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Glycerin, a Biodiesel By-Product with Potentiality to Produce Hydrogen by Steam Gasification

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Abstract: This work investigates the possibility of providing a use to one of the major byproducts generated during biodiesel processing: glycerin. In particular, the steam gasification of water/glycerin mixtures is studied, analysing the influence of temperature (range 600–900 °C), inlet flow rate (0.5–3 mL· min^{-1}) and water/glycerin ratio (6–12 wt/wt, %) on the gas composition (H_2, CO, CH_4 and CO_2), higher heating value, and generated power. In general, a more diluted water/glycerin mixture is more interesting in order to provide a higher fraction of hydrogen in the gas produced, although it also involves a decrease in the power obtained. Higher temperatures cause a greater contribution of water gas and water gas shift reactions in all cases, thus increasing the H_2 proportion of the gas. Finally, a greater inlet flow rate increases gas production, but decreases the hydrogen proportion.

Keywords: glycerin; steam gasification; synthesis gas; hydrogen

1. Introduction

Nowadays, the finite duration of fossil resources, the increasing energy demand and heterogeneous distribution of fossil fuel reserves is generating more and more geopolitical conflicts, which make evident the non-sustainability of the current worldwide energy model. Likewise, the environmental problems associated to the exploitation of fossil fuels are a question of global concern. In this frame, the International Energy Agency (IEA) defines as a primordial target the achievement of a substantial bioenergy contribution to future global energy demands by accelerating the production and use of cost-competitive bioenergy on a sustainable basis, thus providing increased security of supply whilst reducing greenhouse gas emissions from energy use [1].

Especially in the context of transport, biofuels have gained prominence during last years, and they are seen as a near-term alternative. Biodiesel is a non-toxic and biodegradable fuel that can be produced from a variety of crops. Moreover, numerous studies have been carried out using vegetable oils as raw materials [2–4]. The literature also shows works in which unconventional raw materials, as oil obtained from algae, bacteria, mushrooms and microalgae are used [5,6].

Biodiesel is obtained by direct transesterification of vegetable oils and tallows; this process involves the alcohol (glycerol) displacement of the triglyceride structure, by means of the incorporation of another short alcohol chain (methanol or ethanol). This causes the separation of the three fatty acid molecules forming the original triglyceride, which remain as methyl or

ethyl esters [7]. Chemically, the transesterification consists of three consecutive and reversible reactions. The triglyceride is turned consecutively into a diglyceride, monoglyceride and ultimately free glycerol. A mole of ester is freed in each reaction. Stoichiometrically, three moles of alcohol are required per mole of triglyceride and, consequently, three moles of esters are freed. Hence, for each kg of triglyceride another kg of biodiesel is obtained, approximately [8]. During the biodiesel production process, glycerin is formed as by-product in a ratio of approximately 10% (wt. glycerin/wt. biodiesel produced).

Current biofuels production is close to 2 million tons per year, of which Europe and America have a share of more than 90% (the same applied to biofuels consumption) [9]. In the European Union, biodiesel is the main biofuel used for transport and accounts for about 70% of the biofuels market on a volume basis, with a production of some 10000 tons; this production is expected to increase in the coming years, in the frame of Horizon 20/20/20 Strategy, which pursues that transport biofuels (including biodiesel and also other advanced biofuels) rise their contribution up to 10% using renewable energies [10].

These facts make evident the need to look for alternative applications for the glycerin, generated as a byproduct of biodiesel production. If pure, glycerin can be used as raw material for the production of cosmetics and personal care products, medical applications, as lubricant, in the manufacture of explosives, as an antifreeze, in the food processing industry, in the manufacture of resins and paints, in the tobacco industry, for textile and leather applications, *etc.* [11]. However, glycerin is usually contaminated with traces of metals, and this makes it necessary to subject this material to costly cleaning processes, which are usually more expensive than the value of the glycerin itself. The need for alternative uses is therefore pressing, and an interesting option would be to consider energetic applications. In this way, two targets would be achieved: the possibility of providing different uses for this waste, and a reduction of the energetic costs of production.

The potential use of glycerin as an energy source might be carried out by several thermoconversion processes, such as microbial processing [12], pyrolysis [13,14] or supercritical water reforming [15]. Another alternative is the direct combustion of the glycerin in an adapted boiler; however, the heating power of glycerin is low compared with that of the diesel oil. Gasification processes can be of especial interest, since they can promote the production of hydrogen, using steam as gasifying agent [16].

During last years, scientists have focused their attention on hydrogen production technologies, because of its importance in fuel cells and its promising use as a carbon-free energy carrier. Many techniques can be employed to produce hydrogen, however, most of them use depleting sources, which finally make the process unsustainable; in fact, fossil fuel reforming accounts for 98% of hydrogen production. In this frame, obtaining of H_2 from biomass has attracted the interest of researchers worldwide.

To the best of the authors´ known, research on the optimization of steam gasification processes using glycerin as precursor is scarce. Among the studies found in this field, we can highlight the ones by Valliyappan [17], who studied the pyrolysis of glycerin obtaining a gas with a H_2 composition of up to 60%. Also, Adhikari *et al.* [18] investigated the thermodynamics involved in steam reforming of glycerin, finding that the conditions providing the greatest amount of hydrogen were high temperature, low pressure (near atmospheric) and high water-glycerin flow rate, and they achieved hydrogen molar fractions of 56.5%. Other researchers like Ramesh *et al.* [19] have used Cu/Ni catalysts to decrease the glycerin steam gasification temperature, obtaining fraction values near 70%.

With the aim of providing more insight into this topic, this work is focused on the study of steam gasification of glycerin (diluted in water) in order to produce an hydrogen-rich gas, making a systematic investigation on the influence of the temperature, water/glycerin volumetric ratio and inlet feed flow. The novelty of this work is that it uses glycerin obtained from real biodiesel production processes, instead of the pure chemical, as it is the case on most research studies. This research entails

a real application of the by-product, which would otherwise become a harmful residue and would have to be discarded, adding complexity to the process. The obtaining of a high calorific value gas from the gasification of glycerin can be useful to provide part of the energy needed in the biodiesel production or can be stored for further applications.

2. Experimental

2.1. Materials

Glycerin from the transesterification of vegetable oils was provided by the biodiesel manufacturing plant of Bioenergética Extremeña, located in Valdetorres (Extremadura, Spain). It was used as it results from biodiesel production, without any further treatment, and characterized in terms of its chemical composition, which was made according to standard technical specifications, as described in Table 1. In addition, glycerin heating value was determined by a calorimetric bomb (mod. 1351, Parr Instrument Compant, Moline, IL, USA).

Table 1. Characterization of the glycerin.

Analysis		Results (mg· kg^{-1})	Method
Non-glyceric organic matter		6.840	CEA 1705
Sulphated ash		4.2	EP 2002
Water		11	ASTM E-203-1
Purity (%)		77.6	CEA 212
Sulphur		40,000	EN 228:2004
Phosphorus		100	EN 228:2004
Metals	Calcium	3.7	CEA 1574-B
	Tin	2	
	Iron	10	
	Magnesium	11	
	Nickel	2.2	
	Potasium	18,000	
	Sodium	130	

Moreover, the thermal behavior of glycerin was analyzed using a thermobalance (Setsys Evolution, SETARAM, Caluire, France) under an air flow rate of 100 cm^3· min^{-1}. An initial mass of 15.0 ± 0.1 mg was used, employing a heating rate of 20 °C· min^{-1}. The analyses were made in the temperature range 25–800 °C.

2.2. Steam Gasification Experiments

The runs were performed under continuous regime, using a bench-scale experimental set-up like the one shown in Figure 1.

The gasifier, with an inner diameter of 4 cm (outer diameter of 4.3 cm) and total height of 75 cm was placed inside an electrical furnace, which provided the heat for reactions. The furnace was well insulated to prevent major heat losses and a thermocouple was placed inside the furnace, in close contact with the reactor walls, to monitor the temperature in the reaction medium. Nitrogen (100 cm^3· min^{-1}) was fed to the reactor during the heating up and cooling down periods. Once the furnace had achieved the target temperature, the glycerin, diluted in water, was fed into the gasifier and the process was initiated. Previous to experimentation, the influence of water/glycerin ratio showed that these conditions were optimal [20]. The inlet steam was produced in a coil by another electrical furnace and its flow rate was controlled by water pump (M312, Gilson, Middleton, WI, USA) supplying water to the generator. Several inlet water/glycerin ratios were studied (6:1; 9:1, 12:1), also varying the mixture flow rates (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 g· min^{-1}). Moreover, the reactor temperature was varied in the range 600–900 °C. The runs were made once; the suitability of the

procedure can be supported by previous studies on pyrolysis and gasification made by the research group [21–25].

The gas produced was made to pass through a quenching system (glass receivers covered by ice), where the tars and condensable high molecular weight hydrocarbons were collected. The composition of the gas produced (H_2, CO, CO_2 and CH_4) was analyzed by gas chromatography (GC), using two gas chromatographs (HRGC 4000, KONIK, Miami, FL, USA). Both instruments are identical, although their columns are fed with different carrier gases: He and N_2. In the first case CO, CO_2 and CH_4 are monitored, while H_2 is analyzed using N_2 as carrier, in order to avoid interferences due to the similar thermal conductivity of H_2 and He. Both the fed inert gas (nitrogen) and the produced syngas flow rate were measured by appropriately calibrated flow meters. Once analyzed, the gas produced was transported by a pipe and properly evacuated outdoor.

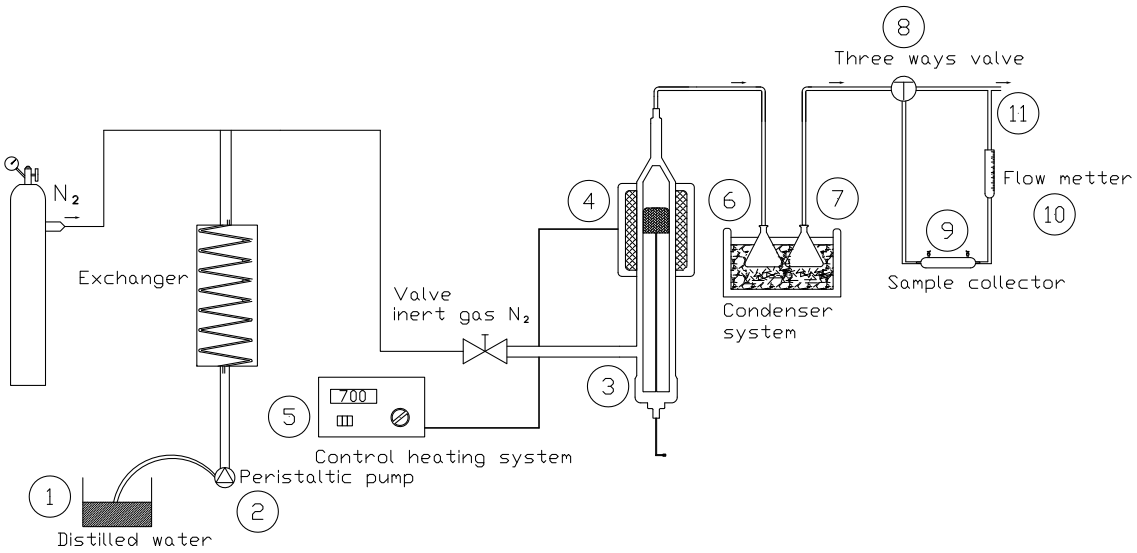

Figure 1. Experimental set-up. Elements: 1-Water container; 2-Bomb; 3-Reactor; 4-Furnace; 5-Temperature controller; 6-Cooling bath; 7-Condensers; 8-Three way valve; 9-Gas sample collecting system; 10-Flow meter; 11-Gas outlet (to chromatograph).

3. Discussion

3.1. Glycerin Characterization

Table 1 shows the chemical analysis of the glycerin feedstock and the analytical method specifications used to perform each analysis. As it can be observed, the glycerin had many impurities, which may be detrimental for its energetic utilization. It is necessary to emphasize the high presence of sulphur and potassium, with 40,000 mg· kg^{-1} and 18,000 mg· kg^{-1}, respectively, and the presence of phosphorus and sodium, in proportions of 100 mg· kg^{-1} and 130 mg· kg^{-1} respectively. Some of these compounds may be harmful for the environment and also damage the experimental installation. For example, and standing out as one of the most toxic pollutants resulting from combustion and gasification processes, organosulphur compounds are converted to H_2S. This gas has been related to fatal diseases for animals and humans, and it also causes stress cracking in metallic installations, reducing the lifetime of processing and handling equipment. Previous studies made by the authors on the thermal degradation of glycerin have confirmed the emission of H_2S [26]. This gas can be successfully reduced by adsorption on selectively functionalized activated carbons as well as other synthetic materials such as zeolites or more costly and sophisticated technologies such as membrane separation [27].

On the other hand, the presence of sodium and potassium can form low melting point eutectics in the gasification bed, which is also a matter of concern [28]. These metals can be removed by chemical pretreatments of glycerin: for instance, Carmona *et al.* [29] have recently studied the elimination of sodium by ion exchange processes on a strong acid resin. Our research group is also investigating the removal of Na and K by dehydration of glycerin, which results in the precipitation of their respective sulphates.

The higher heating value of the glycerin was 3300 kcal· kg^{-1}, which is lower than that of pure glycerin [30], as it can be expected due to its content in water and other impurities.

In Figure 2 the weight loss against temperature (TG) and its derivative (DTG) have been plotted. As it can be inferred, glycerin thermal degradation occurs in several different stages. This decomposition profile can be associated with the chemical characteristics of glycerin: first, there is a slight weight loss up to 115 °C, which becomes more marked in the range 115–350 °C, when most of the glycerin has been pyrolyzed. At temperatures higher than 350 °C, the TG curve only shows a residual mass proportion equal to 2%; which is similar to the ash content of the material. The DTG curve shows two peaks centered at 135 °C and 295 °C, being the latter much wider, in accordance to a more persistent weight loss. The first decomposition stage can be associated with the release of water (glycerin is hygroscopic), as well as some low-temperature volatiles, such as methanol, the co-reactant in the transesterification reaction [31]. The second and larger decomposition stage can be associated the degradation of impurities, such as fatty acid methyl esters as well as residues from previous degradation reactions [32]. The thermal instability of glycerin has been previously observed by other authors, who improved this property by blending glycerin with different plasticizers [33].

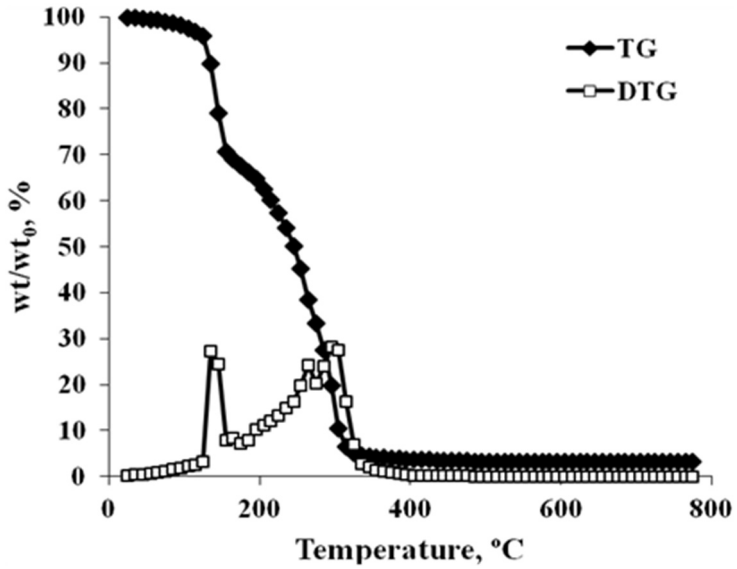

Figure 2. Weight loss against temperature (TG) and its derivative (DTG) profiles of glycerin's thermal decomposition.

3.2. Steam Gasification of Glycerin

3.2.1. Influence of Water/Glycerin Inlet Rate

The effect of water/glycerin inlet rate was studied for all temperatures and water/glycerin ratios. However, as the tendencies found in all cases were similar, and for the sake of brevity, only the mixture of water/glycerin (9/1) and the temperature of 900 °C is presented here. Figure 3 shows the evolution of the concentration of the produced gases for this experimental series.

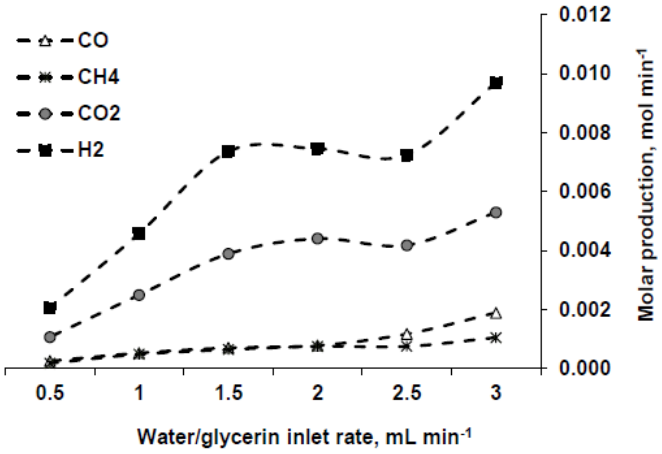

Figure 3. Evolution of gases with inlet flow rate. Water/glycerin ratio: 9/1. Temperature: 900 °C.

From the experimental data, the values of H_2 molar fraction, highest heating value of the gas (HHV, kJ· N· m^{-3}), derived power (kJ· min^{-1}), and energy (kJ) per mL of glycerin, were calculated and are given in Table 2. Also, from the data of power and flow rate, the energy obtained per mL of water/glycerin mixture was obtained:

$$\text{Power (kJ/min)} \cdot \frac{1}{\text{Flow rate (mL/min)}} = \text{Energy per mL of mixture (kJ/mL)} \quad (1)$$

From this value and considering the water/biomass ratio, the parameter "energy per mL of glycerin" can be calculated, as:

$$\text{Energy per mL of glycerin} = \frac{\text{Energy per mL of mixture (kJ/mL of mixture)}}{\text{Ratio (mL of mixture/mL of glycerin)}} \quad (2)$$

Table 2. Characteristic parameters of glycerin steam gasification. Effect of water/glycerin flow rate. Water/glycerin ratio (9/1); Temperature 900 °C; HHV: highest heating value.

Flow rate (g· min^{-1})	H_2 molar fraction (%)	HHV, kJ· Nm^{-3}	Power, kJ· min^{-1}	Energy per mL of glycerin, kJ· mL^{-1}
0.5	67.4	9332.8	0.6	12.5
1.0	63.4	9119.1	1.2	11.6
1.5	60.9	8888.2	2.1	13.7
2.0	59.5	8694.7	2.8	13.8
2.5	58.9	8720.6	3.8	15.0
3.0	59.8	8992.2	4.7	15.7

From Figure 3, it can be seen that as the inlet flow rate increases, there is an increase in the production of all the gases (this effect is not seen in the 2.0–2.5 range). Therefore, the power also gets greater. Regarding hydrogen, in general, its molar fraction decreases as the flow rate increases, being this effect more marked for lower rates (see Table 2). The slight decrease on the HHV is related to the lower proportion of hydrogen.

It is interesting to highlight that the molar fraction of CO_2 as well as that of CH_4 exhibited greater values for higher inlet flow rates. The reactions involved in hydrogen production by steam reforming of glycerin ($C_3H_8O_3$) can be described by Equations (3)–(8):

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \quad (3)$$

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \quad (4)$$

$$C + H_2O \rightarrow CO + H_2 \quad (5)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (6)$$

$$2C + 2H_2O \leftrightarrow CO_2 + CH_4 \quad (7)$$

$$C + CO_2 \leftrightarrow CO \quad (8)$$

All the reactions are favored by low pressure, so the process is usually carried out at atmospheric pressure. If we take into account the abovementioned chemical equilibria, we could attribute the results obtained in this series to the participation of the methanation reaction (Equation (7)), as well as the displacement of the water gas shift reaction towards the production of CO_2 (Equation (6)).

3.2.2. Influence of Temperature

The molar production of the gases analyzed during the glycerin steam gasification processes was investigated under different temperature conditions (600–900 °C). Again, the experiments were made for all the possible experimental conditions of inlet flow rate and water/glycerin ratio. However, in order to avoid excessive graphical information and because the effect was found to be similar for all cases, we present in Figure 4 the results corresponding to an inlet flow rate of 3 mL min^{-1} and a water/glycerin ratio of 9/1.

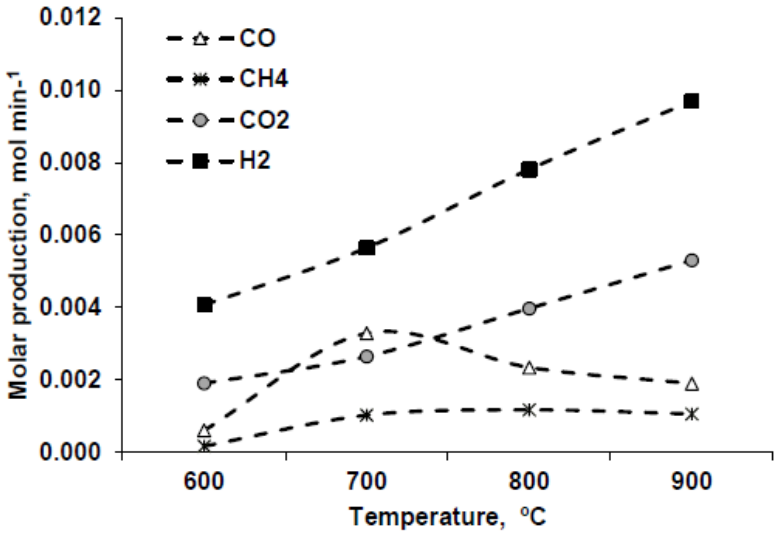

Figure 4. Evolution of gases with temperature. Water/glycerin ratio: 9/1. Flow rate: 3 mL min^{-1}.

From the experimental data, we calculated the previously described characteristic parameters, which are listed in Table 3. From the gas profiles collected in Figure 4, as well as Table 3, one can infer several conclusions; firstly, the molar production of H_2 and CO_2 shows a gradual increase as the temperature gets greater. Also, the evolution of CO shows a defined increase in the 600–700 °C temperature range but then decreases slightly for higher temperatures. CH_4 presents the same tendency than CO, although the changes are very slight. Regarding the molar fraction of hydrogen (Table 3), it is improved at 900 °C as well as the corresponding power. However, the reduction of CH_4 and CO cause a decrease on the heating value of the gas.

Table 3. Characteristic parameters from glycerin steam gasification. Effect of temperature. Water/glycerin ratio (9/1). Flow rate 3 mL· min^{-1}.

Temperature, °C	H_2 molar fraction (%)	HHV, kJ· Nm^{-3}	Power, kJ· min^{-1}	Energy per mL of glycerin, kJ· mL^{-1}
600	51.3	11023.5	5.4	12.3
700	42.8	9637.0	3.8	8.6
800	47.7	9243.1	4.6	11.1
900	57.5	11023.5	5.4	12.3

The literatures show abundant studies on the effect of temperature during steam gasification of biomass [21,22,34]. Changes in this variable within relatively narrow limits can produce significant shifts of the equilibrium composition towards either the starting materials or the end products [35]. In general, an increase in hydrogen production is always found as temperature is raised, which is mainly attributed to the participation of water gas reaction (Equation (5)). The water gas equilibrium shift (Equation (6)) might also be present; in this case, the decrease in CO would support this hypothesis.

3.2.3. Influence of Water/Glycerin Ratio

In this experimental series, the water/glycerin ratio was studied in the range 6/1, 9/1, 12/1, under all the experimental combinations of temperature and inlet flow rate. Figure 5 shows the results corresponding to a temperature of 900 °C, and an inlet flow rate of 3 mL min^{-1}. From the experimental data, we calculated the characteristic parameters previously described for this series, which are listed in Table 4.

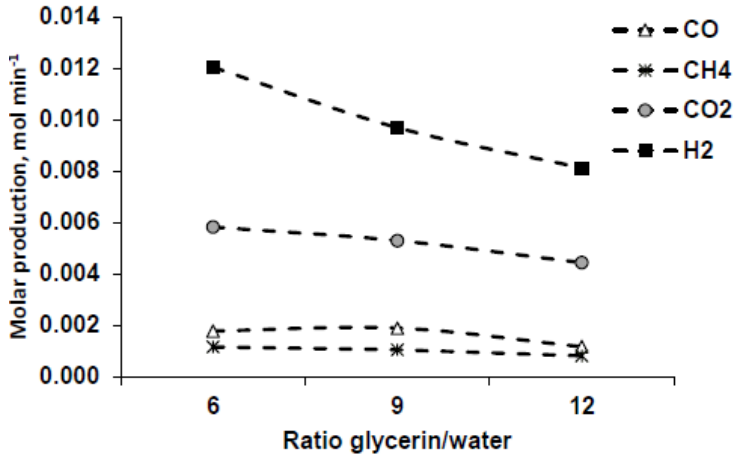

Figure 5. Evolution of gases with water/glycerin ratio. Temperature: 900 °C. Flow rate: 3 mL· min^{-1}.

Table 4. Characteristic parameters from glycerin steam gasification. Effect of water/glycerin ratio. Flow rate 3 mL· min^{-1}. Temperature 900 °C.

Water/glycerin ratio	H_2 molar fraction (%)	HHV, kJ· Nm^{-3}	Power, kJ· min^{-1}	Energy per mL of glycerin, kJ· mL^{-1}
6	56.5	8832,1	4,6	11,2
9	59.8	8992,2	4,6	15,7
12	62.1	8918,0	3,4	20,6

From the analysis of the evolution of gas production for different water/glycerin ratios, under all the conditions analyzed, the following tendencies are inferred: in the first place, there is an increase

in the total production of gases as the proportion of glycerin in the inlet mixture is raised, and on the hydrogen produced per mL of glycerin fed.

This tendency can be related to the fact that an excess in water produces the displacement of Equation (3) towards the products and is consistent with other works which obtained the highest quantity of hydrogen with excess water at all temperatures [13]. Some authors [18] have obtained a cut point temperature showing a decrease in H_2 production for higher water/glycerin ratios. However, in our case, the hydrogen production was favoured with this parameter throughout the whole range studied. It is also noticeable that this effect is more marked at greater temperatures, which is consistent with the endothermicity of equilibrium in Equation (3).

Finally, it is outstanding that the parameter "energy per mL of glycerin" does not follow the trend of the power, as it happened for Tables 2 and 3. While less glycerin dilution causes enhanced gasification, the consideration of the amount of glycerin that is really used in the process can offer a more realistic identification of optimal conditions, if, for example, the aim is to use a lower quantity of raw material.

From the results obtained in this work it can be stated that steam gasification of glycerin can yield a gas with an energy content close to 10 MJ/Nm^3. The literature shows that this value is similar or higher [23,36] than that provided by previous studies on the steam gasification of biomass sources. Taking into account that biomass feedstock needs previous grinding and drying conditioning processing, the interest of the present work can be highlighted, since the glycerin here is used just as it is generated in the biodiesel production process.

On the other hand, the authors are concerned in relation to the energy consumption of the process, and, in this frame, future works will be devoted to study the possibility of installing a heat interchanger at the reactor exit, and thus take advantage of the fumes' heat, which would be used to provide part of the energy needed to produce steam.

4. Conclusions

In this work, the glycerin generated during a biodiesel manufacturing process was used as a feedstock for hydrogen production, in order to valorize this byproduct, which, due to its low purity, cannot be used for the traditional manufacture of other materials. Different variables influencing the process were studied (temperature, water/glycerin ratio and inlet flow rate) in order to optimize the process.

The results obtained allow us to obtain the following conclusions:

(1) Increasing the inlet mixture flow rate is beneficial in order to produce a greater amount of gas and higher power, although it is detrimental if the final goal is to obtain a hydrogen-rich gas.
(2) The addition of water to crude glycerine can be interesting because it provides a greater glycerin reforming. In addition, it moves the equilibria water gas and water gas shift towards the production of hydrogen.
(3) Using higher temperatures is interesting for providing a greater fraction of hydrogen, although it also involves a decrease in the heating value of the gas.
(4) Further research will be devoted to improve the system energy efficiency by studying the incorporation of a heat recovery system and thus taking advantage of the physical exergy of the gas. Also, further studies will address pretreatments of the raw material as well as treatments of the gases in order to mitigate this environmental problem.

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Conflicts of Interest: The authors declare no conflict of interest.

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