

Hydrogen from Biomass via Fast Pyrolysis/Catalytic Steam Reforming Process

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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 problem for this concept is to demonstrate that bio-oil can be efficiently steam reformed. The co-product strategy can be also applied to residual fractions derived from pulping operations and from ethanol production. Hydrogen can be generated from these fractions that are currently available in most pulp mills and that will become available in future ethanol plants using lignocellulosics as feedstocks.

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 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 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. 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. For instance, a series of small size pyrolysis units could be constructed at sites where low cost feedstock is available then the oil would be transported to a central reforming plant located at a site with an existing hydrogen storage and distribution infrastructure. 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, which is presented in Figure 1, the solid line specifies the route leading to co-products hydrogen and “depolymerized lignin”. Lignin-derived oligomer-rich fraction can be used as a feedstock for the production of resins with formaldehyde². Such resins can become valuable co-products (a substitute for phenol-formaldehyde), which will lower the production costs of hydrogen from the aqueous fraction as demonstrated in related technoeconomic studies³. 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/GJ, which is at the low end of the current selling prices.

Another viable application of the lignin-derived fraction is the production of cyclohexylethers, a new class of high-octane fuel additive⁴. The economics of the whole bio-oil reforming are less

favorable than for the co-product strategy. However, the hydrogen yields obtained from the whole oil are higher than when only the aqueous, carbohydrate-derived fraction is processed. In addition, since hydrogen is the only product, this option is independent of co-product markets.

Another concept for producing hydrogen that we are developing is shown in Figure 2. It combines steam-aqueous fractionation of biomass with catalytic steam reforming of the lower-value hemicellulose-rich liquid by-product while cellulose and lignin components would be used for other applications.

Steam reforming can be conceivably conducted with the entire bio-oil or with each of its fractions or with hemicellulose fraction from steam-aqueous processing. Because biomass fast pyrolysis and steam fractionation technologies have almost reached the commercial status, this work has focused on the catalytic steam reforming of bio-oil, its fractions, and hemicellulose solutions. In previous years we demonstrated, initially through micro-scale tests then in the bench-scale fixed-bed reactor experiments⁵ 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. We managed to reduce these undesired reactions by injecting the oil fraction to the reactor in a form of a fine mist. However, 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. The limitations of the fixed-bed reactor were even more obvious for processing whole bio-oil. The hydrogen yield obtained was only 41% of that stoichiometrically possible and the reforming duration was less than 45 minutes. For this reason we decided to employ fluidized bed reactor configuration that can 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 remains in contact with the oil droplets fed to the reactor. This results in increasing the reforming efficiency and extending the catalyst time-on-stream. 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-oils were generated from three feedstocks: poplar and pine wood and from peanut shells using the NREL fast pyrolysis vortex reactor system⁶. The poplar 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. Two other oils will be studied in the near future.

Steam-aqueous fractionation of poplar wood was performed at the University of Sherbrooke in a continuous Stake II unit⁷ employing steam treatment at a severity of $\text{Log } R_o=3.8$. Severity combines the effect of temperature and duration of the process using reaction ordinate defined as $\text{Log } R_o = \text{Log } t + (T-100)/14.75$. This treatment led to solubilization, after washing, of 30% of the biomass into a hemicellulose-rich aqueous solution. The aqueous solution contained 32.1% of solutes having the elemental composition $\text{CH}_{1.36}\text{O}_{0.67}$. These solutes were mostly oligomeric pentosan and a small amount of dissolved lignin.

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 .

.2 Fluidized bed reformer

The bench-scale fluidized bed reactor is shown in Figure 3. 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 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. 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, possibly, char generated in the reactor then 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 gas composition was analyzed every 5 minutes by an 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. Total and elemental balances were calculated as well as the yield of hydrogen generated from the feed.

Results and Discussion

The steam reforming experiments on aqueous extract of poplar bio-oil were carried out in the fluidized bed reactor 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 $G_{C_1}HSV$ was in the range of 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 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 be 99% and 84% respectively.

The catalyst used in this experiment was regenerated by carbon dioxide and steam treatment for two hours at 850°C then reused in the next test, which was carried out at 850°C. We expected that at a higher temperature the formation of char and coke would be less or their gasification by steam would be more efficient than that achieved in the previous conditions. After regeneration the catalyst recovered its initial activity. During eight hours of reforming of the bio-oil carbohydrate-derived fraction, the product gas composition remained constant, as presented in Figure 4. This indicates that no catalysts 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.

Steam reforming of the hemicellulose-rich liquid was carried out at the catalyst bed temperature of 800°C with the feed rate of 4 g/min and steam flow of 2.4 g/min. The produced gas composition is shown in Figure 5. At the beginning of the run the hydrogen concentration was 65% but decreased to 60% after three hours on stream. This suggests that catalyst deactivated during the experiment. Hydrogen yield was 67.3% of that which could be obtained by stoichiometric conversion. Mass balances indicated that 73% of carbon from hemicellulose was converted to CO₂ and CO. The remaining 27% could thus form char entrained from the system and coke deposits on the catalyst surface, which would explain the loss of its activity. The activity of the catalyst used for reforming was easily restored by steam or carbon dioxide gasification of the deposits. The catalyst was reused in next experiments showing the same efficiency. The regeneration also resulted in producing additional amounts of hydrogen. Hemicellulose is more difficult to reform than bio-oil aqueous fraction due to a higher content of oligomeric material that tends to carbonize during the process.

At present, our efforts focus on finding optimum process conditions (temperature, steam to carbon ratio) to maximize hydrogen production and minimize coke formation.

Summary and Conclusion

1. Biomass can be a valuable resource for producing hydrogen provided that an integrated process will also generate higher value co-products. Following this strategy we have considered two process options: fast pyrolysis/steam reforming and steam-aqueous fractionation/steam reforming.
2. Bio-oil from pyrolysis or its aqueous fraction as well as hemicellulose-rich solution from steam-aqueous fractionation can be reformed to generate hydrogen by a thermocatalytic process using commercial, nickel-based catalysts.
3. The hydrogen yield obtained in a fluidized bed reactor from the aqueous fraction of bio-oil was about 90% of the stoichiometric value, which corresponds to almost 6 kg of hydrogen from 100 kg of wood.

4. Hydrogen yield from the hemicellulose solution was about 70% of the stoichiometric potential. Lower performance was due to the higher content of oligomeric material, which is more difficult to reform.
5. Catalysts are easy to regenerate by steam or CO₂ gasification of carbonaceous deposits.
6. The process needs to be optimised to determine conditions that allow for maximum yields of hydrogen and minimum coke formation.

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Figure 1. Process diagram: Hydrogen from Biomass via Fast Pyrolysis/Steam Reforming

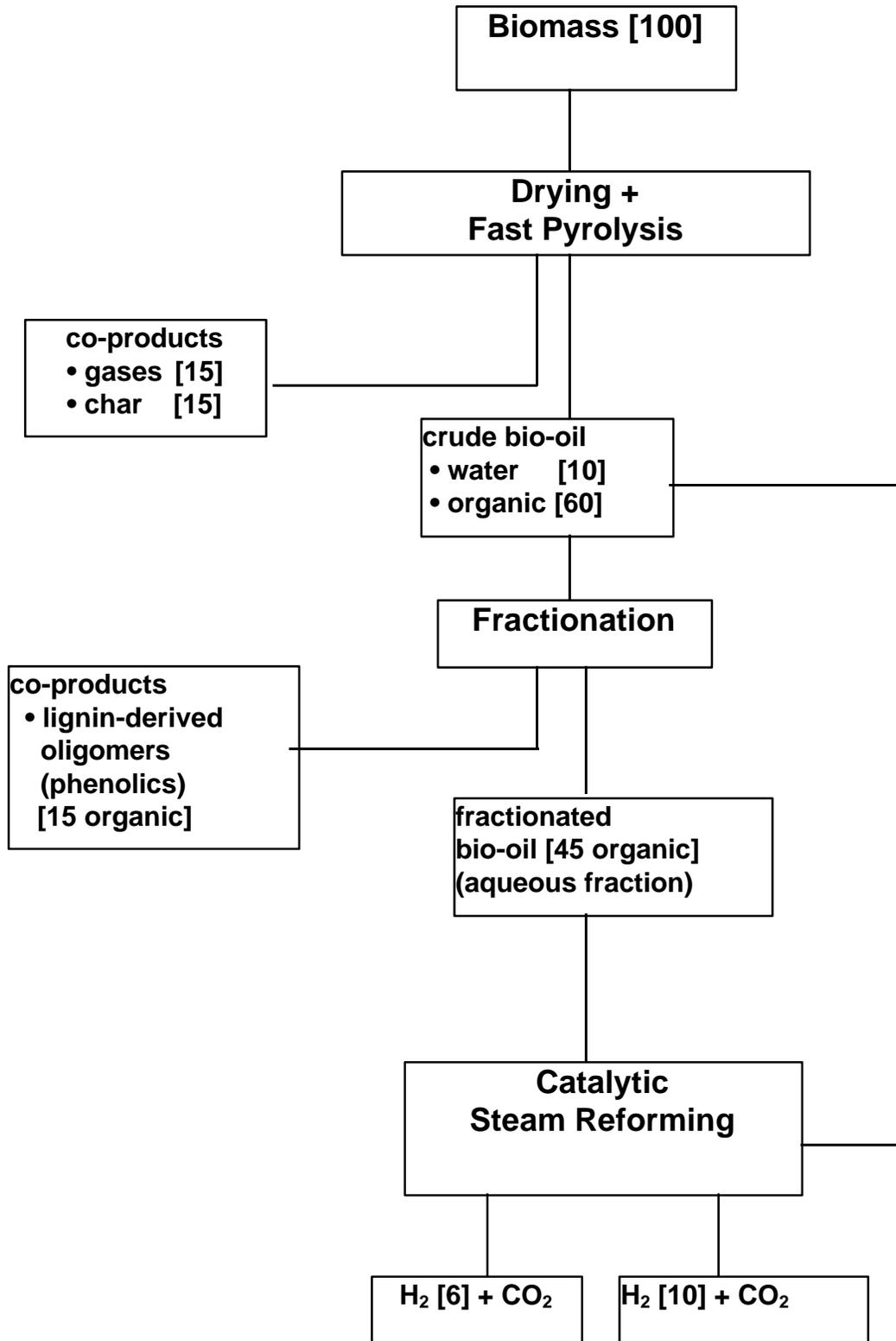


Figure 2. Hydrogen from Biomass via Steam-Aqueous Fractionation/Steam Reforming

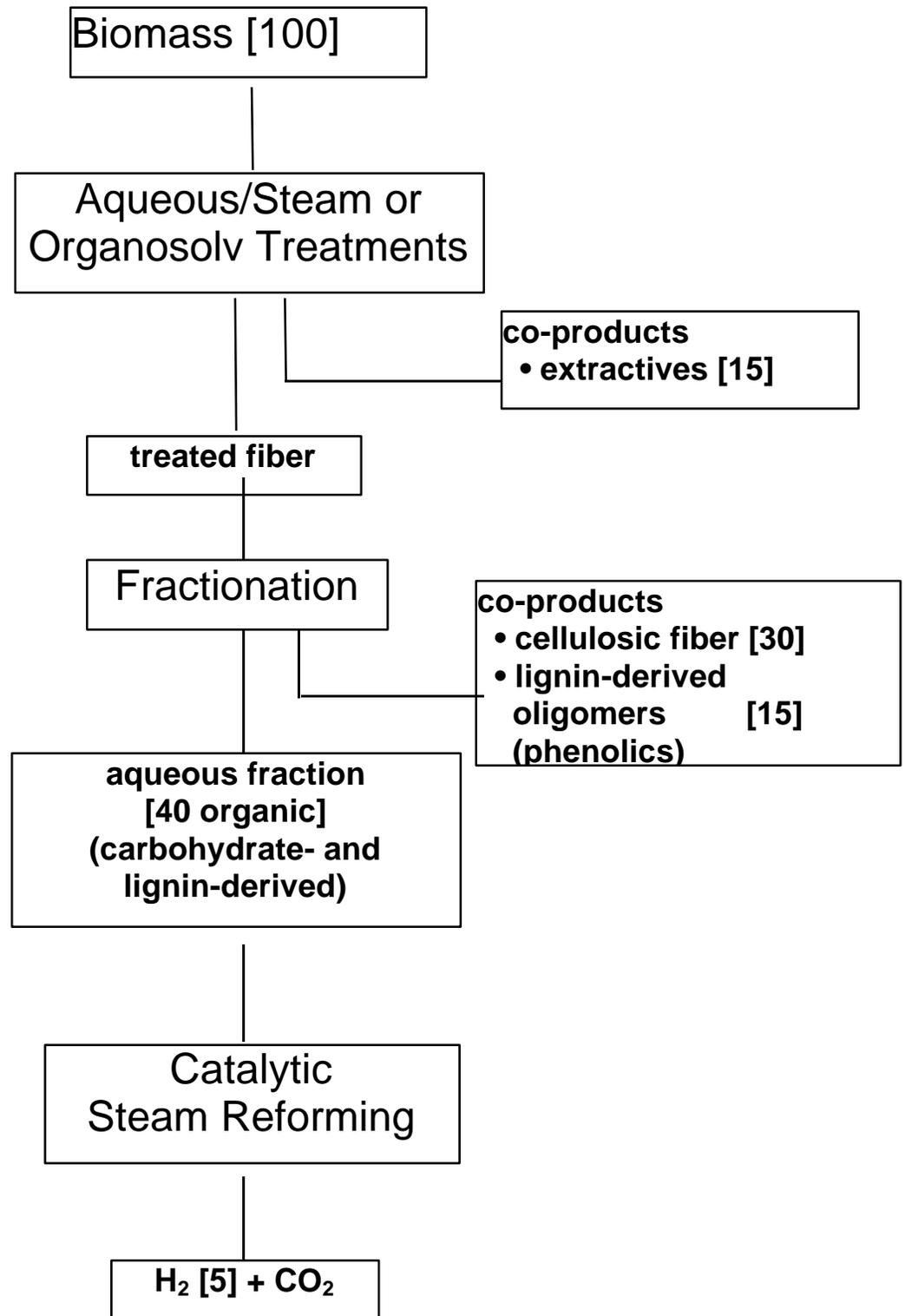


Figure 3. Fluidized bed reforming system.

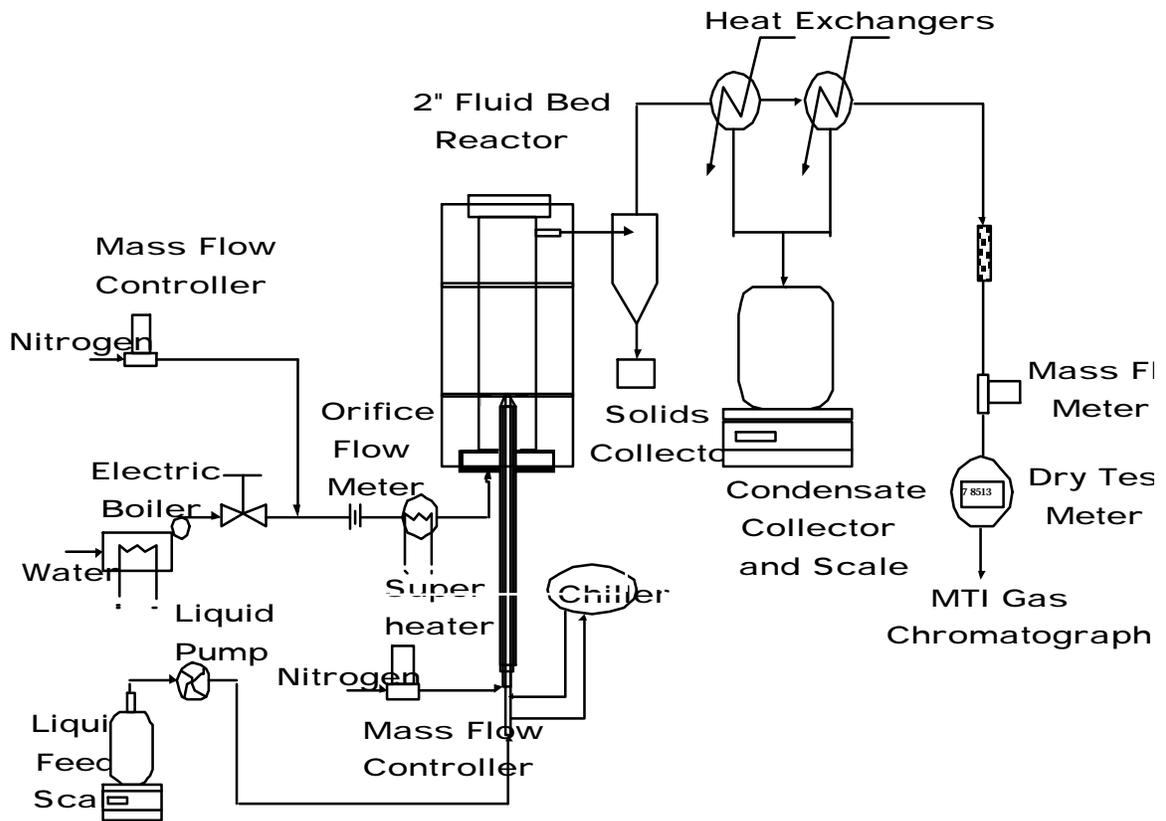


Figure 4. Gas composition from steam reforming of poplar pyrolysis oil aqueous extract

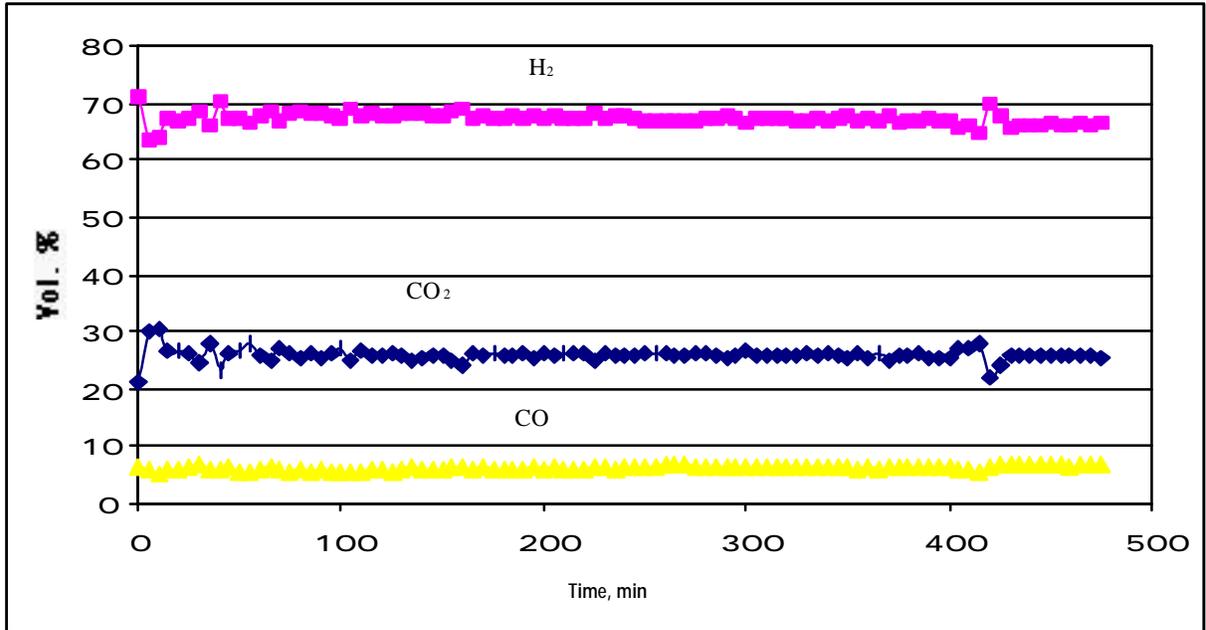


Figure 5. Gas composition from steam reforming of hemicellulose solution obtained by steam-aqueous fractionation of poplar wood.

