

Glycerol Reuse for Obtaining Synthesis Gas through Steam Reforming

J. M. Encinar, J. F. González, N. Sánchez, and S. Nogales

Abstract—Glycerol is generated in biodiesel production. Due to its overproduction, it is necessary to find new applications for glycerol. In this work glycerol underwent steam reforming to obtain synthesis gas, using α -alumina as a filling material, and two cylindrical reactors of 5.2 cm of diameter and 30 cm long, installed in series, and controlling temperature and carrier gas flow. There was also a condensation system for the condensable products and a sample collection system for the gas produced.

The study of the main variables for this process (particle size, temperature, total flow, water/carbon ratio and nitrogen flow) was carried out. The decrease in particle size, as well as the increase in temperature, had positive effects on synthesis gas production. The total flow of the feed mixture and the water/carbon molar ratio should be regulated, establishing a balance between both parameters. Concerning the nitrogen flow, there was an optimum point from which lower or higher flows worsened the results. Finally, the continuous use of the filling material affected the results, proving that the flow of gas produced decreased over time, and its composition became poorer in hydrogen, reaching a stationary regime where the synthesis gas had similar CO and H₂ levels.

Index Terms—Glycerol, steam reforming, synthesis gas, hydrogen.

I. INTRODUCTION

Current energy policies tend to promote sustainable technologies. In that sense, the use of biodiesel is supported by governments. Thus, if they comply with the norms about this fuel, the demand for biodiesel will be considerable [1]-[3]. The main way to obtain biodiesel is by transesterification of vegetable oils or animal fats, obtaining glycerol as a by-product (about 10 % of the biodiesel obtained) [4].

The increase in biodiesel production provokes the incorporation of considerable amounts of glycerol in markets, which is decreasing its price [1], [5]. Therefore, it is important to explore different alternatives for the revaluation of this compound.

In this respect, steam reforming is a suitable alternative for glycerol revaluation due to its ability to produce synthesis gas (rich in hydrogen). In this method the substrate reacts with steam to produce hydrogen, carbon dioxide, carbon monoxide, methane and, to a lesser extent, coke and hydrocarbons [6], [7]. The thermodynamic analysis of the

process has been carried out, finding that an atmospheric pressure, high temperatures and high water/glycerol ratios facilitate the process [8].

In this research work a preliminary study about operating conditions for glycerol reforming with steam was carried out, using a reactor that is from 2 to 10 times bigger than micro reactors usually used in researchs about glycerol reforming [2].

II. METHODOLOGY

Glycerol (Panreac) and α -alumina balls with different diameters (Keratec Advanced Materials S. A.) were used. For the development of the steam reforming experiments, nitrogen (N₂ 5.0, Linde) was used as a carrier gas. The gas produced during the process was analyzed by gas chromatography, using H₂ 5.0, CH₄ 3.5, CO 3.7, CO₂ 4.5, C₂H₄ 2.8, C₂H₆ 2.5 and two mixtures of gases as standards (Linde) for calibration.

The experimental facility was similar to those described in previous works [9], [10] and is shown in Fig. 1. It has two stainless steel cylindrical reactors, positioned in series. Each of them had an inner diameter of 5.2 cm and was 30 cm long. Within the reactors, a small basket made of stainless steel was placed, with the filling material.

Each reactor was placed in an oven and the temperature control was carried out by a thermocouple in the reactor. For the supply of the glycerol/water mixture, a peristaltic pump was used and the carrier gas inlet was controlled by a flowmeter and a mass flow meter. There were several gas traps in containers with cold water, connected to the reactor outlet, in order to collect the condensable products. After that, there was a glass sampler and a gas meter.

In order to carry out an experiment, the reactor was filled with a certain amount of alumina, preparing the glycerol/water solution with the desired water/carbon ratio (S/C) and establishing the flows for the mixture and the carrier gas. The reaction took place when the reactor was filled with N₂ and the reaction temperature was reached, and finished when the stationary regime was achieved. In order to monitor the whole process and know when the stationary regime was reached, the non-condensable gases at the outlet of the reactor were analyzed. At the end of the reaction the condensable products were collected, quantifying their weight and the solid accumulated on alumina balls within the reactor.

The analysis of the gaseous product was carried out by using a chromatograph (Varian 3900), with an injector regulated by a valve that is activated by air pressure and a thermal conductivity detector. The column (Carboxen 1000

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60/80) was 15 ft long and had an inner diameter of 1/8 ft.

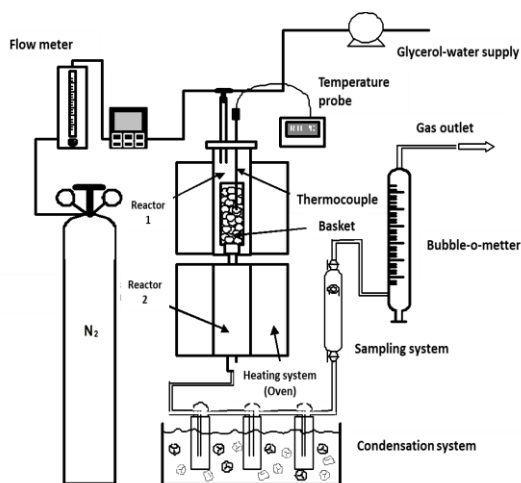


Fig. 1. Diagram of the experimental arrangement.

Finally, the following parameters were calculated: the percentage of carbon of the glycerol converted to gas (% C), the H_2 /glycerol molar ratio (H_2 /glycerol) and the high heating value (HHV) of the gas produced, taking into account the combustion heat for each component of the sample, as follows (Equation 1):

$$HHV = 0.28584 n_{H_2} + 0.28299 n_{CH_4} + 1.4110 n_{C_2H_4} + 1.5599 n_{C_2H_6} \quad (1)$$

where n_{H_2} , n_{CO} , n_{CH_4} , $n_{C_2H_4}$ and $n_{C_2H_6}$ represent, respectively, the moles of H_2 , CO , CH_4 , C_2H_4 and C_2H_6 that have been generated per minute, or during the gasification of a kg of glycerol, expressed in $MJ \min^{-1}$ and $MJ \text{ kg}^{-1} C_3H_8O_3$, respectively.

III. RESULT AND DISCUSSION

The aim of this study was the revaluation of glycerol through steam reforming. For this reason, some operating variables were studied, assessing the yields of the gas product obtained. The variables were: the particle size of the filling material (19 – 25 mm), the reaction temperature (700 – 800 °C), the flow of the glycerol/water mixture ($0.6 - 2.3 \text{ g min}^{-1}$), the water/carbon molar ratio (3 – 15), the flow of the carrier gas ($50 - 325 \text{ mL min}^{-1}$) and the reaction time. The operating conditions and the results obtained, except for the reaction time, are shown in Tables I and II.

A. Effect of the Particle Size of the Filling Material

Fig. 2 represents the composition of exhaust gases for experiments 1 and 2, through which the effect of the particle size of the filling material has been studied. The rest of the results are shown in Table II.

As it can be seen, synthesis gas composition was not affected by particle size; however, Tables I and II shows higher gas production as the diameter of alumina balls decreased. The same happened to % C and the H_2 /glycerol molar ratio. Therefore, higher amount of gas was produced, higher conversions were achieved and this gas was richer in hydrogen. This fact could be due to the fact that shorter particle sizes implied lower porosity and bed permeability

values, causing a more uniform distribution of the reactive, facilitating the reactivity between glycerol and water [11].

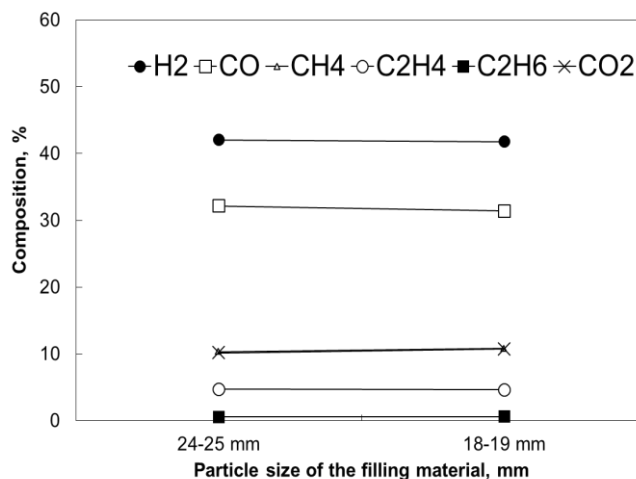


Fig. 2. Synthesis gas composition depending on particle size.

TABLE I: OPERATING CONDITIONS

Exp	Operating conditions				
	Particle size (mm)	T, °C	Mixture flow, g min^{-1}	S/C ratio	N_2 flow, mL g^{-1}
1	24 – 25	800	1.15	5.7	90
2	18 – 19	800	1.15	5.7	90
3	18 – 19	750	1.15	5.7	90
4	18 – 19	700	1.15	5.7	90
5	18 – 19	800	0.58	5.7	90
6	18 – 19	800	1.74	5.7	90
7	18 – 19	800	2.30	5.7	90
8	18 – 19	800	1.15	5.7	49
9	18 – 19	800	1.15	5.7	175
10	18 – 19	800	1.15	5.7	336
11	18 – 19	800	1.15	3.0	175
12	18 – 19	800	1.15	9.0	175
13	18 – 19	800	1.15	15.3	175

TABLE II: EXPERIMENTAL RESULTS

Exp	Experimental results					
	%C	H_2 /glyc ratio	Gas volume		HHV	
			$\text{mL g}^{-1} C_3H_8O_3$	mL min^{-1}	$\text{MJ kg}^{-1} C_3H_8O_3$	MJ min^{-1}
1	80.3	1.60	1012	268	15.7	4.2
2	87.1	1.72	1094	290	17.0	4.5
3	79.8	1.19	887	235	15.0	4.0
4	69.4	1.12	797	211	13.1	3.5
5	98.5	2.13	1284	171	19.3	2.6
6	74.4	1.30	878	351	14.4	5.7
7	64.7	1.11	758	401	12.7	6.8
8	81.3	1.59	1016	269	16.0	4.2
9	90.8	2.25	1277	338	18.1	4.8
10	90.4	2.11	1225	325	17.9	4.7
11	74.7	1.49	938	396	14.8	6.2
12	88.7	1.96	1207	217	17.3	3.1
13	94.7	2.09	1260	140	17.7	2.0

B. Effect of Temperature

The study of temperature was carried out in experiments 2, 3 and 4, and the results are shown in Tables I and II and Fig. 3. As it can be observed in Fig. 3, temperature has an important effect on H₂ production. Its percentage, along with CO₂, increased with this variable. This fact is reasonable, taking into account that the global steam reforming of glycerol (Equation 2) is endothermic and therefore equilibrium will move around to the right-hand as temperature increases. In consequence, the formation of H₂ and CO₂ will be favored at high temperatures [12].

This shift of the global chemical balance to produce H₂ and CO₂, will improve the total gas production, the conversion of glycerol to a gas product (% C) and the heating value of the synthesis gas, as it can be seen in Tables I and II.



On the other hand, there are other reactions that take place (Equations 3-5) whose chemical balance will be shifted to hydrogen production at high temperatures.

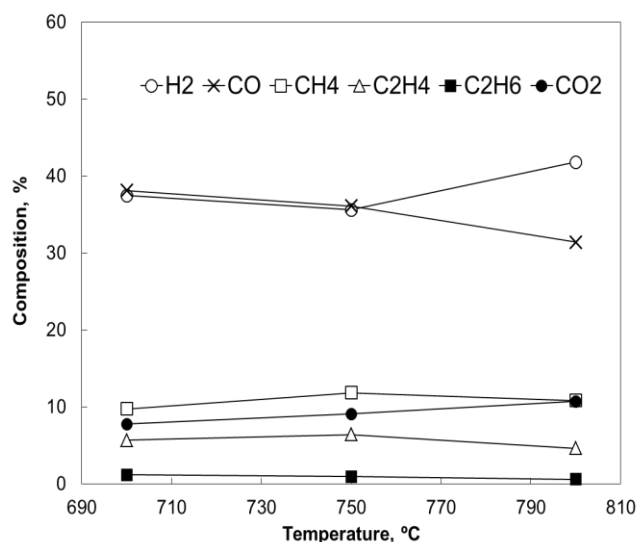
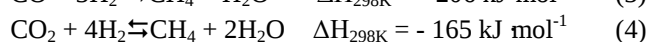
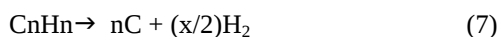


Fig. 3. Synthesis gas composition versus working temperature.

Fig. 3 also shows a decrease in CO production, which could be explained by the thermodynamics of the Water Gas Shift reaction (WGS) (Equation 6):



Finally, higher temperatures did not provoke a decrease in C₂H₄ and C₂H₆ concentration in the synthesis gas obtained. This decrease is explained by the decomposition of non-oxygen-containing hydrocarbons (Equation 7), which is favored at high temperatures.



C. Effect of Glycerol-Water Flow

The total flow of the glycerol/water mixture should be optimized in order to make the most of the system, as it could be possible to work with a lower flow than the maximum that is allowed according to the size of the reactor, which could imply excessive energy costs with low gas production. On the other hand, the flow could be too high, with a poor glycerol conversion to gas. The experiments carried out for this study were Exp. 2, 5, 6 and 7, and their results are shown in Tables I and II and Fig. 4.

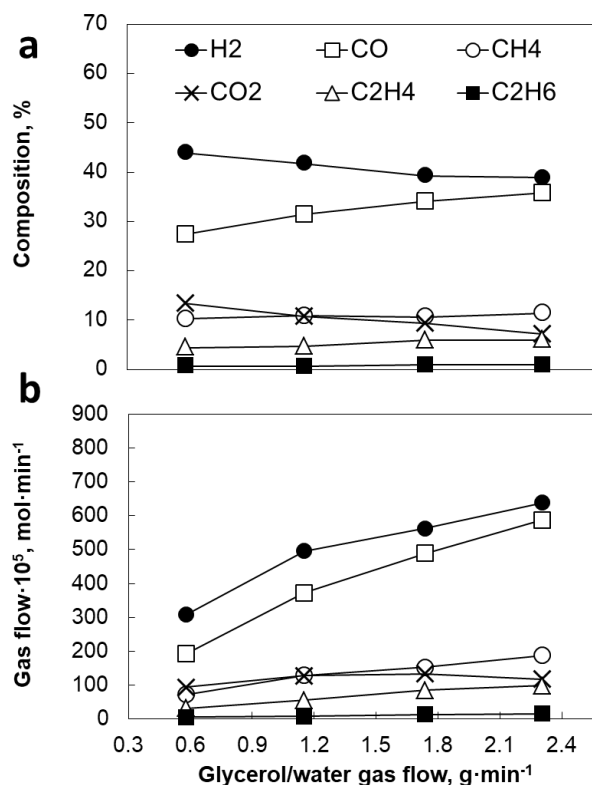


Fig. 4. Synthesis gas composition (a) and gas flow for each compound (b) versus glycerol/water flow.

Fig. 4.b shows an increase in molar flow for most compounds when the mixture flow increased, which is reasonable as more raw material is available. For this reason the flow of the gases generated and the HHV (expressed in MJ min⁻¹) increased. However, these increases were not proportional to the increase in flow, and H₂ and CO₂ composition decreased whereas the composition of the remaining increased and % C decreased, as it happened to H₂/glycerol ratio, gas volume and HHV per unit of mass of glycerol. This fact could be explained by the residence time reduction and its subsequent lower possibility to contact with the filling material. Therefore, for these conditions, it is preferable a compromise solution between the highest conversion per unit of mass and the highest gas production per unit of time, that is, 1.15 g min⁻¹.

D. Effect of the Carrier Gas Flow

Nitrogen, that is an inert gas, was used as a carrier gas. The influence of its flow was studied in this section. As mentioned earlier, it is suitable to consider both the results per unit of mass and unit of time, as it can be seen in Fig. 5, Experiments 2, 8, 9 and 10 and in Tables I and II.

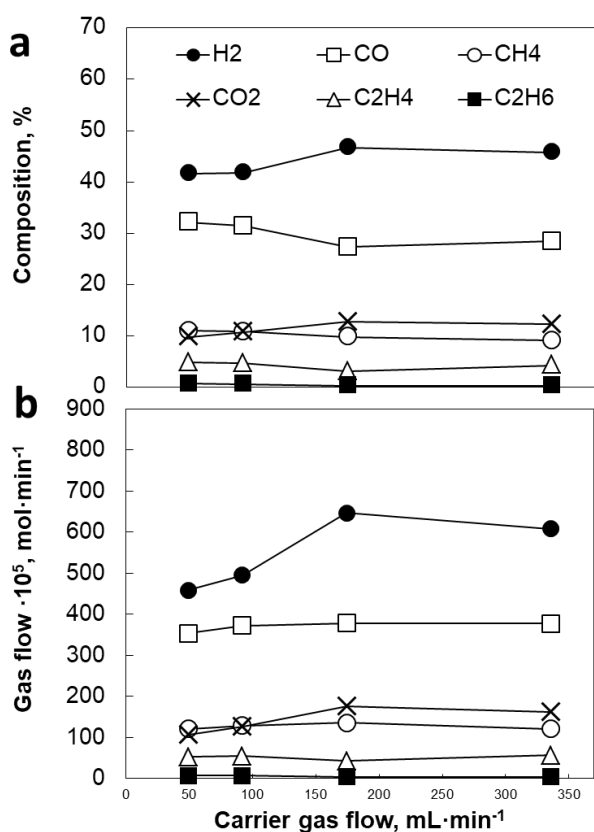


Fig. 5. Synthesis gas composition (a) and gas flow for each compound (b) versus carrier gas flow.

An increase in the carrier gas flow would imply a reduction in the residence time, which could lead to poorer results. Nevertheless, it can be noticed that an increase in the flow from 50 to 175 mL·min⁻¹ improved the results. This fact was already observed by some authors [13], who explained that the “dilution effect” caused the rise of the inert gas concentration. However, if the flow is increased from this range, the results got worse, which could reveal the effect of the residence time reduction.

E. Effect of Water/Carbon Ratio (S/C)

The water/glycerol molar ratio is an important parameter to study. The experiments 9, 11, 12 and 13 are related to it, and the results are shown in Table I, Table II and Fig. 6. Fig. 6.a shows that, as S/C ratio increased in the reactor feeding, the gas is richer in H₂ and CO₂, whereas CH₄ proportion is reduced. This could be due to the fact that the higher proportion of water in the reactor feeding favored the global reaction of reforming (Equation 2), as well as WGS reaction (Equation 6), and it is detrimental to CH₄ production (Equations 3-5) [14, 15]. Concerning the volume of gases generated, as the S/C ratio increased, the amount of glycerol supplied per unit of time was lower. Therefore, it is logical its decline. It should be pointed out that, with S/C values of 3 and 5.7, practically the same gas flow per unit of time was obtained and, however, the results per unit of mass for glycerol were much better for S/C = 5.7. Therefore, this is the most suitable ratio.

F. Study of the Reaction Time

Another aim of this research was to assess the evolution of the steam reforming of glycerol if long reaction times are

used. Thus, the reforming of a water/glycerol mixture was carried out using the same conditions of Experiment 9, showing in Fig. 7 the changes in molar flow for each evolved compounds over time. As it can be seen, reaction times shorter than 200 minutes kept the same flow and composition for the exhausted gases. The most sensitive compound was hydrogen, whose yield decreased considerably with reaction time, and its flow reached a similar value compared to CO.

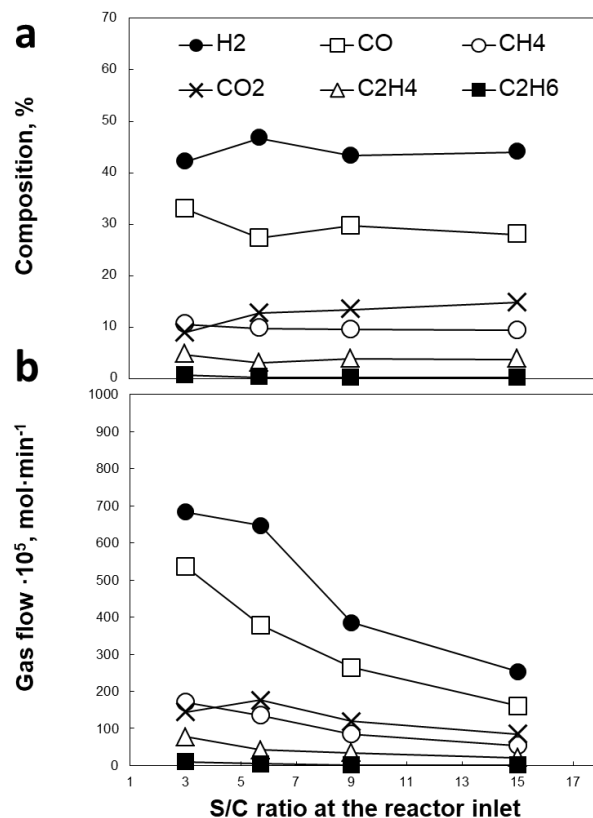


Fig. 6. Synthesis gas composition (a) and gas flow for each compound (b) versus S/C ratio at the entrance of the reactor.

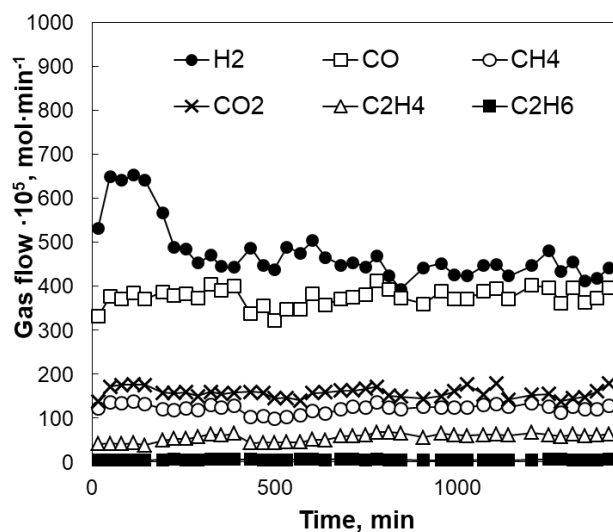


Fig. 7. Gas flow for each compound versus time.

IV. CONCLUSION

It emerges from the study of the main variables of reforming with glycerol, using α -alumina as a filling material,

that smaller particle sizes of the latter favored the reaction. The same effect was found for an increase in temperature. Furthermore, parameters such as total inlet flow water/carbon molar ratio and carrier gas flow should be optimized to establish an intermediate situation between the achievement of high gas flow and the maximum glycerol conversion. Also, it was found that the synthesis gas had less hydrogen over reaction time.

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bioethanol.

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