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## Article

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Energy Reports

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Elsevier

*Suggested Citation:* Almeida, A.; Pilão, R.; Ramalho, E.; Ribeiro, A.; Pinho, C. (2020) : Co-gasification of glycerol/fat mixtures in a downflow fixed bed reactor: Preliminary results, Energy Reports, ISSN 2352-4847, Elsevier, Amsterdam, Vol. 6, Iss. 1, pp. 460-465, <https://doi.org/10.1016/j.egy.2019.09.008>

This Version is available at:

<https://hdl.handle.net/10419/243773>

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6th International Conference on Energy and Environment Research, ICEER 2019, 22–25 July,  
University of Aveiro, Portugal

## Co-gasification of glycerol/fat mixtures in a downflow fixed bed reactor: Preliminary results

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Received 25 July 2019; accepted 7 September 2019

Available online 18 September 2019

### Abstract

The aim of this work was to assess the technical viability of glycerol/fat co-gasification. The gasification performance was studied in a downflow fixed bed reactor using steam as oxidizing agent. Tests were performed with a mixture of 10% of fat and 52% of water, and the effect of temperature was evaluated in the 800 °C to 950 °C range. Samples of dry gas from the gasifier were collected and analysed by gas chromatography in order to determine the CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> content. The results revealed that the co-gasification of glycerol/fat mixtures seems to be a feasible technical option. Best results of the gasification parameters were obtained at the highest tested temperature, 950 °C.

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Peer-review under responsibility of the scientific committee of the 6th International Conference on Energy and Environment Research, ICEER 2019.

*Keywords:* Crude glycerol; Animal fat; Co-gasification; Steam reforming; Fixed bed

### 1. Introduction

The growth of biodiesel industry in Portugal has generated large quantities of crude glycerol. The current solution is the sale of this low purity by-product, which is not economically interesting. In 2018, crude glycerol production reached 32 684 t [1]. On the other hand, animal fat, extracted from wastes of the leather industry, is not currently valued.

In the leather industry one of the wastes with significant impact results from the mechanical operation called hide fleshings. In Portugal, it is estimated that 12 000 t/year of these wastes, the fleshings, are produced. The thermal hydrolysis of fleshings results into two phases, a protein hydrolysate and animal fat (ca. 1800 t/year). One common application of animal fats is transesterification for biodiesel production. However the incorporation of animal fat in this process is limited due to the presence of a high content of saturated carbon chains, which can generate a

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<https://doi.org/10.1016/j.egy.2019.09.008>

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final product with a high CFPP (cold filter plugging point) value, incompatible with the EN 14214 requirements. In addition, its direct burning is also not a viable solution since national law is very restricted. For this reason, a thermochemical conversion process could be a feasible alternative for animal fat valorization.

In this work are presented the preliminary results of the co-gasification of crude glycerol/fat mixtures. Gasification is a thermochemical process, which allows the conversion of high content carbon and hydrogen feedstock into value-added products, such as producer gas, through partial oxidation. The gasification process involves a complex sequence of steps and reactions, depending on operation conditions (such as temperature, pressure, gasifying agent) and reactor type. The following list represents the typical gasification reactions [2,3]:

Water-gas shift:



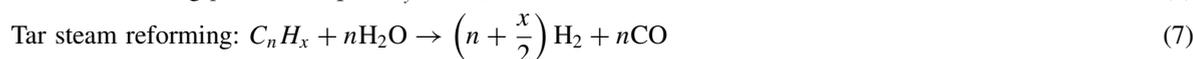
Steam char reaction or H<sub>2</sub>O gasification:



Methane steam reforming:



Methane dry reforming:



Based on product fractions and producer gas composition, the following gasification parameters were defined in order to assess the co-gasification performance [3]:

$$\text{Carbon conversion efficiency (\%): } \eta_c = \frac{MM_c \times A}{(x_{C_{Mat.Org}} \times \dot{m}_{Mat.Org}) + (x_{C_{Fat}} \times \dot{m}_{Fat})} \quad (10)$$

where  $A$  is the total molar flow (kmol/s) of carbon-bearing components (CO<sub>2</sub>, CO, CH<sub>4</sub>) 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 fraction (kg/kg) of organic matter in crude glycerol (glycerol and MONG) and the carbon mass fraction (kg/kg) in animal fat, respectively.  $\dot{m}_{Mat.Org}$  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).

$$\text{Hydrogen conversion efficiency (\%): } \eta_H = \frac{MM_H \times B}{(x_{H_{Mat.Org}} \times \dot{m}_{Mat.Org}) + (x_{H_{Fat}} \times \dot{m}_{Fat})} \quad (11)$$

where  $B$  is the total molar flow (kmol/s) of hydrogen-bearing components (H<sub>2</sub>, CH<sub>4</sub>) 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.

$$\text{Dry gas yield (m}^3\text{/kg): } Y = \frac{\dot{V}_g}{\dot{m}_{Mat.Org} + \dot{m}_{Fat}} \quad (12)$$

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

$$\text{Cold gas efficiency (\%): } \eta_g = \frac{\dot{V}_g \times HHV_g}{(\dot{m}_{Mat.Org} \times HHV_{Mat.Org}) + (\dot{m}_{Fat} \times HHV_{Fat})} \quad (13)$$

The  $HHV_g$  is the producer gas higher heating value ( $\text{kJ/m}^3$ ) and  $HHV_i$  is the higher heating value ( $\text{kJ/kg}$ ) of glycerol and animal fat.

Higher heating value of producer gas:

$$HHV_g = y_{H_2} \times HHV_{H_2} + y_{CO} \times HHV_{CO} + y_{CH_4} \times HHV_{CH_4} \quad (14)$$

where  $y_i$  is the volumetric fraction (%) of component  $i$  present in the producer gas and  $HHV_i$  is its higher heating value ( $\text{kJ/kg}$ ).

Although there is a slight growth of published studies regarding the crude glycerol steam reforming in a fixed bed reactor, as reported by Sabio et al. [4], Suero et al. [5] or Dou et al. [6] concerning to animal fat gasification it is not easy to find published works. There are some studies of gasification of oils [7–9] and about animal fat pyrolysis such as Hassen-Trablesi et al. [10] or Zhang et al. [11], but studies involving the co-gasification of both crude glycerol and animal fat were not found.

## 2. Materials and methods

### 2.1. Raw materials

Crude glycerol was acquired from a Portuguese biodiesel producer and an ion exchange process was performed in order to reduce its salt content. Animal fat was supplied by a technological centre for the Portuguese leather industry (CTIC – Centro Tecnológico das Indústrias do Couro). Table 1 presents the characterization of both raw materials used.

**Table 1.** Crude glycerol and animal fat characterization.

Total basis [% (w/w)]	Crude glycerol after salt removal	Animal fat
C	17.08	74.76
H	9.7	11.93
Glycerol	40.7	–
Water	57.6	1.0
Ash	0.13	1.01
Sulphur	0.12	<0.01
Sodium	0.05	0.2
Potassium	0.01	<0.01
Calcium	–	0.3
Chloride	0.09	–
Phosphorus	0.01	0.04
HHV [ $\text{kJ/g}$ ]	5.7	39.1

A mixture of 10% (w/w d.b.) of animal fat, 38% (w/w d.b.) of crude glycerol and 52% (w/w) of water was studied. Co-gasification of fat/glycerol was studied from 800 to 950 °C, using a mixture fixed flow rate between 2.28 and 2.37 g/min.

### 2.2. Experimental apparatus

The fat/glycerol/water mixture was heated (57 °C) and stirred before being fed up to the reactor. The co-gasification process was studied in a down flow fixed bed reactor, with 54 mm of internal diameter and 500 mm of length. Activated alumina particles were used as inert bed material. A 4 kW external electrical resistance provided the heating. After the gasification process, the product gas followed to a condensing system composed by a heat exchanger, a condensable tank with 500 mL of water and plastic Raschig rings, and two glass flasks, all immersed in an ice bath. After removing the condensable fraction, the producer gas flowed through two filters, the first with activated carbon and glass wool and the second with silica gel and glass wool. Then, the producer gas mass flow was measured in an Alicat flow meter (FIT) and samples were collected (S) for GC-TCD analysis. Fig. 1 shows the experimental apparatus.

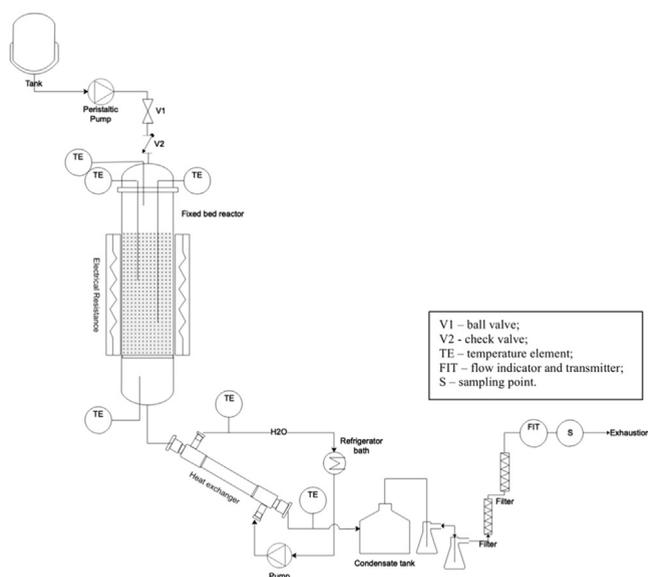


Fig. 1. Diagram of experimental apparatus.

### 3. Results and discussion

For each of the temperatures tested, 3 to 5 trials were performed. The effect of temperature on the average volumetric composition of producer gas is shown in Fig. 2.

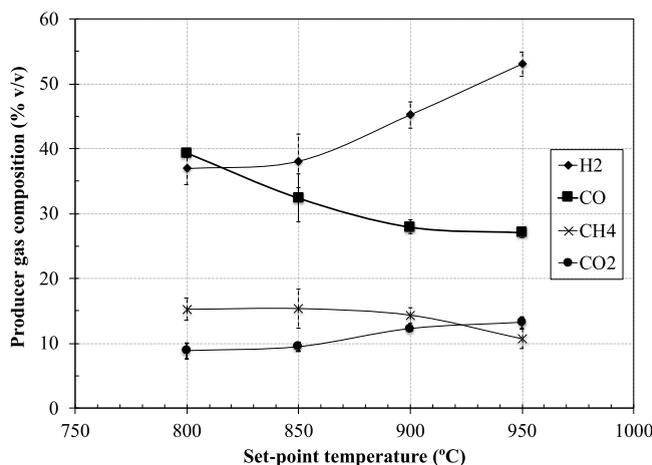


Fig. 2. Effect of temperature on producer gas composition.

The increase of bed temperature resulted in an increase of H<sub>2</sub> and CO<sub>2</sub>, and a decrease of CO and CH<sub>4</sub> volumetric concentrations in producer gas composition. Along the tested temperatures, H<sub>2</sub> concentration increased from 37 to 53% (v/v), CO<sub>2</sub> increased from 9 to 13% (v/v), CO decreased from 39 to 27% (v/v) and CH<sub>4</sub> decreased from 15 to 11% (v/v). As a consequence of composition evolution, it was observed an increase of H<sub>2</sub>/CO ratio from 0.94 to 1.96, with the temperature rise. This behaviour may be explained through a typical gasification mechanism. In the first step of the gasification process, devolatilization seems to be crucial for thermal decomposition of large hydrocarbons molecules into lower molecular weight compounds, which will participate, on both, gasification reactions and tar reactions (6)–(9). Water-gas shift (1) has also a well-known role on the process up to 850 °C, and from this temperature on, methane steam reforming (3),(4) and methane dry reforming (5) become more significant.

The effect of temperature on the gasification parameters was assessed. In the range of tested temperatures it was observed a rise of carbon and hydrogen conversion efficiencies with the increase of temperature (Fig. 3). The evolution of hydrogen conversion efficiency along the temperature presented a higher slope than carbon conversion efficiency. The carbon conversion efficiency increased from 59.5 to 75.8% and the hydrogen conversion efficiency increased from 42.5 to 76.6%.

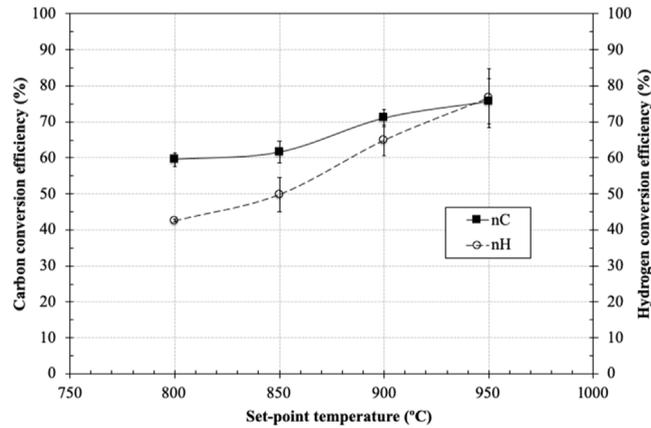


Fig. 3. Effect of temperature on carbon and hydrogen conversion efficiencies.

The increase of temperature from 800 to 950 °C also caused an increase of both the cold gas efficiency and the dry gas yield (Fig. 4). The cold gas efficiency rose between 72.2 and 105.2% and the dry gas yield increased from 0.9 to 1.4 m<sup>3</sup>/kg. Values higher than 100% for cold gas efficiency can be expected when steam is used as gasification agent. The increase of those parameters is related with the increase of producer gas production, with the rise of temperature

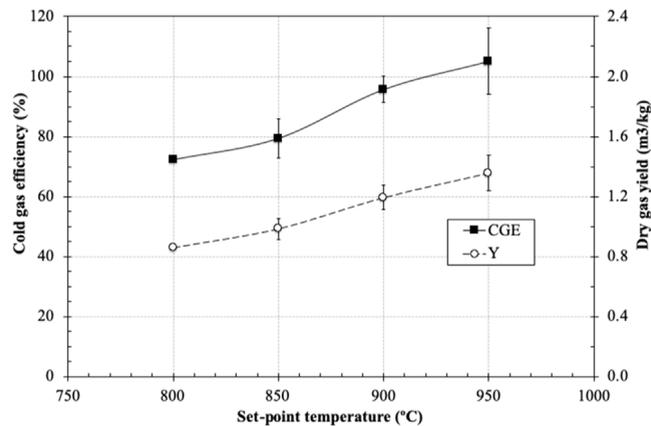


Fig. 4. Effect of temperature on cold gas efficiency and dry gas yield.

The producer gas higher heating value decreased with the temperature rise, from 15.8 to 14.5 MJ/m<sup>3</sup> (Fig. 5) as a consequence of the behaviour observed for the composition of the producer gas (Fig. 2). As the temperature increases, the content of CH<sub>4</sub> and CO, compounds with higher individual HHV, in the producer gas, decreases.

With this preliminary study, good results were obtained for the co-gasification parameters of crude glycerol/fat mixture. At a fat incorporation rate of 10%, there was a small decrease in the values of carbon and hydrogen conversion efficiencies when compared to the values obtained for the steam gasification of crude glycerol with the same order of magnitude of the raw material/H<sub>2</sub>O ratio. Slightly higher values were obtained for the dry gas yield and values of the same order of magnitude were obtained for the cold gas efficiency and for the producer gas HHV.

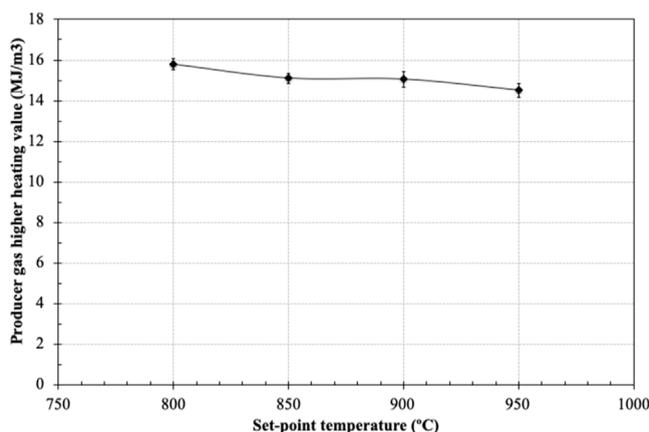


Fig. 5. Effect of temperature on producer gas higher heating value.

#### 4. Conclusions

Although further testing is required using other mixing conditions in order to support the assessment of co-gasification of crude glycerol/fat mixtures, the results obtained in this preliminary study for the gasification parameters indicate that this may be a technical possibility for the disposal of these two by-products. At the tested conditions, maximum mean values of 76% were obtained for carbon and hydrogen conversion efficiency, 105% for the cold gas efficiency, 1.4 m<sup>3</sup>/kg for the dry gas yield and 15.8 MJ/m<sup>3</sup> for the *HHV* of the producer gas.

#### Acknowledgements

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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