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,