Gasification of Crude Glycerol after Salt Removal

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ABSTRACT: The increase in the amount of crude glycerol available on the market, as well as the decrease in its purity due to the use of waste materials in the production of biodiesel, has forced producers to look for alternative ways of valuing this byproduct. In this research work, crude glycerol of a Portuguese biodiesel producer was pretreated using an ion exchange process in order to reduce its salt content. The gasification process was performed using steam as the oxidizing agent in a down-flow fixed-bed reactor using alumina particles as bed material. After the gasification process, the producer gas flowed through a condensing and cleaning system, in order to remove the condensable fraction. Dry gas samples were collected and analyzed by GC in order to quantify the CO, CO_2, CH_4, and H_2 content. Three different feed mixtures were studied with 35%, 39%, and 59% (w/w) water, and the tests were performed at 850, 900, and 950 °C. The results showed that the increase of the water content in the feed mixture led to higher values of H_2 and CO_2, and lower values for CO and CH_4, on the producer gas composition. A slight increase of dry gas yield and hydrogen conversion efficiency with the increase of water content in the feed was observed, while the lower heating value of producer gas decreased. No significant influence of water content was detected in the carbon conversion efficiency and cold gas efficiency. The increase of temperature resulted in the increase of four gasification parameters with maximum mean values of 90% for carbon conversion efficiency, 100% for hydrogen conversion efficiency, 107% for cold gas efficiency, and 1.3 m^3/kg raw material. The maximum lower heating value of 14.5 MJ/m^3 was obtained at 850 °C.

1. INTRODUCTION

In Portugal, biodiesel is the biofuel with the greatest impact on the market. In 2017, the biodiesel sector registered the highest production ever in the country, at 355828 t, where 49% was obtained from virgin oils and 51% from residual matter such as waste cooking oils or animal fat. It was the first time for the Portuguese biodiesel industry that the use of waste materials for biodiesel production exceeded that for virgin oils (Figure 1).[1]

European directives have driven the dynamic of the biofuels sector and biodiesel in particular. However, in the past decade, the biodiesel industry has faced several sustainability and product problems. The use or incorporation of residual matter in biodiesel production is a key requirement for biodiesel producers, since it represents a predominant issue in sustainability criteria. However, the use of residues as part of raw material results in a lower quality of both biodiesel and crude glycerol, a byproduct which represents 10% (w/w) of the conventional process. For this reason, the crude glycerol market price has suffered a huge decrease. In Portugal, the crude glycerol market has become even less competitive, with an estimated decrease above 50% of its liquid value in the past five years. At this moment, it is imperative to find energetic and economic alternatives for its valorization.

Crude glycerol differs from other glycerol nomenclatures since its composition is about 80% of glycerol ($C_3H_8O_3$), and the remaining 20% may be methanol, water, MONG (matter organic non-glycerol), and salts. Due to the low purity of crude glycerol, high-energy costs are required for its purification, which leads to the need to find new valorization alternatives.[2]

Gasification, a partial oxidation process performed at high temperatures, seems to be a feasible option for crude glycerol valorization. This thermochemical process allows for the conversion of residual raw materials into a combustible gas mixture, along with residual fractions of char (solid phase) and bio-oil/tars (liquid phase). The producer gas is mainly composed by hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4). Residual amounts of light hydrocarbons could also be formed (C_nH_m). There are several gasification agents that can be used on the process, such as air, oxygen, steam, and carbon dioxide.[3]

There has been remarkable growth in the experimental research of technical glycerol (product with glycerol content higher than 98%) gasification, possibly in order to study the process feasibility and to extrapolate to the crude glycerol. However, there are few studies regarding the effective use and valorization of crude glycerol, particularly related with noncatalyzed steam gasification in fixed-bed reactors.

Suero et al. (2015) studied crude glycerol steam gasification, reaching conclusions about the influence of the bed temperature (600−900 °C), feed flow rate (0.5−3.0 mL/min), and water/glycerol ratio on the process performance and on the composition of the producer gas. The results showed that higher temperatures contribute for water−gas and water−gas shift reactions and H_2 concentration. Regarding the feed flow rate, with a rate of 3.0 mL/min, an increase in gas production and a decrease in H_2 was obtained.[4]

Sabio et al. (2011) studied the influence of bed temperature (682−1018 °C), water/glycerol ratio (0.7−3.3 w/w), and feed flow rate 8.5−35.5 mL/min on the performance of non-catalyzed crude glycerol steam gasification. The authors concluded that the bed temperature and water/glycerol ratio
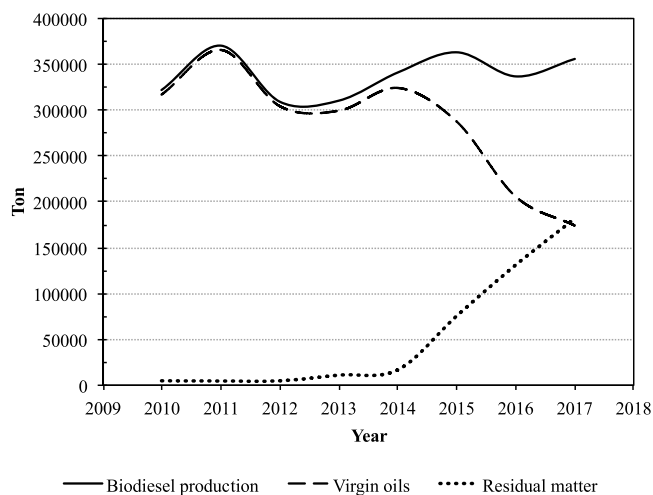
Figure 1. Statistical data regarding the biodiesel industry behavior in the past decade.[1]

have the primary roles in the producer gas composition. The increase of both resulted in an increase of H_2 and CO_2 and in a decrease of CO and CH_4.[5]

Dou et al. (2010) compared crude and technical glycerol steam gasification, with and without dolomite as catalyst, using a fixed-bed reactor between 400−700 °C. Without using a catalyst, for results obtained up to 600 °C, crude glycerol conversions were higher than those obtained for pure glycerol. At 700 °C, both glycerol and pure glycerol gasification presented raw material conversions close to 100%.[6]

There are many other studies, such as those by Demsash et al.,[7] Bastan et al.,[8] Ghani et al.,[9] Wang et al.,[10] Yus et al.,[11] Veiga and Bussi,[12] and Rémon et al.,[13] regarding glycerol gasification but with a catalyst performance approach.

Regarding other technologies involving the valorization of crude glycerol, among many studies the following are worth mentioning. Zhang et al.[14] studied the decomposition of glycerol using a rotating DC arc plasma reactor to produce syngas, Tamošiūnas et al.[15] investigated the crude glycerol gasification using direct current thermal arc plasma, with steam and air as oxidizing mediums. Dianningrum et al.[16] performed a comparative study between technical glycerol and crude glycerol gasification using supercritical water.

In this work, the crude glycerol steam gasification was studied in a down-flow fixed-bed reactor after a crude glycerol salt treatment. The influence of water content in the feed and the bed temperature were evaluated in the gasification process.
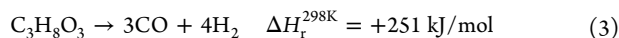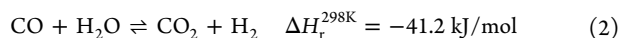
2. MATERIALS AND METHODS

2.1. Process Modeling. Depending on the reactor type and on the oxidizing agent, the overall gasification process includes different steps that can be sequential or simultaneous, i.e., drying, devolatilization, gasification, and combustion. After the devolatilization step, the released products will participate in the homogeneous and heterogeneous gasification reactions.

The global glycerol steam reforming reaction is given by the following eq 1.

$$C_3H_8O_3 + 3H_2O \rightarrow 7H_2 + 3CO_2 \quad \Delta H_r^{298K} = +128 \text{ kJ/mol} \tag{1}$$
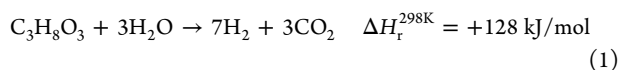
This global reaction results from the addition of two important gasification reactions, namely, water−gas shift reaction 2 and glycerol decomposition reaction 3.[17,18]

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H_r^{298K} = -41.2 \text{ kJ/mol} \tag{2}$$

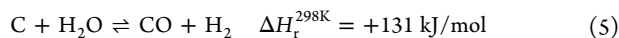$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \quad \Delta H_r^{298K} = +251 \text{ kJ/mol} \tag{3}$$

These reactions, eqs 2 and 3, are part of a complex gasification mechanism. There are many others that can also occur and could have influence in the whole process, as follows:[3,17−20]

Glycerol hydrogenolysis:

$$C_3H_8O_3 + 2H_2 \rightleftharpoons 2CH_4 + CO + 2H_2O$$
$$\Delta H_r^{298K} = -160 \text{ kJ/mol} \tag{4}$$
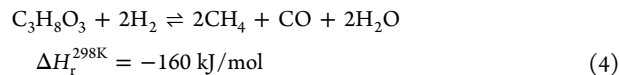
Steam char reaction or H_2O gasification:

$$C + H_2O \rightleftharpoons CO + H_2 \quad \Delta H_r^{298K} = +131 \text{ kJ/mol} \tag{5}$$

Methane steam reforming:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta H_r^{298K} = +206 \text{ kJ/mol} \tag{6}$$

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \quad \Delta H_r^{298K} = +165 \text{ kJ/mol} \tag{7}$$

Methane dry reforming:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad \Delta H_r^{298K} = +247 \text{ kJ/mol} \tag{8}$$

2.2. Gasification Parameters. In crude glycerol steam reforming, the global carbon and hydrogen mass balances are given through the following equations:

$$\dot{m}_{\text{raw material}} + \dot{m}_{H_2O} = \dot{m}_{\text{ashes}} + \dot{m}_{\text{cf}} + \dot{m}_{\text{gas}} \tag{9}$$

$$\dot{m}_{\text{raw material}} \times x_{C_{\text{raw material}}} = \dot{m}_{\text{ashes}} \times x_{C_{\text{ashes}}} + \dot{m}_{\text{cf}} \times x_{C_{\text{cf}}} + \dot{m}_{\text{gas}} \times x_{C_{\text{gas}}} \tag{10}$$

$$\dot{m}_{\text{raw material}} \times x_{H_{\text{raw material}}} + \dot{m}_{H_2O} \times x_{H_{H_2O}}$$
$$= \dot{m}_{\text{ashes}} \times x_{H_{\text{ashes}}} + \dot{m}_{\text{cf}} \times x_{H_{\text{cf}}} + \dot{m}_{\text{gas}} \times x_{H_{\text{gas}}} \tag{11}$$

where $\dot{m}_{\text{raw material}}$ is the mass feed flow rate in a dry basis. The raw material is defined as the organic matter in the feed (such as glycerol and MONG), $\dot{m}_{H_2O}$ is the mass flow of the oxidizing agent in the feed (steam), and $\dot{m}_{\text{ashes}}$, $\dot{m}_{\text{cf}}$, and $\dot{m}_{\text{gas}}$ are the mass flow of generated ashes, the condensable fraction, and the producer gas, respectively. The variables x_{Ci} and x_{Hi} are the carbon and hydrogen mass fractions of each stream (i).

In order to assess the process performance, five gasification parameters were defined:[3]

(a) Carbon conversion efficiency:

$$\eta_C = \frac{MM_C \times A}{x_{C_{\text{raw material}}} \times \dot{m}_{\text{raw material}}} \tag{12}$$

where A is the total molar flow of carbon-bearing components (CO_2, CO, CH_4) present in the producer gas and MM_C is the molar mass of carbon.

(b) Hydrogen conversion efficiency:

$$\eta_H = \frac{MM_H \times B}{x_{H_{\text{raw material}}} \times \dot{m}_{\text{raw material}}} \tag{13}$$

where B is the total molar flow of hydrogen-bearing components (H_2, CH_4) present in the producer gas and MM_H is the hydrogen molar mass.

(c) Dry gas yield (m^3/kg of raw material db):

$$Y = \frac{\dot{V}_g}{\dot{m}_{\text{raw material}}} \tag{14}$$

where $\dot{V}_g$ is the volumetric flow rate of producer gas (0 °C, 1 atm) (m^3/s).

(d) Cold gas efficiency:

$$\eta_g = \frac{\dot{V}_g \times HHV_g}{\dot{m}_{raw\ material} \times HHV_{raw\ material}} \tag{15}$$

The HHV_g is the higher heating value of the producer gas (kJ/m^3) and $HHV_{raw\ material}$ is the higher heating value (kJ/kg) of the raw material.

(e) Lower heating value of producer gas (MJ/m^3):

$$LHV_g = y_{H_2} \times LHV_{H_2} + y_{CO} \times LHV_{CO} + y_{CH_4} \times LHV_{CH_4} \tag{16}$$

where y_i is the volumetric fraction of component i present in the producer gas and LHV_i is its lower heating value.

2.3. Raw Materials Characterization. The high variability of physicochemical properties of the raw materials and all the process conditions of the biodiesel production determine the quality of both biodiesel and crude glycerol. For this reason, the chemical composition of the crude glycerol becomes an important factor when the focus is its thermochemical valorisation. In the gasification process, the salt content of the feed may contribute to increase reactor corrosion, to increase carbonization phase formation, or to increase toxic emissions. Therefore, the crude glycerol salt content should be determined and, if necessary, reduced or eliminated.

Crude glycerol of a Portuguese biodiesel producer was pretreated in order to reduce the salt content, using a two-stage ion exchange process composed by a bed of strong cationic resin in series with a bed of strong anionic resin. In the first stage, a strong acid cation resin gel type (Amberlite IR120), with a minimum total exchange capacity of 2 mol/L, was used in order to reduce the content of potassium and sodium cations. The cationic ion exchange was performed in an acrylic column with 28.7 mm of internal diameter and 593 mm of length. The bed volume was kept between 230 and 255 cm³. In the second stage, the reduction of the anion content was done using a strong base type 1 anion exchange resin (Indion GS300) with a minimum total exchange capacity of 1.3 mol/L. Tests were performed using an acrylic column with 31.2 mm of internal diameter and 598 mm of length. In both steps, treated glycerol samples were collected and qualitatively analyzed by energy dispersive X-ray fluorescence (EDXRF).

Table 1 shows the crude glycerol characterization before and after salt removal using the ion exchange process. Crude glycerol after salt removal presents higher water content than expected because water was used in the displacement rinse after the resins regeneration. The ion exchange process seems to be a feasible option for crude glycerol salt removal, before gasification processes.

2.4. Methodology. After salt removal, the treated crude glycerol gasification process was performed using steam as the oxidizing agent in a down-flow fixed-bed reactor, with a length of 500 mm and internal diameter of 54 mm, operating at atmospheric pressure. Alumina particles, with a mean diameter of 5.9 mm, were used as bed

Table 1. Crude Glycerol Characterization before and after the Ion Exchange Process

	crude glycerol (%, w/w)	crude glycerol after salt removal (%, w/w)	method
carbon	31.07	25.70	ISO 16948
hydrogen	7.97	9.24	–
glycerol	76.1	59.4	BS5711-3
water	8.8	34.5	ASTM D4377
ash	6.8	0.4	ASTM D482
sulfur	0.96	0.07	EDXRF
sodium	2.3	0.1	flame photometry
potassium	0.6	<5 ppm	–
chloride	4.0	0.05	potentiometry
HHV (kJ/g)	13.8	10.7	ASTM D240

material supported by a perforated plate located 100 mm above the bottom of the reactor. The height of the bed was 300 mm, and an external 4 kW electrical resistance was used for bed heating. The crude glycerol/water mixture was continuously stirred in an open tank, and the mixture was fed up to the reactor through a peristaltic pump. The mixture was introduced into the upper chamber of the reactor, 100 mm above the bed. This zone is at about 500 °C, so the mixture vaporizes and the chemical decomposition process begins immediately.

After the gasification process, the producer gas flowed through a condensing and cleaning system, composed of a heat exchanger followed by a condensate tank, with propan-2-ol and water, and two empty flasks, all immersed in an ice bath, in order to remove the condensable fraction (Figure 2). Then, the dry producer gas passed through two columns (filters) with activated carbon, glass wool, and silica gel before its flow rate was measured by an Alicat flow meter (FIT). Dry gas samples were collected (S) and analyzed by a GC-TCD in order to quantify the CO, CO_2, CH_4, and H_2 content.

The effect of glycerol gasification temperature (850−950 °C) and the influence of water content on the feed were studied, using a fixed feed flow rate of 3.6 g/min for all the tested mixtures. The mixtures were prepared by adding, to the treated crude glycerol, the required amount of water to reach the desired water content in the feed. Three mixtures were tested with water contents of 35%, 39%, and 59% (w/w).

3. RESULTS AND DISCUSSION

3.1. Composition of Producer Gas. For all the tested glycerol−water mixtures, the increase of bed temperature resulted in an increase of H_2 and CO_2 concentrations and a decrease of CO and CH_4 concentrations in the producer gas (Figures 3−5).

Bed temperature has a decisive role on gasification processes, particularly in kinetics, and the producer gas composition will directly depend on the gasification temperature. In the tested temperature range (850−950 °C), the water−gas shift reaction 2 has an already-known fundamental role on the producer gas composition. As mentioned in previous works,[21] at those temperatures, the equilibrium constant of water−gas shift is close to 1, which means that in a near-equilibrium situation it is very sensitive to the concentrations of reagents and products involved on it, and Le Châtelier's principle can be applied. For example, an increase in water concentration will favor the forward direction of this reaction and the production of CO_2 and H_2. Besides, the increase of bed temperature, above 700 °C, potentiates methane steam reforming (eqs 6 and 7) and methane dry reforming (eq 8) reactions, which can contribute to the production of CO, H_2, and CO_2 and the consumption of CH_4 and CO_2 as well. For instance, for the mixture with 35% (w/w) of water in the feed, the increase of bed temperature from 850 to 950 °C resulted in an increase (v/v) from 42% to 48% of H_2 and from 8% to 11% of CO_2 and in a decrease from 41% to 34% of CO and from 12% to 11% of CH_4 (Figure 3).

Regarding the effect of water, an increase of H_2 and CO_2 concentrations and a decrease of CO and CH_4 concentrations on producer gas were observed with the increase of water content in the feed mixture. This behavior may be justified by the water−gas shift reaction 2 as mentioned above. No significant changes were observed for producer gas composition between the samples with 35% and 39% (w/w) of water. For the highest amount of water tested, and at a bed temperature of 950 °C, values of 51% for H_2, 26% for CO, 9% for CH_4, and 15% for CO_2 concentrations (all in v/v) were obtained in the producer gas. Therefore, as a consequence of
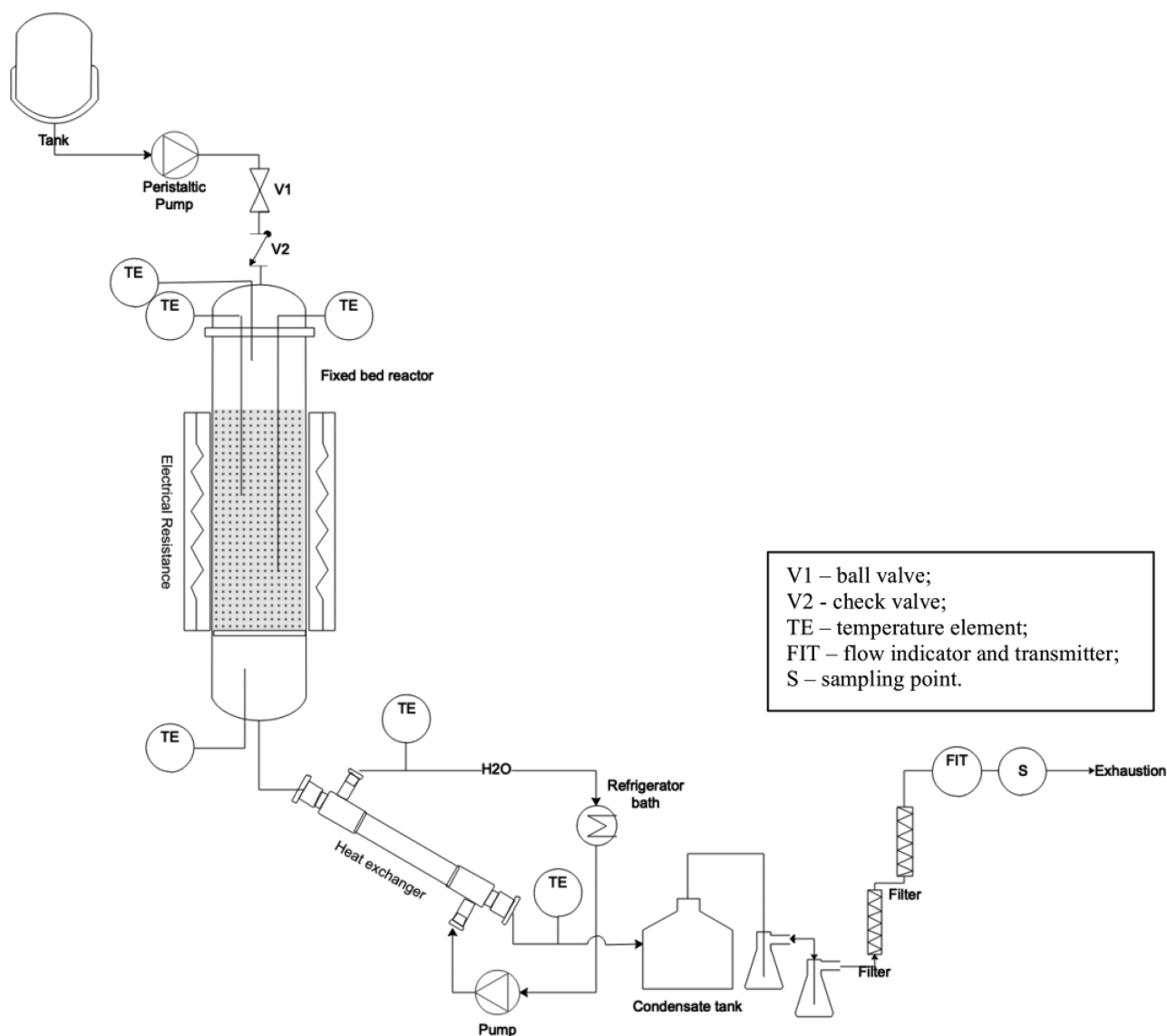
Figure 2. Schematic diagram of the gasification experimental apparatus.
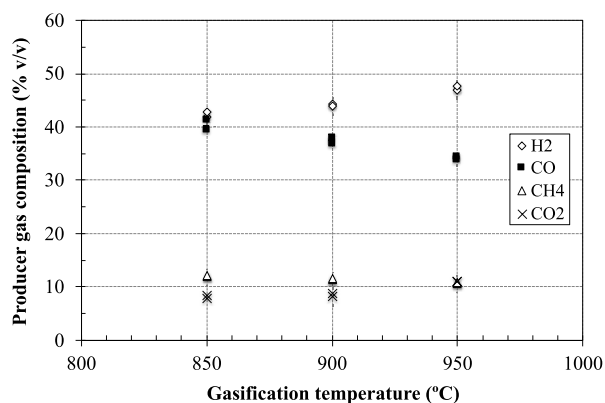

Figure 3. Composition of producer gas obtained from crude glycerol gasification with 35% (w/w) of water in the feed.
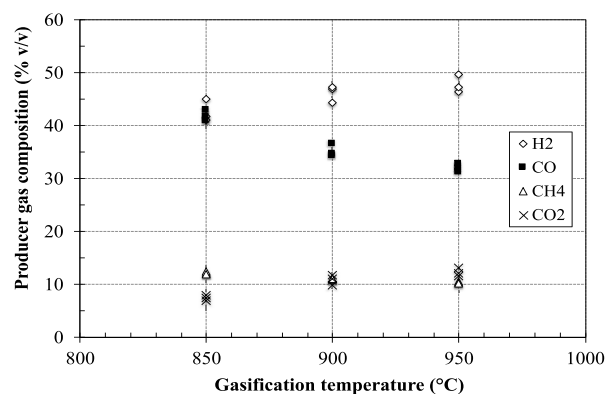

Figure 4. Composition of producer gas obtained from crude glycerol gasification with 39% (w/w) of water in the feed.

producer gas composition, the H_2/CO (v/v) ratio presented values between 1.3 and 2 along the tested temperatures (Figure 6).

3.2. Gasification Parameters. The increase of bed temperature from 850 to 950 °C also contributed to the increase of four of the gasification parameters (carbon conversion efficiency, hydrogen conversion efficiency, cold gas efficiency, and dry gas yield). An increase in carbon
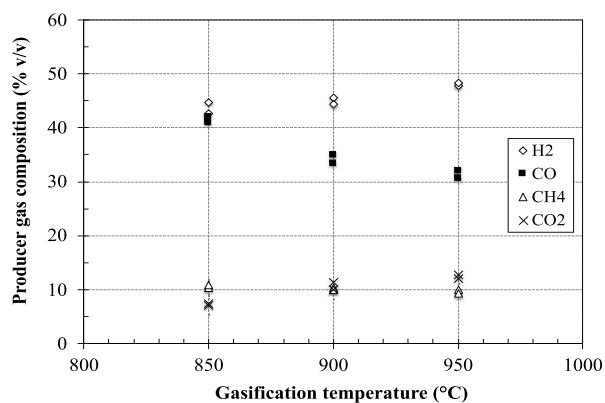
Figure 5. Composition of producer gas obtained from crude glycerol gasification with 59% (w/w) of water in the feed.
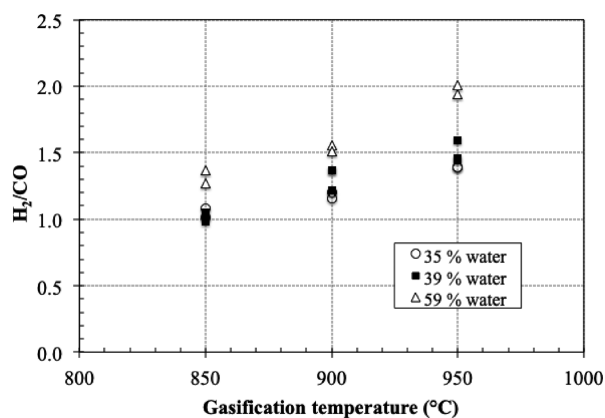

Figure 6. H_2/CO ratio obtained from the three tested mixtures of crude glycerol and water.

conversion efficiency (Figure 7) with the increase of temperature was observed, and mean values from 78% to 90% were obtained. The slight differences obtained between the three tested mixtures at 850 °C were completely narrowed with the increase of temperature.

The hydrogen conversion efficiency (Figure 8) increases with the increase of temperature and water content in the feed stream. This parameter gives information about the amount of hydrogen produced. When the gasifying agent used is water, hydrogen may be added to the producer gas resulting from
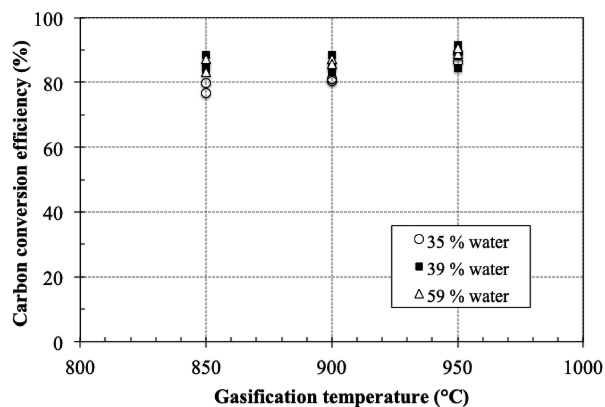

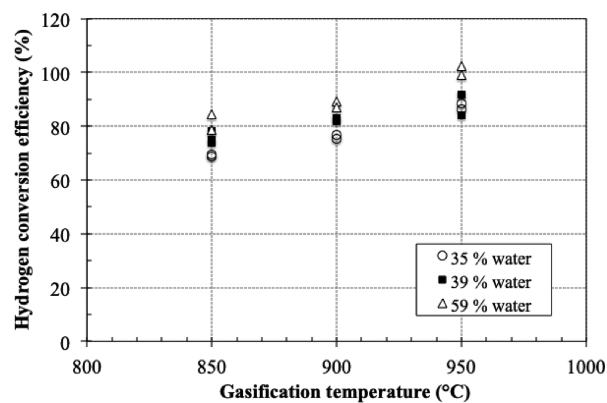**Figure 7.** Effect of temperature and water in the feed on carbon conversion efficiencies.

Figure 8. Effect of temperature and water in the feed on hydrogen conversion efficiencies.

steam dissociation and high values may be obtained for this parameter. Maximum values were obtained with the mixture containing 59% of water, and values in the 80% to 100% range were obtained. For the mixture with 35% of water, values in the 70% to 85% range were obtained.

Cold gas efficiency increased with the temperature rise and values from 90% to 110% were obtained (Figure 9). The effect of water content was detected only for tests performed at 850 °C. At this temperature, low values of cold gas efficiency were obtained with the mixture of 35% of water. By definition, cold gas efficiency (eq 15) is a measure of chemical energy content in raw material transferred to the producer gas. It is not an indicator of the overall process thermal efficiency, and because it does not take into account the energy required to generate steam and heat the reactor, values higher than 100% can be obtained when steam is used as gasifying agent, especially because steam dissociation can also contribute for the increase of hydrogen concentration on the producer gas. Under these conditions, it is possible that more thermal energy may be added to the producer gas, resulting from increased hydrogen production, than it is lost through the small amount of char and tar formed.[22]

Cold gas efficiency values obtained at 950 °C reflect both the high degree of hydrogen and carbon conversions obtained at this temperature. On the other hand, overall values of cold gas efficiency can replicate the degree of uncertainty associated with the determination of the higher heating value (HHV) of
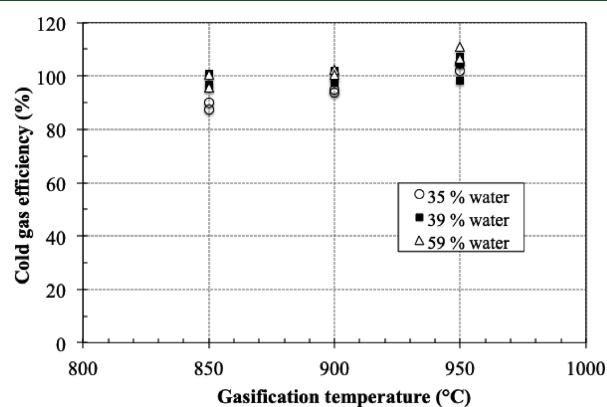

Figure 9. Effect of temperature and water in the feed on cold gas efficiency.

glycerol, due to its high-water content and also due to the uncertainty in determining such water content.

For the dry gas yield (Figure 10), which relates the total amount of producer gas with the raw material content in the feed, a direct relation with the water content in the feed mixture was observed. The increase of water content resulted in better dry gas yield values. The highest values were obtained with 59% of water, with values comprised between 1.1 and 1.3 m^3/kg of raw material (Figure 9). This behavior can be justified by the fact that the increase in temperature favors the reactions of hydrogen formation and the production of gas phase.

Concerning the lower heating value of the producer gas (Figure 11), a reduction from 14.5 to 12 MJ/m^3 with the increase of bed temperature was observed, as a consequence of changes in its volumetric composition. With the increase of temperature a rise in the hydrogen (smaller individual LHV [lower heating value]) content and a decrease in the methane content (highest individual LHV) in the producer gas were observed. The increase of water content from 39% to 59% may result in a reduction of about 1 MJ/m^3 on the LHV of the producer gas.

Overall results showed that the crude glycerol gasification after a salt removal step by ion exchange processes could be a realistic and feasible alternative for crude glycerol valorization. The parameters that assess the gasification performance revealed very good results, of the same order of magnitude of those obtained for technical glycerol (glycerol content >98%) gasification,[21] if the same base of calculation is used (organic matter in the feed). Moreover, with these two sequential steps, operational problems related to salt depositions observed inside the gasifier, mentioned in a previous study by the authors on crude glycerol gasification,[23] were completely eliminated. Thus, the importance of salt removal has a direct impact on the resolution of the operating problems associated with salt deposition inside the reactor. No significant differences were observed in the gasification parameters when compared to the values obtained in the crude glycerol gasification.[23]

4. CONCLUSIONS

Crude glycerol of a Portuguese biodiesel producer was pretreated in order to reduce the salt content. Afterward, steam reforming of treated crude glycerol was studied in a down-flow and fixed-bed reactor.
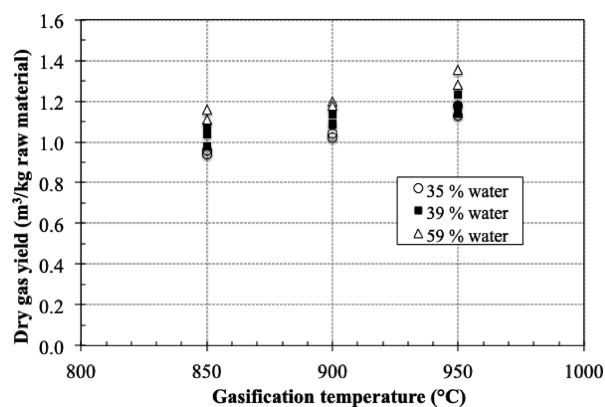

Figure 10. Effect of temperature and water in the feed on dry gas yield.
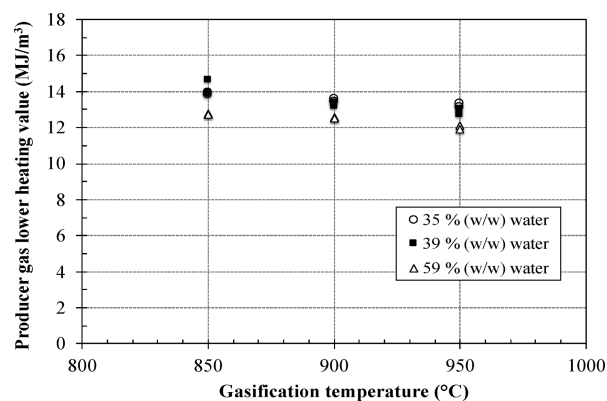

Figure 11. Effect of temperature and water in the feed on the producer gas lower heating value.

For all the tested glycerol–water mixtures, the increase of bed temperature resulted in an increase of H$_2$ and CO$_2$ concentrations and a decrease of CO and CH$_4$ concentrations on producer gas. The same behavior was observed with the increase of water content in the feed mixture. For the highest amount of water content tested, and at a bed temperature of 950 °C, values of 51% for H$_2$, 26% for CO, 9% for CH$_4$, and 15% for CO$_2$ concentrations were obtained, resulting in a H$_2$/CO ratio from 1.3 to 2, along the tested temperatures.

The results have shown that the LHV of producer gas decreased with the increase of temperature with maximum mean value of 14.5 MJ/m^3 obtained at 850 °C. For the other four gasification parameters, an increase on its values with the temperature rise was observed. The highest values of the gasification parameters were obtained at 950 °C, using mixtures with 59% of water; values of 1.3 m^3/kg raw material for dry gas yield, 90% for carbon conversion efficiency, 100% of hydrogen conversion efficiency, and 107% for cold gas efficiency were obtained.

The results revealed that the gasification of crude glycerol seems to be a feasible option after the ion exchange process, reducing supplementary energetic and economic costs, with the addition of water as the oxidizing agent for the gasification process.

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