

Production of hydrogen by co-reforming biomass pyrolysis liquids and natural gas

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At present, hydrogen is produced almost entirely from fossil fuels such as natural gas, naphtha, and coal. We believe that in the future biomass can become an important sustainable source of hydrogen. As a renewable resource, it has an advantage of low environmental impact (almost zero net CO₂ emissions) compared to that for fossil fuels. However, the price of hydrogen obtained by direct gasification of lignocellulosic biomass is at least three times higher than that for hydrogen produced by steam reforming of natural gas [1]. Over the last several years we have been developing a method for producing hydrogen from biomass [2-4] and concluded that only a hydrogen/co-products strategy could compete with the cost of the commercial hydrocarbon-based technologies.

The proposed process combines two stages: fast pyrolysis of biomass to generate bio-oil and catalytic steam reforming of the bio-oil to hydrogen and carbon dioxide. This concept has several advantages over the traditional gasification/water-gas shift technology. First, bio-oil is much easier to transport than solid biomass and therefore, pyrolysis and reforming can be carried out, if needed, at different locations. A second advantage is the potential production and recovery of higher-value co-products from bio-oil. For example, the lignin-derived fraction can be separated from bio-oil and used as a phenol substitute in phenol-formaldehyde adhesives while the carbohydrate-derived fraction is catalytically steam reformed to produce hydrogen. Assuming that the phenolic fraction could be sold for \$0.44/kg (approximately half of the price of phenol), the estimated cost of hydrogen from the proposed process would be \$7.7/GJ [5], which is at the low end of the current selling prices.

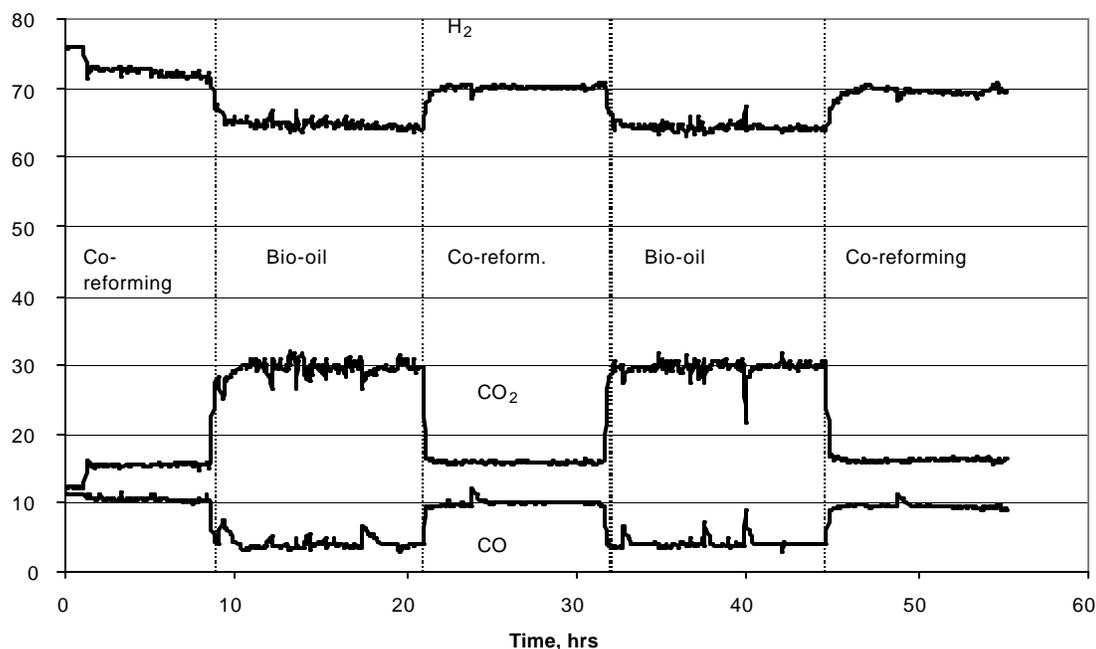
The yield of hydrogen that can be produced from biomass is relatively low, 12-14% based on the biomass weight. It is even lower when only the carbohydrate-derived bio-oil fraction undergoes reforming while the lignin part is used for other applications. At present, the amount of biomass-derived liquids available for reforming is rather limited but a viable way to increase the production of hydrogen in a biomass-based plant could be co-reforming of pyrolysis liquid with natural gas. This approach, similar to co-firing of biomass with coal for power generation, would add environmental benefits to the traditionally fossil-based technology. The objective of this work was to investigate the co-reforming process and validate the concept.

Experimental

C11-NK catalyst obtained from Süd-Chemie, Inc. was ground to the particle size of 300-500 μ and used for co-reforming in the 2"-diameter fluidized bed reformer system that was described in our earlier paper [4]. Bio-oil used for this study was generated from pine sawdust using the NREL fast pyrolysis vortex reactor system. The oil comprised 47.7% carbon, 7.4% hydrogen, and 44.8% oxygen with a water content of 26.7%. It was separated into aqueous (carbohydrate-derived) and organic (lignin-derived) fractions by adding water to the oil at a weight ratio of 1.5:1. The aqueous fraction contained 20.0 wt.% organics and 80.0% water and consisted of 11.8% carbon, 9.6% hydrogen, and 78.6% oxygen. Natural gas from the public utility was compressed and fed to the fluidized bed reformer at the rate of 0.75 L_{STP}/min, while the pyrolysis liquid feed rate was 2 g/min. The reactor operated at 850°C with a methane-equivalent gas hourly space velocity G_{Cl}HSV of app. 1000 h⁻¹ and a molar steam-to-carbon ratio of 4.6. The test was carried out for 56 hours alternating between the co-reforming and the bio-oil-only reforming. The operation was smooth, especially during the co-reforming cycles. Interestingly, co-feeding of natural gas helped maintain and restore the catalyst activity. A sharp increase in methane concentration was observed at the beginning of the second and third cycles of co-reforming but

significantly decreased after 30 minutes. The concentration of major gas components as a function of time is shown in Figure 1.

Figure 1. Gas composition from reforming of bio-oil and from co-reforming of bio-oil with natural gas



The gas composition was almost constant during the stages of reforming and co-reforming, though a small decrease in hydrogen and increase in methane concentration were observed between the first and the second co-reforming cycle. Methane conversion was initially 92.5% and decreased to 80% at the end of the test. Also, the hydrogen yield decreased from initially 80% to 75% of the stoichiometric potential (amount of hydrogen that would be obtained when total organic carbon converts to CO₂) at the final stage. During co-reforming, 23-26% of the hydrogen was generated from bio-oil and 77-73% from natural gas.

Conclusions

The technical feasibility of co-reforming bio-oil and natural gas has been demonstrated. Co-reforming can be an attractive opportunity that enhances the flexibility of the biomass-to-hydrogen process.

References

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