

Catalytic co-gasification of glycerol/fat mixtures: A preliminary study

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Keywords: Glycerol, fat, co-gasification, dolomite

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Abstract: In this work, the co-gasification of treated crude glycerol and animal fat was studied using steam as the gasifying agent. Tests were performed in a downflow fixed bed reactor with a bed composed of catalyst particles of dolomite. The gasification process was studied using a mixture with 59% of glycerol, 3% of fat and 38% of water and tests were carried out at 700 °C and 750 °C.

The producer gas was quantified and analysed by gas chromatography obtaining, for the tested temperatures, between 48% and 47% of H₂, about 13% of CO, 11% of CH₄ and CO₂ content between 30% and 27%. The results showed that the use of dolomite as a catalyst promotes the production of a gas rich in H₂ and CO₂.

The results also show that the gasification parameters increase with temperature having obtained at the maximum working temperature a gas production yield of 0.92 m³/kg at 750°C, a cold gas production efficiency of 70.6% and for the carbon and hydrogen conversion efficiencies the values obtained were 58.0 % and 40.9% respectively.

Keywords: glycerol, fat, gasification, dolomite

1. Introduction

In Portugal more than 39 thousand tons of crude glycerol were produced in 2019 as a by-product of the biodiesel production industry. The crude glycerol produced in this process is of low purity and its purification process is not economically viable. The current surplus of low-quality crude glycerol, combined with the difficulty of its valuation and reuse, is the basis of the sharp drop in its commercial value, observed worldwide.

The tanning industry also produces considerable amounts of solid waste, mainly lime fleshings and green fleshings, containing about 40% (dry basis) of low-value fat and generating more than 2,000 tons of fat in 2019. Fat can be used as a raw material for the production of biodiesel, but animal fat has a high content of saturated carbon chains that generate a biodiesel with a high cold filter plugging point. On the other hand, its direct burning is not a disposal solution since it is not permitted by law. Currently, a large part of this waste is sent to landfill.

This work aims to find a solution for the valorization of these by-products/wastes through a thermochemical conversion process. The co-gasification of glycerol/animal fat mixtures appears, then, as an option for energy recovery of a by-product and as a possibility of disposing of a waste for which, currently, there are no sustainable options.

Crude glycerol gasification is not yet sufficiently studied. Sabio [1] and Suero [2] have studied the influence of some parameters on the performance of non-catalysed crude glycerol steam gasification. Concerning the catalytic glycerol gasification there are other published studies [3-7].

Concerning to animal fat, gasification published works are scarce. Almeida [8] studied the cogasification of mixtures of glycerol and animal fat with various fat mass fractions, 3%, 5% and 10% between temperatures of 800 °C and 950 °C, in a fixed bed reactor of alumina particles using steam as a gasification agent. The study concluded that the best values obtained for the gasification parameters were verified for 3% fat content and at a temperature of 950 °C.

Several studies show that the use of catalysts in gasification reduces the content of methane and tars in the production gas and maximizes the concentration of hydrogen and carbon monoxide. Typical catalysts in this type of processes are alkali metals, carbonates and nickel-based catalysts. One of the most studied catalysts in biomass gasification is dolomite.

Dou [9] studied the effect of using dolomite as a catalyst on the steam gasification of crude and technical glycerol, using a fixed-bed reactor.

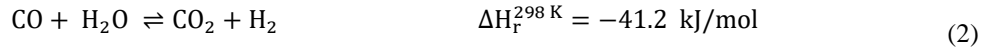
Perez [10] found that using dolomite as a catalyst the composition of the gas produced increased by 7% in H₂ and decreased by 7% in CO by volume. They also found that between 700 °C and 800 °C it was possible to obtain a conversion of tars of almost 100%, and that the activity of dolomite after being calcined increased 10 times compared to non-calcined dolomite.

Several studies have concluded that, with calcined dolomite as a catalyst, there is an increase in the amount of H₂ and CO₂ in the gas produced, that by increasing the temperature, greater yields of gas production are obtained and that increasing the amount of catalyst generates a greater conversion of tars [11-13].

Andrés [14] carried out a study comparing 3 catalysts used in gasification: alumina, dolomite and olivine. According to this study, the activity of the catalysts in decreasing order is dolomite, alumina and olivine. All catalysts studied promote the reforming of tars and, the presence of alumina and dolomite increases the content of H₂ and CO in the producer gas, while the influence of olivine is minimal.

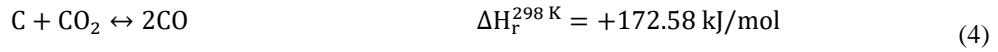
A gasification process involves several sequential steps that comprise a first phase of drying and devolatilization and then a second phase of homogeneous and heterogeneous reactions.

The global steam reforming reaction for glycerol (1) results from the combination of the water-gas shift reaction (2) and the glycerol decomposition reaction (3) [15-17].

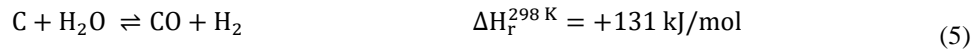


A typical gasification process follows a complex reaction mechanism and some of the typical reactions of gasification processes and the respective heats of reaction are presented below:

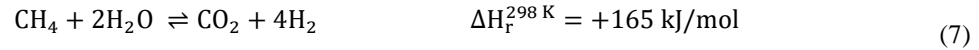
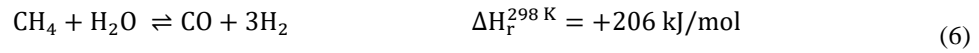
Boudouard reaction:



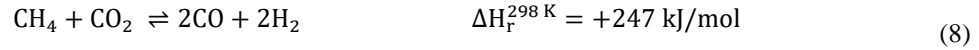
Steam char reaction:



Methane steam reforming:



Methane dry reforming:



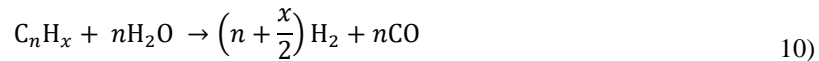
Tar reactions:

$$\Delta H_r^{298\text{ K}} = +[200 - 300] \text{ kJ/mol}$$

Thermal cracking:



Tar steam reforming:



Tar dry reforming:



Tar carbon formation:



In order to assess the co-gasification process, the following gasification parameters were defined:

Dry gas yield (m³/kg):

$$Y = \frac{\dot{V}_g}{\dot{m}_{Mat.Org} + \dot{m}_{Fat}} \quad (13)$$

The dry gas yield corresponds to the amount of gas produced by the amount of biomass fed to the gasifier on a dry basis where \dot{V}_g is the volumetric flow rate (m³/s) of producer gas (0 °C, 1 atm) and $\dot{m}_{Mat.Org}$ is the mass feed flow rate of crude glycerol (kg/s) and \dot{m}_{Fat} is the mass feed flow rate of animal fat (kg/s).

Cold gas efficiency (%):

$$\eta_g = \frac{\dot{V}_g \times HHV_g}{(\dot{m}_{Mat.Org} \times HHV_{Mat.Org}) + (\dot{m}_{Fat} \times HHV_{Fat})} \quad (14)$$

where HHV_g is the higher heating value of the producer gas (kJ/m³) and HHV_i is the higher heating value (kJ/kg) of glycerol and animal fat.

The cold gas efficiency measures the fraction of chemical energy present in the feed that has been transferred to the producer gas. Therefore, this gasification parameter is not a measure of the overall thermal efficiency of the process since, in its definition, the energy required to produce steam and to heat the reactor is not taken into account.

Higher heating value of producer gas (kJ/m³):

$$HHV_g = y_{H_2} \times HHV_{H_2} + y_{CO} \times HHV_{CO} + y_{CH_4} \times HHV_{CH_4} \quad (15)$$

where y_i is the volumetric fraction of component i present in the producer gas and HHV_i is its higher heating values (kJ/m³).

Carbon conversion efficiency (%):

$$\eta_c = \frac{MM_c \times A}{(x_{C_{Mat.Org}} \times \dot{m}_{Mat.Org}) + (x_{C_{Fat}} \times \dot{m}_{Fat})} \quad (16)$$

The carbon conversion efficiency represents the fraction of carbon fed to the reactor that is present in the producer gas where A is the total molar flow (kmol/s) of carbon-bearing components (CO₂, CO, CH₄) present in the producer gas, MM_c is the molar mass of carbon (kg/mol), $x_{C_{Mat.Org}}$ and $x_{C_{Fat}}$ are the carbon mass fractions (kg/kg) of organic matter in crude glycerol (glycerol and MONG) and the carbon mass fraction (kg/kg) in animal fat, respectively.

Hydrogen conversion efficiency (%):

$$\eta_H = \frac{MM_H \times B}{(x_{H_{Mat.Org}} \times \dot{m}_{Mat.Org}) + (x_{H_{Fat}} \times \dot{m}_{Fat})} \quad (17)$$

The hydrogen conversion efficiency represents the fraction of hydrogen present in the reactor feed found in the producer gas where B is the total molar flow (kmol/s) of hydrogen-bearing components (H₂, CH₄) present in the producer gas, MM_H is the hydrogen molar mass (kmol/kg) and x_{H_i} is the hydrogen mass fraction (kg/kg) of glycerol and animal fat.

In addition to the gasification parameters, the indicators H₂/CO ratio and the gas phase yield and liquid phase yield were defined.

The H₂/CO ratio represents the molar ratio between hydrogen and carbon monoxide in the gas produced. This indicator assesses the ability of a gas to be converted into liquid fuels using the Fischer-Tropsch process, the higher the ratio H₂/CO, the better the gas will be to integrate this process.

The gas and liquid phase yields are indicators that allow quantifying the fraction of feed that has been converted to the gas phase and the one that remained in the condensate phase.

2. Materials and Methods

2.1. Raw material

In this work, two raw materials were used: treated crude glycerol and animal fat.

The fat used is a waste from the tanning industry and it was supplied by a technological centre for the Portuguese leather industry (CTIC). This type of fat has a high percentage of saturated carbon chains, for fat in question about 40% of its glycerides, being solid at room temperature.

The crude glycerol used in this work was supplied by a Biodiesel production company and was previously subjected to a pre-treatment process, using a two-stage ion exchange process, in order to reduce its salt content. This step is important because the high initial salt content present in the crude glycerol favors the appearance of operational problems (reactor clogging and corrosion) during the gasification process.

Crude glycerol and animal fat characterizations are presented in Table 1.

Table 1. Crude glycerol and animal fat characterization.

Total Basis [% (w/w)]	Crude Glycerol	Animal Fat
Carbon	27.07	74.76
Hydrogen	9.12	11.93
Water	35.8	1.0
Ash	0.07	1.01
Sulphur	<0.01	< 0.01
Sodium	0.03	0.2
Potassium	<0.01	<0.01
Calcium	-	0.3
Chloride	0.04	-
HHV [kJ/g]	9.3	39.1

2.2 The catalyst

Dolomite is a primary catalyst widely used in gasification processes. It is a mineral mainly composed of magnesium carbonate and calcium carbonate ($MgCO_3CaCO_3$) that is especially attractive for its low cost, for being disposable and for substantially reducing the amount of tar content and increase the H_2 content in the gas produced by gasification. The composition of dolomite varies depending on its origin, but it is usually composed of 30% calcium oxide, 21% magnesium oxide and 45% carbon dioxide by weight. In addition to these components, dolomite also contains traces of silicon oxide, iron (III) oxide and aluminum oxide [18]. Dolomite can be calcined giving rise to the formation of MgO (21.3%) and CaO (30.4%) due to CO_2 loss. Mass loss tests were carried out, placing the catalyst in the muffle for two hours at successively higher temperatures, in order to understand at what temperature the calcium and magnesium carbonates, of the dolomite structure, would pass to calcium and magnesium oxides, by release of CO_2 . Table 2 shows the results of the dolomite calcination tests.

Table 2. Results of dolomite mass loss tests by calcination.

Temperature (°C)	Mass loss (%)
550	0.6
650	1.8
700	4.2
750	11.9
800	27.4
900	44.9

After the calcination test, a change in appearance and texture was observed in the calcined dolomite, verifying that the sample loses hardness and some particles are easily reduced to dust by friction, a behavior that is representative of the presence of CaO and MgO. This behavior is an operating limitation to its use, as a bed of particles, in gasification tests at elevated temperatures.

2.3. Experimental tests

In this work, the co-gasification of treated crude glycerol and animal fat was studied using steam as the gasifying agent. Tests were performed in a fixed bed reactor with a bed composed of catalyst particles of dolomite. The gasification process was studied using a mixture with 59% of glycerol, 3% of fat and 38% of

water and tests were carried out at 700 °C and 750 °C. After the gasification tests, the dolomite bed was cleaned by calcination at 550°C for 2 h, in order to guarantee the removal of the carbonaceous residue and prevent the release of CO₂ with the consequent alteration of its texture. Details on experimental installation and tests can be consulted in Almeida [8].

3. Results

The effect of gasification temperature on producer gas composition, using dolomite as catalyst, was analysed. In figure 1 are presented the results for the average volumetric composition of producer gas, for the two tested temperatures. The results showed that the composition of the producer gas is quite influenced by the bed material used. As evidenced in several published studies, the use of dolomite as a catalyst promotes the production of a gas rich in H₂ and CO₂. The results also show that the increase in temperature favors a decrease in the average concentration of CO₂ from 30% to 27%, with a slight decrease in H₂ from around 48% to 47%. With the increase in temperature, no significant differences were observed for the concentration of CO and CH₄ in the production gas, with average values of around 13% and 11%, respectively.

These results may reflect the combination between the promotion of the water-gas shift reaction (2) and the intensification of the tar reform reactions (10, 11, 12), catalyzed by dolomite.

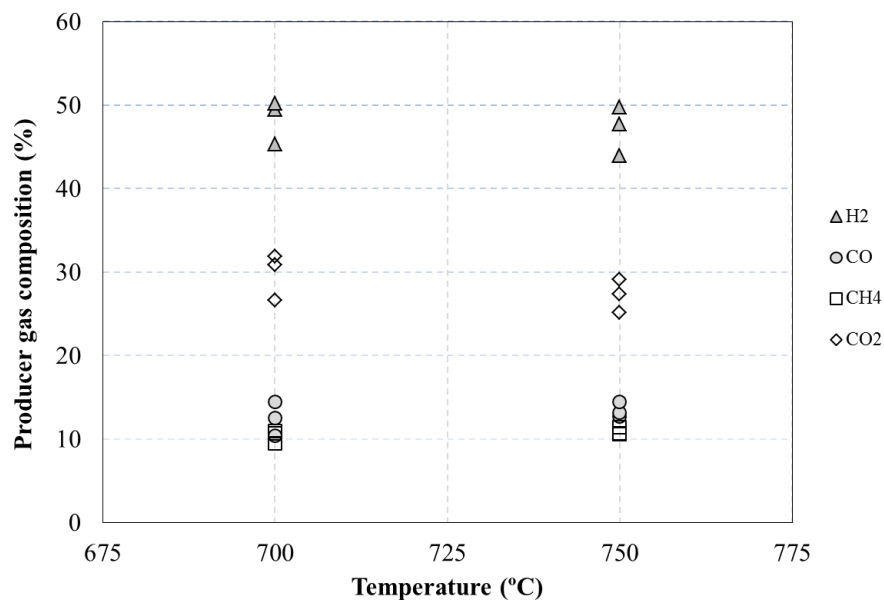


Figure 1. Effect of temperature on producer gas composition.

As a result of the producer gas having a low CO content and a high H₂ content, high values were obtained for the CO/H₂ ratio. For this indicator, at 700°C, the average value of 3.96 ± 0.8 was obtained and at 750°C the value of 3.50 ± 0.2 , making the gas produced using dolomite a good candidate to be used in a Fischer-Tropsch process.

The average values of the yields of the gas and liquid phases obtained at the studied temperatures are shown in Figure 2. The mass flow rate of the dry gas produced was measured experimentally and the mass flow rate of the liquid phase was estimated using the condensed mass quantified at the end of each test and the duration of the test. The results show that the increase in temperature favors the production of gas phase and the decrease in the production of the liquid phase, having obtained at 750°C an average value of about $47.0 \pm 7.5\%$ for the gas phase yield and $53.4 \pm 3.3\%$ for the liquid phase yield. These indicators present great experimental uncertainty but they reflect the behavior of the co-gasification process in the studied conditions.

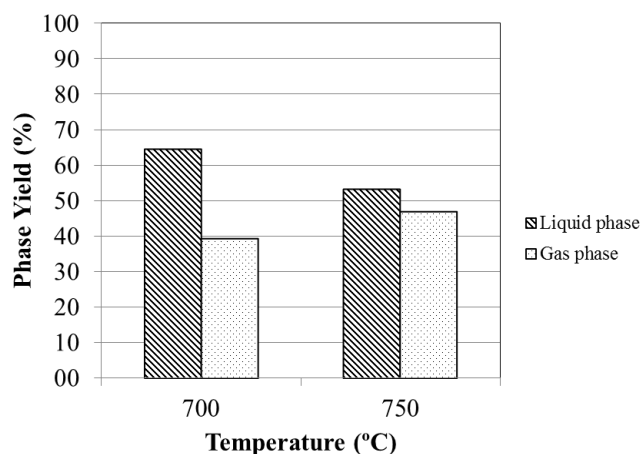


Figure 2. Effect of temperature on phase yields.

The performance of the co-gasification process was assessed using the following indicators: dry gas yield, higher heating value, cold gas efficiency, carbon and hydrogen conversion efficiencies. The mean values obtained for those parameters are presented in Table 3, for the two tested temperatures and, the results show that, in general, the gasification parameters increase with temperature.

Table 3. Effect of temperature on gasification parameters.

	700 °C	750 °C
Dry gas yield (m ³ /kg)	0.80±0.12	0.92±0.08
HHV (MJ/m ³)	11.9±0.4	12.1±0.6
Cold gas efficiency (%)	60.5±9	70.6±7.5
Carbon conversion efficiency (%)	51.5±7.9	58.0±3.8
Hydrogen conversion efficiency (%)	35.6 ±5	40.9 ±4.7

The increase in the dry gas yield is related to the increase in the gas phase yield, observed with the temperature rise. In fact, the molar flow rate of producer gas increased by about 16% with an increase in temperature from 700°C to 750°C.

The HHV of the producer gas is strongly influenced by the composition of the gas, since its value is directly related to the individual contribution of the HHV of each component of the gas produced. As there was no significant change in the composition of the producer gas with the increase in temperature, the HHV value also did not change.

The cold gas efficiency is the parameter that quantifies the chemical energy present in the feed that is transferred to the producer gas. The results show an increase in its average value from 60.5% to 70.6% with the increase in gasification temperature from 700°C to 750°C. This behavior is also directly linked to the increase in gas phase yield observed with the temperature rise.

The results show that the carbon and hydrogen conversion efficiencies increase with the increase in the temperature resulting in, at the maximum temperature tested, the average values of 58% and 40.9%, respectively. The relatively low values of these parameters can be related to the high liquid phase yield obtained under the tested conditions.

4. Conclusions

The results obtained in this study showed that the use of dolomite as a catalyst promotes the production of a producer gas with a high H₂ content and high H₂/CO mass ratio, making this gas an interesting candidate for the production of synthetic fuels. They also show that the use of dolomite as a catalyst enhances the values of the gasification parameters when compared, for example, with those obtained using a bed of alumina particles [8].

Although the results obtained are promising, it would be interesting to increase the operating temperature since the increase in temperature improves process performance.

Acknowledgments

This work was supported by Portugal 2020 - POCI-01-0145-FEDER-024067 and Fundação para a Ciência e Tecnologia – SFRH/BD/137913/2018.

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