

II.E.2 Biomass-Derived Liquids Distributed Reforming

David King (Primary Contact), Yong Wang,
Ayman Karim, James Rainbolt, Kurt Spies
Pacific Northwest National Laboratory (PNNL)
P.O. Box 999
Richland, WA 99354
Phone: (509) 375-3908
Email: david.king@pnnl.gov

DOE Manager

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

Project Start Date: October 1, 2004
Project End Date: September 30, 2013

Overall Objectives

- Identify catalyst, reactor, and operating conditions that maximize hydrogen selectivity and yield from biomass-derived liquids via a catalytic reforming approach
- Quantify hydrogen selectivity and yield requirements for aqueous phase reforming (APR) of biomass-derived liquids to meet the hydrogen 2015 cost target of <\$5.90/gasoline gallon equivalent
- Demonstrate a viable pathway to produce hydrogen from biomass-derived liquids that meets the 2015 target

Fiscal Year (FY) 2013 Objectives

- Develop and demonstrate the feasibility of a two-step approach for the production of hydrogen from cellulose, combining cellulose deconstruction and APR
- Quantify selectivity, yield, and other requirement to enable this two-step approach to meet the 2015 target by H2A analysis
- Demonstrate experimentally the feasibility to meet these requirements in a set of catalytic reactions, generating hydrogen to meet the 2015 target
- Demonstrate the feasibility to apply this technology to the conversion of raw biomass to hydrogen

Technical Barriers

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

- (A) Reformer Capital Costs and Efficiency

(C) Biomass Feedstock Issues

(N) Feedstock Cost and Availability

Technical Targets

There is one primary technical target that we are addressing—H₂ production cost from bio-derived liquids reforming as shown in the following table:

Characteristics	Units	2011 Status	2015 Target	2020 Target
Hydrogen Levelized Cost (Production Only)	\$/kg	6.6	5.9	2.3

Source: Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan (MYRD&D Plan), Hydrogen Production Chapter, July, 2013, <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/production.pdf>

This multi-year project has examined the pathways for production of hydrogen from a variety of biomass-derived liquids. The cost of the starting feedstock has always proven to be a significant factor in the overall economics of hydrogen production. In FY 2013, this project focused on a pathway to convert cellulose to hydrogen, via an initial catalyzed “deconstruction” step to produce a polyol-rich product containing a high fraction of ethylene glycol, followed by APR of the ethylene glycol-rich product into hydrogen and CO₂. Ethylene glycol is one of the most facile molecules for production of hydrogen via APR and this two-step route should allow the use of cellulose, a less expensive feedstock than sugar/sugar alcohols we previously studied. H2A analysis is being used to establish performance targets as well as quantify the current production cost status of this route to meet the hydrogen cost target based on actual performance in catalytic tests. Beyond cellulose as a starting material, the final work on this project will focus on the replacement of cellulose by whole biomass via the same two-step approach. If this can be accomplished, this enables the use of a cheap biomass feedstock and should provide a path for further reducing the cost of hydrogen from biomass through a bio-liquid intermediary route.



INTRODUCTION

Hydrogen production is a significant part of the Fuel Cell Technologies Office mission. It is most easily produced (and demonstrated to meet target cost) through the steam reforming of natural gas, which is seen as a transition fuel for hydrogen production. Natural gas reforming results in the co-production of the greenhouse gas CO₂. For this reason, there is a significant benefit in generating hydrogen from

renewable biomass, since the penalty for co-producing CO₂ is close to zero (the CO₂ co-production product does not need to be captured). Biomass gasification is one option; however this approach is limited by high capital costs. The cost of transporting raw biomass, and biomass availability, also places limits on the size of the gasifier, which results in loss of economies of scale. Steam reforming of some of the products of biomass processing is only possible for a few products (ethanol, methanol, glycerol, acetic acid), but many of the products, such as sugars, decompose on heating and are therefore not viable candidates for steam reforming.

One alternate approach for production of hydrogen from biomass-derived liquid phase (at ambient temperature) products is APR, which allows conversion of these less thermally stable compounds to hydrogen at modest temperatures and pressures without their decomposing or degrading in the reactor. The choice of feedstock with APR remains a consideration, as APR is not 100% selective toward hydrogen with most bio-derived liquid feedstocks, especially those with carbon numbers 5-6 or higher. This dictates that the approach for hydrogen production via APR requires highly active/selective catalysts and inexpensive feedstocks, preferably of low carbon number. Previously, we examined the aqueous fraction of bio-oil as a reactant; conversion of carboxylic acids present in this feedstock, notably acetic acid, was low and its presence in the feed appeared to deactivate the catalyst through a reversible poisoning mechanism. For this reason, in FY 2013 we revamped the program and examined an alternate feedstock and catalytic approach. Cellulose was selected for the initial primary investigation, and a two-step conversion pathway was employed. The first step was to facilitate the deconstruction of cellulose (according to literature precedents) to a mixture of polyols rich in ethylene glycol, followed by APR of this polyol mixture. We and others have established previously that ethylene glycol undergoes conversion to hydrogen with high yield via APR. Since we have focused previous work on the APR, the major focus of research in FY 2013 was on the cellulose deconstruction step. Successful deconstruction of cellulose can lead to a more ambitious effort to convert whole biomass (deconstructing the cellulose and hemicellulose fractions), followed by similar APR for hydrogen production with combustion of the unreacted lignin fraction for process heat.

APPROACH

The production of hydrogen from cellulose follows a two-step conversion process. The first step is described in the literature [1], and involves deconstruction of cellulose using bi-functional catalysis (acid plus metal under hydrogen pressure) to a mixture of oxygenates rich in polyols. In the most favorable cases, high yields of ethylene glycol have been reported. Since cellulose can be considered a polymer of glucose, it seems likely that glucose is the

initial deconstruction product, as suggested by Liu et al. [1]. It is notable in that same work that sorbitol, the sugar alcohol derived from glucose, is unreactive, and therefore it is claimed that ethylene glycol is produced directly from glucose. However, the mechanisms for this transformation have not been fully developed. In the second step of the two-step process, the hydrogen overpressure is removed, and the polyol-rich mixture is converted to hydrogen via APR using a Pt-Re/ZrO₂ catalyst that we previously identified. The combining of these two steps has not been described in the literature prior to our proposing this approach for hydrogen production. The overall H₂ yield will very much depend upon the composition of the compounds that are produced during the cellulose deconstruction.

If we are successful with cellulose, we intend to move to whole biomass as a feedstock. We are expecting that the cellulose and hemicellulose portions of the biomass will be extracted and dissolved (as is cellulose by itself), leaving just the lignin fraction as a filterable by-product. APR will proceed to convert the products of deconstruction of both cellulose and hemicellulose to hydrogen and CO₂. The lignin fraction will be separated from the products of the first reactor by filtration, and can be combusted to provide process heat.

FY 2013 ACCOMPLISHMENTS

- Completed first pass H2A analysis for the two step process; identified key cost contributors to be feedstock cost and capital cost, including cost of processing waste water—indicating the need to demonstrate the ability to recycle the spent feed stream to the reactor and convert residual soluble carbon species to gaseous products to near extinction.
- Optimized the WO₃/Al₂O₃ (45 wt% WO₃) + 5%Ru/C catalyst system for the cellulose deconstruction at a 2:1 weight ratio, maximizing conversion and ethylene glycol yield.
- Obtained an ethylene glycol yield of 42% (carbon basis) at full conversion of cellulose, at 245°C and 180 minutes residence time (0.45 g catalyst and 4 g cellulose), equaling best literature values.

A summary of the key finding of our catalytic studies are provided in Table 1. We found that operation at 245°C provided the best performance compared to operation at lower temperatures (205°C and 225°C). Key points to be noted include:

- In the absence of the WO₃/Al₂O₃ catalyst component, the overall cellulose conversion from 5% Ru/C is low as is the selectivity to ethylene glycol (columns 1 and 2). The acidic function provided by WO₃/Al₂O₃ appears necessary to produce significant quantities of ethylene glycol via glucose.

- With increasing residence time, with the $\text{WO}_3/\text{Al}_2\text{O}_3$ + Ru/C catalyst, sorbitol decreases and ethylene glycol increases (columns 2 and 3). This is also shown more clearly in Figure 1, which includes data obtained at 60 minutes residence time as well. Although sorbitol may not be a primary intermediate in the production of ethylene glycol, neither is it unreactive as suggested by Liu [1]. At longer residence times, sorbitol appears to convert to ethylene glycol with this catalyst system. The long residence time data also suggest that ethylene glycol is stable under reaction conditions.
- The importance of the role of $\text{WO}_3/\text{Al}_2\text{O}_3$ is further supported by comparing performance of the combined catalysts at two different ratios (columns 3 and 4). The catalyst combination 0.17 g $\text{WO}_3/\text{Al}_2\text{O}_3$ + 0.28 g Ru/C performed poorly compared to the combination 0.28 g $\text{WO}_3/\text{Al}_2\text{O}_3$ + 0.17 g Ru/C (columns 3 and 4). Nevertheless, the presence of the 5% Ru/C catalyst component is clearly important in providing a hydrogenation function that generates terminal OH groups in the products.
- We also note that compared with direct APR of sorbitol, which we have described in earlier project work, it appears that this bifunctional catalyst system could provide a better route to hydrogen production from sorbitol via an ethylene glycol intermediate. This is

because the direct APR of sorbitol produces a number of products in addition to hydrogen and CO_2 . Nevertheless, based on the high cost of sorbitol as a feedstock, this new approach is not likely to be economically attractive as a route to hydrogen from bio-derived liquids.

TABLE 1. Comparative Performance of Ru/C and $\text{WO}_3/\text{Al}_2\text{O}_3$ + Ru/C at Two Different Ratios

Temperature (C)	245	245	245	245
Time (min)	30	30	180	180
Catalyst (g)				
Ru/C	0.17	0.17	0.17	0.28
$\text{WO}_3/\text{Al}_2\text{O}_3$		0.28	0.28	0.17
Conversion (%)	54.2	86.3	100.3	62.5
Yield (g/L)				
Ethylene Glycol	1.38	12.89	18.27	3.85
Sorbitol	4.08	7.51	1.42	4.58
Propylene Glycol	1.75	0.87	2.44	1.23
Ethanol	1.5	0.75	0.99	1.06
1,2 Butanediol	0.36	0.74	1.22	0.67
Glycerol	1.67	0	0	0
Methanol	0	0.18	1.05	0
Acetic Acid	0	0	0.37	0

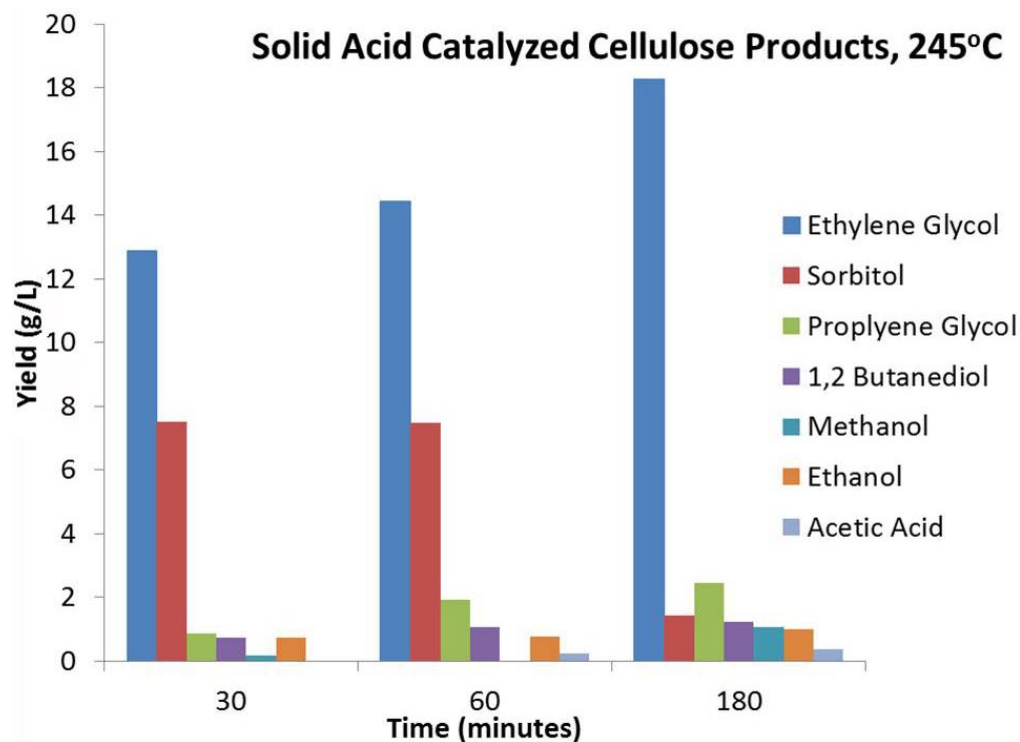


FIGURE 1. Yield of various products from the deconstruction of cellulose using a combination of $\text{WO}_3/\text{Al}_2\text{O}_3$ + Ru/C catalysts at 245°C.

FUTURE DIRECTIONS

The project will end with the end of FY 2013 funding. However, we point out the importance in any future work of determining the ability to recycle the catalyst and the waste water stream in subsequent cycles (cellulose deconstruction step) and as well APR catalyst longevity with the ethylene glycol-rich polyol feedstock.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. A.M. Karim, C. Howard, B. Roberts, L. Kovarik, L. Zhang, D.L. King, Y. Wang “In situ XAFS studies on the effect of pH on Pt electronic density during aqueous phase reforming of glycerol”, *ACS Catalysis*, 2, 2387–2394 (2012).

REFERENCES

1. Yue Liu, Chen Luo, and Haichao Liu, “Tungsten Trioxide Promoted Selective Conversion of Cellulose into Propylene Glycol and Ethylene Glycol on a Ruthenium Catalyst”; *Angew. Chem. Int. Ed.* 2012, 51, 3249–3253.