GLYCEROL CONVERSION TO VALUABLE PRODUCTS BY PRESSURE AQUEOUS PROCESSING USING NI-AL-FE CATALYSTS

R. Raso, J. Ruíz, M. Oliva, L. García, J. Arauzo
Thermochemical Processes Group (GPT), Aragon Institute for Engineering Research (I3A), Universidad de Zaragoza
C/Mariano Esquillor s/n, E-50018, Zaragoza, Spain

ABSTRACT: The present work studied the pressure aqueous processing of glycerol (by-product of biodiesel) without external hydrogen addition to produce value-added products. A series of Ni catalysts supported on Al_2O_3 and Fe as promoter were prepared through co-precipitation technique by changing the Fe/Al ratio (0, 25 and 75% molar). The prepared samples were characterized by several techniques (XRD, H_2-TPR, N_2 adsorption and ICP-OES). All the catalysts showed a low carbon conversion to gas and high carbon conversion to liquid products mainly 1,2-propanediol, acetol and ethylene glycol. This work demonstrates the effects of the molar ratio of Fe/Al on physicochemical characteristics of Ni-Al-Fe catalysts and during the pressure aqueous processing (PAP) of glycerol to value-added products.
Keywords: biodiesel, residues, catalytic conversion, fixed bed

1 INTRODUCTION

In recent decades, the biofuels such as biodiesel are increasing intensively as a result of widespread environmental concerns and firmer regulations for fuel commerce. Currently, the high production of biodiesel produces a glycerol excess, generating a surplus when considering its traditional uses. For every 10 tons of biodiesel generates around 1 ton of glycerol. Considering this, several processes have been investigated in order to valorise the glycerol which is generated as a by-product. The use of glycerol has advantages, on the one hand, the benefits of its valorisation contribute to a more competitive biodiesel production and, on the other hand, the generation of a waste and its necessary treatment are avoided [1-3].

In this bio-refinery context, a promising strategy to obtain value-added chemicals from glycerol is pressure aqueous processing (PAP). PAP is a catalytic process performed at moderate pressures around 40 bar and quite low temperatures around 500 K, allowing the production of gases and liquids from a renewable feedstock. During the PAP of glycerol, several liquid-gas-solid chemical reactions take place. These include cracking and reforming reactions to produce hydrogen, dehydrogenation of alcohols or hydrogenation of carbonyls, deoxygenation and hydrogenolysis as well as cyclisation reactions [3-5]. In addition, it doesn't need external supply of hydrogen, so it is a less expensive and safer process than the conventional hydrogenolysis that requires its contribution. Most of the works published in literature related to this work use batch installations (discontinuous feeding). The use of a continuous feeding is useful due to its greater production potential on an industrial scale.

The catalysts used in the process are noble metals based on Pt, Ni, Pt-Ni, Cu, Ru or Cu supported on various oxides for instance, MgO, Al_2O_3, ZrO_2, SiO_2, CeO_2 or carbon and altered, in some cases, with promoters such as Zr, La, Ce and Mg [3].

Given this background, the aim of this work is develop a stable catalyst to use in the PAP of glycerol to obtain value-added chemicals such as 1,2-propanediol, ethylene glycol, acetol. In previous studies with a catalyst of Ni supported on Al_2O_3, the formation of new phases in the solid has been detected for example, boehmite due to hydration of Al_2O_3, with significant alteration of its surface area and acidity. This may provoke activity decay due to dissolution of the support and sinterisation of metal particles [4, 6].

1,2-propanediol is a major commodity chemical that is mainly used in unsaturated polyester resins, functional fluids, pharmaceuticals and cosmetics, among others. Ethylene glycol is an important bulk chemical with applications in antifreeze and as raw material for the manufacture of polyester fibres. Acetol has uses in food, cosmetics and textile industries [4].

This work studies the effects of the molar ratio of Fe/Al on physicochemical characteristics of the catalyst based on Ni. Moreover, the performance of these catalysts during the PAP of glycerol to value-added products is analysed.

2 EXPERIMENTAL

2.1 Catalyst preparation

Three catalysts based on Ni-Fe-Al were prepared by co-precipitation method and the different between of them was the molar ratio of Fe:Al, but all of them contain a 28% of Ni. The molar ratio of Fe:Al was changed in the order of 0:1, 1:3 and 3:1 and samples were named Fe0, Fe25 and Fe75, respectively. Aluminium nitrate $[Al(NO_3)_3 \cdot 9H_2O]$, nickel nitrate $[Ni(NO_3)_2 \cdot 6H_2O]$ and iron nitrate $[Fe(NO_3)_3 \cdot 9H_2O]$ were used as metal precursors, while NH_4OH acted as precipitant. The hydrated catalyst precursors were dried at 105 ℃ and then calcined at 500 ℃.

2.2 Catalyst characterization

The fresh calcined catalysts were characterized by several techniques such as XRD, H_2-TPR, N_2 adsorption and ICP-OES. The textural properties of the catalyst were determined by N_2 adsorption at 77 K. H_2-TPR (temperature programmed reduction) was employed in order to study the reducibility of the nickel, iron and aluminium oxide species. Crystalline phases of the catalysts were determined by XRD (X-Ray diffraction). The concentrations of Ni, Fe and Al in the fresh catalysts were measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

2.3 Activity test in the PAP of glycerol

Catalytic performance was evaluated using a laboratory-scale continuous feeding unit designed and developed by PID (Process Integral Development Eng &

Tech, Spain). It consists of a stainless steel tubular reactor with an inner diameter of 9 mm, heated up by an electric furnace. A micrometric valve regulates the system pressure. A PID control system keeps the reactor pressure stable during the experiments, while a display shows the live pressure values. A glycerol aqueous solution is fed into the reactor by means of a high performance liquid chromatography (HPLC) pump. A schematic diagram of the experimental system is shown in Fig. 1.
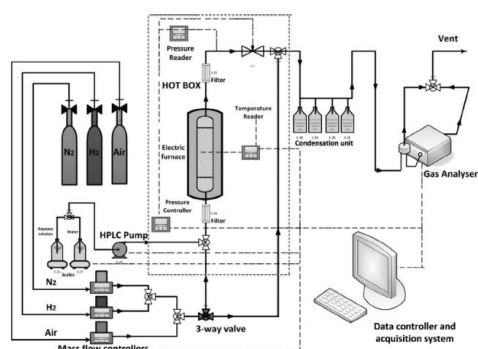

Figure 1: Schematic diagram of the pressure aqueous processing of glycerol experimental rig [3].

The reaction products (gas and liquids) and the unreacted glycerol leave the reactor from its upper part, passing through the micrometric valve where they are depressurized and arrive at the condensation system. This system consists of four condensers where the first one is used to collect the water used to pressurize the system until reaching reaction conditions. An in the rest of them the liquid products are separated from the gas mixture at intervals of 1 h during the experimental test in order to analyse the evolution over time of the liquid phase.

The gas mixture consists of N_2, used as an internal standard, and the different gaseous products of the PAP reaction. This gas stream was analysed online by a Micro-GC equipped with thermal conductivity detectors (TCD). Finally, the liquid fractions were collected in the condensers that were analysed offline by a Total Organic Carbon (TOC) equipment and a gas chromatograph, equipped with Flame Ionization (FID) detector.

Catalytic tests were performed at the same operating conditions to all the catalysts in order to study the effect of the Fe content in the catalyst. Each experiment lasted three hours. Table I shows the values of temperature (T), pressure (P), the glycerol content in the aqueous solution feeding (F) and mass of catalyst/ glycerol mass flow rate ratio (W/m) used in the experiments.

Table I: Experimental conditions

T (ºC)	P (bar)	F (wt.%)	W/m ($g_{catalyst} \cdot min/g_{glycerol}$)
227	33	10	20

3 RESULTS AND DISCUSSION

3.1 Catalyst characterization

The textural properties of the catalysts are listed in Table II.

Table II: Textural properties

	Composition (molar ratio of Fe:Al)	S_{BET}^a (m^2/g)	V_p^b (cm^3/g)	d_p^b (nm)
Fe0	0:1	274	0.170	3.31
Fe25	1:3	223	0.197	3.78
Fe75	3:1	152	0.197	5.81

a: BET method
b: BJH adsorption method

It was observed the influence of the Fe, decreasing the values of specific surface area (S_{BET}), but increasing the average pore diameter (d_p).

The results of ICP-OES are shown in Table III. There are not differences between the analysis and theoretical results, so that means a good preparation of the catalysts.

Table III: Results of ICP-OES expressed as molar %

	Theoretical		Analysis	
	Fe (molar %)	Al (molar %)	Fe (molar %)	Al (molar %)
Fe0	-	72	-	71.72
Fe25	18	54	17.98	54.18
Fe75	54	18	53.02	19.64

H_2-TPR analysis has been performed in order to determine the optimal reduction temperature of the catalyst. Fig. 2 illustrates the H_2-TPR curves of the mixed oxides. It was observed that the Ni reducibility is favoured with the presence of Fe in the catalyst. The highest peak was corresponding the reduction of NiO to Ni at a specific temperature, which value is reduced with the increasing of Fe content in the catalyst such as a 430 ºC with the Fe75 catalyst and 612 ºC with the Fe0 catalyst. The peaks above 805 ºC were corresponding to the reduction of FeO to Fe.
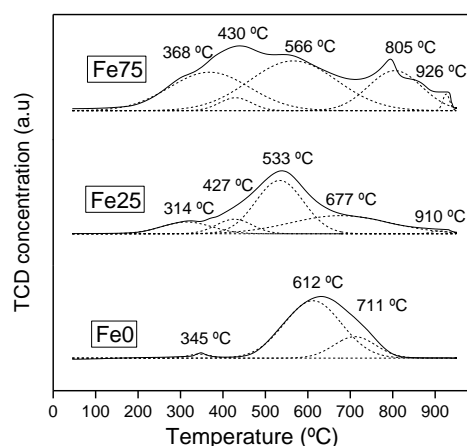

Figure 2: H_2-TPR profiles of the catalysts

Crystalline phases of the catalysts were determined by X-ray diffraction, using JCPDS Data Base. A sample can be observed in Fig. 3.
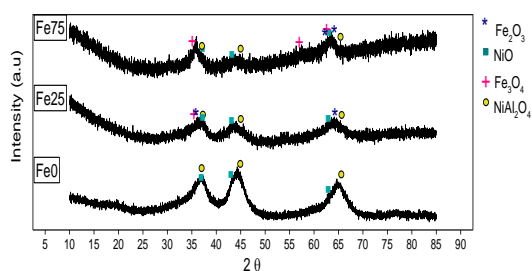
Figure 3: XRD patterns of the catalysts

It was observed that the increase of the Fe content in the catalyst decreases the crystallinity of the catalysts. Also, the peak that corresponds to Fe_3O_4 appears with higher intensity in the Fe75 catalyst than in the Fe25 catalyst.

3.2 Catalytic performance of the catalysts in the PAP of glycerol

PAP of glycerol over the three samples was carried out at the conditions previously shown in Table I.

The average results of the glycerol conversion, carbon conversion to products (gas and liquid) are shown in Table IV.

Table IV: Average glycerol conversion and carbon conversion to products

	Glycerol conversion (%)	CC to gas (%)	CC to liquid (%)
Fe0	35.93	4.77	25.72
Fe25	50.71	6.57	35.46
Fe75	40.76	3.33	29.61

There is a small difference between glycerol conversion and the addition of carbon conversion to products (gas and liquid). An experiment with a value of carbon deficit below of 15% is considered a reliable test, as suggested by other authors [4,7]. The carbon deficit is defined as follows:

Carbon deficit = glycerol conversion – carbon conversion to products

Fig. 4 shows the average results of glycerol conversion over the different catalysts.
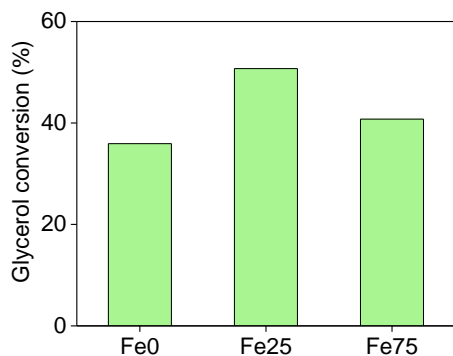

Figure 4: Average conversion of glycerol in PAP

It is observed that the major glycerol conversion it is obtained with the Fe25 catalyst. Besides it is observed that the Fe was increasing the glycerol conversion

because it was obtained more conversion with the catalyst containing some percent of Fe than the catalyst with Fe free.

The main reaction products were H_2 and CO_2 in the gaseous phase, and ethylene glycol, acetol and 1,2-propanediol were collected in the liquid phase besides unreacted glycerol.

Fig. 5 illustrates the average result of carbon conversion to products (gas and liquid).
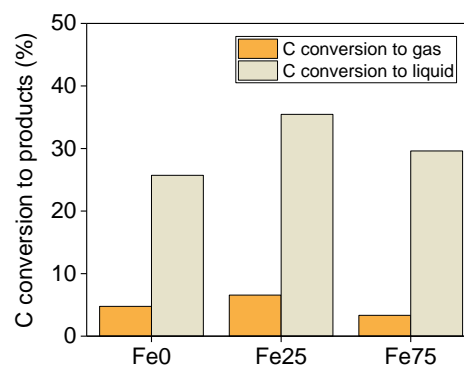

Figure 5: Average carbon conversion to products

It was observed that the presence of a 25% of Fe in the catalyst favours the glycerol conversion, obtaining both more carbon conversion to gas and to liquid. It was obtained more carbon conversion to liquid with the Fe75 catalyst than the Fe0 catalyst. But for the carbon conversion to gas, the Fe75 was the worst.

In respect of the average gas composition without water and nitrogen, Fig. 6 shows its results.
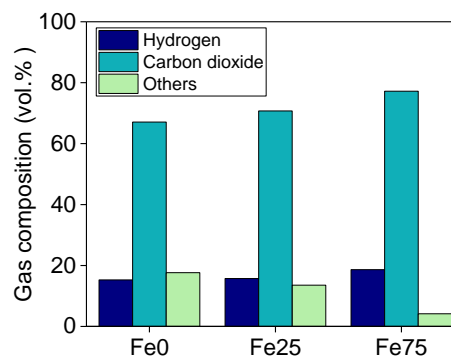

Figure 6: Average gas composition with water and nitrogen free. Others: CO, CH_4, C_2H_6 and C_3H_8

A significant increase in H_2 and CO_2 composition is observed with the increase of Fe percent in the catalyst, from 15.26 and 67.08 vol.% at 0% of Fe to 18.63 and 77.20 vol.% at 75% of Fe, respectively.

In contrast, the others gas composition (CO, CH_4, C_2H_6 and C_3H_8) decrease with the increase of Fe percent, although some of them increase with the increase of Fe such as C_3H_8. The tendency of CH_4 is the most significant because it was obtained major amount of this.

The reaction network of the pressure aqueous processing of glycerol includes gas and liquid products. There are two main routes in the liquid phase that are the following. On the one hand, the route 1 is the dehydration

of glycerol to acetol and further hydrogenation to form 1,2-propanediol. This is the main route in glycerol hydrogenolysis. On the other hand, the route 2 is the dehydrogenation of glycerol, forming glyceraldehyde and further decarbonylated to form ethylene glycol. Ethanol can produce acetic acid, while this alcohol can be generated from ethylene glycol by dehydration/hydrogenation. Also methanol can be produced from ethylene glycol by dehydrogenation/decarbonylation [4].

The average results of carbon selectivity to liquid are shown in Table V.

Table V: Average results of carbon selectivity to liquid

	Acetol (%)	1,2-propanediol (%)	EG* (%)	Others** (%)
Fe0	13.58	58.23	13.48	14.71
Fe25	10.38	68.04	13.39	8.18
Fe75	13.03	61.40	19.14	6.43

EG*: Ethylene glycol
Others**: Methanol, Ethanol and Acetic Acid

The liquid product with the highest carbon selectivity is 1,2-propanediol with the highest value around 68.04% at Fe25. As expected the carbon selectivity to acetol shows the worst value around 10.38% at Fe25.

According to these results at these experimental conditions is the route 1 favoured with the production of 1,2-propanediol from acetol.

Glyceraldehyde, an intermediate product in route 2, has not been detected in the analysis. However, route 2 is carried out because of the existence of ethylene glycol.

Ethylene glycol presents a high carbon selectivity which increases from 13.48 to 19.14% when the amount of Fe increases from 0 to 75%. This suggests, the increase of percent of Fe favours the production of ethylene glycol from a fast reaction of the decarbonylation of glyceraldehyde.

4   CONCLUSIONS

The incorporation of Fe in the catalyst decreases the values of specific surface area and the crystallinity of the sample, but increases the average pore diameter. Furthermore, the catalyst is reduced (NiO to Ni) at lower temperature than the catalyst without Fe.

The presence of a 25% of Fe in the catalyst favours the glycerol conversion, obtaining both more carbon conversion to gas and to liquid, being 1,2-propanediol the liquid product with more carbon selectivity. Moreover, it was obtained more carbon conversion to liquid with the catalyst of 75% of Fe than the sample without Fe. However, it presented the worst in carbon conversion to gas.

In addition, the increase of percent of Fe favours the carbon selectivity to ethylene glycol which is an important bulk chemical.

5   ACKNOWLEDGEMENTS

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7   LOGO SPACE