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OXY-FUEL COMBUSTION OF CRUDE GLYCEROL USING THERMOGRAVIMETRIC ANALYSIS

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Abstract. *The world has experienced a considerable increase in energy demand, a significant reduction of oil reserves and an increase in greenhouse gas emissions. This situation has stimulated research on alternative fuels of renewable origin. Biodiesel is a biofuel capable of meeting part of the energy demand and has great potential for CO_2 reduction, however, their production generates significant amounts of crude glycerol. The literature presents a significant amount of work on the various alternatives for the use of crude glycerol, which range from energy generation, production of biofuels and chemicals. In the context of energy generation, some research has shown that crude glycerol can be used as a fuel. Although there are works involving crude glycerol, there are few studies on the thermal behavior of glycerol under combustion conditions. The study of glycerol oxyfuel combustion is relevant, because besides taking advantage of the energy contained in glycerol, it will be possible to obtain an inlet CO_2-rich gas stream for its subsequent capture. However, studies on glycerol oxy-combustion are still scarce. Thus, this research project proposes the study of the combustion and oxy-combustion of glycerol using thermal analysis techniques.*

Keywords: *Glycerol, TGA, oxy-fuel combustion, energy.*

1. INTRODUCTION

Over the last three decades the world has experienced an increase in demand for energy, depletion of oil reserves, and increased greenhouse gas (GHG) emissions, especially carbon dioxide (CO_2) has stimulated research on alternative fuels (Coronado et al., 2014). Among the various renewable alternative fuels is biodiesel, renewable biofuel, which has great potential for CO_2 reduction. However, its production generates the formation of a by-product called glycerol, which cannot be ruled out in nature and tends to become a growing environmental and economic problem as world production and reserves of glycerol are expanding, making it urgent the search for new uses for glycerol. World biodiesel production has increased rapidly in recent years, reaching 28.3 million metric tons in 2014 (FAO 2014). Thus, the overall production of crude glycerol in 2014 was estimated to be 2.8 million metric tons (Setyawan et al., 2016; Asdrubali et al., 2015).

Crude glycerol, obtained through the production of biodiesel, has characteristics that prevent it from being used in the main current applications, due to the presence of impurities resulting from catalysts used in transesterification (Paz, 2013). In the industrial process, 1 kg of crude glycerol is generated per 9 kg of biodiesel produced. Even though pure glycerol has applications in the food, cosmetics and pharmaceutical industries, it is very expensive for biodiesel producers to refine crude glycerol into high purity glycerol. Therefore, the glycerol generated during the biodiesel process is often considered as a residual product (Jiang and Agrawal 2014; Leoneti et al., 2012).

The literature presents a significant amount of works on the various alternatives for the utilization of crude glycerol, which range from energy generation, biofuel production and chemicals (Monteiro et al., 2018; He et al., 2017; Quispe et al., 2013 Gupta and Kumar 2012). In the context of energy generation, some research has shown that crude glycerol can be used as a fuel, despite its low calorific value and high ignition temperature (Jiang and Agrawal 2014).

Crnkovic et al., (2012) determined the activation energy of the crude glycerol combustion. Angeloni et al. (2016) investigated the combustion of crude glycerol by burning the droplets in a vertical tubular furnace and compared with different blends of pure glycerol with water, alcohol, and salts. Setyawan et al. (2016) studied the combustion and ignition characteristics of crude glycerol compared to other fuels such as diesel, biodiesel and ethanol, and verified the effect of the impurities on the crude glycerol combustion behavior. Yuan et al. (2016) used thermal analysis to study the thermal behavior of glycerol-diesel mixtures (microemulsion), where they verified the effect of different concentrations of glycerol, as well as the kinetics of combustion and pyrolysis.

Despite the studies involving crude glycerol, there are still few studies on the thermal behavior of glycerol under oxy-fuel combustion conditions. In addition, the study of oxy-combustion of glycerol is relevant since, in addition to taking advantage of the energy contained in the glycerol, it will allow a CO_2-rich gas stream to be obtained for its subsequent capture. However, studies of oxy-combustion of glycerol are still scarce.

2. MATERIALS AND METHODS

2.1 Glycerol

Figure 1 shows a sample of glycerol used for the tests.

Figure 1. Glycerol sample.

Properties	Results	Method	Specification
pH	5.61	-	5.00 to 7.00
Salt content	2.73 %	CQGL0001	Max 7.00
Water content	14.47 %	CQ0008	Max 15.00
Glycerol content	83.36 %	CQGL0003	Max 80.00

Table 1. Physical-chemical properties of crude glycerol

2.2 Experimental setup

Figure 2 presents the experimental stand for studies of the thermal behavior of glycerol. The bench was composed mainly of a thermobalance (DSC-Q600 from TA instruments). For the injection of carbon dioxide, a secondary injection of the term scale is used, for this it is necessary to use a flow controller (AALBORG). The tests were carried out starting from the temperature of 30 °C to 600 °C, using atmospheres of Combustion with synthetic air, inert atmosphere with nitrogen and oxy-combustion with 80 % of CO_2 and 20 % of O_2, all using a heating rate of 10 °C per minute, and 30 mg mass of glycerol.

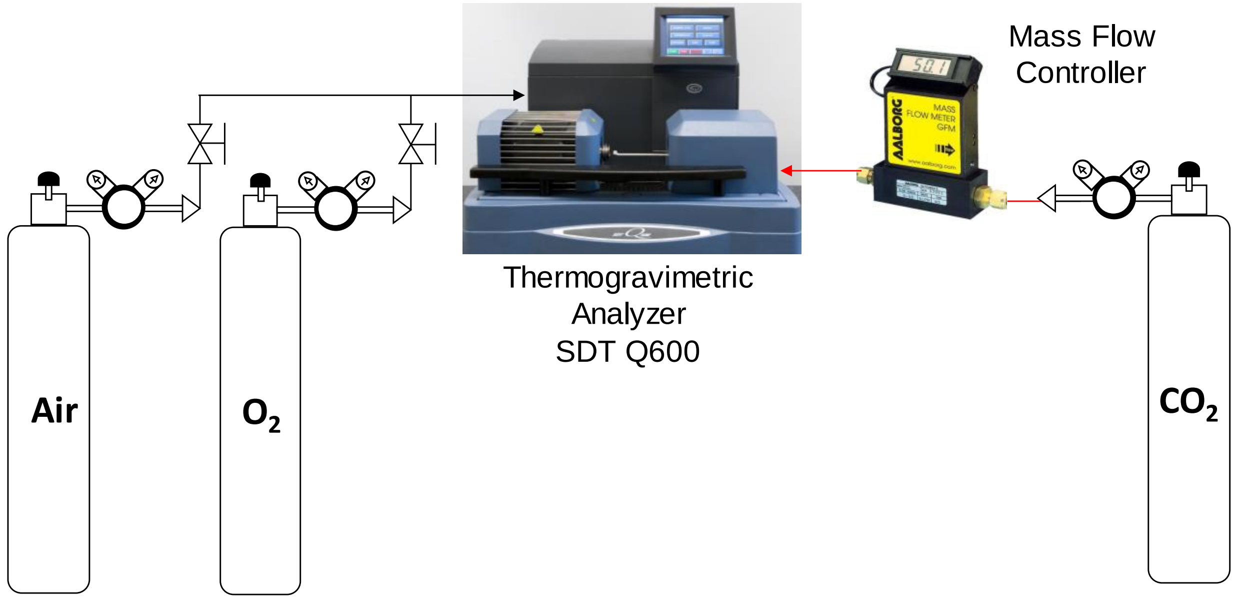


Figure 2. Experimental test.

3. RESULTS AND DISCUSSION

Figure 3 shows the thermal behavior of glycerol under combustion condition. The DTG curve shows two events that were carried out at the heating rate of 10 °C/min, the first in the low intensity range of 50 °C and 150 °C, which may be associated with the content of water and methanol in its composition.

Crnkovic et al. (2012), also observed this small curve for vegetable oil glycerin, but for animal fat this first deviation is not observed. Yuan et al. (2016) found that for biodiesel emulsion samples with glycerol, the first peak is not observed. The second event was much more intense, which started at approximately 150 °C and reached a maximum at 250 °C, but for the experiment of Yuan et al. (2016) which was made with emulsion, the event starts to occur at approximately 75 °C in all of its tests, and reached the maximum value at 180 °C for experiments in which the heating rate was also 10 °C/min, and for Crnkovic et al. (2012) observed that the most pronounced curve also started at approximately 150 ºC obtaining its maximum at about 250 ºC, but with a heating rate of 30 ºC/min, already in the experiment with the rate of 10 ºC/min it is observed that the curve starts at approximately 150 °C plus obtains the highest peak at the maximum of approximately 220 °C.

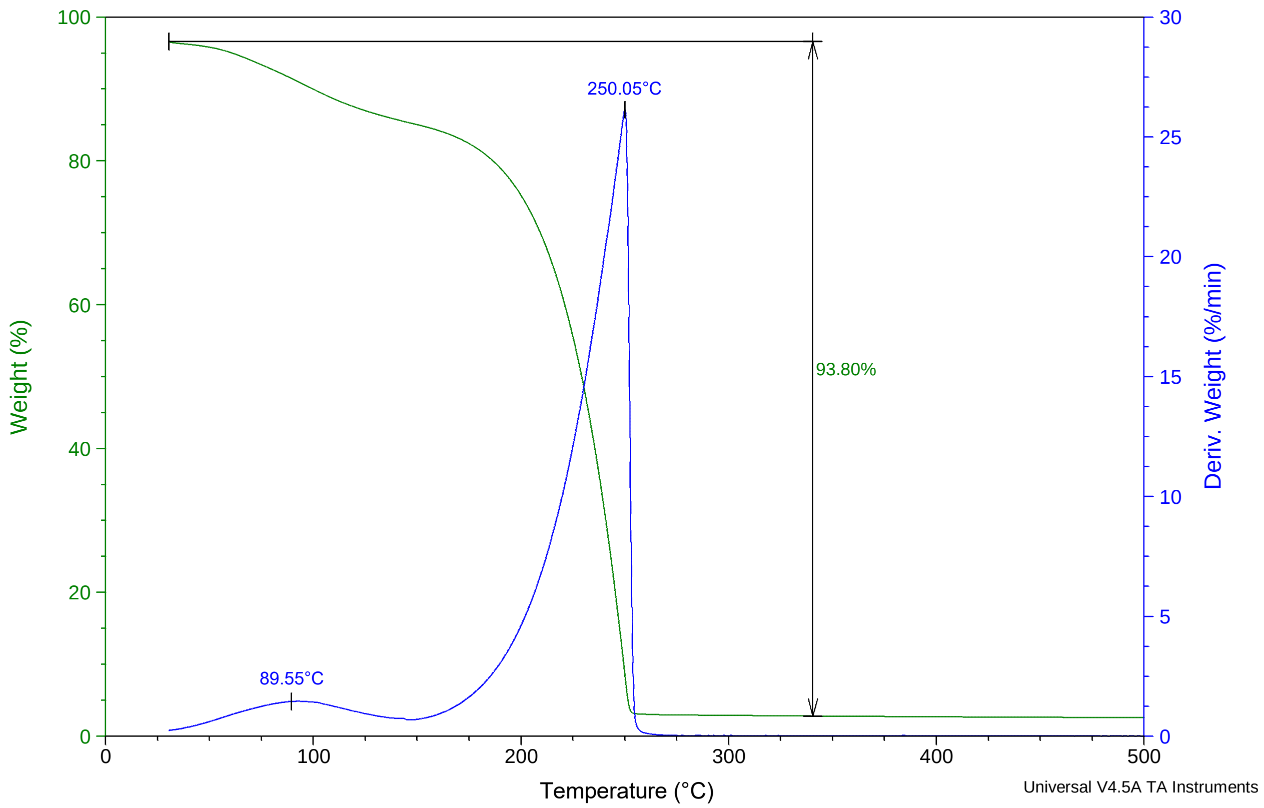
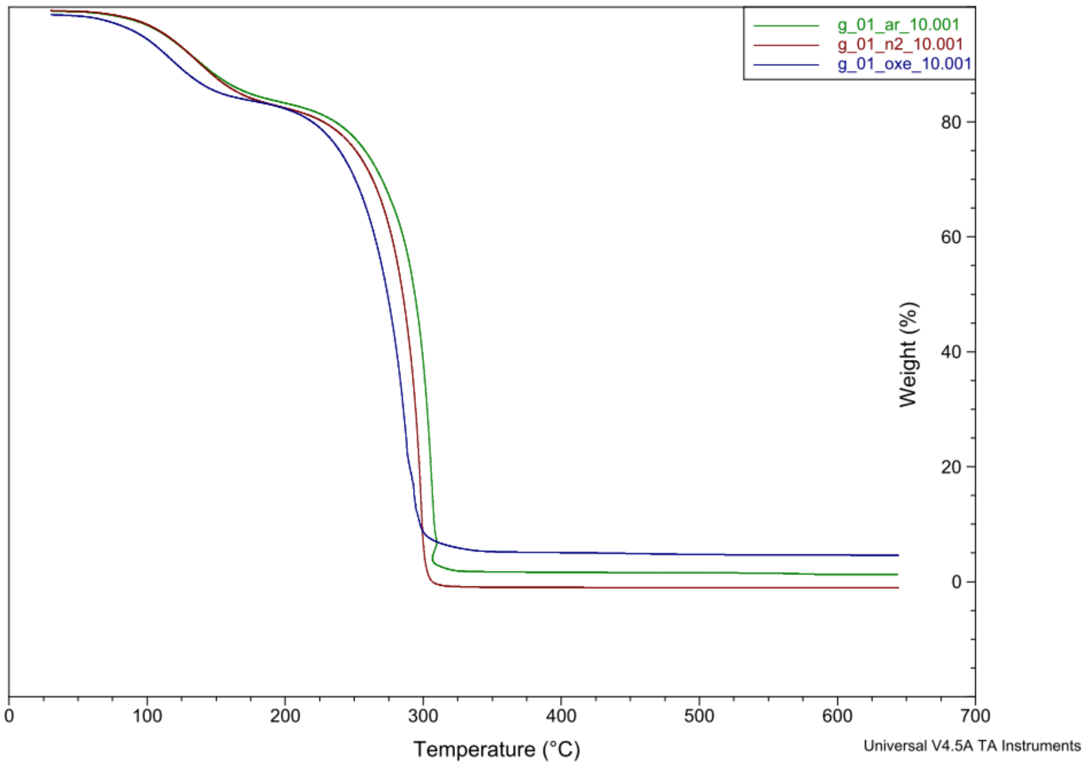


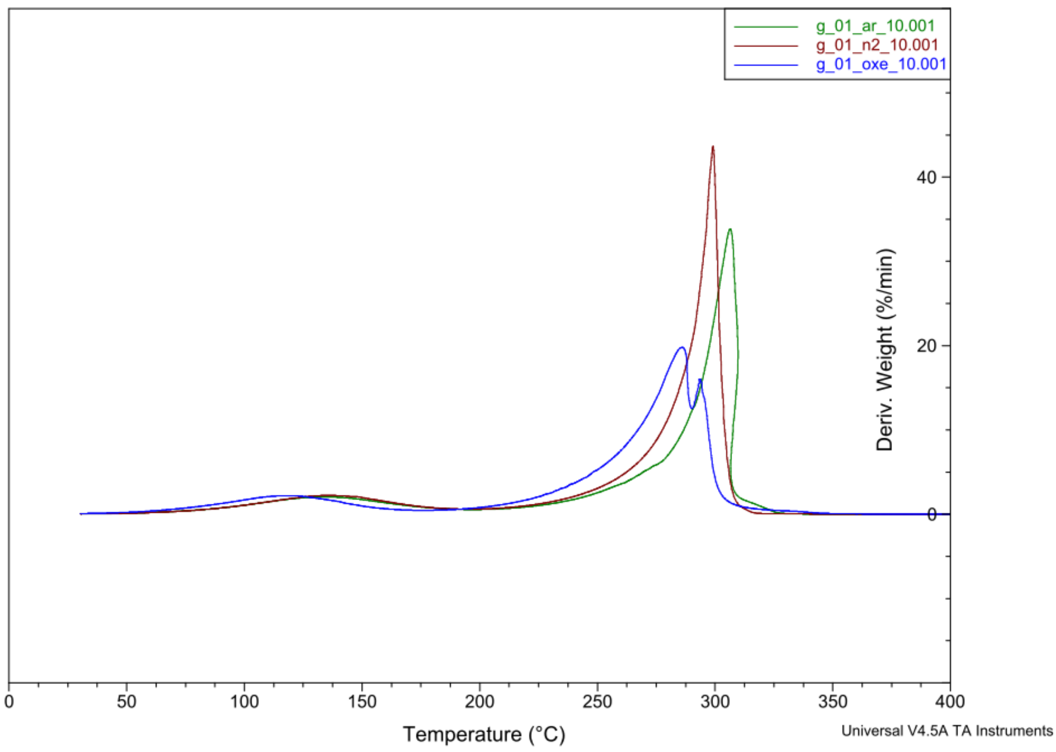
Figure 3. TG/DTG curves of glycerol under combustion condition.

Figure 4a shows mass curves in percentage, where it is possible to see a similarity between the curves, but it can be observed that the oxy-combustion curve begins the reaction in advance of the other two curves, and it is also possible to observe a return in the synthetic air curve at the end of the second degradation, this was probably due to the fact that a large mass was used, and with this a very strong reaction occurred, forcing the equipment to have to decrease the temperature, thus causing this recoil. It is also possible to observe that the degradation in nitrogen atmosphere was complete, there being no ash, and for the other two atmospheres it had little mass of ash, being greater and remarkable for the atmosphere of oxy-combustion with about 5.42 % of content of ashes, this behavior similar as show in Yuan et al. (2016).

Figure 4b shows the curve of the mass derivative, where it is possible to identify that for the three atmospheres the first degradation occurs from 70 °C, but for oxy-combustion the second degradation starts happening at 160 °C and for the two more atmospheres begin to occur at 175 °C, the reaction of greater intensity was that of degradation in nitrogen atmosphere reaching to have more than 40 % of intensity, followed by the reaction in atmosphere of synthetic air where also a retreat of the curve occurs, proving that there was a reaction with a mass greater than it should be used and having an intensity of almost 37 %, since the reaction in oxy-combustion presents us with two peaks of reaction but with lower intensities than in the other atmospheres.



(a)



(b)

Figure 4 – Thermal behavior of crude glycerol (a) TG curve (b) DTG curve.

Figure 5 presents the heat flux curves, where it can be observed that for nitrogen atmosphere, there were only endothermic reactions, both for the first and the second degradation, already for the atmospheres of synthetic air and oxy-combustion there were endothermic and exothermic reactions in the two degradations, with the highest enthalpy release occurring in an air of synthetic air. This may have occurred due to the size of the nitrogen molecules compared to the carbon dioxide molecules, because the nitrogen molecules are smaller thus occupying less space on the contact surface of the sample, thus facilitating the entry of oxygen into the reaction.

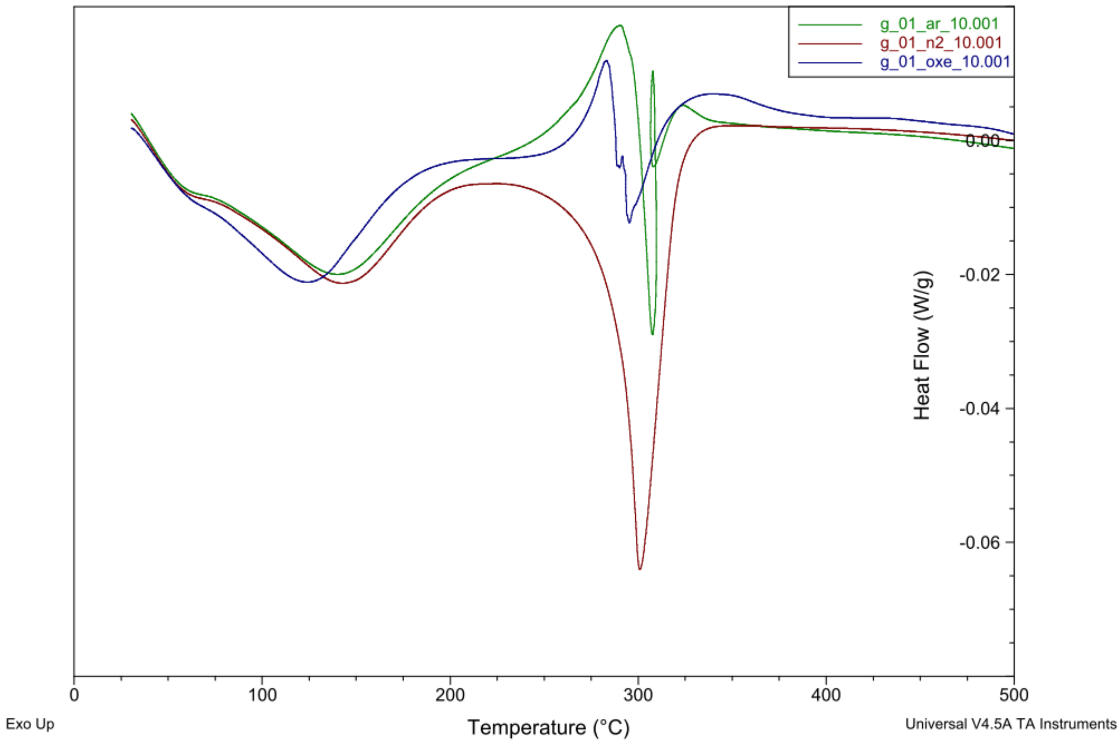


Figure 5 – DSC curve of crude glycerol.

4. CONCLUSIONS

For the tests, the combustion in the atmosphere of synthetic air was more reactive, according to the figures presented, however due to the amount of mass there were unexpected events, with this it is necessary of new tests with less mass to obtain significant results, it is also possible to say that oxy-combustion breaks off if the proportions of the gases change there may be differences, and this needs to be studied.

5. ACKNOWLEDGEMENTS

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