

HYDROGEN FROM BIOMASS VIA FAST PYROLYSIS AND CATALYTIC STEAM REFORMING

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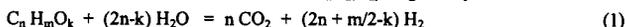
ABSTRACT

Fast pyrolysis transforms biomass into "bio-oil", with yields as high as 75-80 wt.% of the anhydrous biomass. This bio-oil is a mixture of aldehydes, alcohols, acids, oligomers from the constitutive carbohydrates and lignin, and some water from the dehydration reactions. Tests performed using a microreactor interfaced with a molecular beam mass spectrometer and a bench-scale, fixed bed reactor have demonstrated near stoichiometric hydrogen yields from steam reforming of the bio-oil aqueous fraction obtained after precipitation and separation of the lignin-derived oxyaromatics. Reforming of the aqueous fraction required proper dispersion of the liquid to avoid vapor-phase carbonization of the feed in the inlet to the reactor. A spraying nozzle injector has been designed and successfully tested. We will present and discuss the process developed for the pyrolysis and reforming operations and some preliminary product cost estimates. The economics of the process is favored when the separated lignin-derived oxyaromatics are converted to valuable co-products and the aqueous fraction of the bio-oil is used for hydrogen production.

INTRODUCTION

Although renewable lignocellulosic biomass has been considered as a potential feedstock for gasification to produce syngas, the economics of current processes favor the use of hydrocarbons (natural gas, C₂-C₅, and naphtha) and inexpensive coal. An alternative approach to the production of H₂ from biomass is fast pyrolysis of biomass to generate a liquid product (also known as bio-oil) and catalytic steam reforming of the oil or its fractions. This latter approach has the potential to be cost competitive with the current commercial processes for hydrogen production. The yield of bio-oil can be as high as 75-80 wt.% of the anhydrous biomass.

Bio-oil is a mixture of aldehydes, alcohols, acids, oligomers from the constitutive carbohydrates and lignin, and some water from the dehydration reactions. The overall steam reforming reaction of bio-oil (or any oxygenate with a chemical formula of C_nH_mO_k), is given by:



The stoichiometric yield of hydrogen is $2+m/2n-k/n$ moles per mole of carbon in the feed, and k/n is usually in the fractions for the aromatic phenolics from lignin, while k/n is close to 1 for most carbohydrate-derived products such as sugars. In contrast to producer gas, *bio-oil* is easily transportable. Thus, the two key process steps, pyrolysis and reforming, can be carried out independently at different locations. This allows to minimize the costs of feedstock, transportation, and product (H₂) distribution. In this paper, we describe results on catalytic steam reforming of oxygenates. Tests performed using a microreactor interfaced with a molecular beam mass spectrometer and a bench-scale, fixed bed reactor have demonstrated near stoichiometric hydrogen yields from the bio-oil aqueous fraction obtained after precipitation and separation of the lignin-derived oxyaromatics. We will also present results of preliminary economic analysis on this process, which also produces a valuable co-product (lignin-derived oxyaromatics).

EXPERIMENTAL

Tests were carried out in two systems: a microreactor coupled to a molecular-beam mass spectrometer (MBMS) and a bench-scale fixed bed unit. Both systems have been described in detail in our previous work.^{1,2} The microreactor was housed in a tubular furnace with four independently controlled temperature zones. The dual bed configuration of this reactor enabled us to study either the differences between thermolysis and catalysis or to compare the performances of two catalysts under the same temperature conditions. Gaseous products at the exit of the microreactor are sampled in real-time through a supersonic, free-jet expansion nozzle.

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This expansion cools the reaction products and forms a molecular beam that is ionized and analyzed by a quadrupole mass spectrometer.

The bench-scale reactor is a stainless steel tube (1.65 cm id x 42.6 cm length) housed in a tubular furnace equipped with three independently controlled heating zones. The reactor was packed with about 100 g of a commercial, nickel-based catalyst (particle size: 2.4-4.0 mm). Most studies were carried out using the UCI G-90C catalyst and a dual-catalyst bed of 46-1 and 46-4 from ICI Katalco. Steam was generated in a boiler and superheated. The organic feed from a diaphragm metering pump was sprayed using N₂ and mixed with superheated steam in a triple nozzle injector. Products exiting the reactor were passed through a condenser. The condensate (just water in most cases) weight, volume and compositions of the permanent gas output were recorded periodically. An on-line IR gas analyzer was used to monitor CO/CO₂ concentrations and a MTI-QUAD GC was used to measure concentrations of H₂, N₂, O₂, CO, CO₂, CH₄, and other light hydrocarbons. The reformer system was interfaced with a computer to monitor temperatures and other important parameters. All materials used were obtained from commercial suppliers, except the bio-oil and its aqueous fraction that were prepared at NREL.

RESULTS AND DISCUSSION

Rapid Screening Studies. The goal of these experiments was to demonstrate the high efficiency of catalytic steam reforming as a method for conversion of bio-oil to hydrogen, with specific objectives to evaluate and select best catalysts and operating conditions, and to gain mechanistic insight into the chemistry involved in the steam reforming reactions of oxygenates. A series of model oxygen-containing compounds, biomass and its main components (cellulose, xylan, and lignin), and *bio-oil* and its various fractions were screened under identical conditions using a commercial catalyst, G-90C, from United Catalyst Inc. (UCI). We also tested a number of research and commercial steam reforming catalysts and a WGS catalyst and determined H₂ yields using four model compounds (methanol, acetic acid, an aqueous solution of hydroxyacetaldehyde, and a methanol solution of 4-allyl-2,6-dimethoxyphenol) under the same operating conditions. All of the catalysts tested were capable of reforming the model compounds and high conversions (>99%) were observed. The H₂ yields for all catalysts and model compounds were high, averaging 90% (±5%) of the stoichiometric. Within our experimental error limit, there is no clear indication of one catalyst being better than the others. Among the most important parameters for steam reforming are catalyst bed temperature (T), molar steam-to-carbon ratio (S/C), gas hourly space velocity (G_{C1}HSV), and residence time (t, calculated from the void volume of the catalyst bed divided by the total flow rate of gases at the inlet of the reactor; void fraction = 0.4). Temperature was found to have the most profound effect on steam reforming reactions. Within experimental error limits, varying residence time from 0.04 to 0.15 s and increasing S/C from 4.5 to 7.5 showed no significant effects on the yield of hydrogen under the conditions of 600°C and GHSV (gas hourly space velocity, on C₁ basis) = 1680 h⁻¹; however, this affected the yield of CH₄.

From these rapid screening studies of various classes of model oxygenate compounds, we found that steam reforming of oxygenates generally involves a significant competition from the decomposition owing to thermally-induced cracking prior to entering the catalyst bed and the acid-catalyzed reactions at the acidic sites of the catalyst support. These competing thermal decomposition reactions may result in the formation of carbonaceous materials (coke), blocking the reactor and even deactivating the catalyst. This calls for special emphasis on how to feed bio-oil or its fractions into the reactor. However, a complete conversion of both the oxygenate feed and its decomposition products to hydrogen can be achieved with commercial Ni-based catalysts under reasonable operating conditions, if char formation prior to reaching the catalyst bed and coking on the catalyst can be eliminated, or at least controlled.

Bench-Scale Tests. Tests at the bench-scale level were conducted to obtain the global and elemental mass balances and the carbon-to-gas conversion, to quantify the distribution of gas products under conditions of complete conversion of the pyrolysis oil feedstock, and to study catalyst lifetime and regeneration. We used both model compounds (methanol, acetic acid, syringol and *m*-cresol, both separately and in mixtures) and real bio-oil (its aqueous fraction), and representative results are listed in Table 1. Profiles of the output gas composition are shown for the 3-component mixture in Figure 1 and for the poplar oil aqueous fraction in Figure 2. The following discussions are focused on the reforming of a 3-component mixture and a bio-oil aqueous fraction.

The three-component mixture contained 67% acetic acid, 16% *m*-cresol, and 16% syringol. Its composition was close to the proportions of the carbohydrate fraction and the lignin fraction in bio-oil. We observed *some coke deposits* on the top portion of the UCI G-90C catalyst bed. The overall mass balance (carbon, hydrogen, and oxygen) was 99% and the carbon conversion to gas was 96% (Table 1). The other catalyst tested for steam reforming of the 3-component mixture was the 46-series from ICI Katalco (46-1/46-4). This dual catalyst bed is used in commercial naphtha reforming plants to reduce coke formation and extend catalyst lifetime. It showed an excellent and steady performance *without any coke deposition* on the catalyst. The gas composition (Figure 1) remained constant throughout the whole run. The overall mass balance (including carbon, hydrogen, and oxygen) was 104%, and for carbon 105%, indicating that there may be a systematic error in our measurement. An excellent hydrogen yield of 86% was obtained, and the total hydrogen potential may be as high as 98% with a second water-gas shift reactor. These results confirm that both the UCI G-90C and especially the ICI 46-series catalysts can efficiently convert oxygenates to hydrogen.

Steam reforming of bio-oil or its fractions was found to be more difficult than that of model compounds. The main problem that needed to be solved was feeding the oil to the reactor. Bio-oil cannot be totally vaporized; significant amounts of residual solids are often formed that block the feeding line and the reactor. Thus, the simple injection system used for model compounds had to be modified to allow spraying bio-oil and its fractions in to the catalytic reactor without prior char formation.

A poplar oil generated in the NREL vortex reactor system was extracted using ethyl acetate (EA) and water (weight ratios of 1:1:1 for oil:EA:water). The resulting aqueous fraction (55% of the whole oil) contained 25% organics and 75% water. It was successfully fed to the reactor using a triple-nozzle spraying system with minimal accumulation of char in the reactor inlet. A large excess of steam (S/C = 20-30) was used, together with a high flow rate of nitrogen, to allow for proper oil dispersion and heat transfer required to maintain a sufficiently high temperature (>500°C) at the reactor entrance. A portion of water and other volatiles in the sprayed droplets evaporate during mixing with the superheated steam and the remaining will contact the catalyst surface directly. The ICI 46-series catalysts performed satisfactorily with no coke formation. We observed a stable gas production rate and composition throughout the whole 4-hour-long experiment (Figure 2).

The carbon conversion of the aqueous fraction to gas products was almost quantitative in both runs that used the same catalyst bed (Table 1). We observed similar levels of mass balances as in the experiments using model compounds: global 99%, carbon 105%, and hydrogen 97%. The methane concentration (with N₂ excluded) increased from 0.56% in the first run (2 h, $t=0.03$ s) to 2.2% in the second run (4 h, $t=0.02$ s), and both values were much higher than that (0.01%) obtained from the 3-component model compound mixture (17 h, $t=0.09$ s). This was likely caused by the shorter residence time forced by the large flow rate of steam and nitrogen used in the experiment.

Process Design and Preliminary Economics. In the process being evaluated, bio-oil generated from fluid bed pyrolysis of biomass will be refined through a separation step (using water and ethyl acetate) to recover an oxyaromatic coproduct which will be used as a phenolic substitute in resin formulations. The remaining aqueous fraction will be catalytically steam reformed to produce hydrogen, using a process based on that used for natural gas reforming. Because of the low sulfur content of biomass and bio-oil, a sulfur removal system is not likely to be required. Also, according to thermodynamic simulations and the screening results, a temperature reformer ramping up to 700°-750°C (which is lower than 825°-900°C required for reforming natural gas) will be needed. The ratio of steam to oil will be determined by experimental results and economic optimization; it will be in the 5 to 7 range, based on the literature and experimental data already obtained. Laboratory experiments will provide the basis for the choice of the most suitable catalyst and reactor configuration; the base case will use a fixed-bed catalytic reactor. A pressure swing adsorption unit will be used to purify the H₂ produced.

A feasibility analysis was performed on this process to determine if the process could have economic viability and specify areas where research will help to lower the production cost.³ Both laboratory data and standard process data, where applicable, were used. Although this analysis is not of design quality, it does provide useful information on this research project before scale-up and commercialization. The capital investment of the pyrolysis plant was taken from Beckman and Graham.⁴ Biomass was considered available at a cost of \$25/dry tonne. A

15% internal rate of return was assumed for both the pyrolysis and reforming facilities. The phenolics substitute coproduct was assumed to be sold for \$0.44/kg, a fraction of the selling price of phenol. Steam is produced through heat integration and is sold as a by-product.

For our conceptual process, the cost of hydrogen has been estimated to be \$7.70/GJ for the base case (production capacity: 35.5 tonne of hydrogen per day), falling within the range of the current selling price of H_2 in industry (\$5-14/GJ). Several parameters (for instance, a lower cost for biomass) can lower this price to \$3-5/GJ.³ The process can also sustain large changes in coproduct selling price, capital cost, and hydrogen production capacity before the hydrogen becomes more expensive than current markets will allow.

CONCLUSIONS

Reforming biomass-derived oxygenates appears to be possible using available Ni-based catalysts. It involves both thermal decomposition of the labile oxygenates and the catalytic steam reforming of the starting material and its decomposition products. At least 80% of the theoretical maximum hydrogen yield has already been obtained. The excess steam can be reduced to achieve S/C on the order of 5-10, as in cases of natural gas and naphtha reforming, by modification of reactor design. Fast pyrolysis followed by reforming represents a credible alternative to gasification with the following advantages: no oxygen is needed; a co-product strategy is possible; a regionalized system of production units coupled to a central reformer offers greater flexibility. Low biomass costs are required to produce hydrogen economically since feedstock cost is a significant component of the production cost. Co-products from the pyrolysis oil favor the economics.

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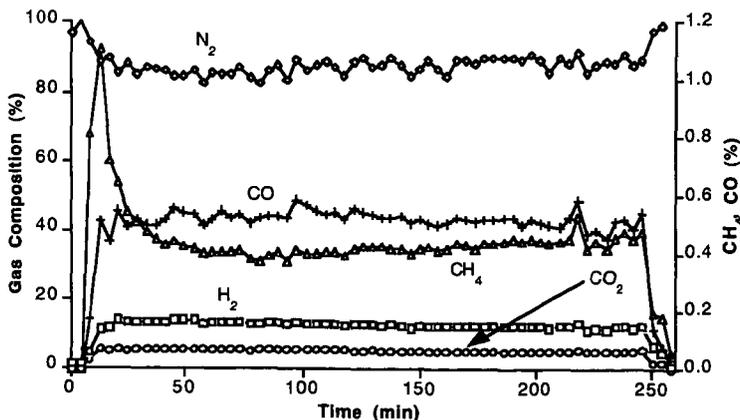


Figure 2. Composition of gaseous products during the steam reforming of a bio-oil aqueous fraction using the ICI 46-series catalyst.

Table 1. Summary of results for catalytic steam reforming experiments on the bench-scale reformer

Feed	Catalyst	S/C ^a	GC ₁ HSV ^b	Temperatures (°C)			Yield (mol/100 mol of carbon fed)				% Carbon-gas conversion	% st. yield of H ₂ (+WGS) ^c	Time on stream (h)
				Top	Middle	Bottom	H ₂	CO ₂	CO	CH ₄			
acetic acid	UCI G-90C	4.7	1973	685	716	833	145.8	50.3	49.7	0.055	101	73 (98)	6
acetic acid	UCI G-90C	12.8	777	710	789	830	171.8	74.9	29.0	0.005	104	86 (100)	8
syringol (in MeOH)	UCI G-90C	6.3	2454	702	745	830	195.0	45.4	53.9	0.2	100	75 (96)	4
syringol (in MeOH)	UCI G-90C	7.4	1985	750	803	863	197.3	46.0	54.9	0.1	101	76 (97)	4
3-component mixture	UCI G-90C	6.5	1053	738	NA	833	167.6	67.4	28.6	0.00	96	78 (91)	11
3-component mixture	ICI 46-1/46-4	4.9	1053	782	753	834	187.8	79.8	27.4	0.03	105	86 (98)	17
poplar oil aq. fraction	ICI 46-1/46-4	19.3	1110	480	730	818	206.7	85.2	9.6	1.7	97	103 (108)	2
poplar oil aq. fraction	ICI 46-1/46-4	30.0	1000	530	744	821	205.8	86.6	8.4	6.9	102	103 (107)	4

^a Molar ratio of steam to carbon. ^b Gas hourly space velocity on C₁ basis (h⁻¹). ^c Assuming all CO being converted to H₂ in a down stream WGS unit. NA = not available.

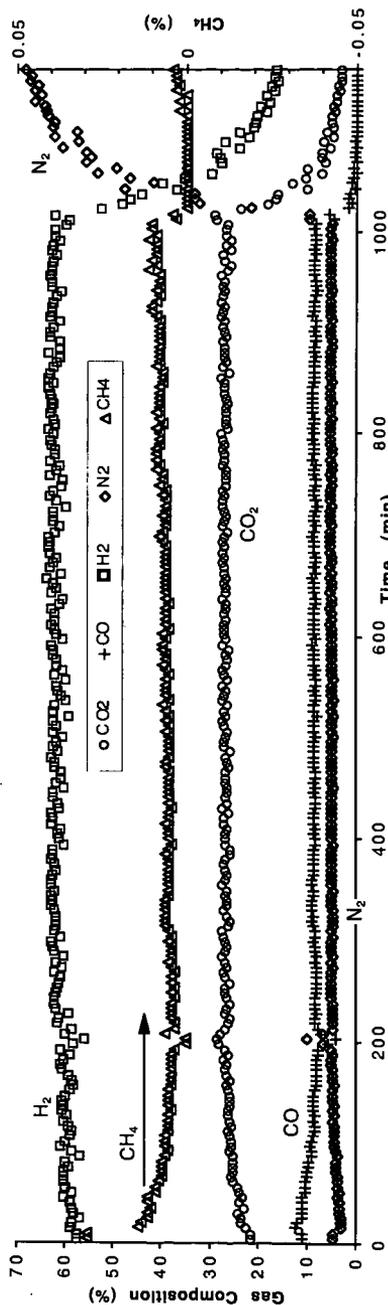


Figure 1. Composition of gaseous products during steam reforming of a 3-component mixture using the ICI 46-series catalyst.