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Characterization and modeling of pyrolysis of the two-phase olive mill solid waste

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ABSTRACT

In this work, first, the two-phase olive mill solid waste was characterized in terms of its physical–chemical properties, which can be useful for its use in pyrolysis units. Then, its behavior on pyrolysis processes was studied by dynamic thermogravimetry and derivate thermogravimetry. For the simulation of pyrolysis processes a kinetic model including three independent parallel reactions was used. The characterization results showed that the solid presents a size distribution with about 66% of particles $>$ 1.00 mm, while the percentage of fines ($<$ 0.250 mm) is only of 1.50%. The moisture content is very high (around 70%), being one of the main characteristics of the solid that makes its direct use as a fuel difficult. However, the low sulfur value ($<$0.1%) is very suitable from the environmental point of view, reducing SO_2 emissions. The results of the proximate analysis are within the range of most biomass waste and the gross calorific value obtained was 4897 kcal/kg. The thermal decomposition in an inert atmosphere can be modeled by separate decomposition of each of the three fractions which constitute the material. The results of both, physical–chemical characterization and thermogravimetric study show that the two-phase olive mill solid waste could be treated in energy recovery installations.

1. Introduction

Over the last 10 years the manufacture of olive oil has undergone important evolutionary changes in the equipment used for the separation of olive oil from the remaining components. The latest development has been the introduction of a two-phase centrifugation process in which a horizontally-mounted centrifuge is used for a primary separation of the olive oil fraction from the vegetable solid material and vegetation water. Therefore, the new two-phase olive oil mills produce three identifiable and separate waste streams. These are: 1) the wash waters from the initial cleansing of the fruit; 2) the wash waters from the secondary centrifuge and 3) the aqueous solid residues from the primary centrifugation. As well as offering process advantages they also reduce the water consumption of the mill. The introduction of this technology was carried out in 90% of Spanish olive oil factories. In addition, the solid residue (two-phase olive mill solid waste, TPOMSW) has a high organic matter concentration giving an elevated polluting load and it cannot be easily handled by traditional technology which deals with the conventional three-phase olive cake [1].

The use of this solid residue is of great economic and social importance for the Mediterranean area, as it accumulates in large amounts during olive oil production. The exploitation of TPOMSW, from an environmental point of view, may be approached in a number of ways, such as composting [2,3], gasification [4], steam explosion treatment for obtaining hydroxytyrosol [5], or the extraction of oils [6]. Specially, in recent years, thermal degradation of olive stone and other olive oil by-products was the subject of interest of a large amount of research, focusing mainly on the degradation mechanism, kinetics and emission of volatile substances [7]. However, there are scarce works concerning pyrolysis of TPOMSW.

On the other hand, thermogravimetric analysis (TG and DTG) is one of the most widely used techniques to study the primary reactions of thermal decomposition of solids. The correct interpretation of the experimental data obtained by thermogravimetric analysis can provide information about the material composition and kinetics of thermal decomposition (number of processes that is taking place, corresponding

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kinetic parameters, etc.) in both pyrolytic and oxidative conditions. All is applied to the design of the pyrolysis or combustion reactors for the generation of chemical compounds or the energy exploitation, respectively [8].

One way to study the kinetics of thermal decomposition is to raise pseudo-mechanistic models. Proposed schemes of reactions for studying the process can be very diverse (reactions in parallel, series, competitive, etc.), and they are proposed in view of the shape of the thermogravimetric curves, the nature of the material (homogeneous or heterogeneous sample) and information provided by the analysis of the products generated (for example, TG coupled with infrared spectrometry (TG-FTIR)). On this basis, the law kinetics of decomposition varies, and may be more or less complex.

Once the model of reactions and the corresponding kinetic equations are created, the next step is to solve these differential equations, and for that the numerical integration methods (Runge–Kutta, Euler, etc.) are very useful. In these methods the equations are numerically integrated for specific values of the supposed kinetic parameters, then the calculated experimental curves are compared with experimental curves by means of an objective function and this is optimized using an optimization method. The determination of kinetic parameters is to find those values with which theoretical thermogravimetry curves that are generated and are experimental ones are as similar as possible, that is to say, it comes to getting the parameters that best simulate or represent the experimental behavior observed.

This work aims to report a complete characterization of the TPOMSW and to deepen the understanding of the processes of thermal degradation in inert atmosphere of "TPOMSW", with emphasis on the kinetics of thermal decomposition. Thus, this study may be helpful for evaluating the possibility of managing this waste in pyrolysis plants as a method of utilization of this waste.

2. Materials and methods

2.1. Two-phase olive mill solid waste (TPOMSW)

TPOMSW was provided by the oil extraction plant, "Vadolivo" located in the province of Jaen (Spain). The sample was dried at room temperature until a constant weight is obtained and then, it was grinded and sieved to obtain the desired particle size (lower than 1 mm).

2.2. Physical–chemical characterization of TPOMSW

2.2.1. Particle size distribution

A sieve study of TPOMSW was performed with the objective of determining the size distribution of this solid after being milled. First, TPOMSW was milled and was subsequently separated by size using standard sieve series A.S.T.M. (American Society for Testing Materials. Mesh ASTM/size mm: 10/2.000; 14/1.400; 18/1.000; 25/0.710; 35/0.500; 45/0.355; 60/0.250).

This study was performed using a screening CISA, model RP-15. A sample of 10 g of TPOMSW (previously sieved to a size less than 1.00 mm) was taken and was then sieved. After that, the amount of TPOMSW retained on each sieve was weighed, and the percentage for each fraction was determined.

2.2.2. BET surface area and porosity

Surface area was determined by mercury intrusion porosimetry (MIP) generated using a mercury porosimeter (Quantachrome, model Poremaster 60).

The porous structure was analyzed by adsorption–desorption N_2 isotherms at 77 K, CO_2 adsorption isotherms at 273 K, and mercury porosimetry tests with the objective of determining all pores sizes: micropores (diameter < 2 nm), mesopores (2 nm < diameter < 50 nm) and macropores (diameter > 50 nm). Finally, the total volume of pores was determined by adding the volume of each of the pore size and the average pore diameter from values of the area surface and the total volume of pores.

2.2.3. FE-SEM analysis

The FE-SEM analysis was performed by a high-resolution scanning electron microscope (Carl Zeiss Merlin) with EDX and WDX analytical capability of Oxford that has a system that can work with all types of samples both in image and analysis. To perform this analysis, the samples were previously assembled on a sample holder of aluminum of 12.5 mm of diameter, using silver glue. To ensure the conductivity of the samples, they were covered with a thin layer of conducting carbon. Then, samples are introduced into the microscope chamber where they are subjected to a high vacuum so that air molecules do not interfere with the electron beam. Samples were metallized utilizing a Polaron SEM E-5000 coating unit.

2.2.4. Elemental analysis and X-ray fluorescence

Elemental analysis of dried TPOMSW sample was performed using an Elemental Fison's Instruments EA 1108 CHNS. This analysis allowed us to determine the percentage of C, H, N and S simultaneously in 15 min. First, TPOMSW was ground to fine powder and a weighed sample was burned in an excess of oxygen, and the mass of the combustion products (NO_2, CO_2, SO_2 and H_2O) was used to calculate the percentages of N, C, S and H contained in each sample. The O content was calculated by a difference of 100%.

The chemical composition of TPOMSW ash was determined by X-ray fluorescence (XRF) in a Philips Magix Pro (PW-2440).

2.2.5. Proximate analysis

A proximate analysis, as defined by ASTM, is the determination by prescribed methods of moisture, volatile matter, fixed carbon and ash.

The moisture content of TPOMSW was determined by the difference in weight between the wet sample and after drying in an oven (at 60 °C) until constant weight [9].

The content of volatile matter was performed according to standard UNE-EN 15148:2010. The sample was introduced into the oven at 900 °C during 7 min, and volatile matter was determined by difference of weight.

The ash content was quantified after combustion for 3 h at 600 °C of 2 g of sample, according to standard TAPPI T 211 [10].

The content of fixed carbon was determined by difference of the other components.

2.2.6. Structural composition (lignin, cellulose and hemicellulose contents)

For these determinations, first removal of soluble extractives was performed according to the standard TAPPI T-264 cm-97 [10]. Then, lignin and α-cellulose were determined according to standard TAPPI T 222 om-83 and TAPPI T 203 os-74, respectively [10], and holocellulose according to Browning [11]. Hemicellulose concentration was calculated as the difference between holocellulose and α-cellulose.

2.2.7. FTIR analysis

TPOMSW was analyzed with a FTIR Spectrometer (Perkin-Elmer, Spectrum 65) in the range of 4000–400 cm^{-1} to identify the chemical groups present in it and to complete the study of the functional groups. No additional preparation of the samples was necessary for this equipment in order to obtain a good quality spectrum.

2.2.8. Real and bulk densities

The real density was measured with helium by picnometry in a ACCUPYC II 1340, from Micromeritics at 27 °C with a total of 10 purges and cycles.

Bulk density was determined by weighing on analytical balance of the amount of TPOMSW needed to fill a given volume, with the solid homogeneously distributed. To minimize the manual error, the values of bulk densities obtained with three different volumes (10, 20 and 30 cm^3) were obtained and an average value of the three values was determined.