

II.A.1 Biomass-Derived Liquids Distributed (Aqueous Phase) Reforming

David King (Primary Contact), Yong Wang,
Ayman Karim, Christopher Howard, Sarah Widder
Pacific Northwest National Laboratory (PNNL)
P. O. Box 999
Richland, WA 99352
Phone: (509) 375-3908
Email: david.king@pnl.gov

DOE Manager

HQ: Sara Dillich
Phone: (202) 586-7925
Email: Sara.Dillich@ee.doe.gov

Project Start Date: October 1, 2004

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

Fiscal Year (FY) 2012 Objectives

- Develop aqueous phase reforming (APR) catalysts and technology to convert bio-derived liquids to hydrogen that meets the DOE 2012 cost target of \$3.80/gge, verified by H2A analysis
- Identify primary compounds in bio-oil that are extractable into an aqueous phase
- Determine the effectiveness of aqueous phase reforming in producing hydrogen from these water-soluble compounds
- Estimate cost of hydrogen production using best catalytic results, given a defined feedstock cost

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.2) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reformer Capital Cost
- (D) Feedstock Issues
- (E) Greenhouse Gas Emissions

Technical Targets

TABLE 1. Progress towards Meeting Technical Targets for Distributed Production of Hydrogen from Bio-Derived Renewable Liquids

Characteristics	Units	2012 Status	2017 Target
Capital Cost	\$/gge	1.77	0.40
Storage, compression, dispensing	\$/gge	2.00	0.35
Fixed operation and maintenance	\$/gge	0.44	0.40
Feedstock Cost	\$/gge	27.08	1.55
Variable operation and maintenance	\$/gge	0.29	0.30
Total hydrogen cost	\$/gge	31.84	3.00

gge – gasoline gallon equivalent

FY 2012 Accomplishments

- Aqueous fraction of bio-oil has been examined as low-cost bio-liquid feedstock for APR
- New catalyst leads, especially 5% Pt-1.5% Co/ZrO₂, have been identified and have potential to improve H₂ yield and economics
- Demonstrated that meeting the 2017 target <\$3.00/kg H₂ (produced and dispensed) will be very challenging, and a much lower feedstock cost than 2012 H2A value of \$1.12/gal is required to meet the target



Introduction

This project focuses on the APR of biomass-derived liquids for the production of hydrogen. We target the development of catalysts and catalytic processes to meet the 2017 DOE target of <\$3.00/gge (dispensed). Our H2A analysis has indicated that the primary driver for the cost of H₂ produced from bio-derived liquids is feedstock cost, assuming good catalytic APR performance. As a result, in FY 2011 we switched from relatively purified (and more expensive) bio-liquids, such as glycerol and sorbitol, to pyrolysis oil. Pyrolysis oil (bio-oil) is lower cost and potentially has much higher availability than other bio-derived liquids. Our specific plan is to carry out APR on the water soluble fraction of bio-oil. This fraction is most conveniently generated by addition of water to the initial bio-oil product. It contains lower molecular weight species and a higher fraction of oxygen-containing functional groups than the water-insoluble fraction. As a result, the water soluble fraction is expected to have a greater potential for successful APR to produce hydrogen. In FY 2012 we proposed to

continue the work initiated in FY 2011, with a greater focus on examining alternative catalysts for H₂ production.

Approach

We started by obtaining a source of non-stabilized bio-oil, and mixed it with water in order to generate a water-soluble fraction. We then proceeded to identify the major compounds, and classes of compounds present in this fraction by high performance liquid chromatography (HPLC). From that, we identified one representative compound from each of the classes of compounds identified: 1-propanol (alcohols, mono-oxygenates); glycerol (polyols); acetic acid (carboxylic acids).

We carried out a preliminary evaluation of catalyst performance in a high throughput combinatorial reactor with each of the three compounds identified above. We used our standard testing conditions of relatively low temperatures (225-265°C) and sufficient pressure (about 30 bar) to maintain liquid phase operation. In one set of experiments we examined performance at 300°C. The purpose of the combinatorial testing was to examine possible alternate catalysts to our Pt-Re/C catalyst, which was deemed inadequate to meet the H₂ cost target. The work examined several catalysts based on bimetallic combinations of metals. We also compared performance with ZrO₂ support in place of carbon. Subsequent studies with single unit reactor testing are scheduled for completion prior to the end of FY 2012, examining performance with the surrogate mixture of aqueous soluble bio-oil and then an actual feedstock sample. Finally, the results will be included in the H2A analysis.

Results

Bio-oil generated from pyrolysis of pine saw dust (480°C, 1.6 sec residence time) was mixed with water at a ratio 4 parts H₂O:1 part bio-oil by weight. The sample was shaken vigorously to form a single phase, and then centrifuged to generate the aqueous and non-aqueous phases. Figure 1 shows that a large fraction of the total carbon in the bio-oil was soluble in the water fraction. Table 2 provides the distribution of identified products comprising the bio-oil (accounting for ~70% of the carbon available), as identified by HPLC. The majority of the products are oxygenated hydrocarbon, primarily having four or fewer carbon atoms in the molecule.

Table 2 shows that it is possible to categorize the products according to oxygen content and type: poly-oxygenates (polyols, sugars); mono-oxygenates (alcohols, aldehydes and ketones); and carboxylic acids. We selected one molecule from each group to carry out further tests to screen improved catalyst formulations: glycerol, 1-propanol, and acetic acid.

Segregation of bio-oil carbon, by phase (wt% C in raw bio-oil)

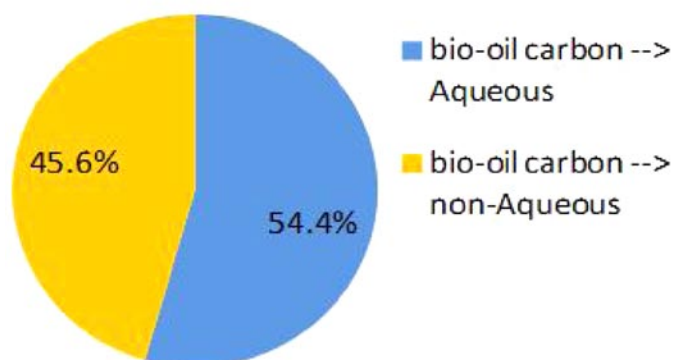


FIGURE 1. Segregation of bio-oil carbon between water and oil fractions; water/oil = 4/1 (wt)/(wt)

TABLE 2. Major Species Identified in the Aqueous Fraction of Bio-Oil by HPLC Analysis

Poly-Oxygenates	Mono-Oxygenates	Carboxylic Acids
glycerol	1-butanol	acetic acid
glycolic acid	isobutanol	propionic acid
ethylene glycol	1-butanol	
glycolaldehyde	ethanol	
levoglucosan	1-propanol	
sorbitol		
glucose		
xylose		

Based on our work in FY 2011, we found that several molecules in the bio-oil were not reactive toward hydrogen formation, and that acetic acid was difficult to reform and moreover tended to deactivate the 5% Pt-3% Re/C catalyst, reversibly. The primary effort in FY 2012 was to make progress was to develop catalysts that were more active and selective toward H₂. For this reason, we carried out a high throughput screening effort to identify better catalysts. Our first effort was to screen catalysts using glycerol as feedstock, representing the poly-oxygenate class of molecules. Figure 2 shows the possible reaction pathways available to even a seemingly simple three-carbon molecule. The cause of these divergent pathways is a competition between the desired C-C bond cleavage which leads to production of H₂ and CO (and with subsequent water gas shift, the CO shifts to CO₂ and a second molecule of H₂ is generated); and a pathway based on loss of water from the molecule (dehydration), which does not produce hydrogen but rather leads to more saturated

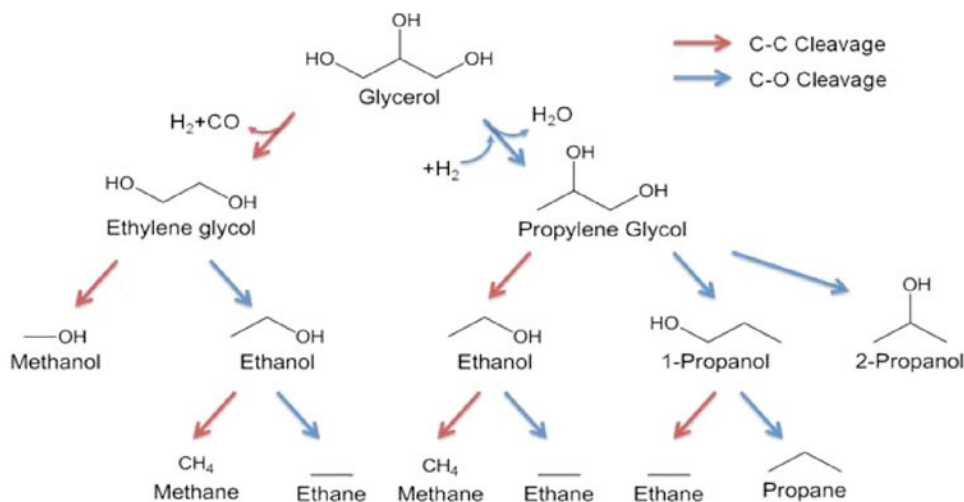


FIGURE 2. Facilitating C-C bond breaking is the key to hydrogen production from glycerol

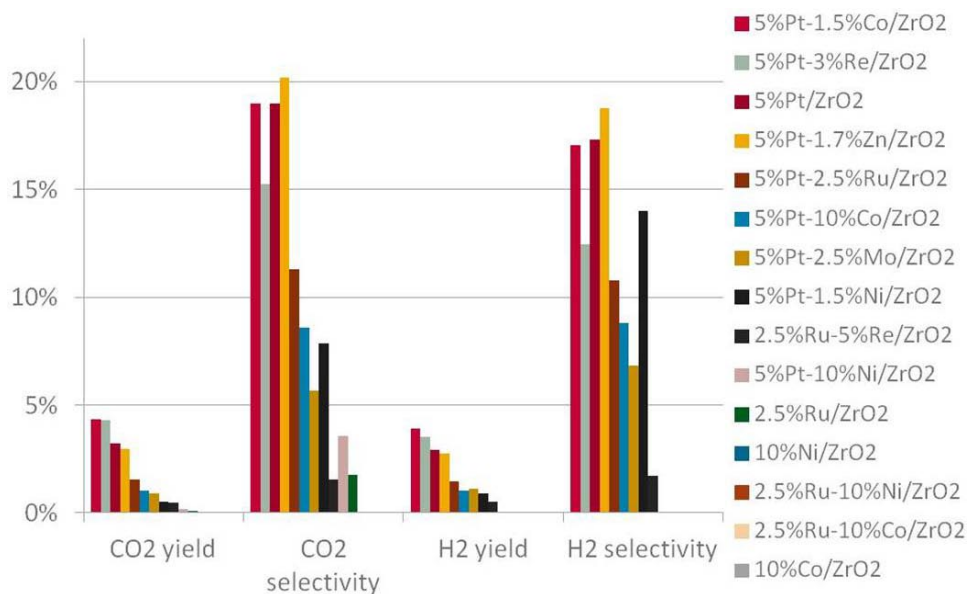


FIGURE 3. Catalyst combinatorial screening for maximum activity and C-C/C-O cleavage: glycerol APR for selected mono- and bi-metallic catalysts supported on ZrO₂

hydrocarbons. Our screening tests were aimed at identifying catalysts that produce the maximum amount of hydrogen. The results of the high throughput test are shown in Figure 3. One thing to notice is that although there were many catalysts screened, fewer provide data in the figure, indicating that many catalysts, including (notably) the single, non-precious metal catalysts, show poor APR activity. A figure of merit was generated (not shown) based on the product of the values for CO₂ yield, CO₂ selectivity, H₂ yield, and H₂ selectivity. The figure of merit was found to be highest for 5% Pt-1.5% Co/ZrO₂, 5% Pt-3% Re/ZrO₂, and 5% Pt/ZrO₂. The new bimetallic combination was the addition of the Pt-Co catalyst.

Studies for 1-propanol APR showed similar behavior and catalyst ranking, although at best 1-propanol generated 1 mole of H₂. This is determined by the fact that ethane was a common product, (rather than ethylene), indicating that one of the two potential molecules of H₂ formed reacted with the C₂ fragment to form ethane. Operation at higher temperature (300°C) did not have any effect on improving selectivity or generating methane, the latter which could be subsequently reformed. Examination of acetic acid performance showed that only the Pt-Re/C catalyst showed the ability to recover activity after being exposed to acetic acid. The remainder of

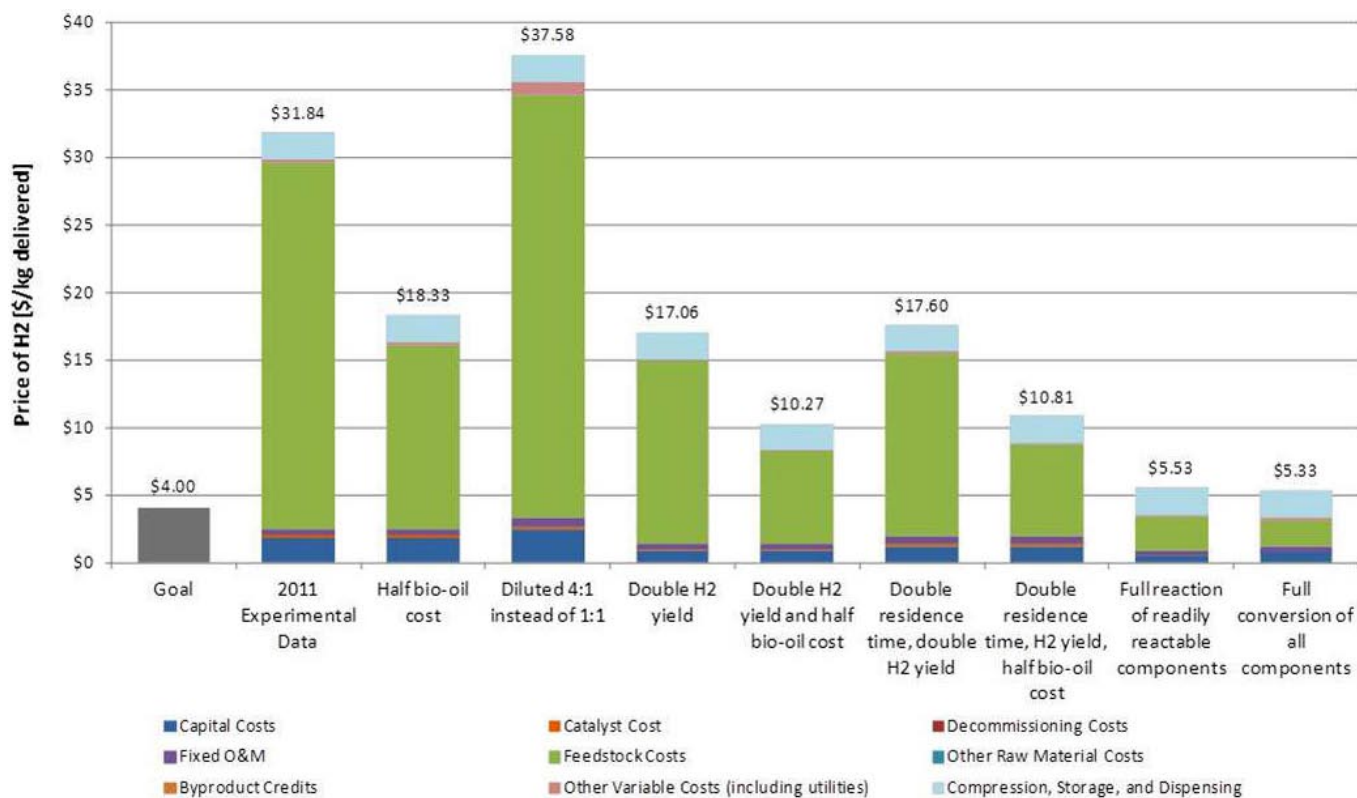


FIGURE 4. H₂Av3 sensitivity analysis

the catalysts showed irreversible deterioration of the catalyst following exposure to acetic acid.

The APR performance with the aqueous fraction of bio-oil is summarized in the H₂Av3 analysis (Figure 4). Part of this summary is based on FY 2011 performance, as FY 2012 studies have not yet been completed. A number of scenarios are considered to determine effects of various factors on H₂ production cost. As expected, a big factor is high feedstock cost. This is based mainly on poor H₂ yield from many of the molecules in the feed, and poses an inherent problem in meeting the delivery target. Improved catalysts are expected to make at best a partial improvement to the H₂ cost, but not to the extent that the \$3.00/kg target can be met.

Conclusions and Future Directions

- Aqueous fraction of bio-oil has been examined as low cost bio-liquid feedstock for APR, and shown to comprise poly-oxygenates, mono-oxygenates, and carboxylic acids, predominantly C₆ or lower. Of these, only the poly-oxygenated components have potential for significant hydrogen production. The theoretical maximum yield of hydrogen with this aqueous bio-oil feed is relatively low in comparison to glycerol, sorbitol, or other predominantly polyol-based feedstocks.

- New catalyst leads, especially Pt-Co/ZrO₂, have been identified and have significant potential to improve H₂ yield and economics compared with FY 2011 results.
- Meeting the target of \$3.00/kg H₂ (produced and dispensed) will be very challenging. The theoretical best H₂ yield case will likely exceed this target, given the feedstock composition and the low potential H₂ yield from mono-oxygenates. A lower feedstock cost than 2012 H₂Av3 value of \$1.12/gal is required to meet the target.
- Concluding work in FY 2012 will be to complete testing with best catalyst of aqueous phase bio-oil, and provide a report and H₂A analysis summarizing findings.
- There are no plans to continue this work in FY 2013, given the challenges to meet the H₂ cost target for 2017.

FY 2012 Publications/Presentations

- Liang Zhang, Ayman M. Karim, Zhehao Wei, David L. King, Yong Wang. Correlation of Pt-Re surface properties with reaction pathways for the aqueous-phase reforming of glycerol. *J. Catal.* 287 (2012) 37-43.