Kinetics of the combustion of olive oil. A semi-global model

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A B S T R A C T

A kinetic study of the combustion of olive oil has been carried out under different conditions by thermogravimetry using two different TG apparatus. Several TG runs were performed at air, $N_2:O_2 = 4:1$ and $N_2:O_2 = 9:1$ under dynamic conditions and a dynamic + isothermal regime (constant heating rate until the set temperature was reached with the set temperature maintained constant thereafter). On the other hand, a number of dynamic runs were carried out on waste olive oil and waste mixed oil. Based on an overall analysis of the data, a scheme of four decomposition steps was proposed and kinetic parameter values were calculated by integration of the differential equations and by minimizing the squared differences between the experimental and calculated values. An examination of the influence of the initial mass on TG runs was performed on the assumption of vaporization + chemical oxidation processes. The thermal decomposition was also carried out in dynamic runs at air atmosphere using TG-MS and TG-IR in order to validate the scheme of proposed reactions, the hypothesis of the formation of a carbonaceous residue and to study the evolution of several compounds.

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1. Introduction

The increasing need of energy by segments of our society, the reduction of petroleum reserves and increased environmental concerns have caused biomass materials to gain much interest with respect to energy utilization. For example, waste vegetable oils can through thermal decomposition be used to directly obtain energy or fuels [1]. It is very important to perform thermal analysis of the oils to predict their behavior in real combustion systems. The combustion kinetics of these fuels gives relevant information on their thermal behavior and on the possible formation of a carbonaceous residue and its subsequent oxidation.

Jansson et al. [2] studied the pyrolysis of olive oils and other vegetable oils, and determined the evolved compounds on a Pyrolyzer/GC/MS. Gases such as propene and liquids such as oleic acid, docosene and octadecenal, with boiling points at around 360 °C (633 K), were found. In a combustion process these compounds are oxidized, which changes the composition of the gas phase.

The subject of a previous paper was a study of the pyrolysis kinetics of olive and used olive oil [3]. The pyrolytic decomposition was analyzed taking into consideration the vaporization process involved, and the results were compared with a number of kinetic considerations discussed in other papers [4–6]. The proposed kinetic model considered two sequential processes: a first process, considering vaporization and decomposition, whose apparent activation energy and reaction order were 112 kJ/mol and 0.606, respectively, and a second process, whose apparent activation energy and reaction order were 194.6 kJ/mol and 2.274, respectively. The values obtained in both of these processes are acceptable; in the first process, the values are between those of the vaporization process and chemical decomposition, and in the second they were common values for decomposition processes.

Others have also studied the oxidative thermal decomposition in order to characterize vegetable oils [7,8]. Tran et al. [9] examined a number of mechanisms of the combustion of oxygenated compounds of biofuels.

Dweck and Sampaio [10] analyzed the thermal decomposition of commercial vegetable oils by TG/DTA and observed four decomposition steps. They proposed that the last one corresponds to the burnout of the residual carbonaceous material.

Concerning the global kinetics, Vecchio et al. [7] studied the oxidative thermal decomposition of single-varietal extra olive oil by TG/DSC, and observed a complex multistep decomposition. They attributed the first apparent peak to two different processes for the purpose of relating them to the chemical composition. From the first decomposition step they obtained apparent activation energies for the de-convoluted peaks ranging between 27 and 158 kJ/mol, and 31 and 278 kJ/mol for the first and second peaks, respectively. No other information concerning kinetic parameters was presented.

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Gouveia de Souza et al. [11] elucidated the oxidation kinetics of sunflower oil by TG, by considering three decomposition steps in which the interaction of the oxidation reactions was important. The first step takes place between 503 and 653 K with reaction order around 1 and activation energy around 90–110 kJ/mol, in which the volatile compounds were removed by the vapor generated during heating. The second is between 653 and 753 K with reaction order around 2 and activation energy of 205–300 kJ/mol. The third step takes place between 753 and 823 K and the deduced reaction orders and apparent activation energies were around 2 and 300–400 kJ/mol, respectively.

Santos et al. [12] considered three decomposition steps in the oxidative decomposition of a number of edible oils, including olive oil. Similar kinetic parameters were obtained. In the first step, the apparent activation energy was between 78 and 106 kJ/mol and the reaction order was between 0.92 and 1.06. In the second step, the apparent activation energy was between 208 and 349 kJ/mol and the reaction order was between 1.86 and 2.11. In the last step, an activation energy between 274 and 370 kJ/mol and a reaction order between 1.87 and 2.13 were obtained. No values were reported for the mass fractions of the volatiles evolved in each step.

Zhengwen [13] recently studied the combustion of cooking oil tar on a TG apparatus. He observed four DTG peaks after the initial evaporation of the absorbed water, and made several plots for correlating the data which suggest a model of First Order Reaction and Three-dimensional Diffusion Separate-stage. However, values for the apparent activation energy were not reported.

Vecchio et al. [14] studied the decomposition of triglycerides contained in olive oil by TG. They observed the presence of four decomposition steps and determined the kinetic parameters of the first two decomposition steps.

More recently, Tomassetti et al. [15] analyzed the thermal decomposition of saturated mono-, di- and tri-glycerides. They also observed four decomposition steps and proposed the kinetic parameters for the two or three first steps.

The decomposition kinetics of complex materials (synthetic polymers, biomass, oils, etc.) is a subject that deals with the examination and analysis of kinetic parameters, with a view to clarifying their significance [16–18]. Thus, efforts to study the decompositions of substances such as vegetable oils can help to reduce the existing chaos in the field of reaction kinetics of complex materials.

In this paper, a kinetic model for the combustion of olive oil at air atmosphere and also in one that is oxygen-poor has been developed by simultaneous determination at each step of the kinetic parameters and the mass fraction of the volatiles. The experimental data are compared with those obtained by simulation using the deduced expressions. We also discuss the possibility of a carbonaceous residue formed during the thermal oxidation of the fuels in question, which has not been considered in previous papers. The kinetic study is analyzed by contrasting with the study on olive oil by Vecchio et al. [7], as well as other studies carried out on other vegetable oils. The kinetic model can be used to characterize certain decomposition steps of the edible oils and/or their corresponding wastes and to analyze the formation of a carbonaceous residue.

2. Experimental

2.1. Raw material

Pure olive oil, waste olive oil and waste mixed oil were selected as materials for studying the kinetics. This study employed the same pure olive oil as a previous pyrolysis kinetic study [3]. The waste olive oil was obtained after four/five frying processes, which corresponds to an average use of this oil, and was also the same waste olive oil employed in the previous pyrolysis kinetic study

[3]. A waste mixed oil, consisting of a mixture of different used cooking oils, was also utilized to determine whether there are any great differences between the oils. An elemental analysis of the samples was carried out on a Perkin-Elmer 2400 to determine the mass fractions of carbon, hydrogen, nitrogen and sulphur; oxygen content was determined by a direct oxygen analysis carried out on a Flash-2000 Thermo Fisher Scientific; a LECO Instruments AC-350 calorimetric bomb was used to obtain the net calorific value. Table 1 shows the results of the elemental analysis and the net calorific values of the three samples tested. As observed, there are no big differences between the samples.

2.2. Apparatus and experimental procedure

The combustion runs at air atmosphere were carried out on two different TG apparatus whereas in the $N_2:O_2 = 9:1$ runs only one of them was used:

(1) A Mettler Toledo Thermobalance model TGA/SDTA851e/LF/1600. This instrument incorporates a horizontal furnace and a parallel-guided balance. In this way, positioning of the sample has no influence on the measurement, and flow gas perturbation and thermal buoyancy are minimized. The sample temperature was measured by a sensor directly attached to the sample holder. Two different atmospheres were used; $N_2:O_2 = 4:1$ and $N_2:O_2 = 9:1$. The crucibles employed in the runs were a nearly cylindrical aluminum crucible of 0.55 cm internal diameter and 0.41 cm height, which is slightly curved at the bottom of the cylinder, and a cylindrical alumina crucible of 0.47 cm internal diameter and 0.42 cm height.
(2) A Perkin Elmer Thermobalance model TGA/SDTA-6000. This instrument incorporates a vertical furnace and a single beam vertical balance. As in the previous case, positioning of the sample has no influence on the measurement, and flow gas perturbation and thermal buoyancy are minimized. The SaTurnA sensor measures both the sample and reference temperature directly for superb performance. The alumina crucible used in all runs was nearly cylindrical with 0.65 cm internal diameter and 0.42 cm height and was slightly curved at the bottom of the cylinder. Synthetic air was used as fluid, so these results can be compared with the results obtained at $N_2:O_2 = 4:1$ using the Mettler Toledo Thermobalance.

Dynamic experiments were carried out at heating rates between 5 and 20 K/min, from the initial room temperature up to 850 K, including thus the entire range of decomposition. Isothermal experiments started at a constant heating rate until the desired temperature was reached and then the final temperature was maintained constant. The experiment was considered to have finished when the weight loss rate was negligible (less than $1 \times 10^{-5}\,s^{-1}$). Small size samples, between 1 and 10 mg, were used in the runs.

A pyrolysis run at a heating rate of 5 K/min using Avicel PH-105 microcrystalline cellulose was done on each apparatus. The kinetic parameter values obtained showed good agreement with the results reported by Grønli et al. [19] in their round-robin study of cellulose pyrolysis kinetics by thermogravimetry (at 5 K/min and 244 kJ/mol, the experimental and calculated data coincide, obtaining logarithmic values of the pre-exponential factors of around 18.8, a value within the accepted interval). These experiments were useful to check how well the two thermobalances performed.

The TG-MS runs were carried out on a Mettler Toledo model TG-ATD TGA/SDTA851e/LF/1600 coupled to a Thermostar GSD301T Pfeiffer Vacuum MS apparatus using $He:O_2 = 4:1$ as carrier gas. The operating conditions were: a mass sample of around 5 mg, a 30 K/min heating rate, a 70 eV ionization energy, and SIR detection