Hydrogen production by steam reforming of bio-oil

J. Román Galdamez[1], M. Carmen Ramos[2], Ana I. Navascues[2], Lucía García[2] and Rafael Bilbao[2].
(1) The Pennsylvania State University, University Park, PA 16802. (2) University of Zaragoza, María de Luna 3, Zaragoza, 50018, Spain

Abstract

Hydrogen production by steam reforming of model compounds of pyrolysis liquids was investigated. Acetic acid and Hydroxyacetone (acetol) were steam-reformed in a fluidized bed reactor using a coprecipitated nickel alumina catalyst at 650 °C. These model compounds were fed as aqueous solution with a concentration of 23 wt % which corresponded to a steam to carbon molar ratio of 5.58 and 4.6 for acetic acid and acetol respectively. The efficiency of the process depends of the nature of the model compounds used. Acetic acid was converted completely to gases even for the non-catalytic experiments. For the two model compounds, the Ni-Al catalyst increases the total gas yield and shifts the gas composition towards the equilibrium values. Then, H_2 and CO_2 yields increase while CH_4 and C_2 yields decrease with the use of the catalyst. Acetol had a carbon conversion to gases of 90 %.

Introduction

Hydrogen is an important raw material in the chemical industry. Most hydrogen is currently produced by catalytic steam reforming of natural gas and oil-derived naphtha, or by partial oxidation (POX) of heavy oils. Consequently, hydrogen production based on fossil fuels is a net contributor to carbon dioxide emissions and the greenhouse effect. Biomass has been proposed as an alternative, because this renewable resource does not contribute to a net increase in atmospheric CO_2.

Catalytic steam reforming of pyrolysis oils (bio-oil) has been explored recently. These liquids can be either converted to hydrogen via catalytic steam reforming, or be used as raw material for the recovery of highly added-value chemicals to improve the economy of the process. In that case, the by-products of the extraction process could be used for hydrogen production. For example, by simply adding water, the bio-oil separates into a water-rich phase that contains mostly carbohydrate-derived compounds and a hydrophobic phase that is composed mainly of lignin-derived oligomers.

Bio-oil is a complex mixture of a large number of compounds, including aldehydes, alcohols, ketones, and acids, as well as more-complex carbohydrate- and lignin- derived oligomeric materials emulsified with water. Several studies[1-2] have analyzed the composition of bio-oil obtained from several woods and by different technologies. The results of chemical characterization were not very consistent. According to the analysis corresponding to the IEA-EU round robin[2], performed in the year 2000, a typical composition of the bio-oil in general could be as follows: 25-50 wt% is pyrolytic lignin, 3-25 wt% are acids, and 3-25 wt % falls into the group of aldehydes, ketones and alcohols. The wide range of composition is due to the different methods used by the laboratories which conducted the analysis. Regardless of the weight percent, two of the major components in bio-oil are acetic acid and acetol. Both compounds are water soluble so they are expected to be present in the water-rich phase of the bio-oil. Therefore, they are chosen as model compounds to study the catalytic steam reforming of the aqueous fraction of bio-oil. The goal of this study is to find the best operational condition to maximize hydrogen production.

Experimental section

Chemicals. Two model compounds, representative of the bio-oil aqueous fraction, were selected for this study. Acetic acid, supplied by PANREAC (99.5% purity), was selected as the model for acids. Acetol, supplied by Sigma-Aldrich (99.9% purity) was used as representative of the ketone and alcohol groups.

Catalyst. A coprecipitated Ni/Al catalysts with a Ni:Al ratio of 1:2 was used in this work. The catalyst was prepared in our laboratory following a preparation method similar to that described by Al-Ubaid and Wolf[3]. In all cases, the calcined catalyst was reduced in the reactor at a temperature of 650ºC for one hour, using hydrogen that has been diluted in nitrogen (H_2:N_2 = 1:10). The hydrogen flow rate was 200 cm^3(STP)/min.

The calcined catalyst was characterized by various techniques such as X-ray diffraction (XRD), nitrogen adsorption, temperature-programmed reduction (TPR), and optical emission spectrometry by inductively coupled plasma (ICP). From those analyses the catalyst was found to have a similar composition than the theoretical formulation; NiO and $NiAl_2O_4$ crystalline phases were identified by XRD and the surface area was 150 m^2/g.

Experimental system. The experimental system was a bench-scale installation using a technology that was very similar to the Waterloo Fast Pyrolysis Process[4] (WFPP). The reactor with a sectional area of 13.14 cm^2 was made of stainless steel and the distributor plate was composed of Inconel. This reactor has been designed for the purpose of processing bio-oil or its fractions. These liquids are fed to the reactor through a lateral arm, provided with a cooling system to prevent the liquids from thermal decomposition before they reach the reaction bed. A more detailed description of the installation used can be found elsewhere[5].

The experimental system was operated at atmospheric pressure. All the experiments were performed using a concentration of the model compounds, (either acetic acid or acetol), in the aqueous solution of 23 wt. %. This solution was delivered by a high-performance liquid chromatography metering pump (Agilent, series 1100). Both catalytic and non-catalytic steam reforming experiments presented in this study were conducted at 650 ºC. The reaction bed was composed of sand (200 g) and catalyst, both previously sieved to 160-320 μm. The catalyst weight (W) ranged from 0 g in the non-catalytic experiments up to 1.29 g. The total nitrogen flow rate into the reactor was 2100 cm^3 (STP)/min. This flow was used to provide the appropriate dispersion of the liquid solution at the feeding point. The total flow rate in the reactor, the sum of the flux of nitrogen and steam from the aqueous solution, is enough to fluidize the reaction bed and no elutriation problem was observed during the experiments.

The composition of the clean and dry product gas was analyzed by two techniques. The concentration of CO and CO_2 was monitored continuously by an infrared (IR) analyzer connected on line. Then the concentrations of H_2, N_2, CO, CO_2, CH_4 and C_2, in the product gas were obtained with an Agilent P200 Micro GC gas chromatograph equipped with thermal conductivity detectors.

Results and Discussion

Among all the parameters that are involved in any reforming process, temperature, the molar ratio between the steam and carbon fed, and the space velocity are very important if any comparisons have to be made. Therefore, the experiments conducted must have similar values for those parameters. The reforming of both model compounds was studied at 650 ºC. The selection of this temperature was based in previous studies[5] for the non-catalytic steam reforming of acetic acid. It was found that all the acetic acid was transformed completely to gases. A maximum in the experimental hydrogen yield was given at that temperature, but equilibrium gas yields for the process are not obtained. It was thought that at that temperature, the use of catalysts would shift the experimental gas yields towards values corresponding to thermodynamic equilibrium. The steam to carbon molar ratio (S/C) was fixed for each model compound. As a composition of 23 wt % was used to simulate the organic compounds content in the aqueous fraction of the bio-oil[6], the experiments were conducted with a S/C molar ratio of 5.58 for the acetic acid, and 4.6 for acetol. Although the S/C ratios for both compounds are not the same, the steam used in any experiment is quite more than the stoichiometric needed and, therefore, no big differences were expected. The space velocity reported here, $G_{C1}HSV$, was defined as the volume of C_1-equivalent species in the feed at standard temperature and pressure (STP) per unit volume of catalyst (including the void fraction) per hour. Values in the range of 13000-34000 for $G_{C1}HSV$ were used in this study. These $G_{C1}HSV$ values are higher than those given in other works in the literature; thus, more-severe conditions have been imposed.

Tables 1 and 2 present the overall results obtained in experiments performed with different weights of catalyst in the reaction bed for both model compounds. These tables show the values of some experimental variables such as temperature, S/C molar ratio, space velocity, liquid feeding rate and total amount of organic compound that has been fed in the system. Also indicated is the percentage of carbon contained in the organic compound that was converted to gases (CO, CO_2, CH_4, and C_2 gases), the yields of total gas (expressed as mass fractions of the sum of organic compound and water and organic compound alone), the yields of different gases (as mass fractions of organic compound), and the gas composition (expressed as molar percentages, N_2 and water free). These tables also contain the calculated gas yields corresponding to the thermodynamic equilibrium for steam reforming of model compounds. The values of the equilibrium gas yields were calculated with a HYSYS program, using the flow rates of water, organic compound (acetic acid or acetol), and nitrogen introduced in the reaction.

Acetic acid. Steam reforming of acetic acid was studied at 650 ºC and using a S/C molar ratio of 5.58 using a coprecipitated Ni-Al catalyst. Experiments of non-catalytic steam reforming with the same operation conditions were conducted as well. A comparison between those experiments enables the study of the specific role of the catalyst in the process.

For the non-catalytic experiment, run 1, the total gas/acetic acid yield is approximately one. As that experiment had a conversion of carbon to gases close to 100 %, it can be deduced that all gases generated come from the reforming of the acetic acid. Nevertheless practically no incorporation of water in the product gases was observed. A comparison, (either in terms of yields or gas composition), between the experimental and the equilibrium values reveals that equilibrium is not achieved for that run. The experimentally obtained H_2, CO_2, and total gas yields are smaller than those expected at equilibrium. Much higher yields for CH_4 and C_2 were observed experimentally if compared with the equilibrium results.

Table 1. Results of acetic acid steam reforming.

run	1	2	3	4	equilibrium
temperature (ºC)	650	650	650	650	650
catalyst	no	Ni-Al	Ni-Al	Ni-Al	
S/C (mol/mol)	5.58	5.58	5.58	5.58	5.58
catalyst weight (g)	0	0.50	0.8	1.29	
W/m_a (g catalyst min/g acetic acid)	0	1.23	2.02	3.19	
space velocity, $G_{C1}HSV$ (h^{-1})	∞	33873	20626	13061	
liquid feeding rate (g/min)	1.84	1.79	1.73	1.77	
time (min)	55.4	55.6	55.5	59.1	
total acetic acid fed (g)	23.4	22.9	22.1	24	
carbon conversion (%)	102.60	114.01	109.87	108.59	100
yields (g/g)					
total gas/(acetic acid + water)	0.222	0.298	0.312	0.317	0.345
total gas/acetic acid	0.964	1.295	1.357	1.377	1.498
gas yields (g/g acetic acid)					
H_2	0.029	0.084	0.120	0.136	0.122
CO	0.384	0.349	0.299	0.352	0.154
CO_2	0.360	0.716	0.854	0.805	1.222
CH_4	0.163	0.138	0.100	0.083	0
C_2	0.028	0.009	0.004	0.002	0
gas composition (% mol, N_2- and H_2O-free)					
H_2	30.31	52.71	62.19	65.31	64.71
CO	28.65	15.64	11.07	12.07	5.83
CO_2	17.37	20.42	20.12	17.57	29.46
CH_4	21.57	10.82	6.48	4.98	0
C_2	2.11	0.40	0.15	0.07	0

Steam seems to have a small effect on the non-catalytic steam reforming of acetic acid[5]. When the catalyst was introduced in the reaction, a considerable increase in the total gas yield was observed. All catalytic steam reforming runs have a total gas yield greater than 1. A comparison of the results of run 1 and runs 2, 3, and 4 shows that the catalyst not only increase the total gas yield, incorporating water to the final product gas, but also it modifies the composition of the product gas. A significant increase in the H_2 and CO_2 yields occurs whereas the CO, CH_4 and C_2 yields decrease when the catalyst is present in the reaction.

The experimental catalytic H_2 yield increases significantly, with respect to the non-catalytic results, because of the steam reforming of CH_4 (reaction 1) and C_2 (reaction 2) and water gas shift (reaction 3) reactions.

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \tag{1}$$

$$C_2H_x + 2\,H_2O \rightarrow 2CO + (\frac{x}{2}+2)\,H_2 \tag{2}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{3}$$

The experimental CO_2 yield increases, because of its formation by the water gas shift reaction, whereas the CH_4 and C_2 yields decrease, because of their decomposition by steam reforming reactions. These tendencies are observed in the experimental results for each catalyst weight used. The experimental CO yield is determined by the steam reforming of CH_4 and C_2 (where CO is formed) and the water gas shift reaction (where CO is consumed). Since this element participates in several reactions of production and consumption, no clear tendency for it was found.

Acetol. Table 2 summarizes the experimental conditions for studying the steam reforming of acetol. All the experiments were performed at 650 °C and using a S/C molar ratio of 4.6. Catalytic and non-catalytic experiments were conducted maintaining the same liquid composition, 23 wt %, and feeding rate.

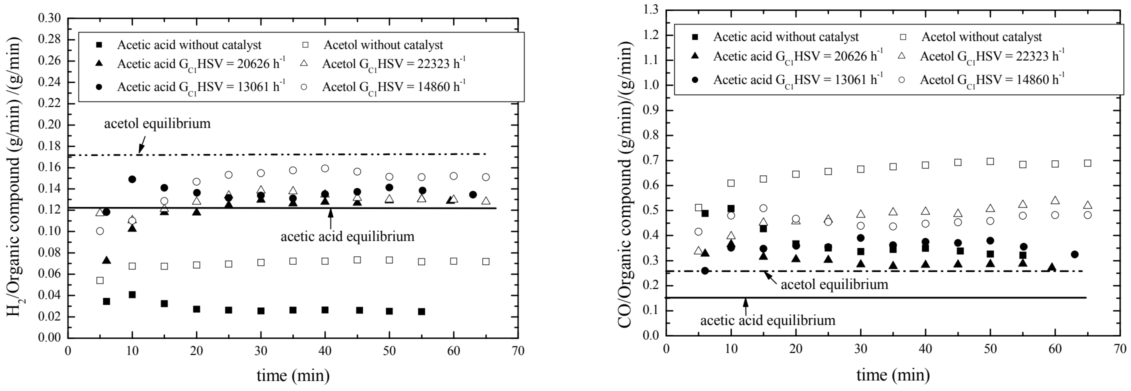
Acetol was not converted completely to gases, having approximately a 90 % of the carbon fed converted into gas. Total gas yield for all experiments are smaller than those obtained for the acetic case. Since high yield for total gases are still obtained, despite of the lower carbon conversion, water may participate, at some degree, in the steam reforming of acetol.

Table 2. Results of acetol steam reforming.

Run	5	6	7	equilibrium
temperature (ºC)	650	650	650	650
catalyst	no	Ni-Al	Ni-Al	
S/C (mol/mol)	4.6	4.6	4.6	4.6
catalyst weight (g)	0	0.8	1.2	
W/m_a (g catalyst min/g acetol)	0	2.27	3.41	
space velocity, $G_{C1}HSV$ (h^{-1})	∞	22323	14860	
liquid feeding rate (g/min)	1.53	1.53	1.53	
time (min)	65	65	65	
total acetol fed (g)	22.9	22.9	22.9	
carbon conversion (%)	87.08	87.06	87.22	100
yields (g/g)				
total gas/(acetol + water)	0.220	0.277	0.292	0.416
total gas/acetol	0.956	1.205	1.268	1.810
gas yields (g/g acetol)				
H_2	0.065	0.119	0.134	0.172
CO	0.609	0.440	0.427	0.255
CO_2	0.112	0.528	0.609	1.382
CH_4	0.127	0.095	0.082	0.001
C_2	0.043	0.023	0.016	0
gas composition (% mol, N_2- and H_2O-free)				
H_2	49.04	63.32	65.82	67.94
CO	32.82	16.72	14.98	7.19
CO_2	3.84	12.77	13.60	24.81
CH_4	11.98	6.32	5.04	0.05
C_2	2.32	0.87	0.56	0

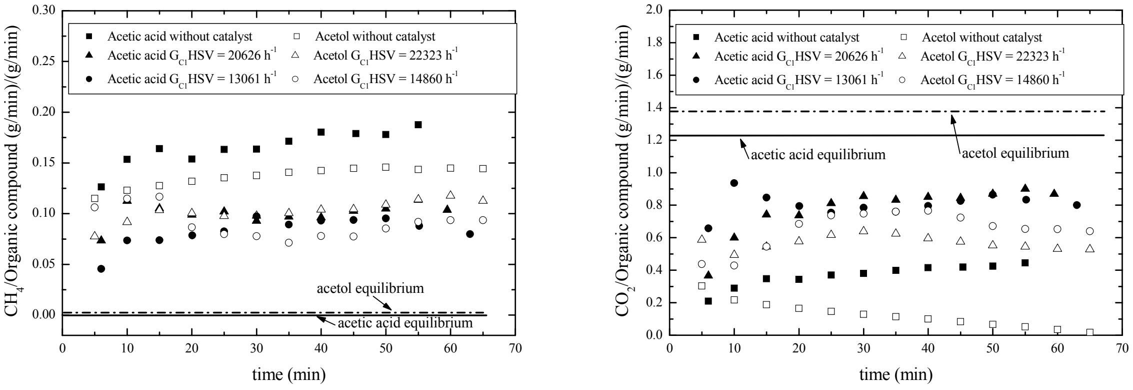
The effects of the catalyst in the steam reforming of acetol are basically two: i) increasing the total yield of gases and, ii) modifying the gas product composition. The expected trends for the yields of the respective gases were observed. An increase on H_2 yield was observed accompanied with a decrease in the yields for CH_4 and C_2 due to reactions 1 and 2. CO_2 yield increases due to the water gas shift reaction (reaction 3).

Comparison of the results obtained with acetic acid and acetol. A comparison between the steam reforming of these two model compounds can be done by directly comparison of the results shown in Tables 1 and 2 or Figures 1.a, 1.b, 2.a, and 2.b. All these figures plot the gas yield evolution with time for the runs shows in Tables 1 and 2. In these figures the thermodynamic equilibrium values for each gas are indicated as well.



a) b)

Figure 1. H_2 and CO yield for the two compounds and different catalyst weight.



a) b)

Figure 2. CH_4 and CO_2 yield for the two compounds and different catalyst weight.

The evolution of gas yields, over time for the different experiments, does not show catalyst deactivation, because product gases of the catalytic experiment such as H_2 and CO_2 do not decrease over time. From Figure 1.a it can be observed that a higher H_2 yield would be obtained for acetol rather than acetic acid. This result is in accordance with the maximum hydrogen production for acetic acid and acetol, given by reactions (4) and (5) respectively.

$$CH_3COOH + 2\ H_2O \rightarrow 2\ CO_2 + 4\ H_2 \tag{4}$$

$$CH_3COCH_2OH + 4\ H_2O \rightarrow 3\ CO_2 + 7\ H_2 \tag{5}$$

Figures 1.a and 1.b show that the yields for H_2 and CO, in the non-catalytic experiments, are higher for acetol than for acetic acid, whereas in Figure 2.a the CH_4 yield is bigger for acetic acid than for acetol. This is consistent with the idea that, in absence of catalyst, acetic acid will follow the decarboxilation reaction[5] (reaction 6) whereas acetol could decompose in other more reactive intermediate molecules that reacts quickly with water increasing the amount of H_2 and CO in the final product.

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{6}$$

The increase of catalyst weight, for any compounds, has the same effect. As the catalyst weight is increased the yields of the different gases are closer to the equilibrium values ones.

Figure 3 shows the total gas yield over time for acetic acid and acetol. Both catalytic and non-catalytic experiments were conducted. Again, the effect of catalyst in the reaction is clear, increasing the total gas yield towards the equilibrium values. As it happens with individuals gases, the total gas yield at equilibrium is higher for acetol, the less oxygenated compound, since oxygen does not participate in the final product. Non-catalytic experiments show yields close to unity. For acetic acid, the conversion was complete and all the carbon converted to gas product. For acetol, which has a conversion ~90%, water must participate into the reaction to give a total gas yield, expressed as g gas/g acetol, close to 1. When catalyst is used, the yield to total gas, for both model compounds, increases. Figure 3 also shows that whereas for acetic acid, the total gas yield is close to the equilibrium values when catalyst is used, for acetol the total gas yield is considerable less than its maximum. That must be due to the incomplete conversion of acetol to gases during the experiments, so not all carbon from the feed can be transformed into valuable gases.

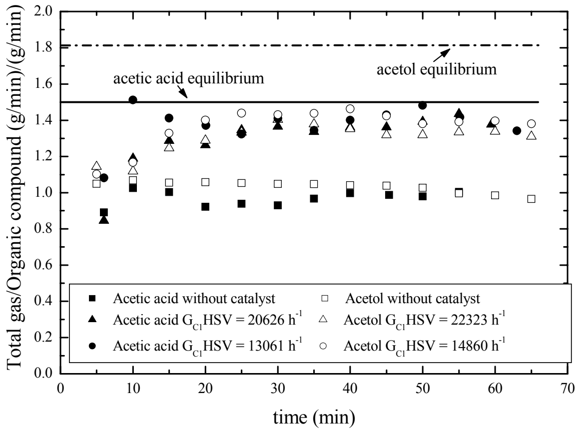


Figure 3. Total gas yields for the two model compounds studied.

Conclusions.

Steam reforming of bio-oil could prove to be a promising technology for obtaining hydrogen. To improve the economy of the process, bio-oil can be used to extract high added-value chemicals such as phenols. The by-products of this process, a water-rich phase with high content in carbonaceous compounds, could be subsequently steam reformed for hydrogen production. Two of the major compounds in this water-rich phase are acetic acid and acetol. In this study, non-catalytic and catalytic steam reforming studies of acetic acid and acetol have been conducted at 650 °C. A coprecipitated Ni-Al catalyst has been used to study the influence of catalyst in the steam reforming of the model compounds.

The efficiency of the process depends on the nature of the model compound. At 650 °C total carbon conversion to gases is achieved in the non-catalytic steam reforming of acetic acid, but not for acetol. At this temperature equilibrium gas yields for the process are not obtained.

The presence of the catalyst in the steam reforming of both compounds increases the total gas, H_2, and CO_2 yields significantly, whereas CH_4 and C_2 yields decrease. Experimentally, it has been obtained a product gas with a H_2 content of 65 % (N_2- and H_2O-free) for both compounds.

References.

(1) Piskorz, J.; Scott, D. S.; Radlein, D. *ACS Symp. Ser*. **1988**, 376, 167-178

(2) Oasmaa, A.; Meier, D. *Fast Pyrolysis of Biomass: A Handbook, Volume 2*; CPL Press: Newbury, U.K., **2002**; pp 41-58.

(3) Al-Ubaid, A.; Wolf, E. E. *Appl. Catal*. **1988**, 40, 73-85.

(4) Scott, D. S.; Piskorz, *J. Can. J. Chem. Eng.* **1982**, 60, 666-674.

(5) Galdamez, J.R.; García, L; Bilbao, R. *Energy & Fuels*, **2005**, 19, 1133-1142.

(6) Czernik, S.; French, R.; Feik, C.; Chornet, E. In *Biomass A Growth Opportunity in Green Energy and Value-Added Products*; Overend, R.P., Chornet, E., Eds.; Proceedings of the 4th Biomass Conference of the Americas, Oakland, CA, USA, August 29-September 2, 1999; Pergamon Press: Oxford, U.K., **1999**; Vol. 1, pp 827-832.