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Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil☆

Stefan Czernik *, Robert Evans, Richard French

National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401, United States

Abstract

Thermo-conversion of biomass is one of the leading near-term options for renewable production of hydrogen and has the potential to provide a significant fraction of transportation fuel required in the future. We propose a two-step process that starts with fast pyrolysis of biomass, which generates high yields of a liquid product, bio-oil, followed by catalytic steam reforming of bio-oil to produce hydrogen. A major advantage of such a concept results from the fact that bio-oil is much easier and less expensive to transport than either biomass or hydrogen. Therefore, the processing of biomass and the production of hydrogen can be performed at separate locations, optimized with respect to feedstock supply and to hydrogen distribution infrastructure. This approach makes the process very well suited for both centralized and distributed hydrogen production. This work demonstrates reforming of bio-oil in a bench-scale fluidized bed system and provides hydrogen yields obtained using several commercial and custom-made catalysts.

Keywords: Biomass; Bio-oil; Steam reforming

1. Introduction

The current production of hydrogen in the U.S. is 9 Mtonne/year, most of which is generated from natural gas and petroleum-derived feedstocks [1]. Thermo-conversion of biomass is one of the leading near-term options for renewable hydrogen production. A Billion-Ton Vision study [2] identified a potential 1.3 billion tonnes biomass in the United States that could be used as a resource to produce transportation fuels. This represents the potential for the annual hydrogen production of 100–130 Mtonne, enough to fuel 300 million fuel cell vehicles [1] and displace more than 30% of the present petroleum usage. Both centralized and distributed production scenarios are possible as hydrogen distribution systems evolve from production at the site of filling stations to future pipeline systems, which can support large-scale dedicated facilities where hydrogen may be co-produced with other fuels, chemicals and materials in an integrated biomass refinery.

Milne et al. [3] published an extensive review of the research on thermo-chemical production of hydrogen from biomass. Gasification coupled with the water-gas shift reaction will likely be the primary thermo-chemical route to hydrogen. Biomass gasification technologies that are under development around the world are based on thermal decomposition and partial oxidation with air, oxygen or steam. The stoichiometric hydrogen yield for air or oxygen gasification followed by water-gas shift is around 14% while that for steam gasification is 17% based on the biomass weight. An alternative approach to the production of hydrogen, proposed and studied at NREL [4,5], is fast pyrolysis of biomass followed by catalytic steam reforming of the liquid pyrolysis product. The main advantage of this concept is based on bio-oil transportability that makes possible implementing pyrolysis and reforming at different locations using low-cost biomass resources and existing infrastructure for hydrogen distribution while saving on high-cost transportation of biomass and hydrogen. This

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* Corresponding author. Tel.: +1 303 384 7703; fax: +1 303 384 6363.
E-mail address: Stefan_Czernik@nrel.gov (S. Czernik).

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approach is especially well suited for smaller-scale reforming plants located at hydrogen distribution sites such as filling stations.

Fast pyrolysis is a thermal decomposition process that converts biomass to liquids with yields as high as 70–80% (including water) based on the starting biomass weight [6]. Fast pyrolysis technologies have been developing since the 1980s, mostly for producing alternative liquid fuels and chemicals, and recently entered the stage of commercialization. The first commercial plant producing bio-oil (70 tonnes/day) for energy application was constructed by DynaMotive in West Lorne, Canada in 2005. Bio-oil is also the feedstock for several processes for producing fuels, chemicals, and materials [7].

Bio-oils are multi-component mixtures comprised of different size molecules derived primarily from depolymerization and fragmentation reactions of three key biomass building blocks: cellulose, hemicellulose, and lignin. Therefore, the elemental composition of bio-oil resembles that of biomass rather than that of petroleum oils. Characteristics of bio-oil physical and chemical properties are provided in several publications, for example [8]. There are concepts to produce hydrogen from either the whole bio-oil or from only the residual fractions after co-products have been separated. The overall stoichiometry gives a maximum yield of 17.2 wt.% based on whole bio-oil (11.2% based on wood). Steam reforming chemistry of biomass-derived liquids has been described in [3,4] and the initial work on the catalyst development for reforming those liquids in [9]. However, that research focused on processing only the carbohydrate-derived bio-oil fraction. It also identified the shortcomings of the traditional fixed-bed steam reforming process used for natural gas or naphtha in the application to bio-oil and thus the necessity to develop a fluidisable catalyst. Recently, Rioche et al. [10] published results of steam reforming whole bio-oil produced by fast pyrolysis of beech wood that includes the oligomeric lignin-derived material. Using fixed-beds of ceria-zirconia supported noble metal catalysts (Pt, Rh) they obtained hydrogen yields between 50 and 60% of the stoichimetric potential and the carbon-to-gas conversion of 90% during a 9-h operation. This work focuses on the demonstration of a fluidized bed reforming of whole bio-oil and on the development of catalysts suitable for such a process.

2. Experimental

2.1. Feedstock

Bio-oil was produced by fast pyrolysis of hardwood by DynaMotive, a developer of fluidized bed pyrolysis technology located in Vancouver, Canada. Because of a long storage time the bio-oil underwent “aging”, polymerization reactions resulting in an increased molecular weight and in partial phase separation. To homogenize the liquid and reduce its viscosity 10 wt.% of methanol was added to the initial bio-oil. The elemental composition of the liquid included 36.5% carbon, 8.4% hydrogen, and 55.0% oxygen. Theoretically, 13.8 g hydrogen can be obtained from 100 g of that bio-oil assuming complete conversion of carbon in bio-oil to CO_2.

2.2. Catalysts

Five catalysts including a commercial catalyst, C11-NK produced by Sűd-Chemie for reforming naphtha and four laboratory formulations were tested for bio-oil reforming efficiency in a fluidized bed reactor. The commercial catalyst pellets were ground to a particle size of 300–500 μm, which allowed for uniform fluidization while avoiding entrainment. NREL catalysts were prepared by impregnating an attrition-resistant support obtained from CoorsTek with various amounts of nickel along with gasification and reforming promoters. The exact composition of the catalysts is not reported here because of the pending patent application.

2.3. Fluidized bed system

The steam reforming experiments were carried out using a bench-scale fluidized bed unit. The tubular 2-in.-diameter Inconel reactor with a perforated gas distribution plate was externally electrically heated. The reactor contained 250 g of catalyst. Before reforming, the catalyst was activated in H_2/N_2 at the process temperature of 850 °C for approximately 2 h. The catalyst was then fluidized using superheated steam, which is also a reactant in the reforming process. The bio-oil was fed into the reactor at 84 g/h through a temperature-controlled injection nozzle and sprayed on the catalyst in the form of very fine droplets. The product collection included a cyclone and a hot-gas filter to capture fine catalyst particles and, possibly, char generated in the reactor. It also contained two heat exchangers to condense excess steam. The condensate weight was continuously monitored. The outlet gas flow rate was measured via a mass flow meter and a dry test meter. The concentrations of H_2, CO_2, CO, and CH_4, C_2H_4, and N_2 in the reformed gas were monitored by infrared (NDIR Model 300 from California Analytical Instruments) thermal conductivity (TCM4 from Gerhard Wagner, Germany) and a micro gas chromatograph (MTI). Temperatures and flows were recorded and controlled by an OPTO22 system.

3. Results and discussion

3.1. Catalyst development

Our initial work established that biomass pyrolysis oil could be steam-reformed to generate hydrogen using non-fluidizable (fixed-bed) commercial catalysts [11]. These multi-component catalysts, which generally contain Ni, K, Ca, and Mg on alumina-based supports, are multifunctional and promote reforming, water gas shift, and gasification reactions that are shown below:

$$C_nH_mO_k + (n-k)H_2O \rightarrow nCO + (n+m/2-k)H_2$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

$$C + H_2O \leftrightarrow CO + H_2$$

The basic assumption underlying this work is that the mechanism of metal-catalyzed reforming of oxygenated organic molecules ought to be similar to that proposed for hydrocarbons as discussed in our previous papers [4,5,9]. Organic molecules dissociatively adsorb on metal (nickel) crystallite sites while water molecules are adsorbed on the support (alumina) surface. Hydrogen is produced via dehydrogenation of adsorbed organic molecules and reaction of adsorbed organic fragments with hydroxyl groups, which migrate from the alumina support to the nickel crystallites/alumina interfaces. The second reaction also results in the formation of carbon oxides. The above chemical processes are accompanied by side reactions leading to the formation of carbon deposits on the catalyst surface. This unwanted effect is enhanced by higher non-saturation, molecular weight, and aromaticity of the organic molecules. Biomass-derived liquids are more reactive than hydrocarbons because they already have some carbon–oxygen bonds. However, at elevated temperatures, they also show greater tendency to form carbon deposits because of the large size and thermal instability of constitutive molecules (carbohydrates, furans, phenols). Therefore, reforming biomass-derived liquids will require process conditions that allow for a good contact of the organic molecules with the catalyst that minimize formation, or facilitate removal by steam gasification, of carbon residues from the catalyst. Our fixed-bed experiments showed that the carbohydrate-derived fraction of poplar pyrolysis oil could be converted to hydrogen, however, process performance decreased with time because of char and coke deposition on the catalyst surface and in the bed itself thus limiting the reforming cycle to 2 or 3 h. This cycle was even shorter when whole bio-oil or polymeric biomass-derived liquids were used as feedstocks for hydrogen production. Process performance was significantly improved by using a fluidized bed of catalyst for reforming whole bio-oil and its fractions [12]. The fluidized bed configuration provides better contact between the reactants and the catalyst and significantly extends time-on-stream. However, commercial steam reforming catalysts that are designed for fixed-bed applications lack the mechanical strength necessary for the use in a fluidized bed reactor, which results in high attrition losses that is economically unacceptable. To address this problem, we identified attrition resistant support materials that could withstand high-temperature fluidization and prepared reforming catalysts using these supports [13]. The catalyst preparation and characterization is discussed in the pending patent application.

3.2. Steam reforming tests

In all tests the process temperature was 850 °C, with a molar steam to carbon ratio (S/C) of 5.8 and a methane-equivalent space velocity of 920 h^{-1}. The experiments proceeded smoothly without any major upsets. The product gas composition and the hydrogen yields (expressed as percent of the stoichiometric potential), obtained using the commercial catalyst C11-NK are shown in Fig. 1a and b.

During 18 h on stream, the concentration of main products H_2, CO_2, and CO did not change significantly. However, the concentration of methane steadily increased to 10,000 ppmv, which is typical of the performance observed with the bio-oil aqueous fraction [4]. The rising methane formation probably resulted from methanation of carbon monoxide as well as from the thermal cracking of complex bio-oil molecules, which became more important when the catalyst deactivated most likely due to carbon deposition that is a major challenge in steam reforming processes. In the reported experiment, about 95% of bio-oil carbon was converted to gaseous compounds, however, at least part of the remaining 5% could form deposits on the catalyst and cause its deactivation. In that test, 12.9 g hydrogen was produced from 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. The negative side was high catalyst losses averaging 1.1%/h on stream (determined as the weight difference of the catalyst put in and recovered from the reactor divided by the initial catalyst weight and the time on stream). However, such an outcome was expected based on the previous fluidized bed tests using different biomass-derived liquids.

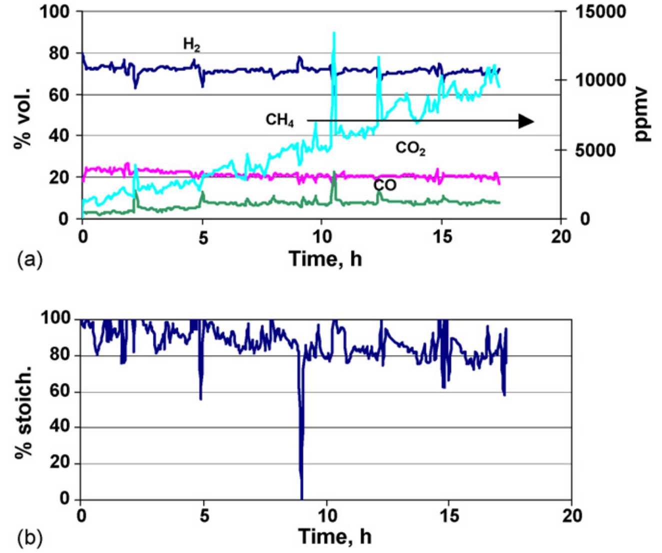

Fig. 1. Gas composition (a) and yield of hydrogen (b) produced by steam reforming of bio-oil using commercial catalyst C11-NK at 850°, S/C = 5.8.

Since these catalyst losses are not acceptable, more robust fluidisable catalysts were produced [13] and tested in the reforming process. Fig. 2a and b shows comparable results for one of laboratory preparations, NREL #20. The performance of this catalyst was not as good as that of C11-NK. Methane concentration increased faster, but the tendency observed for other biomass-derived liquids is for the methane to eventually stabilize at the same level, which may be equilibrium controlled. CO levels start higher and rise more rapidly than for C11-NK as well, which suggests the need for improvement of the water gas shift activity of the NREL catalysts. Likewise, the slow decrease in hydrogen and CO_2 is probably due to low nickel content and the impact of carbon deposition on catalyst active sites. Improving catalyst performance is the target of recent catalyst development activities.

The performance of three other laboratory catalysts tested that had different content of nickel and promoters was

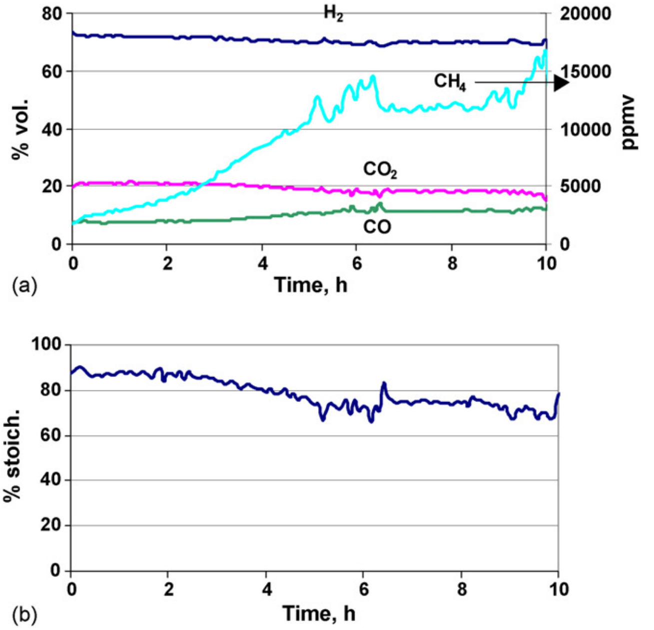

Fig. 2. Gas composition (a) and yield of hydrogen (b) produced by steam reforming of bio-oil using NREL #20 catalyst at 850°, S/C = 5.8.

comparable to the one reported above. For all of them the hydrogen concentration in the product gas was around 70 vol.% and the yield was 70–80% of the stoichiometric potential. These results are significantly better than those reported in [10] for reforming whole bio-oil using more expensive noble metal catalysts.

Because of less nickel and the lower surface area, our catalysts showed somewhat lower yields of hydrogen than those for the commercial catalyst, mostly attributed to lower water-gas shift activity. However, the catalyst losses due to attrition were much less, 0.15%/h compared to 1.1%/h for C11-NK.

4. Conclusions

1. Whole bio-oil was successfully steam reformed using both commercial and laboratory prepared catalysts producing hydrogen with yields of 70–80% of the stoichiometric potential. This can be considered as the concept validation of the two-step process for producing hydrogen from biomass.
2. The four NREL-prepared catalysts showed somewhat lower activity but significantly higher attrition resistance than the commercial naphtha reforming catalyst. The main difference is likely due to lower water-gas shift activity. Increasing nickel and coke gasification promoter contents can likely improve catalyst performance.

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References

[1] Department of Energy, 2003, Hydrogen, Fuel Cells and Infrastructure Technologies Program, Multi-Year Research, Development and Demonstration Plan, Draft, June 3, 2003, U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Washington, D.C.

[2] R.D. Perlack, L.L. Wright, A.F. Turhollow, R.L. Graham, B.J. Stokes, D.C. Erbach, Biomass as Feedstock for a Bioenergy and Bioproducts Industry: the Technical Feasibility of a Billion-Ton Annual Supply, A joint U.S. Department of Energy and U.S. Department of Agriculture report DOE-GO-102995-2135 and ORNL/TM 2005-66, April 2005, http://www1.eereenergy/gov/biomass/pdfs/final_billionton_vision_report2.pdf.

[3] T.A. Milne, C.C. Elam, R.J. Evans, 2002, Hydrogen from biomass, State of the Art and Challenges, IEA/H2/TR-02/001.

[4] D. Wang, S. Czernik, D. Montané, M. Mann, E. Chornet, Ind. Eng. Chem. Res. 36 (1997) 1507.

[5] S. Czernik, R. French, C. Feik, E. Chornet, Ind. Eng. Chem. Res. 41 (2002) 4209.

[6] A.V. Bridgwater, G.V.C. Peacocke, Sustainable Renewable Energy Rev., 4 (1) (Elsevier, 1999) 1–73

[7] S. Czernik, A.V. Bridgwater, Energy Fuels 18 (2004) 590.

[8] A. Oasmaa, S. Czernik, Energy Fuels 13 (1999) 914–921.

[9] L. Garcia, R. French, S. Czernik, E. Chornet, Appl. Catal. A: Gen. 201 (2000) 225–239.

[10] C. Rioche, S. Kulkarni, F. Meunier, J. Breen, R. Burch, Appl. Catal. B: Environ. 61 (2005) 130–139.

[11] D. Wang, S. Czernik, E. Chornet, Energy Fuels 12 (1998) 19.

[12] S. Czernik, R. French, C. Feik, E. Chornet, in: C.E. Gregoire Padro, F. Lau (Eds.), Advances in Hydrogen Energy, Kluwer Academic, New York, 2000, pp. 87–92.

[13] R. French, K. Magrini-Bair, S. Czernik, Y. Parent, M. Ritland, E. Chornet, Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 47 (2) (2002) 759.