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Production of Hydrogen from Biomass-Derived Liquids

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Abstract

Biomass as a product of photosynthesis is a renewable resource that can be used for sustainable production of hydrogen. However, direct production of hydrogen from biomass by gasification/water-gas shift technology is unfavorable economically, except for very low cost feedstocks and very large plants. Our approach proposes an alternative strategy with potentially better economics resulting from the combined production of hydrogen with valuable co-products. The concept is based on a two-stage process: fast pyrolysis of biomass to generate bio-oil; and catalytic steam reforming of the oil or its fractions to produce hydrogen. Fast pyrolysis, a technology near commercial scale, could be carried out in a regional network of plants that would supply bio-oil to a central reforming facility. The preferred option is to separate bio-oil into a lignin-derived fraction, which could be used for producing phenolic resins or fuel additives, and a carbohydrate-derived material that would be steam reformed to produce hydrogen. The key research issue for this concept is to demonstrate that bio-oil can be efficiently steam reformed. The co-product strategy can also be applied to residual fractions derived from pulping operations and from ethanol production. Effluents from other biomass processing technologies such as transesterification of vegetable oils can also be attractive feedstocks for the production of hydrogen. This year, we focused on catalytic steam reforming of different biomass-derived liquids. We employed a fluidized bed reactor configuration with commercial nickel catalysts developed for processing natural gas and naphtha. The hydrogen yields approached or exceeded 90% of the values possible for stoichiometric conversion.

Introduction

At present, hydrogen is produced almost entirely from fossil fuels such as natural gas, naphtha, and inexpensive coal. In such a case, the same amount of CO_2 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 the essentially zero net CO_2 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 a direct conversion process such as the biomass gasification/water-gas shift cannot compete with the well-developed technology for steam reforming of natural gas. Vegetable oils have a better potential for producing hydrogen than lignocellulosic materials but their high costs make the process economics unfavorable. Only an integrated process, in which biomass is used to produce valuable materials or chemicals with the residual fractions utilized for generation of hydrogen, can be an economically viable option. The concept of our approach to producing hydrogen from biomass is shown in Figure 1. In earlier papers[1-3] we proposed a method which 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 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. For instance, a series of small-size pyrolysis units could be constructed at the sites where low cost feedstock is available. Then the oil could be transported to a central reforming plant located at a site with existing hydrogen storage and distribution infrastructure. The second advantage is the potential for production and recovery of higher-value co-products from bio-oil that could significantly impact the economics of the entire process. The lignin-derived fraction can be separated from bio-oil and used as a phenol substitute in phenol-formaldehyde adhesives[4] or converted to cyclohexyl ethers (fuel additives[5]) while the carbohydrate-derived fraction is catalytically steam reformed to produce hydrogen.

In previous years we demonstrated, initially through micro-scale tests[1] then in bench-scale fixed-bed reactor experiments[2,3] that bio-oil model compounds as well as bio-oil carbohydrate-derived fraction can be efficiently converted to hydrogen. Using commercial nickel catalysts, the hydrogen yields obtained approached or exceeded 90% of the yield possible for stoichiometric conversion.

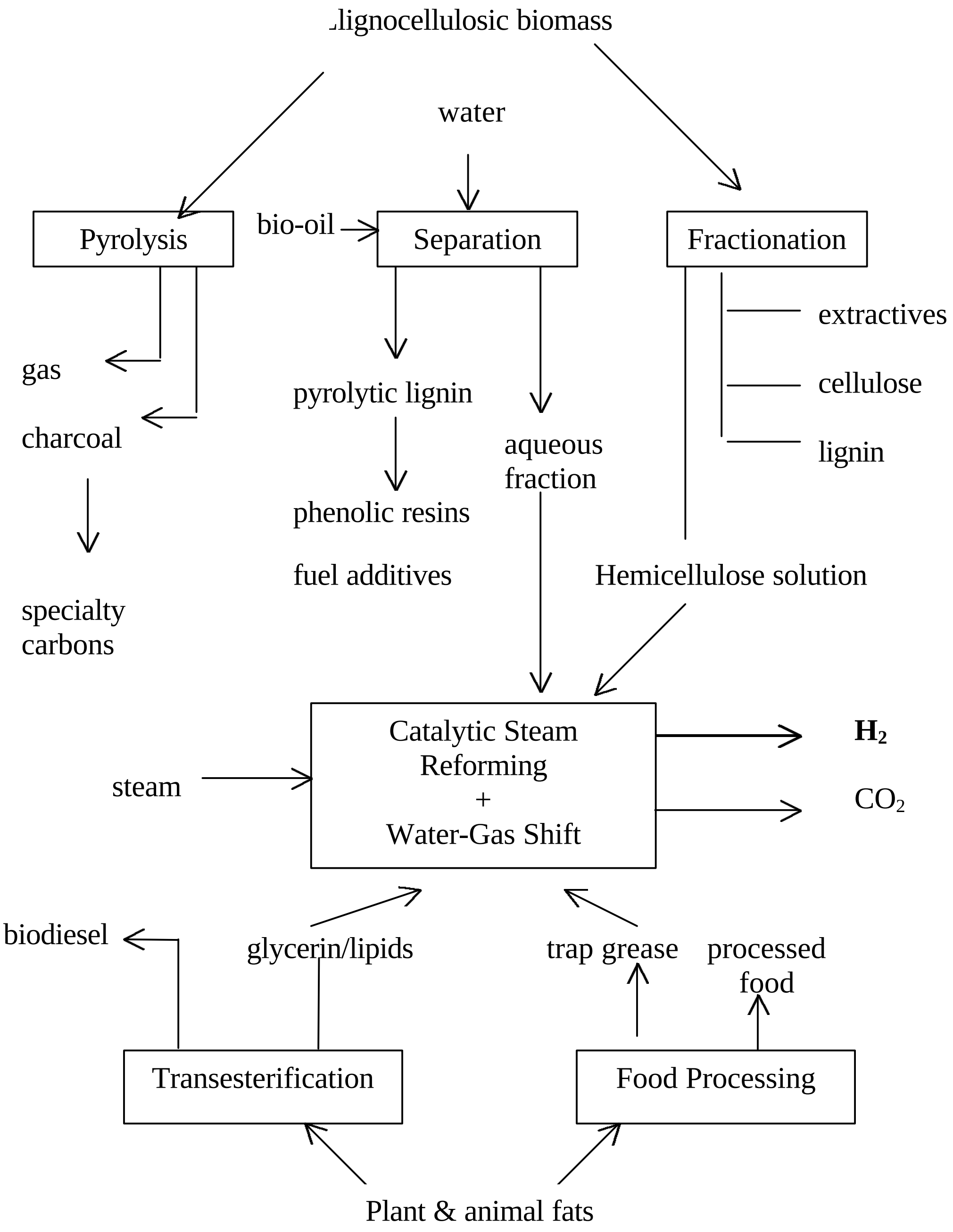

Figure 1. Biomass to hydrogen – Process concept

The carbohydrate-derived bio-oil fraction contains substantial amounts 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 fixed-bed reforming time to 3-4 hours. For this reason we decided to employ a fluidized bed reactor configuration that can overcome some limitations of the fixed-bed unit for this application. Though carbonization cannot be completely avoided, the bulk of the fluidizing catalyst remains in contact with the liquid 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

1. Materials

Bio-oil used for this study was generated from pine sawdust using the NREL fast pyrolysis vortex reactor system[6]. The oil composition was 47.7% carbon, 7.4% hydrogen, and 44.8% oxygen with water content of 26.7%. It was separated into aqueous (carbohydrate-derived) and organic (lignin-derived) fractions by adding water to the oil in a weight ratio of 2:1. The aqueous fraction (75% of the whole oil) contained 21.8% organics ($CH_{1.25}O_{0.55}$) and 78.2% water.

“Crude glycerin” samples were obtained from West Central Co-op bio-diesel plant in Ralston, Iowa. Transesterification of vegetable oils with methanol produces a mixture of bio-diesel (methyl esters of fatty acids) and glycerin. Glycerin settles down at the bottom of a separation tank while bio-diesel forms the top layer. “Crude glycerin” is a very viscous liquid, only partially miscible with water. Its elemental composition includes 54.7% carbon, 9.9% hydrogen, and 35.5% oxygen, which suggests that the phase separation in the tank was not very clean and the liquid is a mixture of glycerin (55%) with methyl esters of fatty acids (45%).

Methane (C.P. grade was supplied by Scott Specialty Gases).

C11-NK, a commercial nickel-based catalyst used for steam reforming of natural gas and naphtha, was obtained from United Catalysts and ground to the particle size of 300-500µ.

2. **Fluidized bed reformer**

The bench-scale fluidized bed reactor is shown in Figure 2.

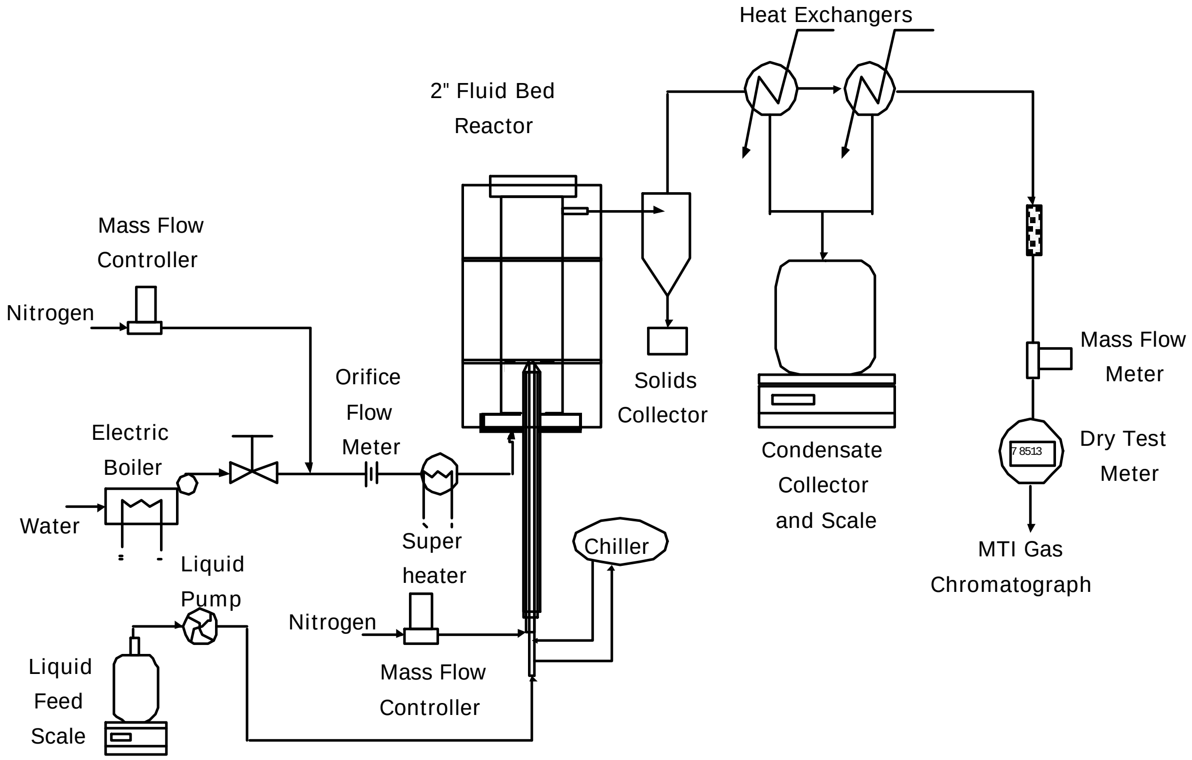

Figure 2. Fluidized bed reformer system

The two-inch-diameter inconel reactor with a porous metal distribution plate was placed inside a three-zone electric furnace. The reactor contained 150-200g of commercial nickel-based catalyst ground to the particle size of 300-500µ. 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. Methane, used in separate experiments to compare the performances of the fluidized bed with the fixed-bed commercial reactors, was fed to the reactor mixed with steam. Liquids were fed at a rate of 4-5 g/min using a diaphragm pump. A 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 coolant flow and maintained below the feed boiling point to prevent evaporation of volatile and deposition of nonvolatile components. The product gas passed through a cyclone that captured fine catalyst particles and any char generated in the reactor, and then through two heat exchangers to remove 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 concentrations of CO_2, CO, and CH_4 in the reforming gas composition were monitored by a non-dispersive infra-red analyzer (NDIR Model 300 from California Analytical Instruments) and that of hydrogen by a thermal conductivity monitor TCM4 manufactured by Gerhard Wagner. In addition, the gas was analyzed every 5 minutes by an on-line MTI gas chromatograph, which provided concentrations of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, and nitrogen as a function of time of the test. The temperatures in the system as well as the flows were recorded and controlled by the OPTO data acquisition and control system. Total and elemental balances were calculated as well as the yield of hydrogen generated from the feed.

Results and Discussion

Reforming of methane.

We measured performances of the fluidized bed reactor for steam reforming of methane in order to compare its performance to that of fixed beds and to verify that fluidized beds could be successfully applied for co-processing biomass-derived liquids or vapors with volatile hydrocarbon feedstocks. We carried out a series of reforming tests at 800°C varying the steam-to-carbon ratio (S/C) and space velocity (WHSV). The reactor operated very smoothly with only minimal fluctuations. Gas composition as a function of the run time is shown in Figure 3.

At the S/C=3.85 and WHSV of 1500 h^{-1} the yield of hydrogen was 81% of that possible for stoichiometric conversion to CO_2 and H_2 and the methane conversion was 97.5%. In industrial processes at the same S/C and WHSV and the temperature of 870-950°C the methane conversion is usually 92-94%. As expected, at a higher steam-to-carbon ratio and lower space velocity, methane conversion to carbon dioxide and hydrogen was even greater. At S/C=4.2 and WHSV of 500 h^{-1} methane conversion was greater than 99%. At S/C=7.1 and WHSV=300 h^{-1} only traces of methane (<20 ppm) were detected in the product gas.

Reforming of carbohydrate-derived bio-oil fraction

The steam reforming experiments on aqueous extract of the pine bio-oil were carried out at the temperature of 800°C and 850°C. The steam to carbon ratio was in the range of 7-9 while methane-equivalent gas hourly space velocity $G_{C1}HSV$ was 1200-1500 h^{-1}. During the experiments at 800°C a slow decrease in the concentration of hydrogen and carbon dioxide and an increase of carbon monoxide and methane 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 85% 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 have been 94% initially, falling to 84% of stoichiometric.

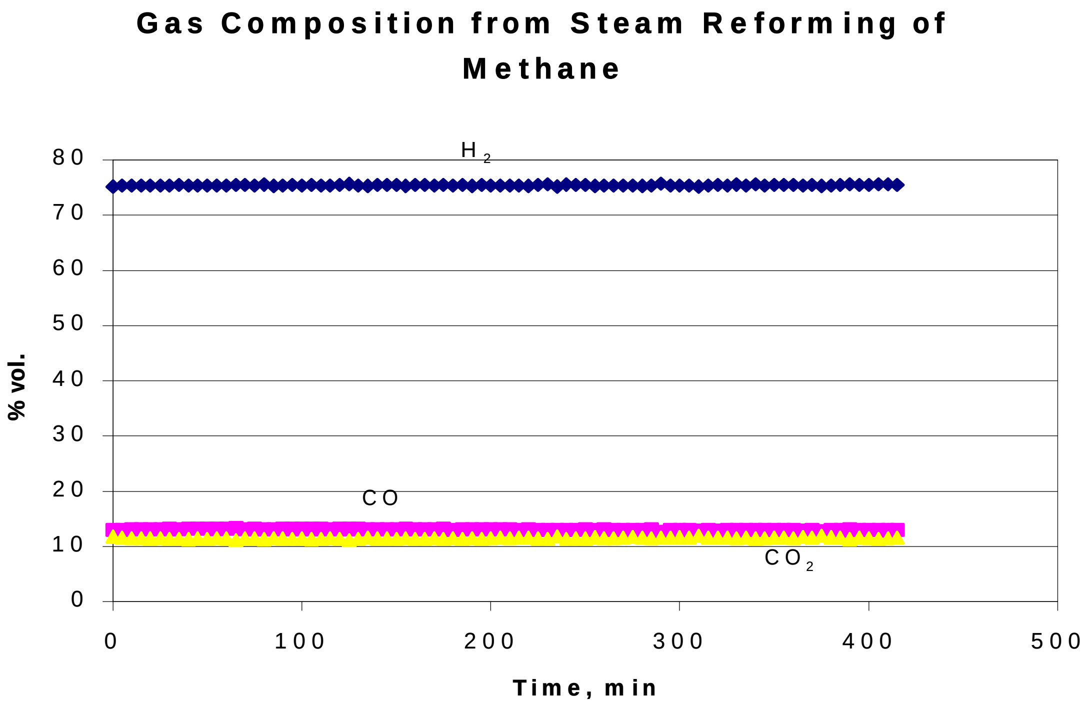

Figure 3. Reforming gas composition as a function of run time

At 850°C, the formation of char and coke was much lower because their gasification by steam was more efficient than that at 800°C. During over 90 hours of uninterrupted reforming of the bio-oil carbohydrate-derived fraction, the product gas composition remained nearly constant and only a small decrease in the concentration of hydrogen was observed, as presented in Figure 4.

Over the run time, the concentration of methane increased and then stabilized at the 2.5% level. This indicates that the catalyst deactivation proceeded very slowly. The yield of hydrogen produced from the bio-oil fraction oscillated around 80% of that possible for stoichiometric conversion (Figure 5). It would be greater than 90% 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.

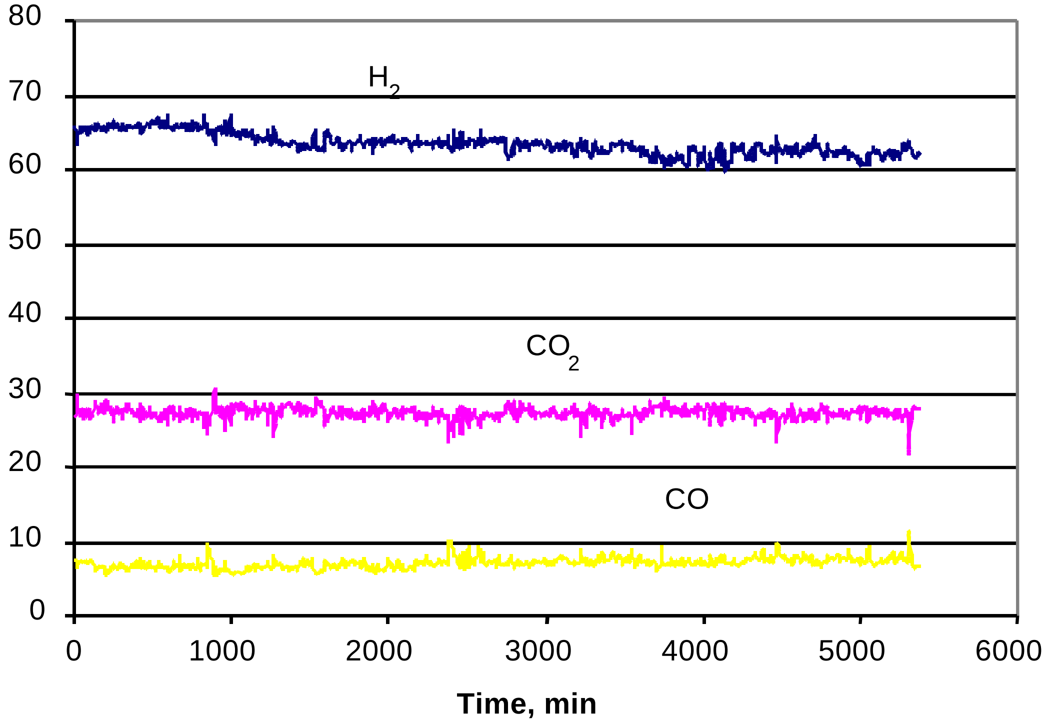

Figure 4. Reforming of bio-oil aqueous extract. Gas composition (vol %) as a function of process time

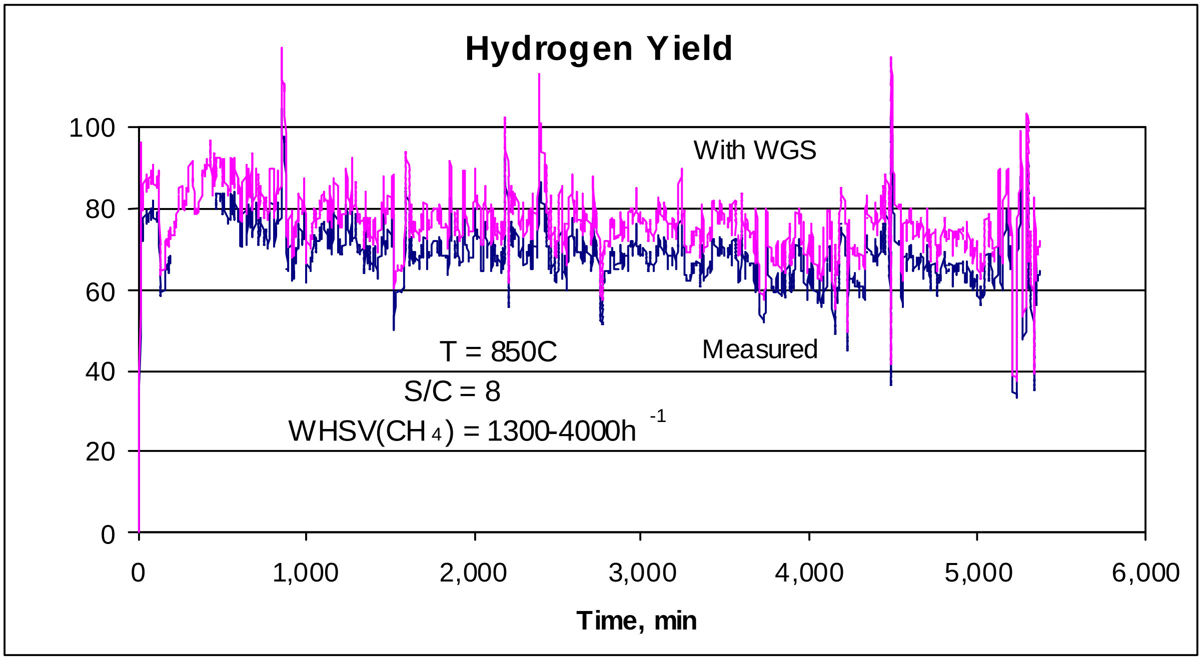

Figure 5. Reforming bio-oil aqueous fraction. % stoichiometric yield of hydrogen as a function of time.

Reforming of "crude glycerin"

"Crude glycerin" is a high viscosity liquid and, therefore, it had to be preheated to facilitate pumping and atomizing (the whole feeding line was maintained at 60-80°C). The liquid was fed at a rate of 78 g/h ($G_{C1}VHSV = 1600\ h^{-1}$) and steam at a rate of 145 g/h, which corresponds to the molar steam to carbon ratio of 2.3. The experiments proceeded very smoothly with only occasional fluctuations in the liquid feed rate resulting from a non-complete homogeneity of the feed. The concentration of the major gas products was constant during the run time but a gradual increase in methane production was noticed (Figure 6). The process performance measured as the yield of hydrogen did not decrease significantly during several hours on stream. The overall mass balance closure was close to 100% at the beginning of the tests then decreased to 95-96% after four hours on stream. Similar closure was also observed for elemental balances of carbon, hydrogen and oxygen. The hydrogen yield oscillated around 77% of the stoichiometric potential, which was 23.6 g per 100 g of feed. It could be significantly higher if more steam were used in the reaction. Conversion of CO in the gas through water-gas shift to CO_2 and H_2 would increase the hydrogen yield to 95% of that theoretically possible. These promising results suggest that a low-value by-product from bio-diesel production could become a viable renewable raw material for producing hydrogen. An integration of these two technologies could significantly improve the economics of both processes.

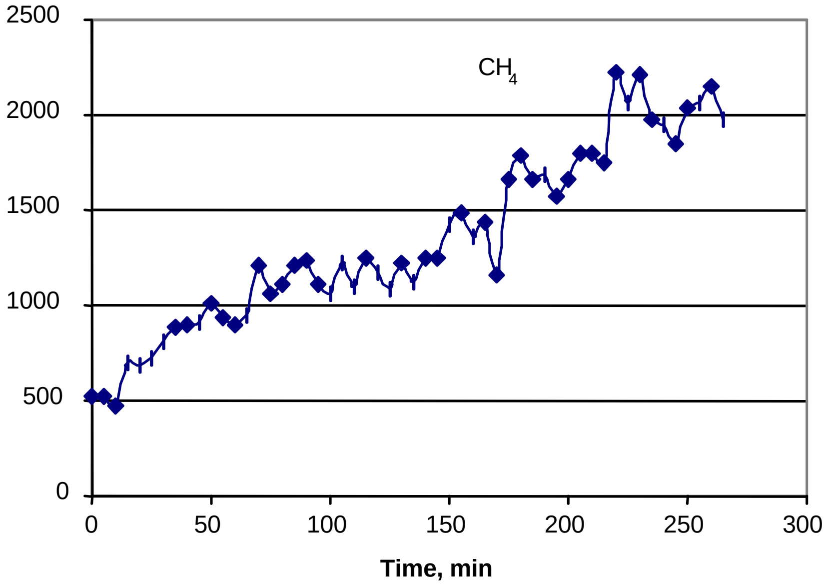

Figure 6. Methane concentration (ppm volume) during steam reforming of “crude glycerin”

SUMMARY AND CONCLUSIONS

- Biomass can be a valuable resource for producing hydrogen if done as an integrated process that also generates higher value co-products. Following this strategy we have presented two process options: fast pyrolysis/steam reforming and transesterification of vegetable oils/steam reforming.
- Bio-oil from pyrolysis or its aqueous, carbohydrate-derived fraction and glycerin from bio-diesel production can be catalytically steam reformed to generate hydrogen using commercial nickel-based catalysts.
- The hydrogen yield obtained in a fluidized bed reactor from the aqueous fraction of bio-oil was about 85% of the stoichiometric value, which corresponds to almost 6 kg of hydrogen from 100 kg of wood.

- The hydrogen yield from “crude glycerin” was 18 g per 100 g of the feedstock, which corresponds to 76% of the stoichiometric potential. If the steam reforming were followed by a water-gas shift process or a higher amount of steam were used in the reforming stage, the hydrogen yield could increase above 90%.
- Fluidized bed reactor configuration proved to be efficient for reforming both methane and biomass-derived liquids. It can be used for producing hydrogen by co-processing bio-oils with natural gas or liquid hydrocarbons.
- The process needs to be optimized to determine conditions that allow for maximum yields of hydrogen and minimum coke formation.

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