Aqueous Phase Reforming of Yellow Poplar to Hydrogen

Timothy D. Davis[1*], Sean C. Emerson[1], Theresa A. Campbell[1], Ying She[1],
Rhonda R. Willigan[1], Thomas Henry Vanderspurt[1]
[1]*United Technologies Research Center, East Hartford, CT 06108*
*DavisTD@UTRC.UTC.com

Introduction

Growing concern over the availability, cost, and environmental impact of traditional petroleum energy sources, has emphasized the need to develop alternative energy technologies that reduce our dependence on non-renewable resources. Hydrogen is a carrier of energy, typically created by conversion of other energy sources. Lignocellulosic biomass is one such low cost source that is renewable and available in significant quantities. It is inherently carbon neutral and sustainable. What remains is providing a low cost, efficient route for its conversion to hydrogen.

One effective means for H_2 production from biomass is by hydrolysis of biomass with concomitant Aqueous Phase Reforming (APR) over a supported metal catalyst. For such a technology to be economically feasible, it be must relatively simple, use raw or minimally processed biomass feedstock, produce a high hydrogen yield with good (~50%) overall energy efficiency, and not produce toxic byproducts or excessive waste streams. Significant work has been reported in the literature for APR of preprocessed biomass derived feed stocks and related oxygenates like ethylene glycol. Solutions of glycerol, glucose or sorbitol have been reformed to H_2, CO_2, and low molecular weight alkanes over Ni, Pt, Ni-Sn catalysts[1,2,3] and other[4,5] catalysts. However, relatively little has been done on raw biomass other than the report of hydrogen production from Southern Pine after acid hydrolysis[6]. In addition, the hydrolysis liquor will be either acidic or basic in nature, leading to significant challenges with regards to catalyst stability, activity, as well as tailoring reaction chemistry. In our overall concept the cellulosic and hemi-cellulosic components of the biomass are reformed to hydrogen and the lignin rich liquor is used to fuel the system.

Materials and Methods

The biomass materials and surrogates used in this work include ethylene glycol, glucose, sorbitol, hemicellulose (xylan), microcrystalline cellulose, and yellow poplar (***Liriodendron tulipifera)*** saw dust. The catalysts used include Pt/alumina, Pt/ceria-zirconia and Pt-Re/ceria zirconia catalyst pellets. The reactor was a custom designed 1.8 cm diameter by 37 cm long vertical tubular, magnetically stirred reactor with a 23 cm heated section and a 10 cm water cooled condenser section at the top designed for a continuous flow of nitrogen purge gas to bubble up through the liquid. The catalyst charge was suspended in a titanium wire mesh basket.

Results and Discussion

Our work has focused on developing a process for base catalyzed hydrolysis of untreated Yellow Poplar (***Liriodendron tulipifera)*** coupled with direct APR of the liquor. Attempts to treat microcrystalline cellulose in the absence of a reforming catalyst resulted in a brown liquor containing a wide variety of cellulose decomposition products. However treatment of 1 wt % microcrystalline cellulose in the presence of $PtRe/Ce_{0.55}Zr_{0.45}O_2$ with a N_2 sweep gas resulted in essentially complete conversion of cellulose to gaseous species. Conversion was confirmed by mass balance and ^1H NMR. Resultant liquors were colorless and without solids. The reaction had 60% selectivity towards H_2 on a hydrogen basis, with ethane being the major byproduct. Tests show that with a microcrystalline cellulose feed the catalyst is not poisoned by the reaction products or the used liquor. Subsequent reactions were performed with 2 wt% untreated Yellow Poplar over $PtRe/ Ce_{0.55}Zr_{0.45}O_2$ by a temperature ramp technique. Assuming only cellulose and hemicellulose were convertible, 45% of the carbon was converted to hydrogen and other gaseous products, with 65% selectivity towards H_2. It was found that at lower temperatures, ethane production was minimal. The initial data suggest that hydrolysis is controlling the evolution of H_2 and that varying the conditions can improve hydrolysis rate and thus reforming and concomitant Water Gas Shift rate and overall yield[7]. Work is ongoing, determining the effects of the process variables on overall conversion and selectivity as well as optimizing catalyst composition for maximum selectivity and stability.

Significance

This work moves the concept of hydrogen production from raw biomass as described in DOE contract DE-FG36-05GO15042 “A Novel Slurry-Based Biomass Reforming Process” a significant step closer to realization.

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