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Glycerol Steam Reforming in a Pilot Plant: Effect of Temperature and Catalyst Load

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Featured Application: Glycerol steam reforming was optimized in a pilot plant, at a semi-industrial scale, to offer useful results for the real implementation of this technology at industrial level.

Abstract: One of the main environmental problems is the use of oil for fuel and plastic production, implying the increase in pollutants that might contribute to the greenhouse gas effect, among others. Thus, the use of vegetable oils to produce biodiesel can be interesting, as it is biodegradable and less pollutant compared to diesel fuels, presenting higher flash and combustion points. Moreover, biodiesel production could take part in a biorefinery concept, to produce products such as biolubricants and obtain interesting byproducts that can be reused (such as methanol) or upgraded for energy or pharmaceutical purposes (like glycerol). Consequently, the valorization of these byproducts could contribute to the higher energy efficiency of the process, improving the atom economy. The aim of this work was to assess the effect of the temperature and the amount of catalyst on glycerol steam reforming to produce hydrogen at a semi-industrial level, regarding some aspects like gas production, hydrogen mole ratio and power, using a Ni-based catalyst. In conclusion, the best results found in this experiment, allowing a plant to work continuously for 9 h, were obtained with the following conditions: S/C ratio: 0.7; inlet flow: 40 mL/min; temperature: 850 °C; La_2O_3 and NiO percentage: 5 and 12%, respectively.

Keywords: glycerin; Ni-based catalyst; lanthanum; semi-industrial scale; hydrogen production; biorefinery

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1. Introduction

Global energy systems are dominated by fossil fuels, which currently represent around 85% of the total energy supply, whereas they will represent 90% of the total supply by 2030. Oil is the main energy source (34%), followed by coal (28%). Almost two-thirds of the increase in the coal supply between 2000 and 2030 will come from Asia. According to future trends, natural gas will represent a quarter of the total energy supply in 2030, on account of an increase in electricity generation [1]. Another environmental problem is oil consumption due to vehicles, which represents a considerable amount of evolved gases, contributing to the greenhouse effect. Apart from these factors, continuous changes in oil prices, as well as its questionable future availability, have contributed to the development of vehicles working with electric power or whose fuel is methanol or ethanol (or other natural sources) that can contribute to environmental protection, such as the use of vegetable oils to produce biodiesel, which is a perfect replacement for diesel as it presents many advantages such as biodegradability, higher lubrication efficiency and similar yields and efficiency in combustion engines, where it can be directly used if it complies with some quality standards [2].

In that sense, many vegetable oils, including safflower, rapeseed, cardoon or waste cooking oil, among others, have been successfully used for biodiesel production, with suitable properties according to UNE-EN 14214 standard [3] in most cases, except for its low oxidative stability, which can be easily improved by an antioxidant addition such as tert-Butylhydroquinone (TBHQ) [4–6], butylated hydroxy anisole (BHA) [4] or propyl gallate (PG) [7]. Apart from that, genetically modified crops, with lower amounts of linoleic and linolenic acid (which cause a considerable decrease in oxidative stability), could be another interesting alternative to comply with the standard [8]. In any case, many studies have been carried out to optimize the effectiveness of biodiesel production and performance in diesel engines to make this process as competitive as possible, with the subsequent sustainable development [9]. This way, the role of biodiesel, especially when it comes to tribology [10] or pollutant emissions and efficiency [11], has been studied. Consequently, biodiesel production is going to play an important role in the short- and long-term, as observed in Figure 1 for global biodiesel production in million liters. This way, biodiesel production will triple in 15 years, pointing out the global concern about the replacement of petrol-based fuels for other sustainable alternatives. This could be due to the fact that many governments or international agencies (for instance, the so-called Sustainable Development Goals, SDGs [12]) are encouraging the use of these kinds of fuels in order to avoid environmental and sustainability problems.

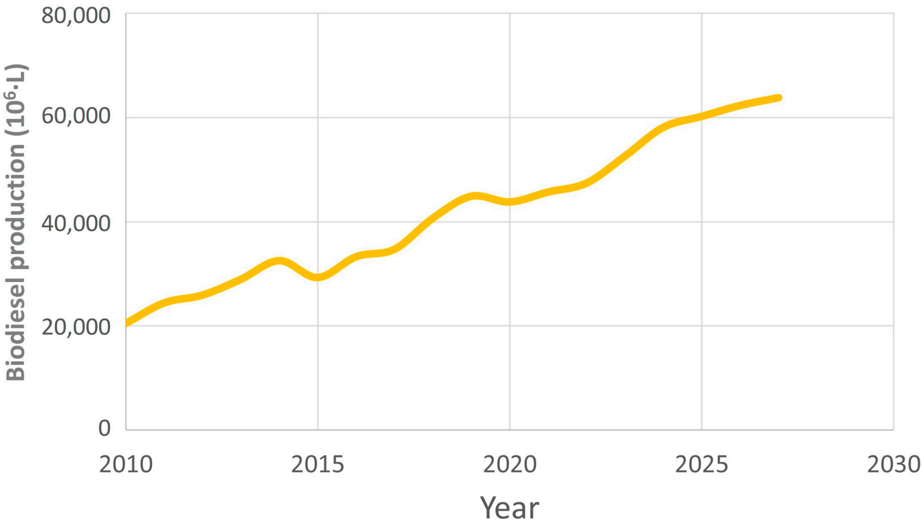


Figure 1. Worldwide biodiesel production from 2010 and forecast for 2027. Source: [13].

As commented above, biodiesel presents many advantages compared to conventional fuels, such as higher biodegradability (it comes from natural sources such as vegetable oils, and the chemical process produces similar molecular structures which are easily processed by microorganisms), zero-net CO_2 emissions, high flash and combustion points, the possibility of a sustainable economic growth in developing areas (as many oilseed crops can be easily adapted to extreme climate conditions such as drought or heat), etc. Biodiesel is mainly obtained from vegetable oils through transesterification with methanol, and triglycerides react with this alcohol to obtain fatty acid methyl esters (FAMEs) and glycerol, as observed in Figure 2. This global reaction takes place in three consecutive and reversible stages where one mol of triglyceride is converted to diglyceride, monoglyceride and glycerol, respectively, obtaining one mol of fatty acid methyl ester in each reaction. The use of catalysts (both homogeneous and heterogeneous [14] or acid and alkaline [15], which present their own advantages and challenges), for instance, sodium methylate, is required to make the process more efficient [16,17]. Once fatty acid methyl esters (that is, biodiesel) are obtained, the purification process usually requires glycerol removal through decantation and washing treatments if homogeneous catalysts are used. Finally, a drying stage takes place, and the final product is obtained (normally biodiesel with at least 96.5% FAME content).

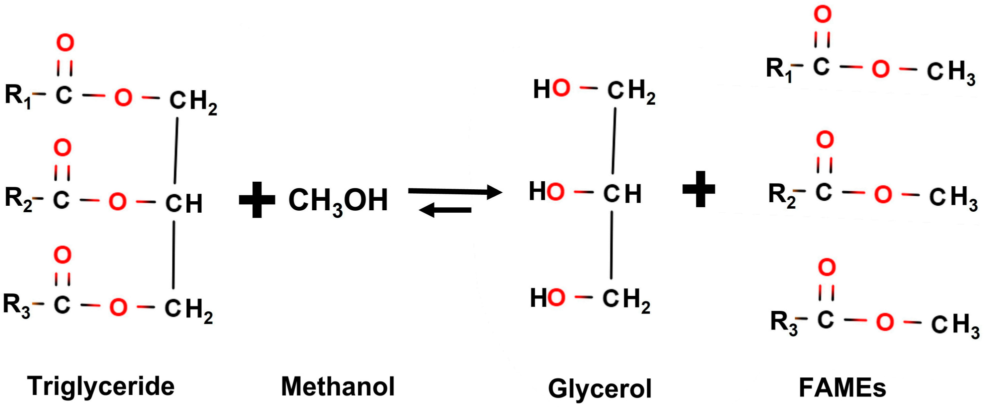
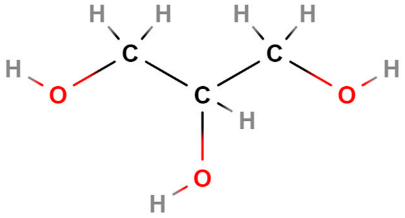


Figure 2. Transesterification of triglycerides with methanol to produce fatty acid methyl esters (FAMEs) and glycerol.

In that sense, the latest trends in biodiesel production are devoted to innovative ways to improve the yield and efficiency of transesterification, mainly focused on machine-learning technology applied to biodiesel research [18] or the use of new dispositions such as bionic flow-induced peristaltic reactors [19].

As can be inferred from this figure, glycerol is obtained as a byproduct in transesterification, representing approximately 10% of biodiesel production. This process can present a high atom economy or efficiency depending on conversion and the use of byproducts [20,21]. Traditionally, glycerol was obtained through several processes such as soap making or fatty alcohol, fatty acid methyl ester and fatty acid production, through synthetic methods or other methods such as microbial fermentation [22,23]. A summary of the main properties of glycerol can be found in Table 1.

Table 1. Glycerol properties and characteristics.

Characteristics	Result
Nomenclature and synonyms	1,2,3-Propanetriol, glycerol, glycerine
Molecular formula	$C_3H_8O_3$
Molecular structure	
Molecular weight (g/mol)	92.09
Viscosity [1] at 20 °C (Poise)	15.0
Density [1], g/cm^3	1.261
Melting point [1], °C	18.2
Boiling point [1], °C	290
Others	Liquid at room temperature, colorless and hygroscopic

[1] Anhydrous and pure.

Thus, glycerol is not toxic nor irritant, it is soluble in water and alcohols and stable at low pressure values and room temperature. Depending on the degree of purity of glycerol, it can be an interesting energy source (such as reforming or pyrolysis for energy [24]) or the starting point for the synthesis of other products such as C3 compounds (such as acrolein, propanediols or carboxylic acids) obtained from routes such as hydrogenation, oxidation or esterification or activated carbons through pyrolysis [21].

Considering the future trend about biodiesel production, it is not surprising that glycerol generation has considerably increased in recent years, which can imply an opportunity for its reuse in industrial processes. A feasible possibility is the use of glycerol as an energy source to obtain synthesis gas (a mixture of hydrogen and carbon monoxide at different ratios) [25]. This synthesis gas, if it is suitably treated, can produce fuel in an environmentally friendly process, as glycerol is obtained from chemical routes by using renewable raw materials [26].

Glycerol steam reforming (GSR) is one of the most typical methods to produce hydrogen in industry, as it is efficient and profitable at an industrial level [21,27]. This technique does not require excessively high pressures and higher hydrogen percentages are produced at high temperatures. Steam reforming consists of the conversion of hydrocarbons to hydrogen or synthesis gas, through a treatment at high temperatures with an oxidizing agent and a catalyst. Thus, glycerol reacts with steam to produce H_2, CO_2 and CO, in a highly endothermal process (ΔH^0 = 123 kJ/mol) represented in Equation (1), which is a combination of glycerol decomposition (ΔH^0 = 251 kJ/mol, Equation (2)) and water–gas shift reaction (WGS, $\Delta H^0 = -41$ kJ/mol, Equation (3)) [28]:

$$C_3H_8O_3 + 3H_2O \leftrightarrow 3CO_2 + 7H_2 \tag{1}$$

$$C_3H_8O_3 \leftrightarrow 3CO + 4H_2 \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3}$$

Consequently, the H_2 and CO ratio depends on the reaction conditions, including the kind of catalyst used, as CO can be converted in the WGS reaction to produce carbon dioxide. Also, other secondary reactions can take place, such as methane generation through exothermal reactions like those included in Equations (4) and (5):

$$CO + H_2 \leftrightarrow CH_4 + H_2O \tag{4}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \tag{5}$$

As a consequence, the presence of these secondary reactions explains the difficulty in reaching 100% H_2 production during glycerol steam reforming. To increase H_2 production, through GSR, a suitable catalyst selection should be carried out to promote the cleavage of C-C, O-H and C-H bonds in the oxygenated hydrocarbon reactant and facilitate the WGS to remove adsorbed CO [28]. Other factors with a strong influence on glycerol steam reforming are the following:

- Feed flow: Overfeeding could reduce the yield of conversion, whereas the contrary could imply a poor gas production. The optimum flow maximizes the energy efficiency of the process.
- Temperature: This is one of the key factors, as it affects the yield of the process and gas composition. In general, high temperature values correspond to a higher gas production and higher H_2 percentage in the outlet gas.
- Steam to carbon (S/C) ratio: As it increases, the gas produced is richer in hydrogen, whereas the gas flow decreases.
- Catalyst use: The use of catalysts (normally transition metals belonging to group VIIIB) is essential in this kind of process to obtain high conversion values. Also, the use of a support (such as Al_2O_3, ZrO_2, SiO_2 or TiO_2) can promote conversion, and the particle size can play an important role in favoring mass transfer and contact among reagents within the reactor. Also, the use of additives or promoters can improve the activity or service life by avoiding problems such as poisoning or carbon deposition [29,30].

Hydrogen production from renewable biomass has gained interest in recent years in the scientific community, international agencies and governments, promoting its implementation through international green chemistry policies [31]. Thus, biomass and glycerol reforming has been studied through gasification to improve glycerol conversion to hydrogen depending on the temperature, pressure and steam to carbon ratio, obtaining favorable results at high temperatures and low pressures.

This study determined that the optimum condition to produce hydrogen was between 700 and 750 °C, at 0.1 MPa, concluding that glycerol and biomass steam reforming is feasible at practical operating temperatures, typical at an industrial level [32]. Similar studies tested glycerol valorization obtained from biodiesel synthesis to obtain a gas rich in H_2 through a sequential process where the first step consisted of glycerol purification to reduce impurities and, afterward, it underwent steam reforming. The theoretical and experimental studies showed that the temperature and glycerol concentration had a considerable influence on the thermodynamics, with an optimum point at 700 °C and a carbon conversion to gas of around 95%, with a gas composition of 67% H_2, 22% CO_2, 11% CO and 1% CH_4 [33]. Equally, hydrogen production through ethanol and glycerol steam reforming was carried out with Ir, Co and Ni catalysts supported on CeO_2, finding that the former (Ir/CeO_2) provided a full conversion of glycerol at 400 °C, whereas the total conversion for Co/CeO_2 and Ni/CeO_2 took place at 425 and 450 °C, respectively [34]. Another study pointed out the role of promoters such as Mg, Zr, Ce or La in Ni-Al_2O_3 catalysts, increasing the hydrogen selectivity during the process and obtaining the full conversion of glycerol at 600 °C (at atmospheric pressure) and a space velocity of 2.5 h^{-1}. Ni, Ir and Co were effective for CeO_2, with a total conversion of glycerol and 90% selectivity for hydrogen at 550 °C [35]. For additional hydrogen purification, membrane reactors can be used to increase the hydrogen percentage in the final gas, with Pd-Ag membranes being one of the most popular alternatives for this purpose [23].

Thus, glycerol turns out to be a good candidate to be a renewable source for hydrogen production. Its conversion to hydrogen (depending on the use of purification technologies such as membrane reactors or pressure swing adsorption [36,37]) or synthesis gas can be reached through reforming processes such as steam reforming (SO), partial oxidation or gasification (PO), autothermal reforming (ATR), aqueous-phase reforming (APR) and steam reforming with supercritical water (SCW). These chemical routes depend on the properties of the catalyst used, generally Ni, Pt and Ru (which favors hydrogen production), as well as the temperature, pressure and reagent ratio. Hence, these factors should be considered when the H_2 yield is evaluated for each process [23]. However, not many studies at a semi-industrial scale or using pilot plants have been observed, as many works show innovative trends that are interesting but only focused on a laboratory scale. Specifically, as observed in Table 2, there are two main trends when it comes to steam reforming applied to glycerol (mainly obtained from biodiesel):

- Firstly, the possible implementation of GSR in a biorefinery context based on biodiesel production was mainly assessed through simulations of integrated processes, proving that hydrogen production could contribute to the total yield found in these systems. In that sense, more works focused on semi-industrial or industrial levels could complement these works to prove the efficiency of GSR in real contexts.
- Secondly, the development of new catalysts, including promoters such as La (included in this work), Ce or Mg, to improve the duration of their activity. Also, different kinds of supports, including nanocatalysts, have been considered to make the chemical conditions more efficient and stable over time. Thus, it is essential to improve the efficiency of GSR at an industrial level, to compete with traditional technologies.

Considering the above, the aim of this work was to carry out the steam reforming of glycerol in an experimental facility at a semi-industrial scale, trying to assess the effect of the temperature and catalyst load to obtain suitable gasification powers, paying attention to the feasibility of the Ni-based catalyst applied to this facility. Specifically, the outlet gas flow was optimized, as well as the hydrogen mole fraction and power. On the other hand, the selection of the best temperature and catalyst percentage to obtain the best catalytic performance was another specific objective, with different NiO concentrations used for that purpose and comparing them with non-catalytic tests. Finally, considering these comparisons, our aim was to establish the optimum operating conditions for the semi-industrial plant according to the gas flow, hydrogen mole ratio, lower calorific value and power. Thus, the real implementation of glycerol steam reforming at a semi-industrial scale is proposed, with useful information about the feasibility of this process.

Table 2. Recent works related to glycerol steam reforming.

Description	Details	Reference
Glycerol steam reforming in an integrated waste cooking oil biodiesel production	A simulation of an integrated process plant was carried out in order to improve the efficiency of the system by maximizing hydrogen production in GSR, with a total yield of 13% and a total yield for biodiesel production of 92.5%	[38]
Integrated hydrogen production from byproducts of cottonseed biodiesel	In a biorefinery or circular economy context, a simulation of an integrated biodiesel and hydrogen production was carried out, obtaining high-quality biodiesel and the following GSR conditions for a high H_2 production: W/G = 4.5, T = 750 °C.	[39]
Use of Ni/CeO_2 catalysts for low-temperature glycerol steam reforming	CeO_2 nanosphere-supported Ni catalysts were prepared through wet impregnation, for GSR. Direct H_2 reduction without calcination was preferred, as high glycerol conversion (95%) and catalytic stability (35 h) were achieved.	[40]
$LaAlO_3$ as a catalyst for glycerol steam reforming, among other processes	Different catalysts were studied, adding Ni, Ni-Ce or Ni-La, among others, observing that the latter showed a high coke resistance.	[41]
Catalytic steam reforming of glycerol over LDH-derived Ni-Al nanosheet to obtain stable hydrogen production	High glycerol conversions (exceeding 83%) were achieved, with a high H_2 yield (85%) and a long catalyst stability (1000 min).	[42]
Effect of noble metals on Ce_2O_3-Al_2O_3 catalysts for hydrogen production via glycerol steam reforming	Different metals like Ir, Pt and Pd were studied, proving that Pt/CeAl catalyst was more selective toward H_2 production, whereas Ir/CeAl tended toward sintering due to the weak metal–support interaction	[43]

2. Materials and Methods

2.1. Glycerol Pretreatment

Glycerol was obtained from a biodiesel plant (Green Fuel Extremadura), which produces approximately 1.1×10^8 kg per year, with the subsequent generation of glycerol (around 1.1×10^7 kg per year). Obviously, this glycerol is not pure and therefore some properties are different compared to pure glycerol, as it presents some impurities that might modify its behavior in different uses. Therefore, a characterization of crude glycerol was carried out, including proximate, ultimate analysis and high heating value determination. The main results are included in Table 3. As can be inferred, it was proven that glycerol presented some impurities that could interfere with a suitable performance of this product during steam reforming. For instance, S content could imply hydrogen sulfide generation during steam reforming, which could be a considerable problem for catalyst deactivation through poisoning. Consequently, to purify glycerol to remove impurities, it was heated at 120–130 °C for 120 h, to reduce moisture and provoke precipitation of salts, which are filtered and removed. Thus, the impurities of glycerol were considerably reduced, allowing its use in further treatments during steam reforming.

Table 3. Crude glycerol: proximate and ultimate analysis.

Proximate Analysis, %	Result
Moisture	16.37 (±0.10)
Volatile fraction	75.18 (±0.95)
Fixed carbon	0 (±0)
Ash content	8.99 (±0.10)

Table 3. *Cont.*

Proximate Analysis, %	Result
Ultimate Analysis, %	
C	30.3 (±0.5)
H	8.68 (±0.30)
N	0.016 (±0.001)
S	0.052 (±0.002)
HHV, kcal/kg	
Crude glycerol	3332 (±25)
Dried glycerol	3467 (±33)

2.2. Catalyst Preparation

Regarding the catalyst used (Ni/La-Al_2O_3 catalyst), it required different steps to be produced, like the following:

- γ-Al_2O_3 rings were calcined in an oven at 750 °C for 3 h.
- Afterward, wet impregnation with a $La(NO_3)_3 \cdot 6H_2O$ solution was carried out in order to obtain 5% La_2O_3. The impregnation took place at different steps (to avoid support saturation), followed by drying in a microwave oven (100 W for 15 min), to make sure that the support adsorbed the solution. Then, the impregnated support was calcined at 650 °C for 6 h, obtaining through weight difference, 4.46% of La_2O_3.
- The following step was the impregnation of the calcined support with $Ni(NO_3)_2 \cdot 6H_2O$ to obtain Ni as the active phase in the final catalyst. Ni content was measured by NiO percentage. Ni concentration was varied, adding the corresponding amount of its nitrate to obtain different NiO percentages (12, 16 and 20% *w*/*w*). Equally, three stages of impregnation took place, with the corresponding drying in a microwave oven as in the previous case. After calcination at 500 °C for 4 h once the nitrate was impregnated, the final catalyst was obtained. Once calcined, NiO content was calculated through weight difference, obtaining the corresponding values depending on each experiment.
- Finally, catalyst reduction at 700 °C for 2 h (at a heating rate of 10 °C/min) in 50% H_2/N_2 atmosphere was carried out, obtaining the final catalyst.

As a result, catalyst characterization was similar to previous studies with the same catalysts [44].

2.3. Experimental Setup

Regarding our experimental facility, Figure 3 shows a general outline of the GSR system and its main components.

Some of the main components of this glycerol steam reforming system will be briefly explained. Thus, the aim of the drying system, a steel tank of 35 L, was to dehydrate wet glycerol. The heating jackets (2 units) were used to cover the drying system and heat it at 120–130 °C to remove salts in glycerol. The glycerol–water mixture steel tank had a capacity of 30 L, with the aim of mixing purified glycerol with distilled water (at a specific ratio) to obtain one single homogeneous phase before introducing it in the reactor. The stirrer was designed to mix highly viscous substances, through a stainless-steel anchor. On the other hand, the distiller obtained distilled water from tap water. The peristaltic pump provided the glycerol–water mix to the reactor, at a constant and controlled flow rate. The aim of the basket was to provoke the contact of gas and heated areas to assure a correct gasification and to retain the carbon residue produced during this process. The reactor (a stainless-steel cylinder) was the element where glycerol steam reforming was going to take place, which was covered by an electric oven covering the central part of the reactor to obtain around 700–800 °C within the reactor. The temperature was controlled by a PID controller, measuring the inner temperature through a thermocouple. Finally, once the outlet gas was produced in the reactor, it was cooled down through a heat exchanger connected to a chiller, obtaining condensate liquids in the corresponding tank. The gas flow was measured by a float-type flowmeter, and dataloggers were used to measure the temperature at different points of the system. The outlet gas composition (mainly H_2, CO, CO_2, CH_4) was determined through gas chromatography, using a Varian 3900 chromatograph coupled to a thermal conductivity detector, with a packed column (Supelco Carboxen 1000 60/80). The carrier gas was argon and synthetic air.

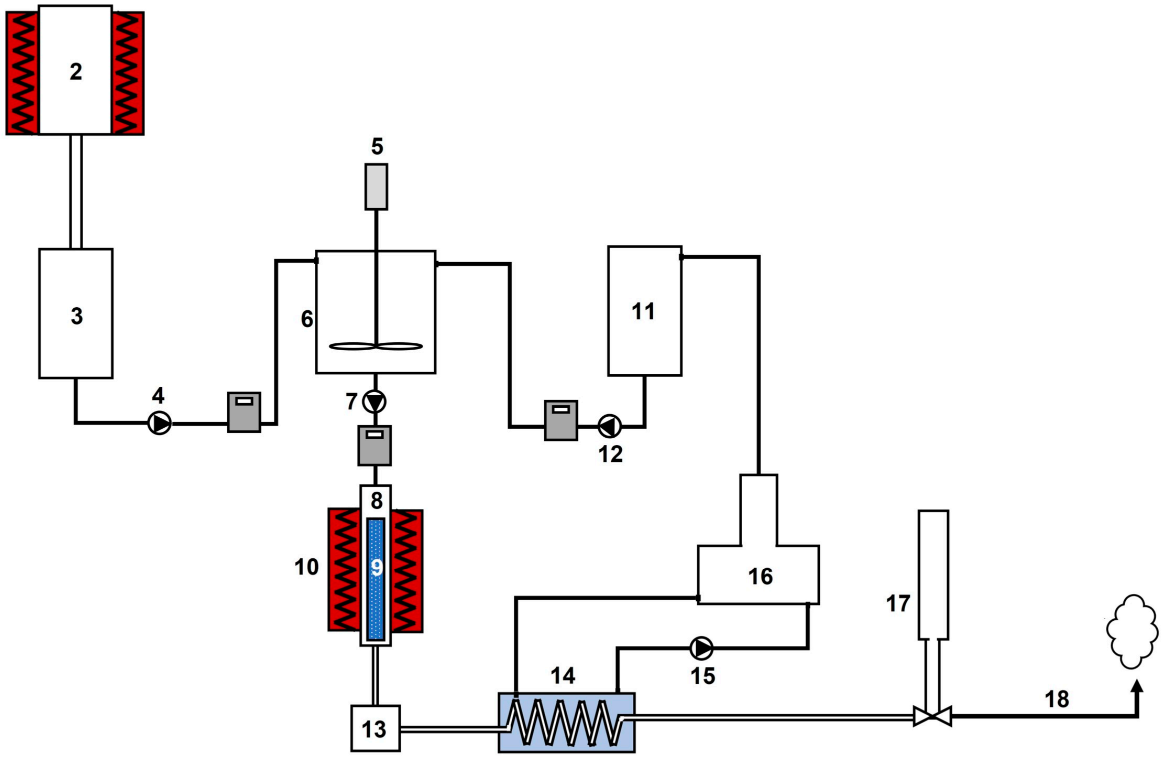


Figure 3. Experimental arrangement, including: (1) heating jacket; (2) glycerol drying system; (3) dried glycerol tank; (4) peristaltic pump; (5) stirrer; (6) glycerol–water mixture tank; (7) peristaltic pump; (8) reactor; (9) basket; (10) oven; (11) distilled water tank; (12) peristaltic pump; (13) condensate tank; (14) gas heat exchanger; (15) peristaltic pump; (16) distiller; (17) flowmeter; (18) exhaust fumes.

In this study, the introduction of certain improvements in the steam reforming system, compared to previous studies, was carried out. The main upgrades are included in Table 4:

Table 4. Improvements in glycerol steam reforming system carried out in this experiment.

Improvement	Details
Installation of an electrical board	A sensor connected to this electrical board was used to control water level in heat exchanger
Insulation joints in reactor	In order to avoid gas leakage in steam reforming reactor, two insulation joints were installed in the reactor, one for each cover. A leak test was carried out to check the effectiveness of these joints
Leak point detection and repair	The system was checked to avoid leak points. The exhaust tube presented leak points, and it was replaced
Basket maintenance	The basket was cleaned during this experiment to avoid rust, by using a polishing machine
Basket modifications	The reactor was modified, being a cylindrical piece with a constriction at the end of it, which was considered to modify the shape of the basket to be perfectly adapted to the end of the reactor, forcing the gas to pass through the basket containing the catalyst
Peristaltic pump calibration	The pump was perfectly calibrated to make sure that the amount of water required by the system was exact and constant

2.4. Glycerol Steam Reforming Tests

To carry out the experiments, 100 g of catalyst (with the suitable Ni and La proportion for each experiment) was added to the basket, closing it perfectly and preparing the corresponding glycerol-distilled water blend, controlling the flow rate to be introduced through the peristaltic pump, previously calibrated. Once the catalyst was activated through a N_2/H_2 flow, the carrier gas was changed to 100% N_2 for 30 min. Then, the oven was set to the corresponding reaction temperature, and once it was reached, the glycerol–water blend was introduced, which was the starting point for glycerol steam reforming. Afterward, different gas samples were taken through Tedlar gas sampling bags to carry out the corresponding gas chromatography, measuring the gas flow once each sample was taken. This way, according to previous experiments, fixed conditions were established for these experiments, such as water/glycerol ratio (W/G) and flow rate, which were previously optimized. Thus, the temperature (in oven) was varied in these experiments. For non-catalytic studies (with no active catalyst added to Al_2O_3 support), the conditions included in Table 5 were followed, whereas in the case of catalytic studies, both the temperature and catalyst proportion (NiO percentage, whereas La_2O_3 percentage was fixed at 5%) were studied (see Table 5).

Table 5. Set of experiments for this work according to water/glycerol (W/G) ratio, inlet flow, reaction temperature and catalyst concentration for catalytic and non-catalytic studies.

Condition	Non-Catalytic Studies	Catalytic Studies
W/G ratio	0.7	0.7
Flow, mL/min	40	40
Temperature, °C	750–850–950	750–850
Catalyst (NiO) concentration, % [1]	0	12, 16, 20

[1] For all the catalysts produced, La_2O_3 concentration (used as promoter) was fixed at 5%.

Thus, for these experiments, the stabilization time of glycerol steam reforming was determined according to the outlet gas flow and gas composition, to assess the feasibility of this catalyst for its use in an industrial plant and to determine its optimum proportion to provide the best results according to the yield and gas quality. Finally, the service life of the catalysts was determined, carrying out a final test on the catalyst with the best yield and measuring the gas composition until its composition decreased. When the experiments were performed in triplicate, the average value (±standard deviation) and the error bars in the tables and figures, respectively, were included.

2.5. Catalyst Characterization

Once the experiments were carried out for the selected chemical condition and catalysts, a characterization of the latter was carried out, comparing SEM images and S_{BET} area for fresh and used or spent catalyst after 700 min of glycerol steam reforming.

Regarding scanning electron microscopy, the sample was characterized by using a Quanta 3D FEG system (Thermo Fisher Scientific, Waltham, MA, USA), working at 20 kV accelerating voltage.

Concerning the Brunauer–Emmett–Teller surface area, it was determined through nitrogen physisorption at 77 K in a Quantachrome Instruments AS-1 Series unit (Boynton Beach, FL, USA). Before the analysis, the samples underwent vacuum conditions at 230 °C for 24 h.

3. Results and Discussion

3.1. Stabilization Test

Firstly, it is important to point out that, before gas sampling, it is necessary to check the stabilization of glycerol steam reforming under these conditions. This test was carried out at the lowest temperature contemplated in this work, whereas the sampling was similar to the criterion obtained from this experiment, as the stabilization time depends on the temperature (an increase in this parameter implies a decrease in stabilization). The experiment took place for 2 h, and gas samples were taken every 15 min. The results are included in Figure 4.

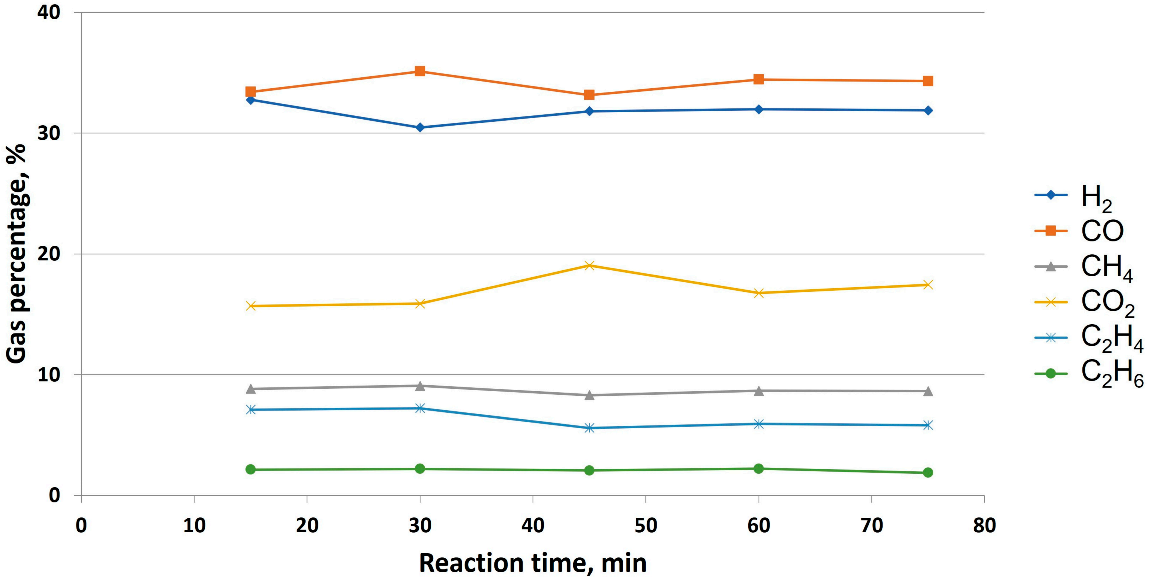


Figure 4. Stabilization test for glycerol steam reforming (reaction conditions: water to glycerol ratio = 0.7; flow = 40 mL/min; T = 750 °C).

As observed, time 0 was the beginning of the reaction once the oven reached 750 °C. Glycerol steam reforming tended to stabilize between 45 and 60 min, as the CO, H_2, C_2H_4 and CO_2 percentages (whose values drastically varied at an initial stage) started to be stable over time. Regarding the non-catalytic tests, gas sampling was carried out once the stabilization time was reached in this experiment, that is, after 60 min of reaction time.

3.2. Non-Catalytic Glycerol Steam Reforming at Different Temperatures

Concerning GSR without the catalyst addition, Figure 5 shows the main results obtained for this experiment at different temperatures, including the gas flow and hydrogen composition in the outlet gas.

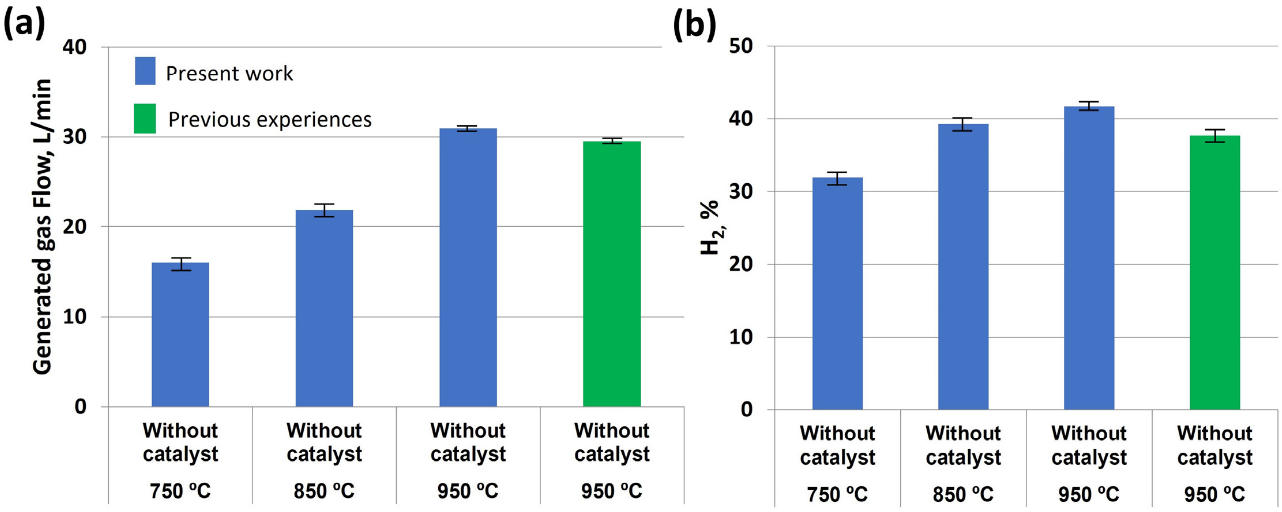


Figure 5. Flow (**a**) and hydrogen percentage (**b**) in outlet gas in glycerol steam reforming without catalyst addition at different temperatures (reaction conditions: water to glycerol ratio = 0.7; inlet flow = 40 mL/min).

As observed in Figure 5a, there was a considerable increase in the gas flow generated with the temperature, from 16.04 to 30.93 L/min at 750 and 950 °C, respectively. Compared with previous experiments at the same chemical conditions, the results obtained in this work at 950 °C were higher, proving that the improvements introduced in the glycerol steam reforming system were effective. Concerning hydrogen production (Figure 5b), its percentage increased with the temperature at the same water/glycerol ratio and feed flow, obtaining slightly higher values compared to previous studies at 950 °C. This could be due to the fact that alumina without a catalyst addition allowed the chemical modification and enrichment in hydrogen. Previous studies did not include any support addition, which provoked a continuous load loss. These hydrogen percentages are in accordance with the literature, where yields ranging from 37 to 99.7% were observed depending on the catalyst used [26]. Regarding the low heating value (LHV) and power, Figure 6 shows the main results obtained. Thus, it can be concluded that, at the same steam/glycerol ratio and inlet flow, higher heating values were obtained at lower temperatures (15,772 kJ/m^{3}N at 750 °C), which could be due to the higher CO and hydrocarbon percentage under these conditions, whereas an increase in the temperature provoked the chemical conversion of hydrocarbons to hydrogen (as observed in Figure 5b) and CO_2, with the latter not contributing to the LHV calculation and therefore decreasing its value.

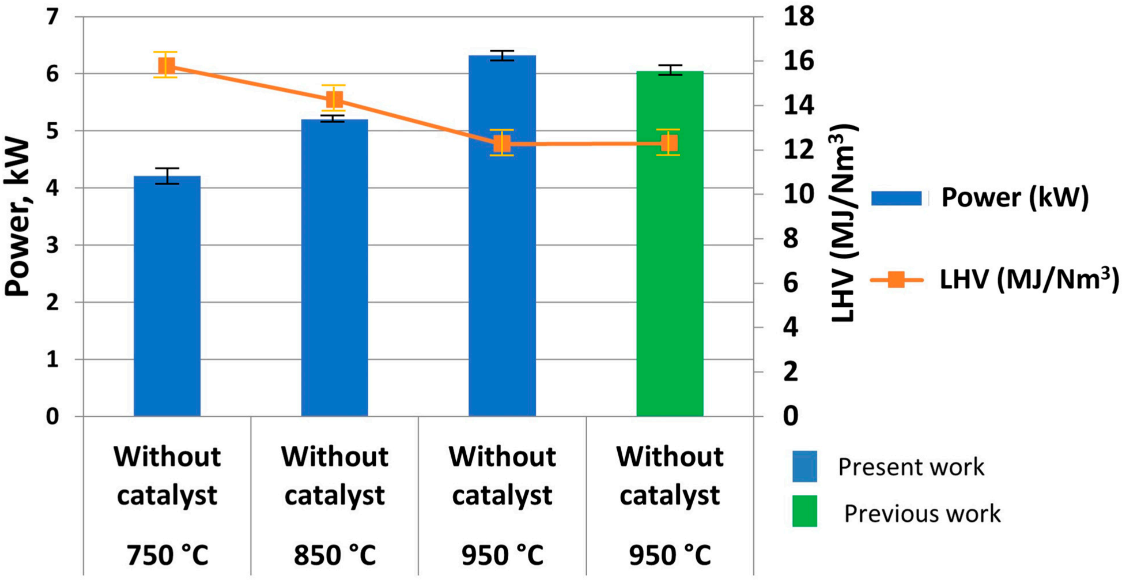


Figure 6. Power and low heating value (LHV) in glycerol steam reforming without catalyst addition (reaction conditions: water to glycerol ratio = 0.7; inlet flow = 40 mL/min).

On the other hand, the power increased with the temperature (from 4216 W at 750 °C to 6325 W at °C) due to its relationship with the outlet gas flow according to Equation (6):

$$\text{Power} = Q_{\text{outletgas}} \times \text{LHV} \tag{6}$$

where $Q_{\text{outlet gas}}$ is the flow of the outlet gas and LHV is the low heating value. Therefore, the influence of the flow gas, which considerably increased with the temperature, as observed in Figure 5a, is higher compared to the LHV (which showed an opposite trend with the temperature). Again, previous studies, where the process was not optimized, offered lower power values compared to the present work, with a 4.43% decrease. This way, it can be concluded that the improvements included in this work implied a better performance when it comes to glycerol steam reforming, as a better outlet gas flow, hydrogen percentage and power values were found compared to equivalent previous studies.

3.3. Catalytic Glycerol Steam Reforming at Different Temperatures and Catalyst Concentrations

In the case of catalytic studies, Table 6 shows the main parameters selected for each experiment, fixing the W/G ratio and inlet flow for all cases and varying the temperature (from 750 to 850 °C) and catalyst concentration (from 12 to 20% NiO).

Table 6. Experiments for catalytic GSR at different temperatures and catalyst concentrations.

W/G Ratio	Inlet Flow, mL/min	Temperature, °C	NiO Concentration, %
0.7	40	750	12
			16
			20
		850	12
			16
			20

For these tests, nitrogen was used as the carrier gas in order to avoid air contact with the catalysts, implying the oxidation and, therefore, deactivation of the active phase. As in the case of non-catalytic experiments, a stabilization test was carried out, with gas sampling at every 15 min, to determine the gas composition and to establish the time at which the outlet gas presented constant composition. This experiment was carried out at the most unfavorable conditions, that is, at 750 °C. As a result, Figure 7 shows the results at different catalyst concentrations (12, 16 and 20% NiO). As can be observed, in the case of 12% NiO (Figure 7a), the reaction time required to stabilize the outlet gas composition was about 70 min (considering the starting point when the carrier gas was disconnected, and the oven reached 750 °C). In the case of 16% NiO (see Figure 7b), some fluctuations were observed, establishing a stabilization time at around 90 min, whereas regarding 20% NiO (Figure 7c), the outlet gas composition was practically constant from 70 min, which was the common sampling time for further analysis. It should be noted that the hydrogen yield was above 30% in all cases, pointing out the effectiveness of the selected catalysts, which was comparable to other Ni-based catalysts found in the literature with hydrogen yields between 32 to 45% [26].

The gas profile obtained was similar to those observed in the literature, where hydrogen was the majority gas, followed by CO and CO_2 and finally, hydrocarbons like methane or ethane were detected at very much lower concentrations [39] for Ni/Al_2O_3 catalysts [30].

When the outlet gas flow and its hydrogen composition were compared at different temperatures and catalyst concentrations, Figure 8 shows the main results, with a considerable improvement in the gas flow and hydrogen yield when the temperature was increased (see Figure 8a), as observed in other studies [45]. However, an increase in the catalyst addition was not effective, obtaining better results with 12% NiO concentration (34.88 kW at 850 °C) compared to 20% NiO (26.55 kW at 850 °C). If these results in Figure 8a referred to the effective amount of catalysts for each catalyst load (that is, per gram of the active phase), the results would be the following: for 12%, 2.91 $L\cdot min^{-1}\cdot g^{-1}$; for 16%, 2.12 $L\cdot min^{-1}\cdot g^{-1}$; and for 20%, 1.32 $L\cdot min^{-1}\cdot g^{-1}$, proving the better efficiency of the catalyst at low concentrations. This fact could be due to a saturation effect when the alumina rings were impregnated, provoking an undesirable active-phase distribution on the support surface. The same effect could have a similar influence on the hydrogen percentage (see Figure 8b), with the best results observed for the lowest NiO concentration (41.35% for 12% NiO at 850 °C, whereas for 20% NiO, 34.42% of hydrogen was obtained). As in the case of non-catalytic tests, there was an increase in the hydrogen purity when the temperature increased.

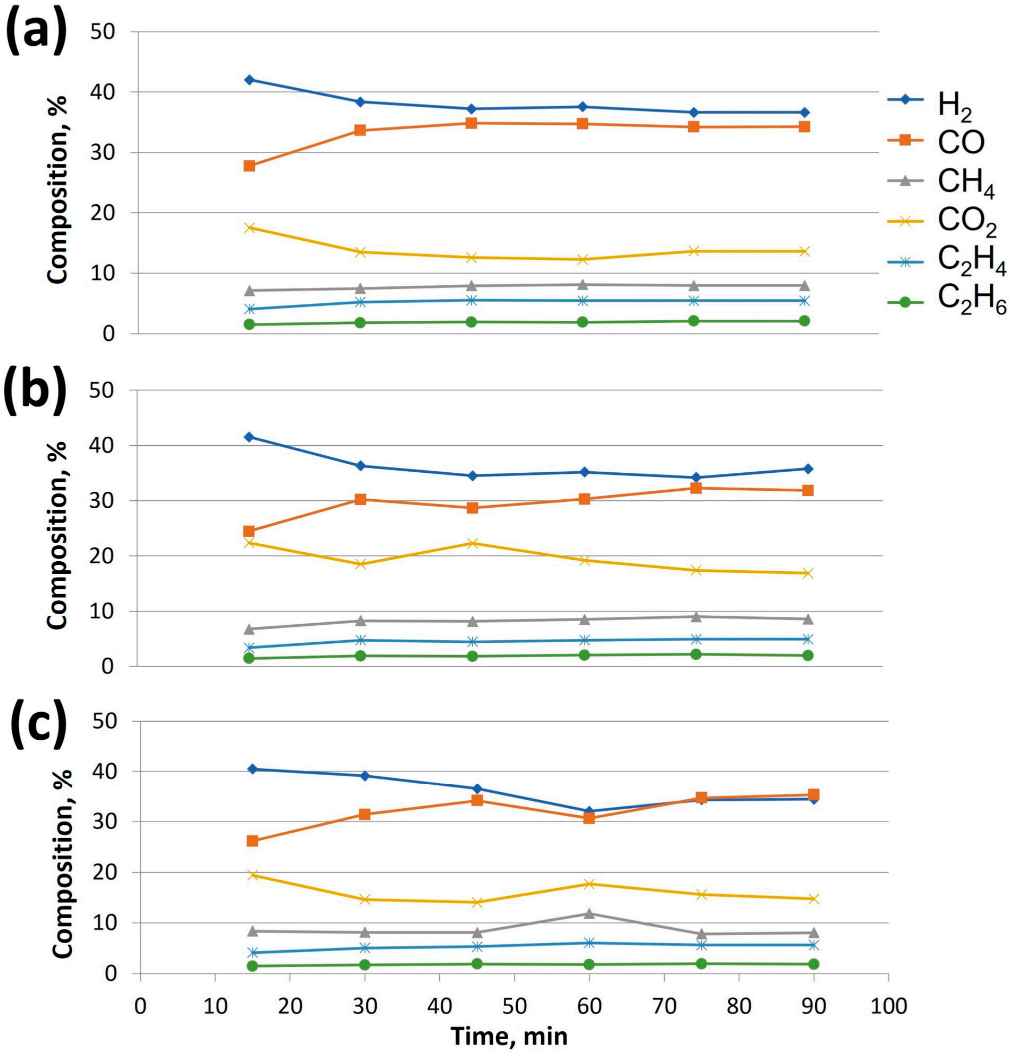


Figure 7. Gas composition over time with different catalyst (NiO) additions: (**a**) 12% (*w*/*w*); (**b**) 16% (*w*/*w*); (**c**) 20% (*w*/*w*). The rest of the operating conditions were common: water to glycerol ratio = 0.7, inlet flow = 40 mL/min, temperature = 750 °C.

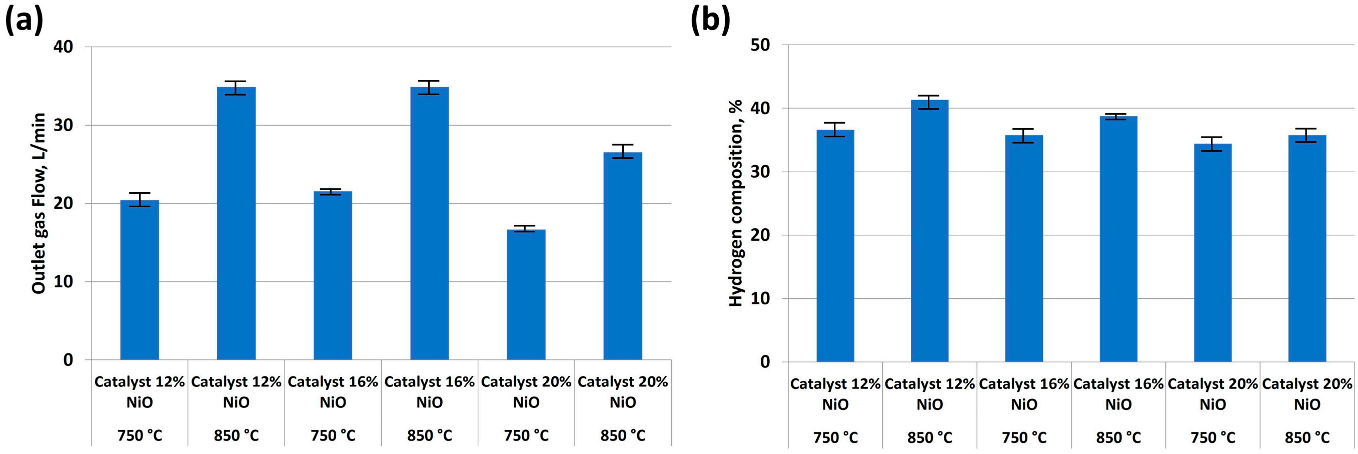


Figure 8. Comparison of outlet gas flow (**a**) and hydrogen composition (**b**) during glycerol steam reforming at different catalyst concentrations and temperatures (reaction conditions: water to glycerol ratio = 0.7, inlet flow = 40 mL/min).

Comparing the power generation and LHV, according to Figure 9, the test with the highest catalyst content and temperature had the highest LHV (15.97 kJ/m^{3}N), due to the lower H_2 content but a higher percentage of hydrocarbons (C_2H_4 and C_2H_6) and CO, which have a strong influence on the LHV. Nevertheless, tests carried out with 12% NiO and 850 °C offered acceptable results regarding the LHV (14.84 kJ/m^{3}N), and the gas composition was kept constant and at higher percentages compared to NiO 16%, whose composition is richer in CO_2, a compound that does not have an influence on the LHV. Consequently, NiO 12% had the highest power generation, observing a strong influence of the outlet gas flow on this parameter. Thus, this catalyst proportion and temperature were selected for further experiments and analysis (considering the optimum reaction conditions as the following: W/G = 0.7; inlet flow = 40 mL/min; oven temperature = 850 °C; NiO concentration = 12%). It should be noted that similar studies with Ni/CaO-Al_2O_3 at different Ni loadings (from 2.5 to 20% wt) offered an optimum Ni loading of 15%, with a high glycerol conversion (99.4% at 700 °C) [46]. In addition, other works offered a high glycerol conversion and yields (83 and 85%, respectively) through the catalytic steam reforming of glycerol over an LDH-derived Ni-Al nanosheet [42].

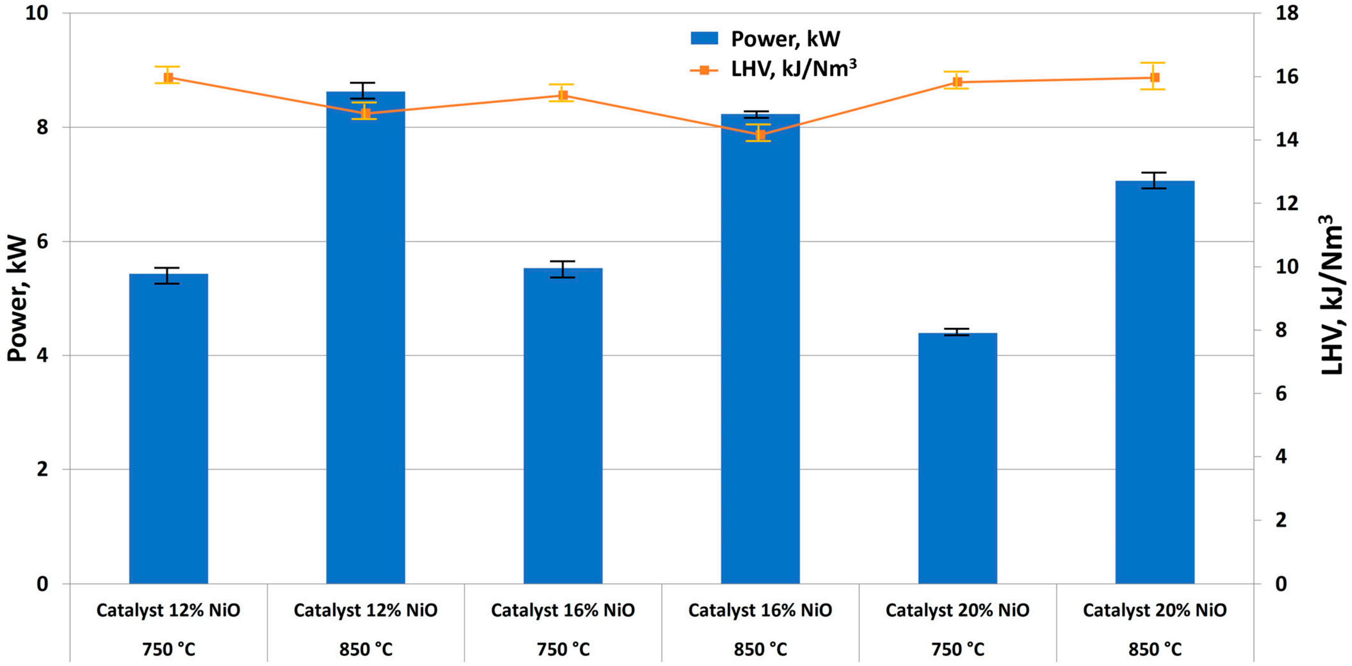


Figure 9. Comparison of power and LHV obtained in glycerol steam reforming at different temperatures and catalyst concentrations (reaction conditions: water to glycerol ratio = 0.7, inlet flow = 40 mL/min).

3.4. Lifetime Determination of Final Catalysts under Optimum Conditions

One of the main problems related to the use of catalysts in steam reforming is the possibility of deactivation during the reaction due to different factors, such as poisoning caused by impurities such as hydrogen sulfide, coke deposition due to hydrocarbon decomposition or sintering of the active phase on account of high temperatures. These problems provoke the decrease in active sites or active areas on the catalyst surface, implying the continuous efficiency loss of the catalyst.

Thus, the use of promoters (such as Ce, Zr or La, in this case, which improved catalyst basicity, metal–support interaction and Ni dispersion, as was proved in similar studies [47]) or mild reaction conditions could lengthen the useful life of catalysts [30,48,49]. Thus, in order to determine the lifetime of the selected catalyst (12% NiO and 5% La_2O_3), an experiment including the selected reaction conditions according to previous sections (that is, W/G = 0.7; inlet flow = 40 mL/min; oven temperature = 850 °C) was carried out, monitoring the gas composition every 30 min for at least 10 h. As a result, as observed in Figure 10, there was a slight change in the H_2, CO and CO_2 composition at around 580 min, possibly due to the lower influence of the WGS reaction (mainly responsible for changes in the syngas composition). At this moment, it is possible that the catalyst did not promote this secondary reaction. On the other hand, the remaining gases (CH_4, C_2H_4 and C_2H_6) come from the thermal decomposition of glycerol, and that is the reason why their mole fraction is not altered at this point.

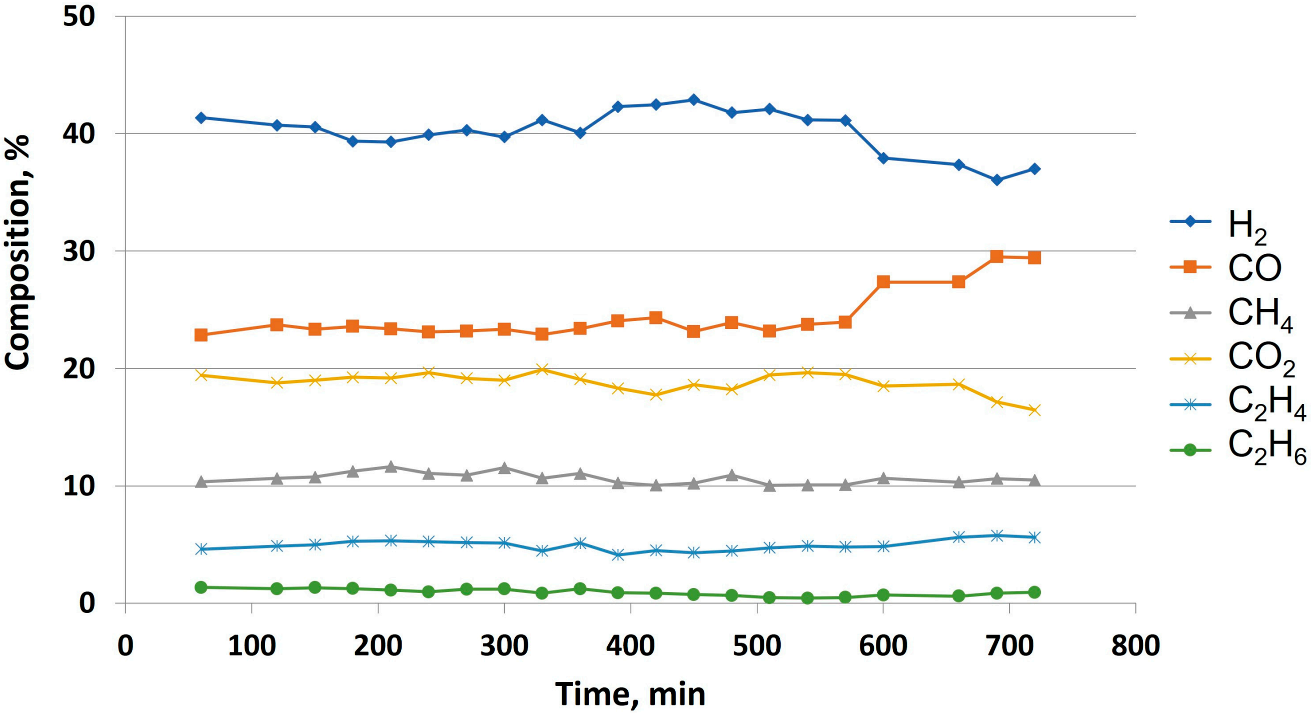


Figure 10. Outlet gas composition for catalyst lifetime determination (reaction conditions: NiO = 12%; water to glycerol ratio = 0.7; inlet flow = 40 mL/min; T = 850 °C).

Consequently, and even though the activity of the catalyst seems to be considerable after 700 min (especially concerning glycerol thermal decomposition), it should be noted that the changes in the gas composition observed from 600 min should be taken into account, especially concerning further syngas processes or purification techniques where the gas composition plays a vital role when it comes to the industrial design. In previous studies, where Ni-La/Al_2O_3 was produced and characterized, the catalyst obtained (16% NiO and 5% La_2O_3) offered a high stability, with a minimum reusability of five times [44]. Other studies based on Ni/CeO_2/Al_2O_3 showed great catalytic stability (with a considerable H_2 production up to 10 h), possibly due to the inhibition effect due to Ce, used as a promoter [30]. Equally, Ni-CeO-based catalysts for glycerol steam reforming offered longer useful times, up to 35 h [40]. Similar catalysts (15% Ni-CaO/Al_2O_3) studied in the literature showed a decline in catalytic conversion after 15 h at lower temperatures (700 °C) [46]. Also, other works covered the catalytic activity of Ni-La-Ti mixed oxide catalysts for glycerol steam reforming, observing that there was a slight and continuous decrease in activity, possibly due to coke deposition on the catalyst [50]. Other studies pointed out the long stability of the hydrogen selectivity (up to 12 h) of the catalyst used for GSR (Ni/CeZrO) at 500 and 600 °C [51]. Thus, the decrease in the catalyst activity could be due to coke deposition, poisoning due to hydrogen sulfide released during steam reforming (on account of the S content in glycerol, as observed in Table 2) and the sintering effect due to the high reaction temperature at which glycerol steam reforming was carried out in this experiment, exceeding 850 °C and, therefore, the corresponding Huttig temperature is exceeded (668 °C) whereas these working temperatures are relatively close to the Tammann temperature (1114 °C). This way, the atoms in the crystal lattice or surface can diffuse, generating recrystallization, agglomeration and sintering.

In this specific way, according to Figure 11, the used catalyst presented filamentous carbon and carbon deposits that could generate encapsulating carbon, hindering the Ni activity. Therefore, in this case, coke deposition seems to be the most influencing factor when it comes to catalyst deactivation. This fact could also explain the decrease in the surface area from the fresh (S_{BET} = 201 $m^2 \cdot g^{-1}$) to used catalyst (S_{BET} = 135 $m^2 \cdot g^{-1}$), with a decrease of around 33%.

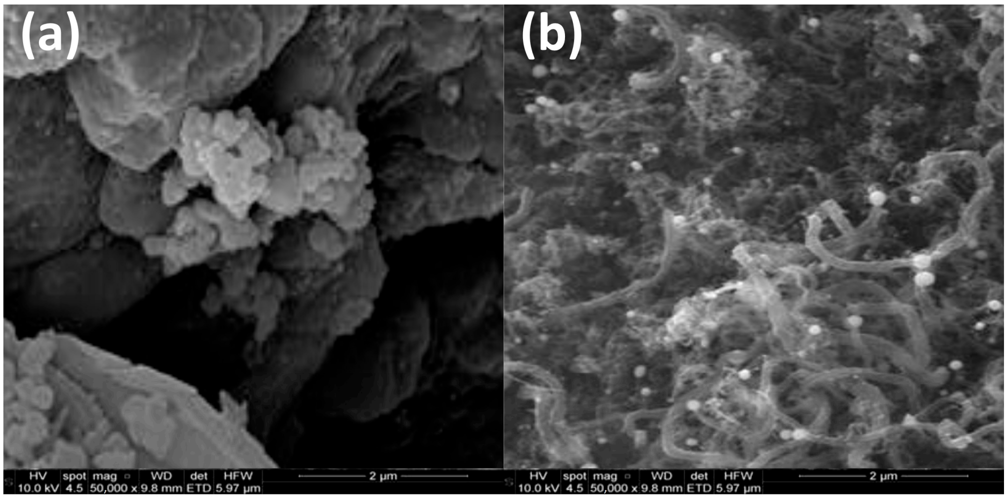


Figure 11. SEM images of fresh (**a**) and used (**b**) catalyst.

3.5. Comparison between Non-Catalytic and Catalytic Steam Reforming

Finally, this final experiment was compared with a non-catalytic steam reforming under the same chemical conditions except for the temperature, which was increased by 100 °C in the case of the non-catalytic experiment. The main results regarding this comparison are included in Table 7:

Table 7. Comparison between non-catalytic and catalytic glycerol steam reforming (reaction conditions: water to glycerol ratio = 0.7; inlet flow = 40 mL/min).

Parameter	Non-Catalytic Studies at 950 °C	Catalytic Studies at 850 °C
Outlet gas flow, L/min	30.93 (±0.65)	34.88 (±0.60)
Hydrogen content, %	41.72 (±0.20)	41.35 (±0.15)
Power, kW	6.32 (±0.15)	8.63 (±0.25)
LHV, kJ/m^3N	12.27 (±0.90)	14.84 (±0.85)

As observed, and even though both experiments were carried out at different temperatures, there was a considerable increase in the outlet gas flow when the catalyst was used, which points out the effectiveness of the Ni catalyst to carry out glycerol steam reforming, allowing the use of lower temperatures for this purpose. Thus, Ni was effective due to its properties, promoting the reaction between water molecules and carbon bounds in the water/glycerol mixture, producing higher and constant amounts of gas. Regarding hydrogen production, a considerable percentage of this gas (exceeding 40%) was found in the catalytic experiment, which proves the effectiveness of NiO to promote hydrogen production in the outlet gas. However, when the non-catalytic experiments at 950 °C were considered, the gas composition was equivalent to the catalytic experiment, as high temperatures promote hydrogen production and therefore its proportion in the final gas outlet. In any case, the catalyst addition allowed the reduction in the temperature reaction, with the subsequent saving on the energy cost. The same trend was observed when non-catalytic GSR was compared to other experiments where zeolite-based Ni catalysts were used, with a considerable increase in the yield and hydrogen percentage for the latter [52]. Finally, the power and LHV were compared, observing a 36% and 21% increase in the power generation and LHV, respectively, when the catalyst was used at lower temperatures. Regarding the LHV, this considerable increase in the case of the catalytic study was possibly due to the use of low temperatures, which implied lower CO_2 amounts in the outlet gas and higher hydrocarbon and CO proportions (which are elements with a strong influence on the LHV). Concerning the power generation, as the outlet gas flow and LHV were higher when using NiO 12% as a catalyst, it is no wonder that the power, obtained by using Equation (6), was much higher compared to non-catalytic experiments.

In view of the above and considering further studies about this subject, once the improvements carried out to the pilot plant were proven to be effective, a thorough sustainability assessment should be carried out to assure the sustainability of the process under these circumstances. Even though bio-based materials present obvious advantages compared to petroleum, they should not be taken for granted, and a rigorous scientific assessment of this subject should be carried out. Thus, advanced sustainability tools such as techno-economic, energy, exergy or life-cycle assessments, among others, should be considered in further studies with these results as a starting point. Moreover, these tools separately present some advantages and disadvantages and their integration was highly recommended according to a recent review work [53]. In any case, and even though there are some methodological problems related to these tools (especially in the case of the life-cycle assessment, where system boundaries, functional units, allocation or carbon accounting can represent some challenges), the system included in this work, in a biorefinery based on a biofuel/bioproduct context, could be promising when it comes to sustainability terms [54]. Also, further characterization of the catalysts should be carried out in order to assess the influence of each deactivation process (coke deposition, poisoning or sintering), taking into account the specific surface area, among other parameters.

4. Conclusions and Prospects

The main findings of this work were the following:

- A study about the steam reforming of glycerol in a pilot plant was carried out, obtaining considerable gas production (up to 35 L/min) at 850 °C with 100 g of catalysts (12% NiO). Under these circumstances, high hydrogen percentages were obtained, exceeding 40%. Thus, a semi-industrial production of hydrogen through GSR was proven.
- The most suitable catalyst for glycerol steam reforming in this experiment was 12% Ni, since, during the impregnation process, the support adsorbed the supplied solution properly, whereas in the rest of the cases, it was not possible, and the support tended to saturate.
- A considerable advantage is achieved when catalysts are used, compared to non-catalytic steam reforming, not reaching very high reaction temperatures.
- Due to the improvements introduced in the reactor, the pressure drop considerably decreased, and, therefore, the catalytic support was in contact with the gas for long enough.
- After several hours of continuous operation in the glycerol steam reforming plant, the results might be altered due to coke deposition and condensate that can be generated.
- For an optimal production in the plant, it should not be operating for more than 9 h, as this is the estimated useful life of the catalyst.
- The main disadvantage when it comes to catalyst implementation in this facility was coke deposition in the basket, which can promote catalyst deactivation.
- For a correct catalytic performance, some steps should be carried out for re-using it, such as oven cleaning, activation processes, placing it in the oven, etc.
- Finally, the main differences between optimal catalytic tests and non-catalytic ones make the use of a catalyst necessary as long as the process takes place for less than 9 h at a temperature of 850 °C.

- Regarding the limitations of this work and prospects, it should be noted that further research about the sustainability of this process should be conducted, including advanced sustainability assessment tools such as a life-cycle assessment or exergy determination to prove the sustainability of the process at an industrial level.
- Also, further characterization of the catalyst (both fresh and spent) should be carried out, paying attention to parameters such as the specific surface area, element and phase composition, to determine key factors affecting its useful life.

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Abbreviations

BHA	Butylated hydroxy anisole
FAMEs	Fatty acid methyl esters
GSR	Glycerol steam reforming
HHV	High heating value
LHV	Low heating value
PG	Propyl gallate
PID	Proportional–integral–derivative
$Q_{\text{outlet gas}}$	Outlet gas flow
S/C	Steam to carbon ratio
SDGs	Sustainable Development Goals
TBHQ	tert-Butylhydroquinone
W/G	Water to glycerol ratio

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