

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

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11 **ABSTRACT**

12 The present work studies the influence of the temperature (200-240 °C), pressure
13 (38-50 bar), glycerol concentration (10-50 wt.%) and mass of catalyst/ glycerol mass
14 flow rate ratio ($W/m_{\text{glycerol}} = 10-40 \text{ g catalyst min/g glycerol}$) during the aqueous
15 phase reforming (APR) of a glycerol solution obtained from the production of
16 biodiesel. The operating conditions exerted a statistically significant influence on the
17 reforming results. Specifically, the global glycerol conversion and the carbon
18 converted into gas and liquid products varied as follows: 4-100%, 1-80% and 16-
19 93%, respectively. The gas phase was made up of H₂ (8-55 vol.%), CO₂ (34-66
20 vol.%), CO (0-4 vol.%) and CH₄ (6-45 vol.%). The liquid phase consisted of a
21 mixture of alcohols (monohydric: methanol and ethanol; and polyhydric: 1,2-
22 propanediol, 1,2-ethanediol, 2,3-butanediol), aldehydes (acetaldehyde), ketones (C3-
23 ketones: acetone and 2-propanone-1-hydroxy; C4-ketones: 2-butanone-3-hydroxy
24 and 2-butanone-1-hydroxy; and cyclic ketones), carboxylic acids (acetic and
25 propionic acids) and esters (1,2,3-propanetriol-monoacetate), together with unreacted

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

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

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1 **1. Introduction**

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

10

11 Given this background, two main options are usually considered to deal with this
12 biodiesel-derived glycerol. The first consists of its purification for further use in other
13 industries such as the food, cosmetics and pharmaceutical sectors [1, 2]. The second
14 option consists of upgrading the crude glycerol employing different valorisation routes.
15 These include gasification, steam reforming, aqueous phase reforming and supercritical
16 reforming, among others [3, 4], allowing the production of different value-added
17 chemicals and/or energy, and thus improving biodiesel economy and sustainability [5,
18 6].

19

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

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

8

9 A promising strategy to obtain value-added chemicals from this biodiesel derived
10 glycerol is aqueous phase reforming (APR). APR is a catalytic process carried out at
11 quite low temperatures and moderate pressures, allowing the production of different
12 chemicals (gases and liquids) from an organic feedstock. During the APR of glycerol,
13 various liquid-gas-solid chemical reactions take place. These include cracking and
14 reforming reactions to generate hydrogen, dehydrogenation of alcohols/hydrogenation
15 of carbonyls, deoxygenation and hydrogenolysis as well as cyclisation reactions. The
16 gas phase consists of a gas with a high H₂ content, the liquid phase being a complex
17 mixture of different organic compounds in water. These include alcohols, ketones,
18 acids, esters, paraffins, aldehydes and other oxygenated hydrocarbons with different
19 compositions depending on the operating conditions of the process and the nature of the
20 feed [6-9]. The versatility of this valorisation process allows the customised conversion
21 of glycerol into chemicals of a different nature to suit the necessities of the market, thus
22 converting this process into a very promising tailor-made route for the treatment and
23 valorisation of the glycerol obtained from the biodiesel industry.

24

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

1 [7, 9-11] and the vast majority of the publications in the literature are focused on
2 understanding the effect of the catalyst type and the operating conditions during the
3 APR of reagent-grade glycerol. The catalysts used in the process are noble metals based
4 on Pt [11-16], Ni [11, 12, 16-20], Pt-Ni, Cu, Co or Ru [9, 12, 16, 18, 21] supported on
5 different oxides such as Al₂O₃, ZrO₂, MgO, SiO₂, CeO₂, or carbon [7, 22] and modified,
6 in some cases, with promoters such as La, Ce, Mg and Zr.

7
8 The influence of the operating variables on the process has been studied in some works.
9 Özgür et al. [14] studied the effect of the temperature (160-280 °C), flow rate (0.05-0.5
10 mL/min), pressure (0-75 atm) and glycerol concentration (5-85 wt.%). The optimum
11 temperature for hydrogen production was 230 °C and the maximum gas production rate
12 was found using feed flow rates of 0.1 mL/min. In addition, they reported that the
13 hydrogen concentration in the gas increased with decreasing the glycerol concentration
14 of the feed. Wawrzetz et al. [23] reported the effect of the glycerol concentration (10-30
15 wt.%) and pressure (26-45 bar) at 498 K. Reaction rates increased with the increase in
16 the glycerol concentration. The pressure was found to have a significant effect on the
17 liquid product distribution without affecting the global conversion of the process.

18
19 Roy et al. [21] investigated the effect of the initial pressure (0-41 bar of N₂) at 493 K
20 using a 9.2 wt.% glycerol solution in a batch reactor, initially fed with 3 g of glycerol
21 and 0.125 g of catalyst, for 6 h. An increase in the initial pressure up to 14 bar of N₂
22 augmented the glycerol conversion from 43.2 to 50.2%, while a further increase up to
23 41 bar decreased the glycerol conversion. The product distribution was not greatly
24 affected by the pressure. An increase in temperature from 473 to 523 K at 14 bar of N₂
25 raised the glycerol conversion from 20.6 to 82.6%, reduced the proportion of ethylene

1 glycol and increased the concentration of ethanol in the liquid.

2

3 Manfro et al. [19] used a batch reactor to study the effect of the glycerol concentration
4 (1-10 wt.%), temperature (523-543 K) and its corresponding pressure (37-52 atm). The
5 highest glycerol conversion (30%) was achieved at 543 K using a 1 wt.% glycerol
6 solution. An increase in the glycerol concentration decreased the glycerol conversion
7 and H₂ formation. A rise in the temperature and pressure increased the glycerol
8 conversion and decreased the proportion of H₂ in the gas. Luo et al. [24] reported the
9 effect of the temperature (180-220 °C) and its corresponding pressure (1.14 -2.5 MPa),
10 glycerol concentration (5-10 wt.%) and liquid hourly space velocity (1.56-3.12 h⁻¹) in a
11 flow reactor. An increase in temperature (and its corresponding pressure) facilitated the
12 reforming process and increased the hydrogen yield. The carbon conversion to gas and
13 the H₂ yield decreased with augmenting the glycerol concentration. Decreasing the
14 hourly space velocity resulted in a higher hydrogen yield, hydrogen selectivity and
15 carbon conversion to gas.

16

17 Seretis and Tsiacaras [25, 26] studied the effect of the reaction time (30-240 min),
18 temperature (200-240 °C), glycerol concentration (1-10 wt.%) and catalyst weight using
19 a Ni/SiO₂-Al₂O₃ catalyst (0.5-10 g) [25] and a Pt/Al₂O₃ catalyst (0.5-2.5 g) [26]. The
20 glycerol conversion increased with increasing the reaction time and temperature. The H₂
21 production was maximised with the use of short reaction times and low glycerol
22 concentrations. An increase in the amount of catalyst increased the C-C cleavage,
23 favouring the formation of ethylene glycol, ethanol and methane. When using the
24 Ni/SiO₂-Al₂O₃ catalyst, the highest conversions to gaseous and liquid products were 74

1 and 36%, respectively, while for the Pt/Al₂O₃ catalyst they were 41 and 39%,
2 respectively.

3

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

12

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

18

19 **2. Material and methods**

20 *2.1 Crude glycerol*

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

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

6
 7 Table 1. Properties of the crude and purified glycerol solutions. Results are presented as
 8 mean \pm standard deviation.

	Crude glycerol	Purified glycerol
Composition		
Glycerol (wt.%)	63.17 \pm 2.26	85.25 \pm 0.79
CH ₃ OH (wt.%)	34.37 \pm 2.13	6.03 \pm 0.17
CH ₃ COOH (wt.%)	0	3.94 \pm 0.86
Ashes (wt.%)	2.06 \pm 0.23	4.56 \pm 0.37
H ₂ O (wt.%)	1.63 \pm 0.02	1.38 \pm 0.002
Ultimate Analysis		
C (%)	40.48 \pm 0.29	36.33 \pm 0.65
H (%)	8.19 \pm 0.06	7.55 \pm 0.03
O (%) ^a	51.33 \pm 0.34	56.11 \pm 0.63
TOC (ppm)	404733 \pm 2850	363333 \pm 6536
Physical properties		
pH	13.1 \pm 0.3	6.0 \pm 0.3
Density (g/mL)	1.060 \pm 0.001	1.043 \pm 0.001
Viscosity (mPa s)	49.93 \pm 1.48	247.41 \pm 3.93
LHV (MJ/kg)	21.89 \pm 0.05	16.96 \pm 0.03

9 ^a Determined by difference

10
 11 The crude glycerol was neutralised with acetic acid using a final pH of 6. Acetic acid
 12 was selected for the glycerol purification as its presence in the refined glycerol solution
 13 can contribute to H₂ formation, without deactivating the catalysts used in APR as occurs
 14 when using H₂SO₄ due to the presence of S. In addition, the work of Manosak et al. [1]
 15 indicates that this acid is suitable for the purification of glycerol obtained from the
 16 biodiesel industry.

17

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

10

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

16

17 *2.2 Experimental system*

18 The experiments were carried out in a small bench scale continuous unit employing a
19 NiAlLa catalyst. A reaction time of 3 hours was selected in order to be able to analyse
20 the evolution over time of the gas and liquid phases while also studying the stability of
21 the catalyst in the process [30-33]. The catalyst was prepared by coprecipitation, having
22 a 28% (relative atomic percentage) of Ni expressed as $\text{Ni}/(\text{Ni}+\text{Al}+\text{La})$, an atomic La/Al
23 ratio of 0.035 and a BET surface area of $187 \text{ m}^2/\text{g}$. The experimental ring used in the
24 experiments was a microactivity unit designed and built by PID (Process Integral

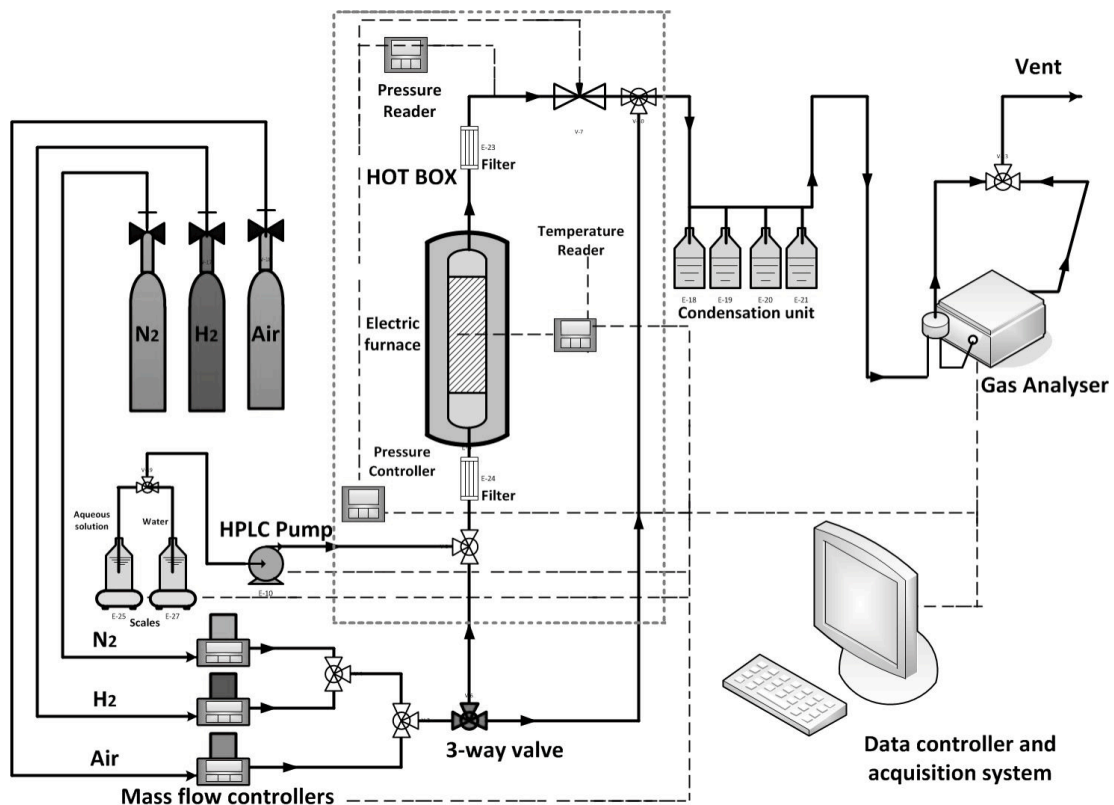
1 Development Eng & Tech, Spain). It consists of a stainless steel tubular reactor with an
2 inner diameter of 9 mm, heated up by means of an electric furnace [33]. The system
3 pressure is reached with the aid of a micrometric valve which automatically adapts its
4 position with the help of a rotor. A pressure gauge, located at the exit of the reactor,
5 measures the pressure of the reaction section. A PDI control system is used to keep the
6 reactor pressure constant during the experiments. The aqueous solutions of crude
7 glycerol are fed into the reactor by means of a high performance liquid chromatography
8 (HPLC) pump. The reaction products (gas and liquids) and the unreacted glycerol leave
9 the reactor from its upper part, pass through the valve, where they are depressurised,
10 and arrive at the condensation system. This system consists of four different condensers
11 where the liquid products are separated from the gas mixture at intervals of 1 h to
12 analyse the evolution over time of the liquid phase. The gas mixture is made up of N₂,
13 used as an internal standard, and the different gaseous products formed during the
14 aqueous phase reforming reaction. A micro chromatograph equipped with thermal
15 conductivity detectors (TCD) was used for the online analysis of the gas phase. At the
16 end of the experiment the liquid fractions were collected and analysed offline with a gas
17 chromatograph equipped with Flame Ionization (FID), and Mass Spectrometry (MS)
18 detectors. A schematic diagram of the experimental system is shown in Figure 1.

19

20 *2.3 Operating conditions, response variables and statistical analyses*

21 The effect of the temperature (200-240 °C), pressure (38-50 bar), glycerol concentration
22 (10-50 wt.%) and catalyst mass/glycerol mass flow rate ratio (10-40 g catalyst min/g
23 glycerol) was experimentally analysed using a design of experiments (DOE) with
24 statistical analysis of the results carried out by means of an analysis of variance
25 (ANOVA).

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2

3

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

5

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

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

8

9 Table 2. Operating conditions employed in the experiments

Run	Glycerol (wt.%)		Pressure (bar)		Temperature (°C)		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

10

11

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

7

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

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

10

11 CC_{liq} = Carbon conversion to liquid products (unreacted glycerol free).

12 CC_{liq}^* = Carbon conversion to liquids including unreacted glycerol

13

14 Some of the used catalysts were characterised by X-Ray diffraction (XRD) and
 15 Thermogravimetric (TG) analyses. XRD patterns of the used catalysts were obtained
 16 with a D-Max Rigaku diffractometer equipped with a $CuK \alpha 1.2$ at a tube voltage of 40
 17 kV and current of 80 mA. The measurements were carried out using continuous-scan
 18 mode with steps of $0.03^\circ/s$ at Bragg's angles (2θ) ranging from 5° to 85° . The phases
 19 present in the samples were defined with reference to the JCPDS-International Centre
 20 for Diffraction Data 2000 database. TG analyses were conducted under a N_2
 21 atmosphere, increasing the temperature from room temperature (around $25^\circ C$) to 600

1 °C at a heating rate of 10 °C/min. The weight loss was measured and the conversion (X),
2 defined as the variation of the mass with the respect to the initial sample mass, was
3 calculated.

4
5 First of all, the evolution over time of the response variables was studied. For each
6 experiment, the results are divided into three intervals. Each interval corresponds to the
7 average value of the studied response variables obtained during each one of the three
8 hours of experiment. All these values (three per experiment) have been compared using
9 a one-way analysis of variance (one-way ANOVA) and Fisher's least significant
10 difference (LSD) test, both with 95% confidence. The results of the ANOVA analyses
11 are provided as p-values. P-values lower than 0.05 indicate that at least two values are
12 significantly different. Furthermore, the LSD test was used to compare pairs of data, i.e.
13 either between two intervals of the same experiment or between two intervals of two
14 different experiments. The results of the LSD tests are presented graphically in the form
15 of LSD bars. To ensure significant differences between any pairs of data, their LSD bars
16 must not overlap.

17
18 Secondly, the effect of the operating conditions was studied considering the results
19 corresponding to the first hour using a statistical analysis of variance (one-way
20 ANOVA) test with 95% confidence. This strategy allows not having to include the
21 effect of the variations with time of the different response variables in the analysis. In
22 addition, the cause-effect Pareto principle was used to calculate the relative importance
23 of the operating variables on each response variable.

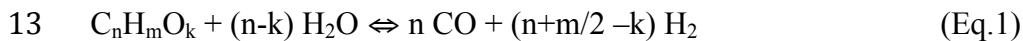
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1 *2.4 Possible reaction network during the aqueous phase reforming of glycerol*

2 A plausible reaction pathway for the aqueous phase reforming of glycerol is shown in
3 Figure 2. The reaction network includes the formation of gases and liquid products.
4 Three possible parallel routes explain the formation of intermediate liquids: glycerol
5 dehydration to 1-hydroxypropan-2-one (A) [6, 7, 21, 23, 34-36] and/or to 3-
6 hydroxypropanal (B) [6, 23, 35, 36] and/or glycerol dehydrogenation to 2,3-
7 dihydroxypropanal (C) [6, 7, 21, 23, 34-36]. Gases, mainly H₂ and CO, are produced by
8 the thermal decomposition and/or reforming reactions of the glycerol and all the liquid
9 intermediates (Eq.1) as well as by all the decarbonylation reactions that release CO. In
10 addition, the water gas shift reaction (Eq.2) and methanation reactions (Eq.3-4) are also
11 possible, explaining the presence of CO₂ and CH₄ in the gas phase [6, 7, 21, 23, 34-36].

12



17

18 *2.4.1 Formation of products via 1-hydroxypropan-2-one: route A*

19 1-hydroxypropan-2-one can undergo further hydrogenation to produce propane-1,2-diol
20 [6, 7, 23, 35, 36] (the preferred and most reported route) and/or dehydration to form
21 acrylaldehyde [35], which can be transformed into propionic acid [35]. Propane-1,2-diol
22 can subsequently be dehydrated to form propan-2-one and/or propionaldehyde, which
23 can be hydrogenated to propan-2-ol and propan-1-ol, respectively [35]. Afterwards,

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

4

5 *2.4.2 Formation of products via 3-hydroxypropanal: route B*

6 The presence of 3-hydroxypropanal in the liquid product has not been detected in the
7 vast majority of works dealing with the aqueous phase reforming of glycerol. This
8 indicates that dehydration forming 1-hydroxypropan-2-one is more likely to occur
9 and/or that 3-hydroxypropanal may be instantaneously converted into other products in
10 subsequent reactions. These reactions produce 3-hydroxypropionic acid, acetaldehyde
11 and formaldehyde via the retro-aldol reaction [35], and/or propane-1,3-diol [34, 35] via
12 hydrogenation. Propane-1,3-diol can be further dehydrated to produce propionaldehyde
13 [35].

14

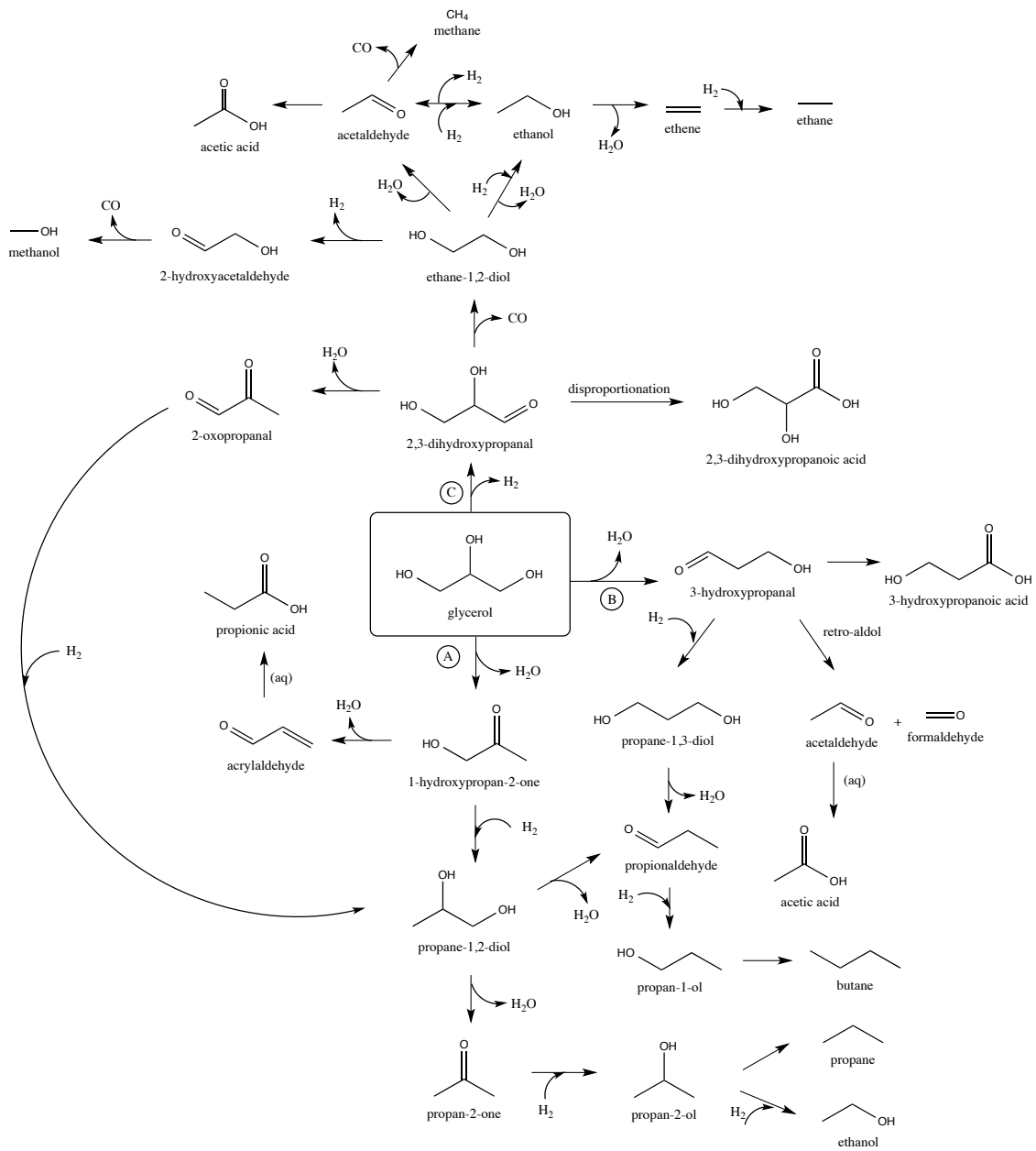
15 *2.4.3 Formation of products via 2,3-dihydroxypropanal: route C*

16 2,3-dihydroxypropanal can be transformed into 2,3-dihydroxypropionic acid,
17 dehydrated to form 2-oxopropanal and/or decarbonylated to produce ethane-1,2-diol.
18 Subsequently, 2-oxopropanal can be further hydrogenated to form propane-1,2-diol.
19 Additionally, 2-hydroxyacetaldehyde can be obtained from the dehydrogenation of the
20 latter and might lead to the formation of methanol by decarbonylation [6, 7]. In
21 addition, acetaldehyde and ethanol can be produced from the dehydration and the
22 dehydration/hydrogenation of ethane-1,2-diol, respectively [6, 7, 23]. Acetaldehyde can
23 subsequently be transformed into acetic acid and/or methane, while light alkanes such

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

2

3



4

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

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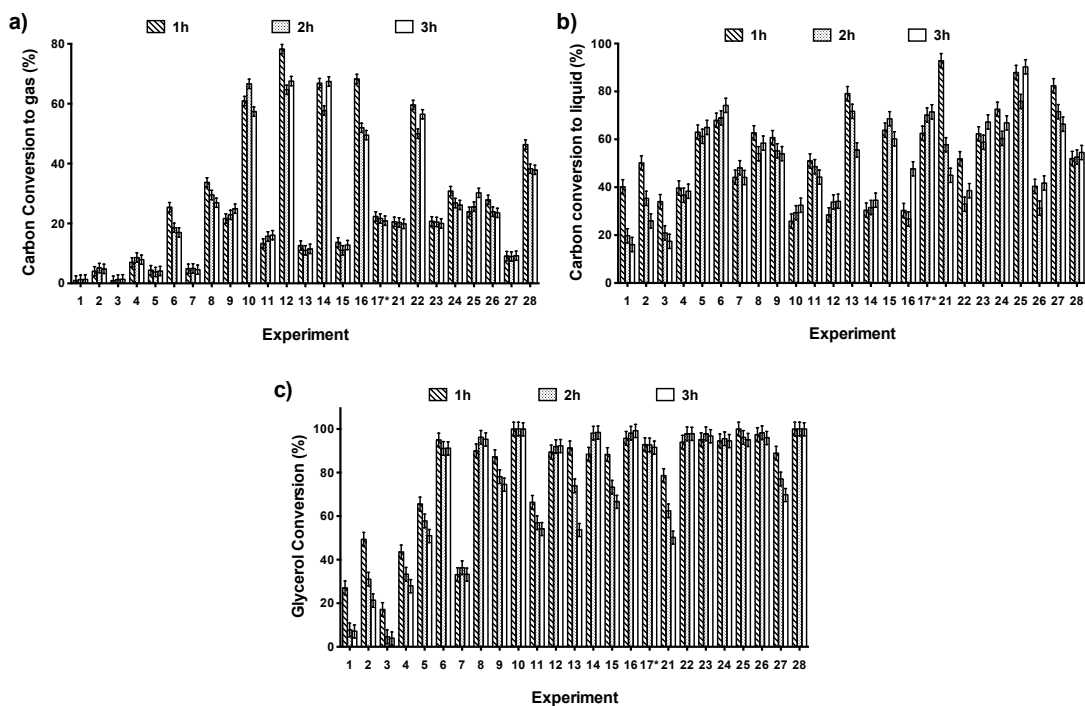
1 **3. Results and discussion**

2 *3.1 Carbon distribution and global glycerol conversion*

3 Figure 3 displays the carbon conversion to gas and liquid (CC gas, CC liq) as well as
4 the global glycerol conversion (X gly) obtained in the experiments. The statistical
5 analysis reveals significant differences between the results obtained in the experiments
6 for the CC gas, CC liq and X gly (p-values < 0.001). Specifically, they vary by 1-80%,
7 16-93% and 4-100%, respectively. The effect of the operating variables on the CC sol
8 was not significant (p-value > 0.05); in all the experiments the CC sol was lower than
9 1.5 %. The evolution over time of these variables shows drops in the X gly together
10 with increases and decreases in both the CC gas and the CC liq. These variations
11 indicate the existence of changes in the product distribution as the reaction advances
12 and/or that a catalyst deactivation may have taken place.

13

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



1

2 Figure 3. Conversion to gas (a), liquid (b) and global glycerol conversion (c) obtained
 3 during the APR experiments. Results are presented as the overall values obtained every
 4 60 minutes and expressed as mean \pm 0.5 Fisher LSD intervals with 95% confidence.

5

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

1 CC liq does not occur in experiment 8, probably due to the lower W/m_{glycerol} ratio
2 employed. High W/m_{glycerol} ratios and elevated temperatures might favour the initial
3 formation of gases and consequently the drop observed in the gas production over time
4 is sharper. These phenomena were also observed by El Doukkali et al. [37], who
5 reported a decrease and an increase over time in the production of gas and liquid
6 products, respectively, due to the progressive deactivation of the catalyst when
7 employing a Ni/Al₂O₃ catalyst for the APR of glycerol. This deactivation was the
8 consequence of the transformation of the alumina of the support into boehmite [37].

9

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

17

18 The CC liq displays increases and decreases over time. Increases occur in experiments
19 6, 12 and 16. These trends have been explained above for the evolution of the CC gas
20 over time. Decreases over time are observed for experiments 1, 2, 3, 21, 22, 24 and 27,
21 which were conducted with W/m_{glycerol} ratios from 10 to 25 g catalyst min/g glycerol
22 and glycerol concentrations lower than 30 wt.%. Additionally, the temperature exerts a
23 significant influence on the evolution of the CC liq with time. The lower the
24 temperature, the greater is the drop over time for this variable. Therefore, the greatest

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

6

7 The evolution of the X gly over time displays significant decreases for experiments 1-5,
8 9, 11, 13, 15, 21 and 27. These drops can be accounted for by the use of either a low
9 temperature or a low W/m_{glycerol} ratio. Experiments 1-5 were conducted with the lowest
10 W/m_{glycerol} ratio employed in this work (10 g catalyst min/g glycerol). Here neither the
11 temperature nor the pressure exerts a significant influence on the X gly evolution with
12 time. Conversely, for the same conditions of temperature and pressure but employing a
13 W/m_{glycerol} ratio of 40 g catalyst min/g glycerol (runs 9-13), drops over time were only
14 appreciated at 200 °C (runs 9, 1, 13 and 15). These results seem to indicate that the
15 catalyst deactivation could be more favoured at a low temperature and/or that the
16 positive kinetic effect of the temperature is able to partially compensate for catalyst
17 deactivation.

18

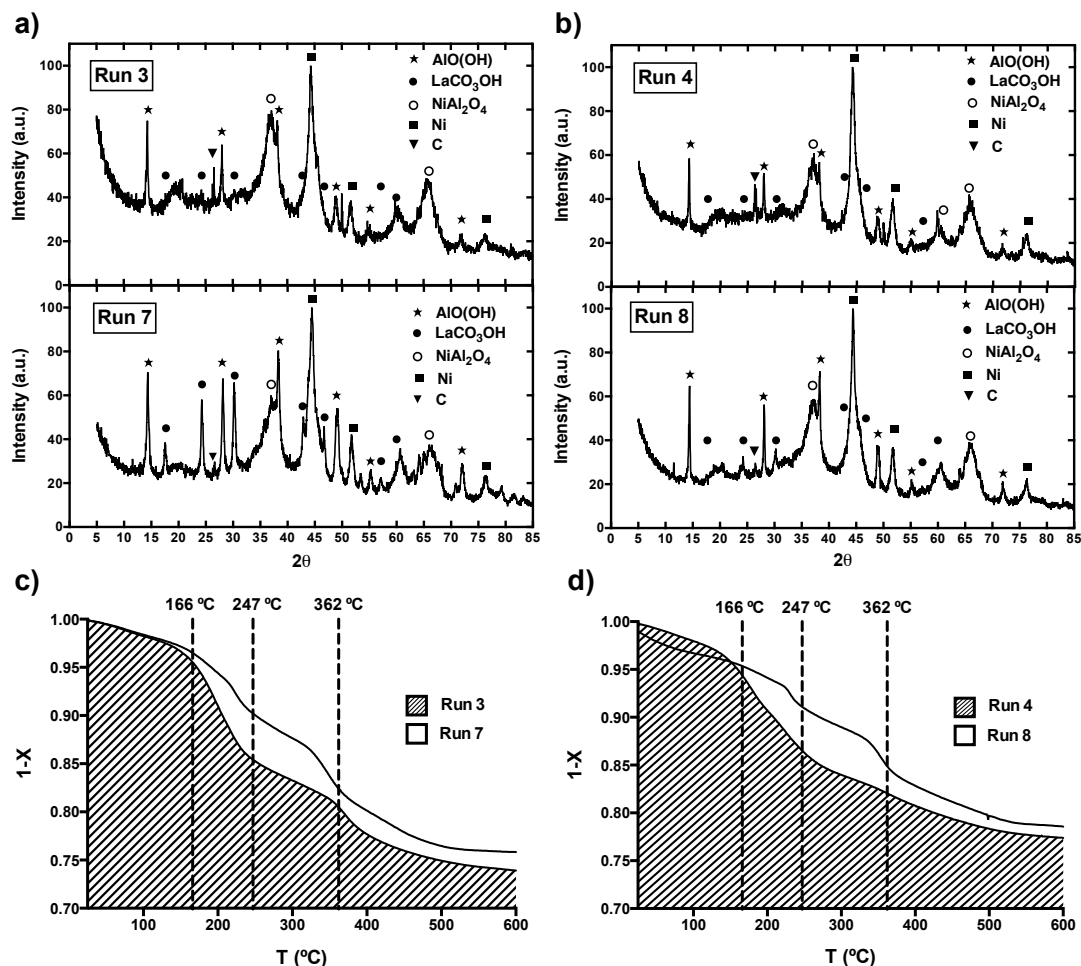
19 Very interestingly, it is observed that an increase in the glycerol concentration
20 diminishes the deactivation of the catalyst, especially at low temperatures. Comparing
21 the experiments conducted with low (1-4) and high (5-8) glycerol concentrations, a
22 higher decrease in the evolution of the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

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

4

5 To corroborate this hypothesis, the spent catalysts for runs 3 and 4 (10 wt.% glycerol)
6 and 7 and 8 (50 wt.% glycerol) were characterised by XRD and TG analyses. Figures 4
7 a and b and Figures 4 c and d show the XRD patterns and TG results of the used
8 catalysts, respectively. The XRD patterns have wide and asymmetric peaks, which
9 denote quite low crystallinity, and indicate the presence of Ni, NiAl₂O₃ and boehmite
10 (AlO(OH)) in the four used catalysts. This finding confirms that under the operating
11 conditions of APR, the alumina of the support can be transformed in boehmite. In
12 addition, C and LaCO₃OH are present in some of the samples. The TG analysis displays
13 four decomposition steps (25-166 °C; 166-247 °C; 247-362 °C and 362-600 °C), which
14 correspond to the decomposition of boehmite into alumina. At constant heating rates
15 this decomposition can be accurately modelled by a 4-reaction mechanism [38-40]
16 involving: (I) the loss of physisorbed water, (II) the loss of chemisorbed water, (III) the
17 conversion of boehmite into transition alumina, and (IV) the dehydration of transition
18 alumina (loss of residual hydroxyl groups). The experimental temperature ranges for the
19 decomposition of the used catalysts are fairly similar to those reported for the
20 decomposition of pure boehmite; the small differences being the consequence of having
21 incorporated different metals on the structure [40]. Very interestingly, a greater mass
22 loss occurs for runs 3 and 4 (conducted using a 10 wt.% glycerol solution) than for 7
23 and 8 (conducted using a 50 wt.% glycerol solution). The greatest differences in terms
24 of mass loss between the former and the latter occur between 166 and 362 °C, which
25 indicates the greater presence of physisorbed water in the structure of the catalyst along

1 with a larger transformation of the alumina of the support into boehmite during the APR
2 reaction. This accounts for the higher deactivation observed with the 10 wt.% than with
3 the 50 wt.% glycerol solutions.
4



5
6 Figure 4. XRD patterns (a and b) and TG analysis (c and d) for the used catalysts
7 employed in runs 3 and 4 (10 wt.% glycerol) and 7 and 8 (50 wt.% glycerol)
8
9 The specific effect of the operating conditions as well as their possible interactions on
10 the process has been studied considering the results obtained during the first hour of
11 reaction. The models created in terms of codec factors considering the ANOVA analysis

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

11

12 Significant interactions between the operating variables also influence the CC gas, CC
13 liq and X gly, as can be appreciated from the models displayed in Table 4. Figure 5
14 illustrates the effect of these interactions according to the ANOVA analysis. Figures 5 a
15 and b, e and f, and i and j show the effects on the CC gas, CC liq and X gly of the
16 reaction temperature, employing a pressure of 38 bar for W/m_{glycerol} ratios of 10 and 40
17 g catalyst min/g glycerol, when feeding 10 and 50 wt.% glycerol solutions, respectively.
18 Figures 5 c and d, g and h, and k and l display the effect of the temperature and the
19 W/m_{glycerol} ratio employing a pressure of 50 bar when glycerol solutions of 10 and 50
20 wt.%, respectively, were used. The most important effects and interactions of the
21 operating variables on the CC gas, CC liq and X gly are discussed in sections 3.1.1,
22 3.1.2 and 3.1.3, respectively.

23

24

1 3.1.1 Carbon conversion to gas: CC gas

2 The CC gas is mainly affected by the temperature and W/m_{glycerol} ratio. An increase in
3 these two variables augments the CC gas due to the positive kinetic effect that both
4 variables exert on the process [14, 19, 21, 23, 24]. At low temperatures, the production
5 of gas is not favoured, since reforming and cracking reactions are not predominant. The
6 prevailing chemical reactions lead to the formation of intermediate liquid products,
7 since their formation is prevalent under low glycerol conversions [23]. Thus, between
8 200 and 220 °C the CC gas is always lower than 30%, and the positive kinetic effect of
9 the temperature within this temperature range is relatively low. Conversely, a further
10 increase in temperature up to 240 °C increases the CC gas very sharply, especially when
11 using a W/m_{glycerol} ratio of 40 g catalyst min/g glycerol, which permits the CC gas to
12 reach 80% in some cases. Under this temperature range, reforming and cracking
13 reactions of both glycerol and its intermediate liquid products might be more favoured.

14

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