INFLUENCE OF OPERATING VARIABLES ON THE AQUEOUS-PHASE REFORMING OF GLYCEROL OVER A Ni/Al COPRECIPITATED CATALYST

L. García*, A. Valiente, M. Oliva, J. Ruiz, and J. Arauzo

Thermochemical Processes Group (GPT), Aragón Institute of Engineering Research (I3A), Universidad de Zaragoza, Mariano Esquillor S/N, 50018 Zaragoza, Spain.

Abstract

A systematic study focused on the aqueous-phase reforming of glycerol has been carried out in order to analyze the influence of several operating variables (system pressure, reaction temperature, glycerol content in feed, liquid feeding rate and catalyst weight/glycerol flow rate ratio) on the gas and liquid products. A continuous flow bench scale installation and a NiAl coprecipitated catalyst were employed. The system pressure was varied from 28 to 40 absolute bar, the reaction temperature was analyzed from 495 to 510 K, the glycerol content in the feed was studied from 2 to 10 wt%, the liquid feeding rate was changed from 0.5 to 3.0 mL/min and the catalyst weight/glycerol flow rate ratio varied from 10 to 40 g catalyst min/g glycerol. The main gas products obtained were H_2, CO_2 and CH_4, while the main liquid products were 1,2-propanediol, ethylene glycol, acetol and ethanol. A $W/m_{glycerol}$ ratio of 40 g catalyst min/g glycerol, 34 bar, 500 K, 5 wt% glycerol and 1 mL/min, resulted in a high yield to H_2 (6.8%), the highest yield to alkanes (10.7%), the highest 1,2-propanediol yield (0.20 g/g glycerol) and the highest ethylene glycol yield (0.11 g/g glycerol). The highest acetol yield (0.06 g/g glycerol) was obtained at 34 bar, 500 K, 5 wt% glycerol, 20 g catalyst min/g glycerol and 3 mL/min.

* Corresponding author. Tel.: +34 976762194; fax: +34 976761879. E-mail address: luciag@unizar.es (L. García).

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1. Introduction

The current energy system dependent on fossil fuels needs to be replaced because of environmental problems and the depletion of natural resources. Biomass can offer a solution due to its renewable nature. The production of biofuels such as biodiesel has increased significantly in recent years. For every 10 tons of biodiesel produced, 1 ton of glycerol is generated as a by-product. Given this high volume of production of glycerol, its valorization represents a significant challenge for the biodiesel industry. The review of Anitha et al. [1] presents a wide range of applications for glycerol, for example, in the synthesis of chemicals, in the fuel industry for the generation of hydrogen gas and also as an additive to improve the quality of fuel, for the development of fuel cells, for the pyrolysis and gasification of glycerol, for methanol production and for wastewater treatment. This review also indicates that the economic viability of these processes is still unknown in large-scale production. Tomishige et al. [2] has extensively worked on glycerol hydrogenolysis to 1,3-propanediol.

Hydrogen has many applications in chemical industries, in petrochemical refineries and for hydrogenation in food industries. Moreover, the use of hydrogen, a clean fuel, is a promising alternative for powering vehicles and as a source of power and heat for industries [3].

Glycerol is a renewable feedstock that could be used for hydrogen synthesis. It has several appropriate properties such as being non-toxic, non-flammable, non-volatile and having high energy density. Hydrogen can be generated from glycerol by biological and thermochemical processes. An example of the former is fermentation using Escherichia coli [4]. The latter include reforming processes such as steam reforming, partial oxidation reforming, autothermal reforming, supercritical water reforming and aqueous phase reforming [3].

In steam reforming, glycerol reacts with steam in the presence of a catalyst. The global reaction is represented by Eq. (1).

$$C_3H_8O_3 + 3\ H_2O \leftrightarrow 3\ CO_2 + 7\ H_2 \quad (1)$$

The main advantage of this process is the high production of hydrogen, with a theoretical maximum of 7 mole H_2/mole glycerol. Because of the endothermicity of steam reforming and the high temperatures used, the high consumption of energy for vaporization of the reaction mixture reduces the energy efficiency of the process. Extensive research work has been reported for this process including thermodynamic studies, catalytic investigations [5-7], studies on the effect of impurities [8], and on the development of new processes [9-11], among others [12-14].

In partial oxidation reforming, glycerol reacts with quantities of oxygen below the optimal stoichiometry for complete combustion. The global reaction of this process can be represented by Eq. (2).

$$C_3H_8O_3 + 1.5\ O_2 \leftrightarrow 3\ CO_2 + 4\ H_2 \quad (2)$$

In autothermal reforming, glycerol reacts with steam and oxygen. Autothermal reforming of glycerol has two important advantages compared to steam reforming: it is

energy self-sufficient and produces less coke formation [3]. A recent thermodynamic study shows high expectations for the sorption-enhanced process [15].

Supercritical water reforming of glycerol requires high temperatures and pressures, with high material costs, making this process economically unattractive. However, some experimental works have studied the use of different catalysts in this process [16, 17].

Aqueous-phase reforming (APR) is a relatively recent process that can be considered for the valorization of glycerol. APR was first investigated by Dumesic and coworkers [18]. The operating conditions of this process are temperatures around 500 K and pressures around 35 bar. The main advantages of this process are that no vaporization of the feedstock is required, which significantly decreases the input energy compared to steam reforming, the product gas has a low CO content (because in this range of temperatures the water gas shift reaction is shifted to H_2 and CO_2 production), and fewer secondary reactions occur [19].

Since 2002 when the first paper on APR was published, intensive work has been carried out in this field. Some authors have used batch installations [20-28] while others have used continuous flow set-ups [21, 29-43]. In the detailed review by Coronado et al. [44], the optimization of the operating conditions and the development of active and stable catalysts were identified as the main challenges for the development of APR technology.

The catalysts used include noble metals (Pt, Ru, Pd, Au, Rh), those based on platinum [21-23, 25-27, 29-35, 45, 46] being the most developed. Nickel catalyst has also been widely used [20, 24, 29, 31, 36, 37, 42, 47]. Bimetallic catalysts such as Pt-Fe, Pt-Co and Pt-Ni, among others, have also been tested in APR [26, 32, 40]. Shabaker et al. [29] employed Ni-Sn catalysts with varying contents of Sn, Manfro et al. [20] used Ni

catalysts supported on CeO_2 prepared by different techniques, while Valiente et al. [31] employed a coprecipitated NiAl catalyst. Iriondo et al. [48] tested alumina-supported nickel catalysts modified with Ce, Mg, Zr and La.

In the APR of ethylene glycol, higher H_2 selectivity and lower alkane selectivity were obtained with the platinum catalysts than with the nickel catalyst. The carbon conversion to gas was similar for the 28% Ni coprecipitated catalyst and the 1%Pt catalyst [31]. Because of the lower price of nickel compared to platinum, the use of nickel catalysts could be an interesting option for this process.

Operating variables that influence APR are temperature, system pressure, spatial velocity and organic content, among others. Valiente et al. [31] studied APR of ethylene glycol using a 3% Pt catalyst analyzing the effect of the system pressure and catalyst weight/ethylene glycol rate (W/m) ratio. When the system pressure increased from 27 to 36 bar at 500 K, carbon conversion to gas increased. A more significant increase in this conversion was observed when the W/m ratio increased from 5 to 30 g catalyst min/g ethylene glycol at 33 bar and 500 K. Small differences were observed in the gas composition when using the 3% Pt catalyst.

Other authors have also studied simultaneously the influence of pressure together with reaction temperature [20, 21, 29, 30, 39, 45]. Luo et al. [30] studied the influence of glycerol content in the feed using the same amount of catalysts. As a consequence, the catalyst weight/glycerol flow rate ($W/m_{glycerol}$) ratio was also changed. This study describes the effect of platinum loading on the catalyst performance and operating variables such as temperature and pressure. It was concluded that a higher reaction temperature and corresponding system pressure produces a higher hydrogen yield.

Most of the previous works in the literature are focused on the gas phase, for example Manfro et al. [20], Ozgür and Uysal [21], Kim et al. [45], Larimi et al. [35] and Subramanian et al. [25]. However, the conversion of glycerol in aqueous phase at temperatures around 473 to 523 K and pressures in the range of 26 to 50 bar produces a liquid phase containing compounds such as 1,2-propanediol, ethylene glycol, acetol and ethanol, among others [23, 24, 26, 32, 46].

Ethylene glycol is an important bulk chemical that is mainly used in antifreeze and as raw material for the manufacture of polyester fibers. 1,2-propanediol is a major commodity chemical with applications in unsaturated polyester resins, functional fluids, pharmaceuticals and cosmetics, among others [49]. Acetol has uses in the food and textile industries and for cosmetics [50].

Remón et al. [47] carried out an experimental work using glycerol derived from biodiesel production with a coprecipitated Ni/Al-La catalyst. This study covered a wide interval of operating conditions. However, the liquid phase was not analyzed quantitatively. The results of the present work and those of Remón et al. [47] will be compared in order to achieve more insights into aqueous phase reforming with coprecipitated catalysts.

This work presents a systematic study of the influence of the operating variables (system pressure, reaction temperature, glycerol content, liquid flow rate and W/m ratio) on the APR of glycerol using a NiAl coprecipitated catalyst. Quantitative results of gas and liquid phases are presented.

2. Material and methods

2.1. Experimental

The experimental system was developed and manufactured by PID Eng&Tech. It consists of a stainless steel tubular reactor with an inner diameter of 9 mm. The bed is composed of a mixture of inert sand and catalyst and is placed inside the tubular reactor between quartz wool supports. The particle sizes of catalyst and sand range between 160 and 250 μm. An aqueous solution of glycerol in deionized water is fed by means of a high performance liquid chromatography (HPLC) pump. The liquid flow exiting from the reactor is depressurized and cooled at atmospheric pressure by means of a Peltier cooler, where a condensable phase is separated consisting of water, liquid products and non-reacted glycerol. The gas flow exiting from the Peltier cooler is then analyzed with an Agilent 3000 Micro GC equipped with a molecular sieve column, a Plot U column and Thermal Conductivity Detectors (TCD), where N_2, H_2, CH_4, CO_2, CO, C_2H_6 and C_3H_8 can be quantified. A schematic diagram of the experimental system is shown in Figure 1.

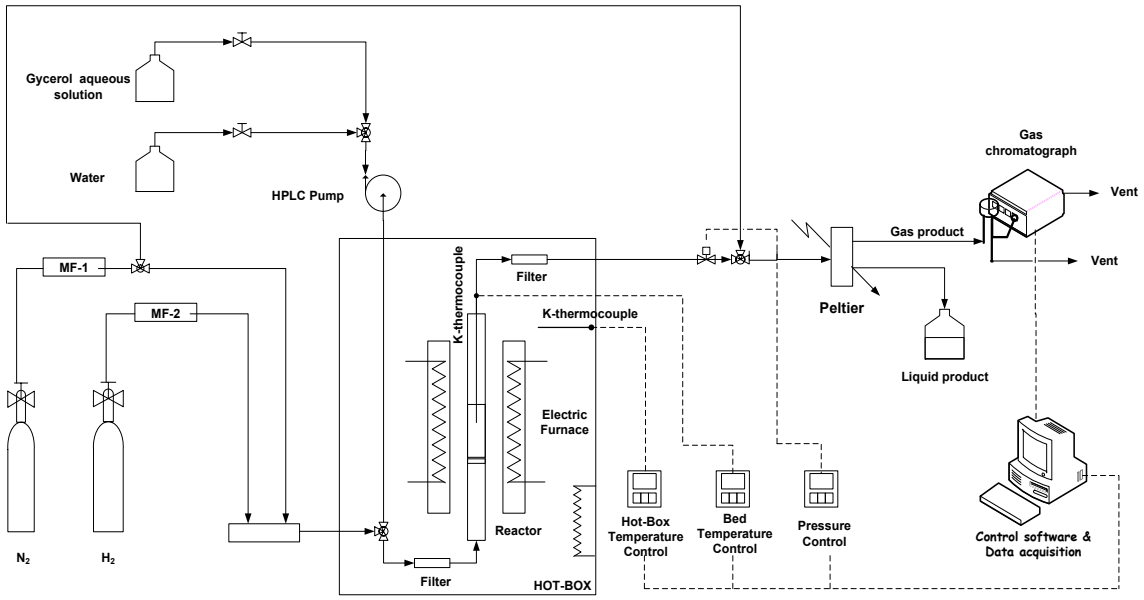

Figure 1. Schematic diagram of the APR experimental system.

The liquid product collected at the end of the experiment was analysed with an Agilent 7820A GC equipped with an Agilent 7693A automatic injector, an HP-FFAP Agilent 19091F-105 capillary column and a Flame Ionization Detector (FID), where acetaldehyde, acetone, methanol, ethanol, acetol, acetic acid, propanoic acid, 1,2-propanediol, ethylene glycol and glycerol were quantified. Previously the compounds in the liquid product were identified by GC-MS.

The total pressure of the system was achieved with pressurized nitrogen. A N_2 flow was directed to the Peltier unit in order to analyze the exiting product gas during the experiment. The nitrogen flow was 75 cm^3 (STP)/min. The reaction data were collected for up to 5 h in order to ensure that the steady state was reached.

The results of a blank experiment without catalyst show a very low glycerol conversion, less than 1%, which indicates the relevant role of the catalyst due to the conditions used in the process. A NiAl catalyst prepared by coprecipitation was used in all the experiments. This catalyst had a relative atomic nickel content of 28% Ni/(Ni+Al). The preparation method and characterization results of this catalyst have been previously reported [51]. The catalyst was in situ reduced with a hydrogen flow rate of 100 cm^3 (STP)/min at 923 K during 1 h.

Different experiments were carried out varying the system pressure (28 to 40 absolute bar), reaction temperature (495 to 510 K), glycerol content in the feed (2 to 10 wt%), feed flow rate (0.5 to 3 mL/min) and the catalyst weight/glycerol flow rate ratio ($W/m_{glycerol}$) from 10 to 40 g catalyst min/g glycerol. The repeatability of the results was checked with a standard deviation of around 3%.

The reagent selected in order to perform the experiments was 99.5% purity glycerol supplied by Sigma-Aldrich. Other chemicals used included commercial high purity

gases (>99.999%): hydrogen, nitrogen, air, helium and argon, as well as a standard gas mixture consisting of H_2, N_2, CO, CO_2, CH_4, C_2H_6 and C_3H_8 for calibration of the Micro GC. For calibrating the GC for the liquid product, reagents with more than 90% purity were employed.

2.2. Data analysis

Gas compositions were determined every four minutes by Micro GC. Because of the high stability over time observed in the results of the gas composition and yields to different gases, overall gas results are shown. These overall results correspond to the gas composition, carbon yield to gases, total gas and hydrogen and alkane yields.

Carbon yield to gases is calculated as the percentage of carbon in the product gases (CO_2, CO, CH_4, C_2H_6 and C_3H_8) compared to carbon in the glycerol fed. Total gas is expressed as moles of gas/moles of glycerol.

Hydrogen and alkane yields are defined as follows:

$$H_2\ yield\ (\%) = \frac{H_2 moles\ produced}{n_{glycerol\ feed} x7} x100$$

$$Alkane\ yield\ (\%)$$

$$= \frac{CH_4 moles\ produced + (C_2H_6 moles\ produced x2) + (C_3H_8 moles\ produced x3)}{n_{glycerol\ feed} x3} x100$$

where $n_{glycerol\ feed}$ are the moles of glycerol in the feed.

The moles of the liquid products acetaldehyde, acetone, methanol, ethanol (EtOH), acetol, acetic acid, propanoic acid, 1,2-propanediol (PG) and ethylene glycol (EG) and unreacted glycerol are quantified from the analysis of the liquid phase by GC-FID.

The global conversion of glycerol is calculated as follows:

$$Glycerol\ conversion\ (\%) = \frac{n_{glycerol\ feed} - n_{glycerol\ exit}}{n_{glycerol\ feed}} x100$$

where $n_{glycerol\ exit}$ are the moles of unreacted glycerol in the exit liquid.

Carbon yield to liquids is calculated as the percentage of carbon in the liquid products acetaldehyde, acetone, methanol, EtOH, acetol, acetic acid, propanoic acid, PG and EG, compared to carbon in the glycerol fed. This value does not include unreacted glycerol. There is a small difference between glycerol conversion and the addition of carbon yield to gases and carbon yield to liquids, due to some experimental errors in the analysis and some unidentified compounds. A carbon deficit smaller than 15% has been used, which is considered acceptable for the experiment reliability. The carbon deficit is defined as follows:

$$Carbon\ deficit = |Glycerol\ conversion - (carbon\ yield\ to\ gases + carbon\ yield\ to\ liquids)|$$

Other authors have also used the term "carbon deficit" [22].

The selectivity to a product is defined as the percentage ratio of carbon in a product to the total carbon in all the analyzed products. Glycerol is excluded from the products. Some studies in the literature [22, 52] employ this selectivity considering the products in the liquid phase as well as in the gas phase.

Liquid carbon selectivity has also been calculated and is defined as the percentage ratio of carbon in a liquid product to the total carbon in all the analyzed liquid products.

Yields of PG, EG and acetol, expressed as g/g glycerol, have been calculated as follows:

$$Yield\ A = \left(\frac{Selectivity\ A}{100}\right) * (carbon\ yield\ to\ gases + carbon\ yield\ to\ liquids) * \left(\frac{1}{100}\right) * \left(\frac{1}{R_A}\right) * R_{Glycerol}$$

Where $R_{Glycerol}$ is the mass fraction of carbon in glycerol (0.391) and R_A is the mass fraction of carbon in the considered compound A, this being PG, EG or acetol.

The units of each variable are specified for PG:

Yield PG is the ratio of grams of PG/grams of glycerol;

$\left(\frac{Selectivity\ PG}{100}\right)$ is the ratio of grams of carbon in PG/grams of total carbon in all the analyzed products from reacted glycerol.

$(carbon\ yield\ to\ gases + carbon\ yield\ to\ liquids) * (\frac{1}{100})$ is the ratio of grams of carbon in all the analyzed products/grams of carbon in the glycerol fed.

$R_{Glycerol}$ is the ratio of grams of carbon in glycerol /grams of glycerol = (3x12)/92 = 0.391

R_{PG} is the ratio of grams of carbon in PG/grams of PG = (3x12)/76 = 0.474.

2.3. The global reaction network

The liquid products identified and quantified were acetaldehyde, acetone, methanol, EtOH, acetol, acetic acid, propanoic acid, PG and EG, while the gas products were H_2, CO_2, CO, CH_4, C_2H_6 and C_3H_8.

Several researchers in the literature have proposed reaction pathways for the aqueous phase reforming of glycerol [19, 46, 53]. The reaction network includes gases and liquid products. There are two main routes in the liquid phase:

Route I: Dehydrogenation of glycerol to glyceraldehyde (or 2,3-dihydroxipropanal). This intermediate can be decarbonylated to produce EG. Acetaldehyde can be generated from EG by dehydration, while EtOH can be generated from EG by dehydration/hydrogenation. EtOH and acetaldehyde can produce acetic acid [54]. EG can be dehydrogenated/decarbonylated to produce MeOH.

Route II: Dehydration of glycerol to hydroxyacetone (or acetol). This intermediate can undergo further hydrogenation to produce PG. This is the main route in glycerol hydrogenolysis [22, 52, 55]. Acetone can be produced from PG by dehydration, while propionic acid can be generated from acetol by isomerization [56].

Glyceraldehyde, an intermediate product in route I, has not been detected. However, route I is carried out because of the existence of EG [28, 43]. Moreover, the decarbonylation of glyceraldehyde to EG is a rapid reaction according to the literature [27]. More details about these reactions can be found in the cited literature.

In gas phase, H_2 and CO are generated by the thermal decomposition and/or reforming reactions of the glycerol and all the liquid intermediates [53] :

$$C_nH_mO_k + (n-k)\ H_2O \leftrightarrow n\ CO + (n+ m/2 –k)\ H_2$$

Route I involves dehydrogenation/decarbonylation with CO production as an intermediate. CO is converted into CO_2 and H_2 by the water-gas shift (WGS) reaction:

$$CO\ (g)+ H_2O \leftrightarrow CO_2\ (g) + H_2(g)$$

Further reaction of H_2 with CO or CO_2 to form alkanes, especially CH_4, is favoured at low temperatures [57]:

$$CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O$$

$$CO_2(g) + 4H_2(g) \leftrightarrow CH_4(g) + 2H_2O$$

Fischer-Tropsch reactions can explain C_2H_6 and C_3H_8 production. Also, these gases can be generated by hydrogenation of C=C bonds such as ethene and propene [53].

The catalyst plays a relevant role in APR. Both the effect of the support and the metal phase are very important [38, 46]. The Ni active sites favour C-C bond cleavage and the WGS reaction [44]. Ni presents activity for hydrogenation/dehydrogenation reactions.

The acid properties of the catalyst have been considered by some authors in the literature. γ-alumina, an acid support, promotes the dehydration reaction of glycerol to acetol [43].

3. Results and discussion

3.1. Influence of the system pressure

The experiments were performed at 500 K with a 5 wt% content of glycerol in the feed, a $W/m_{glycerol}$ ratio of 20 g catalyst min/g glycerol and a liquid feeding rate of approximately 1 mL/min. The absolute system pressure was varied from 28 to 40 bar. Figure 2 shows the carbon yield to gases, carbon yield to liquids and glycerol conversion for the pressure values studied. A significant increase is observed in glycerol conversion with the increase of the system pressure, from 42% at 28 bar to 65% at 40 bar. The carbon yield to liquids is higher than the carbon yield to gases for all the pressures studied. The carbon yield to gases and carbon yield to liquids also increase with the increase of the system pressure. A higher increase is observed in the carbon yield to gases (109% increase, calculated from 10.9% and 22.8% at 28 and 40 bar, respectively) than the carbon yield to liquids (45.1% increase, calculated from 19.3% and 28.0% at 28 and 40 bar, respectively). The increase in the carbon yield to liquids is higher from 28 to 34 bar and then lower up to 40 bar. The increase in the carbon yield to gases is more continuous in the range of pressures analyzed.

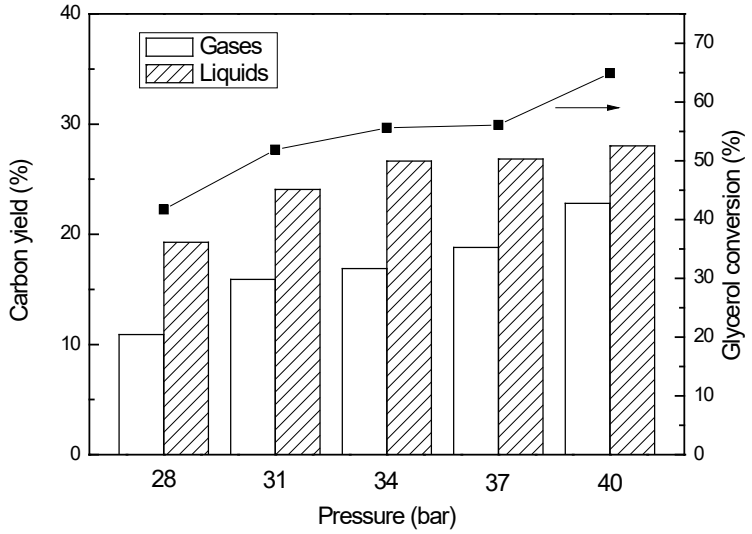

Figure 2. Influence of the system pressure on global results: glycerol conversion, carbon yield to gases and liquids. Operating conditions: 500 K, 5 wt% glycerol, 1 mL/min and $W/m_{glycerol}$ = 20 g catalyst min/g glycerol.

Table 1 shows the overall results corresponding to the gas phase, including the gas composition (mol%, N_2 and H_2O free), total gas and hydrogen and alkane yields. The gas composition analysis shows that the main gases are H_2, CO_2 and CH_4, with low amounts of CO, C_2H_6 and C_3H_8. There is a clear decrease in the H_2 content and an increase in the CH_4 content when the system pressure increases. The CO content in the product gas is low, 1.1% mol at 28 bar, and decreases with the increase in the system pressure. The C_2H_6 content increases from 0.6% to 1.2% when the system pressure increases. The CO_2 and C_3H_8 contents in the product gas barely change with varying the pressure. Total gas follows the same tendency as the carbon yield to gases. The H_2 yield presents values from 4% to 4.8% and no clear tendency is observed with the increase in the system pressure. This is due to the increase in gas yields and the decrease in the H_2 content in the gas as the system pressure increases. The alkane yield varies from 2.4%

to 8.2%, showing a clear increase when the system pressure increases. This is due to the simultaneous increase of the carbon yield to gas and the CH_4 and C_2H_6 content when the system pressure increases.

Table 1. Overall results of the gas phase in the APR of glycerol. Influence of the system pressure. Operating conditions: 500 K, $W/m_{glycerol}$ = 20 g catalyst min/g glycerol, 5 wt% glycerol and 1 mL/min.

Run#	**1**	**2**	**3**	**4**	**5**
Pressure (absolute bar)	28	31	34	37	40
Gas composition (%mol, N_2 and H_2O free)					
H_2	46.3	41.6	38.5	35.6	33.3
CO_2	41.5	42.4	43.8	43.4	43.3
CO	1.1	0.6	1.0	0.5	0.4
CH_4	10.2	14.4	15.6	19.2	21.6
C_2H_6	0.6	0.9	0.9	1.1	1.2
C_3H_8	0.2	0.2	0.2	0.2	0.2
Total gas (mol gas/mol glycerol)	0.60	0.80	0.81	0.86	1.00
Gas yields (%)					
H_2	3.96	4.74	4.44	4.35	4.76
Alkane	2.40	4.47	4.84	6.28	8.21

Figure 3 shows the global carbon selectivity to the analysed products, including gas and liquid products. The gas product with the highest carbon selectivity is CO_2 with a value around 28%, with almost no variation with the system pressure. CH_4 also presents a high carbon selectivity which increases from 7% to 14% when the system pressure increases from 28 to 40 bar.

The main liquid products obtained are PG, EG, acetol and EtOH. The carbon selectivity of PG, EG and EtOH is around 25%, 16% and 8% respectively, with almost no variation with the increase in the system pressure. The carbon selectivity of acetol shows a decrease from 11% to 5% when the system pressure increases from 34 to 40 bar. The same tendencies observed in Figure 3 are also followed by liquid carbon selectivity (Figure S1). Liquid carbon selectivity of PG is around 40%.

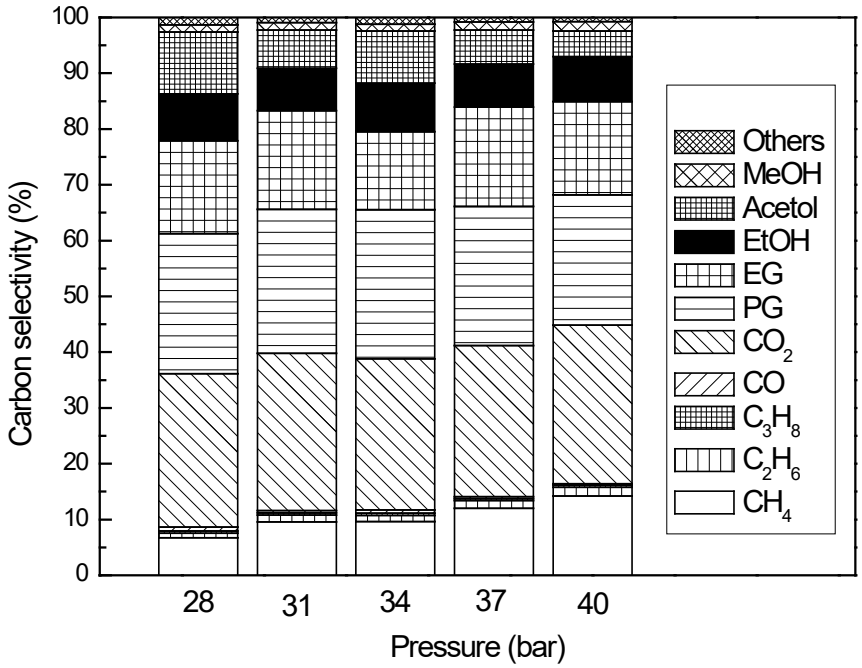

Figure 3. Influence of the system pressure on global carbon selectivity to products. Operating conditions: 500 K, 5 wt% glycerol, 1 mL/min and $W/m_{glycerol}$ = 20 g catalyst min/g glycerol.

Methanation reactions and Fischer-Tropsch reactions are favoured at high pressure [18, 19, 32]. These reactions can explain the increase in CH_4 and C_2H_6 contents and the decrease in H_2 and CO contents at 40 bar. From a thermodynamic point of view, the influence of pressure on the WGS reaction is different in aqueous phase reforming than in steam reforming. In steam reforming, water is in gas phase and the pressure has no influence. In aqueous phase reforming, water is in liquid phase and the increase in pressure does not promote H_2 production. On the other hand, the increase in pressure increases hydrogen solubility in the aqueous phase which favours hydrogenation reactions, for example the production of PG.

The comparison of these results with others published in the literature is not easy. First, the experimental installation may be different: batch or continuous. Second, the operating conditions (temperature, pressure, amount of catalyst, content of glycerol in the aqueous solution, among others) may vary, but they must be similar for the purposes of comparison. Third, the catalyst may be different. Moreover, the published data may be expressed using different parameters or calculations. These points have to be considered in order to obtain valuable conclusions.

Seretis and Tsiakaras [23], using a Pt/Al_2O_3 catalyst in a batch installation, also found a higher conversion to liquid than gases when 0.5 g of catalyst was employed at temperatures from 473 to 513 K. Thus, 30 % glycerol conversion was achieved at 493 K, with around 20% and 10 % of conversion to liquid and gas, respectively [23]. However, when using 1 g of Ni/SiO_2-Al_2O_3 at temperatures of 493 and 513 K, a higher conversion to gases than liquid was observed and 50 % glycerol conversion was achieved at 493 K, with around 20% and 30% of conversion to liquid and gas, respectively [24]. This could be due to the high metal content, 65% Ni. High temperatures correspond to high pressures in batch installations.

Other authors have published results consistent with these. Using a Pt/Al_2O_3 catalyst, Shabaker et al. [29] observed an increase in carbon conversion to gas and a decrease in hydrogen content when the system pressure increased from 29.3 to 56 bar in the aqueous phase reforming of glycerol. Moreover, they reported an increase in CH_4 content when the pressure and temperature were increased. Other feeds used such as sorbitol and ethylene glycol follow these tendencies. Luo et al. [30], also using a Pt/Al_2O_3 catalyst, found an increase in the H_2 yield when the temperature and pressure were increased. Manfro et al. [20], using a Ni/CeO_2 catalyst, observed higher glycerol conversion when the pressure and temperature were increased and also a gas with less

H_2 content. These tendencies were also found by Özgür and Uysal [21] employing a batch reactor and a solution with 80 wt% glycerol.

El Doukkali et al. [32] prepared a NiAl catalyst by the acid sol-gel method and tested this at 503 K, 30 bar, 10 wt% glycerol and 23 g catalyst min/g glycerol, which are operating conditions similar to those of the present work at 31 bar and 500 K. The results of the work of El Doukkali et al. [32] are very similar in glycerol conversion and the carbon yield to gases; moreover, only small differences in the PG and EG yields can be found. Thus, glycerol conversion is 57% (52% in the present work), carbon yield to gases is 12% (16% in the present work), PG yield is 0.165 g/g glycerol (0.085 in the present work) and EG yield is 0.028 g/g glycerol (0.071 in the present work).

High stability over time in the results of the gas composition and yields to different gases has been observed during the five hours of time-on-stream. However, some changes in the catalyst structure are expected, such as the instability of Al in the support that converts into boehmite [27, 37, 38], also the sintering of the active phase [27, 38, 40, 41] and metal leaching, among others. The reusability of the prepared catalyst and the catalyst life are important subjects that require further research. This work backed up with the characterization of spent catalyst will provide significant information about the viability of the catalyst over long reaction times.

It can be concluded that the use of the highest value of the system pressure, 40 bar, produces high H_2 and alkane yields, 4.8% and 8.2% respectively, as well as high yields to liquids: 0.098 g PG/g glycerol and 0.086 g EG/g glycerol. However, the highest yield to acetol is obtained at 34 bar with 0.033 g/g glycerol.

3.2. Influence of the reaction temperature

The experiments were performed at 34 absolute bar pressure, with a 5 wt% content of glycerol in the feed, a $W/m_{glycerol}$ ratio of 20 g catalyst min/g glycerol and a liquid feeding rate of approximately 1 mL/min. The reaction temperature was varied from 495 to 510 K. The highest temperature of 510 K was used in order to be sure to achieve water in liquid phase with an operational safety margin at the system pressure.

Figure 4 shows the carbon yield to gases, carbon yield to liquids and glycerol conversion for the temperature values studied. The general tendency shows that the glycerol conversion, carbon yield to gases and carbon yield to liquids increase when the reaction temperature increases. The glycerol conversion increases from 39% at 495 K to 65% at 510 K. The gas production increase is higher (42% carbon yield to gases, calculated from 12.9% and 18.3% at 495 and 510 K, respectively) than that of the liquid production (24.5% carbon yield to liquid, calculated from 25.7% and 32% at 495 and 510 K, respectively).

Table 2 presents the overall results corresponding to the gas phase. In general, the H_2 and CO contents in the product gas increase when the reaction temperature increases while the CO_2, CH_4 and C_2H_6 contents decrease. Total gas increases with the increase in temperature. The H_2 yields have their highest value, 6.8%, at the highest temperature studied, 510 K. This is a consequence of the increase in the carbon yield to gases and the hydrogen content with the increase in temperature. However, the alkane yield has its highest value, 5.3%, at 505 K. The increase in the carbon yield to gases and the decrease in the CH_4 and C_2H_6 content with the increase in temperature are at a maximum at 505 K.

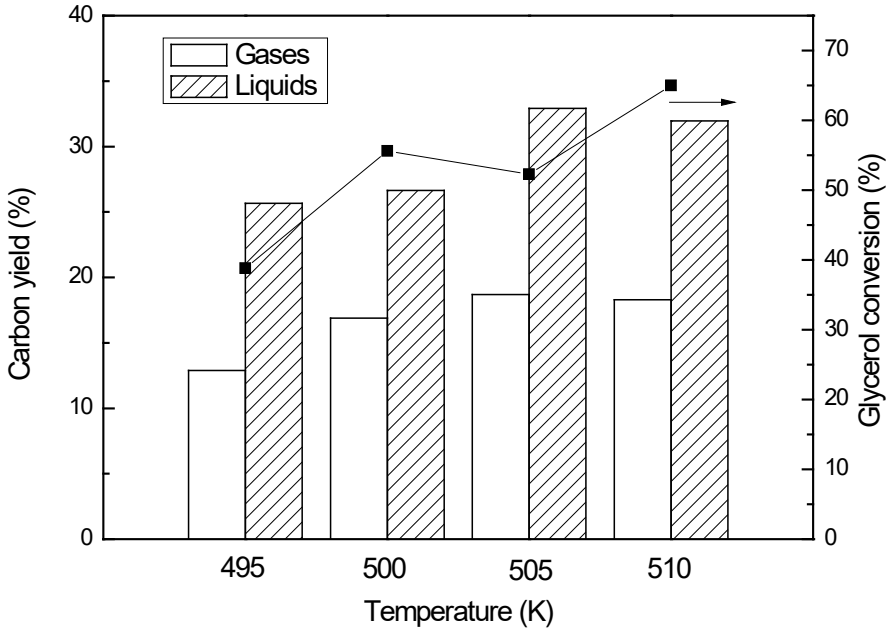

Figure 4. Influence of the reaction temperature on global results: glycerol conversion, carbon yield to gases and liquids. Operating conditions: 34 bar, 5 wt% glycerol, 1 mL/min and $W/m_{glycerol}$ = 20 g catalyst min/g glycerol.

In spite of the small range of temperature studied, a significant increase of total gas from 0.56 to 1.01 mol gas/mol glycerol has been observed when the reaction temperature increases from 495 to 510 K. Also, the H_2 content in the gas increases from 32.8 to 47.0%, the H_2 yield increases from 2.64 to 6.81%, and the CH_4 content in the gas decreases from 18.2 to 10.5% as the temperature increases.

Table 2. Overall results of the phase gas in the APR of glycerol. Influence of the reaction temperature. Operating conditions: 34 bar, $W/m_{glycerol}$ = 20 g catalyst min/g glycerol, 5 wt% glycerol and 1 mL/min.

Run#	**6**	**3**	**7**	**8**
Temperature (K)	495	500	505	510
Gas composition (%mol, N_2 and H_2O free)				
H_2	32.8	38.5	40.4	47.0
CO_2	47.2	43.8	43.2	40.2
CO	0.4	1.0	0.6	1.6
CH_4	18.2	15.6	14.7	10.5
C_2H_6	1.1	0.9	0.9	0.6
C_3H_8	0.2	0.2	0.2	0.2
Total gas (mol gas/mol glycerol)	0.56	0.81	0.92	1.01
Gas yields (%)				
H_2	2.64	4.44	5.32	6.81
Alkane	3.95	4.84	5.25	4.16

Figure 5 shows the global carbon selectivity to the analysed products, including gas and liquid products. The CO_2 has high carbon selectivity with values around 26% for the studied temperatures. The analysis of the selectivity to liquid products shows an increase in the EtOH and acetol selectivities and a decrease in the PG and EG when the reaction temperature increases. Thus, the carbon selectivities to PG and EG decrease from 32% to 25% and from 16% to 11%, respectively, when the temperature increases from 495 to 510 K. On the other hand, the carbon selectivity to EtOH and acetol increases from 8.5% to 10% and 8% to 11%, respectively, with the increase in temperature. An increase in the carbon selectivity of acetaldehyde (1%) and propanoic acid (3%) was observed at the highest temperature studied. The tendencies observed in Figure 5 are also followed in the liquid carbon selectivity (Figure S2).

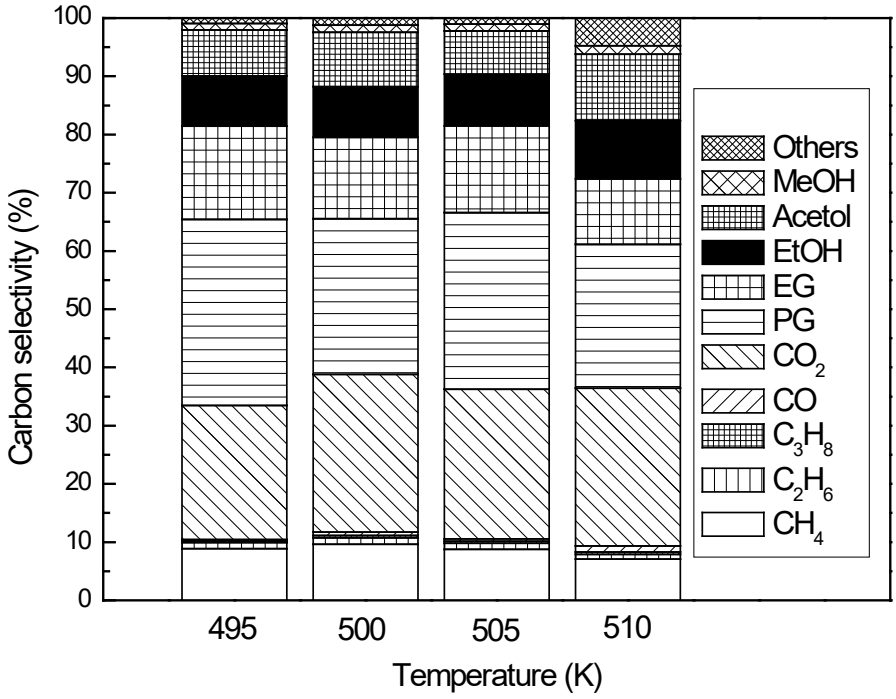

Figure 5. Influence of the reaction temperature on global carbon selectivity to products. Operating conditions: 34 bar, 5 wt% glycerol, 1 mL/min and $W/m_{glycerol}$ = 20 g catalyst min/g glycerol.

The gas composition can be explained considering the thermodynamic data of the reactions involved. Reforming reactions are endothermic and thus these are favoured at high temperatures. Consequently, the H_2 and CO contents would be expected to increase when the temperature increases. In contrast, methanation and Fischer-Tropsch reactions are exothermic and these reactions are thus not favoured at high temperatures. A decrease in CH_4 and C_2H_6 would therefore be expected when the reaction temperature increases.

Remón et al. [47] indicate that temperature significantly influences the carbon yield to gases and glycerol conversion, while the carbon yield to liquids depends on the glycerol content. The models developed in Remón et al. [47] at 38 bar, 10 wt% glycerol and 20 g catalyst min/g glycerol predict the increase in the carbon yield to gases. These values predicted by the model are quite similar to the experimental values in the present work. Thus, the model predicts 10% and 24% of carbon yield to gases at 495 and 510K respectively, while in the present work the experimental values are 13% and 18% at 495 and 510K, respectively. However, the carbon yields to liquids and glycerol conversion do not follow the same tendencies, having very different values. It is probable that the differences in the feed, the catalyst or other experimental details could have a significant influence.

The work of Kim et al. [45], using a Pt-Re catalyst, presents results with similar tendencies to those obtained in this work. They found an increase in the carbon conversion to gases and H_2 yield when the pressure and temperature increased from 22.1 to 42.8 bar and from 483 to 523 K, respectively, at a space velocity (WHSV) of 2.0 h^{-1} when feeding ethylene glycol [45]. The tendencies observed in this work concerning the gas composition are also reflected in other research studies [47].

In contrast, Shabaker et al. [29], using a Pt/Al_2O_3 catalyst and a LHSV of 0.64 h^{-1}, found a decrease in the H_2 content and an increase in the alkane content when the pressure and temperature increased from 29.3 to 56.0 bar and from 498 to 538K, respectively. They used feedstocks such as sorbitol, glycerol and ethylene glycol. The different tendencies observed could be a consequence of the simultaneous study of variables, pressure and temperature.

The decrease in PG selectivity at 510 K indicates that acetol hydrogenation is not favoured at high temperatures, as has been reported in other works [49, 58]. The

decrease in H_2 solubility in the liquid phase when the temperature increases could explain the decrease in acetol hydrogenation to produce PG.

The results of the liquid compositions reported in Remón et al. [47] indicate an increase in the C3-ketones content when the temperature increases from 493 to 513 K, while a maximum is observed in the polyhydric alcohols content at 493K and a decrease when the temperature increases to 513 K. These tendencies are also reflected in the present work when analyzing the carbon selectivity considering only the liquid products (Figure S2).

It can be concluded from the temperatures tested that at the highest temperature, 510 K, the highest value of the H_2 yield, 6.8%, is obtained, while the alkane yield is smaller than at 505 K. The highest yields of PG and EG are obtained at 505 K with values of 0.130 g/g glycerol and 0.078 g/g glycerol, respectively. The highest yield of acetol is obtained at 500 K, with a value of 0.033 g/g glycerol.

3.3. Influence of the glycerol content in the feed

The experiments were performed at 34 absolute bar pressure and 500 K, with a $W/m_{glycerol}$ ratio of 20 g catalyst min/g glycerol and a liquid feeding rate of approximately 1 mL/min. The glycerol content in the feed was varied from 2 to 10 wt%. Figure 6 shows the carbon yield to gases, carbon yield to liquids and glycerol conversion for the values studied of the glycerol content in the feed. The general tendency shows that the glycerol conversion and carbon yield to liquids increase when the glycerol content increases. The glycerol conversion significantly increases from 43.4% to 65.2% when the glycerol content in the feed increases from 2 to 10 wt%. The carbon yield to gas presents values around 15% for the glycerol content values studied. The carbon yield to liquids significantly increases when the glycerol content in the feed

is increased from 14.4% and 40.4% at 2 and 10 wt% glycerol content in the feed, respectively.

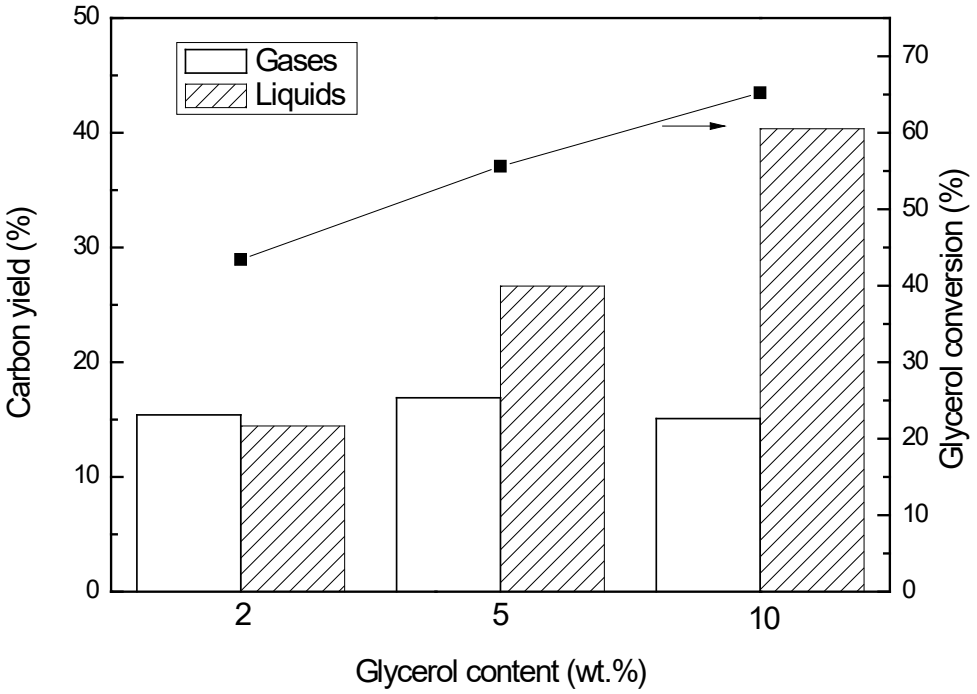

Figure 6. Influence of the glycerol content on global results: glycerol conversion, carbon yield to gases and liquids. Operating conditions: 34 bar, 500 K, 1 mL/min and $W/m_{glycerol}$ = 20 g catalyst min/g glycerol.

Table 3 presents the overall results corresponding to the gas phase. The H_2 content decreases while the CO_2 content increases when the glycerol content increases from 2 to 10 wt%. The CO, CH_4, C_2H_6 and C_3H_8 contents in the product gas increase when the glycerol content increases. Total gas shows values around 0.8 mol/mol glycerol at 2 and 5 wt% glycerol and decreases to 0.68 mol/mol glycerol when the glycerol content is 10 wt%. This decrease is a consequence of the decrease in the H_2 content and the slight decrease in the carbon yield to gases.

The H_2 yield decreases when the glycerol content increases from 2 to 10 wt%. The main tendency of the alkane yield is an increase when the glycerol content increases. These results are a consequence of the evolution of the carbon yield to gases and the gas composition with the glycerol content.

Table 3. Overall results of the gas phase in the APR of glycerol. Influence of the glycerol content in the feed. Operating conditions: 34 bar, 500 K, $W/m_{glycerol}$ = 20 g catalyst min/g glycerol and 1 mL/min.

Run#	**9**	**3**	**10**
Glycerol content (%wt)	2	5	10
Gas composition (%mol, N_2 and H_2O free)			
H_2	44.7	38.5	35.2
CO_2	40.2	43.8	44.8
CO	0.7	1.0	1.1
CH_4	13.8	15.6	17.4
C_2H_6	0.7	0.9	1.1
C_3H_8	0	0.2	0.4
Total gas (mol gas/mol glycerol)	0.82	0.81	0.68
Gas yields (%)			
H_2	5.26	4.44	3.42
Alkane	4.17	4.84	4.71

Figure 7 shows the global carbon selectivity to the analysed products, including the gas and liquid products. The carbon selectivity is significantly affected by the glycerol content. The CO_2 and CH_4 carbon selectivities decrease from 37% to 18% and from 12% to 7%, respectively, when the glycerol content increases from 2 to 10 wt%.

The PG carbon selectivity increases from 13.5% to 37% when the glycerol content increases and the EtOH carbon selectivity also increases (from 5.7% to 13%). A slight increase is also observed for acetol when the glycerol content in the feed increases from 2 to 10 wt%. On the other hand, the EG carbon selectivity decreases from 19% to 11% when the glycerol content increases. Figure S3, representing liquid carbon selectivity,

shows a clear increase of PG, the decrease of EG and a small increase of EtOH and a slight decrease of acetol when the glycerol content in the feed increases.

There is an increase in the products generated from hydrogenations, such as EtOH and PG, which means that hydrogenation reactions in liquid phase are favoured with the increase of the glycerol content in the feed. This result is corroborated by the decrease in the hydrogen content in the gas composition. Thus, the lowest H_2 yield is obtained when 10 %wt of glycerol content is fed. This result is expected as it is consistent with those reported in other works in the literature [30]. It could be due to the participation of hydrogen in the liquid product generation (PG) and methane production.

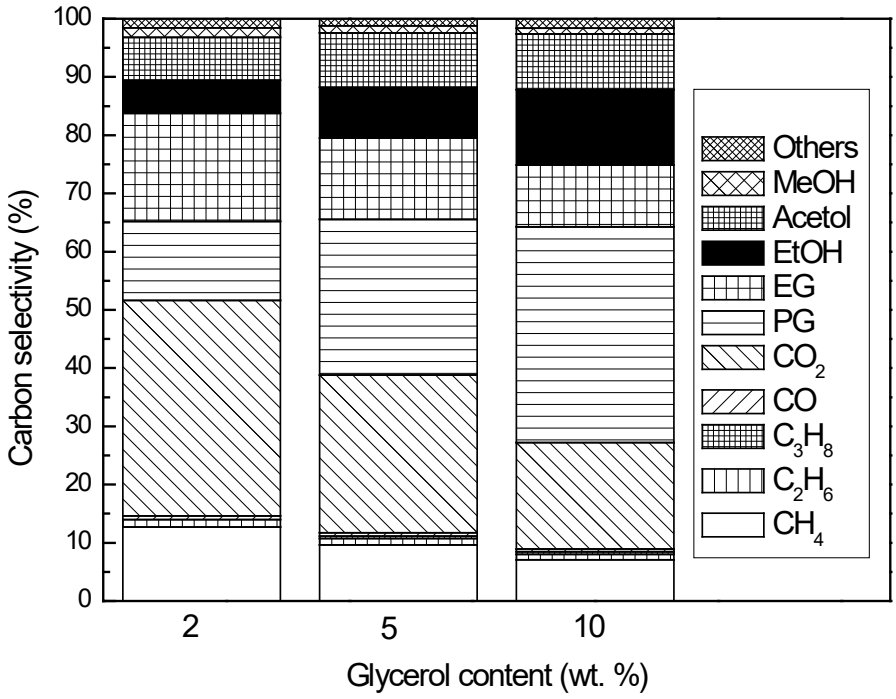

Figure 7. Influence of the glycerol content on global carbon selectivity to products. Operating conditions: 34 bar, 500 K, 1 mL/min and $W/m_{glycerol}$ = 20 g catalyst min/g glycerol.

Considering reaction routes I and II, the increase in the glycerol content favours the selectivity to liquid products following route II. The global carbon selectivity (Figure 7) to liquid products generated in route I (EtOH plus EG) is almost constant with the variation of the glycerol content, while a significant decrease is observed when considering liquid carbon selectivity (Figure S3). This is a consequence of the increase of liquid products when the glycerol content in the feed increases.

Duarte et al. [34] carried out experiments to analyze the effect of the sorbitol concentration at a WHSV of 1.2 h^{-1}. They also found an increase in the sorbitol conversion due to the conversion to liquid products. Seretis and Tsiakaras [23], using a Pt/Al_2O_3 catalyst and 513 K, obtained a decrease in the H_2 yield when the glycerol content in the feed increased, for example at 2 h, the H_2 yield decreased from 6% to less than 2% at 1 wt% and 10%wt of glycerol, respectively. However, they also observed a decrease in the glycerol conversion, carbon yield to gases and carbon yield to liquids when the glycerol content in the feed was increased [23]. For example at 2 h, glycerol conversion decreased from 35% to 11.5%, carbon yield to gases decreased from 9.5% to 1% and carbon yield to liquids decreased from 23.5% to 9.5% when the glycerol increased from 1wt% to 10 wt%. These results could be due to the decrease in the catalyst/glycerol ratio when the glycerol content in the feed increases.

Seretis and Tsiakaras [24], using a Ni/SiO_2-Al_2O_3 catalyst, 513 K and the same ratio catalyst/glycerol = 0.25 g/g, obtained at 2 h around 7.7% and 1.4% of H_2 yields at 1% wt glycerol and 10% wt glycerol, respectively. Moreover, the carbon yield to liquid increased when the glycerol content in the feed increased. These results are around 65%, 40 % and 22% for glycerol conversion, carbon yield to gas and carbon yield to liquid at 1 wt% glycerol and around 58%, 15 % and 32% for glycerol conversion, carbon yield to gas and carbon yield to liquid at 10 wt% glycerol. A decrease in the H_2

content and an increase in the CO content and CH_4 content when the glycerol content in the feed increases was also observed [24].

It can be concluded from the study of the glycerol content in the feed that the highest H_2 yield, 5.3%, is found at 2 wt% glycerol, while the highest alkane yield, 4.8%, is found when feeding 5 wt% glycerol. When feeding 10 wt% glycerol, the highest yields of PG and acetol are obtained with values of 0.169 g PG/g glycerol and 0.043 g acetol/g glycerol. However, the highest yield of EG, 0.062 g/g glycerol, is obtained at 5 wt% glycerol.

3.4. Influence of the liquid flow rate

The experiments were performed at 34 absolute bar pressure and 500 K, with a 5 wt% content of glycerol in the feed and a $W/m_{glycerol}$ ratio of 20 g catalyst min/g glycerol. The liquid feeding rate was varied from 0.5 to 3 mL/min.

Figure 8 shows the carbon yield to gases, carbon yield to liquids and glycerol conversion for the values of liquid flow rate studied. The general tendency shows that the glycerol conversion values are around 53% for all the liquid feeding rates studied. The carbon yield to gas and carbon yield to liquid increase for liquid feeding rates from 0.5 to 2 mL/min, while both decrease for liquid feeding rates from 2 to 3 mL/min. The carbon yield to gases increases from 11.3 to 19.6% at 0.5 and 2 mL/min respectively, while a value of 9.1% is obtained at 3 mL/min. The carbon yield to liquids increases from 26.4 to 35.4% at 0.5 and 2 mL/min respectively, while a value of 31% is obtained at 3 mL/min.

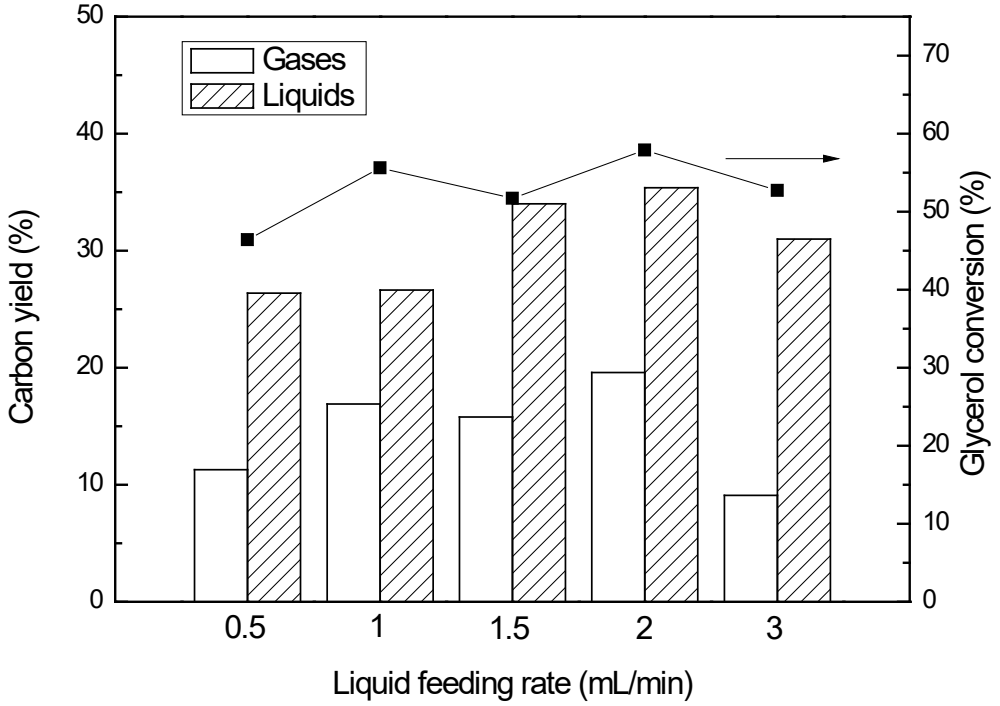

Figure 8. Influence of the liquid flow rate on global results: glycerol conversion, carbon yield to gases and liquids. Operating conditions: 34 bar, 500 K, 5 wt% glycerol and $W/m_{glycerol}$ = 20 g catalyst min/g glycerol.

Table 4 presents the overall results corresponding to the gas phase. The gas composition is similar for liquid feeding rates from 0.5 to 2.0 mL/min, with values around 41% H_2, 42% CO_2, 1% CO, 14.5% CH_4, 0.8 % C_2H_6 and 0.2% C_3H_8. When the liquid feeding rate increases from 2 to 3 mL/min, the gas composition is significantly changed. The H_2 content and CO content increase to 63% and 2.8%, respectively, while the CO_2 and CH_4 contents decrease to values of 24% and 9.2%, respectively. The C_2H_6 content also decreases from 0.8% to 0.5 % when the liquid feeding rate increases from 2 to 3 mL/min.

Total gas increases when the liquid feeding rate increases from 0.5 to 2 mL/min due to the increase in the carbon yield to gases. A decrease in total gas is observed when the

liquid feeding rate increases from 2 to 3 mL/min, which is due to the decrease in the carbon yield to gases in spite of the increase in the H_2 content. The H_2 yield increases from 3.4% to 6.5% when the liquid feeding rate increases from 0.5 to 3 mL/min. The decrease in the carbon yield to gases from 2 to 3 mL/min is compensated for by the increase in the H_2 content, which explains the increase in the H_2 yield from 2 to 3 mL/min. The general tendency shows an increase in alkane yields from 2.9% to 5.5% when the liquid feeding rate increases from 0.5 to 2 mL/min. However, the increase in the liquid feeding rate from 2 to 3 mL/min causes a significant decrease in alkane yields from 5.5% to 2.61%.

Table 4. Overall results of the gas phase in the APR of glycerol. Influence of the liquid feeding rate. Operating conditions: 34 bar, 500 K, $W/m_{glycerol}$ = 20 g catalyst min/g glycerol and 5 wt% glycerol.

Run#	**11**	**3**	**12**	**13**	**14**
Liquid feeding rate (mL/min)	0.5	1	1.5	2.0	3.0
Gas composition (%mol, N_2 and H_2O free)					
H_2	41.4	38.5	42.0	41.3	63.1
CO_2	43.7	43.8	40.9	42.3	24.1
CO	0.8	1.0	1.7	0.7	2.8
CH_4	13.2	15.6	14.4	14.6	9.2
C_2H_6	0.8	0.9	0.9	0.8	0.5
C_3H_8	0.1	0.2	0.2	0.2	0.2
Total gas (mol gas/mol glycerol)	0.57	0.81	0.80	0.98	0.72
Gas yields (%)					
H_2	3.36	4.44	4.79	5.80	6.53
Alkane	2.86	4.84	4.47	5.51	2.61

Figure 9 shows the global carbon selectivity to the analysed products, including gas and liquid products. Small changes are observed in the carbon selectivity to products when the liquid feeding rates increase from 0.5 to 2 mL/min. One exception is the carbon

selectivity to acetol, which decreases from 13.5% to 7.3% when the liquid feeding rate increases from 0.5 to 2 mL/min. When the liquid feeding rate increases from 2 to 3 mL/min, significant changes are observed in the carbon selectivity to products. Thus, CH_4, CO_2 and EG decrease from 8.7%, 25% and 14% to 5.5%, 14.5% and 11% respectively, while acetol and EtOH increase from 7.3% and 10% to 18.6% and 12.6%, respectively. PG is the compound with the highest carbon selectivity values. Its value of around 29% is quite constant for the different liquid feeding rates studied. Significant carbon selectivity to acetaldehyde (2.7%) is obtained at 3 mL/min liquid feeding rate. The tendencies of liquid compounds expressed as global carbon selectivity are clearly represented in Figure S4, showing liquid carbon selectivity.

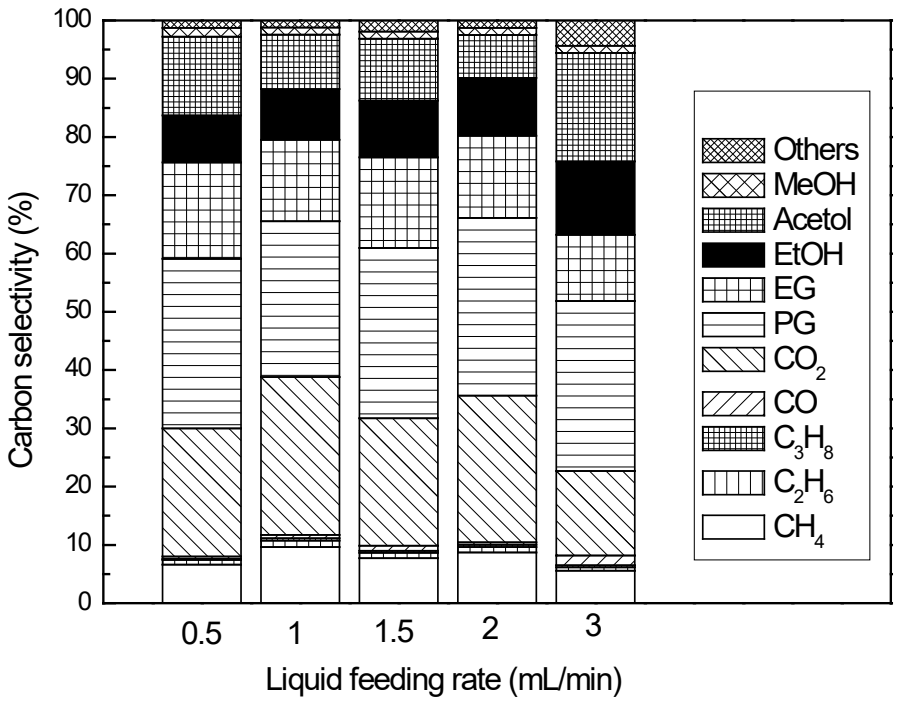

Figure 9. Influence of the liquid flow rate on global carbon selectivity to products. Operating conditions: 34 bar, 500 K, 5 wt% glycerol and $W/m_{glycerol}$ = 20 g catalyst min/g glycerol.

These results can be explained considering the external mass transfer control and the decrease in the residence time. For the 0.5 to 2.0 mL/min increase in the liquid feeding rate, the residence time decreases but the carbon yields to gases and to liquids increase. This result may be due to the existence of external mass transfer control. In contrast, for the 2.0 to 3.0 mL/min increase in the liquid feeding rate, the decrease in residence time diminishes the carbon yields to gases and to liquids, indicating a possibly kinetic regime. Özgür and Uysal [21] proposed a similar explanation for their results. They carried out experiments varying the flow rate and the W/m ratio simultaneously because they used the same amount of catalyst in all the experiments. However, in the present work the amount of catalyst was modified in order to maintain a constant $W/m_{glycerol}$ ratio of 20 g catalyst min/g glycerol.

The increase in the H_2 and CO contents and the decrease in the CO_2, CH_4 and C_2H_6 contents when the liquid feeding rate increases from 2.0 to 3.0 mL/min could indicate that WGS, methanation and Fischer-Tropsch reactions are not favoured at short residence times, possibly indicating that these are not fast reactions.

The acetol carbon selectivity decreases when the liquid feeding rate increases from 0.5 to 2.0 mL/min but increases significantly up to 3.0 mL/min. The carbon selectivity to the main route II products (acetol and PG) is increased at the highest value of the liquid feeding rate, 3 mL/min. From these results we can assume that the hydrogenation reaction of acetol to PG is not a fast reaction, due to the high carbon selectivity to acetol and high H_2 content in the product gas.

Relatively high carbon selectivities to acetaldehyde and propanoic acid are found when using a liquid feeding rate of 3.0 mL/min. The decrease in residence time possibly hinders the conversion of these intermediates to final products. The final products of

acetaldehyde are mainly acetic acid and methane [47], while for propanoic acid they could be ethane and carbon dioxide.

It can be concluded from the values of the liquid feeding rate studied that the highest H_2 yield, 6.5%, is found at 3 mL/min, while the highest alkane yield, 5.5%, is found at 2 mL/min. The highest yields of PG and EG are obtained at the liquid feeding rate of 2 mL/min, with values of 0.139 g/g glycerol and 0.079 g/g glycerol, respectively. However, the highest yield of acetol, 0.060 g/g glycerol, is obtained at 3 mL/min.

3.5. Influence of the $W/m_{glycerol}$ ratio

The experiments were carried out at 34 absolute bar pressure and 500 K, with a 5 wt% content of glycerol in the feed and a liquid feeding rate of 1 mL/min. The $W/m_{glycerol}$ ratio was varied from 10 to 40 g catalyst min/g glycerol. For this purpose the catalyst in the reaction bed was increased from 0.5 to 2.0 g. Figure 10 shows the carbon yield to gases, carbon yield to liquids and glycerol conversion for the values of the $W/m_{glycerol}$ ratio studied. The glycerol conversion, carbon yield to gases and carbon yield to liquids significantly increase when the $W/m_{glycerol}$ ratio increases from 10 to 40 g catalyst min/g glycerol.

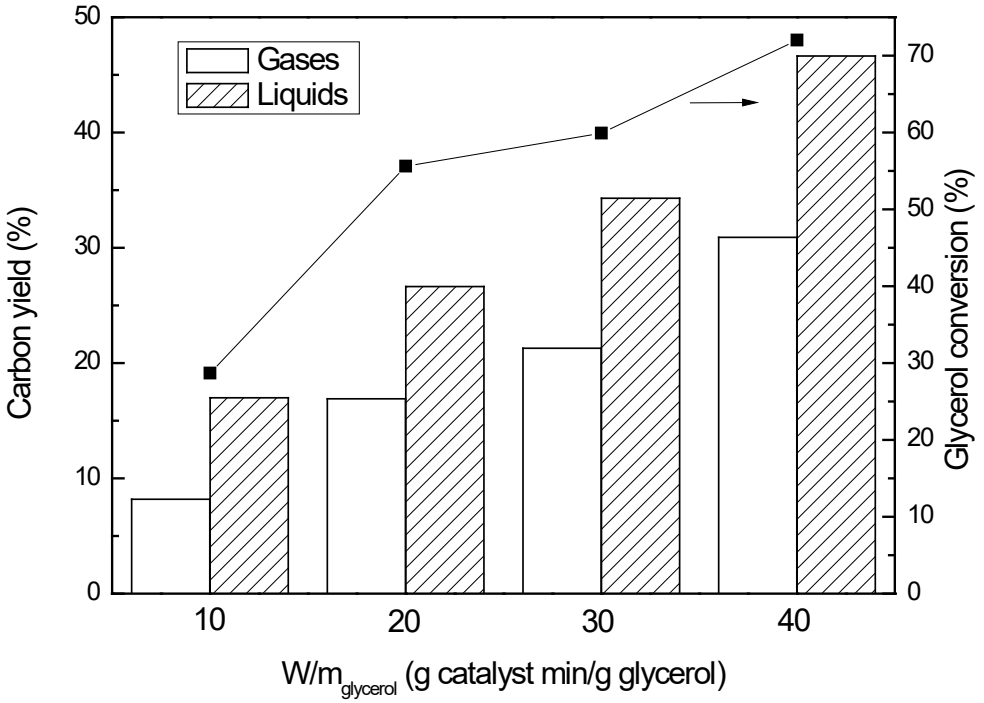

Figure 10. Influence of the W/$m_{glycerol}$ ratio on global results: glycerol conversion, carbon yield to gases and liquids. Operating conditions: 34 bar, 500 K, 5 wt% glycerol and 1 mL/min.

In the range studied, a higher increase is found for product gases (277% carbon yield to gases calculated from 8.2% and 30.9% at 10 and 40 g catalyst min/g glycerol, respectively) than for liquid products (175% carbon yield to liquids calculated from 17% and 46.7% at 10 and 40 g catalyst min/g glycerol, respectively). The influence of the W/$m_{glycerol}$ ratio on the glycerol conversion, carbon conversion to gas and carbon conversion to liquids is higher than for the other variables studied (the system pressure, the reaction temperature, the glycerol content in the feed and the liquid feeding rate). Possibly the wide range of the W/$m_{glycerol}$ ratio studied is the reason for this.

Table 5 presents the overall results corresponding to the gas phase. The general tendencies show a decrease in the H_2 and CO contents and an increase in the CO_2, CH_4 and C_2H_6 contents in the product gas when the W/$m_{glycerol}$ ratio increases. Total gas

increases with the increase of the $W/m_{glycerol}$ ratio, following the same tendency as the carbon yield to gases. The H_2 yield increases from 2.6% to 6.8% when the $W/m_{glycerol}$ ratio increases from 10 to 40 g catalyst min/g glycerol. This is a consequence of the high increase in the carbon yield to gases despite the decrease in the H_2 content in the gas, when the $W/m_{glycerol}$ ratio increases. The alkane yield significantly increases from 2.0% to 10.7% when the $W/m_{glycerol}$ ratio increases from 10 to 40 g catalyst min/g glycerol.

Table 5. Overall results of the gas phase in the APR of glycerol. Influence of the $W/m_{glycerol}$ ratio. Operating conditions: 34 bar, 500 K, 5 wt% glycerol and 1 mL/min.

Run#	**15**	**3**	**16**	**17**
$W/m_{glycerol}$ (g catalyst min/g glycerol)	10	20	30	40
Gas composition (%mol, N_2 and H_2O free)				
H_2	43.3	38.5	34.9	34.3
CO_2	42.4	43.8	45.1	43.7
CO	1.4	1.0	0.4	0.2
CH_4	12.0	15.6	18.3	20.3
C_2H_6	0.8	0.9	1.1	1.1
C_3H_8	0.2	0.2	0.2	0.2
Total gas (mol gas/mol glycerol)	0.42	0.81	0.96	1.38
Gas yields (%)				
H_2	2.62	4.44	4.78	6.78
Alkane	2.01	4.84	6.75	10.65

Figure 11 shows the global carbon selectivity to the analysed products, including gas and liquid products. The general tendencies show an increase in carbon selectivity to CH_4 (6.7 % to 12.1%), CO_2 (23.8% to 26%), PG (27.1% to 30.8%), EG (8.9% to 13.5%) and EtOH (8.7% to 9.8%) while the carbon selectivity to acetol significantly decreases (19.2% to 4%) when the $W/m_{glycerol}$ ratio increases from 10 to 40 g catalyst min/g glycerol. These tendencies of the liquid products are clearly observed in Figure S5, which represents liquid carbon selectivity.

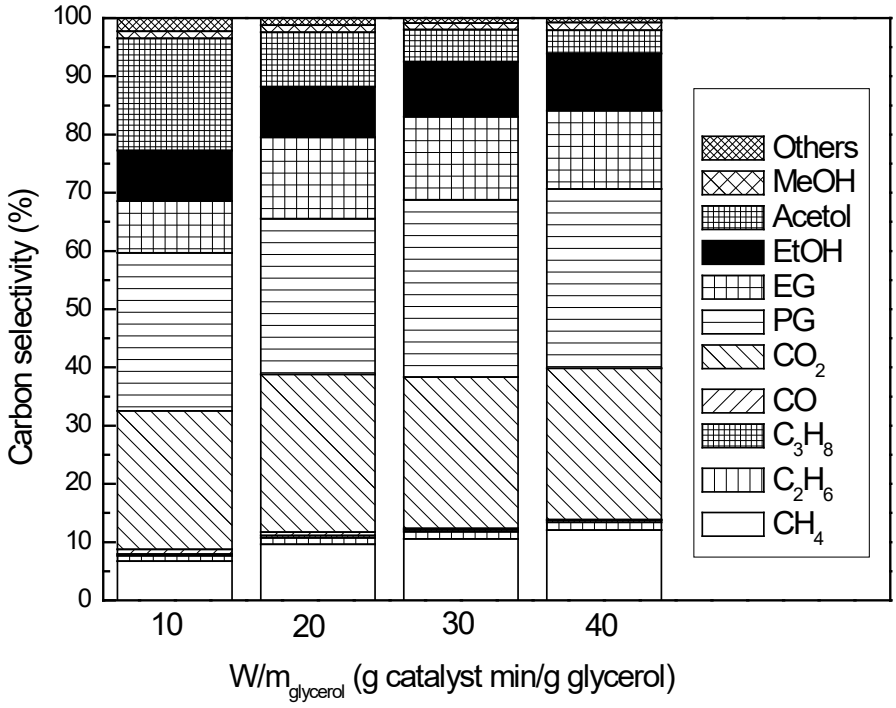

Figure 11. Influence of the $W/m_{glycerol}$ ratio on global carbon selectivity to products. Operating conditions: 34 bar, 500 K, 5 wt% glycerol and 1 mL/min.

The positive effect of the catalyst amount on gas production and glycerol conversion is clear [23-25, 35]. Several authors have reported similar tendencies in carbon yields to gases, although with different space velocities and catalysts. Luo et al. [30] used an impregnated Pt catalyst and space velocities of 1.56 and 3.12 h^{-1}, feeding 5 wt% glycerol. Kim et al. [45] used a Pt-Re catalyst and WHSV values from 6 to 1 h^{-1}, feeding ethylene glycol. In the present work the W/m ratios between 10 and 40 g catalyst min/g glycerol correspond to space velocities from 6 to 1.5 h^{-1}.

Remón et al. [47] indicate that the $W/m_{glycerol}$ ratio significantly influences the carbon yield to gases. The models developed by Remón et al. [47] at 38 bar, 500 K and 10 wt% glycerol predict the increases of the carbon yield to gases and the glycerol conversion when the $W/m_{glycerol}$ increases. However, these values predicted by the model are

different from the experimental values obtained in the present work. Thus, the predicted values of carbon yield to gases and glycerol conversion are 0% and 75.6% respectively at 10 g catalyst min/g glycerol and 45% and 98.5% respectively at 40 g catalyst min/g glycerol.

Seretis and Tsiakaras [24], using a Ni/SiO_2-Al_2O_3 catalyst in a batch installation, observed similar tendencies. They reported a decrease in the hydrogen content and an increase in the methane content when the amount of catalyst was increased. The hydrogen content was around 42% with 0.5 g of catalyst at 4 h, very similar to the result obtained using a W/m ratio of 10 g catalyst min/g glycerol (43% in the present work). However, the methane content reported by Seretis and Tsiakaras [24] was smaller (12%) with 2.5 g catalyst at 4 h than the result obtained with the Ni-Al coprecipitated catalyst using a W/m ratio of 40 g catalyst min/g glycerol (20 % in the present work). A higher H_2 content and smaller CH_4 content were obtained using a Pt/Al_2O_3 catalyst than with the Ni catalyst [23].

The liquid composition reported by Remón et al. [47] shows a decrease in the C3-ketones content when the $W/m_{glycerol}$ ratio increases. This tendency is followed in the present work when analyzing the carbon selectivity considering only liquid products, Figure S5. Seretis and Tsiakaras [23] also observed that acetol is the main product at short reaction times, while the selectivity of PG increases at longer reaction times.

As regards the influence of the $W/m_{glycerol}$ ratio on the selectivities to the main products of routes I and II, the global carbon selectivity to PG and acetol together (products of route II) decreases from 46.3% to 34.8% when the $W/m_{glycerol}$ ratio increases from 10 to 40 g catalyst min/g glycerol, while the global carbon selectivity to EG and EtOH together (products of route I) increases from 17.6% to 23.3%. Thus, a large amount of

catalyst could favour reactions of the cracking of C-C bonds of glycerol to EG and gas products.

EtOH and PG are liquid products generated from the hydrogenation reactions which are favoured using higher values of the $W/m_{glycerol}$ ratio. Moreover, CH_4 could be generated from methanation reactions which consume H_2. These methanation reactions could be favoured by the increase in the $W/m_{glycerol}$ ratio. This could explain the decrease in the H_2 content in the product gas.

It can be concluded from the $W/m_{glycerol}$ ratios studied that the highest H_2 yield and alkane yields, 6.8% and 10.7% respectively, are found at 40 g catalyst min/g glycerol. For this $W/m_{glycerol}$ ratio, the highest yields of PG and EG are also obtained with values of 0.197 g/g glycerol and 0.106 g/g glycerol, respectively. However, the highest yield of acetol, 0.039 g/g glycerol, is obtained at 10 g catalyst min/g glycerol.

3.6. Comparison with other works

Table 6 presents a comparison of the most relevant results obtained in the present work with others concerning the APR of glycerol found in the literature. The results column in this table employs the variables according to the definitions given in the data analysis section. The WHSV ratio is related to the inverse of the $W/m_{glycerol}$ ratio and its units are g glycerol/(g catalyst h). Some results, such as the PG, EG and acetol yields, have been calculated from data provided in the references and are marked in Table 6.

Table 6 shows a high variety of catalysts and operating conditions. Some works [40-42] have employed high values of time-on-stream, equal or higher than 25 h. These studies are relevant in terms of the catalyst life.

High temperatures and pressures, such as 513 K and 40 bar [40], 523 K and 50 bar [42] and 511 K and 39 bar [47] have shown high glycerol conversion and carbon yield to

gases. Low temperatures, such as 463 K [28], 489 K [47] and 500 K, as used in the present work, provide high carbon yield to liquids.

All the results presented in Table 6 indicate the relevant role of the catalyst and the operating conditions in order to valorize glycerol to liquids and gaseous products by APR. The present work is also relevant because it contributes to knowledge about the influence of operating conditions. However, more research work is required to optimize these for a NiAl coprecipitated catalyst.

The data analysis carried out has provided information about the yield of liquids expressed as g/g glycerol. PG and EG yields obtained in the present work are higher than those in other cited references. The calculation of the liquid yield expressed as g/g glycerol requires quantitative analysis of the liquid products. To the best of our knowledge, this is the first time that such analysis has been reported for a coprecipitated NiAl catalyst.

Table 6. Comparison with other works in the literature concerning APR of glycerol.

Catalyst	Installation	Operating conditions	Results	Reference
1Cu-12Ni/MWNT	Continuous flow fixed bed	513 K, 40 bar, 0.05 mL/min, WHSV = 0.2 h^{-1} 1 wt% glycerol; t-o-s = 110 h	X_{Gly} = 84%; C to gas = 76 % H_2 yield = 65.5 % Gas composition: 77% H_2; 16.5% CO_2; 6.5% CH_4	Rahman [40]
Ni/Al_2O_3-MgO	Continuous flow fixed bed	523 K, 50 bar, WHSV = 2.45 h^{-1}; 10 wt% glycerol; t-o-s = 25 h	X_{Gly} = 92%; C to gas* = 90 % H_2 yield = 70 % Gas composition: 79% H_2; 20% CO_2; 1% CH_4	Bastan et al. [42]
Pt(0.5)-Ir-ReOx/SiO_2	Batch	463 K, 20 bar (initial pressure), 17 h, glycerol/catalyst = 20 g/g	X_{Gly} = 30%; C to gas = 4.7 % H_2 yield = 0.6 % PG yield* = 0.05 g/g glycerol; Acetol yield* = 0.14 g/g glycerol	Liu et al. [28]
NiPt/ASGI7	Continuous flow fixed bed	503 K, 30 bar, 0.4 ml/min, WHSV = 2.60 h^{-1}; 10 wt% glycerol; t-o-s = 56 h	X_{Gly} = 79.2%; C to gas = 56.3 % PG yield* = 0.16 g/g glycerol; EG yield* = 0.08 g/g glycerol; Acetol yield* = 0.03 g/g glycerol	El Doukkali et al. [41]
0.625CoAl	Continuous flow fixed bed	508 K, 35 bar, 0.2 ml/min, WHSV = 2.45 h^{-1} 10 wt% glycerol	X_{Gly} = 88.4%; C to gas = 21.7 % H_2 yield = 10.8 % Gas composition: 52% H_2; 30% CO_2; 11% CH_4	Reynoso et al. [43]
Ni-La-Al	Continuous flow fixed bed	[a]489 K, 45 bar, WHSV = 2.73 h^{-1};16 wt% glycerol [b]511 K, 39 bar, WHSV = 1.58 h^{-1};15 wt% glycerol	X_{Gly} = 96%; C to gas = 17 %; H_2 content = 39 % X_{Gly} = 99%; C to gas = 64 % H_2 content = 47 %	Remón et al. [47]
Ni-Al	Continuous flow fixed bed	500 K, 34 bar, WHSV = 1.5 h^{-1}; 5 wt% glycerol	X_{Gly} = 72%; C to gas = 30.9 %; H_2 yield = 6.8 % Gas composition: 34% H_2; 44% CO_2; 20% CH_4 PG yield = 0.20 g/g glycerol; EG yield = 0.11 g/g glycerol; Acetol yield = 0.03 g/g glycerol	Present work

t-o-s = time-on-stream, X_{Gly} = glycerol conversion, C to gas = carbon yield to gases, * estimated values from data provided in the reference, [a] - optimized conditions for liquid production, [b] - optimized conditions for gas production.

4. Conclusions

Aqueous phase reforming of glycerol using a Ni/Al coprecipitated catalyst generates gas and liquid products. The experimental conditions tested have shown that gas yields are favored at high temperature (510 K), high pressure (40 bar) and with a high $W/m_{glycerol}$ ratio (40 g catalyst min/g glycerol). Liquid yields are favored by a high glycerol content (10 wt%) and a high $W/m_{glycerol}$ ratio (40 g catalyst min/g glycerol).

Under the experimental conditions employed (500 K, 5 wt% glycerol, 20 g catalyst min/g glycerol, 1 mL/min) the increase of the system pressure from 28 to 40 bar causes the increase of glycerol conversion and higher increases in the carbon yields to gases than the carbon yields to liquids. Moreover, the H_2 content in the gas decreases while the CH_4 content increases when the system pressure increases. The highest value of the system pressure, 40 bar, produces high yields of PG and EG.

The increase of temperature from 495 to 510 K, maintaining constant the rest of the operating conditions (34 bar, 5 wt% glycerol, 20 g catalyst min/g glycerol, 1 mL/min) increases the glycerol conversion, the increase of gas production being higher than that of liquid production. H_2 content in the gas increases while CH_4 and C_2H_6 contents decrease with the increase of temperature. In the range of temperature studied the highest yields of PG and EG are obtained at 505 K.

The increase of glycerol content in the feed from 2 to 10 wt %, maintaining constant the rest of the operating conditions (34 bar, 500 K, 20 g catalyst min/g glycerol, 1 mL/min) increases the glycerol conversion and carbon yield to liquids, while the carbon yield to gas barely changes. The H_2 content in the gas decreases while the content of CH_4 and other alkanes (C_2H_6 and C_3H_8) increases with the increase of glycerol in the feed. The highest value of glycerol content in the feed, 10 wt %, produces high yields of PG and

acetol. Hydrogenation reactions, which produce PG and EtOH, are favoured with the increase of the glycerol content in the feed.

Using the following operating conditions: 34 bar, 500 K, 5 wt% glycerol and 20 g catalyst min/g glycerol, the liquid flow rate was increased from 0.5 to 3 mL/min. There is external mass transfer control from 0.5 to 2 mL/min, while the increase from 2 to 3 ml/min causes a significant decrease in the carbon yield to gas, an increase of the H_2 and CO contents in the gas and a decrease in the CO_2 and CH_4 contents in the gas. In the range of liquid flow rates studied, the highest yields of EG and PG are obtained at 2 mL/min while the highest yield of acetol is obtained at 3 mL/min.

Under the experimental conditions employed (34 bar, 500 K, 5 wt% glycerol, 1 mL/min), the increase of the $W/m_{glycerol}$ ratio from 10 to 40 g catalyst min/g glycerol causes a significant increase in the glycerol conversion, carbon yield to gases and carbon yield to liquids. Moreover, the H_2 and CO contents in the gas decrease while the CH_4 and C_2H_6 contents increase when the $W/m_{glycerol}$ ratio increases. The highest yields of PG and EG are obtained at 40 g catalyst min/g glycerol, while the highest yield of acetol is obtained at 10 g catalyst min/g glycerol.

A high yield to H_2 (6.8%), the highest yield to alkanes (10.7%), and the highest PG (0.20 g/g glycerol) and EG (0.11 g/g glycerol) yields were obtained under the following experimental conditions: $W/m_{glycerol}$ ratio of 40 g catalyst min/g glycerol, 34 bar, 500 K, 5 wt% glycerol and 1 mL/min. The highest acetol yield (0.06 g/g glycerol) was obtained at 34 bar, 500 K, 5 wt% glycerol, 20 g catalyst min/g glycerol and 3 mL/min.

More research work is required in order to optimize product yields and the viability of the catalyst over long reaction times.

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