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Influence of alumina fixed-bed in steam reforming of glycerol for hydrogen production

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Abstract

In this study, hydrogen production by steam reforming was carried out in a tubular fixed-bed reactor. The influence of some operating variables such as temperature, flow rate of the feeding glycerol solution and space velocity on hydrogen production under a non-catalyzed reaction was analyzed. The results showed that the hydrogen yield increased with temperature and decreased with the space velocity. As the feedstock flow rate increased, the hydrogen yield decreased rapidly. Compared with a reference experiment without fixed-bed, the use of non-porous alumina fixed-bed showed better results. Under the best reaction conditions (900 °C and a feedstock flow rate of 0.85 g/min), 17 L/h of syngas were obtained, with a purity of about 55% of hydrogen and a production of 2.7 moles of hydrogen by mol of glycerol.

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Keywords: Hydrogen; Glycerol; Steam reforming; Fixed-bed; Non-catalyzed reaction

1. Introduction

Currently, the development of alternative fuels is being very important due to the increase in energy demand. In this way, hydrogen could be a suitable alternative and an important energy vector in the future. Hydrogen can be obtained from different renewable and non-renewable sources (natural gas, methane, ethanol, glycerol) and processes: steam reforming, gasification, partial oxidation, autothermal reforming, dark-fermentation, electrolysis [1]. Among all of them, steam reforming is the most dominant method to obtain hydrogen from glycerol and other feedstocks. However, glycerol presents some advantages compared with other sources: lower temperatures (700–900 °C) and higher hydrogen molar flow by the same molar feedstock. According to the global steam reforming reaction (Eq. (1)),

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it is possible to obtain 7 mol of hydrogen from 1 mol of glycerol. This equation included glycerol decomposition and water–gas shift reaction. As final product, it is obtained a gaseous mixture that contains as main components hydrogen, methane, carbon dioxide and carbon monoxide, called synthesis gas. This syngas can be used to generate heat and electricity, hydrogen, or synthesis of liquid fuels such as ammonia and methanol [2,3].



On the other hand, reforming of glycerol for hydrogen production needs to be improved since other reactions, like methane and coke formation, occur decreasing the rate and purity of obtained hydrogen [4]. According to literature [5–7], high temperature, low pressure, and high water/glycerol molar ratio are suitable for hydrogen production from glycerol steam reforming. Therefore, it is important to analyze the effect of these parameters.

Catalytic reforming is also used in the steam reforming of glycerol for hydrogen production. The most used catalysts for this process are noble metals (Pt, Ru, Rh, Ir) or non-noble transition metals (Ni, Co, Ce, Zr) [6]. The noble metals are highly active and less susceptible to deactivation through coke depositions, but they are expensive and present lower availability. Then, nickel is the most used in glycerol steam reforming. Regarding catalyst support, some materials such as alumina, zirconium dioxide or silica, have been used as metal supports for their high surface areas, its stability of the catalyst via metal-support interactions. However, for its higher availability and low cost, the most commonly used media are silica and alumina. The most widely used support for catalysts reformed is $\gamma\text{-Al}_2\text{O}_3$ due to its high chemical stability and its high specific surface.

Many researchers have investigated the effect of different catalyst and supports to obtain high yields [8], but there are few studies related to the study of the effect of the support on the process without any other catalyst. In this research, non-catalyzed glycerol steam reforming has been carried out in a fixed-bed reactor with alumina. The aim of this research is to examine the effect of an alumina fixed-bed reactor on steam reforming of glycerol, and the influence of feedstock flow rate, temperature, and space velocity.

2. Experimental

2.1. Experimental system and procedure

Fig. 1 shows a schematic drawing of the setup used, which consist of four main elements: feeding system, fixed-bed reactor, condensates tank and gas analyzer. A mixture of water and glycerol (20 wt%) is feed to the center of the reactor through a peristaltic pump (D25Vplus, Dinko Instruments) at different flow rates (0.35, 0.85, 1.04, and 1.48 mL/min).

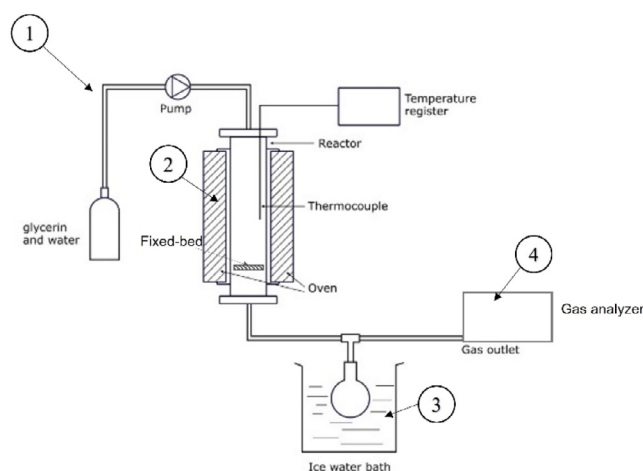


Fig. 1. Scheme of the experimental system: feeding system (1), fixed bed-reactor (2), condensates tank (3), and gas analyzer (4).

The fixed bed reactor consists of a boiler steel cylindric reactor with a length of 700 mm and inner diameter of 48 mm. It was placed in an electrical tubular furnace (TR4, Hobersal) for heating the reactor at two different

operation temperatures (800 °C and 900 °C). To analyze the influence of bed height, two different operating conditions were assessed: without alumina (named as Reference), using only a perforated metal cylinder of 70 mm length and 30 mm of inner diameter, and with the cylinder loaded with a nonporous alumina spheres of 3 mm diameter, 92% Al₂O₃, density of 3670 kg m³ (named as AL). In the last operating condition, two different heights were assessed: 30 mm (which correspond with 40 g of alumina), and 60 mm (which corresponds with 80 g).

The gas products were condensed in a thermostatic bath and the condensable liquids were collected in borosil transparent gas wash bottles of 250 mL. Finally, composition and flow rate of the dry gas was measured in a gas analyzer (Mamos, Madur), which allows a continuous measurement and data stored of the concentration of CO, CO₂, CH₄ and H₂ (in this study, only the data related to the latter gas are shown). In all experiments, the final reaction time was 45 min, and the measurements was carried out each minute.

2.2. Data analysis

Based on the measurements registered in each case, and considering that seven is the maximum number of moles of hydrogen that can be produced per mol of glycerol (Eq. (1)), the following parameters were analyzed:

Gas flow rate and compositions. Both values were measured directly in the experimental system.

Feedstock flow rate. The optimization of this parameter is a considerable point since, as previous studies point out [9], a high liquid flow rate can produce low conversion (a fact that will reduce the purity of the hydrogen produced) while a low flow rate can provoke a low gas production (this fact would improve hydrogen purity, but the process is less efficient). For that, hydrogen production from steam reforming of glycerol was analyzed at different liquid flow rate (from 0.35 to 1.48 g/min).

Hydrogen production (P_{H_2}), which can be obtained as follows:

$$P_{H_2} = \frac{\text{moles } H_2 \text{ in gas products}}{\text{moles glycerol in the feedstock}} \quad (2)$$

Hydrogen yield (Y), which can be defined according to Eq. (3).

$$Y (\%) = \frac{\text{obtained moles } H_2}{\text{theoretical moles } H_2} \times 100 \quad (3)$$

The weight hourly space velocity (WHSV), which is inversely proportional to residence time, and gas hourly space velocity (GHSV). Both parameters can be defined with the following equations:

$$WHSV(h^{-1}) = \frac{\text{mass flow rate}}{\text{mass of alumina}} \times 100 \quad (4)$$

$$GHSV(h^{-1}) = \frac{\text{syngas flow rate}}{\text{volume occupied by alumina}} \times 100 \quad (5)$$

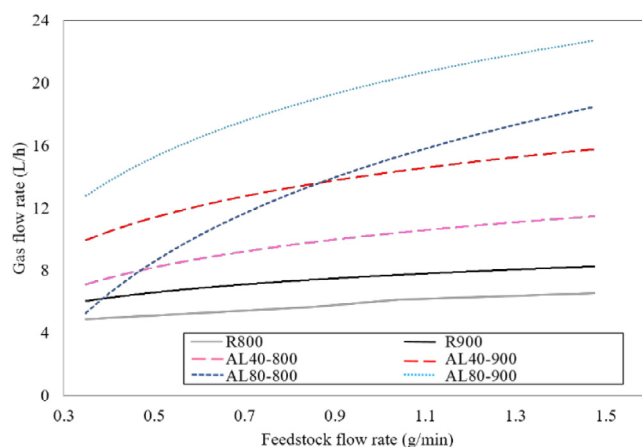
3. Results and discussion

Table 1 shows the operating conditions of all experiments and the results obtained under different bounding conditions of temperature, fixed-bed height, material of the bed and feedstock flow rate. Some of these parameters, such as the existence of a larger fixed-bed or the application of a higher temperature, have a direct influence on the gas outlet flow rate. As shown in Fig. 2, the higher the temperature (considering the same fixed-bed size), the higher the flue gas flow rate (a logical fact considering the excess of energy supplied to the reaction). What is noteworthy is the influence of fixed-bed height on gas production. As it was observed, as the bed height was increased and the flow rate was analyzed for different feedstock flow rates, the shape of the output flow curve changed from a linear shape with a very low slope to a logarithmic shape with a much steeper slope. This fact shows that this parameter has a significant influence on the gas outlet flow rate produced.

Regarding the hydrogen production (P_{H_2}) and yield (Y) obtained in the process, it was observed (Table 1) that increasing the temperature by 100 °C, under the same bed conditions, causes an increase in the order of 50%–100% in both parameters (especially at low feedstock flow rates: 0.35 and 0.85 g/min) [10]. This fact again shows that (1) a higher energy input favors the glycerol steam reforming endothermic reactions (1), i.e., when the temperature increases, the reaction shifts towards hydrogen production; (2) the glycerin flow rate influences the reaction yield, as reported in [9]. As shows in Fig. 2 the feed flow rate increases, the flow rate of gases produced increases. However,

Table 1. Experimental conditions and results, for different bed types: only a metal cylinder (R), and cylinder loaded both with nonporous alumina (AL).

Exp	Acronym	T (°C)	Alumina amount (g)	Feedstock flow rate (g/min)	P_{H_2}	Y (%)	H ₂ purity (%)
1	R800-0.35	800	0	0.35	1.08	15.48	26.7
2	R800-0.85	800	0	0.85	0.55	7.92	37.7
3	R800-1.04	800	0	1.04	0.58	8.35	39.0
4	R800-1.48	800	0	1.48	0.42	5.98	37.0
5	R900-0.35	900	0	0.35	2.23	31.88	53.8
6	R900-0.85	900	0	0.85	1.06	15.19	50.9
7	R900-1.04	900	0	1.04	0.95	13.59	45.4
8	R900-1.48	900	0	1.48	0.61	8.76	43.0
9	AL40-800-0.35	800	40	0.35	1.17	16.72	51.6
10	AL40-800-0.85	800	40	0.85	0.53	7.51	53.2
11	AL40-800-1.04	800	40	1.04	0.62	8.91	46.9
12	AL40-800-1.48	800	40	1.48	0.51	7.22	45.8
13	AL40-900-0.35	900	40	0.35	2.24	31.99	62.2
14	AL40-900-0.85	900	40	0.85	1.04	14.86	58.0
15	AL40-900-1.04	900	40	1.04	0.93	13.36	54.5
16	AL40-900-1.48	900	40	1.48	0.63	8.95	45.5
17	AL80-800-0.35	800	80	0.35	1.67	23.88	43.4
18	AL80-800-0.85	800	80	0.85	1.45	20.72	41.8
19	AL80-800-1.04	800	80	1.04	1.54	21.98	38.2
20	AL80-800-1.48	800	80	1.48	1.21	17.25	36.8
21	AL80-900-0.35	900	80	0.35	5.19	74.19	57.7
24	AL80-900-0.85	900	80	0.85	2.66	38.01	50.7
23	AL80-900-1.04	900	80	1.04	2.45	35.04	46.2
24	AL80-900-1.48	900	80	1.48	1.59	22.78	43.1

**Fig. 2.** Influence of glycerin feed flow rate on the gas outlet flow rate, under different temperature and fixed-bed height conditions.

this does not cause an increase in the yield of $H_{2(g)}$ produced. In fact, the data obtained showed that, regardless of the working temperature, in the Reference and AL40 experiments, less than one mole of $H_{2(g)}$ per mole of glycerol was produced at high flow rates (1.04 and 1.48 g/min), which means that more than 50% of the gases produced at the end of the process were not $H_{2(g)}$.

With respect to the fixed bed influence, it was observed that, for the same conditions of temperature and flow rate, generally, the yield increases as the bed height increases as occurs in [11], achieving in consequence the lowest yield in the reference experiments and the highest in the AL80 experiments. In addition, it was observed that the increase of the fixed-bed up to a considerable value (in this case 60 mm), caused that although working at temperatures of

800 °C, the yields, gas outlet flow rates, and purity of hydrogen, were higher than those obtained in the reference experiments, regardless of the feedstock flow rate supplied. This fact could be due to (1) the longer retention time of the glycerin inside the reactor which favors the conversion, and (2) to the fact that the alumina acts in a certain way as a catalyst of the reaction favoring that this takes place at a lower temperature than necessary. This would mean that at 800 °C with a higher alumina content, an excess of energy is provided for the conversion to take place.

As it can be observed in Table 1, the syngas composition was also influenced mainly by the temperature and feedstock flow rate. The highest amount of hydrogen purity (62%) was obtained at higher temperature (900 °C), lower feedstock flowrate (0.35 g/min) and 40 g of alumina; however, a lower gas outlet flow rate (10 L/h) was obtained in comparison with 80 g of alumina at same conditions (14 L/h). Thus, it is necessary to look for a compromise solution between obtaining higher gas flows, their purity and maximum use of the glycerol feedstock.

When the alumina is placed into the reactor, it is expected that the residence time increases and the ability to process the reagent, improving the glycerol steam reforming and therefore the hydrogen production and yield (Y) [12]. Similar results should be obtained when feedstock flow rate decreases [13]. Fig. 3 shows that hydrogen yield increase when de WSHV decreases for the same amount of alumina. The same behavior was observed when the amount of alumina was increased for the same feedstock flow rate. The values of space velocity increased gradually with the flow rate, resulting in shorter residence time. This provoked that glycerol did not react totally inside the reactor. According to the experimental results, the appropriated values of WSHV depend strongly on temperature, being 1.3 h^{-1} at 800 °C and 0.6 h^{-1} at 900 °C.

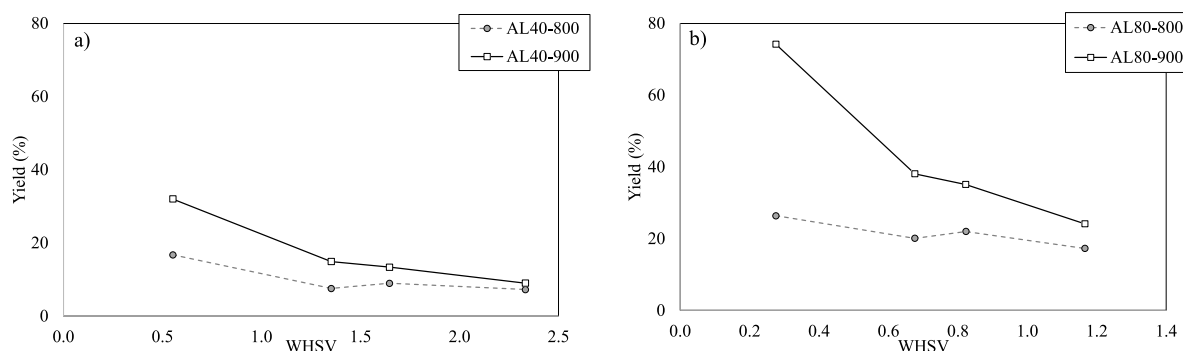


Fig. 3. Influence of WSHV on hydrogen yield at different amount of alumina: (a) 40 g, (b) 80 g.

The effect of gas hourly space velocity on hydrogen yield (Y) is shown in Fig. 4a for different conditions: 40 g of alumina at 800 °C (AL40-800) and at 900 °C (AL40-900), 80 g of alumina at 800 °C (AL80-800) and at 900 °C (AL80-900). It can be observed that hydrogen yield decreased when GHSV increased, especially for AL80-900, where this parameter dropped from 74% to 22%. For AL80-800, with the same amount of alumina and lower temperature than before, the values of Y keep constant around 20%. Similar behavior was observed for AL40-800 and AL40-900, at the highest temperature the hydrogen yield decreased from 62% to 45% when GHSV increased, whereas at 800 °C the values were around 50%.

The gas hourly space velocity is also influenced by feedstock flow rate (Fig. 4b). High GHSV, give high synthesis gas yields; however, the feed rate is so high that the contact time decreases and the ability to process the glycerol is reduced, resulting in a lower yield. At longer contact times, the activity of the alumina increases since the interaction of the glycerol and water molecules increases [12]. Combining the obtained results in both figures, it can be said that the best results are at 80 g of alumina, 900 °C and a feedstock flow rate of 0.85 g/min.

4. Conclusions

The hydrogen production of glycerol steam reforming was carried out in an alumina fixed-bed reactor. From the study of the main variables of steam reforming of glycerol, it can be concluded that the presence of alumina as a fixed-bed inside the reactor favors the reaction. The same effect was observed increasing the temperature. On the other hand, by increasing the feedstock flowrate, a greater amount of syngas is produced with lower purity, being

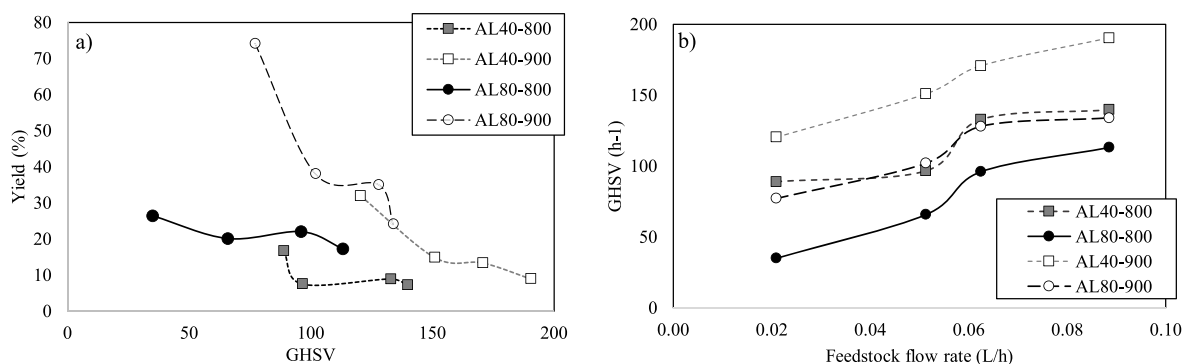


Fig. 4. (a) Influence of GHSV on hydrogen yield. (b) Effect of feedstock flow rate on GHSV.

necessary to find a compromise solution between both parameters. Under the optimal reaction conditions, 17 L/h of syngas were obtained, with a purity of about 55% of hydrogen and a production of 2.7 moles of hydrogen by mol of glycerol.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Rocio Maceiras reports financial support was provided by Defense University Center at the Spanish Naval Academy (CUD-ENM).

Data availability

Data will be made available on request.

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References

- [1] Martino M, Ruocco C, Meloni E, Pullumbi P, Palma V. Main hydrogen production processes: An overview. *Catalysts* 2021;1:547–78.
- [2] Chimpaie S, Wongsakulphasatch S, Vivanpatarakij S, Glinrun T, Wiwatwongwana F, Maneepakorn W, et al. Syngas production from combined steam gasification of biochar and a sorption-enhanced water–gas shift reaction with the utilization of CO₂. *Processes* 2019;7(6):349–64.
- [3] Boerrigter H, Rauch R. Syngas production and utilization. In: *Handbook biomass gasification*. the Netherlands: Biomass Technology Group (BTG), Enschede; 2005.
- [4] Menezes JPSQ, Manfro RL, Souza MMVM. Hydrogen production from glycerol steam reforming over nickel catalysts supported on alumina and niobia: Deactivation process, effect of reaction conditions and kinetic modelling. *Int J Hydrogen Energy* 2018;43(32):15064–82.
- [5] Remón J, Mercado V, García L, Arauzo J. Effect of acetic acid, methanol and potassium hydroxide on the catalytic steam reforming of glycerol: Thermodynamic and experimental study. *Fuel Process Technol* 2015;138:325–36.
- [6] Qingli X, Zhengdong Z, Lifang L, Ping L, Rui W, Shoutao C, et al. Hydrogen production by glycerol reforming in a two-fixed-bed reactor. *Int J Hydrogen Energy* 2022;47(38):16805–14.
- [7] Cheng CK, Foo SY, Adesina AA. Thermodynamic analysis of glycerol-steam reforming in the presence of CO₂ or H₂ as carbon gasifying agent. *Int J Hydrogen Energy* 2012;37(13):10101–10.
- [8] Saeidabad NGhaffari, Noh YS, Alizadeh Eslami A, Song HT, Kim HD, Fazeli A, et al. A review on catalysts development for steam reforming of biodiesel derived glycerol; Promoters and supports. *Catalysts* 2020;10(8):910–32.
- [9] Encinar JM, González JF, Sánchez N, Núñez F. Aprovechamiento de glicerol para la obtención de gas de síntesis mediante reformado con vapor. In: *VIII Congreso nacional de ingeniería termodinámica*. 2013, p. 1045–52.
- [10] Xin S, Qingli X, Lifang L, Yongjie Y. Hydrogen production by glycerol reforming in a fixed-bed reactor. *Energy Sourc, Part A: Recovery, Util Environ Effects* 2017;39(24):2195–202.

- [11] Ming F, Qingli X, Wei Q, Zhikai Z, Suping Z, Yongjie Y. Hydrogen production from glycerol steam reforming over Ni/La/Co/Al₂O₃ catalyst. *Energy Source, Part A: Recovery, Util, Environ Effects* 2016;38(14):2128–34.
- [12] Sahoo DR, Vajpai S, Patel S, Pant KK. Kinetic modeling of steam reforming of ethanol for the production of hydrogen over Co/Al₂O₃ catalyst. *Chem Eng J* 2007;125(3):139–47.
- [13] Sánchez N, Encinar JM, Nogales S, González JF. Lanthanum effect on Ni/Al₂O₃ as a catalyst applied in steam reforming of glycerol for hydrogen production. *Processes* 2019;7(7):449–67.