European Association for the
Development of Renewable Energies,
Environment and Power Quality (EA4EPQ)

International Conference on Renewable Energies and Power Quality
(ICREPQ'11)
Las Palmas de Gran Canaria (Spain), 13th to 15th April, 2011

Providing an added-value to biodiesel by-products: Pyrolysis of glicerin. Thermogravimetric study and analysis of sulphur emissions

J. F. González[1], G. Engo[1], S. Román[1], J. I. Arranz[2] and J. M. Encinar[3]

1Departament of Applied Physics, 2Department of Mechanical, Energetics and Materials Engineering,
3Department of Chemistry Engineering and Physical Chemistry,
University of Extremadura, Avda. Elvas s/n, 06006 Badajoz (Spain)
Phone/Fax number:+0034 924 289619/003492428960
e-mail **J. F. jfelixgg@unex.es, S. sroman@unex.es**

Abstract. This work aimed to study the thermal degradation process of the glycerine generated as by-product during biodiesel production. For this task, thermogravimetric analyses (TG) were conducted under argon atmosphere at various heating rates, and the different stages occurring during the pyrolysis were elucidated.

Also, by the coupled use of TG and Mass spectrometry analyses (MS) it was possible to monitorize the gas emissions released during the pyrolysis, and thus have a better knowledge of the mechanisms governing the degradation process.

From the experimental data, it was found that glycerin degradation occurs at various stages which are not apparently affected by the heating rate. The MS analyses on the emission of sulphur dioxide and dimethyl sulfide allowed identifying the release of these compound around the temperature of 370ºC.

Key words

Glycerine, pyrolysis, thermal degradation, sulphur emissions

1. Introduction

There are many reasons that evidence the need of shifting our current energy system, mainly based on fossil fuels exploitation (up to 84% of global energy demand is based on fossil fuels) [1], towards a new scenery, in which alternative sources of energy will participate. Some of these reasons are the close and unavoidable fossil fuels exhaustion, the energetic dependence on traditional energy sources which is the basis of many geopolitical problems, the environmental problems associated with their exploitation and the increasing energy demand.

The alternative energy resources such as nuclear power and renewable energy sources are nowadays being employed to generate electricity. In the transport field (which is responsible for the 18% consumption of primary energy worldwide) there are several alternatives able to substitute the fossil fuels role, such as biofuels.

In this context, biomass stands as one of the most important renewable sources of energy, due to the well-known advantages it provides. In the particular case of biodiesel, another attractive feature is added: it has potential to be used as alternative liquid transportation fuel.

Of the several methods available for producing biodiesel, trastesterification of oils and fats is the most common method. In this process, the oil/fat reacts with an alcohol to form the biodiesel in the presence of a catalyst, and glycerin is formed as a by-product. As biodiesel production is increasing, so does the formation of glycerin. In view of this situation, the research community has recently showed more and more interest in studying possibilities to revalorize the glycerin produced during biodiesel production [2-5]. Up to now, the chemical synthesis of glycerin-derivative products (food, pharmaceutical, cosmetics, and others), is the most common option [4].

As a consequence of the massive production of glycerol, its value is lower and lower, up to the point that it is currently considered as a waste product. Moreover, crude glycerol derived from biodiesel production possesses very low value because of the impurities.

Further refining of the crude glycerol will depend on the economy of production scale and/or the availability of a glycerol purification facility. All the same, the knowledge of the glycerin degradation mechanisms provides important information for the improvement of the processes design.

With these premises, this work aimed to study the thermogravimetric degradation of glycerin under an argon atmosphere, studying the process under different approaches:

a) On the one hand, the effect of heating rate (in the range 20-100 K min^{-1}) was studied, analyzing its influence on the weight loss profiles.

b) Also, the emission of sulphur compounds was monitorized and related to thermal degradation events.

2. Experimental

Glycerin was provided by the Biodiesel manufacture plant of Bioenergética Extremeña, located in Valdetorres (Extremadura, Spain). The TG study was carried out using a thermobalance (Setsys Evolution, SETARAM) under an Ar flow of 100 cm^{3}min^{-1}. An initial mass of 15.0±0.1 mg was used, employing argon as carrier gas (100 cm^3 min^{-1}) and varying the heating rate conditions in the range previously described. The analyses were made in the temperature range 25-800 ºC.

The study of the emissions released was made by coupling mass Spectrometer (Pfeiffer Tecnovac Thermostar GDS301 T3). The gas line between the TG and MS was heated to 200 ºC in order to avoid cold points and thus prevent the condensation of some of the gaseous products. The following mass spectrometer signals were monitorized: SO_2 (m/z=64), $S(CH_3)_2$ (m/z=62), H_2O (m/z= 17 and 18), CO2 (m/z=44) and glycerin (m/z=73).

In order to guarantee reproducibility of results each run was made three times and the signals were normalized to the initial mass of the sample. Thus, it was possible to compare the peak height of the same compound evolved from different samples.

3. Results

From the results obtained it was found that glycerin thermal degradation occurs following various different stages, at it can be seen from Figure 1.

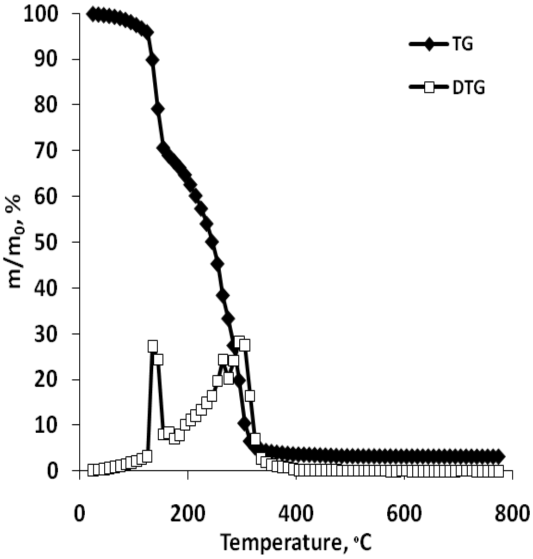

Figure 1. TG and DTG profiles of glycerin thermal decomposition.

This decomposition profile can be associated with the chemical characteristics of glycerin (Figure 2):

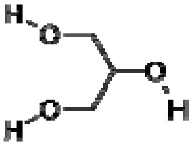

Figure 2. Molecular structure of glycerin.

From Figure 1, it can be inferred that there is a slight weight loss up to 115ºC, which becomes more marked in the range 115-350ºC, when most of the glycerin has been pyrolyzed. At temperatures higher than 350 ºC, the TG curve only shows a residual mass proportion equal to 2%; which is similar to the ash content of the material. The DTG curve shows two peaks centered at temperatures 135 and 295ºC, being the latter much wider, in accordance to a more persistent weight loss.

The first decomposition stage can be associated with water release (glycerin is hygroscopic; i.e., it absorbs water from the air), while the second wide one is associated to its boiling and decomposition at 290°C [6].

The thermal instability of glicerin has been previously observed by other authors, which improved it by blending it with different plastiziers [7].

Figure 3 shows the TG profiles corresponding to runs made at the different heating rates.

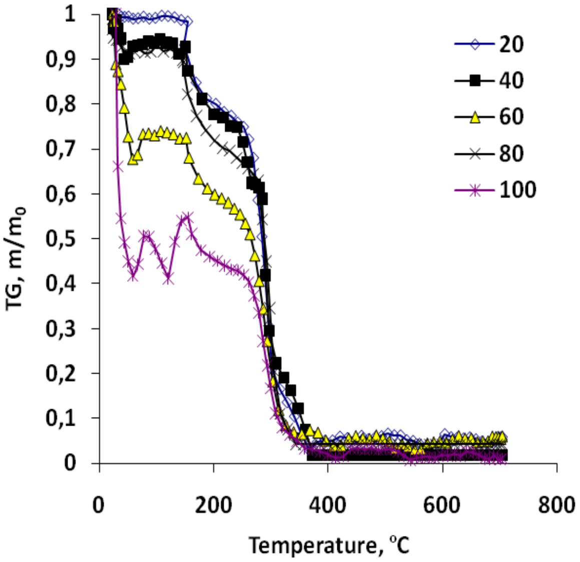

Figure 3. TG profiles under different heating rates.

From Figure 3 it can be infered that the effect of this variable was more marked at the first stages of the decomposition, giving rise to a greater weight loss and a slight shift of the temperatures defining each stage towards lower temperatures.

Finally, the course of various emissions during thermal degradation processes was monitorized by coupled TG_MS analyses at a heating rate of 40 ºCmin^{-1}.

Figure 4 shows the ion intensity profiles of signals corresponding to m/z= 17 and 18, which can be related to water. From this Figure, it can be seen that the ion intensity starts increasing at temperatures close to 100 ºC, and then shows a continuous marked rise.

While the former increase might be related to the water absorbed by glycerin, the subsequent one could be due to the release of water during the cracking reactions occurring when the decomposition temperature of glycerin is reached, although the saturation of the signal might also be postulated.

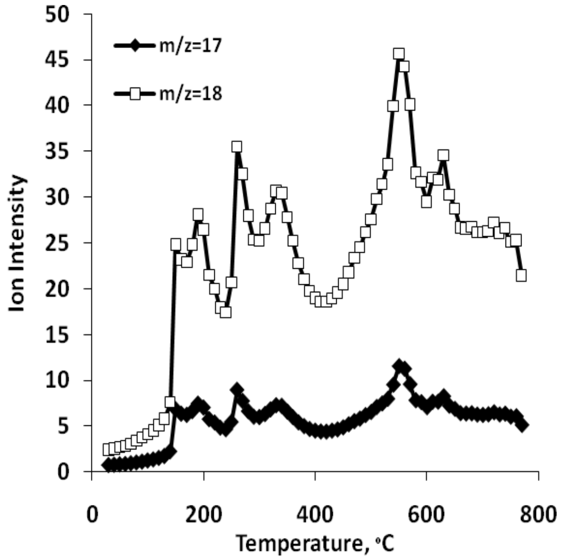

Figure 4. Mass spectra associated to water, (m/z=17) and (m/z=18).

Regarding the specie SO_2 (as associated to the ion intensity signal of m/z=62) it was identified as a very well defined peak centered at 370ºC, corresponding to the second stage, attributed to glycerin decomposition (see Figure 5). The release of this compound can be related to the presence of K_2SO_4 (around 4-7 wt.%) in technical glycerin.

Also, a well-defined signal was found for the ratio m/z=64, which could be related to the presence of dimethyl sulfide.

Finally, the mass spectra signals associated to carbon dioxide (m/z=44) and pure glycerin (m/z=73) [8] have been plotted in Figure 6.

First, the carbon dioxide profile is consistent with the hypothesis made before: its release is outstanding at temperatures higher than 200 ºC aproximatelly, as the previous weight loss was related to water. However, the ion intensity of carbon dioxide get greater as temperature is risen above this value, presenting a well defined peak around 280-300 ºC, which is consistent with the decomposition of glycerin. This signal gets more marked at higher temperatures, coinciding with the peak found for pure glycerin (m/z=73), which is released at the final stages of the decomposition.

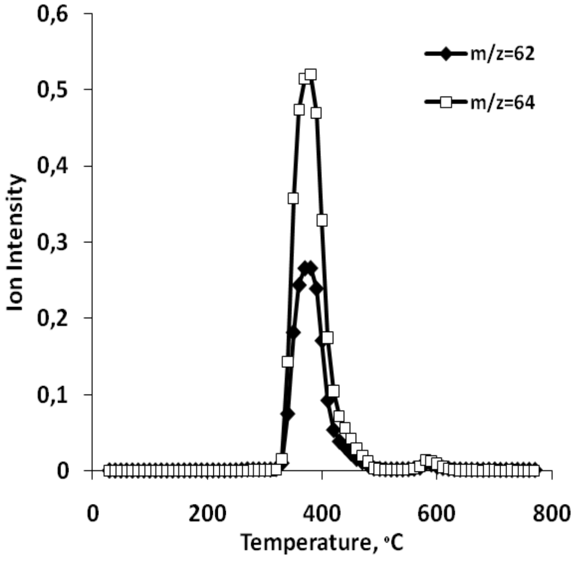

Figure 5. Mass spectra associated to sulphur dioxide (m/z=62) and dimethyl sulfide (m/z=64)

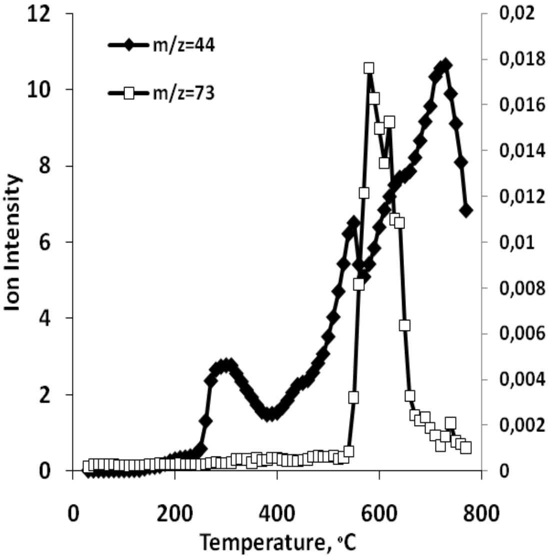

Figure 6. Mass spectra associated to carbon dioxide (m/z=44) pure glycerin (m/z=73).

Acknowledgement

The authors express their gratitude for the financial support through project PDT09A024.

References

[1] World energy outlook. Executive Summary. International Energy Agency, 2008. Available online on: http://www.worldenergyoutlook.org/docs/weo2009.

[2] T. Valliyappan, N.N. Bakhshi, A.K. Dalai Pyrolysis of glycerol for the production of hydrogen or syn gas. Bioresource Technology 99 (2008) pp. 4476-4483.

[3] Y. S. Stein, M. J. Antal Jr., M. Jones Jr. A study of the gas-phase pyrolysis of glycerol. Journal of Analytical and Applied Pyrolysis 4 (1983) pp. 283-296.

[4] M. I. Galana, J. Boneta, R. Sireb, J. M. Reneaumeb and Alexandra E. Pleşu. From residual to useful oil: Revalorization of glycerine from the biodiesel synthesis. Bioresource Technology 100(15) (2009) pp. 3775-3778

[5] N. Pachauri, B. He. Value-added Utilization of Crude Glycerol from Biodiesel Production: A Survey of Current Research Activities. ASABE Annual International Meeting. Oregon Convention Center Portland, Oregon, 2006

[6] R.H. Perry, and D.W. Green.. Perry's Chemical Engineers' Handbook. pp2-39. McGraw-Hill: New York, 1997.

[7] D. Schlemmer, E. R. de Oliveira and M. J. Araújo Sales Polystyrene/thermoplastic starch blends with different plasticizers. Preparation and thermal characterization. Journal of Thermal Analysis and Calorimetry 87 pp.137-142.

[8] R. M. Smith Understanding mass spectra: a basic approach. Second Edition. Wiley Interscience, Canada, 2004.