

II.A.10 Distributed Bio-Oil Reforming

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

Objectives

- By 2015, reduce the cost of distributed hydrogen production from bio-oil to \$2.50/gallon of gasoline equivalent (gge; delivered, untaxed) at the pump.
- By 2010, develop and demonstrate distributed reforming technology for producing hydrogen from bio-oil at \$3.60/kilogram (kg) purified hydrogen.
- By 2008, 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 (FY) 2006, develop a system for partial oxidation and catalytic reforming of volatilized/atomized whole bio-oil and develop an oxidative cracking database that will be used to define process parameters for syngas generation.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4.2.1) of the Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Fuel Processor Capital Costs
- (B) Fuel Processor Manufacturing

- (C) Operation & Maintenance (O&M)
- (D) Feedstock Issues
- (F) Control & Safety

Technical Targets

The table below outlines the DOE technical targets to which this project contributes, excerpted from the Hydrogen Production section of the Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan.

Distributed Production of Hydrogen from Bio-Derived Renewable Liquids

Characteristics	Units	2010 Target	2015 Target
Total Energy Efficiency	%	66	70
• Production Energy Efficiency	%	70	
• Storage, Compression, Dispensing Efficiency	%	94	
Total Hydrogen Costs	\$/gge	3.60	2.50

Accomplishments

- Demonstrated bio-oil volatilization by two methods with less than 10% residue.
- Demonstrated oxidative cracking process conditions that give 80% conversion of bio-oil to CO on a carbon basis with only 10% conversion to CO₂.
- Demonstrated oxidative cracking of bio-oil at tatures less than 650°C.

Introduction

Renewable biomass is an attractive near-term alternative to fossil resources because it essentially has zero life-cycle carbon dioxide (CO₂) impact. Recent assessments have shown that more than 500 million tonnes of biomass could be available in the United States each year at less than \$50/ton. This biomass could be converted to 50 million tons of hydrogen; enough to supply the light-duty transportation needs of the United States. Although low-cost biomass sources, such as agricultural and forest residues, can be used in the near term, large-scale, sustainable energy crops will need to be produced to realize the biomass potential. In addition, these energy crops must be tailored to several different growing regions in the country. The challenges for this variety of feedstock include handling and drying,

regional and seasonal availability, and compositional variability, with emphasis on the potential range of impurities that could be present and have an impact on conversion technology and final product gas purity. Any process developed, then, must be shown to be feedstock-flexible, and any approach taken must minimize costs for feedstock collection, transport, and processing. Additionally, given the high cost of hydrogen storage and delivery, technologies that can be distributed at or near the point of use are attractive.

Approach

This project is based on a two-step approach focused on addressing these challenges. First, pyrolysis is used to convert the feedstock into a liquid that can be transported more easily. This “bio-oil” can then be catalytically steam reformed to H_2 and CO_2 in a distributed manner at refueling stations or stationary power sites. Previous work at NREL [1, 2, 3] has used a fluid bed reactor with a nickel catalyst that operated at $850^\circ C$, but these conditions are not optimum for distributed reforming. The work for FY 2006 targets the barriers to automated, low-cost operation of appropriately-sized systems for a prototypical filling station that would service 1,500 cars/day.

The thermally reactive compounds (e.g., anhydro-sugars and phenolics) found in bio-oil do not evaporate cleanly. They tend to decompose and react, and may form carbonaceous deposits or undergo conversion to aromatic hydrocarbons that are thermally stable and more difficult to convert to hydrogen. Because of this, conventional fixed bed reformers have not proven efficient for this highly reactive feedstock. Reactors that fluidize or circulate the catalyst are much more suitable for this application, but are not an optimal choice for small-scale and unattended operation.

In FY 2006, NREL is

- Developing a system for partial oxidation and catalytic reforming of volatilized/atomized whole bio-oil.
- Developing an oxidative cracking database that will be used to define process parameters for syngas generation.

These tasks will allow us to develop an understanding of the process chemistry of bio-oil handling and conversion to optimize the next phase of work on catalyst chemistry, deactivation, and regeneration strategy. This work is foundational for efforts to evaluate engineering systems for distributed application at the refueling station, for fuel quality standards, and for ongoing techno-economic evaluations.

Results

Bio-Oil Injection

In this task, we are developing systems for introducing the bio-oil to the reactor and for the initial heat-up to the target temperature. Initially, we employed the spray injection nozzle systems used in the fluid bed systems. The resulting incomplete carbon conversion and low carbon mass closures were attributed to carbonaceous deposit formation that was blown out of the reactor. We subsequently studied bio-oil film volatilization, which showed a 6% residue at $400^\circ C$. This was much less than expected, and this system was used to study batch samples using molecular beam mass spectrometry (MBMS) for product detection. Experiments showed promising conditions in which the pyrolysis oil was converted to syngas at low temperature without aromatic hydrocarbon formation as typified by benzene.

We then began developing a reactor system based on ultrasonic nebulization as shown in Figure 1. A fine mist of oil was generated at ambient conditions and

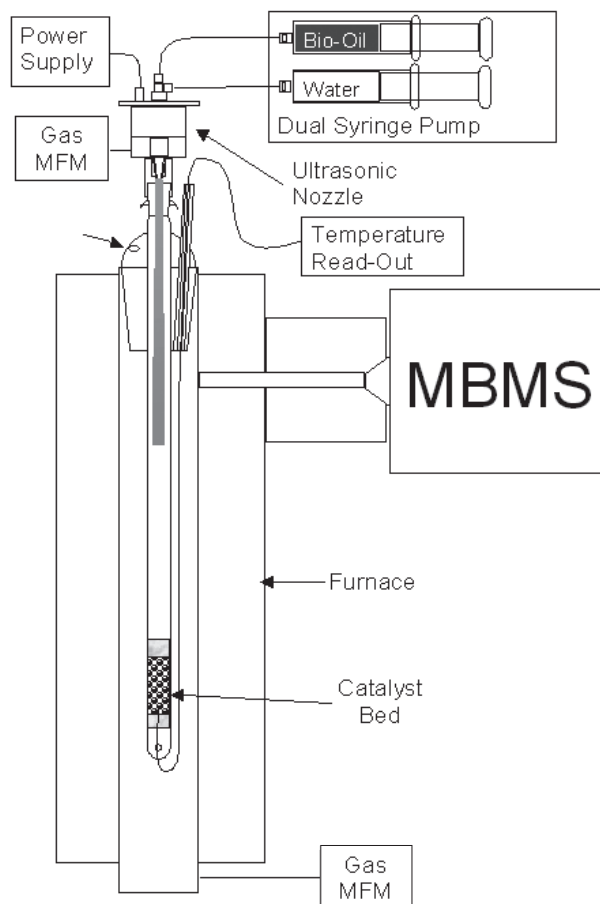


FIGURE 1. Autothermal Reforming Reactor Based on Ultrasonic Nebulization and MBMS Detection

heated to the target temperature, typically 650°C, where a residence time of 0.5 s was achieved.

A catalyst bed will eventually be placed at the bottom of the tube, but in this year's work a bed of quartz particles was placed to capture any deposits that formed in the volatilization and cracking zones. The bio-oil injection system was tested with 50% bio-oil solutions in methanol, and the system performed well, allowing steady-state operation. Results are reported below for those experiments. The target feed composition is 10% methanol, but improvements in the nebulizer must be made to allow that concentration due to the higher viscosity of the liquid. A new power supply is needed with better feedback control.

Oxidative Cracking

This year we are conducting lab-scale experiments to develop a partial oxidation database that will be the basis for the first part of the process model. Parametric studies include bio-oil composition, temperature, residence time, and oxygen level with the objective of breaking carbon-carbon bonds while avoiding oxidation to CO₂ and H₂O and aromatic hydrocarbon formation.

Using the quartz reactor system described above and completing MBMS analysis to determine product composition, we conducted experiments to determine the extent of low-temperature oxidation of the volatilized bio-oil. We have evidence from experiments conducted this quarter indicating significant conversion of revolatilized bio-oil to CO and H₂ with minimal aromatic hydrocarbon formation when the temperature is 650°C and at a low and steady oxygen level. This stage will reduce the required catalyst load in the next catalytic stage, reduce coking tendencies, and provide some of the required heat for the process.

A typical experiment run is shown in Figure 2. At time zero, oxygen is introduced to the system, which is indicated by the line m/z 32 in the spectrum. When bio-

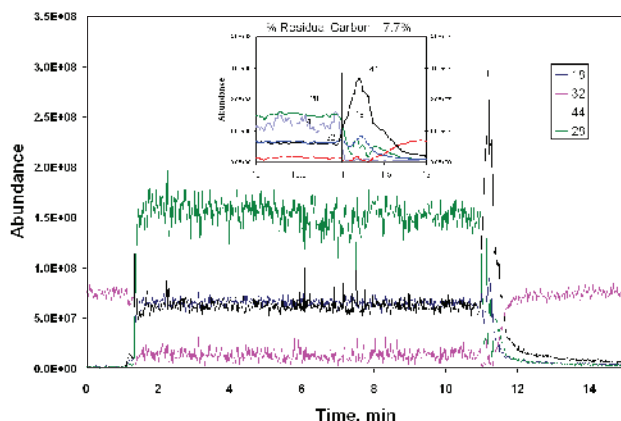


FIGURE 2. MBMS Ion Traces for Bio-Oil/Methanol Oxidative Cracking

oil/methanol feeding begins, the m/z 32 signal declines but does not go to zero because methanol also produces an m/z 32 mass spectrum line. The traces for CO at m/z 28, water at m/z 18, and CO₂ at m/z 44 are shown and remain constant over the 10-minute experiment. When the feeding is stopped at approximately 11 minutes, the oxygen does not immediately rise, and it begins to oxidize carbon deposited in the quartz bed as shown by the increase in m/z 44 as well as sustained signals at m/z 28 and 18. An expanded scale from 10 to 12 minutes also shows benzene at m/z 78 (plotted on the expanded scale shown on the right of the insert). The benzene signal immediately disappears when the feeding stops, implying that benzene is not being formed from the oxidation of deposited carbon but rather is the result of either gas phase chemistry or the reaction of particulate matter formed early in the process.

The average product spectrum for the thermal cracking of the bio-oil/methanol feed in the absence of oxygen is shown in Figure 3. The higher molecular weight lignin-derived products are altered, and three representative products, phenol, catechol, and methylsalicylaldehyde, are shown in Figure 3 (respectively at m/z 94, 110, and 136). The structures shown at m/z 60 are hydroxyacetaldehyde and acetic acid, which are perhaps the most important carbohydrate-derived products. Methanol is present at m/z 32 and 31.

The spectrum for oxidative cracking is shown in Figure 4. The primary and secondary products are essentially removed, and CO is the dominant product. Note that there is residual methanol as shown by m/z 31 (m/z 32 was removed by background subtraction of oxygen). This means that the bio-oil (or at least its volatile part) is more reactive than methanol under these conditions. The striking presence of the aromatics is a major finding. Note that with the film evaporation experiments, there was no benzene present. One explanation is that the material not volatilized (~6%) in film volatilization, which is now in the vapor phase

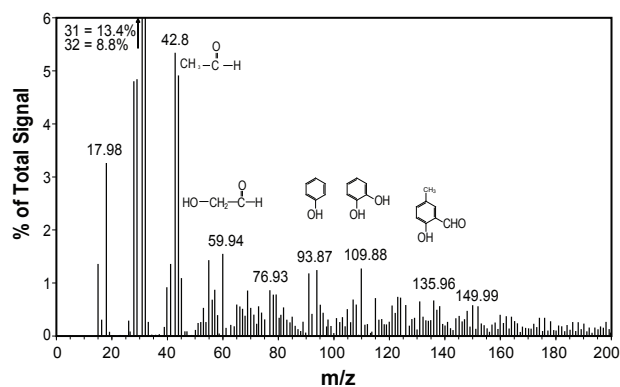


FIGURE 3. Average Spectra for Thermal Cracking (no added oxygen) at 650°C for 0.5 s

resulting from ultrasonic nebulization, is giving rise to the aromatics at this low temperature in the presence of oxygen. Additional experiments will be performed in FY 2006 to address this issue, including lower temperature and longer residence time runs to find the conditions that minimize aromatics formation. Several modifications of the volatilization process are possible to control the chemistry once the parameters of formation are known in detail.

The new system allowed us to calibrate and determine carbon mass balances. The results of key experiments are shown in Figure 5. The CO from bio-oil/methanol is highly correlated with oxygen to carbon (O/C) ratio. At a ratio of 1.6, the carbon conversion

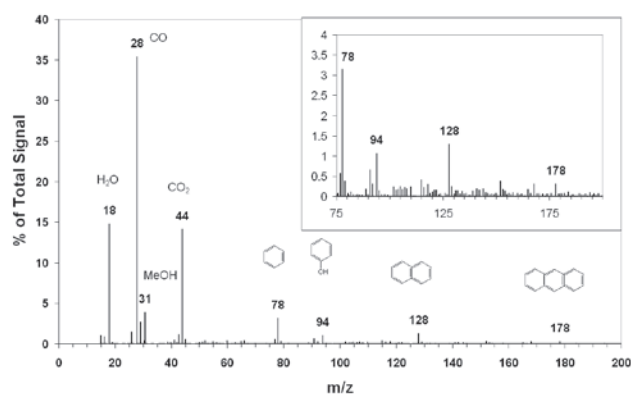


FIGURE 4. Average Spectra for Oxidative Cracking of Bio-Oil/Methanol at 650°C for 0.5 s

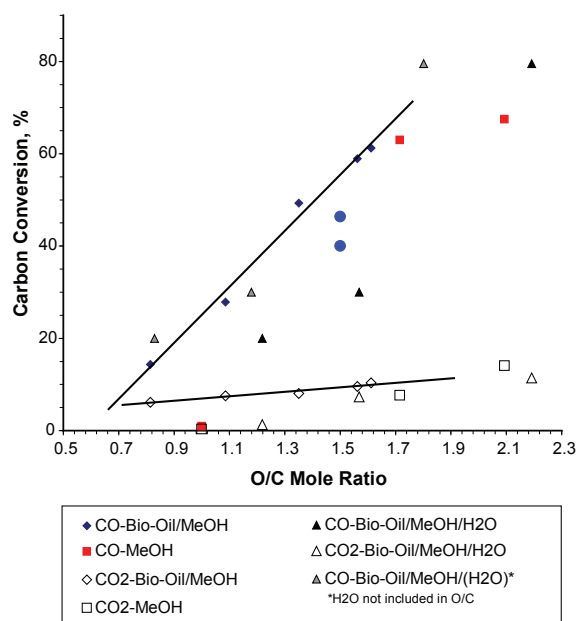


FIGURE 5. Conversion of Feed Carbon to CO and CO₂ as a Function of O/C Molar Ratio for Experiments Performed at 650°C and 0.5 s Residence Time

to CO was 60%. This corresponds to a CO₂ carbon conversion of only 10%. For comparison, the calculated equilibrium at an O/C ratio of 1.5 for both CO and CO₂ was around 40%. Methanol alone shows less conversion to CO, but the corresponding CO₂ levels are comparable to the bio-oil/methanol results. The flat CO₂ response to O/C is encouraging since it means that the downstream water-gas shift reaction can be used to recover the hydrogen that may have been consumed in oxidative cracking. No attempt was made in this work to monitor hydrogen since it requires special mass spectrometer tuning and the emphasis here was on carbon conversion and the removal and formation of high molecular weight products. Several runs are also included in Figure 5 for added steam. These points were plotted with the O/C ratio, not including the added steam, and these latter points fall close to the CO line. This means that H₂O is not playing a significant role in the gas phase cracking, and the water in the bio-oil should not be included in the effective O/C ratio.

Conclusions and Future Directions

The results to date have shown the promise of the staged, low-temperature approach to converting bio-oil to hydrogen using controlled volatilization and oxidative cracking prior to catalytic autothermal reforming. This work has shown that by converting the complex suite of oxygenates to CO, the catalyst loading can be reduced, which allows catalyst reactor configurations that will enable integrated product separation. Catalyst selection, reaction configuration, and integrated hydrogen separation will be explored in FY 2007 and FY 2008.

FY 2006 Publications/Presentations

1. Czernik, S. and French, R., Production of Hydrogen from Plastics by Pyrolysis and Catalytic Steam Reforming, *Energy & Fuels*, 2006, 20, 754-758.
2. Czernik, S., Evans, R., and French, R., Hydrogen from Biomass; Distributed Production by Steam Reforming of Biomass Pyrolysis Oil, 1st International Symposium on Hydrogen from Renewable Resources, 231 ACS National Meeting, Atlanta, GA, March 26-30, 2006.

References

1. Czernik, S., French, R., Feik, C., and Chornet, E. (2002). *Ind. Eng. Chem. Res.* **41**, 4209-4215.
2. Evans, R. J., et al. (2002). Renewable hydrogen production by catalytic steam reforming of peanut shells pyrolysis products. In *Proceedings of 14th World Hydrogen Energy Conference*. Montreal, Quebec, Canada, June 19-13, 2002.
3. Evans, R., and Czernik, S. (2005). *Reforming of Biomass Pyrolysis Oils—Report on Technical Status, Assessment, and Planning*.