

Homogeneous Partial Oxidation of Bio-Oil: We have demonstrated previously that we can get significant conversion of revolatilized bio-oil to CO (up to 90% carbon conversion) with minimal aromatic hydrocarbon formation if we keep the temperature at 650ºC 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. We need to improve bio-oil revolatilization and partial oxidation if the more refractory components of bio-oil are to be converted to CO. We will establish the underlying chemical understanding of the process, as well as identify optimized conditions. The Colorado School of Mines is working as a subcontractor with NREL on this activity.

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. Professor Lanny Schmidt at the University of Minnesota has identified 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 system. The University of Minnesota is a subcontractor and works with NREL on this activity to develop less expensive catalysts that will be effective for the conversion of bio-oil derived gas.

Further work is needed to assess the impact of increased feed complexity on reaction mechanisms and to develop a robust model for catalyst activity and performance at different process conditions (temperature, oxygen-to-carbon and steam-to-carbon ratio, space velocity). Also, the kinetics of catalyst regeneration by steam gasification and by oxidation of carbon deposits from the catalyst surface will be determined. Catalyst formulations need to be optimized for reforming, gasification, and water-gas shift (WGS) performance. Other deactivation mechanisms, including poisoning by S and Cl, also should be evaluated and addressed either through catalyst development or system design.

Most importantly, research will be 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.

Results

The reactor system was previously described [3] and is based on ultrasonic nebulization of the bio-oil. A fine mist of oil is generated at ambient conditions and heated to the target temperature, typically 650ºC, at which point a residence time of 300 ms is achieved. Oxygen, steam, and helium are mixed with the bio-oil vapors in the nebulizer region in varying amounts depending on the experiment. A catalyst bed is located at the bottom of the tube. The catalyst used in this report was a 1% rhodium on alumina that was prepared in the laboratory of Prof. Lanny Schmidt of the University of Minnesota under a subcontract which began in FY 2008. The reactor is coupled with a molecular beam mass spectrometer. The gases exiting the reactor are expanded through an orifice on the apex of a sampling cone into a vacuum chamber at 40 mtorr. A second expansion forms a molecular beam, which next 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 [3,4].

A major goal in 2008 was to improve the nozzle so that atomization of non-diluted bio-oil is possible, which eliminates the need for the use of methanol. The new nozzle uses higher power input that allows the use of the higher feed viscosity. The new nozzle will accommodate both the current micro-reactor (0.2 g/min) and the bench-scale reactor (~2 g/min) that is under development. Tests have shown that it works with the viscous neat bio-oil but only at the upper end of the feed rate range, which is where the new bench-scale reactor will be operated. The micro-reactor underwent several modifications to allow the mounting of the new nozzle, which required new geometry for the nozzle area and sealing system. However, to date, methanol addition of at least 30% is still required, therefore work continued with the micro reactor at 50% methanol to be consistent with past experiments.

The oxidative cracking study was performed in collaboration with the Colorado School of Mines under a subcontract to develop a model that will be used to define process parameters for low temperature syngas generation and a mechanistic and kinetic model of the process chemistry. Hydrogen and CO yields produced by partial oxidation of bio-oil were determined as a function of O:C ratio at two levels of bio-oil dilution with methanol. In Figures 1 and 2 there are essentially no differences between 50% and 30% methanol addition for hydrogen and CO, respectively. Experiments were also performed at two different gas phase residence times which are shown in Figure 3 for both gas phase and catalytic experiments. Only minor differences were observed in the major products although the differences appear to be statistically significant. The minor products are shown in Figure 4.

A series of experiments were performed at 650°C over the new rhodium catalyst prepared by the University of Minnesota. Results are shown in Figures 3 and 4. However, standard steam-to-carbon ratios (S/C) were not used because of the shorter residence time in the reactor.

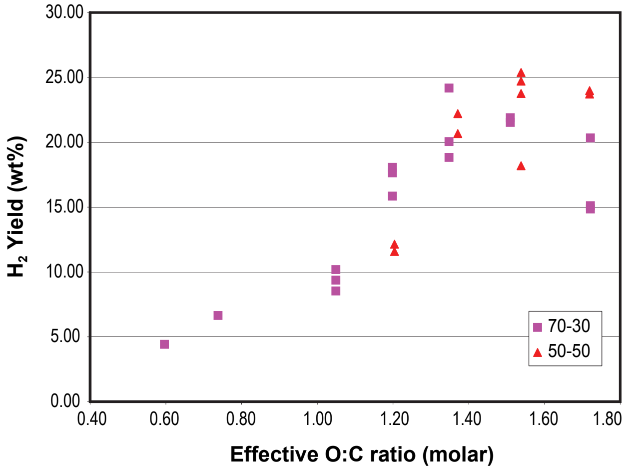


FIGURE 1. Effect of Effective O:C Ratio for Two Methanol Addition Levels on H_2 Yields

A typical series of experiments under standard conditions are shown in Figure 5 with a S/C of 2.5. Major products (mmol/min) are shown for three sequential bio-oil runs of the integrated system under standard conditions:

- Vapor residence time at 650°C of 0.3 s.
- Effective oxygen-to-carbon molar ratio, O/C_{eff}, of 1.3. This is based on the O_2 added and the oxygen in the bio-oil, but does not include the oxygen in water, which has been shown to be inert in the gas phase step.

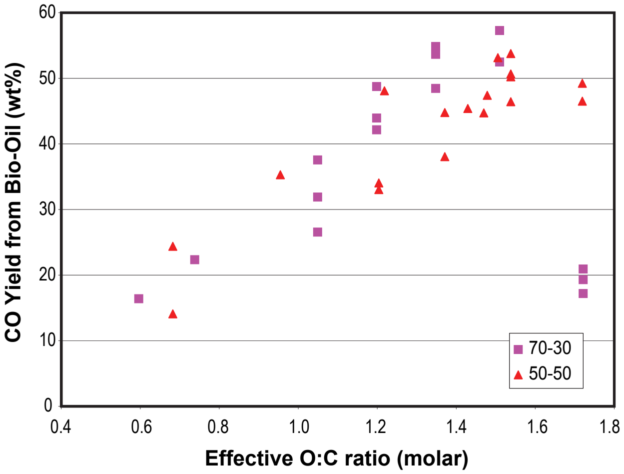


FIGURE 2. Effect of Effective O:C Ratio for Two Methanol Addition Levels on CO Yields

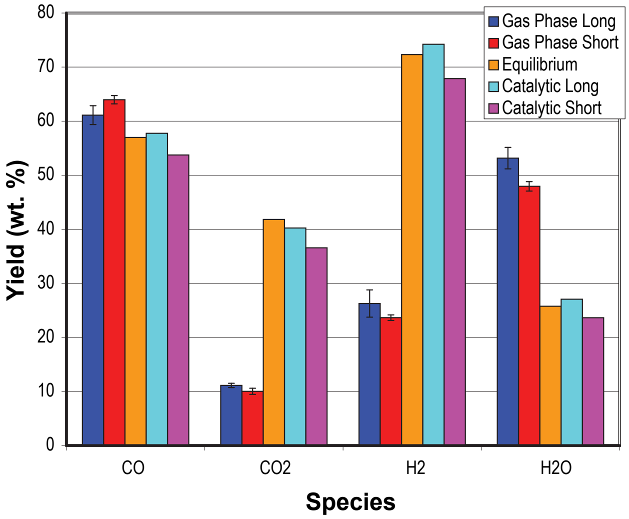


FIGURE 3. Effect of 200 ms (short) and 300 ms (long) gas residence times on gas-phase and catalytic products compared to equilibrium calculations for experiments using a 50:50 bio-oil:methanol mixture (wt%) at 650°C and a O:C ratio of 1.7.

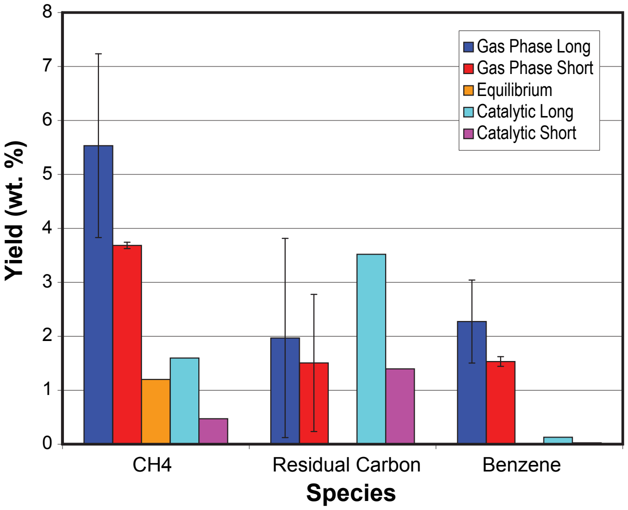
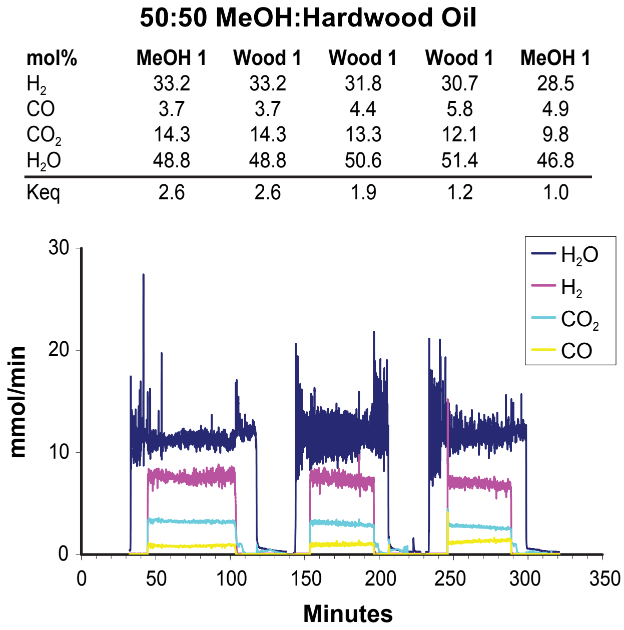


FIGURE 4. Effect of 200 ms (short) and 300 ms (long) gas residence times on gas-phase and catalytic minor products (see legend and conditions described in Figure 2).



mol%	MeOH 1	Wood 1	Wood 1	Wood 1	MeOH 1
H_2	33.2	33.2	31.8	30.7	28.5
CO	3.7	3.7	4.4	5.8	4.9
CO_2	14.3	14.3	13.3	12.1	9.8
H_2O	48.8	48.8	50.6	51.4	46.8
Keq	2.6	2.6	1.9	1.2	1.0

FIGURE 5. Major products for three sequential bio-oil runs of the integrated system under standard conditions (vapor residence time=0.3 s; catalyst bed of 0.5%Rh/Al_2O_3, weight hourly space velocity=3.5; S/C=2.5; O/C_{eff}=1.3). The table insert also includes methanol before and after the series. K_{Eq} is an index of WGS activity = $([H_2]*[CO_2])/([CO]*[H_2O])$. The O_2 in the gas flow reacts with carbon deposits generating CO_2 between runs.

- The catalyst bed in this experiment is 0.5%Rh/Al_2O_3 with a weight hourly space velocity of 3.5.
- The added oxygen is consumed in the gas phase and does not interact with the catalyst under standard conditions. When the bio-oil feed is stopped the O_2 then reacts with carbon deposits generating CO_2 between runs, which is used to measure carbon deposition.

The table insert in Figure 5 gives the average major products and also includes methanol runs before and after the series. K_{Eq} is $([H_2]*[CO_2])/([CO]*[H_2O])$, which is a sensitive indicator of changes in the catalyst as a function of time on stream. It is an index of WGS activity, which is obviously greatly diminished in this experiment. For this reason a WGS reactor is included in the process flow sheet shown in Figure 6.

Process Engineering

In order to assist with estimation of the gasification (thermal) efficiency, we have begun to develop an ASPEN model of the process (model based on diagram shown in Figure 6). Thermal efficiency was defined as the lower heating value of the hydrogen produced (i.e. recoverable hydrogen) divided by the lower heating value of the bio-oil required (both for heat and reaction). Several major assumptions were made:

- In order to perform the simulation, it was necessary to develop a surrogate bio-oil. This surrogate was based on components typically found in bio-oil and was tuned to have the same carbon, hydrogen, and oxygen composition as the bio-oil used in experiments.
- The laboratory-scale experimental partial oxidation results were assumed to scale-up without major changes: the yields of major species were specified (based on experimental yields) using the RYIELD unit operation in ASPEN. Because carbon balances were typically around 90% (i.e. bio-oil was not completely converted), small amounts of naphthalene and anthracene (both observed experimentally) were added as products of the RYIELD reactor in order to get reasonable mass closure (within 3% for carbon, hydrogen, and oxygen).
- Equilibrium was assumed to be achievable in both the steam reforming and water gas shift reactions; the RGIBBS unit operation was used to calculate equilibrium at the temperature of these reactors.
- Heat losses were neglected (i.e. perfect heat exchangers).
- 85% of the hydrogen was assumed to be recoverable via pressure swing absorption.
- A steam to carbon ratio of three was used.
- Air was used as the oxygen source for partial oxidation.

It should be noted that this first version is a preliminary effort and only concerned with mass and energy balances. Critical review must be performed

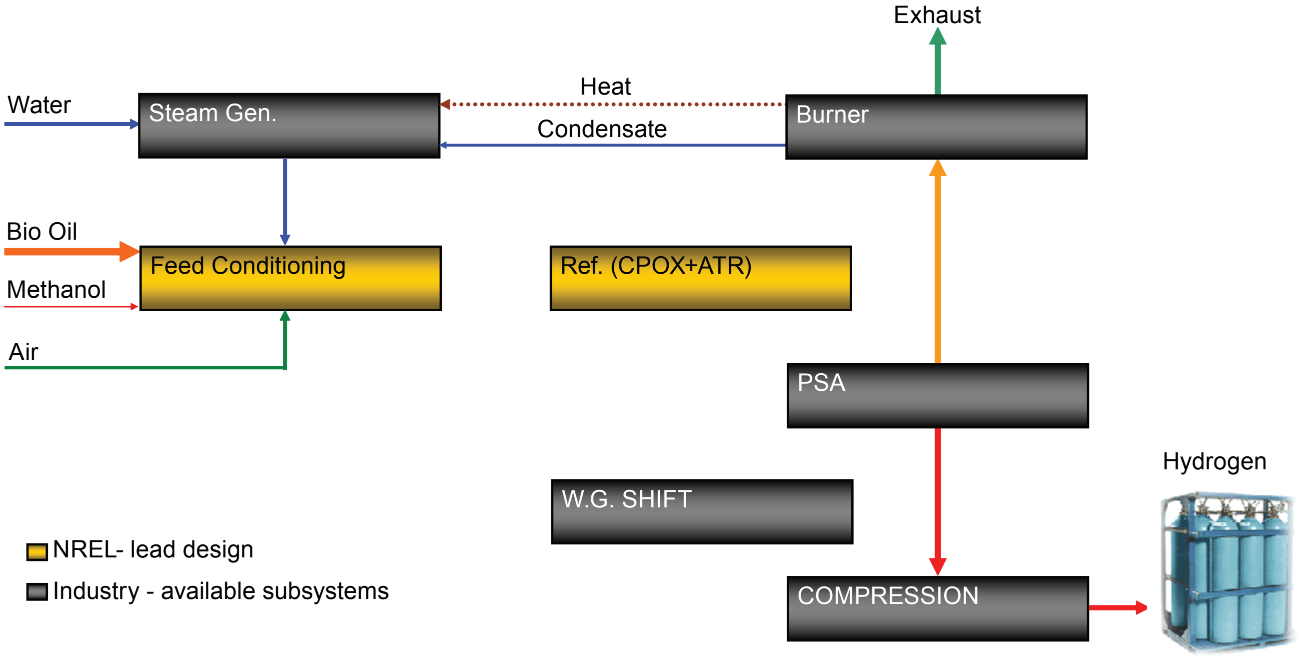


FIGURE 6. Process Sub-System Outline used in First Generation ASPEN Model

before conclusions can be drawn and revisions made to the H2A analysis.

FY 2008 Publications/Presentations

1. Czernik, S.; Evans, R.; French, R. "Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil." *Catalysis Today;* Vol. 129, 2007; pp. 265-268.

2. Evans, R.J.; Czernik, S.; French, R.; Ratcliff, M.; Marda, J.; Dean, A.M.; "Distributed Bio-Oil Reforming." Presented at the ACS National Meeting, Fuel Chemistry Symposium: Fuel Processing for Hydrogen Production: Perspectives on Hydrogen Generation. Boston, Massachusetts. August 19, 2007.

3. Marda, J.R.; Dean, A.M.; Czernik, S.; Evans, R.J.; French, R.J.; Ratcliff, M.A. "Intermediate temperature conversion of bio-oil to synthesis gas for distributed hydrogen production." Presented at the ACS/AIChE Rocky Mountain Regional Meeting. Denver, Colorado. August 30, 2007.

4. Marda, J.R.; Dean, A.M.; Czernik, S.; Evans, R.J.; French, R.J.; Ratcliff, M.A. "Intermediate temperature conversion of bio-oil to synthesis gas for distributed hydrogen production." Presentaed at the AIChE Annual Meeting. Salt Lake City, UT. November 7, 2007.

5. Marda, J.R.; Dean, A.M.; Czernik, S.; Evans, R.J.; French, R.J.; Ratcliff, M.A. "Intermediate Temperature Catalytic Reforming of Bio-Oil for Distributed Hydrogen Production." Presented at the AIChE 2008 Spring National Meeting. New Orleans, Louisiana. April 8, 2008.

6. Marda, J.R.; Dean, A.M.; Czernik, S.; Evans, R.J.; French, R.J.; Ratcliff , M.A.; "Importance of a Non-Catalytic Step in the Distributed Reforming of Bio-oil for Hydrogen Production." Presented at the 235th ACS National Meeting. New Orleans, Louisiana. April 9, 2008.

7. Marda, J.R.; Dean, A.M.; Czernik, S.; Evans, R.J.; French, R.J.; Penev, M.; Ratcliff, M.A. "Distributed Reforming of Bio-Oil for Hydrogen Production." Presented at the AIChE 2008 Spring National Meeting. New Orleans, Louisiana. April 9, 2008.

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1. U.S. Department of Energy. Hydrogen, Fuel Cells and Infrastructure Technologies Program, Multi-Year Research, Development and Demonstration Plan. Section 3.1 Hydrogen Production. U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy: Washington, D.C., 2006.

2. Czernik, S.; Elam, C.; Evans R.; Milne, T. "Thermochemical routes to hydrogen from biomass – a review." Bridgwater, A.V.; Boocock , D.G.B., eds. *Science in Thermal and Chemical Biomass Conversion*.Newbury, UK: CPL Press, 2006; pp.1752–1761.

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

4. Evans, R.J.; Milne, T.A. *Energy & Fuel*. 1987. pp. 1,123.