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Title: On the gas-phase reforming of glycerol by Pt on carbon black: Effects of metal particle size and pH value of the glycerol stream

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Highlights

- Low-temperature glycerol gas-phase reforming demonstrates being a structure-sensitive reaction over Pt/C catalyst
- Activity and selectivity change with the size of the platinum particle size
- The pH of the glycerol aqueous solution has not any remarkable effect under the reaction condition

Abstract

We investigate the effect of the platinum particle size and the pH of the feed solution in the glycerol gas-phase reforming reaction at low-temperature (623 K) over carbon black-supported Pt catalyst with different platinum loadings (1, 3, 5, and 10 wt. %). We also verify the influence of the aqueous glycerol (30 wt. %) feeding solution pH in the reaction at low-temperature (WHSV = 33 min⁻¹ and P = 1 bar) over the 5 wt. % Pt/C catalyst. Glycerol gas-phase reforming demonstrates being a structure-sensitive reaction and it has its activity and selectivity changed with the size of the platinum particle size. The size increasing leads to an increasing of the CO and Glycerol TOF and selectivity towards gaseous products, formed by consecutive C-C cleavages. Despite no remarkable change is observed in the selectivity under the reaction condition with different pHs of the glycerol aqueous solution, there is an activity decrease.

Keywords: glycerol gas-phase reforming; Pt/C-black catalysts; metal particle size effect; glycerol aqueous solution pH

1. Introduction

Biodiesel production can be one of the main efforts to obtain "green fuels". Its production has grown from 19.6 thousand barrels per day in 2001 to 294.7 thousand barrels in 2010 [1]. Biodiesel is mainly obtained by the transesterification of triglycerides,-from vegetable oils and fat with methanol. As a result, crude glycerol (10 wt. % of total product) is produced as a co-product. Since crude glycerol is a residue from the biodiesel production, its valorization represents a way to enhance the biodiesel economy. Moreover, the amount of glycerol used in commercial applications, sometimes becomes much less than its production, thereby creating an oversupply crisis [2].

Glycerol of high purity is an important industrial feedstock for applications in food, cosmetics and pharmaceutical, and others industries; however, it is costly to refine crude glycerol, especially for medium or small sized plants. Therefore, many researches focused on innovative processes to convert pure glycerol, as well as the crude one, into valuable products [3,4].

Glycerol is considered as one of the top twelve building block chemicals that can be also derived from carbohydrates and converted into to numerous valuable commodity chemicals (e.g. glyceric acids, propylene glycol, 1,3- and 1,2-propanediol, branched polyesters and polyols) [5]. These chemicals can be formed by different routes, including: selective oxidation, hydrogenolysis, dehydration, transesterification, etherification, oligomerization and polymerization, as reviewed very well by Zhou *et al.* [6]. Among possible uses for glycerol, hydrogen and/or synthesis gas production from glycerol have been attracting much attention due to their importance in the petrochemical and energy industries and because they are currently produced from fossil non-renewable

sources. Hydrogen is widely used to power fuel cell systems and syngas is a vital building block to prepare various chemicals [7]. Moreover, its productions from biomass process waste or residue has become key to make biorefinery feasible.

Different pathways to produce H₂ or syngas from glycerol÷ (e.g. aqueousphase reforming [8,9], gasification or thermal reduction [10], steam reforming [11-13], auto-thermal or partial oxidation reforming [14,15], pyrolysis [16] and photocatalysis reforming [17]) have been reported. Recently, a comprehensive review was published [7], which complemented other important ones [6,8-20].

In this context, Soares *et al.* [21] have reported a pioneering lowtemperature (e.g., 550 K) gas-phase catalytic process that converts aqueous glycerol into H₂/CO gas mixtures over a carbon-supported Pt catalyst. Furthermore, they demonstrated that this glycerol conversion process can be combined with Fischer-Tropsch synthesis or water-gas-shift (WGS) reaction in a single reactor process. In this way, the heat generated by the exothermic Fischer-Tropsch or WGS reaction can supplied to the endothermic glycerol reforming reaction [21,22]. These combined gas-phase processes produce liquid alkanes suitable for transportation applications [22] or hydrogen production with low CO content directly from aqueous glycerol [23,24].

In spite of this advance, only a few studies [25-29] on low-temperature (< 673 K) gas-phase glycerol reforming were published after the work by Soares et al. [21]. Simonetti *et al.* [26] and Kunkes *et al.* [27] have shown that Re addition to 5%Pt/C has a great promotional effect on the rate of glycerol conversion. Pompeo *et al.* [28] have shown the influence of the nature of the support on the catalytic performance of Pt or Ni-based catalysts, and Sutar *et al.* [29] has proposed a kinetic model for a Pt/C catalyst.

Since, biodiesel can be synthesized by homogeneous basic or acid catalysis [2-4,30]; the aqueous glycerol solution derived may be basic or acidic. Studies on the influence of this solution pH for glycerol or sorbitol liquid-phase reforming or hydrogenolysis showed that basic aqueous solution enhanced the hydrogen yield. However, this pH effect on gas-phase glycerol reforming is hitherto unknown. Therefore, in this work, we investigate in more detail the effect of the platinum particle size and the pH of the feed solution in the glycerol steam reforming reaction over carbon-supported Pt catalyst, in various catalytic reaction conditions with different platinum loadings.

2. Experimental

2.1. Catalyst preparation and characterization

Commercial catalysts containing 5 and 10 wt.% Pt supported on carbon black (Vulcan X-72C) were purchased from BASF FUEL CELL INC. Catalysts with low platinum loadings, 1 (1.07) and 3 (2.97) wt.%, were prepared by incipient wetness impregnation of H₂PtCl₆.6H₂O (SIGMA-ALDRICH) aqueous solution on Carbon black (CABOT; Vulcan XC72, Lot-1105528). Then, all the catalysts were dried at 393 K for 12 h in air. The real Pt contents (in parentheses) were determined by X-Ray Fluorescence spectrometer (BRUKER – S8 Tiger).

Prior to any CO chemisorption measurements and reaction kinetics studies, the catalysts were reduced *in-situ* by heating up in flowing H₂ [35 cm³ (NTP) min⁻¹] with a ramp rate of 0.5 K.min⁻¹, and then maintained at 623 K for 2 h. In a special case for 5 wt. % Pt the reduction temperature was 473 K giving the sample with tag 5 wt. %*. Another sample was then generated from this sample as follows. After remaining at 2h at 473 K under hydrogen flow, the

temperature was increased at 10 K.min⁻¹ to 623 K and then kept for 2h under He atmosphere.

CO chemisorption measurements were carried out on all catalysts using a standard gas adsorption apparatus (MICROMERITICS, model ASAP 2020 C). The irreversible CO uptake of the catalysts at 300 K was used to determine the platinum dispersion and crystallite size.

Some samples of spent catalysts (1 and 5 wt. %) were also characterized by CO chemisorption. Before the analysis, the catalysts were purged with helium (50 cm³.min⁻¹) at reaction temperature for 30 min. Next, the material was cooled down to 273 K and passivated by an air flowing for 30 min.

2.2. Glycerol Gas-Phase Reforming Tests

Isothermal reaction kinetics studies were conducted on an apparatus described elsewhere [21-23,26,27]. The reactor consisted of a 26 mm outer diameter stainless steel tube with a wall thickness of 0.71 mm. A bed consisting of fresh powder catalyst (20–100 mg) mixed with an equal volume of crushed fused SiO₂ granules (to decrease pressure drop across the bed) was loaded between a quartz wool plug and fused SiO₂ granules (-4 + 16 mesh; Sigma Aldrich). The reactor was heated with a homemade furnace. A J-type thermocouple was attached to the outside of the reactor to measure temperature, which was controlled with a temperature controller (THERMA Instruments - TH 2131P series type). Aqueous glycerol solution (30 wt. % in glycerol, with 99.5% purity, diluted in deionized water of pH \cong 6.3; VETEC) was introduced into the reactor in a down-flow configuration. In some experiments, the pH value of the feeding solution was adjusted to 3 or 10 by adding droplets of an HNO₃ (0.5 M)

or NH₄OH (0.5 M) solutions respectively.

The liquid feed flowing rate was controlled by a pump (ELDEX; Model 1440-A-30-S-2 CE), which is connected to a syringe needle (Hamilton; point 5 tip) to introduce droplets of the feed into the reactor where vaporization occurs. Part of the effluent was condensed in a gas–liquid separator at 279 K, and drained periodically for gas chromatography analysis (Shimadzu equipped with a flame-ionization detector and a RTx-5 capillary column). Each drain portion was analyzed for glycerol and trace amounts of other condensable byproducts. The effluent gas stream was separated by packed column (HAYESEP DB), and analyzed for H₂, CO, CO₂, and light hydrocarbons and oxygenates (C₁–C₄) using another Shimadzu gas chromatograph (17AF) equipped with a thermal conductivity detector followed by with a flame-ionization detector.

The glycerol conversion $(X_G)_{GP}$ (%) to gaseous products, H₂, CO, CO₂, and light hydrocarbons and oxygenates (C₁–C₄) and to liquid products (condensate molecules), $(X_G)_{LP}$ (%), were calculated based on the following equation (1) and (2), respectively:

$$(X_{G})_{GP}(\%) = \frac{F_{CO} + F_{CO_2} + F_{CH_4} + 2F_{C_2} + 3F_{C_3} + 4F_{C_4}}{3.(F_{glycerol})_0} \times 100 \text{ (1)}$$

$$(X_{G})_{LP}(\%) = \frac{{}^{n}C^{\cdot}F(\text{condensate molecule})}{3.(F_{glycerol})_{0}} \times 100 \text{ (2)}$$

Then, the overall glycerol conversion was calculated by equation (3):

$$(X_G)_{T1}(\%) = (X_G)_{GP}(\%) + (X_G)_{LP}(\%)$$
 (3)

Alternatively, the overall glycerol conversion was also calculated by equation (4):

$$(X_{G})_{T2}(\%) = \frac{(F_{glycerol})_{0} - (F_{glycerol})}{(F_{glycerol})_{0}} \times 100$$
 (4);

Where (F_j) and $(F_j)_0$ are the molar flow rate (mols.min⁻¹) of the molecule "j" at any time and at the inlet, respectively, and n_c is the number of carbon atoms in the molecule. The selectivities towards any molecule were calculated by:

$$(S)_{j}(\%) = \frac{({}^{n}C)_{j} \cdot F_{j}}{3.(F_{glycerol})_{0}} \times 100 (5)$$

The carbon balance CB (%) was evaluated by:

CB (%) =
$$\frac{(X_G)_{T2}(\%) - (X_G)_{T1}(\%)}{(X_G)_{T2}(\%)} \times 100$$
 (6);

The space velocity, WHSV (min⁻¹) was calculated after dividing the feeding glycerol mass flow (g.min⁻¹) rate by the platinum weight (g) in the catalyst bed.

The values of catalytic activity are expressed by the Turnover Frequencies (TOF/min⁻¹), which were calculated for glycerol (G) and carbon monoxide (CO) by the same way calculated elsewhere for same systems [21-23,27]:

G - TOF =
$$\frac{(F_G)_0 - (F_G)}{(\text{mols CO uptaken})}$$
(7);

$$CO - TOF = \frac{(F_{CO})}{(mols CO uptaken)} (8);$$

This calculation is acceptable for any conversions values, since the reaction is first-order with respect to glycerol, as demonstrated by Sutar *et al.* [29].

3. Results and Discussion

3.1. Catalyst characterization: CO uptake, platinum crystallite size and dispersion

Table 1 shows the irreversible CO uptakes as well as the metal dispersion and particle size calculated from it, for monometallic Pt/C with different platinum contents. The average of the platinum crystallite size for the low Pt content catalysts (1 and 3 wt. % Pt/C) are almost the same, 2.2 nm. When the platinum content increases to 5 and 10 wt. %, the Pt crystallite sizes increase to 3.56 and 6.10, respectively. This result indicates a trend of platinum agglomeration with the increase in metal content, especially above 3 wt. %. The ease in sintering for the high Pt loading is more evident when comparing the Pt crystallite average sizes obtained from different reduction procedures using the same Pt catalyst (5 wt.%). The average platinum crystallite size increased from 2.07 to 3.56 when the sample reduced at 473 K was heated to 623 K in He, and then further reduced for 2h at this temperature.

3.2. Glycerol Gas-Phase Reforming Tests: effect of the platinum crystallite size on activity

Figure 1 exhibits the glycerol conversion as a function of time-on-stream for all catalysts under atmospheric pressure and at 623 K. The profiles show that all catalyst presents a good stability, without any significant deactivation even after 24 h time-on-stream. This observation confirms previous result [21-23,26,27], which demonstrated the excellent catalytic stability of the 5 wt. % Pt/C catalysts under low-temperature gas-phase glycerol reforming. The platinum crystallite sizes of the catalysts (with 1 and 5 wt. % loading of Pt) measured after reaction, were 2.41 and 3.85 nm, respectively. Hence, no remarkable difference

was detected between the particle sizes of the fresh and spent catalysts.

Table 2 shows the conversions, catalytic activity values, and H₂/CO ratios attained after 30 hours of reaction. Good material balance was obtained as shown by two methods of computing the overall glycerol conversions: $((X_G)_{T2}$ and $(X_G)_{T1})$. Their differences were less than 10% for all runs. The catalysts exhibited high conversions to gaseous products $((X_G)_{GP})$ and H₂/CO ratios close to 1.33, the stoichiometric glycerol decomposition value $(C_3H_8O_3 \rightarrow 3CO + 4H_2)$ (6). This indicates that Pt/C-black catalysts are selective towards synthesis gas under the test conditions, without significant contribution from water-gas shift (WGS) to the product mixture. The CO₂ selectivity was very low. This result was also similar to the ones reported in the literature [21-23,26,27].

Two considerations demonstrate that our system is free from transport limitations. First, theoretical analyses based on dimensionless groups [31] indicate interphase mass transfer can become limiting for particle sizes higher than 100 µm. The catalysts particle sizes of the catalysts used in this study were less than 70 µm. Further, the TOF measured increased with the particle size. Second, the CO-TOF and Glycerol-TOF values are quite similar for the catalysts 1% Pt/C and 5 wt. % Pt/C (after reduction at 473 K, with similar dispersion as that of 1% Pt/C). Thus, the Madon-Boudart criterion for the absence of transport limitations is satisfied for these catalysts [32]. Therefore, our tests results were obtained under kinetics regime.

Notably the CO-TOF and Glycerol-TOF values increased with the platinum crystallite size (CO-TOF from 107 to 580 min⁻¹ and Glycerol-TOF from 42 to 226 min⁻¹ for catalysts with 1 wt. % to 10 wt. % Pt). More interestingly is the difference between the TOF values obtained from the catalysts with the same Pt content,

but different platinum crystallite sizes prepared at different reduction temperatures. A 4-fold increase in TOF was observed when Pt crystallite size increases 79%. These results suggest that the glycerol reforming reaction is a structure-sensitive reaction.

3.3. Glycerol Gas-Phase Reforming Reaction: effect of the Pt crystallite size on selectivity

Table 3 summarizes selectivity results under different conversions (conversions given in Table 2). The selectivity to CO was the highest among all products. It increased from 74% for catalyst with higher Pt dispersion to 90% or above for those with lower Pt dispersion. At the same time the selectivity towards molecules with 2 and 3 carbon atoms size decreases. Moreover, the ratio of conversion to gaseous products and to condensed ones $[(X_G)_{GP}/(X_G)_{LP}]$ increased as well (Table 2). It implies that more C-C bond cleavages occurred as compared to C-O ones. However, the selectivities in Table 3 were recorded under different glycerol overall conversions. Hence, we carried out the glycerol reforming using the 5 wt. % Pt/C catalysts by using different space velocities to obtain different conversions. With these results, we can then discuss and compare with the selectivity values obtained with the low metal-loading catalysts. As shown in table 4, the overall glycerol conversion attains a value around 20 and 34% when the space velocity is 99 and 66 min⁻¹, respectively. This latter value in the same range obtained by the catalysts with 1 wt. % and 3 wt. % Pt under typical conditions. In these conditions, the selectivity towards gaseous products is still higher for the platinum catalyst with a larger crystallite size (5 wt. %), by comparing the selectivity ratio (gaseous to condensed/liquid). The CO selectivity was above

80% (higher than that of 1 and 3% Pt) and the selectivity values for two or three carbons were lower. These results indicate that the gas-phase reforming of glycerol is also structure sensitive regarding its selectivity. Here, we should point out that aqueous-phase glycerol hydrogenolysis has been shown to be structure sensitive concerning to the selectivity [34-36] and activity [36].

3.4. General consideration on structure sensitivity

Even though we observed remarkable changes in reaction rates and important changes in selectivity in the reforming reaction comparing Pt catalyst of not very different in Pt crystallite sizes, the reaction being structure sensitive is rather reasonable. Simonetti et al [26] have indicated that this reaction was structure sensitive using a catalyst system similar to this work, in a less severe reaction condition (T = 548 K). Claus and Lehnert [34] also proposed that the aqueous phase reforming (APR) reaction is structure sensitive as the selectivity in hydrogen production increased with crystallite size of Pt even though the rate of reaction was not affected. For the hydrogenolysis of glycerol on ruthenium catalysts, Miyazawa et al. [35] and Wang et al. [36] reported that the reaction might be structure sensitive.

As according to Claus and Lehnert [34], one may assume that the adsorption of the oxygenated hydrocarbons for subsequent cleavage of a C-C bond occurs preferably at face positions rather than at the edges and corners. The former positions are more abundant for larger metal crystallites. Hence, catalysts containing these type of crystallites are more active per surface atom exposed.

In the steam reforming reaction of glycerol, in addition to the C-C bond

cleavage, C-O bonds cleavages also occurs. The competition of C-C adsorption and C-O adsorption on adjacent metal sites and their subsequent cleavage may result in a complex dependence on the crystallite sizes.

3.5. Glycerol Gas-Phase Reforming Tests: the pH effect of the glycerol aqueous feed solution

The catalytic performances of the commercial 5 wt. % Pt/C (BASF) catalysts at using glycerol aqueous feed solutions with various pH (3, 6, and 10) are shown in Figure 3 and Tables 6 and 7. The tests were performed under typical conditions: under atmospheric pressure, at 623 K, with a space velocity (WHSV) of 33 min⁻¹. It is worthy to mention that no activity was observed when that blank tests using the support as catalyst were made.

Figure 3 illustrates stable conversion profiles for all feed solutions with different pH values in the first 25 h time-on-stream, which demonstrates that basic and acidic species not poisoning the catalyst as well as no significant deactivation occurs. The conversion to gas-phase products was the highest at pH=6, $(X_G)_{GP}$ = 77.4, and was lower in basic and acidic medium. Again, both methods of calculation of conversions agreed within 10%, as shown in Table 6. The activities observed, TOF, follow the same trend. They decreased considerably, which indicates that ionized feed does not favor the main reaction. Despite the gaseous to liquid products ratio increase with the pH of the feed solution, the selectivities to all identified molecules, shown in Table 7, did not change significantly. Chaminand *et al.* [21] obtained a similar result after adding HCI in the aqueous feed solution.

In summary, an activity decreased and no remarkable changes in selectivity were observed in the glycerol steam reforming under the reaction

condition with different pH value of the glycerol aqueous solution. Nevertheless, catalytic performances of the APR or liquid-phase hydrogenolysis reactions were changed when the pH of the glycerol solution was varied. In basic medium, selectivity to break C-C bonds leading to carbon monoxide was higher compared in neutral medium, whereas in acidic media, the cleavage of the C-O, by a reaction dehydration became competitive with the former. In acidic medium was also observed a small inhibition of successive falls of the C-C, providing the formation of acetol, ethylene glycol and methanol.

4. Conclusions

Carbon black supported platinum catalysts with low Pt-content can also be used to produce syngas at low temperature (623 K) with reasonable stability until 3024 h at least. Moreover, a stable steady state is established even under high space velocity (99 min⁻¹) under acidic and basic condition. The Pt/C system provides synthesis gas with a H₂/CO ratio around 1.33.

As the activity and selectivity changed with the size of the platinum particle size, the current results also indicate that the gas-phase reforming of glycerol is a structure-sensitive reaction. The size increasing leads to an increasing of the CO and Glycerol TOF and selectivity towards gaseous products, formed by consecutive C-C cleavages. The Pt-C bonds are more stable than the Pt-O ones in the Pt/C system. Then, adsorbed species are probably bonded to the catalyst surface through Pt-C bonds. This enables further subsequent C-C cleavages, avoiding C-O breakages, which would lead to hydrogenolysis products. The activity decreases and no remarkable changes in selectivity are observed in the glycerol gas-phase reforming under the reaction condition with different pHs of

the glycerol aqueous solution.

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Figure Captions

Figure 1. Glycerol Steam (30 wt.%) Reforming (P = 1 bar, T = 623 K, and WHSV = 33 min⁻¹) of 1, 3, 5, and 10 wt.% Pt/C catalysts after reduction at 623 and 473 K (w/ 5 wt.%*)

Figure 2. Glycerol Steam (30 wt. %) Reforming at P = 1 bar, T = 623 K of 5 wt. % Pt/C catalyst with different WHSV (33, 66, and 99 min⁻¹)

Figure 3. Glycerol Steam (30 wt. %) Reforming (P = 1 bar, T = 623 K, WHSV = 33 min^{-1}) of 5 wt. % Pt/C catalyst with different glycerol aqueous solution pH (3, 6, 10).

Figure 1.



Figure 2.







Table 1. CO chemisorption results

Results	1%	3%	5% *	5%	10%
µmolCO uptaken/gcat	26.00	78.80	97.50	81.30	95.70
Metal Dispersion (%)	50.81	51.26	53.01	31.74	18.67
Pt particle size (nm)	2.22	2.21	2.97	3.56	6.10

(*) The reduction temperature was 473 K, using the same temperature ramp (0.5 K.min⁻¹) and H₂ flow rate (35 cm³.min⁻¹). After remaining 2h at 473 K under hydrogen flowing, the temperature was increased (10 K.min⁻¹) to 623 K under He flowing (35 cm³.min⁻¹), remaining 1h at it.

Table 2. Influence of the metal (Pt) particle size on the conversion to Liquid $(X_G)_{LP}$ and gas $(X_G)_{GP}$ phases, overall glycerol $((X_G)_{T1}$ and $(X_G)_{T2})$ conversions (%), CO (CO-TOF) and Glycerol (G-TOF) Turnover frequencies (min⁻¹), and H₂/CO ratio.

Cotolyst		(V)			CO-TOF	G-TOF	
Catalyst	(A G)LP	(AG)GP	(A G)T1	(A G)T2	(min ⁻¹)	(min ⁻¹)	H ₂ /CO
1%	2.89	26.51	29.4	27.3	107.42	42.28	1.36
3%	2.42	20.56	22.98	23.86	97.53	37.77	1.38
5%	4.42	77.45	81.87	81.09	422.25	197.57	1.36
5% *	4.47	27.00	31.47	32.71	101.02	43.61	1.38
10%	3.58	54.07	57.65	58.96	580.26	226.62	1.35

Table 3. Influence of the metal (Pt) particle size on the selectivity (%) to gas and liquid phases products: CO, CH₄, Ethylene ($C_2^=$), Ethane (C_2), Propene($C_3^=$), Propane(C_3), CO₂, Acetone, Metanol (MeOH), Acetol, Ethylene glycol (EG), Glyceraldehyde (GA).

Cataly	С	СН	C.=	C.	C.=	C.	CO	MeO	Aceto	Acet	Ε	G	
st	0	4	C_2	C_2	C3	C 3	2	Н	ne	ol	G	Α	
10/	75.	3.2	1.8	3.1	1.0	1.3	1.3	2 42	1 20	176	2.	25	
1 70	2	7	6	1	8	8	0	2.42	1.39	4.70	1	2.3	
20/	75.	2.8	2.4	2.7	2.2	2.5	1.0	2 1 2	1 20	2.05	2.	21	
3%	6	1	8	0	2	0	9	2.12	1.20	2.95	1	5.1	
50/	90.	2.8	0.3	0.4	0.3	0.0	1.6	1 47	1 47 0 02	0.02	1.05	1.	0.1
570	8	1	2	3	0	6	1	1.4/	0.02	1.95	2	0.1	
50/ *	74.	3.1	1.3	1.7	0.7	0.1	1.3	2 71	0.96	756	1.	52	
5% *	5	5	8	8	2	4	0	2.71	0.80	7.30	8	5.5	
100/	93.	2.2	0.2	0.3	0.1	0.0	1.3	1 27	0.12	1 1 5	0.	0.2	
10%	4	6	9	4	8	0	8	1.27	0.12	1.15	4	0.5	

Table 4. Influence of the WHSV on the conversion to Liquid $(X_G)_{LP}$ and gas $(X_G)_{GP}$ phases, overall glycerol $((X_G)_{T1}$ and $(X_G)_{T2})$ conversions (%), CO (CO-TOF) and Glycerol (G-TOF) Turnover frequencies (min⁻¹), and H₂/CO ratio.

WHSV(min ⁻¹)		(V)	(V)		CO-TOF	G-TOF	
	(AG)LP	(A G)GP	(A G)T1	(A G)T2	(min ⁻¹)	(min ⁻¹)	112/00
33	4.42	77.35	81.77	80.78	404.44	156.53	1.35
66	2.14	29.39	31.53	34.20	300.96	158.89	1.38
99	1.72	16.03	17.75	19.87	266.0	126.11	1.36

Table 5. Influence of the WHSV on the selectivity (%) to gas and condensed phases products: CO, CH4, Ethylene ($C_2^=$), Ethane (C_2), Propene($C_3^=$), Propane(C_3), CO₂, Acetone, Metanol (MeOH), Acetol, Ethylene glycol (EG), Glyceraldehyde (GA).

WHSV	CO	СЦ	C.=	C.	C.=	C.	CO.	МоОН	Acotono	Acotol	FC	CA
(min ⁻¹)	co	CII4	C_2	C_2	C3	C3		Meon	Action	Accion	ĽŪ	UA
33	85.32	3.38	1.06	1.41	0.53	0.06	1.46	2.01	0.02	1.49	0.84	1.01
66	85.40	3.29	0.94	0.38	0.28	0.00	1.19	2.29	0.29	3.93	1.23	2.12
99	80.20	2.68	1.07	0.32	0.32	0.00	1.24	2.84	0.42	5.29	1.85	5.37

Table 6. Influence of the pH of the feed solution on the conversion to Liquid $(X_G)_{LP}$ and gas $(X_G)_{GP}$ phases, overall glycerol $((X_G)_{T1}$ and $(X_G)_{T2})$ conversions (%), CO (CO-TOF) and Glycerol (G-TOF) Turnover frequencies (min⁻¹), and H₂/CO ratio.

рН				(V)	CO-TOF	G-TOF	
	(AG)LP	(AG)GP	(A G)T1	(A G)T2	(min ⁻¹)	(min ⁻¹)	H ₂ /CO
3	3.04	65.70	68.74	68.35	337.98	133.13	1.46
6.07	4.42	77.35	81.77	80.78	404.44	156.53	1.38
10	4.00	45.39	49.40	53.20	248.65	103.11	1.35

Table 7. Influence of the pH of the feed solution on the selectivity (%) to gas and condensed phases products: CO, CH₄, Ethylene ($C_2^=$), Ethane (C_2), Propene($C_3^=$), Propane(C_3), CO₂, Acetone, Methanol (MeOH), Acetol, Ethylene glycol (EG), Glyceraldehyde (GA).

pН	CO	CH ₄	$C_2^=$	C ₂	C3 ⁼	C ₃	CO ₂	MeOH	Acetone	Acetol	EG	GA
10	88.8	2.83	0.50	0.38	0.13	0.00	1.09	2.74	0.02	0.88	1.60	1.92
6.0	85.3	3.38	1.06	1.41	0.53	0.06	1.35	2.01	0.02	1.49	0.84	1.01
3	86.7	3.61	0.67	0.56	0.33	0.00	2.28	2.76	0.02	1.18	1.60	2.28