Production of gaseous and liquid chemicals by aqueous phase reforming of crude glycerol: Influence of operating conditions on the process

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ABSTRACT

The present work studies the influence of the temperature (200-240 ºC), pressure (38-50 bar), glycerol concentration (10-50 wt.%) and mass of catalyst/ glycerol mass flow rate ratio ($W/m_{glycerol}$ = 10-40 g catalyst min/g glycerol) during the aqueous phase reforming (APR) of a glycerol solution obtained from the production of biodiesel. The operating conditions exerted a statistically significant influence on the reforming results. Specifically, the global glycerol conversion and the carbon converted into gas and liquid products varied as follows: 4-100%, 1-80% and 16-93%, respectively. The gas phase was made up of H_2 (8-55 vol.%), CO_2 (34-66 vol.%), CO (0-4 vol.%) and CH_4 (6-45 vol.%). The liquid phase consisted of a mixture of alcohols (monohydric: methanol and ethanol; and polyhydric: 1,2-propanediol, 1,2-ethanediol, 2,3-butanediol), aldehydes (acetaldehyde), ketones (C3-ketones: acetone and 2-propanone-1-hydroxy; C4-ketones: 2-butanone-3-hydroxy and 2-butanone-1-hydroxy; and cyclic ketones), carboxylic acids (acetic and propionic acids) and esters (1,2,3-propanetriol-monoacetate), together with unreacted

glycerol and water. The relative amount (free of water and un-reacted glycerol) of these compounds in the liquid phase was as follows: monohydric alcohols: 4-47%, polyhydric-alcohols: 14-68%, aldehydes: 0-5%, C3-ketones: 2-33%, C4-ketones: 0-10 %, ciclo-ketones: 0-6%, carboxylic acids: 2-43%, and esters: 0-46%. This process turned out to be highly customisable for the valorisation of crude glycerol for the production of either gaseous or liquid products. Gas production is favoured at a low pressure (39 bar), high temperature (238 ºC), high $W/m_{glycerol}$ ratio (38 g catalyst min/g glycerol) and employing a 15 wt.% glycerol solution. A high pressure (45 bar), medium temperature (216 ºC), medium $W/m_{glycerol}$ ratio (22 g catalyst min/g glycerol) and the feeding of a 16 wt.% glycerol solution favours the production of liquid products.

Keywords: crude glycerol, aqueous phase reforming, value-added liquids, gas production, renewable hydrogen

1. Introduction

Worldwide biodiesel production is increasing intensely as a result of widespread environmental concerns and firmer regulations for fuels. This biofuel is commonly produced by the transesterification of triglycerides using an alcohol in the presence of a catalyst. Unfortunately, despite the environmental benefits of biodiesel, its production originates glycerol as a by-product: 1 kg of crude glycerol is yielded with the production of 10 kg of biodiesel. This scenario could create a surplus of crude glycerol unable to be absorbed by its current market, which may cause economic and environmental problems, hampering the development of the biodiesel industry [1].

Given this background, two main options are usually considered to deal with this biodiesel-derived glycerol. The first consists of its purification for further use in other industries such as the food, cosmetics and pharmaceutical sectors [1, 2]. The second option consists of upgrading the crude glycerol employing different valorisation routes. These include gasification, steam reforming, aqueous phase reforming and supercritical reforming, among others [3, 4], allowing the production of different value-added chemicals and/or energy, and thus improving biodiesel economy and sustainability [5, 6].

The glycerol discharged from biodiesel production plants consists not only of glycerol but also of many other chemicals [1], which can significantly reduce the yields and efficiencies of the valorisation processes. Therefore, an intermediate option that includes a first purification of the crude glycerol up to an appropriate level for use in the subsequent valorisation processes should be addressed. This pre-treatment helps to reduce troublesome impurities such as fatty acid methyl esters (FAMES) and soaps. A

cost-effective purification method consists of the physical separation of the FAMES and the elimination of the soaps by an initial acidification, normally with acetic, sulphuric or phosphoric acid, and a subsequent liquid-liquid extraction with a polar solvent [1]. This pre-treatment using acetic acid provides a glycerol solution with 85-90% purity, which still contains some of the acid used in the neutralization, part of the catalyst employed in the biodiesel production (usually KOH or NaOH) as well as the alcohol used during the transesterification reaction and/or in the purification step.

A promising strategy to obtain value-added chemicals from this biodiesel derived glycerol is aqueous phase reforming (APR). APR is a catalytic process carried out at quite low temperatures and moderate pressures, allowing the production of different chemicals (gases and liquids) from an organic feedstock. During the APR of glycerol, various liquid-gas-solid chemical reactions take place. These include cracking and reforming reactions to generate hydrogen, dehydrogenation of alcohols/hydrogenation of carbonyls, deoxygenation and hydrogenolysis as well as cyclisation reactions. The gas phase consists of a gas with a high H_2 content, the liquid phase being a complex mixture of different organic compounds in water. These include alcohols, ketones, acids, esters, paraffins, aldehydes and other oxygenated hydrocarbons with different compositions depending on the operating conditions of the process and the nature of the feed [6-9]. The versatility of this valorisation process allows the customised conversion of glycerol into chemicals of a different nature to suit the necessities of the market, thus converting this process into a very promising tailor-made route for the treatment and valorisation of the glycerol obtained from the biodiesel industry.

Works dealing with the aqueous phase reforming of crude glycerol are extremely scarce

[7, 9-11] and the vast majority of the publications in the literature are focused on understanding the effect of the catalyst type and the operating conditions during the APR of reagent-grade glycerol. The catalysts used in the process are noble metals based on Pt [11-16], Ni [11, 12, 16-20], Pt-Ni, Cu, Co or Ru [9, 12, 16, 18, 21] supported on different oxides such as Al_2O_3, ZrO_2, MgO, SiO_2, CeO_2, or carbon [7, 22] and modified, in some cases, with promoters such as La, Ce, Mg and Zr.

The influence of the operating variables on the process has been studied in some works. Özgür et al. [14] studied the effect of the temperature (160-280 ºC), flow rate (0.05-0.5 mL/min), pressure (0-75 atm) and glycerol concentration (5-85 wt.%). The optimum temperature for hydrogen production was 230 ºC and the maximum gas production rate was found using feed flow rates of 0.1 mL/min. In addition, they reported that the hydrogen concentration in the gas increased with decreasing the glycerol concentration of the feed. Wawrzetz et al. [23] reported the effect of the glycerol concentration (10-30 wt.%) and pressure (26-45 bar) at 498 K. Reaction rates increased with the increase in the glycerol concentration. The pressure was found to have a significant effect on the liquid product distribution without affecting the global conversion of the process.

Roy et al. [21] investigated the effect of the initial pressure (0-41 bar of N_2) at 493 K using a 9.2 wt.% glycerol solution in a batch reactor, initially fed with 3 g of glycerol and 0.125 g of catalyst, for 6 h. An increase in the initial pressure up to 14 bar of N_2 augmented the glycerol conversion from 43.2 to 50.2%, while a further increase up to 41 bar decreased the glycerol conversion. The product distribution was not greatly affected by the pressure. An increase in temperature from 473 to 523 K at 14 bar of N_2 raised the glycerol conversion from 20.6 to 82.6%, reduced the proportion of ethylene

glycol and increased the concentration of ethanol in the liquid.

Manfro et al. [19] used a batch reactor to study the effect of the glycerol concentration (1-10 wt.%), temperature (523-543 K) and its corresponding pressure (37-52 atm). The highest glycerol conversion (30%) was achieved at 543 K using a 1 wt.% glycerol solution. An increase in the glycerol concentration decreased the glycerol conversion and H_2 formation. A rise in the temperature and pressure increased the glycerol conversion and decreased the proportion of H_2 in the gas. Luo et al. [24] reported the effect of the temperature (180-220 ºC) and its corresponding pressure (1.14 -2.5 MPa), glycerol concentration (5-10 wt.%) and liquid hourly space velocity (1.56-3.12 h^{-1}) in a flow reactor. An increase in temperature (and its corresponding pressure) facilitated the reforming process and increased the hydrogen yield. The carbon conversion to gas and the H_2 yield decreased with augmenting the glycerol concentration. Decreasing the hourly space velocity resulted in a higher hydrogen yield, hydrogen selectivity and carbon conversion to gas.

Seretis and Tsiacaras [25, 26] studied the effect of the reaction time (30-240 min), temperature (200-240 ºC), glycerol concentration (1-10 wt.%) and catalyst weight using a Ni/SiO_2-Al_2O_3 catalyst (0.5-10 g) [25] and a Pt/Al_2O_3 catalyst (0.5-2.5 g) [26]. The glycerol conversion increased with increasing the reaction time and temperature. The H_2 production was maximised with the use of short reaction times and low glycerol concentrations. An increase in the amount of catalyst increased the C-C cleavage, favouring the formation of ethylene glycol, ethanol and methane. When using the Ni/SiO_2-Al_2O_3 catalyst, the highest conversions to gaseous and liquid products were 74

and 36%, respectively, while for the Pt/Al_2O_3 catalyst they were 41 and 39%, respectively.

The large number of operating variables significantly influencing the process increases its intrinsic complexity. Some interactions between some of the operating variables can occur so that the effects of some variables may depend on others, resulting in different consequences for the process. These interactions have never been considered in the parametric studies reported in the literature, and they could be responsible for some of the contradictory results reported. In addition, the effect of the operating conditions on the production and selectivity to the different liquid products is not yet well understood; therefore, an in-depth study is needed for gaining a better understanding of this process.

Given this background, this work addresses the effect of the temperature (200-240 ºC), pressure (38-50 bar), glycerol concentration (10-50 wt.%) and $W/m_{glycerol}$ ratio (10-40 g catalyst min/g glycerol) on the aqueous phase reforming process of biodiesel-derived glycerol using a Ni-based catalyst. Optimal values for the production of gas and liquid products were also sought for their selective production.

2. Material and methods

2.1 Crude glycerol

The crude glycerol used for this work was obtained from the transesterification of sunflower oil with methanol, employing potassium hydroxide as a catalyst. The characterisation results of the crude glycerol, including the Total Organic Carbon (TOC), density, viscosity, pH and chemical composition, are listed in Table 1. The

chemical composition was calculated by means of a Gas Chromatography-Mass Spectrometry analysis, Karl Fischer titration and ash content. The GC-MS analysis of the glycerol also revealed the presence of a small proportion of some FAMES (linoleic, palmitic, oleic and stearic). The properties of this crude glycerol are consistent with those reported in other works in the literature [27-29].

Table 1. Properties of the crude and purified glycerol solutions. Results are presented as mean ± standard deviation.

	Crude glycerol	**Purified glycerol**
Composition		
Glycerol (wt.%)	63.17±2.26	85.25±0.79
CH_3OH (wt.%)	34.37±2.13	6.03±0.17
CH_3COOH (wt.%)	0	3.94±0.86
Ashes (wt.%)	2.06± 0.23	4.56± 0.37
H_2O (wt.%)	1.63±0.02	1.38±0.002
Ultimate Analysis		
C (%)	40.48±0.29	36.33±0.65
H (%)	8.19±0.06	7.55±0.03
O (%)[a]	51.33±0.34	56.11±0.63
TOC (ppm)	404733±2850	363333±6536
Physical properties		
pH	13.1±0.3	6.0±0.3
Density (g/mL)	1.060±0.001	1.043±0.001
Viscosity (mPa s)	49.93±1.48	247.41±3.93
LHV (MJ/kg)	21.89±0.05	16.96±0.03

[a] Determined by difference

The crude glycerol was neutralised with acetic acid using a final pH of 6. Acetic acid was selected for the glycerol purification as its presence in the refined glycerol solution can contribute to H_2 formation, without deactivating the catalysts used in APR as occurs when using H_2SO_4 due to the presence of S. In addition, the work of Manosak et al. [1] indicates that this acid is suitable for the purification of glycerol obtained from the biodiesel industry.

The glycerol was then subjected to a vacuum distillation where acetic acid and methanol were recovered for further use in the subsequent neutralisation and purification steps. This strategy improves the economics of this purification-valorisation process. As a result of this two-step strategy, a rich glycerol solution was obtained and used for the aqueous phase reforming experiments. The characterisation results of the rich glycerol phase (Table 1) reveal a significant increase in the glycerol purity (up to 85 wt.%) and a decrease in the concentration of methanol. Additionally, an increase in the viscosity and a decrease in the LHV of the glycerol solution also occur as a result of the reduction in the methanol and FAMES contents in the solution.

As listed in Table 1, the glycerol used in this work also contains CH_3COOH, CH_3OH, KOH and H_2O as major impurities. For better readability, the glycerol solutions are only defined by indicating their glycerol concentrations throughout the text, although they contain the corresponding amounts of impurities resulting from the dilution of the glycerol solution in water.

2.2 Experimental system

The experiments were carried out in a small bench scale continuous unit employing a NiAlLa catalyst. A reaction time of 3 hours was selected in order to be able to analyse the evolution over time of the gas and liquid phases while also studying the stability of the catalyst in the process [30-33]. The catalyst was prepared by coprecipitation, having a 28% (relative atomic percentage) of Ni expressed as Ni/(Ni+Al+La), an atomic La/Al ratio of 0.035 and a BET surface area of 187 m^2/g. The experimental ring used in the experiments was a microactivity unit designed and built 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 means of an electric furnace [33]. The system pressure is reached with the aid of a micrometric valve which automatically adapts its position with the help of a rotor. A pressure gauge, located at the exit of the reactor, measures the pressure of the reaction section. A PDI control system is used to keep the reactor pressure constant during the experiments. The aqueous solutions of crude glycerol are fed into the reactor by means of a high performance liquid chromatography (HPLC) pump. The reaction products (gas and liquids) and the unreacted glycerol leave the reactor from its upper part, pass through the valve, where they are depressurised, and arrive at the condensation system. This system consists of four different condensers where the liquid products are separated from the gas mixture at intervals of 1 h to analyse the evolution over time of the liquid phase. The gas mixture is made up of N_2, used as an internal standard, and the different gaseous products formed during the aqueous phase reforming reaction. A micro chromatograph equipped with thermal conductivity detectors (TCD) was used for the online analysis of the gas phase. At the end of the experiment the liquid fractions were collected and analysed offline with a gas chromatograph equipped with Flame Ionization (FID), and Mass Spectrometry (MS) detectors. A schematic diagram of the experimental system is shown in Figure 1.

2.3 Operating conditions, response variables and statistical analyses

The effect of the temperature (200-240 ºC), pressure (38-50 bar), glycerol concentration (10-50 wt.%) and catalyst mass/glycerol mass flow rate ratio (10-40 g catalyst min/g glycerol) was experimentally analysed using a design of experiments (DOE) with statistical analysis of the results carried out by means of an analysis of variance (ANOVA).

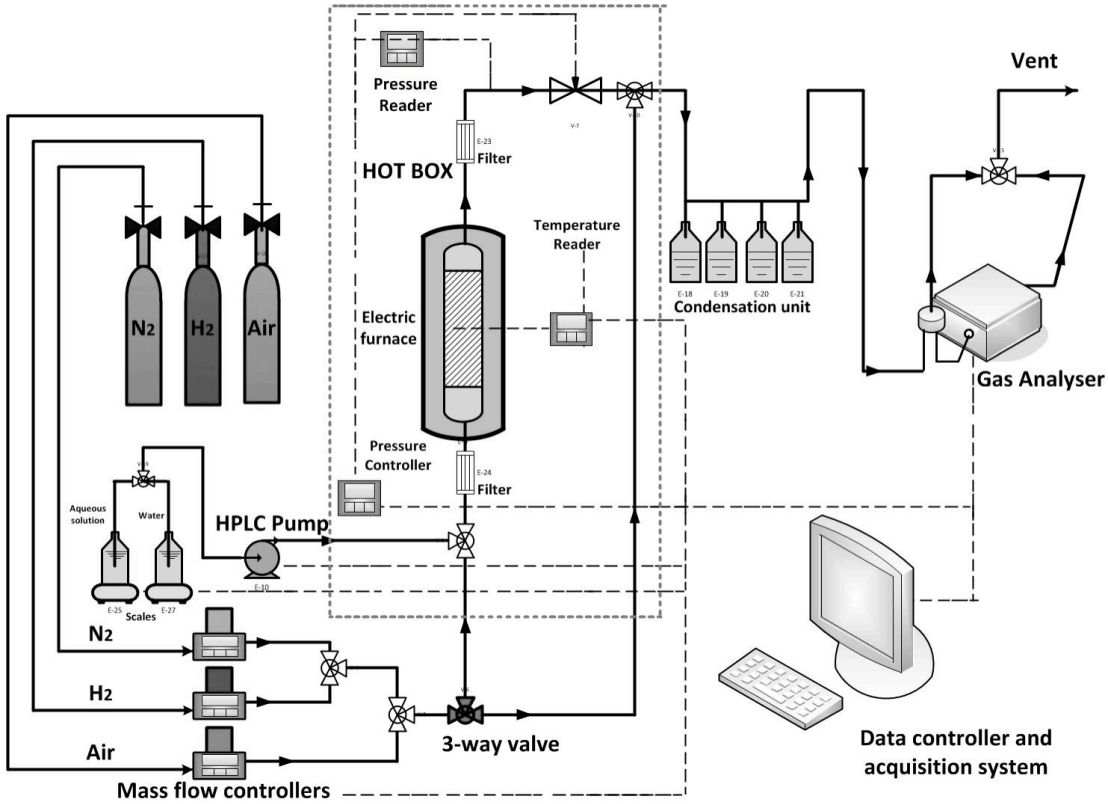

Figure 1. Schematic diagram of the aqueous phase reforming experimental rig.

The experiments were designed using a 2^k factorial design, where k indicates the number of factors studied (in this case 4 operating conditions) and 2^k represents the number of runs (in this case 16). In addition, 4 replicates at the centre point (centre of the variation interval of each factor) were carried out in order to evaluate both the experimental error and the curvature shown by the evolution of each variable, i.e. whether or not this evolution is linear within the experimental range studied. This factorial design minimises the number of experiments needed to understand the effect on the process of the operating variables and the interactions between them. As the response variables did not show a linear trend, this design was increased with 8 axial runs following a Box-Wilson Central Composite Face Centred (CCF, α: ± 1) design,

enabling the operating variables and interactions responsible for the curvature to be identified without modifying the range of study initially considered for the operating variables. The values for the operating conditions employed in the experiments according to this experimental design are listed in Table 2. The lower and upper limits of all the operating variables were normalised from -1 to 1 (codec factors). This codification enables all factors to vary within the same interval and helps to identify their influence in comparable terms.

Table 2. Operating conditions employed in the experiments

Run	**Glycerol (wt.%)**		**Pressure (bar)**		**Temperature (ºC)**		**Wcatalyst/$m_{glycerol}$ (g cat min/g glycerol)**	
	Actual	codec	actual	codec	actual	codec	Actual	codec
1	10	-1	38	-1	200	-1	10	-1
2	10	-1	38	-1	240	1	10	-1
3	10	-1	50	1	200	-1	10	-1
4	10	-1	50	1	240	1	10	-1
5	50	1	38	-1	200	-1	10	-1
6	50	1	38	-1	240	1	10	-1
7	50	1	50	1	200	-1	10	-1
8	50	1	50	1	240	1	10	-1
9	10	-1	38	-1	200	-1	40	1
10	10	-1	38	-1	240	1	40	1
11	10	-1	50	1	200	-1	40	1
12	10	-1	50	1	240	1	40	1
13	50	1	38	-1	200	-1	40	1
14	50	1	38	-1	240	1	40	1
15	50	1	50	1	200	-1	40	1
16	50	1	50	1	240	1	40	1
17* (17,18,19, 20)	30	0	44	0	220	0	25	0
21	30	0	44	0	200	-1	25	0
22	30	0	44	0	240	1	25	0
23	30	0	38	-1	220	0	25	0
24	30	0	50	1	220	0	25	0
25	10	-1	44	0	220	0	25	0
26	50	1	44	0	220	0	25	0
27	30	0	44	0	220	0	10	-1
28	30	0	44	0	220	0	40	1

The effect of the operating conditions on the process was analysed for the following response variables: global glycerol conversion (X gly, %), carbon conversion to gas, liquid and solid products (CC gas %, CC liq %, and CC sol %) as well as the composition of the gas (N_2 and H_2O free, vol.%) and liquid (relative chromatographic area free of water and un-reacted glycerol, %). Table 3 summarises the response variables and the analytical methods used for their calculation.

Table 3. Response variables. Definitions and analytical techniques used in their determination.

Product	Response variable	Analytical method
Gas	$\text{CC gas (\%)} = \frac{\text{C in the gas (g)}}{\text{C fed (g)}} 100$	Micro Gas Chromatograph (Micro GC). N_2 as internal standard
	$\text{Composition (vol.\%)} = \frac{\text{mol of each gas}}{\text{total mol of gas}} 100$	Online analyses
Liquid	$\text{CC liq (\%)} = \frac{\text{C in the liquid products (g)}}{\text{C fed (g)}} 100$	Total Organic Carbon (TOC)
	$\text{Composition (area \%)} = \frac{\text{area of each compound}}{\text{total area}} 100$	GC-MS (Gas Chromatography-Mass Spectrometry)
	$\text{X gly (\%)} = \frac{\text{glycerol fed (g)} - \text{glycerol in the liquid (g)}}{\text{glycerol fed (g)}} 100$	GC-FID (Gas Chromatography-Flame ionization detector)
		Offline analyses
Solid	$\text{CC sol (\%)} = 100 - \text{CC gas (\%)} - \text{CC liq}^{*}\text{ (\%)}$	

CC liq = Carbon conversion to liquid products (unreacted glycerol free).
CC liq* = Carbon conversion to liquids including unreacted glycerol

Some of the used catalysts were characterised by X-Ray diffraction (XRD) and Thermogravimetric (TG) analyses. XRD patterns of the used catalysts were obtained with a D-Max Rigaku diffractometer equipped with a CuK α1.2 at a tube voltage of 40 kV and current of 80 mA. The measurements were carried out using continuous-scan mode with steps of 0.03°/s at Bragg's angles (2θ) ranging from 5° to 85°. The phases present in the samples were defined with reference to the JCPDS-International Centre for Diffraction Data 2000 database. TG analyses were conducted under a N_2 atmosphere, increasing the temperature from room temperature (around 25 ºC) to 600

ºC at a heating rate of 10 ºC/min. The weight loss was measured and the conversion (X), defined as the variation of the mass with the respect to the initial sample mass, was calculated.

First of all, the evolution over time of the response variables was studied. For each experiment, the results are divided into three intervals. Each interval corresponds to the average value of the studied response variables obtained during each one of the three hours of experiment. All these values (three per experiment) have been compared using a one-way analysis of variance (one-way ANOVA) and Fisher´s least significant difference (LSD) test, both with 95% confidence. The results of the ANOVA analyses are provided as p-values. P-values lower than 0.05 indicate that at least two values are significantly different. Furthermore, the LSD test was used to compare pairs of data, i.e. either between two intervals of the same experiment or between two intervals of two different experiments. The results of the LSD tests are presented graphically in the form of LSD bars. To ensure significant differences between any pairs of data, their LSD bars must not overlap.

Secondly, the effect of the operating conditions was studied considering the results corresponding to the first hour using a statistical analysis of variance (one-way ANOVA) test with 95% confidence. This strategy allows not having to include the effect of the variations with time of the different response variables in the analysis. In addition, the cause-effect Pareto principle was used to calculate the relative importance of the operating variables on each response variable.

2.4 Possible reaction network during the aqueous phase reforming of glycerol

A plausible reaction pathway for the aqueous phase reforming of glycerol is shown in Figure 2. The reaction network includes the formation of gases and liquid products. Three possible parallel routes explain the formation of intermediate liquids: glycerol dehydration to 1-hydroxypropan-2-one (A) [6, 7, 21, 23, 34-36] and/or to 3-hydroxypropanal (B) [6, 23, 35, 36] and/or glycerol dehydrogenation to 2,3-dihydroxypropanal (C) [6, 7, 21, 23, 34-36]. Gases, mainly H_2 and CO, are produced by the thermal decomposition and/or reforming reactions of the glycerol and all the liquid intermediates (Eq.1) as well as by all the decarbonylation reactions that release CO. In addition, the water gas shift reaction (Eq.2) and methanation reactions (Eq.3-4) are also possible, explaining the presence of CO_2 and CH_4 in the gas phase [6, 7, 21, 23, 34-36].

$$C_nH_mO_k + (n-k)\ H_2O \Leftrightarrow n\ CO + (n+m/2 - k)\ H_2 \qquad \text{(Eq.1)}$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad \text{(Eq.2)}$$

$$CO + 3\ H_2 \Leftrightarrow CH_4 + H_2O \qquad \text{(Eq.3)}$$

$$CO_2 + 4\ H_2 \Leftrightarrow CH_4 + 2\ H_2O \qquad \text{(Eq.4)}$$

2.4.1 Formation of products via 1-hydroxypropan-2-one: route A

1-hydroxypropan-2-one can undergo further hydrogenation to produce propane-1,2-diol [6, 7, 23, 35, 36] (the preferred and most reported route) and/or dehydration to form acryaldehyde [35], which can be transformed into propionic acid [35]. Propane-1,2-diol can subsequently be dehydrated to form propan-2-one and/or propionaldehyde, which can be hydrogenated to propan-2-ol and propan-1-ol, respectively [35]. Afterwards,

these two chemicals can be further transformed into light alkanes, such as butane and propane [6, 23, 35, 36]. Ethanol might be formed from the hydrogenation of propan-2-ol [6].

2.4.2 Formation of products via 3-hydroxypropanal: route B

The presence of 3-hydroxypropanal in the liquid product has not been detected in the vast majority of works dealing with the aqueous phase reforming of glycerol. This indicates that dehydration forming 1-hydroxypropan-2-one is more likely to occur and/or that 3-hydroxypropanal may be instantaneously converted into other products in subsequent reactions. These reactions produce 3-hydroxypropionic acid, acetaldehyde and formaldehyde via the retro-aldol reaction [35], and/or propane-1,3-diol [34, 35] via hydrogenation. Propane-1,3-diol can be further dehydrated to produce propionaldehyde [35].

2.4.3 Formation of products via 2,3-dihydroxypropanal: route C

2,3-dihydroxypropanal can be transformed into 2,3-dihydroxypropionic acid, dehydrated to form 2-oxopropanal and/or decarbonylated to produce ethane-1,2-diol. Subsequently, 2-oxopropanal can be further hydrogenated to form propane-1,2-diol. Additionally, 2-hydroxyacetaldehyde can be obtained from the dehydrogenation of the latter and might lead to the formation of methanol by decarbonylation [6, 7]. In addition, acetaldehyde and ethanol can be produced from the dehydration and the dehydration/hydrogenation of ethane-1,2-diol, respectively [6, 7, 23]. Acetaldehyde can subsequently be transformed into acetic acid and/or methane, while light alkanes such

as ethene and ethane can be produced from ethanol [6, 7, 23].

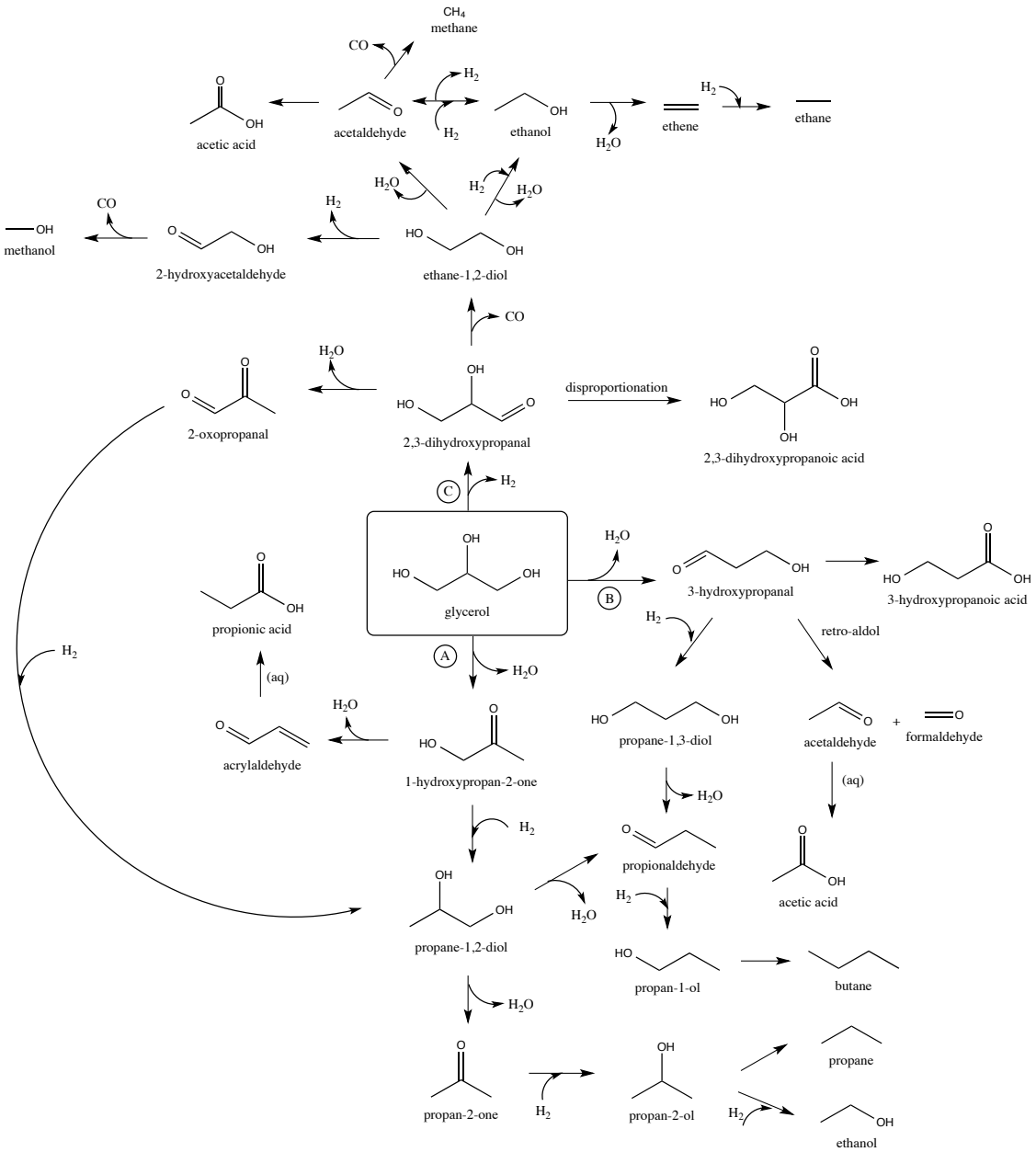

Figure 2. Possible reaction pathways during the aqueous phase reforming of glycerol.

3. Results and discussion

3.1 Carbon distribution and global glycerol conversion

Figure 3 displays the carbon conversion to gas and liquid (CC gas, CC liq) as well as the global glycerol conversion (X gly) obtained in the experiments. The statistical analysis reveals significant differences between the results obtained in the experiments for the CC gas, CC liq and X gly (p-values < 0.001). Specifically, they vary by 1-80%, 16-93% and 4-100%, respectively. The effect of the operating variables on the CC sol was not significant (p-value > 0.05); in all the experiments the CC sol was lower than 1.5 %. The evolution over time of these variables shows drops in the X gly together with increases and decreases in both the CC gas and the CC liq. These variations indicate the existence of changes in the product distribution as the reaction advances and/or that a catalyst deactivation may have taken place.

Significant drops in the CC gas occurred in experiments 6, 8, 12, 16, 22, 24, 26 and 28, which were conducted at temperatures higher than 220 ºC and where initially relatively high amounts of CC gas (>20 %) were obtained. In addition, the greatest drops for this variable are observed for the experiments employing $W/m_{glycerol}$ ratios higher than 25 g catalyst min/g glycerol. This variation is particularly marked for experiments 12 and 16, where the highest temperature (240 ºC), pressure (50 bar) and $W/m_{glycerol}$ ratio (40 g catalyst min/g glycerol) were employed. These two experiments display both the highest initial CC gas (greater than 65%) and the biggest drop in this variable. The X gly remained constant over time while an increase in the CC liq is observed for both experiments.

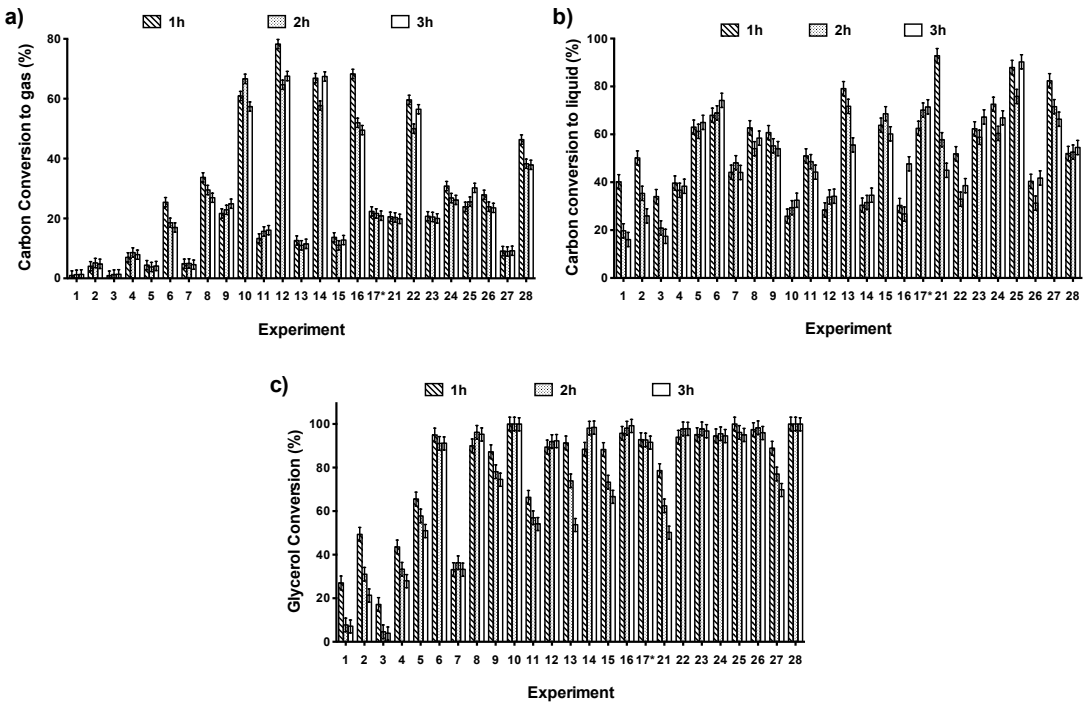

Figure 3. Conversion to gas (a), liquid (b) and global glycerol conversion (c) obtained during the APR experiments. Results are presented as the overall values obtained every 60 minutes and expressed as mean ± 0.5 Fisher LSD intervals with 95% confidence.

These variations might indicate a change in the product selectivity over time. The production of gases is highly favoured during the first reaction steps due to a substantial extension of all the reactions involved in the process: cracking and reforming reactions of glycerol, reactions to produce intermediate liquids as well as all the reforming reactions of these intermediates towards gas production. This is consistent with the work of Wawrzetz et al. [23], which demonstrated that the formation of H_2 and CO_2 via dehydrogenation followed by decarbonylation with the subsequent water gas shift is one of the fastest reactions in this process. The progressive deactivation of the catalyst over time could lead to the reforming reactions occurring to a lesser extent, decreasing the CC gas and augmenting the CC liq [23]. These trends also apply to experiments 6 and 8. However, lesser decreases over time for the CC gas are observed and the increase in the

CC liq does not occur in experiment 8, probably due to the lower $W/m_{glycerol}$ ratio employed. High $W/m_{glycerol}$ ratios and elevated temperatures might favour the initial formation of gases and consequently the drop observed in the gas production over time is sharper. These phenomena were also observed by El Doukkali et al. [37], who reported a decrease and an increase over time in the production of gas and liquid products, respectively, due to the progressive deactivation of the catalyst when employing a Ni/Al_2O_3 catalyst for the APR of glycerol. This deactivation was the consequence of the transformation of the alumina of the support into boehmite [37].

Conversely, when lower $W/m_{glycerol}$ ratios are employed (25 g catalyst min/g glycerol), the drop in the CC gas is less pronounced (experiments 24 and 26). In these conditions, the production of intermediate liquid products is more favoured than the formation of gases, as the amount of catalyst in the bed is not high enough for their complete transformation to gases. Lower initial amounts of CC gas are obtained compared with experiments using higher $W/m_{glycerol}$ ratios. The CC liq remains steady over time and a smaller decrease in the CC gas occurs.

The CC liq displays increases and decreases over time. Increases occur in experiments 6, 12 and 16. These trends have been explained above for the evolution of the CC gas over time. Decreases over time are observed for experiments 1, 2, 3, 21, 22, 24 and 27, which were conducted with $W/m_{glycerol}$ ratios from 10 to 25 g catalyst min/g glycerol and glycerol concentrations lower than 30 wt.%. Additionally, the temperature exerts a significant influence on the evolution of the CC liq with time. The lower the temperature, the greater is the drop over time for this variable. Therefore, the greatest

drops were observed for the experiments conducted at 200 ºC (1, 3, 13 and 21). An increase in the $W/m_{glycerol}$ ratio exerts an effect on the kinetic of the process, increasing the reaction rate of reactions leading to the formation of liquid products. This circumstance can partially compensate for the deactivation of the catalyst, as can be observed comparing experiments 1 with 9 and 3 with 11.

The evolution of the X gly over time displays significant decreases for experiments 1-5, 9, 11, 13, 15, 21 and 27. These drops can be accounted for by the use of either a low temperature or a low $W/m_{glycerol}$ ratio. Experiments 1-5 were conducted with the lowest $W/m_{glycerol}$ ratio employed in this work (10 g catalyst min/g glycerol). Here neither the temperature nor the pressure exerts a significant influence on the X gly evolution with time. Conversely, for the same conditions of temperature and pressure but employing a $W/m_{glycerol}$ ratio of 40 g catalyst min/g glycerol (runs 9-13), drops over time were only appreciated at 200 ºC (runs 9, 1, 13 and 15). These results seem to indicate that the catalyst deactivation could be more favoured at a low temperature and/or that the positive kinetic effect of the temperature is able to partially compensate for catalyst deactivation.

Very interestingly, it is observed that an increase in the glycerol concentration diminishes the deactivation of the catalyst, especially at low temperatures. Comparing the experiments conducted with low (1-4) and high (5-8) glycerol concentrations, a higher decrease in the evolution of the X gly over time takes place for the former than for the latter. This result indicates that the greater the amount of water, the greater the catalyst deactivation. Under the operating conditions of the APR process, the alumina of

the catalyst support can be transformed into boehmite by water. This transformation is enhanced employing high water concentrations, which might cause the catalyst deactivation to be greater [16, 24, 37].

To corroborate this hypothesis, the spent catalysts for runs 3 and 4 (10 wt.% glycerol) and 7 and 8 (50 wt.% glycerol) were characterised by XRD and TG analyses. Figures 4 a and b and Figures 4 c and d show the XRD patterns and TG results of the used catalysts, respectively. The XRD patterns have wide and asymmetric peaks, which denote quite low crystallinity, and indicate the presence of Ni, $NiAl_2O_3$ and boehmite (AlO(OH)) in the four used catalysts. This finding confirms that under the operating conditions of APR, the alumina of the support can be transformed in boehmite. In addition, C and $LaCO_3OH$ are present in some of the samples. The TG analysis displays four decomposition steps (25-166 ºC; 166-247 ºC; 247-362 ºC and 362-600 ºC), which correspond to the decomposition of boehmite into alumina. At constant heating rates this decomposition can be accurately modelled by a 4-reaction mechanism [38-40] involving: (I) the loss of physisorbed water, (II) the loss of chemisorbed water, (III) the conversion of boehmite into transition alumina, and (IV) the dehydration of transition alumina (loss of residual hydroxyl groups). The experimental temperature ranges for the decomposition of the used catalysts are fairly similar to those reported for the decomposition of pure boehmite; the small differences being the consequence of having incorporated different metals on the structure [40]. Very interestingly, a greater mass loss occurs for runs 3 and 4 (conducted using a 10 wt.% glycerol solution) than for 7 and 8 (conducted using a 50 wt.% glycerol solution). The greatest differences in terms of mass loss between the former and the latter occur between 166 and 362 ºC, which indicates the greater presence of physisorbed water in the structure of the catalyst along

with a larger transformation of the alumina of the support into boehmite during the APR reaction. This accounts for the higher deactivation observed with the 10 wt.% than with the 50 wt.% glycerol solutions.

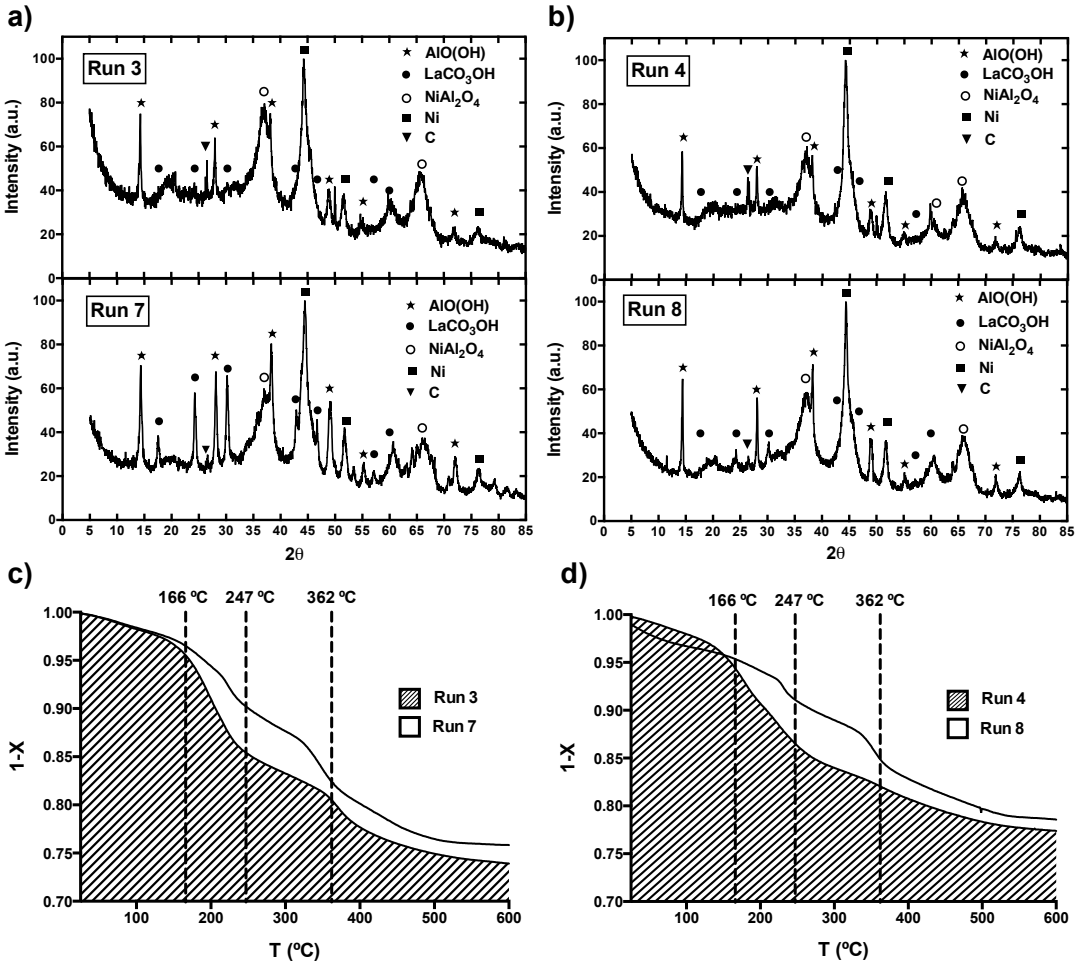

Figure 4. XRD patterns (a and b) and TG analysis (c and d) for the used catalysts employed in runs 3 and 4 (10 wt.% glycerol) and 7 and 8 (50 wt.% glycerol)

The specific effect of the operating conditions as well as their possible interactions on the process has been studied considering the results obtained during the first hour of reaction. The models created in terms of codec factors considering the ANOVA analysis

are shown in Table 4. The CC gas is strongly affected by the temperature, the $W/m_{glycerol}$ ratio and an interaction between these two variables. An increase in these two variables increases the CC gas. The temperature, glycerol concentration, $W/m_{glycerol}$ ratio and their interactions are the operating variables with the greatest effect on the CC liq. For this variable some quadratic terms of the temperature exert a high influence, which indicates the existence of maxima and minima within the range of temperatures considered in this work. The glycerol conversion is greatly affected by the temperature, the $W/m_{glycerol}$ ratio and the interaction between these two variables. The CC sol was lower than 1.5 % in all cases and the effect of the operating variables on the CC sol is not significant with 95% confidence.

Significant interactions between the operating variables also influence the CC gas, CC liq and X gly, as can be appreciated from the models displayed in Table 4. Figure 5 illustrates the effect of these interactions according to the ANOVA analysis. Figures 5 a and b, e and f, and i and j show the effects on the CC gas, CC liq and X gly of the reaction temperature, employing a pressure of 38 bar for $W/m_{glycerol}$ ratios of 10 and 40 g catalyst min/g glycerol, when feeding 10 and 50 wt.% glycerol solutions, respectively. Figures 5 c and d, g and h, and k and l display the effect of the temperature and the $W/m_{glycerol}$ ratio employing a pressure of 50 bar when glycerol solutions of 10 and 50 wt.%, respectively, were used. The most important effects and interactions of the operating variables on the CC gas, CC liq and X gly are discussed in sections 3.1.1, 3.1.2 and 3.1.3, respectively.

3.1.1 Carbon conversion to gas: CC gas

The CC gas is mainly affected by the temperature and $W/m_{glycerol}$ ratio. An increase in these two variables augments the CC gas due to the positive kinetic effect that both variables exert on the process [14, 19, 21, 23, 24]. At low temperatures, the production of gas is not favoured, since reforming and cracking reactions are not predominant. The prevailing chemical reactions lead to the formation of intermediate liquid products, since their formation is prevalent under low glycerol conversions [23]. Thus, between 200 and 220 ºC the CC gas is always lower than 30%, and the positive kinetic effect of the temperature within this temperature range is relatively low. Conversely, a further increase in temperature up to 240 ºC increases the CC gas very sharply, especially when using a $W/m_{glycerol}$ ratio of 40 g catalyst min/g glycerol, which permits the CC gas to reach 80% in some cases. Under this temperature range, reforming and cracking reactions of both glycerol and its intermediate liquid products might be more favoured.

The effect of the temperature also depends on the $W/m_{glycerol}$ ratio. This variable positively influences the CC gas due to its positive kinetic effect on cracking and reforming reactions. The higher the $W/m_{glycerol}$ ratio, the greater is the increase in the CC gas with temperature. This effect is especially marked when the highest value for this variable is employed (40 g catalyst min/g glycerol).

Table 4. Relative influence of the operating conditions on the CC gas, CC liq and X gly according to the ANOVA analysis for the first hour of reaction.

	R^2	Indep..	T	P	C	W	T·P	T·C	T·W	P·C	P·W	C·W	T^2	P^2	C^2	W^2	T·P·C	T·P·W	T·C·W	P·C·W	T^2·P	T^2·C	T^2·W	T·P^2	T·P·C·W
CC gas (%)	0.99	24.36	17.29	1.85	2.6	16.2	2.3	2.83	9.62	n.s	n.s	-4.26	10.12	-4.18	n.s	n.s	n.s	n.s	-2.25	n.s	n.s	n.s	n.s	n.s	-1.88
			(27)	(3)	(4)	(25)	(3)	(4)	(14)			(6)	(3)	(4)					(3)						(3)
CC liq (%)	1	67.06	-20.49	5.15	-23.77	-15.2	2.3	-1.05	-11.17	-0.98	1.14	-2.27	n.s	-3.65	-6.96	-3.91	1.29	1.14	-2.04	n.s	-9.11	30.74	13.18	14.21	-0.94
			(10)	(4)	(5)	(5)	(3)	(1)	(14)	(1)	(1)	(3)		(3)	(13)	(4)	(2)	(1)	(2)		(4)	(12)	(5)	(6)	(1)
X gly (%)	0.98	98.72	n.s	n.s	n.s	n.s	2.82	n.s	-5.91	n.s	n.s	-6.34	-10.96	-5.63	n.s	-6.7	n.s	n.s	-4.29	3.3	-5.3	11.98	19.4	10.96	n.s
							(3)		(6)			(7)	(7)	(3)		(14)			(5)	(4)	(6)	(13)	(21)	(12)	

n.s: Non significant with 95% confidence

Response = Indep. + Coefficient T·T + Coefficient P·P + Coefficient C·C + Coefficient W·W + Coefficient T·C·T·C + Coefficient T·W·T·W + Coefficient P·C·P·C + Coefficient P·W·P·W + Coefficient C·W·C·W + Coefficient T^2·T^2 + Coefficient P^2·P^2 + Coefficient C^2·C^2+ Coefficient W^2·W^2+ Coefficient T·P·C·T·P·C + Coefficient T·P·W·T·P·W + Coefficient T·C·W·T·C·W + Coefficient P·C·W·P·C·W + Coefficient T^2·P T^2·P + Coefficient T^2·C T^2·C + Coefficient T^2·W T^2·W + Coefficient T·P^2·T·P^2 + Coefficient T·P·C·W·T·P·C·W.

Numbers in brackets indicate the percentage Pareto influence of each factor on the response variable. Pareto values represent the percentage of the orthogonal estimated total value.

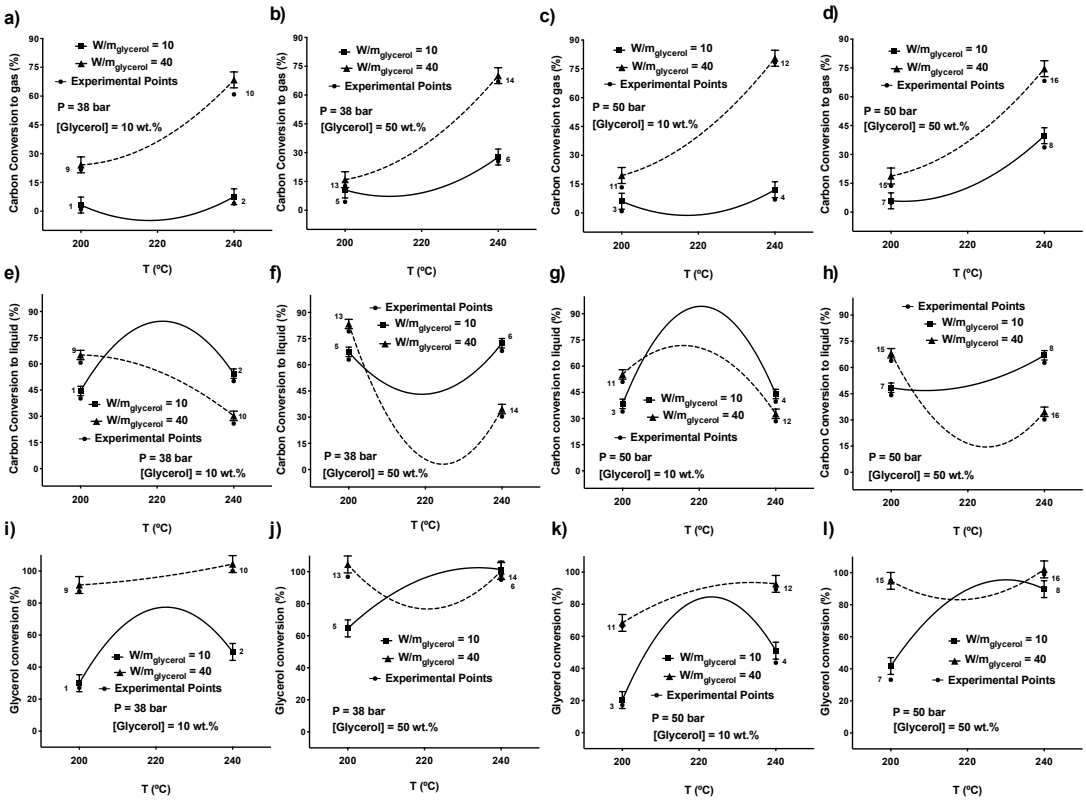

Figure 5. Interaction plots for the initial CC gas (a), CC liq (b) and global glycerol conversion (c). Bars are LSD intervals with 95% confidence.

The effects of the pressure and glycerol concentration on the CC gas are lower than the effect of the temperature, as previously explained using the Pareto analysis. This lower influence has also been reported by other authors [21, 23]. The influence of the pressure can be gathered comparing Figures 5 a and c and 5 b and d. This comparison illustrates that the effect of the pressure is only significant at high temperatures. For a 10 wt.% glycerol solution, an increase in pressure from 38 to 50 bar only increases the CC gas for a $W/m_{glycerol}$ ratio of 40 g catalyst min/g glycerol when using temperatures higher than 220 ºC. Conversely, when 50 wt.% glycerol is used, the same increment in pressure only exerts a significant influence on the CC gas at temperatures higher than 220 and employing a low spatial velocity (10 g catalyst min/g glycerol). In both cases, the effect of pressure is only significant when gas production is favoured. The pressure

exerts a significant influence on the kinetics of the process, since an increase in the total pressure of the system also increases the partial pressures of glycerol and its intermediates. This produces an increase in the reaction rates and consequently makes the effect of the glycerol concentration significant.

The increase in the glycerol partial pressure when the total pressure of the system is increased is lower for a 10 wt.% glycerol solution than for 50 wt.%. For a 10 wt.% solution this effect is only observed employing high $W/m_{glycerol}$ ratios, while for a 50 wt.% solution the increase in the CC gas only occurs for low $W/m_{glycerol}$ ratios. Under high pressure, the increase in the glycerol partial pressure is higher and the positive kinetic effect of the $W/m_{glycerol}$ ratio can mask the effect of the increase in the partial pressure. Consequently, this circumstance is only observed for low $W/m_{glycerol}$ ratios. An increase in the CC gas when increasing the total pressure of the system has also been reported in other works concerning the aqueous phase reforming of glycerol [15, 21, 41].

The effect of the glycerol concentration can be studied comparing Figures 5 a and b and 5 c and d. An increase in the glycerol concentration from 10 to 50 wt.% significantly influences the CC gas at 240 ºC when using a $W/m_{glycerol}$ ratio of 10 g catalyst min/g glycerol. The CC gas is little affected by the glycerol concentration and therefore this effect is only observed under low spatial time. At high spatial time the positive kinetic effect of the catalyst is higher than that of the glycerol concentration. Additionally, the increase in the CC gas when the glycerol concentration increases is greater at 50 than at 38 bar, since the increase in the glycerol partial pressure is also higher.

3.1.2 Carbon conversion to liquid products: CC liq

The temperature exerts two different effects on the CC liq depending on the glycerol concentration. For a 10 wt.% solution, in most cases the CC liq increases between 200 and 220 ºC and drops with a further increase in the temperature to between 220 and 240 ºC. The temperature exerts a kinetic effect on the process, augmenting the reaction rates of the reactions involved. At low temperatures (200-220 ºC) the positive kinetic effect helps to shift the reaction towards the formation of intermediate liquids, increasing the CC liq. Conversely, a further increase in temperature up to 240 ºC favours the transformation of these liquid products into gases, decreasing the CC liq. These results are in accordance with the reaction pathway of the process [6, 7, 21, 23, 34-36] and with the experimental observations reported in the work of Wawrzetz et al. [23], where the proportions of gas and liquid products augmented and dropped, respectively, as the glycerol conversion increased. An increase in the $W/m_{glycerol}$ ratio from 10 to 40 g catalyst min/g glycerol increases the CC liq between 200 and 210 ºC, where the formation of liquid products is more favoured, while at temperatures higher than 210 ºC it decreases the CC liq, as the catalyst favours the production of gas from glycerol and its intermediate products.

For a 50 wt.% glycerol solution, the CC liq generally diminishes with temperatures between 200 and 220 ºC and increases between 220 and 240 ºC. When a concentrated glycerol solution is employed, the partial pressure of the organics inside the reactor increases, and gas formation is more favoured, especially when using a $W/m_{glycerol}$ ratio of 40 g catalyst min/g glycerol. Thus, under these conditions an increase in temperature between 200 and 220 ºC decreases the CC liq and increases the CC gas. A further

increase in temperature up to 240 ºC increases the CC liq. This phenomenon will be further described below when explaining the effect of the total pressure. The effect of the $W/m_{glycerol}$ ratio displays the same trends as described for a 10 wt.% glycerol solution.

A comparison between Figures 5 e and f and 5 g and h illustrates the effect of the glycerol concentration. An increase in the glycerol concentration from 10 to 50 wt.% increases the partial pressure of the organics inside the reactor, increasing the reaction rate of the reactions involved in the process. At low temperatures (200-210 ºC), where liquid formation is favoured, an increase in the glycerol concentration increases the CC liq, while at high temperatures (210-230 ºC), where the formation of gases becomes predominant, the CC liq decreases. A rise in the CC liq is observed between 230 and 240 ºC, especially for low $W/m_{glycerol}$ ratios. This is a consequence of an increase in the global glycerol conversion due to the increase in the partial pressure of the organics inside the reactor and will be discussed when explaining the evolution of the X gly.

The influence of the pressure can be gathered comparing Figures 5 e and g and 5 f and h. The effect of the pressure on the CC liq is related to the glycerol concentration. For a 10 wt.% solution, an increase in the pressure from 38 to 50 bar has different effects depending on the temperature. Between 210 and 230 ºC, where the formation of liquid products is favoured, an increase in the CC liq occurs with an increase in the total pressure. Between 230 and 240 ºC the CC liq decreases due to gas formation. These results mean that at low temperature (200 ºC) liquid production is favoured under low pressure (38 bar). At medium temperature (220 ºC) liquid production is enhanced at high pressure (50 bar), while at high temperature (240 ºC) similar liquid production

occurs within the whole range of pressure when the greatest amount of catalyst is used ($Wm_{glycerol}$ = 40 g catalyst min/g glycerol). Conversely, for a $W/m_{glycerol}$ ratio of 10 g catalyst min/g glycerol, liquid production is favoured at low pressure (38 bar).

When a 50 wt.% glycerol solution is employed, the same increase in pressure decreases the CC liq from 200 to 220 ºC and increases it from 220 to 240 ºC. This increment is related to an increase in glycerol conversion. At 220 ºC the CC liq is greater at 50 than at 38 bar for a $W/m_{glycerol}$ ratio of 40 g catalyst min/g glycerol. The effect of the pressure is not significant under the following conditions: at 240 ºC regardless of the $W/m_{glycerol}$ ratio; and at 220 ºC when using a $W/m_{glycerol}$ ratio of 10 g catalyst min/g glycerol.

3.1.3 Global glycerol conversion: X gly

The global glycerol conversion is greatly affected by the reaction temperature especially when using a $W/m_{glycerol}$ ratio of 10 g catalyst min/ g glycerol. An increase in temperature between 200 and 220 ºC leads to an increase in glycerol conversion. The endothermicity of the aqueous phase reforming and the fact that the reaction rates of all the reactions involved in the process are intensified with temperature [14, 19, 21, 23, 24] accounts for this finding. Within this temperature range, the lower the $W/m_{glycerol}$ ratio, the higher is the increase in the conversion with temperature. These results indicate that the effect of the temperature is kinetically less important than the $W/m_{glycerol}$ ratio and that the catalyst is active even at low temperatures. A further increase in temperature up to 240 ºC produces different tendencies depending on the glycerol concentration. For a 10 wt.% solution, an increase in the temperature has two effects. On the one hand, employing 10 g glycerol min/g catalyst, the X gly drops with

the temperature. This low spatial time is insufficient for achieving the production of the H_2 needed for the extension of the hydrogenation reactions of the liquid intermediates. This accounts for the drop in the CC liq and the small increase in the CC gas that takes place under these conditions. On the other hand, when a spatial time of 40 g glycerol min/g catalyst is used, the X gly slightly increases with temperature. These results are in agreement with the high increase in the CC gas observed between 220 and 240 ºC.

Interestingly, the drop in the X gly disappears when a 50 wt.% glycerol solution is fed in the reactor. Between 220 and 240 ºC the X gly is very high and does not depend on the temperature. Additionally, the effect of the $W/m_{glycerol}$ ratio on the X gly becomes insignificant, indicating that it is possible to achieve high conversions with the lowest amount of catalyst employed. This increase in the glycerol concentration increases the partial pressure of all the organic species inside the reactor, raising the reaction rate of the reactions involved in the process.

The effect of the total pressure depends on the temperature. At low temperatures (200-220 ºC) where gas formation is not preferential, an increase in the total pressure of the system results in a drop in the X gly. This decrease is the consequence of the drop in the CC liq with pressure under this temperature range. Since the process is not shifted towards gas production, the negative effect of the pressure on the CC liq is greater than the positive effect on the CC gas, resulting in a drop in the global conversion (X gly). This phenomenon is not observed between 220 and 240 ºC because the gas production is preferential.

Other authors have also reported the different effects that pressure can have on the global glycerol conversion. This is explained by having used different temperatures, glycerol concentrations, catalysts and/or spatial velocities. Manfro et al. and Roy et al. [19, 21] reported an increase in glycerol conversion with pressure, while Wawrzetz et al. [23] found that the pressure had a significant effect on the liquid product distribution without affecting the global glycerol conversion.

3.2 Effect of the operating conditions on the volumetric composition of the gas

Figure 6 shows the composition of the gas obtained for the different experiments divided into three intervals of 60 minutes each. The gas phase is made up of a mixture of H_2 (8-55 vol.%), CO_2 (33-73 vol.%), CO (0-4 vol.%) and CH_4 (6-44 vol.%). The ANOVA analysis reveals significant differences between experiments and time intervals (p-values < 0.05). As regards the evolution of the gas composition over time, statistically significant increases and decreases are detected for the proportions of both H_2 and CH_4. The proportion of CO increases slightly in some experiments while the concentration of CO_2 remains relatively steady over time.

A drop in the proportion of H_2 together with an increase in the proportion of CH_4 takes place in experiments 2 and 3. These two experiments were conducted employing a low spatial velocity (10 g catalyst min/g catalyst) and feeding a glycerol solution of 10 wt.%. The high water content of the solution favours the transformation of alumina into boehmite, causing the deactivation of the catalyst [16, 24, 37]. The low $W/m_{glycerol}$ ratio employed and the catalyst deactivation helps to promote the methanation reaction. Experiments 14, 16, 22 and 28 display an increase in the proportion of H_2 as well as a

decrease in the proportion of CH_4. These experiments were conducted employing a high $W/m_{glycerol}$ ratio (25-40 g catalytst min/g glycerol), a high glycerol concentration (30-50 wt.%) and a high temperature (220-240 ºC).

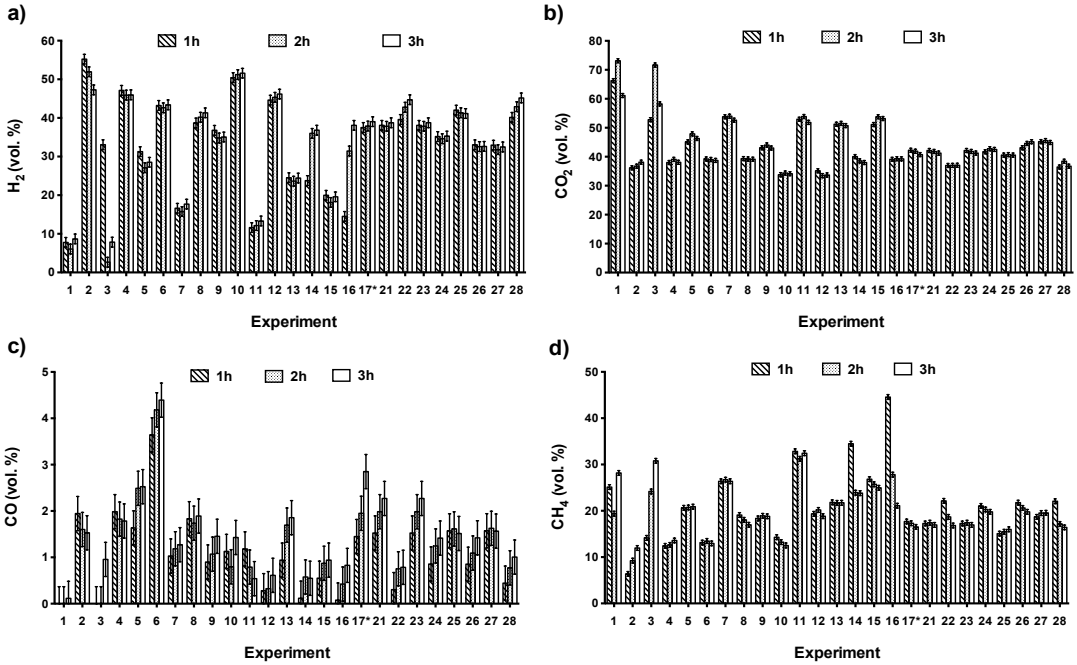

Figure 6. Relative amounts (vol.%) of H_2 (a), CO_2 (b) CO (c) and CH_4 (d) in the gas obtained during the APR experiments. Results are presented as the overall values obtained every 60 minutes and expressed as mean ± 0.5 Fisher LSD intervals with 95% confidence.

A multivariate analysis by means of Spearman´s test revealed a significant relationship between the concentration of H_2 and CH_4 in the gas (p-value = 0.0001). In addition to being significant, this relationship is strong (R^2=0.83). The relationship might account for the methanation reaction ($CO + 3\ H_2 \Leftrightarrow CH_4 + H_2O$). Significant relationships between CO and H_2 (p-value = 0.019) and between CH_4 and CO (p-value = 0.007) were also found, helping to corroborate this hypothesis.

The specific effects of the operating conditions as well as their possible interactions on the volumetric composition of the gas were studied considering the results obtained during the first 60 minutes of reaction. Table 5 shows the results of the statistical analyses performed. This analysis shows that the glycerol concentration and the pressure-temperature and glycerol concentration-temperature interactions are the operating variables with the greatest influence on the proportion of H_2 in the gas. The temperature is the operating variable with the greatest influence on the proportion of CO_2. The interactions of the glycerol concentration with the $W/m_{glycerol}$ ratio and the temperature also exert a significant influence on this gas, although their relative importance is lower. The concentration of CO in the gas is mostly affected by the $W/m_{glycerol}$ ratio and the following interactions: temperature- $W/m_{glycerol}$ ratio, $W/m_{glycerol}$ ratio-glycerol concentration and temperature-pressure. The $W/m_{glycerol}$ ratio, the glycerol concentration and its interaction with temperature substantially influence the relative amount of CH_4 in the gas.

Figure 7 illustrates the effect of these interactions according to the ANOVA analysis. The effects of the reaction temperature, at 38 bar and 50 bar for $W/m_{glycerol}$ ratios of 10 and 40 g catalyst min/g glycerol, feeding a 10 wt.% glycerol concentration, are shown in Figures 7 a and b, e and f, i and j, and m and n. Figures 7 c and d, g and h, k and l, and o and p display the effect of the temperature and the $W/m_{glycerol}$ ratio at 38 and 50 bar for a 50 wt.% glycerol solution.

Table 5. Relative influence of the operating conditions on the composition of the gas and liquid phases according to the ANOVA analysis for the first hour of reaction.

	R^2	Indep..	T	P	C	W	T·P	T·C	T·W	P·C	P·W	C·W	T^2	P^2	C^2	W^2	T·P·C	T·P·W	T·C·W	P·C·W	T^2·P	T^2·C	T^2·W	T·P^2	T·P·C·W
H_2 (vol.%)	1	38.02	n.s	2.76 (5)	4.61 (9)	3.59 (4)	n.s	5.02 (9)	3.44 (6)	1.2 (2)	2.68 (5)	2.95 (5)	n.s	2.91 7	n.s	2.98 (3)	1.21 (2)	2.37 (4)	1.59 (3)	3.35 (6)	n.s	ns	6.51 (4)	8.5 (16)	4.22 (8)
CO_2 (vol.%)	0.98	41.56	2.58 (27)	n.s	n.s	4.37 (7)	n.s	1.77 (7)	0.93 (4)	n.s	0.81 (3)	2.02 (8)	n.s	2.13 8	n.s	n.s	1.01 (4)	1 (4)	1.29 (5)	2.05 (8)	n.s	ns	2.85 (4)	4.65 (6)	1.97 (7)
CO (vol.%)	0.98	1.29	0.61 (6)	0.23 (7)	0.36 (3)	0.44 14	0.12 (4)	0.11 (3)	0.54 (16)	0.14 (4)	0.09 (3)	0.38 (11)	0.33 (4)	n.s	n.s	n.s	n.s	n.s	n.s	0.16 (5)	0.51 (5)	ns	n.s	0.91 (9)	0.17 (5)
CH_4 (vol.%)	1	18.04	2.44 (3)	2.51 (7)	3.93 (12)	1.68 (13)	0.81 (2)	3.35 (9)	3.01 (8)	0.76 (2)	1.74 (5)	1.36 (4)	1.35 (1)	0.8 1	n.s	2.02 (6)	n.s	1.35 (4)	2.64 (7)	1.31 (4)	n.s	ns	3.01 (3)	3.85 (4)	1.96 (5)
Aldehydes (%)	0.95	1.45	0.57 (21)	0.19 (7)	n.s	0.49 (2)	n.s	0.33 (11)	0.25 (9)	0.12 (4)	n.s	0.28 (10)	0.53 (13)	n.s	n.s	n.s	n.s	n.s	0.19 (7)	n.s	n.s	0.24 (8)	0.62 (7)	n.s	n.s
Mono-OH (%)	0.99	23.65	17.58 (11)	0.93 (2)	11.92 (10)	16.43 (13)	2.88 (6)	1.99 (4)	1.23 (2)	n.s	n.s	3.1 (6)	n.s	n.s	3.05 (10)	n.s	1.01 (2)	1.28 (3)	3.84 (8)	1.68 (3)	n.s	13.5 (9)	11.4 (8)	14.03 (9)	1.91 4
Poly-OH (%)	0.99	47.18	17.22 (25)	4.11 (8)	8.45 (7)	14.271	n.s	2.3 (4)	6.35 (12)	n.s	n.s	n.s	10.16 (9)	2.7 (3)	3.86 (2)	6.92 (4)	n.s	1.35 (3)	1.31 (2)	1.92 (4)	n.s	5.71 (4)	16.57 (10)	5.23 (3)	n.s
C. Acids (%)	0.95	6.35	n.s	n.s	-6.23 (22)	n.s	n.s	-1.44 (5)	2.77 (9)	n.s	n.s	1.45 (5)	n.s	n.s	3.98 (19)	3.47 (8)	n.s	-1.76 (6)	-1.04 (3)	n.s	-1.3 (4)	n.s	-3.53 (12)	1.79 (6)	n.s
C3-Ketones (%)	0.97	11.95	n.s	n.s	n.s	-5.15 (8)	n.s	n.s	n.s	1.71 (7)	1.19 (5)	4.71 (19)	3.04 (8)	n.s	n.s	n.s	2.14 (9)	1.16 (5)	3.48 (14)	n.s	n.s	n.s	3.66 (5)	2.94 (12)	1.71 (7)
C4-Ketones (%)	1	1.87	2.64 (17)	-0.68 (6)	0.44 (9)	n.s	-0.97 (8)	0.62 (5)	0.94 (7)	0.35 (3)	-0.92 (7)	n.s	1.47 (5)	n.s	-0.7 (3)	n.s	0.26 (2)	-0.64 (5)	-0.29 (2)	0.55 (4)	n.s	0.68 (2)	1.08 (9)	-0.75 (2)	0.62 (5)
C. Ketones (%)	0.86	0.9	n.s	n.s	n.s	-0.31 (6)	-0.55 (10)	0.81 (15)	n.s	-0.6 (11)	n.s	n.s	n.s	n.s	n.s	n.s	-0.55 (10)	n.s	n.s	n.s	-0.6 (11)	1.02 (19)	n.s	0.81 (15)	n.s
Esters (%)	0.98	3.63	-0.95 (6)	n.s	2.4 (22)	2.09 (6)	-1.08 (6)	-0.85 (5)	1.41 (8)	n.s	-0.62 (3)	-1.27 (7)	1.9 (5)	n.s	-1.34 (10)	n.s	-0.99 (5)	-0.64 (4)	1.32 (7)	-0.53 (3)	n.s	1.62 (3)	-3.45 (6)	n.s	-0.73 (4)

3.2.1 H_2 and CO_2

The reaction temperature exerts a significant influence on the concentrations of H_2 and CO_2. In general, an increase in the temperature from 200 to 240 ºC results in an increase in the H_2 concentration and a drop in the CO_2 concentration, as reported in other works [7, 15]. The H_2 solubility in the liquid phase decreases with the temperature, diminishing the extent of the hydrogenation reactions, thus augmenting the proportion of H_2 in the gas [23]. In addition, the reforming reactions are endothermic, while the WGS reaction is exothermic, which also results in an increase in H_2 and a decrease in CO_2 with the temperature.

The effect of the pressure on the proportion of these two gases depends on the glycerol concentration and $W/m_{glycerol}$ ratio. For a $W/m_{glycerol}$ ratio of 10 g catalyst min/g glycerol, an increase in the total pressure of the system from 38 to 50 bar has two different effects depending on the glycerol concentration. On the one hand, when a 10 wt.% glycerol solution is used, increases in the H_2 and decreases in the CO_2 concentrations take place between 200 and 230 ºC. A diminution in the consumption of H_2 during the hydrogenation of the liquid products might account for this increment. Furthermore, the analysis of the liquid phase, which will be discussed in detail in section 3.3, shows that this increase in pressure leads to a drop in the proportion of poly-alcohols. This depletion is the consequence of the decline in the proportion of 1,2-propane-diol, which is obtained from the hydrogenation of acetol [42, 43]. This drop in the proportion of H_2 causes the relative amount of CO_2 in the gas to increase.

On the other hand, for a 50 wt.% glycerol solution, the same increase in pressure exerts the opposite effect on the concentrations of H_2 and CO_2. Hydrogen solubility increases with

pressure, thus hydrogenation reactions in the liquid phase may be more favoured with the increase in pressure for this glycerol concentration. The higher the glycerol concentration, the lower the amount of water and consequently the higher the partial pressure of H_2. The rise in the proportion of CO_2 is basically a consequence of the decline in the proportion of H_2 in the gas.

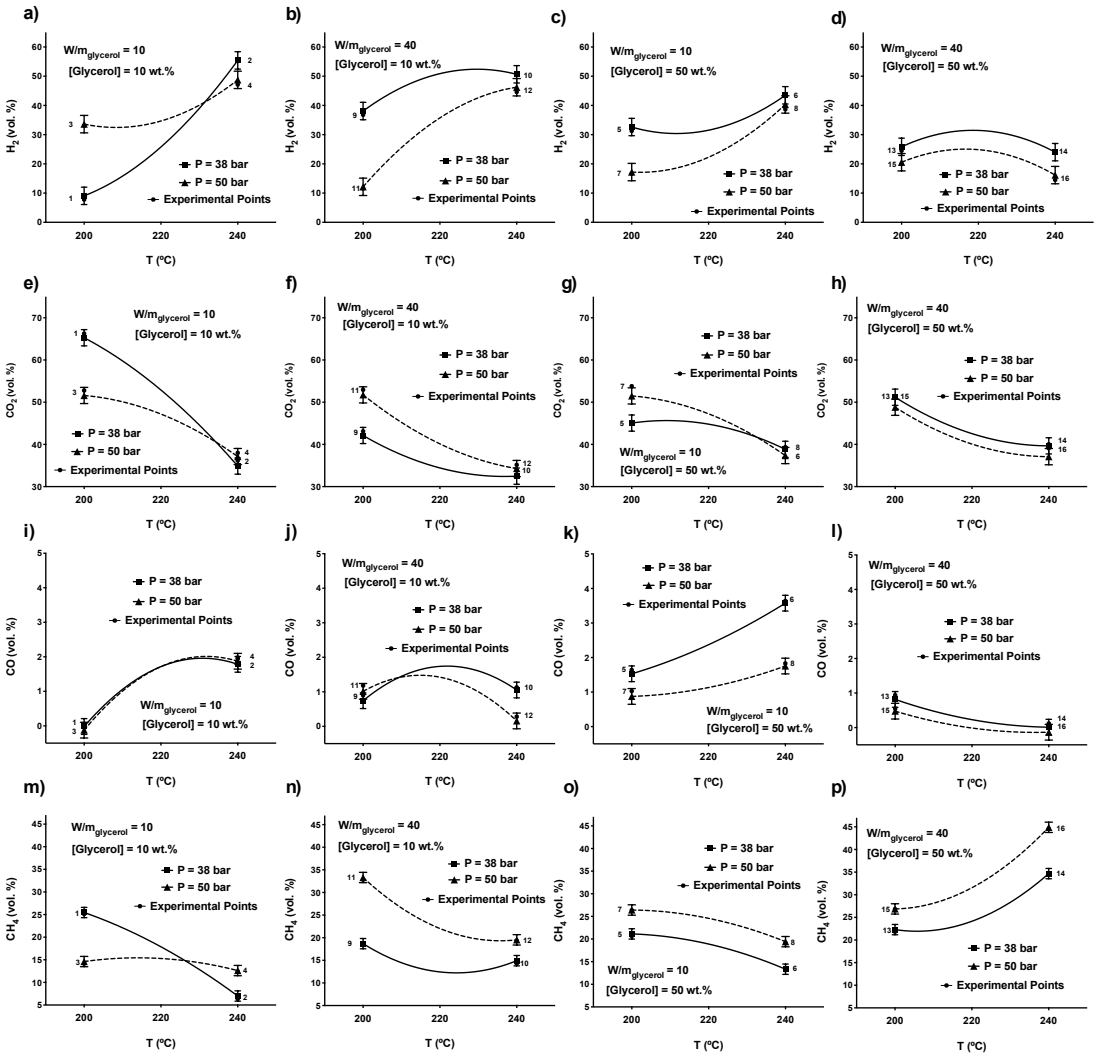

Figure 7. Interaction plots for initial relative amounts (vol.%) of H_2 (a), CO_2 (b) CO (c) and CH_4 (d) in the gas. Bars are LSD intervals with 95% confidence.

Different effects for the total pressure have been reported in other works. Luo et al. [24] found an increase in the proportion of H_2 when increasing the pressure, while Manfro et al. [19] and Özgür and Uysal [14] reported a drop in the proportion of H_2.

When a $W/m_{glycerol}$ ratio of 40 g catalyst min/g glycerol is used, an increase in pressure from 38 to 50 bar reduces the proportion of H_2 regardless of the glycerol concentration and increases the proportion of CO_2 only for a 10 wt.% glycerol solution. In the case of H_2, this decrease is greater when employing a 10 wt.% than a 50 wt.% solution. For a 10 wt.% glycerol solution, the higher the pressure, the higher the solubility of H_2 in the liquid phase, which might promote the hydrogenation reactions due to the high $W/m_{glycerol}$ ratio employed. Under these conditions, an increase in the proportion of mono-alcohols in the liquid takes place, ethanol being the alcohol responsible for this increment. Ethanol is a hydrogenation end product in glycerol aqueous phase reforming, which justifies that this trend is only observed for a high $W/m_{glycerol}$ ratio. Conversely, for a 50 wt.% glycerol solution little variation in the proportions of H_2 and CO_2 are observed. Under these conditions, a high increase in the proportion of CH_4 takes place, indicating that CH_4 formation might be favoured. CH_4 is an end product in glycerol aqueous phase reforming. It can be formed by an initial hydrogenation of ethane-1,2-diol to produce ethanol, which undergoes posterior dehydrogenation to produce CH_4. These reactions explain the increase in the proportion of CH_4 and the steady evolution of H_2.

The greatest effect of the $W/m_{glycerol}$ ratio on the concentrations of H_2 and CO_2 occurs when a 10 wt.% glycerol solution is fed. This effect depends on the total pressure. For 38 bar, an

increase in the $W/m_{glycerol}$ ratio from 10 to 40 g catalyst min/g glycerol increases the H_2 and decreases the CO_2. This increase in the H_2 concentration was also reported in the work of Luo et al. [24], conducted at relatively low pressure (25 bar). Conversely, an increase in the pressure up to 50 bar has the opposite effect, although little variation occurs for the proportion of CO_2 in the gas. An increase in the $W/m_{glycerol}$ favours reforming reactions, increasing the H_2 production. When a total pressure of 50 bar is used, the partial pressure of H_2 could be high enough to carry out hydrogenation reactions in the liquid phase, reactions that are promoted with the increase in the $W/m_{glycerol}$ ratio. These phenomena lead to a decrease in the proportion of H_2. Conversely, hydrogenation reactions might take place to lesser extent at 38 bar due to the lower H_2 partial pressure. An increase in the $W/m_{glycerol}$ ratio increases the concentration of H_2 in the gas.

A multivariate analysis by means of Spearman´s test was conducted to find evidence for the relationship between the concentrations of H_2 and CO_2 in the gas. The relationship between the two gases was found to be statistically significant (p-value=0.0001) and direct (R^2=0.89).

3.2.2 CO and CH_4

During the aqueous phase reforming of glycerol, CO is mainly obtained from cracking and decarbonylation reactions [23]. Under the temperatures studied in this work, the water gas shift (WGS) reaction is shifted towards H_2 and CO_2, which explains the low proportion of CO in the gas. The temperature has two different effects on the concentration of CO depending on the $W/m_{glycerol}$ used. For 10 g catalyst min/g glycerol, an increase in temperature increases

the proportion of CO, while for 40 g catalyst min/g glycerol the effect of the temperature is lower and it is only significant for low glycerol concentrations (10 wt.%).

The pressure exerts a weak effect on the concentration of CO, being statistically significant only for a high glycerol concentration (50 wt.%) when a $W/m_{glycerol}$ ratio of 10 g catalyst min/g glycerol is used. Under these conditions, an increase in pressure reduces the proportion of CO in the gas. An increase in the $W/m_{glycerol}$ ratio from 10 to 40 g catalyst min/g glycerol causes the relative amount of CO in the gas to drop, especially at temperatures between 220 and 240 ºC where CO production can be intensified by decarbonylation and WGS reactions occur to a lesser extent.

In general, an increase in temperature provokes a decrease in the relative amount of CH_4. This drop is the consequence of the exothermic character of the methanation reaction [15]. Conversely, when a 50 wt.% glycerol concentration and a $W/m_{glycerol}$ ratio of 40 g catalyst min/g glycerol are employed, the proportion of CH_4 with temperature increases sharply. This increase might be caused by acetaldehyde decarbonylation, as was previously explained for the concentration of H_2.

An increase in the total pressure between 38 and 50 bar increases the proportion of CH_4 in the gas. This increase can have a thermodynamic background as the pressure shifts CH_4 formation through the methanation reaction. As an exception, it is observed that this increase does not occur between 200 and 230 ºC when a 10 wt.% glycerol solution and a $W/m_{glycerol}$ ratio of 10 g catalyst min/g glycerol were used, conditions at which a reduction in the concentration of

CH_4 occurs. This decrease is the consequence of the high increase in the concentration of H_2 in the gas, as previously explained. This rise in H_2 diminishes the formation of acetaldehyde, which leads to a decrease in the proportion of CH_4 in the gas. In the vast majority of cases, an increase in the $W/m_{glycerol}$ ratio increases the concentration of CH_4.

The effect of the glycerol concentration on the concentration of CH_4 depends on the temperature and the $W/m_{glycerol}$ ratio. Between 200 and 220 ºC at high pressure and employing a low $W/m_{glycerol}$ ratio, an increase in the glycerol concentration increases the proportion of CH_4 in the gas. Under these conditions the methanation reaction is favoured. Conversely, for a high $W/m_{glycerol}$ ratio and pressure, the same increase in the glycerol concentration decreases the proportion of CH_4 in the gas. An increase in the $W/m_{glycerol}$ ratio increases the reaction rates of the reactions in the liquid phase. This shifts the process towards the production of liquid end products, such as acetaldehyde, which can be converted into CH_4 by decarbonylation [23].

3.3 Effect of the operating conditions on the composition of the liquid phase

Figure 8 summarises the relative amount of each of the different families of liquid compounds for the different experiments represented in 3 intervals of 60 minutes each. The liquid phase is made up of a mixture of alcohols, aldehydes, ketones, carboxylic acids and esters together with unreacted glycerol and water. Alcohols include monohydric alcohols (methanol and ethanol), polyhydric alcohols (1,2-propanediol, 1,2-ethanediol, 2,3-butanediol) and, in lower proportions, monohydric substituted and alicyclic alcohols. Ketones include C3-ketones such as 2-propanone (acetone) and 2-propanone-1-hydroxy, C4-ketones (2-butanone-3-hydroxy

and 2-butanone-1-hydroxy) and cyclic ketones. Acetaldehyde is the most abundant compound for the aldehydes, while the carboxylic acids are mainly made up of acetic and propionic acids. The presence of these compounds in the condensates is consistent with the pathway proposed in Figure 2 and those proposed by several authors [6, 7, 21, 23, 34-36]. Glycerol monoacetate is the most abundant ester compound, indicating that esterification reactions can also take place under some operating conditions.

The statistical analysis reveals significant differences (p-values<0.005) in the relative amounts of these compounds in the liquid phase. The results of the Fisher´s LSD test are plotted in Figure 8. The relative concentration for these compounds, expressed as relative chromatographic area, varies as follows. Monohydric alcohols: 4-47%, polyhydric-alcohols: 14-68%, carboxylic acids: 2-43%, aldehydes: 0-5%, C3-ketones: 2-33%, C4-ketones: 0-10 %, cyclic-ketones: 0-6% and esters: 0-46%. Increases and decreases in the proportions of these families with time are detected. The highest variations occur for aldehydes, polyhydric alcohols, C3-ketones and esters. These variations have been analysed with the multivariate Spearman´s test to find significant relationships between the increases and decreases of the families of compounds with time.

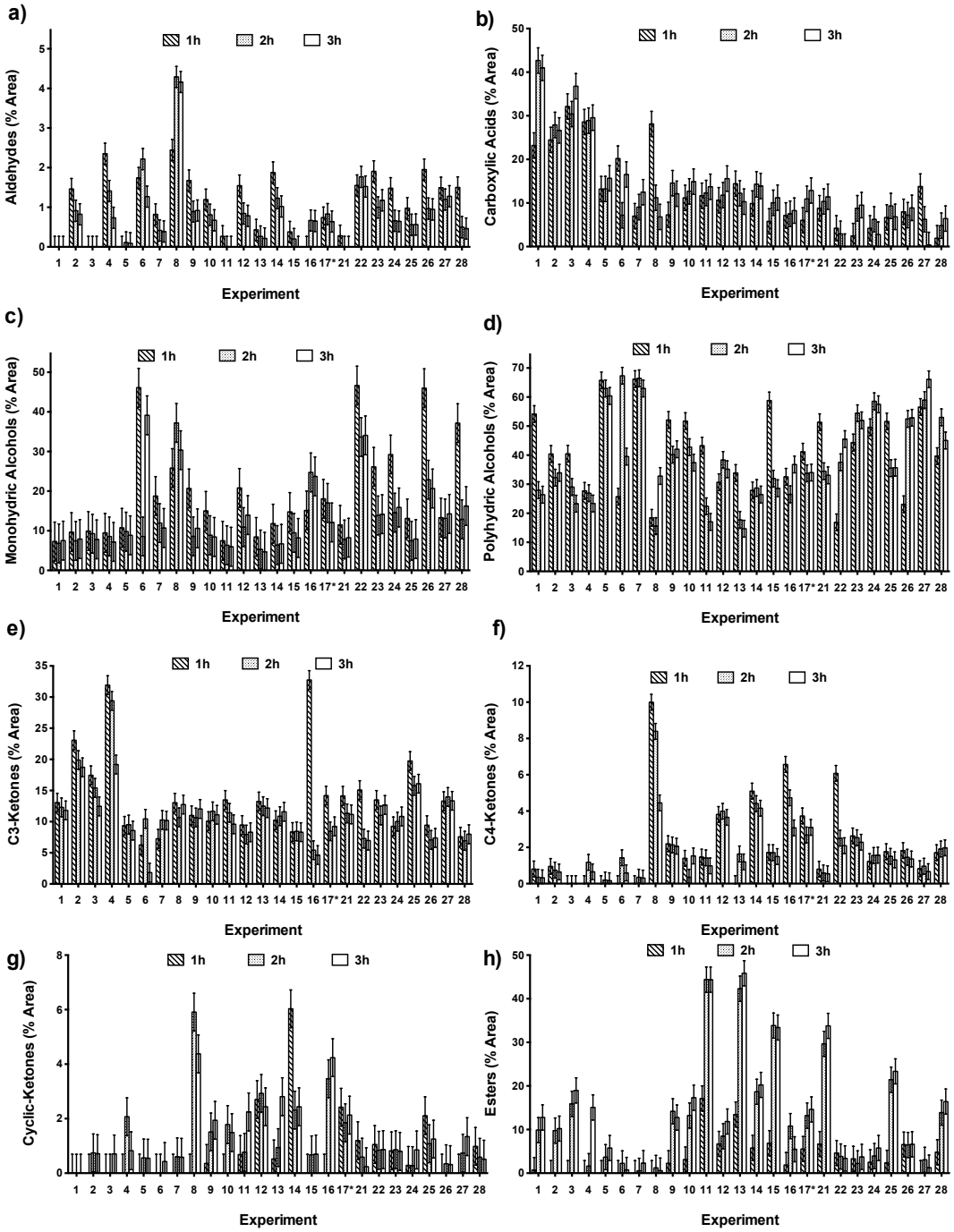

Figure 8. Proportions (% chromatographic area) of carboxylic acids (a), monohydric alcohols (b), polyhydric alcohols (c), aldehydes (d), C3-ketones (e), C4-ketones (f), cyclic ketones (g) and esters (h) in the liquid obtained during the APR experiments. Results are presented as the overall values obtained every 60 minutes and expressed as mean ± 0.5 Fisher LSD intervals with 95% confidence.

Aldehydes show increases with time for runs 8 and 16. The increases take place along with decreases with time in the CC gas and increases in the CC liq or X gly. According to the pathway shown in Figure 2, aldehydes are end products of glycerol aqueous phase reforming; therefore, their proportions increase as the X gly increases. Conversely, the proportion of aldehydes drops with time for runs 2, 4, 9, 12, 14, 23, 24, 26 and 28. These decays occur along with decreases in the relative amount of monohydric alcohols (runs 23, 24, 26 and 28) together with increases in the proportion of esters (runs 2, 4, 9, 14 and 28) or polyhydric alcohols (runs 23, 24, 26 and 28). The multivariate analysis reveals significant relationships for the proportions of aldehydes with the proportions of carboxylic acids (p-value = 0.002; R^2 = 0.33), monohydric alcohols (p-value = 0.0001; R^2 = 0.57) and esters (p-value = 0.0001; R^2 = 0.48). In addition, the proportion of carboxylic acids depends on the proportion of monohydric alcohols (p-value = 0.0001; R^2 = 0.55) and polyhydric alcohols (p-value = 0.0001; R^2 = 0.44). These relationships confirm the pathway shown in Figure 2.

The proportions of carboxylic acids in the condensate remain steady over time for the vast majority of the experiments. Runs 1, 17 and 23 display a mild increase with time, while drops can be observed for runs 8 and 27. The multivariate analysis reveals a significant relationship between the relative amount of monohydric and polyhydric alcohols and carboxylic acids. This relationship explains the experimental trend since 1,2-propane-diol and ethanol are intermediate compounds for acetic acid production.

The relative amount of monohydric alcohols shows decreases for runs 9, 22, 23, 24, 26 and 28. These drops occur at the same time as increases in the proportion of polyhydric alcohols and decreases in the proportion of aldehydes (runs 9, 22, 23, 24, 26 and 28). Polyhydric

alcohols display increases (runs 6, 8, 22, 23, 24, 26, 27 and 28) and decreases (runs 1, 2, 3, 9, 10, 11, 13, 15, 17, 21 and 25) with time. In general, the increases occur together with decreases in the proportion of monohydric alcohols. Exceptionally, this decrease is not observed for experiments 6 and 27. These trends are in concordance with the multivariate analysis (p-value = 0.05; R^2 = 0.20). However, although the relationship is significant, it is not strongly direct, which indicates that this drop is more related to the drop observed in the proportion of aldehydes. This result suggests that the limiting step for the production of ethanol is the dehydration of ethane-1,2-diol to produce acetaldehyde. In general, increases in the proportion of esters occur together with decreases in the relative amount of polyhydric alcohols (p-value = 0.0002; R^2 = 0.40).

The variations over time for the relative amount of ketones and esters in the liquid are scarce. C3-ketones exhibit decreases with time for runs 2, 3, 4, 6, 11, 16, 17, 22 and 25, while increases were not detected. The multivariate analysis indicates a relationship between the proportion of C3-ketones and monohydric alcohols in the liquid (p-value = 0.0004; R^2 = 0.38). This relationship is not strongly direct, which is consistent with the intermediate condition that ketones have in the aqueous phase reforming process of glycerol, participating in a great number of reactions. The relative amount of C4-ketones and cyclic-ketones in the liquid is low and steady, as they are not major products in the process. Increases in the relative amount of esters, coinciding with increases in the proportion of carboxylic acids, take place in some experiments, as explained above.

The specific effects of the operating conditions as well as all the interactions between the variables on the liquid composition have been studied considering the results obtained during

the first 60 minutes of reaction. Table 5 shows the significant terms in the codec model and their relative influence in the process according to the ANOVA analysis. The reaction temperature is the operating variable with the greatest influence for the relative amount of aldehydes in the liquid. The glycerol concentration and the interaction temperature-$W/m_{glycerol}$ ratio exert the greatest influence on the proportion of carboxylic acids. Monohydric alcohols are strongly influenced by the temperature, glycerol concentration and $W/m_{glycerol}$ ratio; while the temperature and the interaction temperature-$W/m_{glycerol}$ ratio greatly influence the relative amount of polyhydric alcohols. The proportions of ketones and esters mainly depend on the temperature and the glycerol concentration, respectively. The temperature exerts a low influence on the relative amount of C3-ketones, the glycerol concentration-$W/m_{glycerol}$ ratio interaction being more influential for this family of ketones.

To gain a deeper understanding of the influence of the operating variables and the interactions on the proportion of the most important liquid families, Figures 9 illustrates the effect of these interactions according to the ANOVA analysis for the proportions of carboxylic acids, monohydric and polyhydric alcohols, and aldehydes. Figure 10 displays these effects for the proportions of C3, C4 and cyclic ketones, and esters. Specifically, the effects of the reaction temperature, employing a pressure of 38 bar for $W/m_{glycerol}$ ratios of 10 and 40 g catalyst min/g glycerol, feeding glycerol concentrations of 10 and 50 wt.%, are shown in Figures 9 and 10 a and b, e and f, i and j, and m and n. Figures 9 and 10 c and d, g and h, k and l, and o and p display the effects of the temperature and the $W/m_{glycerol}$ ratio employing a pressure of 50 bar when glycerol solutions of 10 and 50 wt.% were used, respectively.

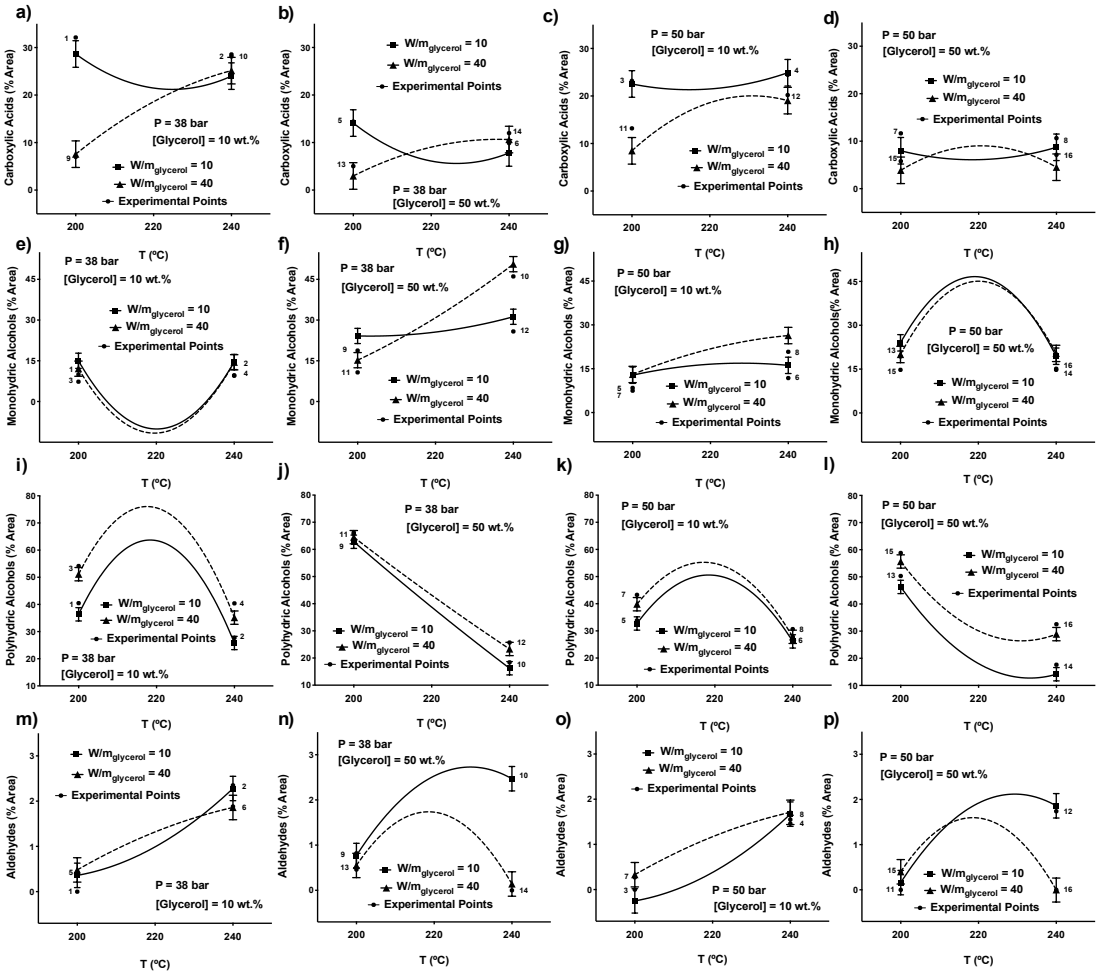

Figure 9. Interaction plots for the relative amounts in the liquid of carboxylic acids, monohydric alcohols, polyhydric alcohols and aldehydes. Bars are LSD intervals with 95% confidence.

3.3.1 Carboxylic acids

Acetic and propionic acids are the most abundant carboxylic acids in the liquid phase. Figure 2 shows that acetic acid is produced through routes B and C, while propionic acid is formed through route A. Propionic acid formation occurs to a lesser extent due to the higher proportion of 1-hydroxypropan-2-one hydrogenated compounds than dehydrated compounds in the liquid.

The temperature exhibits two different effects on the proportion of carboxylic acids depending on the other operating conditions (pressure, $W/m_{glycerol}$ ratio and glycerol concentration) due to the interaction of these variables with the temperature. When a 10 wt.% glycerol solution is fed to the reactor, two different trends are found depending on the $W/m_{glycerol}$ ratio. For 10 g catalyst min/ g glycerol, an increase in temperature between 200 and 240 ºC does not have a statistically significant influence on the relative amount of this family of compounds. Conversely, when a $W/m_{glycerol}$ ratio of 40 g catalyst min/g glycerol is used, this same increment in temperature causes the proportion of carboxylic acids to increase. Under these conditions, an increase in the $W/m_{glycerol}$ ratio from 10 to 40 g catalyst min/g glycerol decreases the proportion of carboxylic acids. Acetic acid is present in the crude glycerol solution as an impurity; therefore, an increase in the amount of catalyst favours its decomposition. However, as the temperature increases, the reaction rate of acetic acid formation from glycerol could be higher than its rate of decomposition, leading to an increase in the proportion of acetic acid and thus augmenting the relative amount of carboxylic acids in the liquid. This formation-transformation scenario might make the effect of the temperature insignificant when employing a low $W/m_{glycerol}$ ratio (10 g catalyst min/g glycerol) due to the compensatory effect of these two developments. At a low temperature this $W/m_{glycerol}$ ratio is not high enough for the decomposition of acetic acid to take place.

In general, similar interactions and trends as those described for a 10 wt.% glycerol solution are apparent when feeding a 50 wt.% glycerol solution, although they are more appreciable at 38 than at 50 bar. Increasing the concentration from 10 to 50 wt.% causes the proportion of carboxylic acids to decrease. As the glycerol concentration increases, the partial pressure of acetic acid also increases, enhancing its decomposition rate. This effect is greater for the

lowest $W/m_{glycerol}$ ratio. The greater kinetic effect of the $W/m_{glycerol}$ ratio masks the effect of the concentration for high $W/m_{glycerol}$ ratios. In addition, the effect of the $W/m_{glycerol}$ ratio decreases when increasing the glycerol concentration. It can be seen that for a 50 wt.% solution the effect of the $W/m_{glycerol}$ ratio is only significant between 200-210 ºC at 38 bar, as the transformation of acetic acid could be more favoured when feeding a more concentrated glycerol solution.

3.3.2 Alcohols: monohydric and polyhydric alcohols

The compounds with the highest relative amounts in the liquid phase are alcohols, essentially mono and polyhydric alcohols. The proportion of monohydric alcohols varies between 0 and 45 %. This basically corresponds to variations in ethanol, as the relative amount of methanol in the liquid phase shifts from 2 to 6%. The proportion of polyhydric alcohols increases from 10 to 80%. A slightly negative proportion of monohydric alcohols is predicted under some operating conditions due to the empirical character of the models.

The temperature has different influences on the proportion of monohydric and polyhydric alcohols depending on the glycerol concentration, pressure and $W/m_{glycerol}$ ratio due to the large number of interactions detected between these variables. When a 10 wt.% glycerol solution is used, an increase in temperature exerts two different effects on the proportion of alcohols depending on the total pressure. At 38 bar the proportion of monohydric alcohols decreases between 200 and 220 ºC, and increases between 220 to 240 ºC, while polyhydric alcohols exhibit the opposite trend (increases between 200 and 220 ºC and decreases between 220 and 240 ºC). The decrease with temperature in the proportion of monohydric alcohols

between 200 and 220 ºC might be the consequence of fewer hydrogenation reactions of 1,2-ethane-diol due to the lower solubility of H_2 in the liquid phase when the temperature increases. This leads to an increase in the proportions of H_2 and polyhydric alcohols in the gas and the liquid phases, respectively [23]. In addition, an increase in temperature shifts the glycerol decomposition, which also causes an increase in the relative amount of polyhydric alcohols in the liquid. Between 220 and 240 ºC, the proportion of monohydric alcohols increases while that of polyhydric alcohols drops [23, 35]. The lesser extent of the hydrogenation reactions of 1-hydroxy-2-propanone due to the lower solubility of H_2 in the liquid phase, favouring route C over route A, might be responsible for this variation [23].

An increase in pressure up to 50 bar when feeding a 10 wt.% glycerol solution weakens the effect of the temperature on the proportion of monohydric alcohols for a $W/m_{glycerol}$ ratio of 40 g catalyst min/ g glycerol. The effect is insignificant for 10 g catalyst min/ g glycerol. The proportion of polyhydric alcohols decreases with pressure, while monohydric alcohols slightly increase between 215 and 230 ºC. The solubility of H_2 in the liquid increases with pressure, favouring hydrogenation reactions. This shifts the hydrogenation of 1,2-ethane-diol to ethanol, increasing and decreasing the proportions of monohydric and polyhydric alcohols, respectively. In addition, the partial pressure of polyhydric alcohols also increases, which also favours the advancement of the reactions in the liquid phase. At high pressure, the proportion of monohydric alcohols does not drop with temperature, as the positive effect of the pressure can compensate for the negative effect of the temperature. Furthermore, the increase in the proportion of polyhydric alcohols between 200 and 220 is lower at 50 than at 38 bar, due to their quicker transformation into other liquid intermediates.

When a 50 wt.% glycerol solution is used, an increase in temperature from 200 to 240 ºC at 38 bar increases and decreases the proportions of monohydric and polyhydric alcohols, respectively. This increase in the glycerol concentration increases the concentration of liquid intermediates, intensifying their partial pressure inside the reactor and favouring the displacement of the reactions in the liquid phase towards end products. This causes the maximum in the relative amount of polyhydric alcohols to be reached at lower temperatures (220 and 200 ºC for 10 and 50 wt.% solutions, respectively). Therefore, under these conditions, thanks to the high total pressure employed which helps to increase the partial pressure of the organics in the reactor, an increase in temperature moves the process towards end products, i.e. it reduces the proportion of polyhydric alcohols and increases the relative amount of monohydric alcohols to their lowest and highest values, respectively.

An increase in pressure up to 50 bar for a 50 wt.% glycerol concentration causes the maximum in the proportion of monohydric alcohols and the minimum in polyhydric alcohols to be reached at a lower temperatures (220 ºC) due to the positive effect the pressure exerts on the process. An increase in the total pressure increases the partial pressure of the organics inside the reactor, favouring hydrogenation reactions. Furthermore, a rise in the glycerol concentration helps to intensify this effect. As a consequence, an increase in temperature from 200 to 220 increases and decreases the proportions of monohydric and polyhydric alcohols, respectively. Wawrzetz et al. [23] found the highest proportion of polyhydric alcohols (1,2-propanediol and 1,2-ethanediol) in the liquid when the glycerol conversion was around 50%. With the increase in the glycerol conversion the proportions of these liquids decreased while the proportion of ethanol increased, which accounts for the experimental observations of this work.

The effect of the $W/m_{glycerol}$ ratio exerts a weaker influence on the proportions of alcohols than the other operating variables. The greatest effect of this variable on the proportion of monohydric alcohols occurs feeding a 50 wt.% glycerol solution at 38 bar. Under these conditions, an increase in the $W/m_{glycerol}$ ratio increases the proportion of monohydric alcohols, helping to increase their maximum. An increase in the $W/m_{glycerol}$ ratio slightly increases the proportion of polyhydric alcohols for a 10 wt.% glycerol solution at 38 and 50 bar. A higher amount of catalyst favours a greater spread of glycerol dehydration and hydrogenation reactions. However, the higher the pressure, the weaker is the effect of the $W/m_{glycerol}$ ratio. The positive kinetic effect of the pressure makes the effect of the catalyst less important. When feeding a 50 wt.% glycerol solution, this increase in the $W/m_{glycerol}$ ratio also increases the proportion of polyhydric alcohols due to the decrease in the proportion of the relative amount of aldehydes in the liquid. Under these conditions, the methanation reaction is favoured and an increase in the $W/m_{glycerol}$ ratio favours the transformation of acetaldehyde into CH_4.

3.3.3 Aldehydes

Acetaldehyde is the major compound of this family. It is obtained in the final steps of route C, which indicates that many reactions are involved during its production. It can also be produced in route B.

The relative amount of this compound in the liquid phase is low (0-3%), probably because it is one of the end products of glycerol aqueous phase reforming and can be easily transformed into gas in the final steps of the process. An increase in temperature from 200 to 220 ºC

increases the proportion of this family regardless of the other operating conditions. A temperature increase within this range results in an increase in the CC liq due to the positive kinetic effect of the temperature in the process, favouring the advancement of the reaction in the liquid phase towards the formation of final products.

However, a further increase in temperature up to 240 ºC has different consequences depending on the other operating variables. On the one hand, for a low glycerol concentration (10 wt.%), this increase in temperature slightly increases the proportion of aldehydes and the effect of the $W/m_{glycerol}$ ratio is not significant. On the other hand, when increasing the glycerol concentration up to 50 wt.%, the same increase in the temperature exerts two different effects on the proportion of aldehydes depending on the $W/m_{glycerol}$ ratio. For 10 g catalyst min/g glycerol, the temperature does not exert a significant influence and the proportion of aldehydes remains constant, while for 40 g catalyst min/g glycerol there is a drop in the proportion of aldehydes. These differences in the evolution of the proportion of aldehydes depending on the glycerol concentration could be the consequence of the different partial pressure of aldehydes inside the reactor.

An increase in the glycerol concentration increases the partial pressure of aldehydes. This increase inside the reactor as the glycerol concentration increases from 10 to 50 wt.% could raise the decomposition velocity to give liquid (acetic acid and ethanol) and gaseous (methane, ethane and ethylene) products. Furthermore, an increase in the $W/m_{glycerol}$ ratio might increase the decomposition reaction towards gases, decreasing the proportion of aldehydes. This accounts for the differences observed when using glycerol concentrations of

10 and 50 wt.%. For a 10 wt.% glycerol solution, the increase in the proportion of aldehydes with the temperature is small and the subsequent decay is not observed. This is probably due to the lower partial pressure of aldehydes that hinders their production and subsequent transformation into end liquids and gases.

In general, high temperatures, glycerol concentrations and $W/m_{glycerol}$ ratios lead to a greater gas production, thus decreasing the proportion of liquid intermediates. These patterns are consistent with the experimental observations of Wawrzet et al. [23], where the proportion of aldehydes in the liquid initially increases with the increase in the glycerol conversion from 0 to 50 % and then decreases as the glycerol conversion reaches 100 %.

The effect of the total pressure is only significant at a high glycerol concentration (50 wt.%) and low $W/m_{glycerol}$ ratio (10 g catalyst min/g glycerol). Under these concentrations, an increase in pressure from 38 to 50 bar reduces the relative amount of aldehydes in the liquid due to the increase in the partial pressure of acetaldehyde, which favours its transformation into gases.

3.3.4 Ketones: C3-ketones, C4-ketones and cyclic ketones

The ketonic fraction in the liquid shifts from 0-30% and is made up of ketones of three and four carbon atoms (C3-ketones and C4-ketones) together with cyclic ketones. C3-ketones, mainly obtained from dehydration reactions through route A, are the most abundant ketones in the liquid phase. The statistical analysis reveals that the operating variables exert different

effects on the proportions of C3-ketones in the liquid due to the numerous interactions between the variables detected for the proportion of this family.

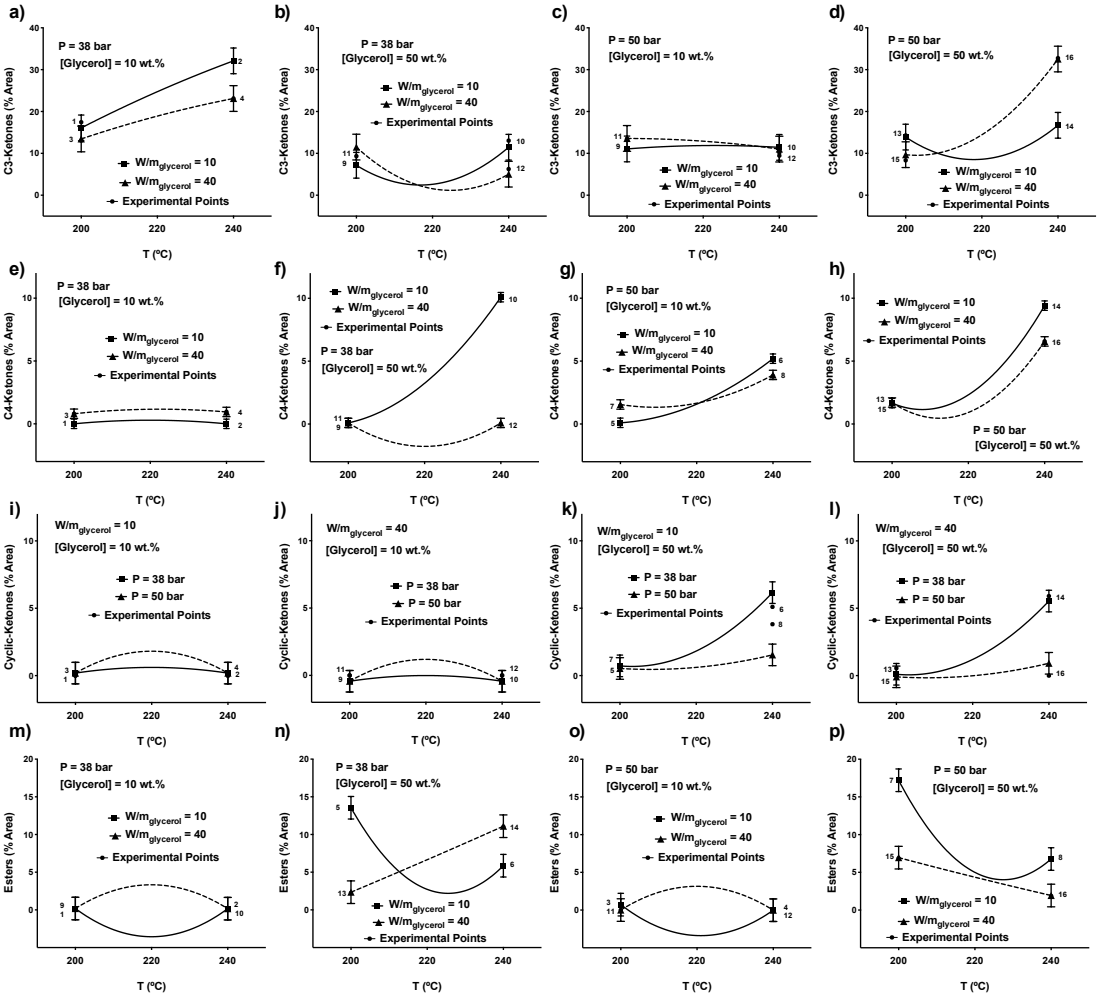

Figure 10. Interaction plots for the relative amounts in the liquid of C3-ketones, C4-ketones, cyclic ketones and esters. Bars are LSD intervals with 95% confidence.

For a 10 wt.% glycerol solution, an increase in temperature from 200 to 240 ºC has two different consequences depending on the total pressure of the system. At 38 bar, it increases the proportion of C3-ketones, while at 50 bar the proportion of ketones remains steady (Figures 10 a and c). At low pressure, the temperature shifts the reaction towards liquid

intermediates, which increases the dehydration rate of glycerol and increases the proportion of 1-hydroxypropan-2-one. In addition, the solubility of H_2 decreases with temperature, hindering the hydrogenation of 1-hydroxypropan-2-one, thus increasing the proportion of H_2 in the gas as previously explained. This circumstance increases the proportion of 1-hydroxypropan-2-one in the liquid, which leads to an increase in the proportion of C3-ketones.

Conversely, at 50 bar and feeding a 10 wt.% glycerol solution the temperature and $W/m_{glycerol}$ ratio do not significantly influence the relative amount of C3-ketones. An increase in the total pressure raises the solubility of H_2 in the liquid, which can compensate for the decrease in the solubility of this gas with temperature. At low temperature, the reaction rate of glycerol dehydration is slow and the temperature promotes its dehydration to 1-hydroxypropan-2-one, increasing the proportion of C3-ketones. However, the subsequent hydrogenation of 1-hydroxypropan-2-one at high pressure is also favoured, decreasing the proportion of C3-ketones. These two consecutive reactions might be responsible for the insignificant effect of the temperature.

When a 50 wt.% glycerol solution is used, two different trends on the proportion of the ketone family with pressure can also be observed. The effect of the temperature does not have a significant effect at 38 bar regardless of the $W/m_{glycerol}$ ratio, while a sharp increase in the proportion of C3-ketones takes place at 50 bar when a $W/m_{glycerol}$ ratio of 40 g catalyst min/g glycerol is used. This increase accounts for a sharp increase in the proportion of acetone in the liquid. Under these conditions, the high partial pressure of liquid products inside the reactor

together with the large amount of catalyst present in the bed can favour the dehydration of 1,2-propanediol to acetone, increasing the proportion of C3-ketones in the liquid [23]. The chemical composition of the liquid phase accounts for these results as the proportion of acetone increases from 1 to 27% and the relative amount of 1,2-propanediol in the liquid drops from 55 to 32%.

The proportion of C4-ketones and cyclic-ketones in the liquid phase is relatively small. 2-butanone and cyclopentanone are the most abundant compounds of these two families. These types of ketones can be obtained by the reaction of an alcohol with a ketone [44]. Therefore, it is suggested that their presence in the liquid might be the consequence of the reaction of glycerol with acetone.

In general, the proportion of C4-ketones increases with temperature, suggesting that their formation is favoured at high temperatures. The higher the glycerol concentration, the greater is the proportion of C4-ketones in the liquid. An increase in the glycerol concentration not only increases the glycerol available in the liquid, it also increases the proportion of acetone to react with, such as the increases observed in the proportions of C3-ketones (mainly acetone). Therefore, the highest proportion of C4-ketones in the liquid is obtained when feeding a 50 wt.% glycerol solution. For this concentration, two different trends are found depending on the total pressure of the system. On the one hand, at 38 bar the effect of the temperature is only significant for a $W/m_{glycerol}$ ratio of 10 g catalyst min/g glycerol. Under these conditions, reforming reactions take place to a lesser extent, allowing part of the glycerol to react with the acetone formed in the process. However, when increasing the

$W/m_{glycerol}$ ratio up to values of 40 g catalyst min/g glycerol, reforming reactions occur to a greater degree, reducing the amount of glycerol available and thus decreasing the formation of C4-ketones in the liquid. On the other hand, at 50 bar, an increase in temperature from 200 to 240 ºC increases the proportion of C4-ketones regardless of the $W/m_{glycerol}$ ratio, since under this pressure the formation of acetone is favoured, increasing the proportion of acetone in the liquid to react with glycerol.

The presence of cyclic-ketones in the liquid phase is scarce (lower than 5%), being detected only under few experimental conditions. This compound is only observed at 38 bar when a high temperature (240 ºC) and high glycerol concentration (50 wt.%) are used, regardless of the $W/m_{glycerol}$ ratio.

3.3.5 Esters

The proportion of esters (basically glycerol monoacetate) in the liquid phase is quite small. In general, their formation consists of the reaction between an acid and an alcohol. Therefore, glycerol monoacetate can be formed by the reaction of glycerol with the acetic acid present as an impurity and/or formed in the process. In addition KOH, also present in the feed, can catalyse this reaction. The concentration of glycerol exerts a great impact on the proportion of glycerol monoacetate. An increase in the glycerol concentration increases the proportion of esters.

When feeding a 50 wt.% glycerol solution, where the presence of esters is significant, the temperature and $W/m_{glycerol}$ ratio significantly influence the relative amount of esters in the

liquid. For a $W/m_{glycerol}$ ratio of 10 g catalyst min/g glycerol, an increase in temperature reduces the proportion of esters in the liquid. Conversely, for a $W/m_{glycerol}$ ratio of 40 g catalyst min/g glycerol, the effect of the temperature depends on the total pressure of the system. At 38 bar an increase in temperature increases the proportion of esters, while at 50 bar the proportion of esters decreases.

3.4 Theoretical prediction of optimal operating conditions within the range of study

Optimal conditions for gas and liquid production were sought for this process making use of the experimental models developed, bearing in mind the possibility of scaling-up this process. Modelling and optimisation tools are gaining increasing attention from the research community for their use in various processes related to biomass/bio-product conversion/production [45, 46]. The predicted R^2 of all the models is higher than 0.90, allowing their use for prediction purposes. Six different optimisations were carried out. The first comprised the maximisation of the X gly. In the second and the third optimisations, apart from the X gly, the CC gas and CC liq were also maximised. The fourth maximised the production of H_2 and the fifth and sixth maximised the proportion of monohydric and polyhydric alcohols, respectively. In addition, the evolution over time for the CC gas, CC liq and X gly were minimised for all the optimisations. Table 6 lists the criteria used in the optimisations, together with the optimums for the operating variables and the values for the response variables considered.

The highest glycerol conversion (Opt. 1) is obtained using intermediate values for the temperature and $W/m_{glycerol}$ ratio, at high pressure and feeding a concentrated glycerol

solution. Conversely, if the optimisation includes the maximisation of the CC gas (Opt. 2), high values (close to the maximum values studied in this work) for the temperature and $W/m_{glycerol}$ ratio are needed. In addition, low pressure and glycerol concentrations are also required. The comparison between the values obtained in Opt. 1 and Opt. 2 reveals slight decreases for the X gly and CC liq and a considerable increase (by a factor of three) in gas production (CC gas). The proportion of H_2 in the gas is enlarged, the proportion of polyhydric alcohols drops and the relative amount of monohydric alcohols increases. The composition of the liquid phase shows a greater spread of the reactions leading to the formation of liquid products, which is in agreement with the results previously discussed in the parametric study.

Table 6. Theoretical optimisation: Objectives, optimum values for the operating variables and optimised values for some responses

Opt	Variable/s maximised	T (ºC)	P (bar)	[Gly] (wt.%)	W/m_{gly} g_{cat} min/g_{gly}	X gly (%)	CC gas (%)	CC liq (%)	H_2 (vol.%)	Mono-Alcohols (%)	Poly-Alcohols (%)
1	X gly	222	42	49	18	100	22	42	34	27	46
2	X gly, CC gas	238	39	15	38	99	64	35	47	36	17
3	X gly, CC liq	216	45	16	22	96	17	86	39	7	61
4	X gly, CC gas, H_2	236	38	14	36	100	54	43	51	28	24
5	X gly, CC liq, Mono-Alcohols	209	39	24	40	93	26	63	41	30	41
6	X gly, CC liq, Poly-Alcohols	218	49	16	20	91	15	82	45	7	66

Var CC gas = 0.79 + 1.5 T + 6 P + 14.5 C + 7.5 W + 1.44 TP + 2.31 TC + 0.81 TW + 0.31 PC + 2.81 PW -1.06 CW -0.078 T^2 + 4.42 P^2 - 6.08 C^2 + 5.92 W^2 + 0.19 TPC + 2.94 TPW - 3.19 TCW + 1.81 PCW - 4.69 T^2P - 10.06 T^2C - 8.81 T^2W +4.81 TP^2 +1.69 TPCW (R^2 = 1)

Var CC liq = -1.91-10.61 T -9.83 W-3.19 TW + 8.31 CW + 26.3 T^2 -8.7 C^2 - 5.06 TCW -8.69 PCW -7.31 T^2P - 9.69 T^2C -3.56 TPCW (R^2 = 0.97)

Var X gly = 1.43 – 16 T- 9.44 W + 2.38 PW + 14 CW + 12.54 T^2 +5.54 W^2 + 4 TPC – 4.38 TCW – 3.12 T^2P – 10.75 T^2C +5.87 TP^2 (R^2 = 0.95)

For the production of liquid products, the maximisation of the CC liq (Opt. 3) implies medium values (within the interval studied in this work) for the temperature and the $W/m_{glycerol}$ ratio together with the use of high pressure and a relatively diluted glycerol solution. Under these conditions the CC liq increases up to 86%. The liquid phase is mainly

made up of alcohols (68 %), the vast majority being polyhydric alcohols (61%). These results suggest that for maximising the production of intermediate liquids, the reaction should be stopped at the early reaction steps. The advancement of the reaction with the formation of end products facilitates their transformation into gases, decreasing the CC liq [21, 23].

As regards the properties of the gas and liquid phases, the maximisation of the production of H_2 (Opt. 4) is achieved employing a high temperature, a high $W/m_{glycerol}$ ratio, low pressure and feeding a diluted glycerol solution. The highest proportion of monohydric alcohols in the liquid (Opt. 5) is achieved at low pressure and temperature, feeding a medium glycerol solution, and using a high $W/m_{glycerol}$ ratio. The maximisation of monohydric alcohols implies the use of conditions for temperature and pressure where the formation of liquid products is highly favoured combined with high $W/m_{glycerol}$ ratios to favour the extension of the reaction in the liquid phase towards end products, minimising their subsequent transformation into gases. Optimum conditions for the production of polyhydric alcohols (Opt. 6) are medium temperature, high pressure, low glycerol concentration and an intermediate value for the $W/m_{glycerol}$ ratio. These conditions are able to stop the advancement of the reactions in the liquid phase, thus providing a high production of liquids together with an excellent selectivity to polyhydric alcohols.

4. Conclusions

This work addresses the valorisation process of a crude glycerol solution obtained from biodiesel production by aqueous phase reforming (APR). The process has been experimentally evaluated and optimised in a flow reactor using a Ni-based catalyst. A design of experiments with statistical analysis of the results has been used to analyse the effect on the

process of the temperature, pressure, glycerol concentration, $W/m_{glycerol}$ ratio and all the interactions between these variables. As a result, this work provides a good understanding of the aqueous phase reforming of glycerol in general and the effect of the operating variables on the process in particular. In addition, appropriate operating conditions for the selective production of liquids and gases are provided. The most important conclusions obtained from this work are summarised as follows.

1. The operating variables exert a significant influence on the global results of the aqueous phase reforming (glycerol conversion and carbon converted into liquid and gas products) as well as on the composition of the gas and liquid phases.

2. Gas production is favoured at low pressure, high temperature and employing a concentrated glycerol solution. Under these conditions, reforming and cracking reactions of glycerol and its intermediate liquids are enlarged. Conversely, a high pressure and medium temperature and $W/m_{glycerol}$ ratio favour the production of liquid products. A high selectivity to liquids is achieved maximising the proportion of polyhydric alcohols in the liquid, i.e. detaining the process at early reaction steps.

3. The gas phase is composed of H_2, CO_2, CO and CH_4. The proportion of H_2 in the gas does not only depend on the extent of the chemical reactions involved in its production, such as reforming and/or cracking reactions, but also of those where it is consumed, such as hydrogenation. The temperature is the variable with the greatest impact on the composition of the gas. An increase in temperature increases the proportion of H_2 and decreases the proportion of CO_2 due to the decrease in solubility of H_2 with temperature as well as the endothermic reactions of the process.

4. The liquid phase is made up of a mixture of carboxylic acids (2-32%), aldehydes (0-3%),

monohydric alcohols (4-47%), polyhydric alcohols (14-68%), C3-ketones (2-33%), C4-ketones (0-10 %) ciclo-ketones (0-6%) and esters (0-46%).

5. Alcohols are the most abundant compounds in the liquid phase. Monohydric alcohols are formed under conditions of temperature and pressure (209 ºC and 39 bar) where the formation of liquid products is highly favoured together with the use of high $W/m_{glycerol}$ ratios (40 g catalyst min/g glycerol) to favour the extension of the reactions in the liquid phase towards liquid end products. The production of polyhydric alcohols is favoured at an intermediate temperature (218 ºC), high pressure (49 bar), low glycerol concentration (16 wt.%) and a medium $W/m_{glycerol}$ ratio (20 g catalyst min/g glycerol). These conditions are able to stop the advancement of the reactions in the liquid phase at the early steps.

Acknowledgements

The authors wish to express their gratitude to the Aragon Government (GPT group), ESF and Spanish MINECO (projects ENE2010-18985 and ENE2013-41523-R) for providing financial support. The authors would also like to acknowledge the use of the Servicio General de Apoyo a la Investigación- SAI of the Universidad de Zaragoza. In addition, Javier Remón Núñez would like to express his gratitude to the Spanish MINECO for the FPI grant awarded (BES- 2011-044856).

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