

PRODUCTION OF HYDROGEN FROM BIOMASS BY PYROLYSIS/STEAM REFORMING

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INTRODUCTION

Hydrogen is the most environmentally friendly fuel that can be efficiently used for power generation. While burning or oxidising it generates steam as the only emission. At present, however, hydrogen is produced almost entirely from fossil fuels such as natural gas, naphtha, and inexpensive coal. In such a case, the same amount of CO₂ as that formed from combustion of those fuels is released during hydrogen production stage. Renewable biomass is an attractive alternative to fossil feedstocks because of essentially zero net CO₂ impact. Unfortunately, hydrogen content in biomass is only 6-6.5% compared to almost 25% in natural gas. For this reason, on a cost basis, producing hydrogen by the biomass gasification/water-gas shift process cannot compete with the well-developed technology for steam reforming of natural gas. However, an integrated process, in which biomass is partly used to produce more valuable materials or chemicals with only residual fractions utilised for generation of hydrogen, can be an economically viable option.

The proposed method, which was described earlier¹, 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 at different locations to improve the economics. A second advantage is the potential production and recovery of higher value added co-products from bio-oil that could significantly impact the economics of the entire process. In this concept, the lignin-derived fraction would be separated from bio-oil and used as a phenol substitute in phenol-formaldehyde adhesives while the carbohydrate-derived fraction would be 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 this conceptual process would be \$7.7/GJ², which is at the low end of the current selling prices.

In previous years we demonstrated, initially through micro-scale tests then in the bench-scale fixed-bed reactor experiments³ that bio-oil model compounds as well as its carbohydrate-derived fraction can be efficiently converted to hydrogen. Using commercial nickel catalysts the hydrogen yields obtained approached or exceeded 90% of those possible for stoichiometric conversion. The carbohydrate-derived bio-oil fraction contains a substantial amount of non-volatile compounds (sugars, oligomers) which tend to decompose thermally and carbonize before contacting the steam reforming catalyst. Even with the large excess of steam used, the carbonaceous deposits on the catalyst and in the reactor freeboard limited the reforming time to 3-4 hours. For this reason we decided to employ fluidized bed reactor configuration that should overcome at least some limitations of the fixed-bed unit. Even if carbonization of the oil cannot be avoided, still the bulk of the fluidizing catalyst would be in contact with the oil droplets fed to the reactor. Catalyst regeneration can be done by steam or carbon dioxide gasification of carbonaceous residues in a second fluidized bed reactor providing additional amounts of hydrogen.

EXPERIMENTAL

The bio-oil was generated from poplar wood using the NREL fast pyrolysis vortex reactor system⁴. The oil was comprised of 46.8% carbon, 7.4% hydrogen, and 45.8% oxygen with water content of 19%. It was separated into aqueous (carbohydrate-derived) and organic (lignin-derived) fractions by adding water to the oil at a weight ratio of 2:1. The aqueous fraction (55%

of the whole oil) contained 22.9% organics ($\text{CH}_{1.34}\text{O}_{0.81}$) and 77.1% water.

U91, a commercial nickel-based catalyst used for steam reforming of natural gas, was obtained from United Catalysts and ground to the particle size of 300-500 μ .

The aqueous solution was steam reformed using a bench-scale fluidized bed reactor shown in Figure 1. The two-inch-diameter inconel reactor supplied with a porous metal distribution plate was placed inside a three-zone electric furnace. The reactor contained 150-200g of commercial nickel-based catalyst from United Catalysts ground to the particle size of 300-500 μ . The catalyst was fluidized using superheated steam, which is also a reactant in the reforming process. Steam was generated in a boiler and superheated to 750 C before entering the reactor at a flow rate of 2-4 g/min. Liquids were fed at a rate of 4-5 g/min using a diaphragm pump. Specially designed injection nozzle supplied with a cooling jacket was used to spray liquids into the catalyst bed. The temperature in the injector was controlled by a coolant flow and maintained below the feed boiling point to prevent evaporation of volatile and deposition of nonvolatile components. The product collection line included a cyclone that captured fine catalyst particles and, possibly, char generated in the reactor and two heat exchangers to condense excess steam. The condensate was collected in a vessel whose weight was continuously monitored. The outlet gas flow rate was measured by a mass flow meter and by a dry test meter. The gas composition was analyzed every 5 minutes by a MTI gas chromatograph. The analysis provided concentrations of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, and nitrogen in the outlet gas stream as a function of time of the test. The temperatures in the system as well as the flows were recorded and controlled by the G2/OPTO data acquisition and control system.

The measurements allowed to determine total and elemental balances as well as to calculate the yield of hydrogen generated from the biomass-derived liquid feed.

RESULTS AND DISCUSSION

The overall steam reforming reaction of any oxygenated organic compound can be presented as follows:



Thus the maximum (stoichiometric) yield of hydrogen is $2+m/2n-k/n$ moles per mole of carbon in feed. The steam reforming experiments in the fluidized bed reactor were carried out at the temperature of 800°C and 850°C. The steam to carbon ratio was held at 7-9 while methane-equivalent gas hourly space velocity $G_{CH_4}HSV$ was in the range of 1200-1500 h^{-1} . At 800°C a slow decrease in the concentration of hydrogen and carbon dioxide and an increase of carbon monoxide and methane in the gas generated by steam reforming of the carbohydrate-derived oil fraction was observed. These changes resulted from a gradual loss of the catalyst activity, probably due to coke deposits. As a consequence of that, the yield of hydrogen produced from the oil fraction decreased from the initial value of 95% of stoichiometric (3.24 g of hydrogen from 100 g of feed) to 77% after 12 hours on stream. If a water-gas shift reactor followed the reformer the hydrogen yields would increase to 99% and 84% respectively. During eight hours of reforming at 850°C, the product gas composition remained constant, as presented in Figure 2. This indicates that no catalyst deactivation was observed throughout the run time. The yield of hydrogen produced from the bio-oil fraction was approximately 90% of that possible for stoichiometric conversion. It would be greater than 95% if carbon monoxide underwent the complete shift reaction with steam. Only small amounts of feed were collected as char in the cyclone and condensers, and little or no coke was deposited on the catalyst.

CONCLUSIONS

We successfully demonstrated that hydrogen could be efficiently produced by catalytic steam reforming carbohydrate-derived bio-oil fraction using a commercial nickel-based catalyst in a fluidized bed reactor. Greater steam excess than that used for natural gas reforming was necessary to minimize the formation of char and coke (or to gasify these carbonaceous solids) resulting from thermal decomposition of complex carbohydrate-derived compounds.

At 850°C with a steam to carbon ratio of 9 the hydrogen yield was 90% of that possible for stoichiometric conversion during eight hours of the catalyst on-stream time. This yield could be 5-7% greater if a secondary water-gas shift reactor followed the reformer.

Coke deposits were efficiently removed from the catalyst by steam and carbon dioxide gasification, which restored the initial catalytic activity.

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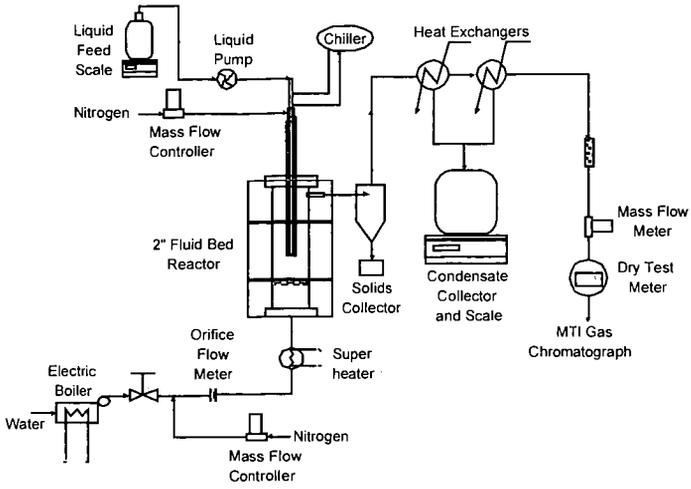


Figure 1. Schematic of the 2" fluidized bed reactor system

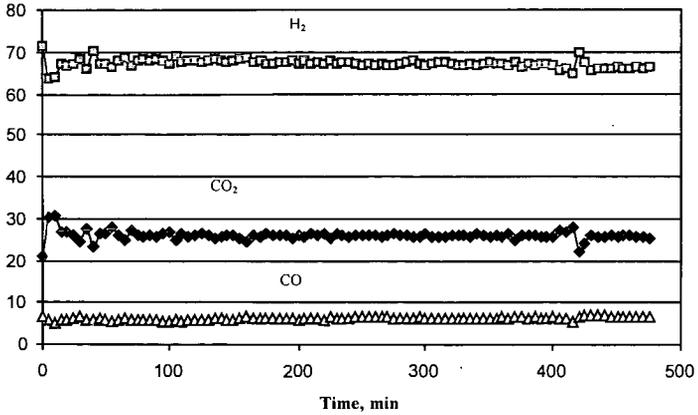


Figure 2. Reforming Gas Composition