

IV.A.13 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 injection, homogeneous partial oxidation, and catalytic autothermal reforming.
- Develop the necessary understanding of the process chemistry, bio-oil compositional effects, catalyst chemistry, and deactivation and regeneration strategy as a basis for process definition for automated distributed reforming to meet the DOE targets.
- In fiscal year (FY) 2005, determine the process performance of the catalytic reforming of whole bio-oil using the catalytic fluid bed and the NREL catalyst.

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. Fuel Processor Capital
- B. Fuel Processor Manufacturing
- C. Operation & Maintenance (O&M)
- D. Feedstock Issues
- F. Control & Safety

Technical Targets

Table 1. 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

Approach

- Review past work on pyrolysis oil reforming.
- Prior to FY 2005, only the aqueous fraction of bio-oil [1] and directly coupled, whole vapors [2] had been reformed in the catalytic fluid bed reactor. As a result, the technical approach in FY 2005 was to use the fluid bed reactor system to test whether whole bio-oil could be successfully revolatilized (partly evaporated and partly converted to aerosol) and reformed.
- Because bio-oil can change physically and chemically over time and during revolatilization, we added 10% methanol to stabilize the oil.
- Screen several catalysts, including a derivative of a commercial nickel catalyst that has been modified for fluid bed operation and a few fluidizable, attrition-resistant formulations developed by NREL to operate in the fluid bed reformer.
- Prepare a detailed plan of the distributed reforming approach.

Accomplishments

- Completed the review of past work and prepared report summarizing all aspects of producing hydrogen from biomass by pyrolysis/reforming studied in past projects [3].
- Whole bio-oil was successfully reformed. With 10% methanol addition, bio-oil processing was trouble-free over runs of up to 16 hours (h).
- The NREL catalysts were shown to be effective for whole bio-oil. Four NREL catalysts showed comparable performance with a modified commercial reforming catalyst. We are filing a patent on the fluidizable catalyst formulations.

Future Directions

- Focus on developing a compact, low capital cost, low/no maintenance reforming system to enable the cost and energy efficiency targets for distributed reforming of renewable liquids to be achieved.
- Move the process away from fluidized nickel catalysts and high temperatures (to accomplish the distributed reforming objective).
- Investigate bio-oil pretreatment options to increase stability and physical and chemical processing.
- Adapt high-pressure injection techniques for the first stage volatilization of the bio-oil.
- Investigate homogeneous partial oxidation of bio-oil as the next stage to break large molecules and minimize the demands on the catalyst system.
- Use heterogeneous auto-thermal reforming of bio-oil derived gas and vapor using non-nickel reforming catalysts in a third stage to finish the conversion to the equilibrium molecular hydrogen (H₂)/carbon monoxide (CO) mixtures.
- Evaluate integrated separation of hydrogen from product gas techniques.
- Conduct additional research to assess the impact of increased feed complexity on reaction mechanisms.
- Develop a robust model for catalyst activity and performance at different process conditions (feedstock composition, temperature, oxygen, steam-to-carbon ratio, and space velocity).
- Determine the kinetics of catalyst regeneration by steam gasification and by oxidation of carbon deposits from the catalyst surface.
- Optimize catalyst formulations for reforming, gasification, and water-gas-shift performance. Deactivation mechanisms, including poisoning by sulfur (S) and chlorine (Cl), need to be evaluated and addressed either through catalyst development or system design.

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. These could be converted to 50 million tons of hydrogen, enough to displace about 37% of the current light-duty transportation fuel used in the U.S. 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 H₂ and CO₂ in a distributed manner at refueling stations or stationary power sites. This proposed work for FY 2006 will target the barriers to automated, low-cost operation of appropriately sized systems for the prototypical filling station that will deliver 1500 kg hydrogen per 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, with the potential of forming carbonaceous deposits or undergoing 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 suited for this application, but are not an optimal choice for small-scale and unattended operation.

Results

We obtained bio-oil—produced in 2002 from mixed hardwood—from DynaMotive, a developer of fast pyrolysis technology located in Vancouver, Canada. To assist in volatilization, we diluted whole bio-oil with 10% methanol. Reforming test durations ranged from 6 to 18 h. The elemental composition of the homogenized bio-oil included 36.5% carbon, 8.4% hydrogen, and 55.0% oxygen. Theoretically, 13.8 grams (g) hydrogen can be obtained from 100 g of that bio-oil assuming that the carbon in bio-oil is completely converted to CO₂.

Five catalysts were tested including a commercial catalyst for reforming naphtha, C11-NK, produced by Sd-Chemie (Louisville, KY). The catalyst pellets were ground to a particle size of 300–500 micrometers (μm), which allowed for uniform fluidization in the reactor while avoiding entrainment. NREL catalysts were prepared by impregnating an attrition-resistant support obtained from CoorsTek (Golden, Colorado) with various amounts of nickel along with gasification and reforming promoters. The exact composition of the catalysts is not reported here because of the ongoing patent review.

All the tests were carried out in a 10 centimeter (cm) fluidized bed reactor operating with 250 g of the catalyst. Bio-oil fed at 84 g/hr was sprayed on the catalyst in the form of very fine droplets. Superheated steam was used as the fluidizing gas and as the reforming reagent. The process temperature was 850°C, with a molar steam to carbon (S/C) ratio of 5.8 and a methane-equivalent space velocity of 920 h⁻¹. The experiments proceeded smoothly without any major upsets. Figure 1 shows the product gas composition and the hydrogen yield (expressed as percent of the stoichiometric potential) obtained using the commercial catalyst. In that experiment, 12.9 g hydrogen was produced from

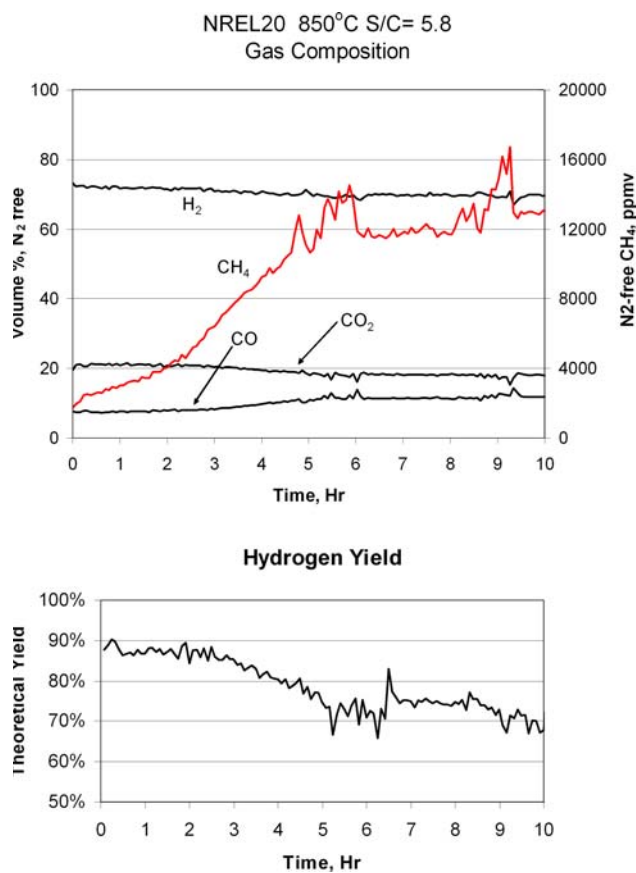
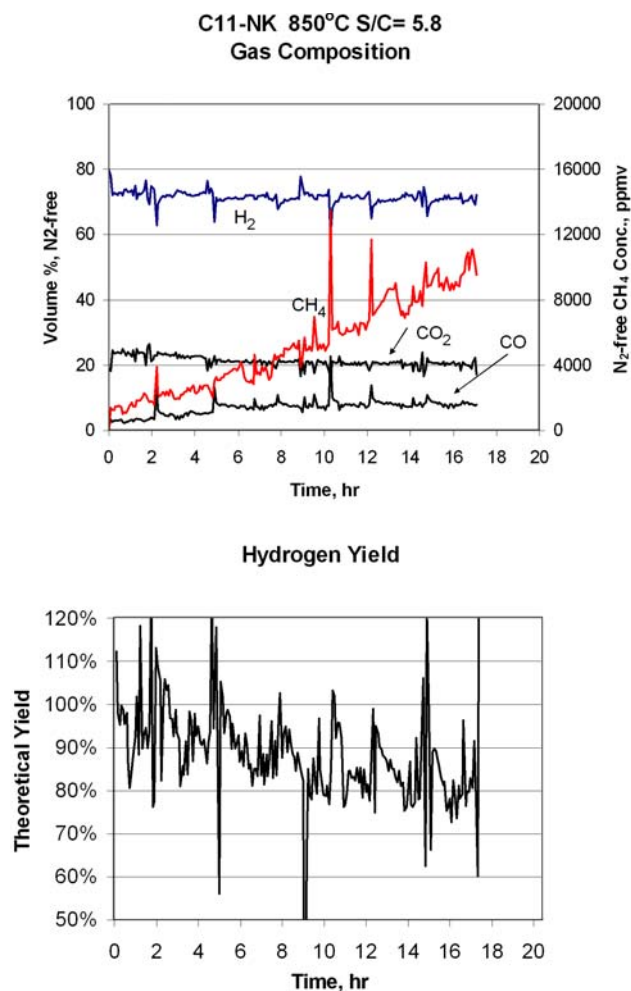


Figure 2. Product Gas Composition and Hydrogen Yield Obtained by Reforming Whole Bio-Oil Using NREL20 Catalyst

Figure 1. Product Gas Composition and Hydrogen Yield Obtained by Reforming Whole Bio-Oil Using a Commercial Catalyst

100 g bio-oil (compared to the stoichiometric potential of 13.8 g/100 g bio-oil). This yield would increase by 10% if CO in the gas were further converted by water-gas shift. These results are very encouraging considering that they are the first obtained for reforming whole bio-oil. Catalyst losses of 1.1%/h were observed for the test, but we had expected this outcome based on the previous fluidized bed tests using different biomass-derived liquids.

We conducted four tests using four NREL-developed attrition-resistant catalysts. The nickel content of our catalysts was significantly lower than that of C11-NK. Typical results are shown in Figure 2. Because of the lower nickel content as

well as the lower surface area, our catalysts showed somewhat lower yields of hydrogen, mostly attributed to lower water-gas-shift activity. The catalyst losses from attrition, however, were much less (0.15%/hr).

The run with C11-NK was the longest in this test series with 18 h on stream. The hydrogen yield decreased slightly over that time as methane slowly rose to 10,000 parts per million by volume (ppmv) where it would probably level off if operation were continued. This is typical of the performance observed with the bio-oil aqueous fraction. We did not attempt lower S/C ratios in this experiment, but this is an important variable that will need to be tested. One potential problem that has not been addressed by past work is the possibility of more extensive and rapid carbonization as the whole bio-oil is introduced into the reactor, making the action by both steam and catalyst more difficult. It appears

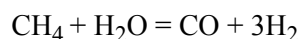
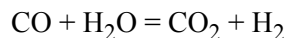
that the injected whole bio-oil in our laboratory testing behaves similarly to the directly coupled whole vapor reformer runs conducted in the pilot-scale reactor, which ran for 100 h in FY 2003 [2] and is currently the subject of a 1000-h test at the University of Georgia. In other words, deactivation rates are on the order of hundreds of hours on stream and not tens of hours. The spraying of the more complex feedstock does not cause excessive carbonization as we anticipated for the lignin-derived phenolics. The level of methanol addition was not varied and could prove to be a key variable in the process.

Figure 2 shows comparable results for the NREL20 catalyst. The results are typical with a more rapid increase in methane than observed for C11-NK, but the tendency is for the methane level to eventually rise to the same level, which may be equilibrium controlled. CO levels start higher and rise more rapidly than for C11-NK as well. Improvement of the water-gas-shift activity of the NREL catalysts has been the subject of recent work. Likewise, the slow decrease in hydrogen and CO₂ probably results from low nickel content and the impact of carbon deposition on the catalyst site. These are also the targets of recent catalyst development activities.

The results for the NREL catalysts are difficult to compare because the performance of any one parameter, such as hydrogen yield, varies by only a small amount at any given time. In addition, each run includes process upsets caused by discontinuities in bio-oil or steam feeding. To utilize the time-series information that is in each experiment, we used multivariate statistical analysis to determine correlated behavior across all six experiments. In addition to the five catalyst runs, we performed a sixth experiment, NREL21, on just the support material used in NREL20.

We used ten process variables and calculated correlation coefficients using factor analysis. The first factor explained 45% of the variance in the entire data set. More than 700 sets of measurements from the six experiments were included in the analysis. After the first calculations, we eliminated outliers, which were either caused by spikes or interruptions in steam or bio-oil feed. The products

were all weighted equally in this calculation so hydrogen and ethylene had equal impact in the analysis. We assigned these equal weights because the trace components are a more sensitive indicator of changes in conditions. In addition, the product gases were entered as masses, again reducing hydrogen in importance. No normalization effect was included as would be the case if gas composition data were used. The process parameters—bio-oil feed rate, steam feed rate, and nitrogen concentration (used for atomizing bio-oil)—were included to evaluate the variation that may have been encountered over the many hours of run time. The coefficients show high positive correlations for H₂ and CO₂, which are the desired final products, so higher scores for a sample indicate better performance. Steam is also positively correlated, so a positive deviation in the steam rate improved performance. The trace hydrocarbons methane, ethylene, and ethane had the highest negative scores, which was expected because they represent incomplete reactions, as did potential coke deposition. The mass closure was included to represent potential undetected products; it too had a high negative correlation coefficient, which is difficult to interpret. If a variable is unimportant, it would have a value close to zero (e.g., feed rate), so it is unclear why total and nitrogen show high negative values. The CO coefficient is only half as influential as methane even though both are intuitively used as indicators of catalyst performance, but this analysis shows that the latter is less strongly related to maximum hydrogen yield than to methane. Considering the following equilibria may be helpful, although CO levels are much greater than methane levels.



All hydrocarbons are strongly correlated with each other and with the tars, and together they may represent 20% of the carbon. Modeling the carbon balance rather than the total may make more sense. The total tends to be low for the first hour that steam is on because the condenser is not yet wet. The highest conversion also takes place during the first hour of steam, so if no methanol was run at the start to wet the condenser, the total balance may be negatively correlated with hydrogen yield. The

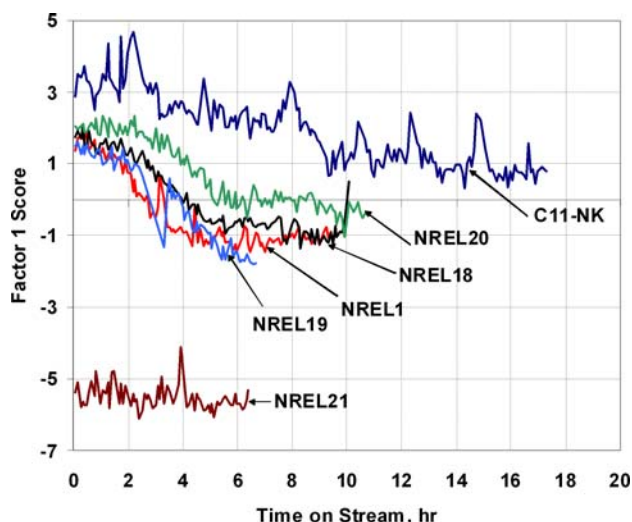


Figure 3. Factor score plot of the factor defined by the linear combination of 10 variables that explained 45% of the variance in the entire data set of 700 sampling points \times 10 variables. Because the six individual runs were included in the analysis, this graph is proposed as a basis for comparison of relative catalyst performance. The magnitude of the score is not physically meaningful (the units are standard deviation units). Instead, the calculation is intended to allow a higher level of discrimination among catalysts than is possible by simple univariate comparisons that are typically made from the data in Figures 1 and 2. NREL21 is the support material used in catalyst 20 and therefore can be used to represent a completely deactivated catalyst.

nitrogen is probably negatively correlated because when nitrogen flow is constant, a high concentration of nitrogen indicates a low yield of product gas.

The first factor score is plotted in Figure 3 for the catalysts we compared. The C11-NK performance degraded slightly over the 16 h, which is consistent with the results of past tests with the aqueous fraction, where conversion was acceptable for up to 200 h [1]. The factor score used here is a sensitive indicator of change so the plot of the four NREL catalysts and the support material allows direct comparisons to be made and leads to the choice of NREL20 as the best-performing catalyst. The difference between NREL20 and C11-NK is due to reduced water-gas-shift activity, and as with C11-NK we expect that the catalyst will perform at an

acceptable level for more than 100 h (as was experienced with the aqueous fraction [1]). The immediate coking of the catalyst from the volatilization of the more reactive and recalcitrant components of the whole bio-oil was not seen in these experiments.

Conclusions

Whole bio-oil was successfully converted to hydrogen in five experiments using five different catalysts. Chemically, the four NREL catalysts did not perform as well as the commercial catalyst, but they showed better attrition resistance. Catalyst NREL20 has been selected as the best catalyst for reforming whole bio-oil, and we will use this catalyst as the basis for performing economic analysis of the distributed reforming of bio-oil concept. It is likely that increased levels of nickel and coke gasification promoters can make improvements in this formulation. The main difference is likely caused by lower water-gas-shift activity, which further development work promises to overcome.

FY 2005 Publications/Presentations

1. Czernik, S., Evans, R. J., and French, R. (2005). *Initial Evaluation of NREL's Catalysts for Reforming Whole Bio-Oil*. Milestone Progress Report
2. Evans, R. J., and Czernik, S. (2005). *Reforming of Biomass Pyrolysis Oils—Report on Technical Status, Assessment and Planning*. Milestone Progress Report.
3. Elam, C. C., and Evans, R. J. (2004). Overview of hydrogen production. *Preprints of Papers—American Chemical Society, Division of Fuel Chemistry* 49(2), 481–482; NREL Report No. CP-510-36887.
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5. Day, D., Evans, R. J., Lee, J. W., and Reicosky, D. (2005). Economical CO₂, SO_x, and NO_x capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration. *Energy* 30(14), 2558–2579.
6. Evans, R. J. (2004). Hydrogen from Biomass. Presented at the Renewable Energy from Organics Recycling Conference, Minneapolis, Minnesota, November 17–18.

7. Evans, R. J. (2004). Options for Renewable Hydrogen Production. Presented at the Conference on Energy & Agricultural Carbon Utilization, Athens, Georgia, June 11–12.

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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*.