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Hydrogen production by means pyrolysis and steam gasification of glycerol

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Abstract. The objectives of this work were to optimize the variables affecting pyrolysis and steam gasification of glycerol (by-product formed during biodiesel production); and to characterize the gaseous phase formed, in order to carry out its energetic use. The studied operation variables were reaction temperature (700-900 ºC), water flow rate (0-0.173 g·min^{-1}), glycerol flow rate (0.009-0.676 g·min^{-1}) and carrier gas (nitrogen) flow rate (30-180 cm^3·min^{-1}). The most interesting phase (analyzed by gas chromatography) was the gas fraction. In this work, gas fraction was composed by H_2, CH_4, CO, C_2H_6, C_2H_4 and CO_2. The main gas generated was the hydrogen. Its generation was favoured by steam presence and its yield was increased in 224% in relation with pyrolysis process (default of water steam). The better conditions for studied process were 800 ºC, 0.074 g·min^{-1} of water flow rate, 0.009 g·min^{-1} of glycerol flow rate and 60 cm^3·min^{-1} of nitrogen flow rate. In these conditions, the volume of synthesis gas was 1.86 L·$(g_{glycerol})^{-1}$ and its higher heating value (HHV) was 26.70 MJ· $(kg_{glycerol})^{-1}$. This study indicated that the bio-glycerol is an excellent raw material in the obtaining of medium heating value gases. These gases could be used as fuel in industrial furnaces or domestic use.

Key words

Hydrogen production, glycerol, pyrolysis, steam gasification.

1. Introduction

Biodiesel is an alternative fuel to petrodiesel technically feasible, economically competitive, environmentally acceptable and easily available. For these reasons, biodiesel is attracting increasing attention world wide as a blending component or a direct replacement for diesel fuel in vehicle engines [1]. Globally, current energy policies reflect environmental issues including developing environmentally friendly technologies and increasing energy security and clean energy supplies. The implementation of the current directives about biodiesel triggers a huge demand for biodiesel [2].

The main way to make biodiesel is the transesterification of vegetable oils and animal fats. In this way the triglycerides from the feedstock react with a short-chain alcohol to form fatty acid methyl ester and glycerol. The reaction turn a mol of triglyceride into a mol of glycerol, in fact, 100 tons of glycerol per 1000 tons of biodiesel are obtained when transesterification occurs [1]. Glycerol is a highly versatile product and has a lot of uses. Almost two third of the industrial uses of glycerol are in food and beverage (23%), personal care (24%), oral care (16%) and tobacco (12%) [3]. In this way, the glycerol marketing would have a positive impact on the biodiesel manufacturing cost. However, the increasing available amount of glycerol due to the rapid growth of the biodiesel production has provoked a huge excess in glycerol market. In fact, the worldwide production of glycerol was more than 0.9 million tons in 2006, and in 2010 its production is estimated as high as 1.2 million tons [4]. This huge excess triggers glycerol market price depreciation because of this market is unable to absorb high amounts of the product. For these reasons and because of the glycerol contains impurities, the biodiesel industries are managing the glycerol excess as a waste. Therefore they suffer the impact of the increasing storage and management costs [5]. Taking into account these problems, it is important to explore other alternatives able to valorize high amount of glycerol. One of these glycerol valorization alternatives is its conversion into hydrogen.

Hydrogen is an environmentally friendly fuel as a feedstock for ammonia-based fertilizers or other chemicals as well as is gaining widespread applications with the advent of fuel cell technologies. At present, almost 95% of the world's hydrogen is produced from fossil fuels, hence, to develop an alternative source of hydrogen is very interesting [6]. Glycerol is a potential feedstock to produce hydrogen because 1 mol of glycerol can theoretically produce up to 4 mol of hydrogen. The main methods for the production of hydrogen from glycerol are pyrolysis [7-9], steam reforming [10-12], dry reforming [13], autothermal reforming [14], aqueous-phase reforming [15] and supercritical water reforming [16].

Pyrolysis consists of the oxygen free thermal cracking of substance and at high temperature; the obtained products are in the three phases: gaseous, liquid and solid. Gas phase is composed mainly by hydrogen, carbon monoxide, carbon dioxide and methane, the liquid phase is composed by hydrocarbons like ethylene, acetylene, and the solid phase is char. The most important phases are gas and liquid [7]. Gas fraction is normally the most important and usually content high amount of H_2 or high amount of the mixture H_2+CO (synthesis gas). Syngas could be used as a feedstock in Fischer-Tropsh synthesis to produce green diesel (long chain hydrocarbon). Pyrolysis has been studied by different authors; for example, Valliyappan et al.[8] carried out the pyrolysis of glycerol; it was observed that temperature, carrier flow rates and particle diameter of packing material had profound effects on the conversion of glycerol as well as product distribution. Moreover, this study indicated that the glycerol has potential in making syngas and medium heating value gases. Pyrolysis of mixtures of bio-oil and glycerol was also reported [9].

On the other hand, the steam reforming or steam gasification is the most commonly used method for producing hydrogen in the chemical industry. In this process, the substrate is reacted with steam, the gasifying agent, to produce, as by pyrolysis, hydrogen, carbon monoxide, carbon dioxide and methane, and to a lesser extent liquid and solid phases [10]. Thermodynamic analysis of steam gasification of glycerol has been performed, founding that the process at atmospheric pressure is favoured in high temperature and high water/glycerol ratio, having this parameter the most important effect on H_2 yield. Under these conditions methane production is minimized and the carbon formation is thermodynamically inhibited. Moreover, glycerol with possible contaminants (chloride and sodium ions) present in crude glycerine as byproducts of biodiesel synthesis was tested in the reformer, producing similar results [17, 18]. On the other hand, catalytic steam has been tested. This process gets the valorization of glycerol in economic and effective way. The catalysts usually used are metal supported on metallic oxides [19].

The aim of this study is to produce hydrogen by pyrolysis and steam gasification of glycerol and, in this way, to revalorize the byproduct of biodiesel.

2. Materials and Methods

A. Experimental Section

Glycerol (PRS) was supplied by Panreac and α-alumina with diameter 20 mm (filler material), by Keratec Advanced Materials S.A. Carrier gas (N_2 5.0) and gases for chromatograph calibrate (H_2 5.0, CH_4 3.5, CO 3.7, CO_2 4.5, C_2H_4 2.8, C_2H_6 2.5) were supplied by Linde.

Experimental set-up, similar to previous works [20, 21] is shown in Figure 1. Reactor consisted of a cylindrical tube of stainless steel 316. It was arranged vertically and its sizes were 75.5 cm longitude, 5.2 cm internal diameter and 6.0 cm outer diameter. At the top, it had a suspension system of the basket where filler material (α-alumina) was contained, maintaining the tightness of system. Also at the top were located, on the one hand, N_2 gas and water-glycerol solution feeding systems; and on the other hand, the thermocouple for temperature control inside reactor. After the first reactor was a second reactor in series. The aim of this was to increase residence time at reaction temperature. Its dimensions were 36.0 cm longitude, 5.2 cm internal diameter and 6.0 cm outer diameter. It also contained a thermocouple for temperature control and accessories to collect liquid and gas phases. Reactors were provided with heating systems, consisting of ceramic furnace and power source. Temperature was controlled to within ± 2 ºC automatically, and all experiments were carried out isothermally.

Each experiment consisted of pyrolysis-gasification of a glycerol solution. Water-glycerol flow rate was supplied to the system using a KONIC pump, calibrated previously. In first reactor, the basket filled with porous material (alpha alumina) was located. The role of porous material was to increase the contact surface between glycerol and water vapor. Following the launch of carrier gas flow rate, heating system was connected at programmed temperature reaction. Once temperature was reached, water-glycerol feeding system was connected to desired flow.

At this time, samples of non-condensable gases were analyzed chromatographically until concentrations remained constant, that is, until steady state.

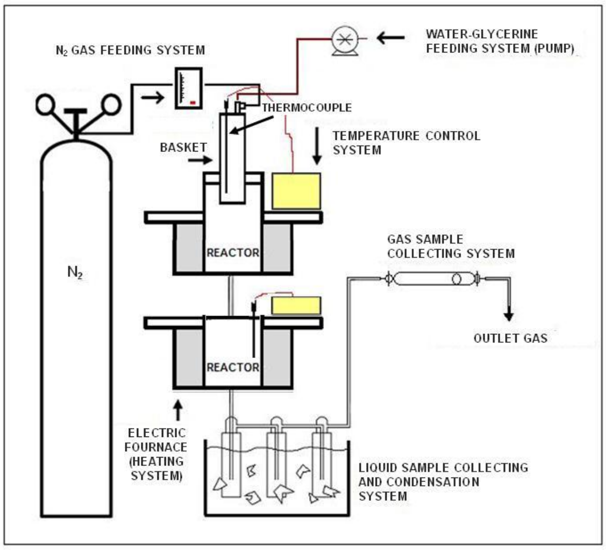

Fig. 1. Experimental set-up.

B. Product analysis

Gas phase was assayed by gas chromatography in a VARIAN 3900 chromatograph, provided with a thermal conductivity detector and automatic injector by air-actuated valve (Valco 2 positions). Silica semi-capillary column of 50 m length, 0.53 mm ID, and 0.50 μm film thickness was employed. Carrier gas was argon at a flow rate of 0.7 $mL\cdot min^{-1}$. Injector temperature was kept at 200 ºC, and the detector temperature, 160 ºC. Temperature ramp starts with 40 ºC during 7 min, then

55 °C·min^{-1} up to 150 °C during 20 min.

On the other hand, higher heating value, HHV, of syngas was calculated. Heating value of fuel is the amount of heat released in complete combustion of a fuel unit, 1 kg if it is a solid or liquid fuel and 1 m^{3}N (at 0 °C and 760 mmHg) in the case of a gaseous fuel. Gaseous fuels are mixtures of simple combustible components, and therefore, its heating value is deduced with sufficient precision and accuracy from the percentage volume composition by its heats of combustion. Knowing the composition of gas produced (H_2, CO, CH_4, C_2H_6, C_2H_4 and CO_2), we should take into account the following combustion reactions:

$$CO + 1/2O_2 \rightarrow CO_2 \qquad +0.2827\ \text{MJ/mol} \qquad (1)$$

$$H_2 + 1/2O_2 \rightarrow H_2O_{(l)} \qquad +0.2856\ \text{MJ/mol} \qquad (2)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(l)} \qquad +0.8895\ \text{MJ/mol} \qquad (3)$$

$$C_2H_6 + 7/2O_2 \rightarrow 2CO_2 + 3H_2O_{(l)} \qquad +0.1561\ \text{MJ/mol} \qquad (4)$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O_{(l)} \qquad +0.1411\ \text{MJ/mol} \qquad (5)$$

According to the above, HHV (MJ·kg$_{\text{glycerol}}^{-1}$) is given by equation (6):

$$HHV = 0.2827 \cdot nCO + 0.2856 \cdot nH_2 + 0.8895 \cdot nCH_4 + 0.1561 \cdot nC_2H_6 + 0.1411 \cdot nC_2H_4 \qquad (6)$$

where *nX* represents mols of each gas generated per 1 kg of glycerol.

3. Results and Discussion

The studied operation variables were reaction temperature (700, 800, 850, 900 °C), water flow rate (0, 0.030, 0.074, 0.173 g·min^{-1}), glycerol flow rate (0.009, 0.030, 0.074, 0.173, 0.676 g·min^{-1}) and carrier gas flow rate (30, 60, 120, 180 cm^3·min^{-1}).

As mentioned previously, three phases (gas, liquid and solid) are obtained from the pyrolysis and gasification processes of organic matter. However, since the objective of this research is hydrogen production, the presentation and discussion of results will primarily focus on gas phase production and its composition.

Solid phase consists of solid residue formed in small quantities on filler material, and liquid fraction consists of complex organic products, mainly tars, and it was collected together with water process.

As had been indicate the gas fraction, analyzed chromatographically, was mainly composed by H_2, CH_4, CO, C_2H_6, C_2H_4 and CO_2.

A. Temperature influence

To study temperature influence, experiments at 700, 750, 800 and 900 °C were tested. In all cases we employed water-glycerol total flow rate of approximately 0.247 g·min^{-1}, with 30% by weight of glycerol (0.074 g·min^{-1}) and carrier gas flow rate was set at 60 cm^3·min^{-1}. Specific values of mass and volume flow rates, used in each experiment, are reflected in figure captions.

Figure 2 shows temperature effect on syngas composition during gasification of glycerol. It can be seen that H_2 production changed from 35 to 50.3% when temperature increased from 700 to 800 °C, and then it remained constant from this temperature.

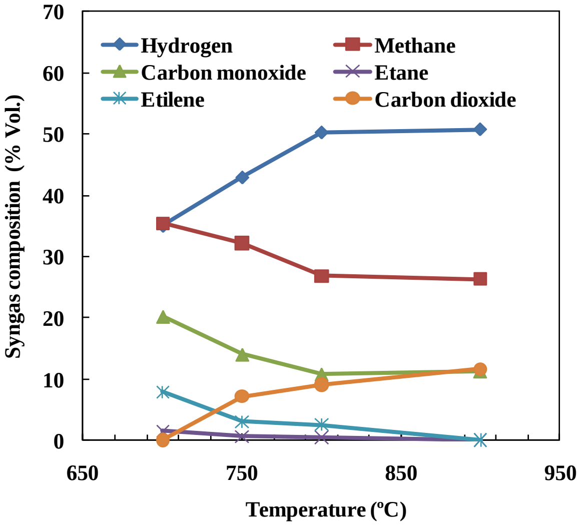

Fig. 2. Influence of temperature on syngas composition. Reaction conditions: water flow rate, 0.173 g·min^{-1}; glycerol flow rate, 0.074 g·min^{-1}; carrier gas flow rate, 60 cm^3·min^{-1}.

However, CO production at 700 °C was 20.22%, decreasing to 10% at 800 °C, after which it remained almost unchanged. On the other hand, hydrocarbons production decreased when temperature increased: CH_4 production was reduced from 35.43 to 17.54%, C_2H_6 production of 1.46 to 0% and C_2H_4 production of 7.88 to 0% when the temperature increased from 700 to 900 °C. Thus, an increase in temperature from 700 to 800 °C gave rise to an increase in H_2 and CO_2 productions, while for the rest there was a decline. These facts are due to cracking suffering by glycerol and hydrocarbons of low boiling when temperature increases. Specifically, the increase in H_2 production could be due to decomposition of hydrocarbons CH_4, C_2H_6 and C_2H_4 to coke and to H_2, as reflected in the reaction (7) [8, 22-24]. Moreover, this explains the decrease in generation of CH_4, C_2H_6 and C_2H_4, and even the total decomposition of C_2H_6 and C_2H_4 at 900 °C.

$$C_xH_y \Leftrightarrow mH_2 + nC_s \qquad (7)$$

From 800 °C syngas composition remained almost unchanged, however volume of syngas and percentage of glycerol converted were significantly improved at 900 °C (see Table I). That is, when temperature increased from 800 to 900 °C, the amount of glycerol converted was increased; thereby obtaining a syngas volume higher, but its composition was practically identical to composition of syngas obtained at 800 °C.

As can be seen in Table I, higher heating value of syngas increased when reaction temperature was increased. As explained previously, HHV of gases is a function of moles of H_2, CO, CH_4 and other hydrocarbons, produced per kilogram of pure raw material (see equation (6)). Although CO and CH_4 productions decreased in the syngas, amount of this gas phase increased with temperature. Therefore, quantitatively the amount of these three gases increased, causing an increase in HHV global of gas obtained.

Table I.- Operating conditions and results in steam gasification of glycerol.

OPERATING CONDITIONS				**RESULTS**		
T, ºC	**Water, g·min^{-1}**	**Glycerol, g·min^{-1}**	**Carrier gas, cm^3·min^{-1}**	**Glycerol reacted yield, %**	**Gas volume, L·g$_{glycerol}$$^{-1}$**	**HHV gas, MJ·kg$_{glycerol}$$^{-1}$**
700	0.173	0.074	60	73.46	0.79	15.22
750	0.173	0.074	60	78.64	1.03	18.95
800	0.173	0.074	60	83.26	1.26	21.28
900	0.173	0.074	60	97.98	1.59	26.70
800	0	0.074	60	81.51	1.14	15.08
800	0.030	0.074	60	85.66	1.23	17.68
800	0.074	0.074	60	91.89	1.35	20.59
800	0.074	0.009	60	92.20	1.83	25.64
800	0.074	0.030	60	96.17	1.45	20.86
800	0.074	0.173	60	70.43	0.92	15.80
800	0.074	0.676	60	75.55	0.88	16.45
800	0.074	0.009	30	93.32	1.86	26.39
800	0.074	0.009	120	64.74	1.24	14.04
800	0.074	0.009	180	54.78	0.93	9.35

Taking H_2 production as variable to maximize, the optimal temperature would be 900 ºC. It is even doubt what would have happened if the temperature had increased even more. However, we must take into account the limitations of reactor materials and their wear with increasing temperature. Another consideration, obviously, is the energy expenditure. In these circumstances, we opted for a compromise situation, choosing a temperature of 800 ºC to carry out the study of the other variables influence.

B. Water flow rate influence

In this series, all experiments were performed at 800 °C with a nitrogen flow rate of 60 cm^3·min^{-1} and glycerol flow rate of 0.074 g·min^{-1}.

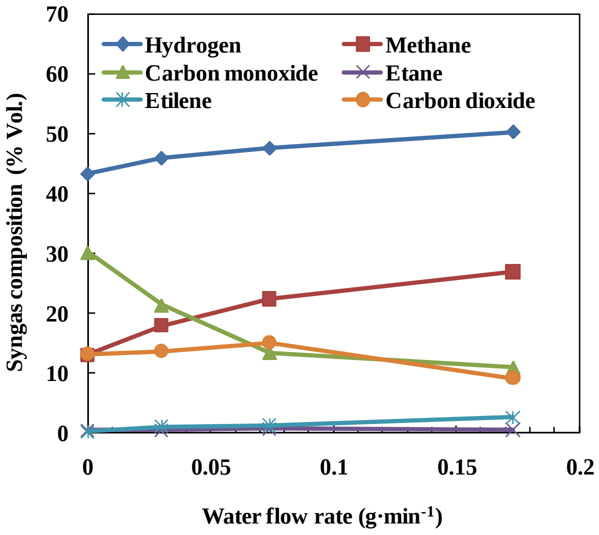

Fig. 3. Influence of water flow rate on syngas composition. Reaction conditions: temperature, 800 ºC; glycerol flow rate, 0.074 g·min^{-1}; carrier gas flow rate, 60 cm^3·min^{-1}.

In Figure 3, effect of gasifying agent (steam) flow on composition of gas phase is shown. It is observed that there was a mild increase in H_2 production (from 43.3 to 50.3%) when amount of water was from 0 (pyrolysis) to 0.173 g·min^{-1}. CO_2 production remained virtually constant. CO production decreased sharply (from 30.1% to 13.3%) when glycerin increased from pyrolysis to gasifying with water flow rate of 0.074 g·min^{-1}, when gasifying agent flow further increased, CO production continued to decline but more slow. Hydrocarbons production increased when water flow was increased. In the case of C_2H_6 and C_2H_4, this increase was not pronounced. However, CH_4 production increased from 13% when the operation was performed without gasifying agent, to 26.9% when water flow rate was 0.173 g·min^{-1}.

As can be seen in Table I, gas volume generated (1.35 L·g$_{glycerol}$$^{-1}$) and process yield (91.89%) reached the maximum when water flow rate was 0.074 g·min^{-1}. Probably, steam addition enhances the distribution of reagents through the filler material, causing a greater number of reactions and an improvement in the thermal cracking of glycerol. From this maximum, gas production and process yield decreased, probably due to a decrease in residence time of reagents when amount of water increased. The increase in H_2 production and the decrease in CO production were probably due to the reaction occurring between CO and steam to produce CO_2 and H_2, water gas shift reaction (8).

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad -41\ \text{kJ/mol} \qquad (8)$$

HHV of gas phase increased when water vapor was introduced into the system, up to a water flow rate of 0.074 g·min^{-1}. This is because CH_4 production doubled in the same interval. This gas has a HHV higher than H_2 and CO and, consequently, an increase in total count of HHV was produced. From 0.074 g·min^{-1} HHV increased but less sharply, because the main gases (H_2, CH_4 and CO) did not change over their productions.

The gas produced with the highest percentage in moles (or volume) of H_2 was obtained with a water flow rate of 0.173 g·min^{-1}. With a water flow rate of 0.074 g·min^{-1}, a lower percentage of H_2 was obtained in the gas mixture, but also a greater volume of gas was generated which leads to the relationship between them produced bigger amount of H_2 per gram of glycerol. Thus, we chose a flow rate of 0.074 g·min^{-1} to carry out the study of the other variables.

C. Glycerol flow rate influence

All experiments, in this study, were performed at 800 °C with a nitrogen flow rate of 60 cm^3·min^{-1} and water flow rate of 0.074 g·min^{-1}.

Figure 4 shows that as when glycerol flow rate was increased, H_2 production decreased (from 60.3% to 36.2% across the range tested). CO_2 production showed the same trend, however, the production of other gases increased when the amount of glycerol increased. This behavior could be because the water exerts a limiting effect as gasifying agent. Thus, by increasing glycerol flow rate, water flow rate remains in default, causing part of the glycerol undergo a thermal cracking, that is, a simple pyrolysis.

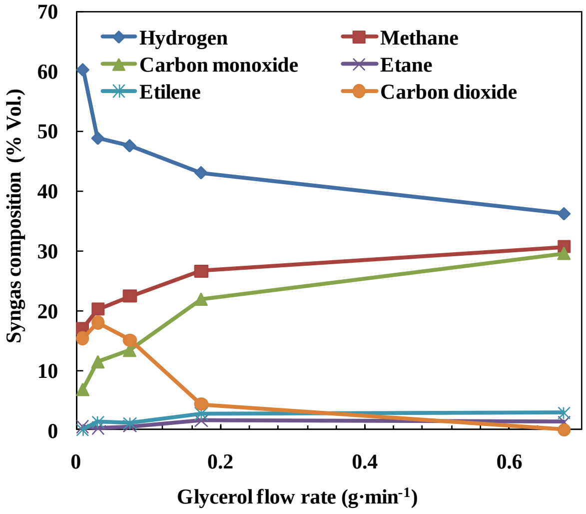

Fig. 4. Influence of glycerol flow rate on syngas composition. Reaction conditions: temperature, 800 ºC; water flow rate, 0.173 g·min^{-1}; carrier gas flow rate, 60 cm^3·min^{-1}.

In addition, increasing the ratio of glycerol/water flows are likely to impede the distribution of the reactants through the fill material, resulting in less intimate contact and worse reaction conditions. In this context, it should consider the main reactions involved in the reforming of glycerol with steam [25, 26]. In addition to the reactions (7) and (8), we should consider the following:

$$C_3H_8O_3 + 3H_2O \Leftrightarrow 7H_2 + 3CO_2 \quad +128\text{kJ/mol} \quad (9)$$

$$C_3H_8O_3 \Leftrightarrow 4H_2 + 3CO \quad +250\text{ kJ/mol} \quad (10)$$

$$C + H_2O \Leftrightarrow CO + H_2 \quad +131\text{ kJ/mol} \quad (11)$$

$$C + 2H_2 \Leftrightarrow CH_4 \quad -75\text{ kJ/mol} \quad (12)$$

$$CO + 3H_2 \Leftrightarrow CH_4 + H_2O \quad -206\text{ kJ/mol} \quad (13)$$

$$CO_2 + 4H_2 \Leftrightarrow CH_4 + 2H_2O \quad -165\text{ kJ/mol} \quad (14)$$

$$C + CO_2 \Leftrightarrow 2CO \quad +172\text{ kJ/mol} \quad (15)$$

In the experiments with glycerol flow rate equal or less than water flow rate, a yield of 93% was observed, whereas when glycerol flow rate exceeded water flow rate, yields fell to 70% (see Table I). These facts can be explained by reactions (9) and (10). According to (9), if water vapor is the limiting reagent, the hydrogen formation would be conditioned by this fact. In the absence of water vapor (or otherwise) reaction (10), regardless of their strong endothermic, acquire ownership, and this would explain the increasing of CO formation in syngas. Finally, (regardless of route pyrolysis) CH_4 formation would be affected by reactions (12) to (14). Specifically, reaction (13) could be of key importance when operating in conditions where CO concentration is very high.

HHV of gas fraction decreased with increasing glycerol flow rate. As shown, the amount of H_2 produced decreased and the amounts of CH_4 and CO increased. However, the decrease rate of H_2 production was much greater than the growth rate of CH_4 and CO productions, causing a global decrease in HHV of syngas.

Given the amount of H_2 produced as variable to maximize, we can conclude that must be operated in conditions of water vapor excess. Therefore, to carry out the study of carrier gas flow influence, we chose to work with 0.009 g·min^{-1} of glycerol.

D. *Carrier gas flow rate influence*

As is know, this variable is one of the most important for optimizing gasification processes because it is directly related to residence times [8, 16, 27-29]. In this experimental series, operating conditions were 800 ºC, water flow rate of 0.074 g·min^{-1} and glycerol flow rate of 0.009 g·min^{-1}.

With regard to the composition of gas produced, it remained practically constant, only a slight decrease in CH_4 and H_2 productions were observed, when nitrogen flow rate was increased.

By increasing carrier gas flow rate, residence time of the components in the reactor decreases, which produces, on the one hand, a poor distribution of the reagents on the filler material and, secondly, a decrease in time reaction. This fact was reflected in the volume of gas phase and its yield, because they decreased when nitrogen flow rate was increased (see Table I). Moreover, as the nitrogen flow rate was increased, more amount of glycerol did not react, probably because his time spent in the reactor was too small to give it time to react.

Similarly, HHV of gas produced decreased when the carrier gas flow was increased. In this case, this decrease was due to a decrease in the amounts generated of H_2 and CH_4, and to a decline in the volume of gases generated per weight of glycerol.

When carrier gas flow rate was reduced below 60 cm^3·min^{-1} significant changes were not observed. Probably below this value, the residence time is sufficiently large so that process was chemically controlled, that is, residence time would ensure that the reagents could react at the speed of reaction that marked the thermodynamic conditions. Thus, in these conditions, an increase of gas volume and of its HHV could not be reached. Similarly, significant variations in the composition of syngas were not appreciated.

4. Conclusions

In the study of pyrolysis and steam gasification of glycerol, tested in this research, syngas was consisted of H_2, CH_4, CO, C_2H_6, C_2H_4 and CO_2, and H_2 was the majority (and the objective of this research). Temperature and steam/glycerol flows relation exerted greater influence. Carrier gas flow rate did not significantly influence on products distribution, but it influenced on quantity and HHV of syngas: when carrier gas flow decreased, these increased.

An increase in reaction temperature produced a marked increase in gas fraction production. This was because condensable gases suffered a sharp cracking when temperature increased. In addition, increasing temperature favors the most interesting reactions to the process. As with the water flow, temperature had a positive influence across the range: quantity and HHV syngas increased always, and H_2 production did it to 800 ºC (at higher temperatures there was not variability in composition gas).

Presence of water vapor produced a notable increase in syngas yield, since the steam favors cracking of heavy hydrocarbons, reforming of methane and other reactions with carbonaceous solid residue. In fact, the increase in water/glycerol flows ratio gave rise to increased syngas production. Within range of variability used, water flow rate has always had a positive effect on the amount and HHV of syngas. Hydrogen increased its production by 224% in gasification process with respect to that produced in pyrolytic process (without water).

Volume of syngas ranged from 0.79 to 1.86 $L\cdot(g_{glycerol})^{-1}$; and its HHV did it between 9.33 and 26.70 $MJ\cdot(kg_{glycerol})^{-1}$. Therefore, this study proves that bio-glycerol is suitable for generating syngas with medium calorific value by steam gasification. This gas could be used as fuel in industrial furnaces or domestic use.

Although H_2 production obtained in this research was very high, it would be desirable to try different catalysts to increase the selectivity towards hydrogen formation from production of the rest.

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