

## **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. Direct production of hydrogen from biomass by gasification/water-gas shift technology is economically unfavorable, except for very low cost feedstocks and very large plants. An alternative strategy, with potentially better economics, results 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, followed by catalytic steam reforming of the oil or its fractions to produce hydrogen. The preferred option is to separate bio-oil into a lignin-derived fraction that could be used for producing phenolic resins or fuel additives, and a carbohydrate-derived material that would be steam reformed to produce hydrogen. In order to increase the hydrogen production in a biomass-based plant, co-reforming of the bio-oil fraction and natural gas has also been considered. The co-product strategy can also be applied to residual fractions derived from pulping operations and from ethanol production. Effluents from other biomass conversion technologies such as transesterification of vegetable oils and food processing residues (“trap grease”) can also be attractive low-cost feedstocks for the production of hydrogen. This work focused on catalytic steam co-reforming of (a) carbohydrate-derived fraction of bio-oil and natural gas and (b) “trap grease.” We employed a fluidized bed reactor configuration with commercial nickel catalysts developed for processing natural gas and naphtha. The hydrogen yields obtained were 80-90% of the potential values for stoichiometric conversion of feed to CO<sub>2</sub> and H<sub>2</sub>.

## Introduction

At present, hydrogen is produced commercially from fossil fuels such as natural gas, naphtha, and coal. In such a case, the same amount of CO<sub>2</sub> 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 CO<sub>2</sub> impact. However, the hydrogen content in lignocellulosic biomass is only 6-6.5%, compared to almost 25% in natural gas. Consequently, the yield of hydrogen from biomass is relatively low, 12-14% based on the dry feedstock weight. Vegetable oils have a better potential for producing hydrogen than lignocellulosic materials but their high costs make the process economically non-viable. Only an integrated process, in which biomass is partly used to produce valuable materials (such as fibers) or chemicals (such as phenolics) while the residual fractions are utilized for generation of hydrogen, can be an economically viable option.

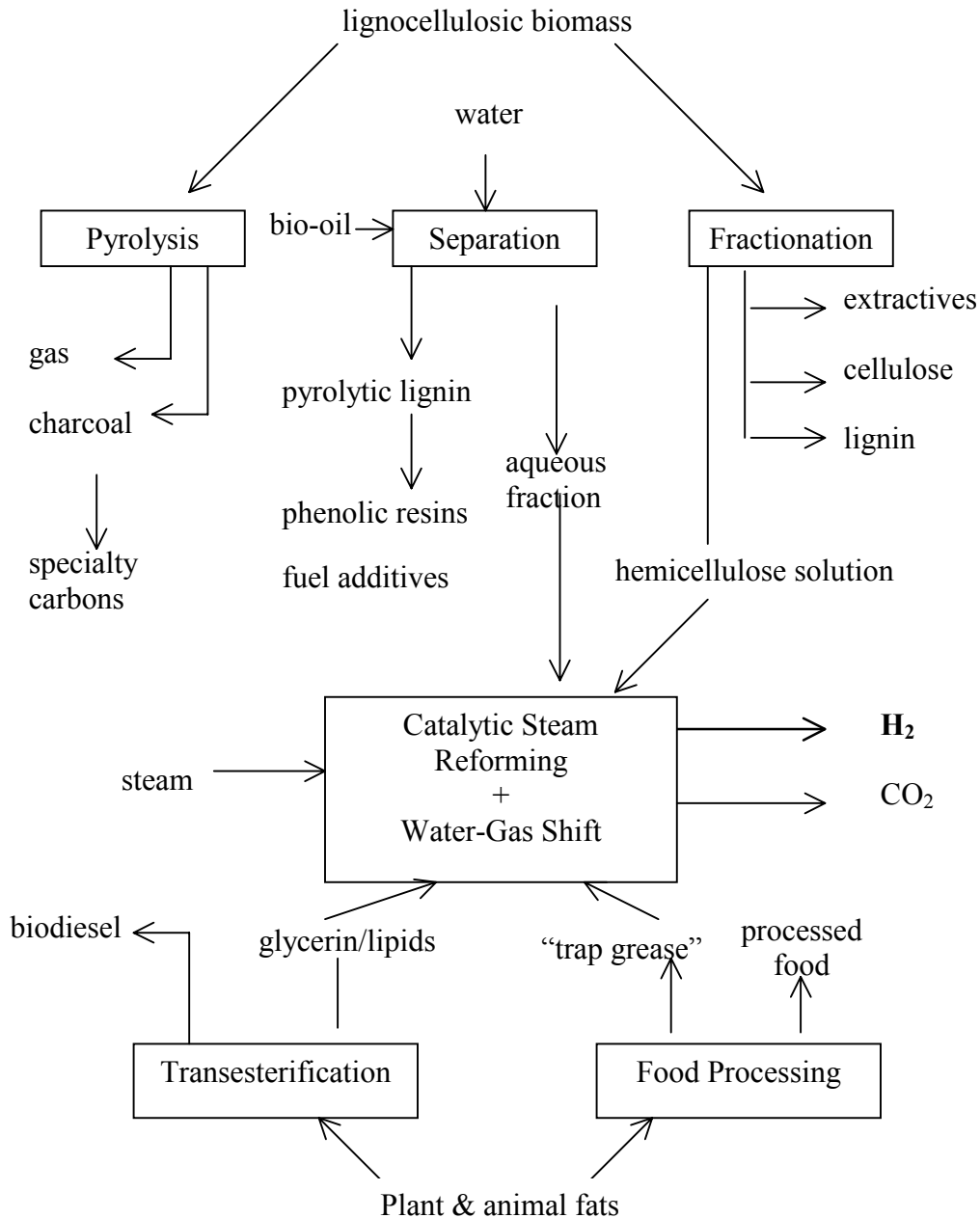
Our approach to the production of hydrogen from biomass is depicted in Figure 1. In earlier papers (Wang et al. 1997 and 1998, Czernik et al. 1999) we proposed a method that combines fast pyrolysis of biomass to generate bio-oil and catalytic steam reforming of the bio-oil to hydrogen and carbon dioxide. A significant advantage of this method is its potential for production and recovery of higher-value co-products from bio-oil, which would help to improve 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 (Kelley et al. 1997) or converted to cyclohexyl ethers fuel additives (Shabtai et al. 1997) while the carbohydrate-derived fraction is catalytically steam reformed to produce hydrogen.

The carbohydrate-derived bio-oil fraction includes non-volatile compounds (sugars, oligomers) that do not evaporate and tend to decompose thermally, forming carbonaceous deposits in the reactor freeboard before contacting the steam reforming catalyst. Because of this, a fixed-bed catalytic reactor configuration used for steam reforming natural gas did not prove to be efficient for processing pyrolysis liquids. Therefore, we decided to employ a fluidized bed reactor that can overcome the limitations of the fixed beds. 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.

In previous years we demonstrated that bio-oil carbohydrate-derived fraction could be efficiently converted to hydrogen. The hydrogen yields approached or exceeded 90% of theoretical (defined as the stoichiometric conversion of this fraction to CO<sub>2</sub> and H<sub>2</sub>) when using commercial nickel-based catalysts. The proposed strategy improves the process economics but reduces the amount of hydrogen that can be produced from biomass to about 6% based on the initial weight of the feedstock.

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 twofold: (a) to validate the co-reforming approach; (b) to determine the feasibility of producing hydrogen from “trap grease.” The latter is

a widely available low-cost waste material recovered from restaurants, food processing plants, and water treatment facilities. The estimated amount of 13 lbs/person/year of “trap grease” (Wiltsee, 1998) translates into a potential source of 1 billion pounds (0.5 Mt/year) of hydrogen.



**Figure 1. Biomass to hydrogen – Process concept**

## Experimental

### Materials

Bio-oil used for this study was generated from pine sawdust using the NREL fast pyrolysis vortex reactor system (Diebold and Scahill, 1988). The oil composition (wt%, dry basis) was 47.7% carbon, 7.4% hydrogen, and 44.8% oxygen. Water content was 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 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.

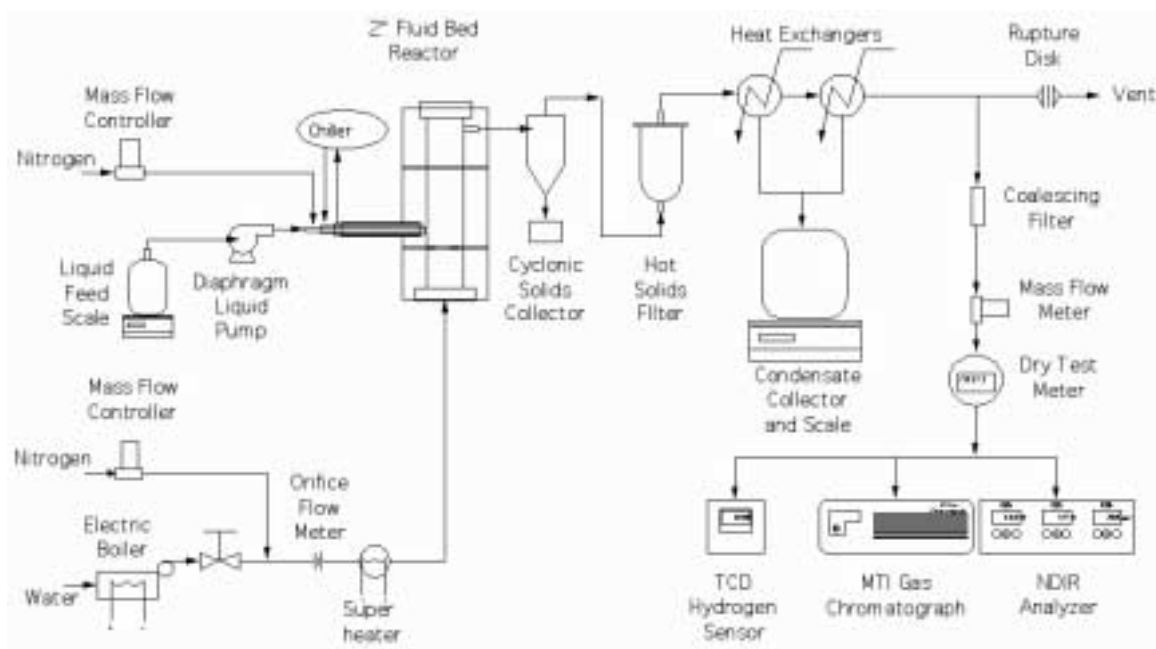
Natural gas from the public utility had the following composition: 82.4% CH<sub>4</sub>, 6.6% C<sub>2</sub>H<sub>6</sub>, 2.6% CO<sub>2</sub>, and 8.4% N<sub>2</sub> (by volume.)

“Trap grease” was obtained from Pacific Bio-Diesel, a company collaborating with the DOE Bio-Diesel Program. The raw “trap grease” was filtered (at Pacific Bio-Diesel) to remove solid impurities. The grease was a dark-colored liquid of very high viscosity at room temperature. However, at 45°C its viscosity decreased to ca. 80 cP, which made it easy to pump. The grease mainly consisted of fatty acids and their mono-, di-, and triglycerides. The overall elemental analysis of the grease showed 75.5% carbon, 11.8% hydrogen, and 12.7% oxygen.

C11-NK, a commercial nickel-based catalyst used for steam reforming of natural gas and naphtha, was obtained from Süd-Chemie (formerly United Catalysts) and ground to a particle size of 300-500 $\mu$ .

### Fluidized bed reformer

The bench-scale fluidized bed reactor is shown in Figure 2. A two-inch-diameter Inconel reactor having a porous metal fluidizing gas distribution plate was placed inside a three-zone electric furnace. The reactor contained 250-300g of commercial nickel-based catalyst ground to the particle size of 300-500 $\mu$ . 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. In the co-reforming experiments, natural gas was compressed and fed to the reactor at a rate of 0.75 L (standard)/min. Liquids were fed at a rate of 2 g/min using a diaphragm pump. In the case of “trap grease,” the feed was preheated and the feeding lines were heat-traced and maintained at 60-80°C to facilitate liquid flow and atomization. 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 and hot-gas filter that captured fine catalyst particles and, possibly, char generated in the reactor, then through two heat exchangers that removed excess steam. The condensate was collected in a vessel whose weight was continuously monitored.



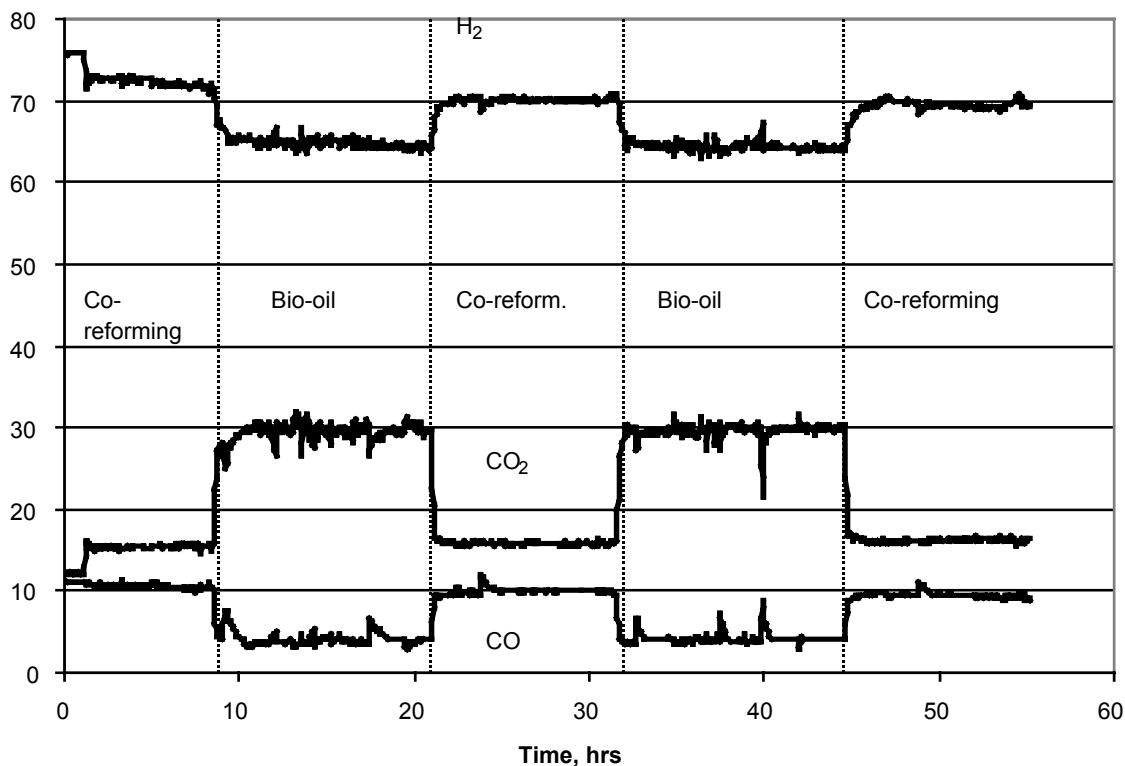
**Figure 2. Fluidized bed reformer system**

The flow rate of the outlet gas was measured using a mass flow meter and a dry test meter. The concentrations of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  in the reforming gas composition were monitored by a non-dispersive infra-red analyzer (NDIR Model 300) and that of hydrogen by a thermal conductivity monitor (TCM4). In addition, the gas was analyzed every 5 minutes by an on-line MTI gas chromatograph that provided concentrations of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, and nitrogen as a function of time. The temperatures and flows in the system 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

### Co-reforming of bio-oil and natural gas

The reactor operated at  $850^\circ\text{C}$  with a methane-equivalent gas hourly space velocity  $G_{\text{C}_1\text{HSV}}$  of ca.  $1000 \text{ h}^{-1}$  and a molar steam-to-carbon ratio of 4.6. The test was carried out without interruption for 56 hours alternating between co-reforming and bio-oil-only reforming. The operation was smooth, especially during the co-reforming cycles. Co-feeding of natural gas helped maintain and restore the catalyst activity. The concentration of major product gas components as a function of time is shown in Figure 3.



**Figure 3. Reforming gas composition (vol %) as a function of run time**

The gas composition was almost constant during the reforming phase and the co-reforming phase, 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% but decreased to 80% by the end of the test. A sharp increase in methane concentration at the reactor outlet was observed at the beginning of the second and third cycles of co-reforming but  $\text{CH}_4$  significantly decreased after 30 minutes (Figure 4). The hydrogen yield was initially 80% then decreased to 75% of the theoretical (stoichiometric) potential (amount of hydrogen that would be obtained when total organic carbon converts to  $\text{CO}_2$ ) via reforming + water gas shift, WGS) as shown in Figure 5. During co-reforming, 23-26% of the hydrogen was generated from bio-oil and 73-77% from natural gas.

### Reforming of “trap grease”

“Trap grease” reforming was carried out at  $850^\circ\text{C}$  with a methane-equivalent gas space velocity ( $G_{\text{Cl}}\text{VHSV}$ ) of  $950\text{ h}^{-1}$  and a molar steam to carbon ratio of 5. The experiments proceeded very smoothly and the concentration of the major gas products was constant during the whole run of 17 hours as shown in Figure 6.

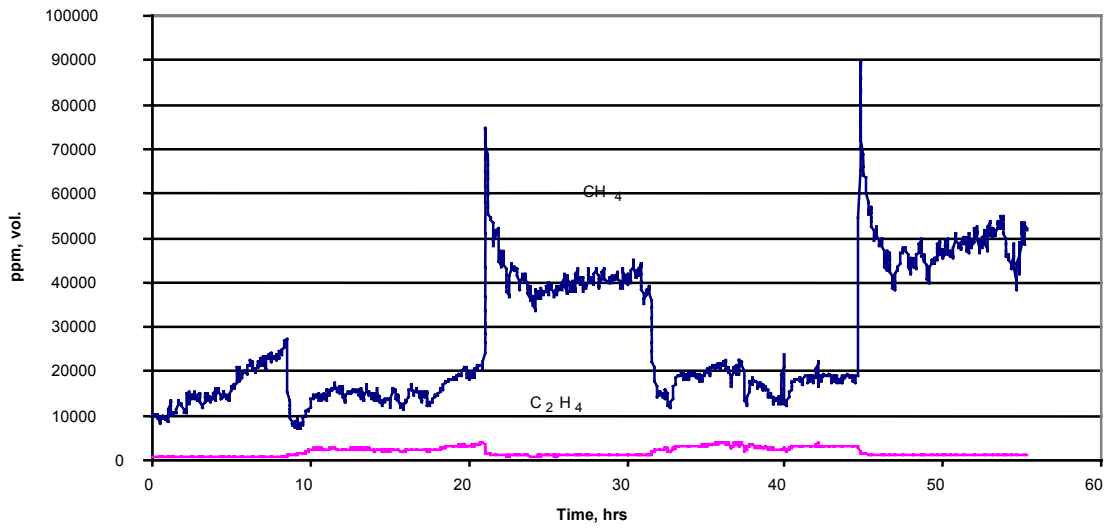


Figure 4. Concentration of hydrocarbons in the co-reforming gas

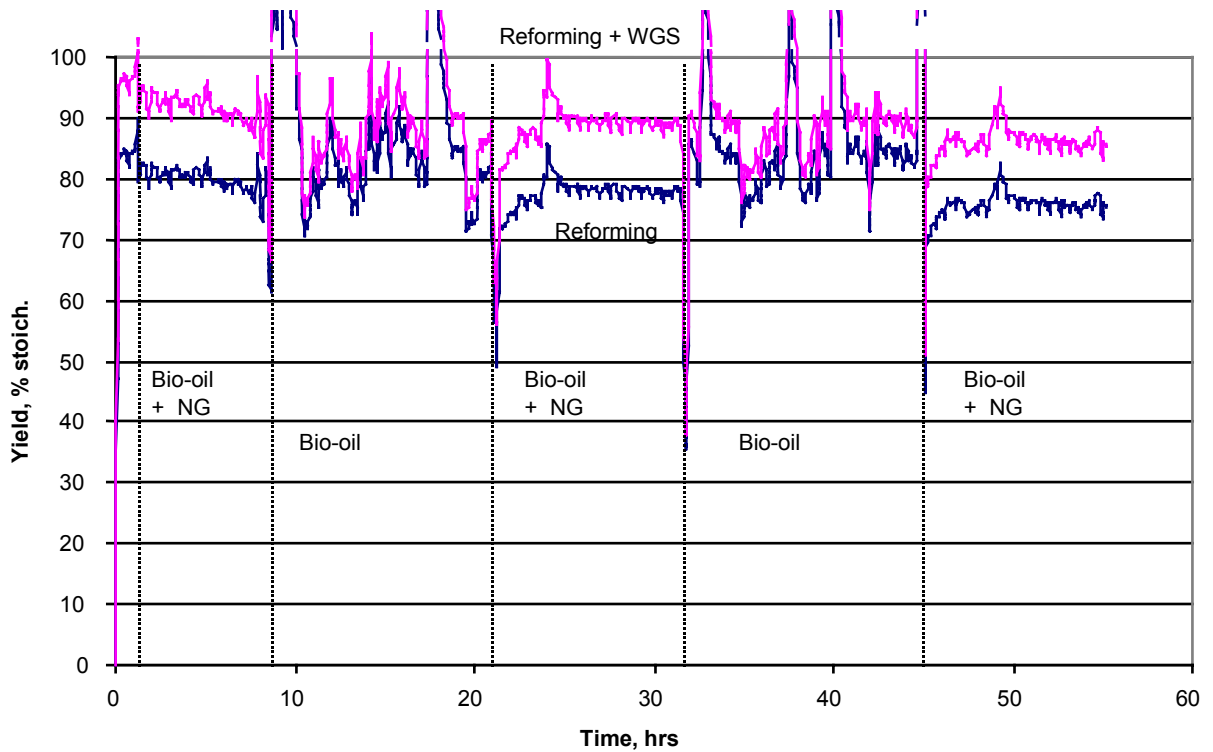
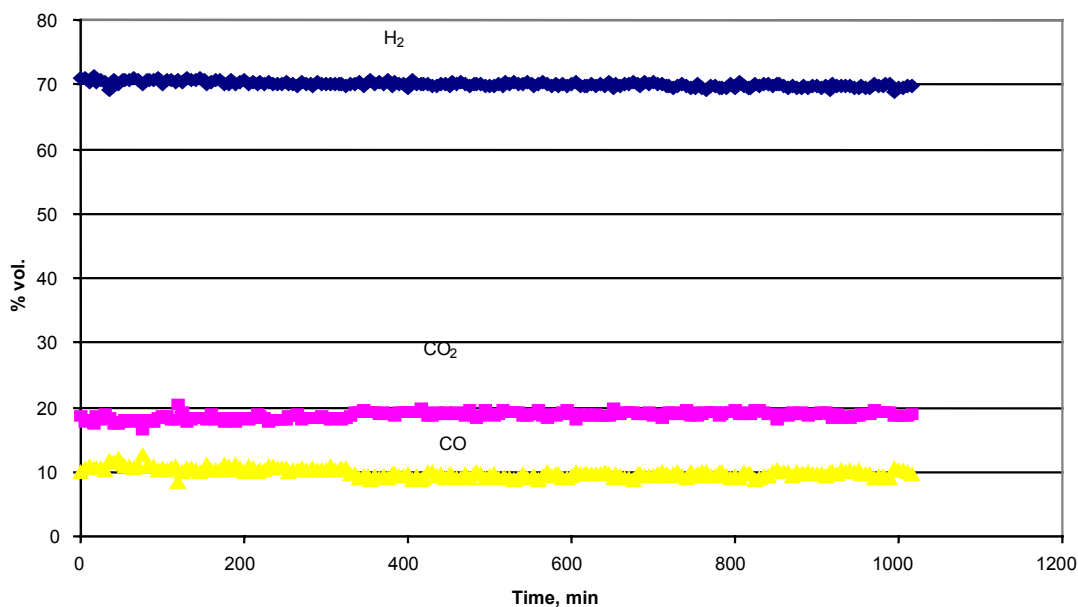
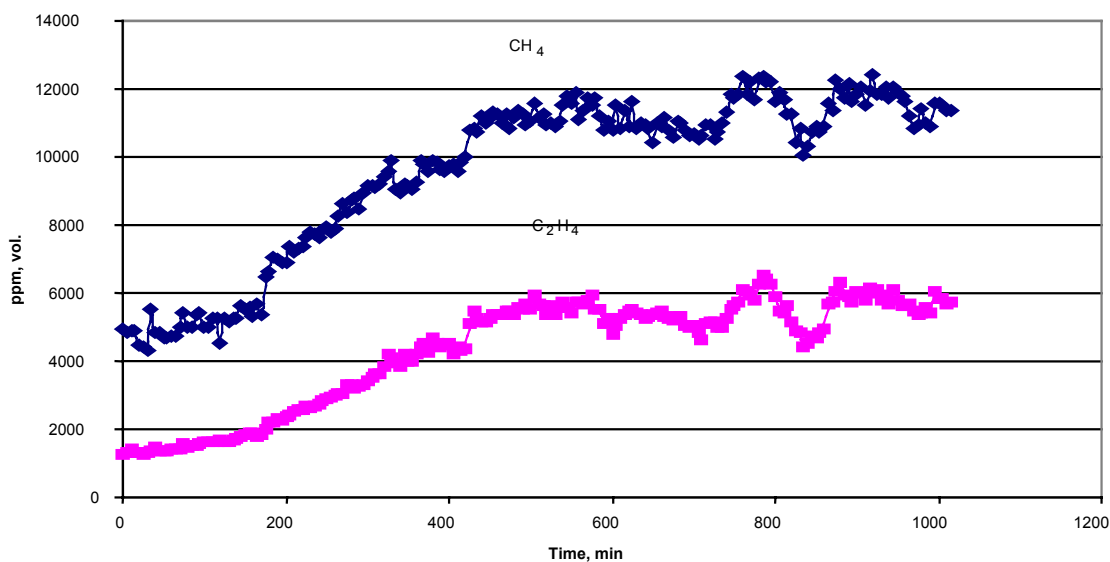


Figure 5. Yield of hydrogen from co-reforming of bio-oil and natural gas



**Figure 6. Product gas composition obtained by reforming of “trap grease”**

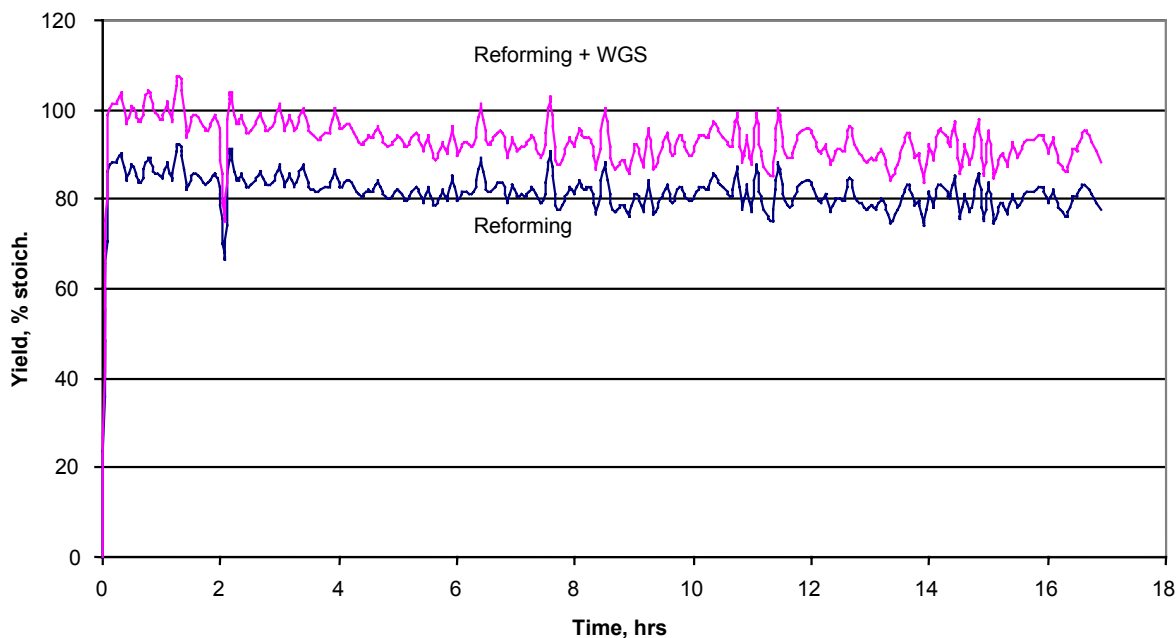
The concentrations of minor products, methane and ethylene (Figure 7), increased during the first ten hours of the experiment, which could be due to a decreasing catalyst activity. However, they leveled off in the second half of the test.



**Figure 7. Concentration of hydrocarbons during steam reforming of “trap grease”**



The hydrogen yield that was initially 31.1 g per 100 g of “trap grease” decreased to 28.7 g after 17 hours of operation. This corresponds respectively to 88% and 81% of the amount that could be achieved if total organic carbon were converted to CO<sub>2</sub> (Figure 8). These yields could be 10% higher if the reforming were followed by water-gas shift to convert CO to CO<sub>2</sub> (upper curve). The overall mass balance closure was essentially 100% throughout the duration of the test. Closures were also observed for elemental balances of carbon, hydrogen and oxygen, indicating that all the carbon from “trap grease” was converted to gases.



**Figure 8. Hydrogen yield obtained from reforming of “trap grease”**

The above results indicate that “trap grease” can be a convenient feedstock for producing hydrogen. It is available at a price of 2-4¢/lb. Since over 30 kg of hydrogen can be obtained from 100 kg of “trap grease,” the feedstock costs contributes only \$1-2/GJ to the total cost of hydrogen. With current market prices for hydrogen in the \$6-9/GJ range, “trap grease,” which can be processed directly without any expensive pretreatment, offers an opportunity for further development. The technology needs to be further studied to determine the catalyst time on stream and the efficiency of regeneration. Also effects of possible contaminants in “trap grease,” especially inorganics, should be thoroughly investigated.

### Summary and Conclusions

1. Biomass can be a valuable resource for producing hydrogen if used in an integrated process that also generates higher value co-products. Following this strategy we have presented two process options: fast pyrolysis/steam reforming (extended to co-reforming bio-oil and natural gas) and steam reforming of biomass residues (“trap grease” in this study).

2. We have demonstrated feasibility of co-reforming the aqueous fraction of bio-oil and natural gas. The hydrogen yield obtained in a fluidized bed reactor using a commercial catalyst was about 80% of the stoichiometric value. This yield would increase by 10% if CO present in the gas were further converted by water-gas shift. In our tests, about 75% of the hydrogen was obtained from natural gas while 25% was from bio-oil.
3. We have successfully proven the concept of using a fluidized bed catalytic steam reforming process for the production of hydrogen from “trap grease,” a low-cost feedstock available at food processing and sewage treatment plants. The hydrogen yield was about 30 g per 100 g of feed, which is above 81% of theoretical (stoichiometric conversion), for 17 hours of catalyst time on stream. This yield could increase by 10% if a secondary water-gas shift reactor followed the reformer.
4. The catalytic fluidized bed process should be further studied to determine the catalyst time on stream and efficiency of regeneration. The effect of possible inorganic impurities on the catalyst needs to be determined.

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