Characterization of the physical and chemical properties of olive cake for its use as fuel

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Abstract

In this work, a waste from olive industry, the olive cake, was characterized in terms of its physical–chemical properties, which can be useful for its use in thermal units. Then, its behavior on pyrolysis and combustion processes was studied by dynamic thermogravimetry. The characterization results showed that the solid presents a size distribution with about 56.6% of particles > 1.00 mm and with a low percentage of fines (11%). The carbon content was relatively high (22.15%), being one of the main characteristics of the solid that makes useful to be use as fuel. Besides, the low sulfur value (<0.1%) was very suitable from the environmental point of view, reducing SO_2 emissions. The amount of volatile compounds and fixed carbon was similar to other biomass; however the olive cake showed high percentages of ashes. The obtained heating value was around 17 MJ/kg, which is adequate to be used as fuel. Finally, experimental thermogravimetric and differential thermogravimetric curves showed a characteristic profile of lignocellulosic materials, with three stages of weight loss.

Keywords

Olive cake; biomass; characterization; dynamic thermogravimetry.

1. Introduction

Nowadays, a high amount of waste is generated in different industrial processes, which can be valorized as a renewable feedstock. It achieves two important goals: to recover of materials and energy from them and to reduce the landfill of waste to safeguard the environment and enabling the shift toward a circular bioeconomy. Inside wastes are two important groups: agroindustrial and organic wastes [1]. They are largely available, cheap, rich in functional groups potentially and with energetic potential and therefore they present good properties to be reused as secondary raw materials [2].

Spain is the world-leading of olive oil production. Only, Andalusia maintains an area of almost constant cultivation that reaches 1,500,000 hectares of olive groves approximately. Thus, a great amount of wastes is produced by olive oil production [3]. Moreover, due to the important evolutionary changes in the equipment used for the separation of olive oil from the remaining components, one waste from the new two-phase centrifugation process is the olive cake. In that sense, raw olive cake (alperujo in Spanish) is generated in large amounts by

olive industries in Mediterranean areas without any industrial application. Thus, the study of the properties of this waste to be use is of great economic, environmental and social importance, mainly for the Mediterranean area.

This work aims to report a complete characterization of the olive cake, with emphasis on its properties as fuel to evaluate the possibility of managing this waste in thermal processes.

2. Materials and methods

2.1. Material

The material used in this study was the olive cake, a waste from olive industry. The solid was supplied by the company Daniel Espuny S.A.U, located in Linares-Baeza, province of Jaen, Spain.

2.2. Physic-chemical characterization

A full physic-chemical characterization was performed by studying eight properties of the solid, which are intimately related with their properties as fuel. These properties are the most commonly studied for this kind of waste.

2.2.1. Particle size distribution

For obtained the particle size distribution of olive cake, the solid was milled and separated by size using standard sieve series A.S.T.M. (American Society for Testing Materials) and using a screening CISA, model RP-15. A sample of 100 g approximately of olive cake was taken to sieve. After that, the amount of solid retained on each sieve was weighed, and the percentage for each fraction was determined.

2.2.2. Elemental analysis

The elemental composition (C, H, N, S, O) analysis was performed using an elemental analyzer Fison's Instruments EA 1108 CHNS. It is based on a flash combustion of organic samples, which allows the simultaneous determination of percent carbon, hydrogen, nitrogen and sulfur in 15 min. Oxygen was obtained by difference.

2.2.3. Proximate analysis

Proximate analysis allowed the determination of the moisture, volatile matter, fixed carbon and ash contents. The moisture was determined following the UNE-EN-3 14774 using a drying oven with a temperature of 105 ± 2 ºC. The ash content was obtained according to the UNE-EN 14775, which is used for solid biofuels. The volatile content was performed following the procedure outline in the UNE-EN 15148, appropriate for solid biofuels. Finally, the fixed carbon content was determined by difference with the other components.

2.2.4. Holocellulose and lignin contents

The determination of holocellulose and lignin contents was performed following a sequential procedure (see Fig. 1). First, soluble hot water extractives were removed according to the TAPPI T 257. Then, ethanol-benzene extractable was separated according to TAPPI T 204.

Finally, the lignin and holocellulose contents of the solid free of extractive compounds were determined according to TAPPI T 222 and Wise method respectively [4-7].
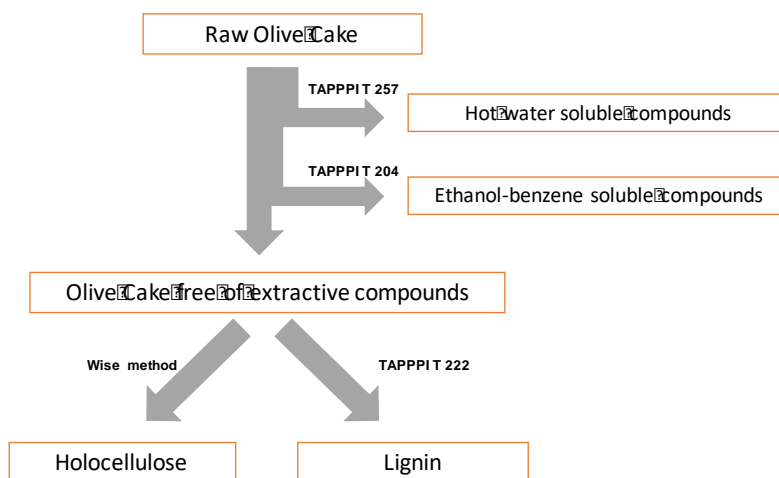

Fig. 1: Scheme of the sequential procedure followed to determine the holocellulose and lignin contents.

2.2.5. Bulk density

The bulk density was determined following the procedure described in the UNE-EN 15103 and represented as the ratio of the dry weight of solid sample and the volume occupied by it.

2.2.6. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The infrared analysis was performed using a Fourier Transform Spectrophotometer of Perkin-Elmer (model Spectrum-65) for detecting functional groups and characterizing covalent bonding information in sample.

2.2.7. Heating value

The determination of high heating value was performed using a Phywe LEC-02 calorimeter according to the procedure described in the standard UNE-EN 14918:2011.

2.2.8. Scanning electro-microscopy (SEM)

The SEM micrographs of materials were obtained using a Phenom-World (Phenom G2 pro, the Netherlands).

2.3. Thermal properties

The thermal properties of the olive cake were determined by studying its thermal decomposition using a Perkin-Elmer thermobalance (model STA 6000). Thermogravimetric tests were performed by duplicated with approximately 26 mg of sample and a heating rate of 15 ºC/min under a flow of 20 mL/min of nitrogen. The temperature range analyzed was from 30 to 800 ºC.

3. Results

3.1. Physic-chemical characterization

3.1.1. Particle size distribution

The particle size distribution is a useful property which determines the necessary physic pretreatments of the biomass to be use in thermochemical process. Thus, a low particle size makes easier the management and transport of the solid, improves the thermal decomposition by increasing the thermal yield and reducing the pollutants emissions. However, the crushing is a pretreatment which needs a high cost, and therefore it has been taken into account to choose the best particle size. On the other hand, an excessive low particle size can be cause smouldering of the solid during the storage. Table 1 shows results of the particle size analysis of the olive cake. It is observed that the most of the solid (56.60 %) are formed by particles > 1 mm. The other 53.40 % presents a very homogeneous distribution and all fractions present a similar percentage respect to total amount. The particle size distribution is appropriate to be used directly in the most of the energetic valorization technologies, without any additional pretreatment cost.

Table 1: Particle size distribution of the olive cake.

Tamaño de partícula	Masa %
2.00-1.00	44.50
1.00-0.710	12.10
0.710-0.500	12.94
0.500-0.355	10.68
0.355-0.250	8.72
<0.250	11.06

3.1.2. Elemental analysis

The elemental analysis of solid allows to know approximately the calorific value (by empirical equations as Milne or Dulong equations), to know the theoretical amount of oxygen necessary for the combustion and to identify other aspects related with the pollutants emissions (CO_2, NO_x and SO_2, mainly). Results from elemental analysis of the olive cake are showed in the Table 2. It is observed that the solid has a similar composition of other biomass waste [8-11]. It is mainly compound by carbon and oxygen and at lower proportion hydrogen and nitrogen. Moreover, the amounts of sulphur and nitrogen are negligible, which is useful to an environmental point of view in thermal applications.

Table 2: Elemental analysis of the olive cake.

C, %	H, %	N, %	S, %	O, %
44.03	7.03	1.70	<0.1	47.24

3.1.3. Proximate analysis

Table 3 shows the proximate analysis of the olive cake. It is observed that the moisture content is moderate, which allows that it is use directly without a previous drying step. Moreover, the amount of volatile compounds and fixed carbon is similar to other biomass and they are suitable to its use as fuel [12]. However, the amount of ashes is high compared with

similar waste [9, 11-13]. This fraction represents the inorganic content of the solid, and they can be generating operational problems and waste management. Moreover, it decreases the energetic content of the biomass.

Table 3: Proximate analysis of the olive cake.

Moisture, %	6.65
Volatile compounds, %	60.83
Fixed carbon, %	22.15
Ashes, %	10.37

3.1.4. Holocellulose and lignin contents

The holocellulose and lignin contents were determined following the sequential procedure described in the section 2.2.4 and results are showed in the Table 4. The high amount of hot water soluble compounds (40.3 %) presents a problem from an environmental point of view, due to the leaching products in contact with water. Respect to the solid free of extractive compounds, it is formed by similar fractions of lignin and holocellulose compounds, in the range of similar waste [9,13].

Table 4: Chemical analysis of the olive cake.

Hot water soluble compounds, %	40.30
Ethanol-benzene soluble compounds, %	0.50
Lignin (from free extractive), %	42.40
Holocellulose (from free extractive), %	57.60

3.1.5. Bulk density

The bulk density is a parameter of special interest in aspects related to the management and transport and storage of the solid. It is also important for the operational conditions of some thermal processes (as in the gasification in fluid bed). The bulk density of the olive cake was 571.43 kg/m^3 and it is consistent with waste densities reported in literature [13].

3.1.6. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR is a useful tool to know the chemical composition of a solid and the functional groups present in it. The Figure 2 shows the FTIR spectra of the olive cake. It indicates a complex composition of the solid with a high number of peaks. The most important peaks in the solid exist between 400 and 1700 cm^{-1}. Interpretations of the spectra were based on the information acquired from the literature [14–17] and results are showed in Table 5.
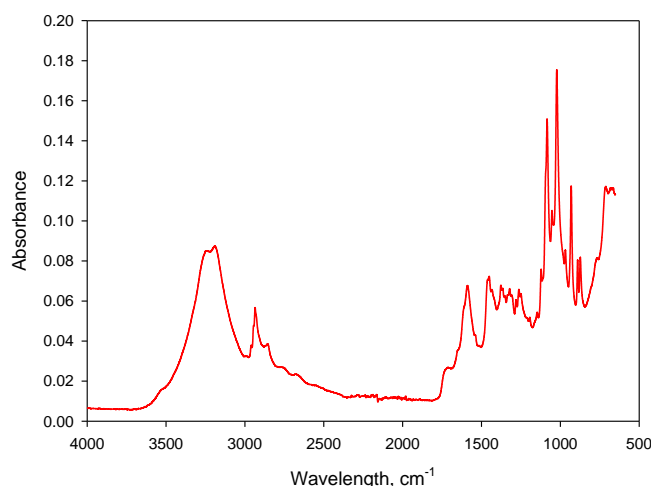
Fig. 2: FTIR spectra of the olive cake.

Table 5: Main functional groups observed on the olive cake by FTIR spectroscopy and their corresponding wavenumbers (v, cm^{-1}).

v cm^{-1}	Functional groups
3190.7	O-H in polymeric compounds
2935.0	C-H symetric aliphatic C
1711.5	COO$^-$ (cellulose and hemicellulose)
1588.5	Vibration of aromatic group in lignin, streching C=O
1451.1	Deformation C−H in −CH$_3$ and −CH$_2^-$ and metoxi groups (O−CH$_3$) in lignin
1377.0	COO−, deformation C−H in cellulose and hemicellulose
1321.2	Vibration C−H in carbohydrate, syringil and guaiacyl strings
1280.8	Syringil string and stretching C−O in lignin and xylane
1193.6	Vibration C−O−C in cellulose and hemicellulose
1083.6	Aromatic bonds and streching C-O
1022.4	Deformation C-H n aromatic, deformation C−O in primary alcohols and streching C=O
967.7	C–C in alcanes and cycloalcanes; C–H in aromatic rings
890.2	Deformation C−H in cellulose and hemicellulose
711.8	C-H aromatics
674.2	Glycosidic group in hemicelluloses

The most significant results observed are commented bellow:

- A wide band around 3200 cm^{-1}, which is associated to vibration of –OH bonds in alcohols and phenols and bonds between OH-N and hydrogen [18].

- In the range 1500-1000 cm^{-1} very significant peaks appear and they are assigned to vibration of C-O bonds and deformation of O-H bonds in organic compounds with oxygen (alcohols, phenols and ethers) [15].

- Bellow to 1000 cm^{-1} appear significant groups, which are associated the presence of aromatic groups in the material.

3.1.7.   Heating value

The heating value obtained for olive cake was 17.34 MJ/kg. Value is similar to other biomass and it is adequate for the use of the olive cake as fuel [9, 19-20].

3.1.8. Scanning electro-microscopy (SEM)

The scanning electron-microscope is an important tool for studying the morphology of individual particles of solid fuels. Figure 3 shows the SEM image of the olive cake and the corresponding microanalysis. These images clearly show that olive cake particles have a regular flat shape with semi-porous surface and contains mainly potassium and magnesium oxides.
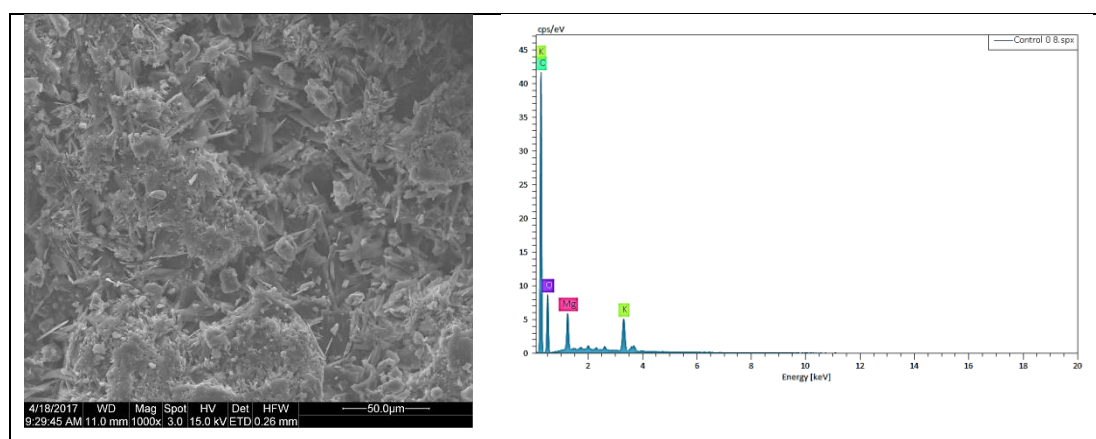

Fig. 3: SEM image and microanalysis of the olive cake.

3.2. Thermal properties

Figure 4 shows the experimental thermogravimetric (TG) and the derivative thermogravimetric (DTG) curves for the olive cake under nitrogen and air atmospheres respectively. The TG curve indicates the loss of mass ($w=m/m_0$, ratio between total mass at each time (m) and the intial mass (m_0)) versus the temperature and the DTG represents the values of dw/dt versus temperature.

The thermogravimetric and differential thermogravimetric analyses are characteristic of lignocellulosic materials, with three stages of weight loss. To a better analysis of curves a summary of the different stages on thermal decomposition of olive cake under nitrogen atmosphere and air atmosphere is showed in Table 6.

In nitrogen atmosphere, the first one takes place at temperatures below 200 ºC and it corresponds mainly to the moisture (5.5 % weight loss). Several authors have found the same stage corresponding to the loss of moisture in their studies with different types of biomass [21, 22].

The second one, at temperatures between 150 ºC and 355 ºC with maxima in the DTG curve at 200 ºC and 301 ºC, is attributable primarily to the thermal degradation of hemicellulose and cellulose (44,1 % weight loss). Authors such as Chen et al. [23] Zabaniotou et al. [24] or

Garima et al., [25] found the degradation peaks of hemicellulose and cellulose within the ranges presented in the present work. It should be noted here that the two weight loss peaks of hemicellulose and cellulose in the DTG curves do not differ significantly. Decomposition of hemicellulose is often seen as a "less marked peak", linked to the cellulose decomposition peak which is a better defined peak and occurs at higher temperatures [26].
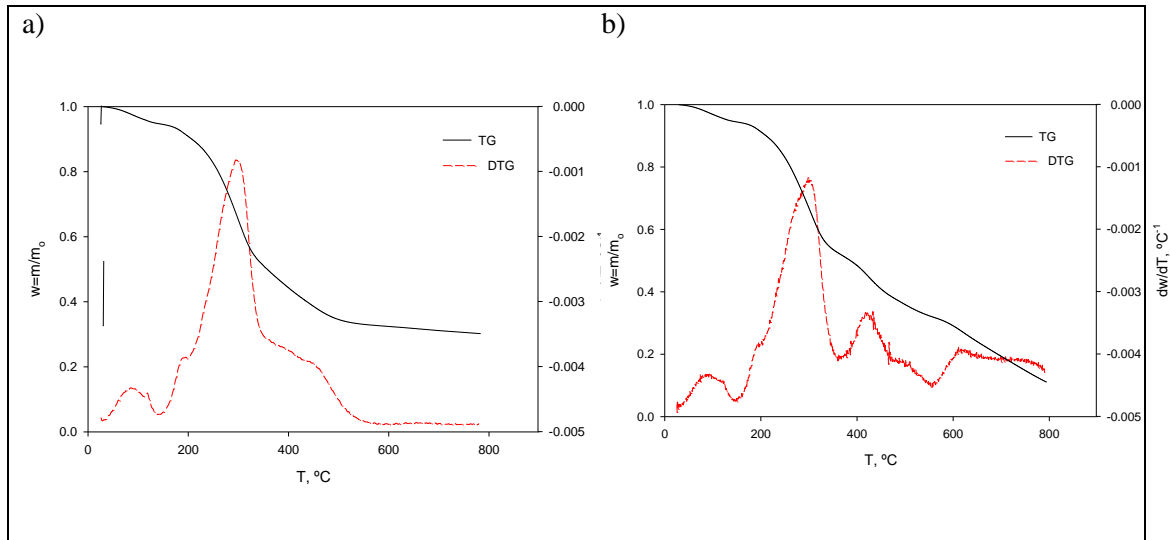

Fig. 4: Experimental TG (black) and DTG (red) curves for the olive cake under nitrogen atmosphere (a) and air atmosphere (b).

Table 6: Summary of the different stages on thermal decomposition of olive cake under nitrogen atmosphere and air atmosphere.

		N_2 atmosphere	Air atmosphere
First stage of decomposition (moisture)	T_i, ºC	30	30
	T_f, ºC	148	142
	$T_{máx}$, ºC	90	96
	$w_{volatilized}$ (%)	5.5	5.4
	$(dw/dT)_{máx}$, ºC^{-1}	$-6.714e^{-4}$	$-6.783e^{-4}$
Second stage of decomposition (hemicellulose and cellulose)	T_i, ºC	148	142
	T_f, ºC	355	364
	$T_{máx}$, ºC	200	198
	$w_{volatilized}$ (%)	44.1	42.4
	$(dw/dT)_{máx}$, ºC^{-1}	$-1.125e^{-3}$	$-1.171e^{-3}$
Third stage of decomposition (Lignin)	T_i, ºC	355	364
	T_f, ºC	800	800
	$T_{máx}$, ºC	-	-
	$w_{volatilized}$ (%)	20.3	41.2
	$(dw/dT)_{máx}$, ºC^{-1}	-	-

In the third stage, the gradual mass reduction in the solid fraction at temperatures between 355 ºC and 800 ºC is attributable to the progressive carbonization of thermally resilient components, mainly lignin (20.3 % weight loss). This step does not show a significant peak, providing a gently sloping baseline to the DTG curve. This behavior is similar to that of other lignocellulosic biomass compounds [27, 28].

In air atmosphere, stages of weight loss are similar to those found in nitrogen atmosphere. However, there are two significant differences. A new peak in the DTG curve appears at a temperature of approximately 421 ºC which may correspond to the combustion of the char generated during the decomposition. There is a lower amount of final residue (11 % vs. 30 % under nitrogen atmosphere). In air atmosphere new reactions occur, so that the decomposition is more complex. The reactions that can place take are: the pyrolysis reaction of the main constituents (hemicellulose, cellulose and lignin), the combustion of these components and the combustion of the carbonaceous residues that are generated in the pyrolysis reactions. All these reactions can be competitive.

Conclusions

Physico-chemical characterization of olive cake has been performed. Its particle size distribution is appropriate to be used directly in the most of the energetic valorization technologies, without any additional pretreatment cost. It is mainly compound by carbon and oxygen and at lower proportion hydrogen and nitrogen. Moreover, the amounts of sulphur and nitrogen are negligible, which is useful to an environmental point of view in thermal applications. Proximate analysis showed a high amount of ashes that can generate operational problems. FT-IR spectroscopy revealed that olive cake is composed by a great variety of groups as it presents a complex composition. The heating value obtained for olive cake was 17.34 MJ/kg. Finally, thermogravimetric (TG) and the derivative thermogravimetric (DTG) curves were analysed in two different atmospheres (nitrogen and air). The results are characteristic of lignocellulosic materials, with three stages of weight loss. In air atmosphere, stages of weight loss are similar to those found in nitrogen atmosphere, however new reactions occur, so that the decomposition is more complex.

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