

Hydrogen production by catalytic steam reforming of acetic acid, a model compound of biomass pyrolysis liquids

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Abstract

An environmentally friendly and cost-competitive way of producing hydrogen is the catalytic steam reforming of biomass pyrolysis liquids, known as bio-oil, which can be separated into two fractions: ligninic and aqueous. Acetic acid has been identified as one of the major organic acids present in the latter, and catalytic steam reforming has been studied for this model compound. Three different Ni coprecipitated catalysts have been prepared with varying nickel content (23, 28 and 33% expressed as a Ni/(Ni + Al) relative at.% of nickel). Several parameters have been analysed using a microscale fixed-bed facility: the effect of the catalyst reduction time, the reaction temperature, the catalyst weight/acetic acid flow rate (W/m_{HAc}) ratio, and the effect of the nickel content. The catalyst with 33% Ni content at 650 °C showed no significant enhancement of the hydrogen yield after 2 h of reduction compared to 1 h under the same experimental conditions. Its performance was poorer when reduced for just 0.5 h. For W/m_{HAc} ratios greater than 2.29 g catalyst min/g acetic acid (650 °C, 33% Ni content) no improvement was observed, whereas for values lower than 2.18 g catalyst min/g acetic acid a decrease in product gas yields occurred rapidly. The temperatures studied were 550, 650 and 750 °C. No decrease in product gas yields was observed at 750 °C under the established experimental conditions. Below this temperature, the aforementioned decrease became more important with decreasing temperatures. The catalyst with 28% Ni content performed better than the other two.

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1. Introduction

There is increasing interest in the use of hydrogen as an energy carrier for providing a possible substitute for fossil fuels in small scale energy generation systems and in the transportation sector, either directly combusted in internal combustion engines or through high-efficiency systems such as fuel cells.

One of the limitations of current hydrogen generation is that it is based on natural gas and naphtha catalytic steam reforming, or coal gasification, as its main sources. These well established industrial processes release almost as much carbon dioxide into the atmosphere as the direct combustion of the original fossil fuels, with a net production of greenhouse gas. One of the

reasons for seeking alternative hydrogen sources is therefore environmental.

An additional reason is economic. The increasing demand for fossil fuels resulting from new consumers coming onto to the global market has raised prices dramatically during the last few years. This effect will continue or even accelerate in the near future with the reduction and eventual exhaustion of fossil fuel stocks.

Various liquids have been studied from the point of view of obtaining hydrogen by catalytic steam reforming, such as glycerin [1] obtained as a subproduct of biodiesel production, ethanol [2,3], or vegetable oils [4]. The added value of trap grease has also been investigated [5].

Hydrogen can also be produced by thermochemical processes of biomass: pyrolysis and gasification [6]. Of the various pyrolysis processes, the catalytic steam reforming of bio-oil or its fractions is of particular interest [7–9]. This is a two step process: first, a fast pyrolysis of biomass to produce an oil or bio-oil at levels of 75% per biomass weight [10,11]; and a

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second step where the bio-oil or a fraction of it is transformed into a gas rich in hydrogen by steam catalytic reforming followed, if necessary, by a water–gas shift conversion step.

Bio-oil is a complex mixture, whose major components are oxygenated compounds such as alcohols, acids, aldehydes and ketones, as well as more complex carbohydrates and lignin derived materials [12,13]. This bio-oil can be reformed as a whole or separated by water extraction into two fractions: an organic fraction with lignin derived materials that can be used for the production of more valuable products [14,15], and a water soluble fraction that can be catalytically steam reformed.

Due to the complexity of bio-oil, some researchers have used model compounds. Of these, acetic acid has been widely employed [16–24]. In these works noble metal catalysts have been used [18,19,21,24], and a bifunctional mechanism has also been proposed for steam reforming of acetic acid on Pt/ZrO₂ [18,24]. Nickel based catalysts, both commercial [16,17] and research [20,23], have also been employed. Basagiannis and Verykios [23] have found that carbon formation is affected by reaction temperature, steam to carbon molar ratio and catalyst composition.

In the work of Galdámez et al. [20] coprecipitated nickel catalysts were investigated, some of them promoted with lanthanum. The results indicate that the highest hydrogen yield was produced with the Ni–Al catalyst. This catalyst had a nickel content (Ni/(Ni + Al)), relative at.% of Ni equal to 33.

The influence of the nickel content has been previously investigated. Thus, coprecipitated Ni–Al catalysts with three different nickel contents (15, 33 and 53 relative at.% of nickel) have been tested in steam reforming of methane by Al-Ubaid and Wolf [25]. Sahli et al. [26] have recently studied Ni–Al catalysts prepared by the sol gel method with different nickel contents. They concluded that it would be of interest to study nickel contents in the catalyst smaller than 33 relative at.% of nickel.

However, these works have not studied the influence of the nickel content in nickel coprecipitated catalysts on the catalytic steam reforming of acetic acid, which is the aim of this paper.

The present work constitutes a part of a more detailed study with the aim of developing a nickel coprecipitated catalyst for the catalytic steam reforming of the aqueous fraction of biomass pyrolysis liquids. Our intention is first to select the

most suitable nickel content and secondly to incorporate modifiers into the catalyst. This work constitutes the initial part of the study.

In the present work, acetic acid is steam reformed in a fixed bed using an experimental coprecipitated Ni/Al catalyst of different Ni contents (23, 28 and 33 relative at.% of nickel) at relatively low temperatures. We analyse the behaviour of the catalyst over time and the effect on the hydrogen yield. The reduction time, catalyst weight/acetic acid flow rate (W/m_{HAc}) ratio and reaction temperatures are also studied.

2. Experimental

2.1. Experimental system

The experimental system is based on a micro-reactor test facility consisting of a fixed bed placed inside a tubular quartz reactor. The inner diameter of the quartz reactor is 9 mm, and the height of the bed is about 25 mm. The bed is a mixture of sand, used as an inert filler, and a Ni coprecipitated catalyst. The particle sizes of both catalyst and sand are between 200 and 320 μm . A schematic flow diagram of the experimental system is shown in Fig. 1. Two mass flow controllers (MFC) (Bronkhorst HI-TEC EL-FLOW[®] F201C) constitute the gas inlet, one for nitrogen and the other for hydrogen, needed in the reduction process. The liquid is fed in by means of a high-performance liquid chromatography (HPLC) metering pump (GILSON 307). It flows through 316 stainless steel tubing of 1/16 in. o.d. that is pre-heated at 150 °C inside an insulated cabin, called a hot box, thus allowing evaporation of the feed prior to its mixture with the nitrogen coming from the MFC01. As a result, the exiting current flowing through 316 stainless steel tubing of 1/8 in. o.d. constitutes a gaseous mixture fed directly into the upper part of the reactor, placed inside an electric furnace that is also sheltered inside the aforementioned hot box. The temperature is controlled by two K-type thermocouples, one placed inside the reactor directly measuring the temperature of the bed, and the other measuring the temperature inside the cabin.

The exiting flow is forced into a condenser cooled by means of the Peltier effect (depicted as Peltier in Fig. 1). Here, condensable substances are collected and the exiting gas flow is

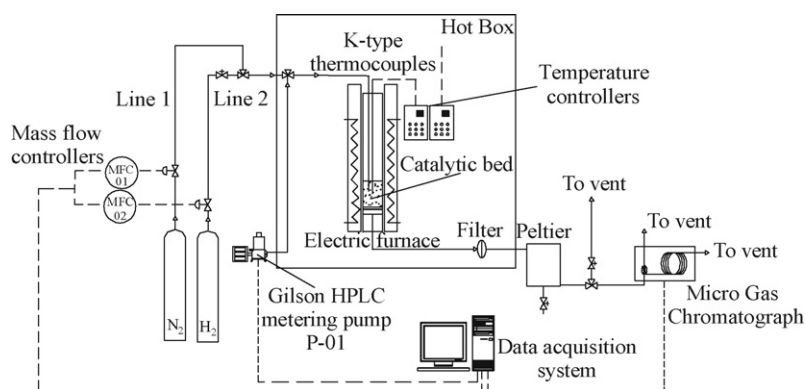


Fig. 1. Schematic flow diagram of the experimental system.

then analysed with an Agilent M3000 Micro GC (G2801A) equipped with a Plot U column (with a Plot Q pre-column), a Molsieve molecular sieve column (with a Plot U pre-column) and Thermal Conductivity Detectors (TCD), where N_2 , H_2 , CO_2 , CO , CH_4 and C_2 's (C_2H_2 , C_2H_4 , C_2H_6) can be quantified.

The experimental system was operated at atmospheric pressure. The concentration of acetic acid was established at 23 wt.% in an aqueous solution, corresponding to a steam-to-carbon (S/C) molar ratio of 5.58. The concentration of acetic acid was selected with an organic content similar to that of the aqueous fraction of bio-oil. The nitrogen flow rate was fixed at 40 cm^3 (STP)/min. Experiments were conducted varying several parameters such as the reaction temperature (550, 650 and $750 \text{ }^\circ\text{C}$), reduction time (0, 0.5, 1 and 2 h), the catalyst weight/acetic acid flow rate (W/m_{HAC}) ratio, ranging from 0.00 to $8.70 \text{ g catalyst min/g acetic acid}$, and the nickel content in the catalyst.

The experimental procedure involves in situ reduction of the catalyst, with hydrogen diluted in nitrogen (10%, v/v) at a fixed temperature of $650 \text{ }^\circ\text{C}$. Nitrogen is subsequently fed in until the reaction temperature is reached after which the model compound is fed in. After the reforming reaction, nitrogen is again fed in as a sweeping gas while the temperature is decreased.

2.2. Catalysts

Three different catalysts were prepared in the laboratory by coprecipitation. The preparation method was similar to that described by Al-Ubaid and Wolf [25]. The catalysts had 23, 28 and 33% of nickel content (expressed as a Ni/(Ni + Al) relative at.% of nickel). All were prepared adding ammonium hydroxide (NH_4OH) to a solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ in distilled water until the pH attained a value of 7.9. The precipitation medium was maintained at $40 \text{ }^\circ\text{C}$ and moderately stirred. The precipitate obtained was filtered, washed at $40 \text{ }^\circ\text{C}$ and dried overnight at $105 \text{ }^\circ\text{C}$. The precursor thus obtained was ground and sieved (particle size ranging from 200 to $320 \mu\text{m}$) prior to calcination for 3 h in air atmosphere at $750 \text{ }^\circ\text{C}$.

The calcined catalysts were characterized by various techniques, including optical emission spectrometry by inductively coupled plasma (ICP-OES), X-ray diffraction (XRD), nitrogen adsorption and temperature-programmed reduction (TPR). Several catalyst samples, after their use in reforming, were also characterized by XRD. The elemental analysis of the metals (nickel and aluminium) done by means of ICP-OES (Thermo Elemental IRIS INTREPID) shows good concordance with the theoretical formulations: 22.0% versus a theoretical 23% value, 26.9% versus a theoretical 28% value and 32.1% versus a theoretical 33%.

Results obtained using XRD analyses (D-Max Rigaku), Fig. 2, show that the samples present wide and asymmetric peaks. Crystalline phases of NiO and spinel ($NiAl_2O_4$) have been detected. The intensities of NiO phase ($2\theta = 43.3^\circ$ and 62.9°) decrease when the nickel content diminishes. These results are consistent with the work of Al-Ubaid and Wolf [25].

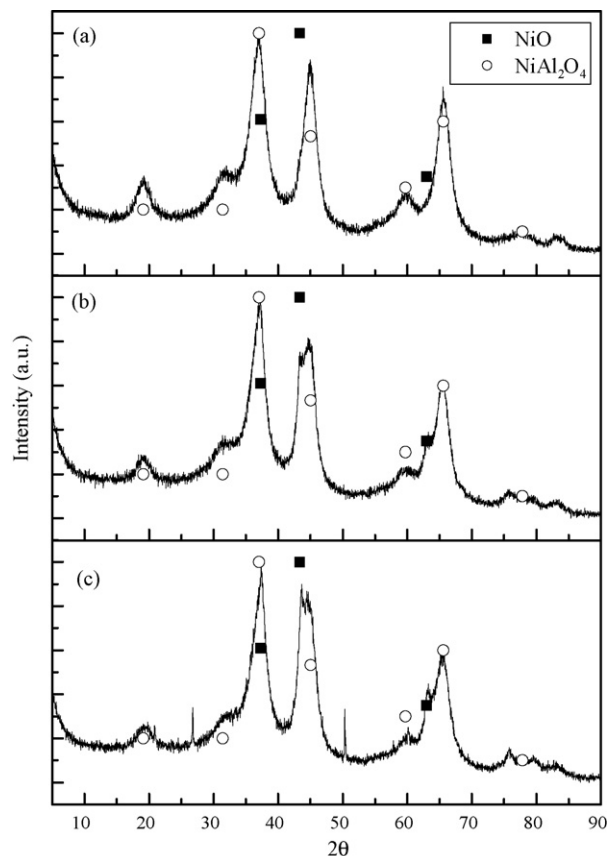


Fig. 2. XRD patterns of calcined catalysts for different nickel content: (a) 23%, (b) 28% and (c) 33%.

Temperature-programmed reduction (TPR) analyses of the catalysts with different nickel content were carried out. In these experiments the catalyst weight was determined using a thermobalance, CAHN TG131. The maximum reduction peak was found at 710, 742 and $734 \text{ }^\circ\text{C}$ for 33, 28 and 23 relative at.% of nickel, respectively. From this result it is concluded that the catalyst with 33 relative at.% of nickel is the easiest to reduce and, according to XRD analysis, is the catalyst with the highest amount of NiO phase. The percentage of weight loss between 400 and $820 \text{ }^\circ\text{C}$ reveals that this value increases when the nickel content increases.

The total surface area of the Ni–Al catalysts was measured in a Micromeritics ASAP 2020. The values obtained for the three different catalysts prepared were as follows: $205 \text{ m}^2/\text{g}$ for the 23% Ni catalyst, $205 \text{ m}^2/\text{g}$ for the 28% Ni catalyst and $180 \text{ m}^2/\text{g}$ for the 33% Ni catalyst. These values indicate that the total surface area of the catalysts is quite large, being slightly higher for the catalysts with lower nickel contents.

2.3. Chemicals

The model compound selected for the tests (acetic acid) was supplied by PANREAC (99.5% purity). Other chemicals used included commercial gases at purity $>99.999\%$: hydrogen, nitrogen, air, helium and argon, as well as standard gas mixture

(N₂, H₂, CO₂, CO, CH₄ and C₂'s) for the calibration of the gas chromatograph.

3. Results and discussion

3.1. Influence of reduction time

The purpose of these experiments was to select the most appropriate conditions of catalyst reduction to obtain a high hydrogen yield. The experiments were performed at 650 °C using a liquid feeding rate of 0.15 mL/min and a W/m_{HAc} ratio of around 5.80 g catalyst min/g acetic acid. The catalyst used had a 33% nickel content (relative at.% of nickel). The reduction was carried out at 650 °C, using a hydrogen flow rate of 4 cm³ (STP)/min diluted with nitrogen (H₂:N₂ = 1:10).

Table 1 presents the overall results obtained in experiments performed at different reduction times. The table shows the values of various experimental variables such as catalyst weight, liquid feeding rate, reduction time, reaction time and W/m_{HAc} ratio. The $G_{\text{C}_1\text{HSV}}$ is also included for the purposes of comparison with other works. The $G_{\text{C}_1\text{HSV}}$ was defined as the volume of C₁-equivalent species in the feed at standard temperature and pressure (STP) per unit volume of catalyst (including the void fraction) per hour. Also indicated are gas and liquid yields expressed as mass fractions of the sum of acetic acid and water, the recovery, the percentage of carbon contained in the acetic acid converted to gases (CO and CO₂), the gas yield (expressed as mass fractions of acetic acid), and the gas composition (expressed as molar percentages; N₂ and H₂O free).

Table 1

Results at 650 °C, W/m_{HAc} = 5.80 g catalyst min/g acetic acid, using the catalyst with 33% nickel content: influence of reduction time

	Run			
	1	2	3	4
Catalyst weight (g)	0.2004	0.2001	0.2000	0.2007
Liquid feeding rate (mL/min)	0.15	0.15	0.15	0.15
Reduction time (h)	0	0.5	1	2
Reaction time (h)	2	4	4	8
W/m_{HAc} (g catalyst min/g acetic acid)	5.81	5.80	5.80	5.82
$G_{\text{C}_1\text{HSV}}$ (h ⁻¹)	7,171	7,183	7,183	7,159
Yields (g/g liquid fed)				
Gas	0.255	0.285	0.341	0.364
Liquid	0.732	0.693	0.652	0.647
Recovery	0.987	0.978	0.994	0.981
Carbon conversion (%)	73.2	80.7	98.0	101.7
Gas yields (g/g acetic acid)				
H ₂	0.098	0.101	0.120	0.130
CO	0.107	0.084	0.130	0.151
CO ₂	0.903	1.052	1.234	1.300
Gas composition (mol%, N ₂ and H ₂ O free)				
H ₂	66.65	65.33	64.73	65.11
CO	5.22	3.85	4.99	5.39
CO ₂	28.06	30.82	30.27	29.50

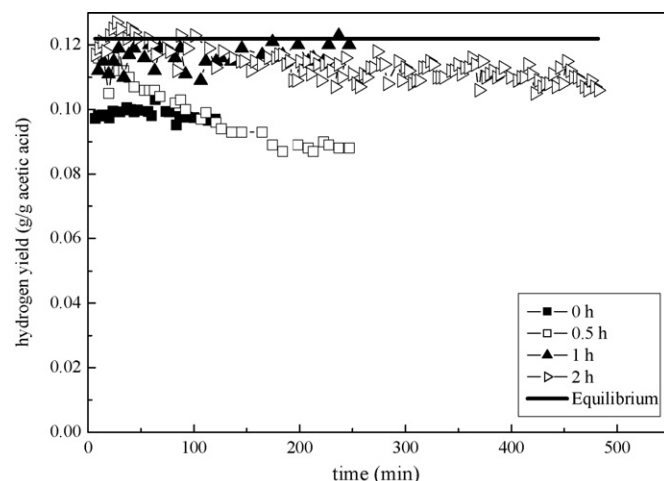


Fig. 3. Hydrogen yield evolution with time, influence of reduction time. $T = 650$ °C, $W/m_{\text{HAc}} = 5.80$ g catalyst min/g acetic acid and nickel content = 33%.

It must be borne in mind when analysing the results presented in Table 1 that the reaction time is not the same for all the experiments. The general tendency shows that the gas yields to H₂, CO and CO₂ increase, as does the carbon conversion to gases, when the reduction time increases. The gas composition (mol%, N₂ and H₂O free) hardly changes with the reduction time; the H₂ content is around 65%, the CO content around 5% and CO₂ around 30%. However, little improvement in the product gas yields was observed with 2 h of reduction time compared to 1 h.

In order to show more clearly the effect of the reduction time on the gas yields, Figs. 3–5 show the H₂, CO and CO₂ yields, respectively, as well as their corresponding equilibria values calculated with AspenTech HYSYS 3.2 simulation software.

The experimental results indicate that the calcined precursor without previous reduction has a significant catalytic activity, though lower than that of reduced catalysts. The results of a blank experiment (reaction bed without catalyst) under the same experimental conditions gave 1.45×10^{-4} , 0.008 and

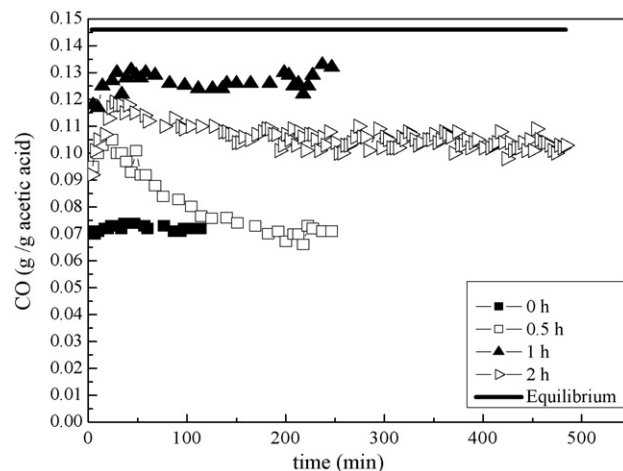


Fig. 4. CO yield evolution with time, influence of reduction time. $T = 650$ °C, $W/m_{\text{HAc}} = 5.80$ g catalyst min/g acetic acid and nickel content = 33%.

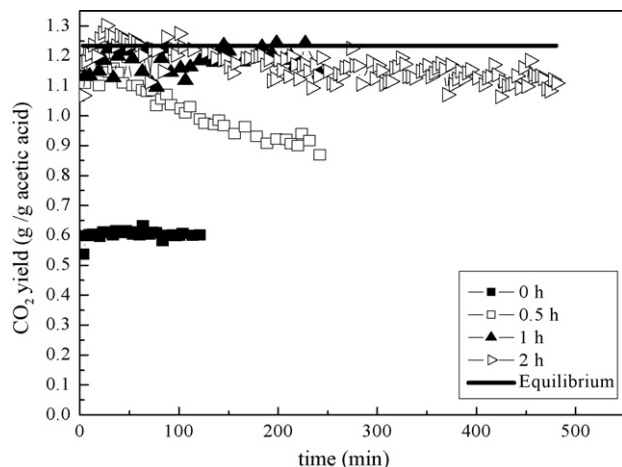


Fig. 5. CO_2 yield evolution with time, influence of reduction time. $T = 650^\circ\text{C}$, $W/m_{\text{HAc}} = 5.80$ g catalyst min/g acetic acid and nickel content = 33%.

0.020 g gas/g acetic acid for H_2 , CO and CO_2 yields, respectively. The catalyst reduced for 0.5 h shows a poor performance, with low product gas yields after the first minutes of reaction, and reaching H_2 and CO yields, at the end of the experiment, very close to those of the aforementioned calcined precursor.

No significant enhancement was observed for the catalyst reduced for 2 h compared to that reduced for just 1 h. Both catalysts present similar values for H_2 and CO_2 yields, though the catalyst reduced for 1 h shows higher values for the CO yield. The reduction time was therefore set at 1 h for further experiments.

The results obtained show as a general tendency that the increase in reduction time causes a shift in gas yields relative to those corresponding to thermodynamic equilibrium, as depicted in Figs. 3–5. This fact is in accordance with the work

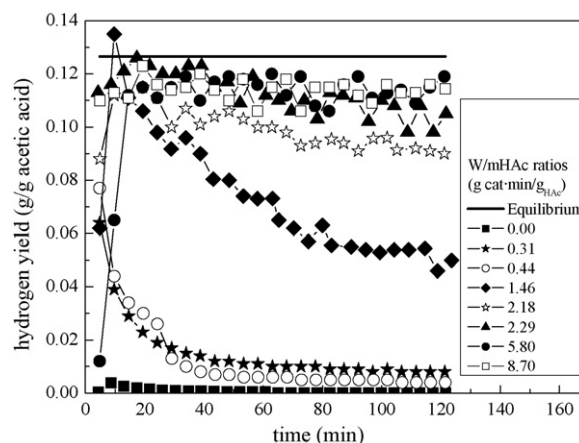


Fig. 6. Hydrogen yield evolution with time, influence of W/m_{HAc} . $T = 650^\circ\text{C}$, reduction time = 1 h and nickel content = 33%.

of Galdámez et al. [20], though gas yields in non-catalytic steam reforming are very different to those in the present work.

3.2. Influence of catalyst weight/acetic acid flow rate (W/m_{HAc}) ratio

These experiments were performed at 650°C , using the catalyst with a stoichiometric nickel content (33 relative at.% of nickel) previously reduced for 1 h. The results are summarized in Table 2. The experiment with a zero value for the W/m_{HAc} ratio is the blank experiment.

The general tendency observed is that for increasing W/m_{HAc} ratios, the gas yields increase with a consequent decrease in the respective liquid yields. The carbon conversion to gas also increases with higher W/m_{HAc} ratios.

Table 2
Results at 650°C using the catalyst with 33% nickel content and reduced for 1 h: influence of the W/m_{HAc} ratio

	Run							
	5	6	7	8	9	3	10	
Catalyst weight (g)	0.0108	0.0101	0.0505	0.0502	0.0526	0.2000	0.2000	
Liquid feeding rate (mL/min)	0.15	0.10	0.15	0.10	0.10	0.15	0.10	
Reaction time (h)	4	4	4	4	2	4	2	
W/m_{HAc} (g catalyst min/g acetic acid)	0.31	0.44	1.46	2.18	2.29	5.80	8.70	
G_{C1HSV} (h^{-1})	134,400	94,961	28,537	19,112	18,194	7,183	4,789	
Yields (g/g liquid fed)								
Gas	0.032	0.026	0.172	0.274	0.293	0.341	0.316	
Liquid	0.956	0.969	0.807	0.706	0.658	0.652	0.646	
Recovery	0.988	0.995	0.979	0.980	0.951	0.993	0.962	
Carbon conversion (%)	9.2	7.6	49.1	79.1	84.6	98.0	90.6	
Gas yields (g/g acetic acid)								
H_2	0.012	0.009	0.062	0.097	0.109	0.120	0.115	
CO	0.006	0.013	0.063	0.114	0.134	0.130	0.123	
CO_2	0.121	0.089	0.621	0.981	1.031	1.234	1.136	
Gas composition (mol%, N_2 and H_2O free)								
H_2	65.47	63.62	65.63	64.93	65.85	64.73	65.53	
CO	2.52	6.50	4.72	5.41	5.78	4.99	5.01	
CO_2	31.21	28.91	29.65	29.67	28.37	30.27	29.46	

Table 3

Results for the catalyst with 33% Ni content reduced for 1 h, $W/m_{\text{HAc}} = 1.46$ g cat min/g acetic acid: influence of the steam reforming temperature

	Run					
	11	12	7	13	14	15
Catalyst weight (g)	0.0505	0.0505	0.0505	0.0500	0.0503	0.0501
Temperature (°C)	550	550	650	650	750	750
Liquid feeding rate (mL/min)	0.15	0.15	0.15	0.15	0.15	0.15
Reaction time (h)	2	2	4	2	2	2
W/m_{HAc} (g catalyst min/g acetic acid)	1.46	1.46	1.46	1.45	1.46	1.45
$G_{\text{C}_1\text{HSV}}$ (h^{-1})	28,537	28,537	28,537	28,748	28,576	28,690
Yields (g/g liquid fed)						
Gas	0.133	0.130	0.172	0.173	0.337	0.328
Liquid	0.870	0.826	0.807	0.804	0.589	0.621
Recovery	1.003	0.956	0.979	0.977	0.926	0.948
Carbon conversion (%)	37.8	37.3	49.1	51.36	99.5	96.5
Gas yields (g/g acetic acid)						
H ₂	0.048	0.045	0.062	0.063	0.125	0.126
CO	0.038	0.036	0.063	0.104	0.211	0.203
CO ₂	0.490	0.479	0.621	0.580	1.128	1.096
Gas composition (mol%, N ₂ and H ₂ O free)						
H ₂	65.63	64.39	65.63	64.79	65.29	66.22
CO	3.67	3.73	4.72	7.63	7.89	7.63
CO ₂	30.35	31.17	29.65	27.10	26.83	26.15

Individual gas yields for H₂, CO and CO₂ follow the same tendency, rising progressively up to values close to equilibrium with W/m_{HAc} ratios of 5.80 and 8.70 g catalyst min/g acetic acid. The amounts of methane obtained with the lowest W/m_{HAc} ratios (0.31 and 0.44 g catalyst min/g of acetic acid) were too small (around 0.002) to be taken into account and are thus not included in the table.

Fig. 6 depicts the effect of the W/m_{HAc} ratio on the H₂ yield. The CO and CO₂ yields show the same behaviour. The value of the hydrogen yield under equilibrium conditions at 650 °C appears as a line indicating the maximum value of hydrogen yield achievable at this temperature.

W/m_{HAc} ratios above 2.29 g catalyst min/g acetic acid do not significantly enhance the performance of the catalyst. All of the ratios above this value display reaction conditions close to equilibrium. Below 2.29 g catalyst min/g acetic acid, the decrease in product gas yields becomes more significant with decreasing W/m_{HAc} ratios.

The intermediate value of 1.46 g catalyst min/g acetic acid was chosen for analysing the rest of the parameters.

3.3. Influence of the steam reforming temperature

The temperature at which the steam reforming reaction develops was also studied. Three different temperatures were chosen: 550, 650 and 750 °C. Table 3 shows the experimental data obtained. Replicas of the experiments carried out at the three temperatures studied are shown in order to check reproducibility. Results for these replicas are also given in Table 3. All the experiments were carried out under the same conditions (catalyst with 33% Ni content, W/m_{HAc} ratio of 1.46 g catalyst min/g of acetic acid, and 1 h reduction).

It can be inferred that increasing the steam reforming temperature results in higher gas yields, therefore obtaining greater carbon conversions. Gas composition (mol%, N₂ and H₂O free) is again around 65% for H₂. CO and CO₂ gas yields vary significantly with temperature, increasing from around 4% at 550 °C up to around 8% for CO, whereas CO₂ decreases from around 30% down to 26%.

Fig. 7 shows the hydrogen yield and the influence of the steam reforming temperature for a W/m_{HAc} ratio of 1.46 g catalyst min/g of acetic acid. The figure shows a clear tendency of the hydrogen yield to increase when the reaction temperature rises. Moreover, there is a decrease in the hydrogen yield with the reaction time at 550 and 650 °C, whereas this decrease was not observed at 750 °C.

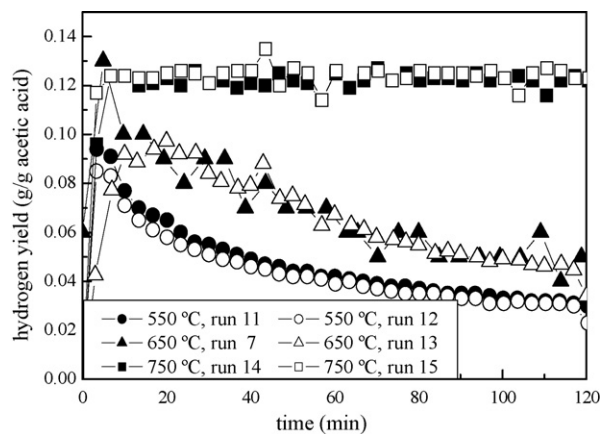


Fig. 7. Hydrogen yield evolution with time, influence of reaction temperature. $W/m_{\text{HAc}} = 1.46$ g catalyst min/g acetic acid, reduction time = 1 h and nickel content = 33%.

Table 4

Results at 550 and 650 °C for $W/m_{\text{HAc}} = 1.46$ g min/g acetic acid, 1 h reduction time: influence of the nickel content in the catalyst

	Run					
	16	17	11	18	19	7
Nickel content (%)	23	28	33	23	28	33
Catalyst weight (g)	0.0501	0.0503	0.0505	0.0500	0.0503	0.0505
Temperature (°C)	550	550	550	650	650	650
Liquid feeding rate (mL/min)	0.15	0.15	0.15	0.15	0.15	0.15
Reaction time (h)	2	2	2	2	2	4
W/m_{HAc} (g catalyst min/g acetic acid)	1.45	1.46	1.46	1.45	1.46	1.46
G_{C1HSV} (h^{-1})	28,691	28,537	28,537	28,691	28,537	28,537
Yields (g/g liquid fed)						
Gas	0.136	0.205	0.133	0.246	0.312	0.172
Liquid	0.826	0.781	0.870	0.745	0.628	0.807
Recovery						
Carbon conversion (%)	0.962	0.986	1.003	0.991	0.940	0.979
Gas yields (g/g acetic acid)						
H ₂	0.051	0.071	0.048	0.090	0.118	0.062
CO	0.049	0.063	0.038	0.126	0.130	0.063
CO ₂	0.490	0.751	0.490	0.850	1.109	0.621
Gas composition (mol%, N ₂ and H ₂ O free)						
H ₂	66.42	64.46	65.63	65.14	66.30	65.63
CO	4.51	4.05	3.67	6.53	5.23	4.72
CO ₂	28.91	30.81	30.35	27.95	27.95	29.65

The data sets for the three temperatures show acceptable reproducibility. For the hydrogen yields, depicted in Fig. 7, the average relative errors for runs at 550, 650 and 750 °C were ca. 5, 6 and 3%, respectively, while the standard deviations were lower than 0.006, 0.008 and 0.010, respectively.

3.4. Influence of nickel content

To test the effect of the nickel content, expressed as Ni/(Ni + Al) relative at.% of nickel, three catalysts were tested with 33, 28 and 23%. The experiments were performed at 550 and 650 °C using a W/m_{HAc} ratio of 1.46 g catalyst min/g acetic acid. All the catalysts were reduced at 650 °C during 1 h

using hydrogen diluted with nitrogen ($\text{H}_2:\text{N}_2 = 1:10$). The overall results of these experiments are presented in Table 4.

For each reaction temperature the highest gas yield, expressed as a mass fraction of the sum of acetic acid and water, was obtained for the catalyst with 28% nickel content while the smallest gas yield was obtained for the catalyst with 33%. H₂, CO and CO₂ yields obtained for the catalyst with 28% nickel content were the highest for each temperature. At 650 °C it is observed that H₂, CO and CO₂ yields were higher for 23% than for 33% of nickel content. At 550 °C similar results for H₂ and CO₂ yields were obtained for 23 and 33% nickel contents.

Figs. 8–10 show the H₂, CO and CO₂ yield evolution with time respectively for the two reaction temperatures.

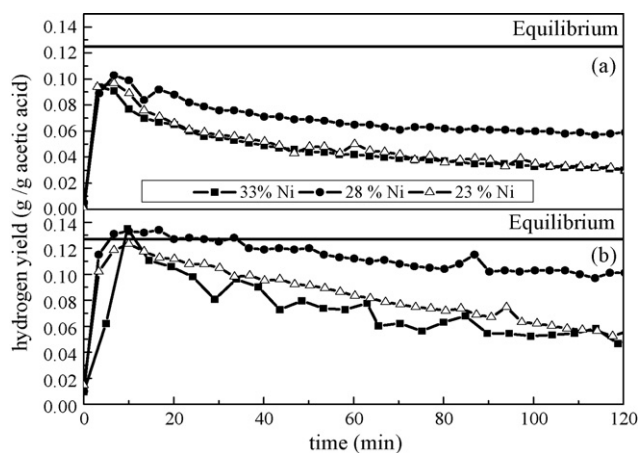


Fig. 8. Hydrogen yield evolution with time, influence of nickel content: (a) 550 °C and (b) 650 °C. Reduction time = 1 h, $W/m_{\text{HAc}} = 1.46$ g catalyst min/g acetic acid.

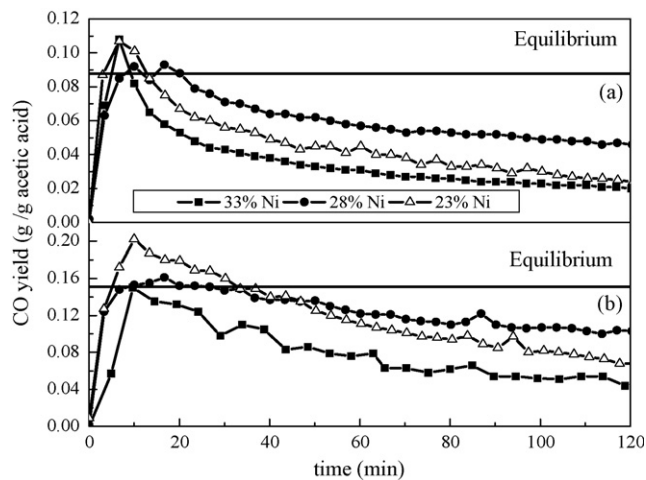


Fig. 9. CO yield evolution with time, influence of nickel content: (a) 550 °C and (b) 650 °C. Reduction time = 1 h, $W/m_{\text{HAc}} = 1.46$ g catalyst min/g acetic acid.

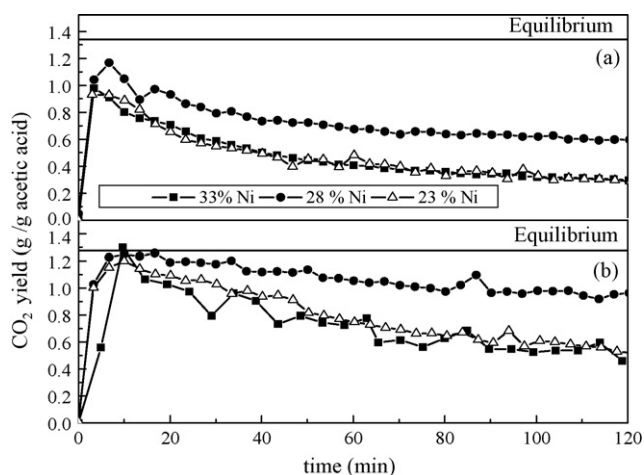


Fig. 10. CO₂ yield evolution with time, influence of nickel content: (a) 550 °C and (b) 650 °C. Reduction time = 1 h, $W/m_{\text{HAc}} = 1.46$ g catalyst min/g acetic acid.

The best performance of the catalyst with a nickel content of 28% could be a consequence of nickel dispersion after reduction and its stabilization in the reaction conditions. The crystalline phases, NiO and NiAl₂O₄, present in the calcined precursor, identified by XRD analysis, and the highest temperature of the maximum reduction peak probably have a significant influence.

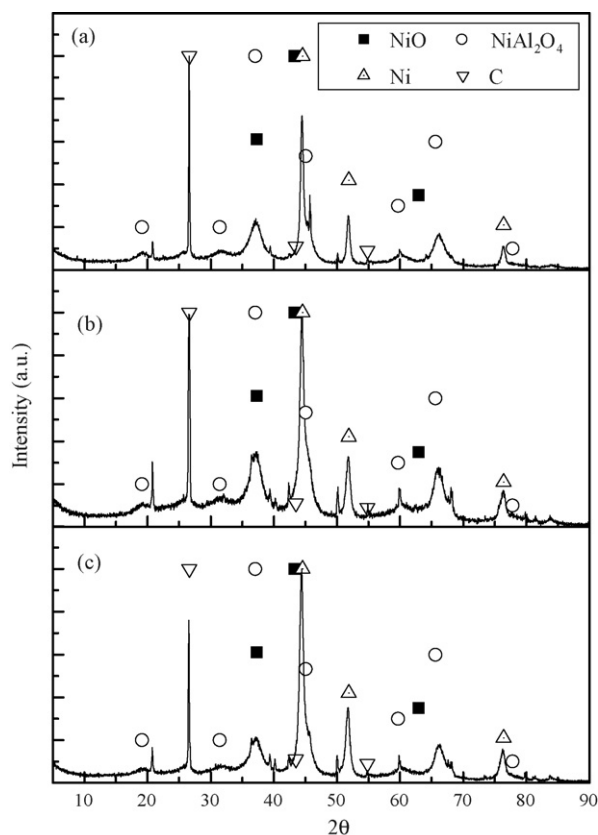


Fig. 11. XRD patterns of used catalyst samples for different nickel content: (a) 23%, (b) 28% and (c) 33%.

In order to obtain information from the used catalysts, XRD characterization was carried out on the 23, 28 and 33% Ni content samples used under the following operational conditions: 1 h reduction, 650 °C reaction temperature, W/m_{HAc} of 1.46 g catalyst min/g acetic acid. Fig. 11 shows the results obtained. The three samples show similar patterns, with a clear peak at $2\theta \sim 26^\circ$ that has been identified as coke and peaks at $2\theta = 44.5^\circ$, 51.9° and 76.4° , identified as metallic nickel. Comparing these patterns with those corresponding to fresh samples (see Fig. 2), the major difference observed is the great diminution of the peaks corresponding to NiO and NiAl₂O₄. In addition, the peaks corresponding to metallic Ni are narrower than those of the fresh samples.

4. Conclusions

Acetic acid has been selected as a model compound of bio-oil. Catalytic steam reforming of this acid has been studied with the purpose of obtaining high hydrogen yields, the catalysts chosen being coprecipitated Ni–Al. The variables analysed were reduction time, W/m_{HAc} ratio, reaction temperature and nickel content in the catalyst. The main conclusions of this work are as follows:

- (1) The calcined precursor of the catalyst with 33% nickel content has significant activity without previous reduction at a reaction temperature of 650 °C. The increase in reduction time (reduction temperature 650 °C) causes an increase in H₂, CO and CO₂ yields although no significant differences were observed for 2 h of reduction time as against 1 h.
- (2) The W/m_{HAc} ratio has a significant influence on gas yields. Using W/m_{HAc} ratios higher than 2.29 g catalyst min/g acetic acid, the H₂ yields reached values close to thermodynamic equilibrium. A W/m_{HAc} ratio smaller than 2.18 g catalyst min/g acetic acid leads to a decrease in H₂, CO and CO₂ yields.
- (3) The influence of the reaction temperature has been studied using a catalyst with 33% nickel content and a W/m_{HAc} ratio of 1.46 g catalyst min/g acetic acid. At 750 °C no decrease in product gas yields was observed. The decrease noted at 550 °C was greater than that observed at 650 °C.
- (4) The effect of the nickel content of the catalyst has been analysed at 550 and 650 °C. For the three catalysts tested (33, 28 and 23 relative at.% of nickel) the best performance with the highest H₂ yield was obtained for the catalyst with 28% nickel content at both reaction temperatures.

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