

# Hydrogen from Biomass: Steam Reforming of Model Compounds of Fast-Pyrolysis Oil

Maximiliano Marquevich,<sup>†</sup> Stefan Czernik,<sup>‡</sup> Esteban Chornet,<sup>‡,§</sup> and Daniel Montané<sup>\*,†</sup>

Rovira i Virgili University. Department of Chemical Engineering, Carretera de Salou s/n, 43006 Tarragona (Catalunya), Spain, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401, and Université de Sherbrooke, Department of Chemical Engineering, Sherbrooke, Québec, J1K 2R1, Canada

Received March 2, 1999

We investigated the production of hydrogen by the catalytic steam reforming of model compounds of biomass fast-pyrolysis oil (bio-oil). Acetic acid, *m*-cresol, dibenzyl ether, glucose, xylose, and sucrose were reformed using two commercial nickel-based catalysts for steam reforming naphtha. The experiments were conducted at a methane-equivalent gas hourly space velocity ( $G_{CH_4}HSV$ ) from 500 to 11790 h<sup>-1</sup>. Steam-to-carbon ratios (S/C) of 3 and 6 and catalyst temperatures from 550 to 810 °C were selected. Rapid coking of the catalyst was observed during acetic acid reforming at temperatures lower than 650 °C. Acetic acid, *m*-cresol, and dibenzyl ether were completely converted to hydrogen and carbon oxides above this temperature, and hydrogen yields ranged from 70 to 90% of the stoichiometric potential, depending on the feedstock and reforming conditions. Sugars were difficult to reform because they readily decomposed through pyrolysis in the freeboard of the reactor. This led to the formation of char and gases before contacting the catalyst particles.

## Introduction

The use of hydrogen as fuel for transportation<sup>1</sup> and the production of electricity with fuel cell systems<sup>2</sup> is becoming an attractive option for a sustainable energy system. Most hydrogen is currently produced by catalytic steam reforming of natural gas and oil-derived naphtha, or by partial oxidation (POX) of heavy oils.<sup>3</sup> Consequently, hydrogen production based on fossil fuels is a net contributor to carbon dioxide emissions and the greenhouse effect. The use of renewable biomass as a major feedstock for hydrogen production has received considerable attention in recent years<sup>4–7</sup> since it is an environmentally friendly alternative to hydrogen derived from fossil fuels. Biomass is the sole renewable source of carbonaceous materials,<sup>8</sup> and hydrogen pro-

duction from biomass feedstocks—either residual or from dedicated crops—may reduce, or even suppress, the net generation of carbon dioxide during hydrogen manufacture.<sup>9</sup> Current technology allows two thermochemical methods for producing hydrogen from biomass: (a) gasification and water-shift, and (b) fast pyrolysis coupled with steam reforming of the resulting biomass-derived oil (bio-oil). We have focused our research on the second option because it allows a coproduct strategy by fractionation of the bio-oil to recover valuable chemicals, thus improving the economics of the process.<sup>10</sup>

The composition of bio-oil differs substantially from that of crude oil and its fractions. Bio-oil is formed by a complex mixture of highly oxygenated compounds derived from the pyrolytic decomposition of the three polymers that constitute biomass: cellulose, hemicellulose, and lignin. Typical composition for poplar-derived bio-oil indicates that it is a complex mixture of acids (4–6%), aldehydes (6–16%), alcohols (8–16%), lignin-derived phenolics (17–26%) with a broad distribution of molar masses, and other unidentified oxygenates.<sup>11,12</sup> In this work, steam reforming of oxygenates using commercial and research nickel-based catalysts

\* Corresponding author.

<sup>†</sup> Rovira i Virgili University.

<sup>‡</sup> National Renewable Energy Laboratory.

<sup>§</sup> Université de Sherbrooke.

(1) Berry, G. D.; Pasternak, A. D.; Rambach, G. D.; Smith, J. R.; Schock, R. N. *Energy* **1996**, *21*, 289–303.

(2) Appleby, A. J. *Energy* **1996**, *21*, 521–653.

(3) Steinberg, M.; Cheng, H. C. *Int. J. Hydrogen Energy* **1989**, *14*, 797–820.

(4) Arauzo, J.; Radlein, J.; Piskorz, J.; Scott, D. S. In *Advances in Thermochemical Biomass Conversion*; Bridgewater, A. V., Ed.; Elsevier Applied Science: London, 1993; pp 201–215.

(5) Mann, M.; Czernik, D.; Wang, D.; Gregoire, C.; Chornet, E. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1994**, *39*, 1034.

(6) Hausermann, W. B. *Int. J. Hydrogen Energy* **1994**, *19*, 413–419.

(7) Chughtai, M. Y.; Kubiak, H. In *10th European Conference on Biomass for Energy and Industry*; Kopetz, H.; Weber, T.; Palz, W.; Chartier, P.; Ferrero, G. L., Eds.; C.A.R.M.E.N.: Rimpfing (Germany), 1998; pp 284–286.

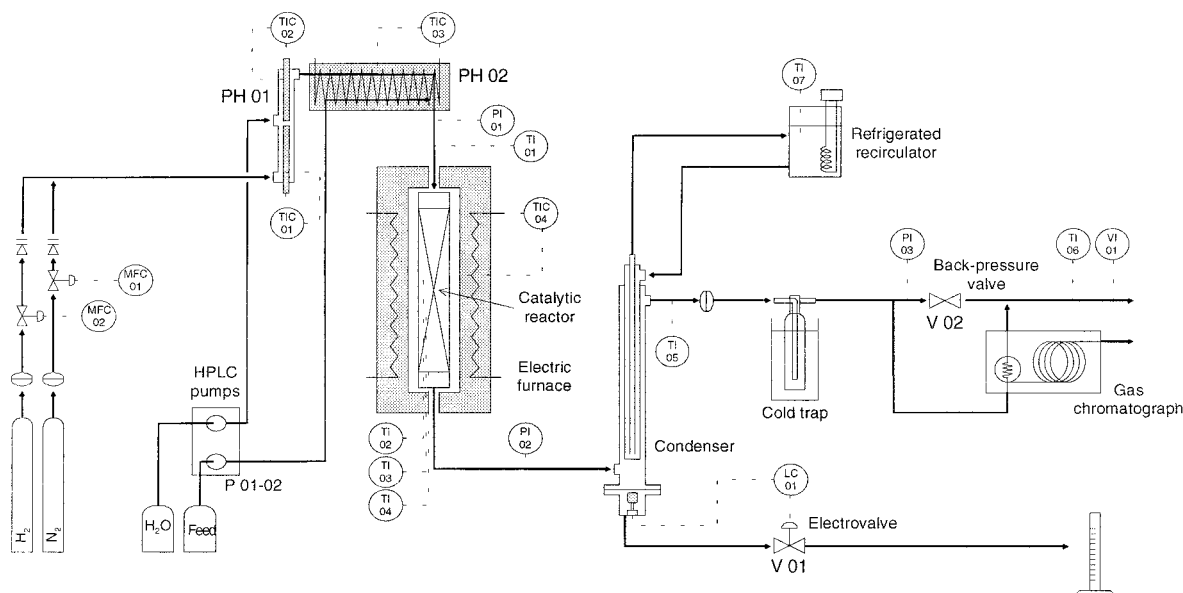
(8) Hall, D. O.; House, J. I. *Sol. Energy Mater. Sol. Cells* **1995**, *38*, 521–542.

(9) Gustavsson, L.; Börjeson, P.; Johansson, B.; Stenningsson, P. *Energy* **1995**, *20*, 1097–1113.

(10) Mann, M. K. In *Proceedings of the Annual DOE/NREL Hydrogen Program Review Meeting*; National Renewable Energy Laboratory: Golden, CO; NREL/CP-430-20036, 1995; pp 707–730.

(11) Piskorz, J.; Scott, D. S.; Radlein, D. In *Pyrolysis Oils from Biomass: Producing, Analyzing and Upgrading*; Soltes, E. J., Milne, T. A., Eds.; ACS Symposium Series 376; American Chemical Society: Washington, DC, 1988; pp 167–178.

(12) Radlein, D.; Piskorz, J.; Scott, D. S. *J. Anal. Appl. Pyrolysis* **1991**, *19*, 41–63.



**Figure 1.** Schematic diagram of the small reactor setup.

was first studied using a packed-bed microreactor coupled to molecular-beam mass spectrometer (MBMS).<sup>13,14</sup> The reforming tests of the model compounds and the aqueous fraction of bio-oil were then carried out using a fixed-bed bench-scale reactor.<sup>15</sup> In this paper we focus on a more systematic bench-scale steam reforming study of model compounds which are representative of the major chemical families present in bio-oil: acids, carbohydrates, and oxygenated aromatics. We based the selection of the operating conditions for the experiments on our previous results and the usual conditions for steam reforming hydrocarbons. In industrial reformers the mixture of naphtha and steam enters the catalyst bed at a temperature of around 600 °C and the products leave the reactor at 790–900 °C. Steam-to-carbon molar ratios range from 2.5 to 6.5, depending on the catalyst preparation and the desired purity for hydrogen. Methane-equivalent gas hourly space velocity ( $G_{C1}HSV$ ) for naphtha reforming typically ranges from 700 to 2000  $h^{-1}$ .<sup>16,17</sup> We have tested steam-to-carbon ratios of 3 and 6 and reforming temperatures from 550 to 810 °C at near atmospheric pressure (1.5–2 bar), using methane-equivalent space velocities ( $G_{C1}HSV$ ) from 500 to 11790  $h^{-1}$ .

## Experimental Section

**Chemicals.** Three groups of model compounds were selected for the tests: organic acids, carbohydrates, and oxygenated aromatics. Acetic acid (Sigma, 99.7% purity) was used as the model for acids. Xylose (Sigma, 99.0%), glucose (Sigma, 99.5%), and sucrose (Sigma, 99.5%) were selected as representatives of the alcohol group. The saccharides were dissolved in deionized water at a concentration of 20 wt %. Finally, *m*-cresol (Merck, 98.0%) and dibenzyl ether (Fluka, 98.0%) were chosen for the aromatics group. Other chemicals used in this study included commercial high purity gases, hydrogen (99.995%) and nitrogen (99.995%), HPLC-grade water, as well as standard gas mixtures (hydrogen, nitrogen, carbon monoxide, carbon dioxide, and methane) for the calibration of the gas chromatograph.

**Catalysts.** We used two commercial nickel-based catalysts for steam reforming naphtha: the UC G-90C manufactured by United Catalyst Inc. and the ICI 46-1 produced by ICI Katalco. The catalysts were crushed and sieved to 2.4–4.0 mm or 1.0–2.0 mm, depending on the reactor size. They were reduced at 600 °C for 4 h in the reactor under a constant flow of 0.8 SLM (standard liters minute) of an equimolar mixture of nitrogen and hydrogen.

**Reactor Setup.** We used two fixed-bed reactors of different size. The larger one (2.64 cm i.d. × 41.0 cm length) was constructed in Inconel and was packed with 100 g of catalyst (the size of the particles ranged from 2.4 to 4.0 mm) diluted with  $\alpha-Al_2O_3$  of the same size at a weight ratio of 50%. The acetic acid and saccharides were studied in this unit. The small reactor (1.27 cm o.d. × 28 cm length) was built of 316L stainless steel and was packed with 10 g of catalyst with particles of 1 to 2 mm. This reactor was used for reforming *m*-cresol, dibenzyl ether, and acetic acid.

The larger reactor has been described elsewhere,<sup>18</sup> and its specific feature is a nozzle injector to spray the organic feed directly on top of the catalyst bed. This nozzle is needed to feed solutions that contain compounds with very high boiling points or that are thermally unstable. Figure 1 shows a schematic of the smaller system. The reactor is located inside a tubular furnace. The temperature profile along the bed is measured by three thermocouples (type K, 0.5 mm o.d.), which are placed axially inside a 1/8-in. o.d. 316L SS sheath. Typically, the first thermocouple (TI 02) measured the temperature at the top of the bed of catalyst,

(13) Wang, D.; Montané, D.; Chornet, E. *Appl. Catal. A: General* **1996**, 143, 245–270.

(14) Wang, D.; Czernik, S.; Montané, D.; Mann, M.; Chornet, E. *Ind. Eng. Chem. Res.* **1997**, 36, 1507–1518.

(15) Wang, D.; Czernik, S.; Chornet, E. *Energy Fuels* **1998**, 12, 19–24.

(16) Rostrup-Nielsen, J. *Chem. Eng. Prog.* **1977**, 73, 87–92.

(17) Satterfield, C. N. *Heterogeneous Catalysis in Industrial Practice*, 2nd ed.; McGraw-Hill: New York, 1991.

(18) Czernik, S.; Wang, D.; Montané, D.; Chornet, E. In *Developments in Thermochemical Biomass Conversion*; Bridgwater, A. V., Boocock, D. G. B., Eds.; Blackie Academic & Professional: London, 1997; pp 672–686.

**Table 1. Steam Reforming of Acetic Acid Using the UC G-90C Catalyst; Experimental Conditions and Yield of Gas Products**

run	S/C ratio mol/mol	M <sub>C1</sub> HSV mol h <sup>-1</sup> L <sup>-1</sup>	G <sub>C1</sub> HSV h <sup>-1</sup>	average temperatures (°C)			yield (mol/100 mol of carbon feed)				run time min
				TI 02	TI 03	TI 04	H <sub>2</sub>	CO <sub>2</sub>	CO	CH <sub>4</sub>	
29 <sup>a</sup>	6.0	67	1500	476	487	511	124.3	61.9	9.4	4.0	45
34 <sup>a</sup>				497	498	520	119.3	58.6	9.8	2.4	45
24 <sup>a</sup>				504	547	661	132.6	61.3	17.6	3.0	51
26 <sup>a</sup>				505	533	594	131.8	61.4	17.1	2.8	45
25 <sup>a</sup>				507	535	599	137.6	59.3	23.7	1.3	45
27 <sup>a</sup>				508	547	658	142.0	61.4	25.1	1.5	51
23 <sup>a</sup>				510	560	708	141.7	59.3	28.6	0.4	60
28 <sup>a</sup>				510	558	706	141.8	58.1	28.9	0.6	60
30 <sup>a</sup>				548	610	709	153.7	62.5	35.0	0.6	45
31 <sup>a</sup>				555	615	708	154.4	61.8	35.5	0.7	60
32 <sup>a</sup>				608	667	710	152.2	58.7	39.2	0.7	60
33 <sup>a</sup>				617	661	709	150.3	56.3	42.2	0.9	84
63 <sup>b</sup>		244	5466	595	592	604	153.4	66.5	25.1	<i>d</i>	60
62 <sup>b</sup>				646	628	659	157.7	66.6	26.7	<i>d</i>	50
61 <sup>b</sup>				690	669	709	158.2	64.9	30.0	<i>d</i>	62
60 <sup>b</sup>				734	747	763	152.6	59.8	32.4	<i>d</i>	54
70 <sup>b</sup>	3.0	232	5200	680	652	727	156.1	47.7	38.6	0.6	53
74 <sup>b</sup>				678	649	<i>c</i>	156.1	46.8	38.7	0.8	55
68 <sup>b</sup>				742	725	805	153.1	42.4	44.8	<i>d</i>	55
73 <sup>b</sup>				746	696	<i>c</i>	149.4	38.3	46.9	<i>d</i>	54
69 <sup>b</sup>				757	729	806	155.0	55.3	30.7	<i>d</i>	57
67 <sup>b</sup>				816	813	878	146.0	35.6	51.3	<i>d</i>	53
72 <sup>b</sup>				817	790	<i>c</i>	146.3	33.5	52.7	<i>d</i>	53
50 <sup>a</sup>	4.7	88	1971	685	716	833	145.8	50.3	49.7	0.055	360
49 <sup>a</sup>	12.8	35	784	710	789	830	171.8	74.9	29.0	0.005	480

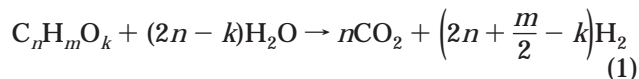
<sup>a</sup> Large reactor (100 g of catalyst). <sup>b</sup> Small reactor (10 g of catalyst). <sup>c</sup> Thermocouple failure. <sup>d</sup> Not detected.

the second (TI 03) at one-third of the length of the bed, and the last one (TI 04) at the bed outlet. Water and organic compounds were fed by two HPLC metering pumps. Water was vaporized and superheated to 300–400 °C by two electric cartridge heaters (PH 01). The organic liquid was vaporized and mixed with steam and nitrogen at the reactor inlet. Nitrogen was used as a carrier and internal standard for the analysis of the gas by GC. The flow rate of nitrogen was controlled by a mass flow controller (MFC 01). The gas produced in the reactor was cooled in a heat exchanger to condense steam, which was collected (water) and measured in a graduated cylinder. The flow rate of the gas was measured by a volumetric meter. The pressure in the system was adjusted by a back pressure regulator (V 02). Temperatures, pressures, and the flow rate of gas were continuously monitored and recorded by a data acquisition system. The composition of the gas was determined by an on-line gas chromatograph equipped with a thermal conductivity detector, an automatic 10 port injection valve, and two packed columns. The first column was a Chromosorb 102 (3.6 m; 1/8-in. o.d.; 60/80 mesh), and the second column was a molecular sieve 13× (2 m; 1/8-in. o.d.; 80/100 mesh).

## Results and Discussion

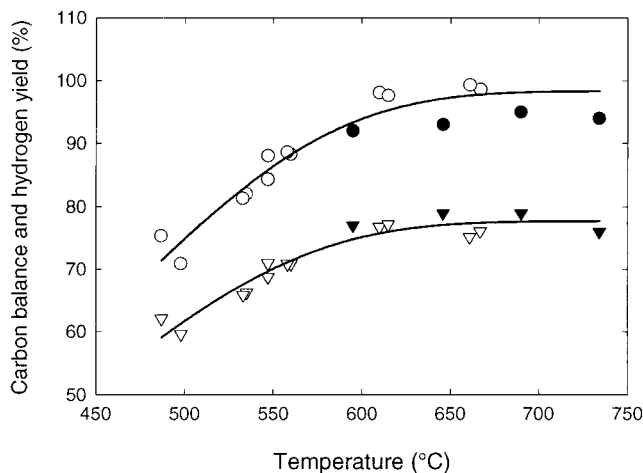
The most important parameters for this process are temperature, the amount of steam used to reform the feed, expressed as a molar steam-to-carbon ratio (S/C), and the amount of feed processed per unit of catalyst, measured as space velocity. The space velocity reported in this paper, M<sub>C1</sub>HSV, represents a number of moles of carbon in the feed per volume of catalyst (L) and time (h), and the methane-equivalent gas hourly space velocity, G<sub>C1</sub>HSV (h<sup>-1</sup>), defines the volume of the feed, stated in terms of methane equivalents, that was processed by

a unit volume of the catalyst in 1 h. The process performance was measured as hydrogen yield calculated as a percentage of the stoichiometric potential, assuming complete conversion of carbon to CO<sub>2</sub> according to eq 1. Thus the potential yield of hydrogen gas from an oxygenated feedstock is  $(2 + m/2n - k/n)$  moles of H<sub>2</sub> per mole of carbon in the feed.



**Acetic Acid.** Steam reforming of acetic acid was studied at temperatures from 500 to 750 °C and S/C of 3 and 6 using the UC G-90C catalyst. Runs at S/C 6 were performed in the larger reactor setup using around 100 g of catalyst at a space velocity (M<sub>C1</sub>HSV) of 67 mol h<sup>-1</sup> L<sup>-1</sup>. Additional runs at S/C 6 and all runs at S/C 3 were performed in the small reactor setup at space velocities of 244 and 232 mol h<sup>-1</sup> L<sup>-1</sup>, respectively. In both cases, duplicate experiments were performed randomly using the same batch of catalyst for all runs. The yield of hydrogen, the amount of carbon converted to gas products (CO<sub>2</sub>, CO, and CH<sub>4</sub>), the volumetric flow rate of gas and the differential pressure in the catalyst bed were monitored for each experiment and related to the temperature profile inside the bed. Table 1 lists the operating conditions for each experiment and the yield of gas products based on 100 mol of carbon entering the reactor. The duration of each run ranged from 45 min to 8 h.

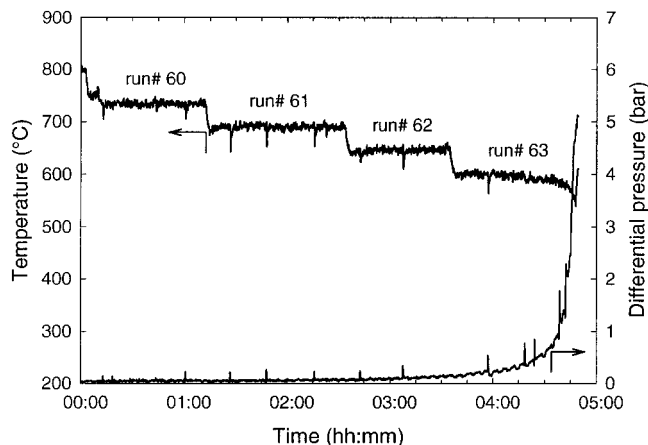
The amount of carbon converted to gas products and the yield of hydrogen based on the stoichiometric potential are plotted in Figure 2 as a function of the temperature of the reforming zone of the catalyst bed (TI 03) for the experiments performed at a S/C ratio of 6. Results from the larger reactor show that the temperature of the reforming section of the bed determines



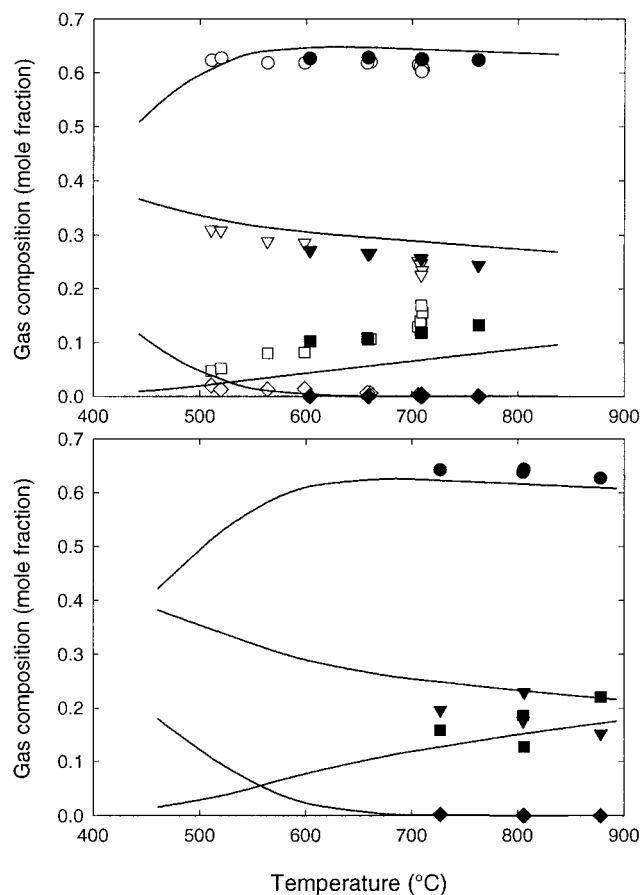
**Figure 2.** Steam reforming of acetic acid at an S/C ratio of 6 using the UC G90-C catalyst. Comparison of the carbon balance and hydrogen yield at different reforming temperatures for the large and small reactors. (Carbon balance: ○ large reactor; ● small reactor. Hydrogen yield: ▽ large reactor; ▼ small reactor. Lines only indicate trends).

the efficiency of the carbon conversion to gas products. At 500 °C (runs 29 and 34) only 73% of the carbon contained in the feed was converted to gas products and a significant amount of char was deposited on the catalyst bed. Raising the reforming temperature improved conversion of carbon to gas products; at temperatures above 600 °C carbon conversion to gases was complete. Agreement between the hydrogen yield and carbon conversion to gases was reasonable for the experiments performed in both reactors, though the conversion of carbon to gases was incomplete in the smaller reactor, even at a high temperature (from 92 to 95%). Results at a S/C of 3 (Table 1) show that the conversion of carbon to gases was only 86% at all the temperatures tested, even when carbon was not substantially deposited on the catalyst bed. This may be due to a low activity of the catalyst, which was not able to reform acetic acid completely at the high space velocity (and low contact time) used for these experiments, specially at a S/C of 3 where the rate of the reforming reactions will be smaller due to the lower partial pressure of steam.

The deposition of carbon caused a continuous rise in the differential pressure through the bed (Figure 3) for runs 60 to 63. The differential pressure grew slowly at 650 °C (run 62), but increased sharply when temperature was lowered to 600 °C (run 63). These results show that the influence of temperature on carbon deposition on the catalyst during steam reforming of acetic acid is similar to the observed for hydrocarbons.<sup>19</sup> During steam reforming of naphtha, carbon is deposited onto the catalyst surface at high rates at a temperature below 650 °C, either as low-density filaments inside the pores or as an encapsulating film, while at temperatures above 700 °C coking is dramatically reduced. The carbon deposited on the catalyst during steam reforming of acetic acid at low temperature (below 600 °C) was gasified by steam, at least partially and, after steam treatment, the differential pressure in the reactor recovered its initial value.



**Figure 3.** Steam reforming of acetic acid at an S/C ratio of 6 using the UC G-90C catalyst. Reforming temperatures and pressure drop in the catalyst bed as a function of run time.

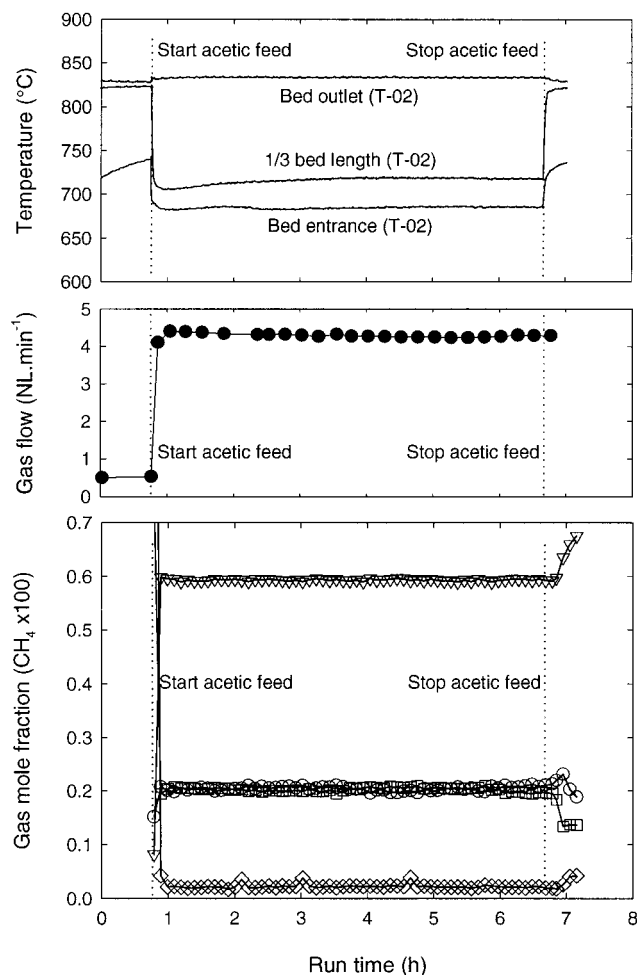


**Figure 4.** Steam reforming of acetic acid using the UC G-90C catalyst. Gas composition at an S/C ratio of 6 (top) and 3 (bottom): H<sub>2</sub>, ● ○; CO<sub>2</sub>, ▼ ▽; CO, ■ □; CH<sub>4</sub>, ◆ ◇. Open symbols: large reactor; solid symbols: small reactor. Lines are equilibrium compositions.

Results from the larger reactor (Table 1) show that below 600 °C hydrogen yield grew as the reforming temperature increased due to the higher conversion of carbon to gas products. Above 650 °C, where carbon conversions are close to 100%, hydrogen yield stabilizes at around 78% of the potential. This behavior is due to the thermodynamics of the process, since equilibrium is displaced toward the formation of CO and water at high temperature. This is clearly seen in Figure 4 where gas composition, expressed as mole fraction, is plotted

(19) Cromarty, B. J. *Carbon Formation and Removal in the Primary Reforming Process*; ICI-Katalco Technical Papers, 1990.





**Figure 5.** Steam reforming of acetic acid using the UC G-90C catalyst at an S/C ratio of 5 (run 50). Temperature profiles (top), gas flow rate (middle) and gas composition (bottom:  $\text{CO}_2$ ,  $\circ$ ;  $\text{H}_2$ ,  $\nabla$ ;  $\text{CO}$ ,  $\square$ ;  $\text{CH}_4$ ,  $\diamond$ ).

as a function of the temperature at the exit of the catalyst bed and compared with the equilibrium composition at a S/C ratio of 6. As the temperature increases, the equilibrium shifts toward the formation of carbon monoxide and the concentration of carbon dioxide and methane decreases. This results in a maximum for the hydrogen mole fraction at around 650 °C, where methane has been completely converted, and a slow decrease in concentration at higher temperatures as more carbon is shifted from carbon dioxide to monoxide. Gas compositions obtained in the small reactor at an S/C of 6 agree strongly with results from the larger unit; even if the conversion of carbon to gas products was not complete, the products generated from the fraction that was reformed tended to the same relative distribution among carbon oxides, methane, and hydrogen.

Two long experiments were performed in the larger reactor to test the activity of the catalyst after a few hours of operation at constant conditions (runs 49 and 50). Monitoring the temperature profile in the bed, the differential pressure, the gas flow-rate, and the gas composition during the experiment showed that stability was good for all parameters, as Figure 5 shows for run 50. Carbon was quantitatively transformed into gas products and deposition of carbon on the catalyst bed was not significant. The conditions used in run 50 may

**Table 2.** Experimental Conditions for Steam Reforming *m*-Cresol Using the UC G-90C Catalyst<sup>a</sup>

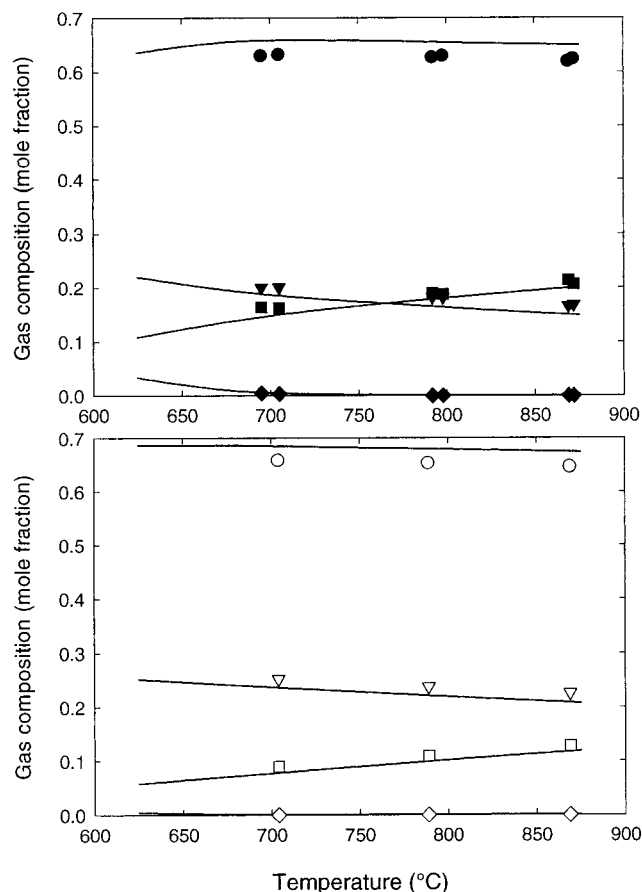
run	S/C ratio (mol/mol)	average temperatures (°C)				carbon balance (% feed)	hydrogen yield (% potential)	run time (min)
		furnace	TI 02	TI 03	TI 04			
87	6.0	875	766	815	869	97	77	52
88		800	701	687	789	98	76	53
90		725	651	638	704	99	74	53
83	3.0	875	811	858	872	98	68	53
91		875	810	854	869	100	67	52
84		800	716	706	798	97	68	52
92		800	722	704	792	99	69	53
86		725	678	662	705	98	70	52
94		725	685	665	695	100	71	53

<sup>a</sup> All experiments were conducted at a space velocity ( $M_{\text{C}_1\text{HSV}}$ ) of  $386 \text{ mol h}^{-1} \text{ L}_{\text{catalyst}}^{-1}$ , equivalent to a gas hourly space velocity ( $G_{\text{C}_1\text{HSV}}$ ) of  $8650 \text{ h}^{-1}$ .

be considered close to the optimal for the production of hydrogen by steam reforming of acetic acid using the UC G-90C catalyst: a steam-to-carbon ratio below 5 and a bed temperature higher than 650 °C. This resulted in a hydrogen yield of 73% of the potential. This yield could increase to 97% if the reforming was followed by a water-gas shift process.

***m*-Cresol.** Table 2 summarizes the experimental conditions for studying the steam reforming of *m*-cresol. All the experiments were performed in the small reactor unit with a single load of UC G-90C catalyst at a methane-equivalent space velocity ( $G_{\text{C}_1\text{HSV}}$ ) of  $8650 \text{ h}^{-1}$ . Two levels of S/C ratio (3 and 6) and three furnace temperatures (875 °C, 800 °C, and 725 °C) were tested. For each experiment, carbon balance, expressed as the percentage of the carbon feed recovered in the gas, and hydrogen yield are also reported in the same table. Cresol was converted completely to gases in all the experiments, even for an S/C ratio as low as 3. Moreover, the differential pressure on the catalyst bed remained constant in all the experiments, which indicates that carbon was not deposited substantially onto the surface of the catalyst. This agrees with the previous observation that at reforming temperatures above 650 °C encapsulating carbon was not deposited. At an S/C ratio of 6, hydrogen yields were from 74 to 77% of the stoichiometric, while an S/C ratio of 3 produced yields from 67 to 71%, which are close to the yields calculated from equilibrium for this system. Figure 6 plots the composition of gas against the temperature of the catalyst at the exit of the bed. Gas composition was close to equilibrium in the whole range of temperatures at both steam-to-carbon ratios.

**Benzyl Ether.** Steam reforming of dibenzyl ether was carried out in the same conditions as the reforming of *m*-cresol except for the methane-equivalent space velocity ( $G_{\text{C}_1\text{HSV}}$ ), which was  $11800 \text{ h}^{-1}$ . All the experiments were performed in the small reactor unit with a single load of 10 g of UC G-90C catalyst. Table 3 summarizes the operating conditions, the carbon balance and the yield of hydrogen for each experiment. As for *m*-cresol, conversion was complete and all the carbon converted to gas products, mainly carbon oxides; carbon recovery as gases was 98 to 105%. Hydrogen yields were approximately 83% at an S/C ratio of 6, and 67% at an S/C of 3. Figure 7 plots the gas composition against the temperature at the exit of the catalyst bed at both S/C ratios. Gas composition was close to equilibrium at an



**Figure 6.** Steam reforming of *m*-cresol using the UC G-90C catalyst. Gas composition at an S/C ratio of 3 (top, solid symbols) and 6 (bottom, open symbols): H<sub>2</sub>, ● ○; CO<sub>2</sub>, ▼ ▽; CO, ■ □; CH<sub>4</sub>, ◆ ◇. Lines are equilibrium compositions.

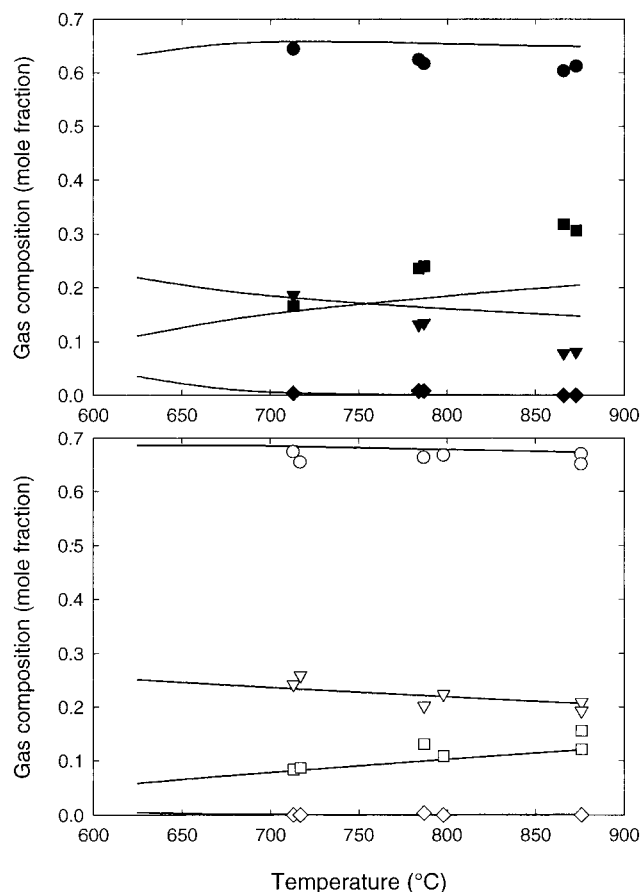
**Table 3. Experimental Conditions for Steam Reforming Dibenzyl Ether Using the UC G-90C Catalyst<sup>a</sup>**

run	S/C ratio (mol/mol)	average temperatures (°C)				carbon balance (% feed)	hydrogen yield (% potential)	run time (min)
		furnace	TI 02	TI 03	TI 04			
95	6.0	875	695	777	876	102	85	52
102		875	727	782	876	101	81	51
96		800	673	684	787	99	84	53
103		800	679	669	798	101	84	52
97		725	621	620	713	98	83	52
104	3.0	725	635	620	717	105	83	52
98		875	770	765	873	100	66	57
105		875	778	765	866	104	65	52
100		800	714	710	784	100	69	53
107		800	720	703	787	104	70	52
109		725	675	652	713	102	67	52

<sup>a</sup>All experiments were conducted at a space velocity ( $M_{C1}HSV$ ) of  $526 \text{ mol h}^{-1} \text{ L}^{-1}$  catalyst, equivalent to a gas hourly space velocity ( $G_{C1}HSV$ ) of  $11790 \text{ h}^{-1}$ .

S/C of 6, but shifted toward a mixture with less hydrogen and carbon dioxide and more carbon monoxide than the equilibrium composition at an S/C of 3.

**Sugars.** The steam reforming of sugars was studied for xylose, glucose, and sucrose in the larger reactor using the ICI 46/1 catalyst. Since sugars are nonvolatile, this unit was equipped with a nozzle that allowed the sugar solution to be sprayed directly on top of the catalyst bed, thus minimizing thermal decomposition and carbonization in the freeboard of the reactor.<sup>15</sup> Experimental conditions are shown in Table 4, where carbon balance and hydrogen yield are also reported.



**Figure 7.** Steam reforming of dibenzyl ether using the UC G-90C catalyst. Gas composition at an S/C ratio of 3 (top, solid symbols) and 6 (bottom, open symbols): H<sub>2</sub>, ● ○; CO<sub>2</sub>, ▼ ▽; CO, ■ □; CH<sub>4</sub>, ◆ ◇. Lines are equilibrium compositions.

Each catalyst load was used for several consecutive runs. In all cases, the catalyst was regenerated before each run for 4 h with high steam flows (12–15 g/min) to gasify possible carbon deposits from previous runs. The catalyst was then reduced for 3 h following an procedure identical to that for the fresh catalyst.

Results for all sugars were similar. Steam-to-carbon ratio appears to play a key role in the conversion of the saccharides to gas products. At high S/C ratios xylose was completely converted into gaseous products. The results obtained for reforming glucose also show that very high S/C ratios were necessary to ensure a high carbon-to-gas conversion, but even at an S/C ratio as high as 17, the carbon conversion to gases was 92% and it was only 78% at an S/C ratio of 7. In these conditions, carbon mostly deposited in the freeboard of the reactor and not on the catalyst. The accumulation of the carbonaceous deposits above the catalyst bed caused a rapid rise in the differential pressure in the system and did not allow for longer experiments (2 h maximum). Reforming sucrose was even more difficult because only 88% of the carbon was converted to gas products at an S/C ratio of 34. The carbonaceous deposits are formed by thermal decomposition of the saccharides. When injected through the nozzle at high temperature, water is vaporized and mixed with the flow of nitrogen carrier, but the sugar molecules quickly decompose through pyrolysis. This leads to the formation of char particles and gases. It is therefore unlikely that variations in the S/C ratio may affect the chemistry of char formation by

**Table 4. Steam Reforming of Mono- and Disaccharides Using the ICI 46/1 Catalyst; Experimental Conditions, Carbon Balance, and Hydrogen Yields**

sugar	S/C ratio (mol/mol)	$M_{C_1HSV}$ (mol h <sup>-1</sup> L <sup>-1</sup> catalyst)	$G_{C_1HSV}$ (h <sup>-1</sup> )	average temperatures (°C)			carbon balance (% feed)	H <sub>2</sub> yield (% potential) H <sub>2</sub>	run time (min)
				TI 02	TI 03	TI 04			
glucose	47	32	717	590	735	843	98	82	65
	32	32	717	582	745	860	102	89	65
	17	28	627	630	797	897	92	80	66
	7	24	538	610	782	869	78	67	65
xylose	37	36	806	569	679	787	100	84	55
	27	33	739	535	685	806	103	89	60
	14	33	739	514	751	860	105	90	55
sucrose	34	38	851	562	723	835	88	72	45

gas-phase pyrolysis, although greater partial pressures of steam may favor gasification of the char. The most likely effect of adding large flows of steam is a reduction in residence time of the sugar molecules in the freeboard and, consequently, in the extent of the pyrolysis process. Research is still being developed to verify this hypothesis; the steam reforming of oligosaccharides is currently being studied in a fluidized bed catalytic reactor in order to decrease sugar carbonization and improve contact between the feed and the catalyst.

### Conclusions

We converted several model compounds of biomass fast-pyrolysis oil to hydrogen through steam reforming with commercial nickel-based catalysts. The efficiency of the process depends on the nature of the model compound. Acetic acid is almost completely converted to hydrogen and carbon oxides provided that the catalyst temperature is above 650 °C. Carbonaceous deposits are formed on the catalyst particles when temperatures are

lower than this. Oxygenated aromatics (*m*-cresol and dibenzyl ether) can also be completely converted to gases if the catalyst temperature is above 650 °C, even at a steam-to-carbon ratio of 3 and a space velocity ( $G_{C_1HSV}$ ) above 8500 h<sup>-1</sup>. Sugars (glucose, xylose, and sucrose) were difficult to process, mainly because they are readily pyrolyzed upon injection and form char in the reactor freeboard. The reforming of sugars apparently requires very high steam-to-carbon ratios, but this may partly be due to the reduction in the residence time of the sugar feed in the high-temperature freeboard above the catalyst bed.

**Acknowledgment.** The authors are indebted to the U.S. Department of Energy Hydrogen Program (Contract DE AC 36-83CH10093), and to the Commission for Cultural, Educational and Scientific Exchange between the U.S.A. and Spain (Project 5.2/309) for funding. M. Marquevich is grateful to the Spanish Government for financial support (Grant AP96 22313698).

EF990034W