On the search of efficient uses for glycerine: steam gasification

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Abstract. This work deals with the steam gasification of the glycerine generated during the biodiesel manufacture in an industrial plant. Glycerine (diluted in water) was gasified with the aim of producing an hydrogen-rich gas, making a systematic investigation on the influence of the gasification temperature in the range 600-1000 ºC. It was found that the change in this parameter influences the composition of the gas generated during gasification, driving the process towards a higher hydrogen production as the temperature gets greater. On the other hand, if the aim is to produce a gas with a higher energy content, a lower temperature would be more favourable.

Key words

Glycerine, gasification, hydrogen, biodiesel

1. Introduction

Biodiesel is one of the alternative fuels used to meet the current energy requirements. Apart from the null net CO_2 emissions it provides, it can be used for automotive applications, which makes it more interesting than other alternative energy sources.

During biodiesel production by means of transesterification of oils and animal fats, glycerine is formed as by-product in a ratio of approximately 10% (weight referred to biodiesel production). This quantity of glycerin is huge if we consider that biodiesel production is increasing to get a more significant role in the next energy scheme. As more biodiesel is produced, the price of glycerin decreases and the need of searching new ways to provide an added value to this product becomes an imperative. With increased production of biodiesel, a glut of glycerol ($C_3H_8O_3$) is expected in the world market, and therefore it is essential to find useful applications for glycerol. Currently, glycerol is used in many applications including personal care, food, oral care, tobacco, polymer and pharmaceutical applications. However, explosive growth of biodiesel industry has created a glut in glycerol that has demeaned the market value of this commodity. Therefore, finding alternative uses for glycerol is important. One possibility is using glycerol as a source for producing hydrogen.

In this line, some studies regarding the steam gasification of glycerine for the production of hydrogen, syn gas and medium heating value gas have been made [1-9]. These works showed that glycerin steam gasification is a very complex process in which concurrent, consecutive, dehydration and cracking reactions all compete to transform glycerin into H_2, syn gas and char [1]. Theoretically, one mole of glycerin would give four moles of H_2. However, up to now, the most interesting results found in the bibliography show conversions lower than 60% [1], which is already very attractive.

Although this field is a hot topic for research, given the many advantages it can offer once the process has been optimized, the knowledge on the mechanisms governing glycerine degradation reactions is very scarce.
With these premises, this work studied the steam gasification of glycerine (diluted in water) with the aim of producing an hydrogen-rich gas, making a systematic investigation on the influence of the temperature (600, 700, 800, 900 and 1000 ºC). The water-to-glycerol feed ratio and steam flow rate were 12:1 and 2.5 cm^3 min^{-1}, respectively.

2. Experimental

Glycerine was provided by the Biodiesel manufacture plant of Bioenergética Extremeña, located in Valdetorres (Extremadura, Spain).

The runs were performed under continuous regime, using a two stage gasification system as the one shown in Figure 1.

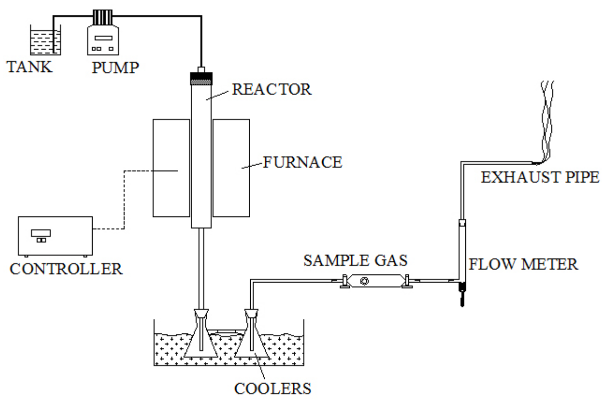

Figure 1. Experimental set-up

It consists basically on a stainless steel tubular reactor (inner diameter of 3.5 cm and length of 70 cm) where the glycerine gasification processes with steam takes place. A peristaltic bomb introduces the adequate glycerine/water ratio directly into the reactor. The gas produced is then passed through a quenching system (glass recipients covered by ice), where the condensable liquids are collected. Once the steady regime has been reached, a gas sample is collected for further analysis. This operation is repeated several times to confirm the reliability of the results obtained. Therefore the data presented in this work is an average value.

The composition of the gas produced; mainly H_2, CO, CO_2 and CH_4, was analysed by a 4000 HRGC KONIK gas chromatograph provided with two thermal conductivity detectors, connected to two columns: Porapack Q and Carboxen-1000 (15 ft length, 1/8 inch diameter).

3. Results and discussion

In this paper, the results obtained in the reforming process of glycerine with water vapour are discussed. The hydrogen or syngas production and energy power obtained per kg of glycerine are valorized.

This work is a part of a wider investigation in which tree experimental series have been performed, varying the water-to-glycerol feed ratio, WGFR in the range 2:1, 6:1, 9:1 and 12:1. In each series the temperature and flow rate has been varied in the ranges 600-1000 ºC and 0.5 a 3 $cm^3\ min^{-1}$, respectively.

In this case, the influence of the temperature on the main parameters of the reaction thus as quality and energetic value of gas, moles of gas/min, moles of each gas/mol of glycerine, molar fractions of gas compounds, lower heating value of gas (in kJ/Nm^3) and energetic power generated (in kW) are analyzed. The results obtained for the experimental series carried out at different temperatures with a WGFR of 12:1 and a flow rate of 2.5 $cm^3\ min^{-1}$ are discussed here.

The reforming of glycerine with vapour produces H_2, CH_4, CO, CO_2, and C, together with non-reacted water and glycerol. Only the discussion of these compounds will be analysed because they are the primary products formed in the reforming of glycerine with vapor [5, 6].

First, it is necessary to study the global reaction of vapor reforming of glycerine, which is:

$$C_3H_8O_3\ (g) + 3H_2O\ (g) \leftrightarrow 7H_2\ (g) + 3CO_2\ (g) \qquad (1)$$

$\Delta H = 225.29$ kJ/mol

Thermodynamically, the reforming reaction is an endothermic reaction and the equilibrium constant is high enough to convert glycerine completely at appropriate temperatures (227 °C) [7]. Therefore, it is viable to reform glycerine for hydrogen production from a liquid phase at relatively low temperature. However, the reforming in aqueous phase of polyalcohols is very complex and many secondary reactions are possible, including parallel and consecutive [8].

The glycerol reforming for hydrogen production involves complex reactions. As a result, various intermediary by-products are formed and finish in the product stream affecting the final purity of hydrogen produced. Moreover, the hydrogen yield depending of several variables of process, such as pressure, temperature, feeding caudal and water-to-glycerol feed ratio [8, 9].

Figure 2 shows the temperature influence on the moles of each gas/min generated for a feeding flow rate of 2.5 $cm^3\ min^{-1}$. One can be observe that increasing temperature produces a practically lineal increase of H_2, a decrease of CO, an increase of CO_2 until 900 ºC (decreasing after). The same tendency is observed for CH_4 although less accused than in the case of CO_2.

Also, in Figures 2 and 3 an increase of the mol number of H_2 obtained per each mol of glycerine can be appreciated (although it is far from the 7 moles of H_2 per mol of glycerine that is the maximum production of this gas according to the equation 1) and the molar fraction of H_2 increases as the reaction temperature increases. Also an increase of CO_2 and CH_4 up to 900 ºC and a decrease of CO can be appreciated as the temperature increases. Adhikari et al., (2007b) have observed an increase in the CO and H_2 production with the increase of temperature until 1000 K, while they found a decrease of the CH_4 production. Moreover, they obtained a maximum in the CO_2 production at 800-850 K for the different water-to-glycerol feed ratios tested by those authors. This effect is somehow also observed in this work, (respect to H_2 and CO_2 produced), but the maximum in the CO_2 production is observed at 900 ºC. In the case of CH_4 production, a maximum is also observed at 900 ºC, therefore the participation of secondary reactions such as:

Water gas shift reaction:

$$CO\ (g) + H_2O\ (g) \leftrightarrow H_2\ (g) + CO_2\ (g) \qquad (2)$$

$\Delta H = -40.\ 9$ kJ/mol

Steam reforming reactions:

$$CH_4\ (g) + 2H_2O\ (g) \leftrightarrow 4H_2\ (g) + CO_2\ (g) \qquad (3)$$

$\Delta H = 165.0$ kJ/mol

$$CH_4\ (g) + H_2O\ (g) \leftrightarrow 3H_2\ (g) + CO\ (g) \qquad (4)$$

$\Delta H = 206.3$ kJ/mol

These equilibria can explain the composition of final gas obtained. The reactions 3 and 4 must be favoured with the temperature because they are endothermic reactions. However, the reaction (2) is slightly exothermic. The justification of the final gas composition can be analyzed, evaluating the effects of the ratios showed in Table 1.

In this series, the ratio CO/CH_4 decreases from 4.94 to 1.24 and the ratio H_2/CO increases strongly as one can see in Table 1, consequently, the reaction (4) participates scantily in the composition of the generated gas. The reaction water gas shift must participate in the final gas composition, because this reaction must be favoured with the increase of the reaction temperature. This circumstance can be justified, if one observes the reduction of the ratios CO/CO_2 and H_2/CO_2 (in this case until 900 ºC) and the strong increase experimented by the ratio H_2/CO. Logically, the final gas composition can be also influenced by the participation of the reforming of glycerine (equation 1), which is endothermic.

The reforming reactions must be favoured because of the strong increase of the ratio H_2/CH_4 (see Table 1). In Figure 4 (where the molar fractions of gases versus temperature is plotted), one can see an increase and decrease of the molar fractions of H_2 and CH_4, respectively, as the reaction temperature is increased. Also, a decrease of molar fraction of CO with increasing temperature is observed. The molar fraction of CO reaches a maximum at a temperature of 900 ºC. An hydrogen-rich gas with a molar fraction of 61.3% was obtained for a temperature of 1000 ºC.

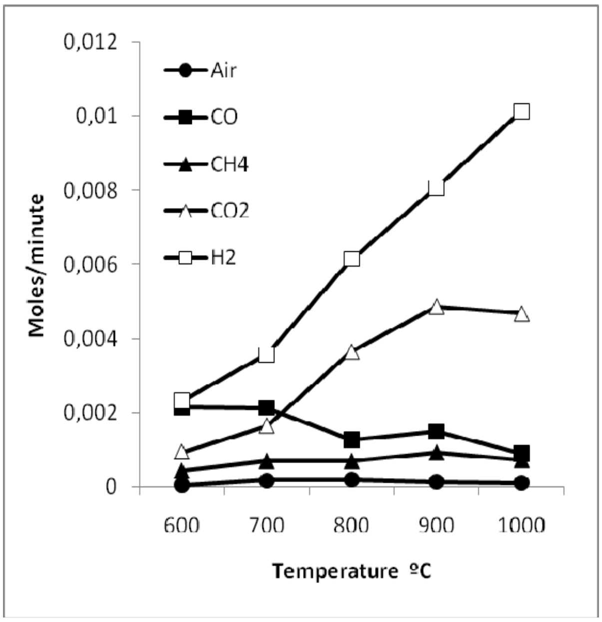

Figure 2. Influence of the temperature on the generated moles de gases per minute (WFGR = 12:1, Q= 2.5 cm^3 min^{-1}).

Figure 1 shows the number of moles of each gas per volume unit of glycerine (mole mL^{-1}) for the different runs made.

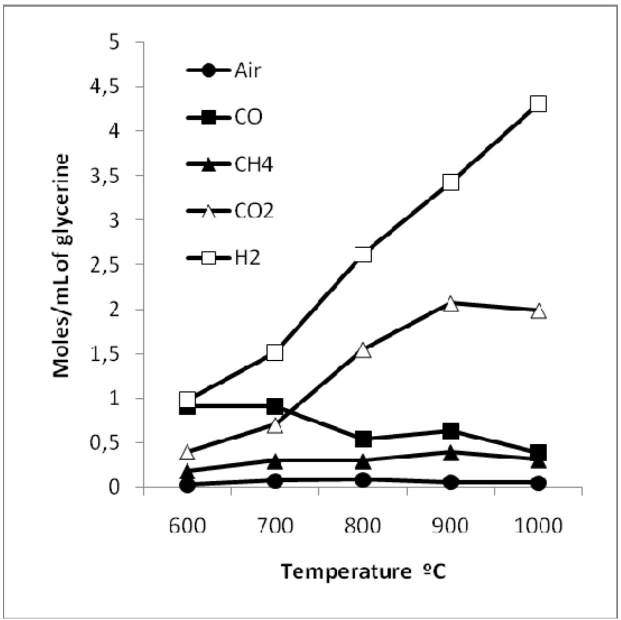

Figure 3. Influence of temperature on the moles of gases per cm^3 of glycerine (WFGR = 12:1, Q= 2.5 cm^3 min^{-1}).

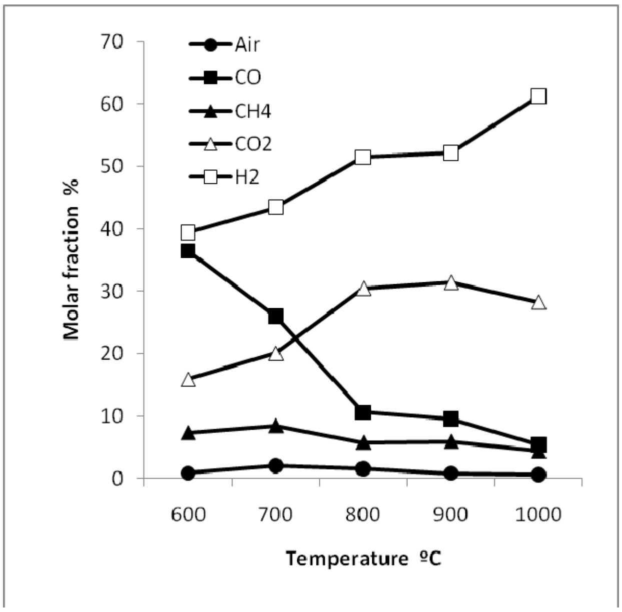

Fig. 4. Influence of temperature on the molar fractions of generated gases (WFGR = 12:1, Q= 2.5 cm^3 min^{-1}).

Table 1. Influence of temperature on the Ratios H_2/CO, H_2/CH_4, CO/CO_2, CH_4/CO_2 e H_2/CO_2 (WFGR = 12:1, Q= 2.5 cm^3 min^{-1}).

T, ºC	Ratio H_2/CO	Ratio H_2/CH_4	Ratio CO/CO_2	Ratio CH_4/CO_2	Ratio H_2/CO_2
600	1.08	5.35	2.29	0.46	2.48
700	1.67	5.11	1.29	0.42	2.16
800	4.84	8.85	0.35	0.19	1.68
900	5.45	8.73	0.30	0.18	1.66
1000	11.28	13.96	0.19	0.15	2.16

The results obtained allowed concluding that the use of different water/glycerine ratios influenced the composition of the gas obtained: a more diluted glycerine/water ratio gives rise to a higher hydrogen fraction, in coherence with other studies [1].

On the other hand, using the molar composition (H_2, CO, CO_2, CH_4 and air) of the gases generated, the low calorific value has been calculated. These results are collected in Table 2.

Table 2. Lower Heating Value of the gases generated

T, ºC	LHV (kJ/Nm^3)
600	11488.5
700	11000.8
800	8959.9
900	8956.1
1000	8846.3

From Table 2 it can be inferred that the use of higher temperatures is not interesting if the aim is to produce an energetic gas. The decrease in the heating value could be associated with the cracking of gases as CH_4, as it has been suggested [3], and also due to the strong decrease observed in the CO content of final gas.

In Figure 5 the influence of temperature on the power generated (in W) is plotted. This parameter is strongly influenced by the gas flow rate generated. One can observe that the temperature increase produces a strong increase of the generated power. This result is interesting for the design of an industrial plant of glycerine reforming, because the power is increased one hundred percent with increasing temperature from 600 to 1000 ºC. However, the energy consumption would be higher as the temperature is increased. In this sense, the participation of a catalyst in the reaction medium could reduce the temperature and thus to diminish the energy consumption in the global process. We are studying the cited effect using catalysts derived of Ni.

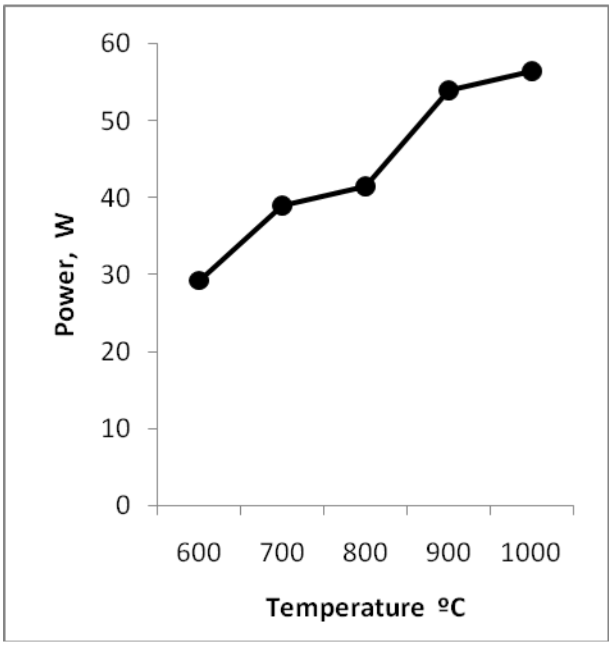

Figure 5. Influence of temperature on the generated power (WFGR = 12:1, Q= 2.5 cm^3 min^{-1}).

Conclusions

Glycerine reforming at higher temperatures (temperatures in the range 600-1000 ºC, WFGR = 12:1, Q= 2.5 cm^3 min^{-1}) was investigated in this work with the aim of to produce an hydrogen-rich gas. A molar fraction of 61.3 % was obtained for a temperature of 1000 ºC. Increasing temperature gave place to a strong increase in H_2 production and the decrease of CO and CH_4 probably due the participation of secondary reactions that modify the final gas composition. From the results obtained, a decrease of lower heating value of gas was observed with the increase of temperature. However the power generated from the gas increased, which is interesting for the design of industrial plant.

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