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Study of the wet pomace as an additive in ceramic material

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ABSTRACT

The olive oil industry is a very important economic activity in the southeast of Spain. In the European Union, Spain produces more than the 50% of the olive oil. Twenty percent of world production is produced in the province of Jaen, Spain. This industry generates annually thousands tons of vegetable and water waste. Currently, these residues do not have an industrial application and are disposed in large quantities in ponds or landfills. It is essential to find a sustainable solution for the treatment of this kind of organic waste. The ceramics industry can incorporate large amounts of waste materials without important modifications in the manufacturing process. Its use represents a saving of raw materials and energy, incorporating inert organic and inorganic matter in the internal structure of the ceramic matrix. This study determines the characteristics of the residue from the production of olive oil (wet pomace) for its possible reuse in the production of ceramic materials.

Keywords: Olive oil industry; Wet pomace; Ceramic material

1. Introduction

The growing demand from the olive oil in the market, motivated by its beneficial properties to health and its presence in the Mediterranean diet, makes the agro-industry of the olives' groves an economic activity with enormous importance in Spain.

Spain is the first world power in the sector of olive oil, with an average production between 40 and 60% of total world production. Within Spain, the region of Andalucia clearly shows a strong presence in the sector, highlighting the province of Jaen as the first olive oil producer in the world (the International Olive Oil Council, 2010 data).

In the production of olive oil, around 80% of the processed olives become residue which may reach four million tons a year. In recent years, this fact has been the subject of much research [1,2], being the disposal from the industrial waste of olive oil production a serious environmental problem.

The wet pomace can be treated by composting or gasification [3–5]. In recent years, the thermal

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degradation of olive stone and other byproducts was the subject of a large amount of research. There are also investigation works related to pyrolysis of wet pomace [6,7].

However, these kinds of treatments are insufficient to treat the amount of waste produced in a year. Therefore, it is very important to find alternatives to its comprehensive treatment and reuse [2]. In this context, the industries of ceramics and cement [8,9] present a manufacturing processes that makes possible the recovery of this kind of waste, taking advantage of the calorific value during the combustion of the organic materials, and the incorporation of inorganic waste in the internal structure of the matrix [10–25,26].

A way to reduce the thermal conductivity is to introduce organics' additives to lightening the ceramic matrix [27,28]. Through these procedures, waste ceases to be a problem for the environment and in some cases, can be part of manufactured materials and incorporate their best properties.

Wet pomace contains water, olive stone and pulp residue. This waste has slightly acidic pH and very high organic matter content. By its organic nature can serve as an internal fuel during sintering of the materials, reducing the amount of fuel required in the oven, producing lighter bricks and saving raw materials. Further, the ashes produced in the combustion become part of the ceramic matrix, due to the formation of crystalline or vitreous phase during the sintering process [8–11].

The present study characterized the technological properties of bricks manufactured with the addition of different quantities of wet pomace to the clay matrix. The influence of the amount of wet pomace and the optimum concentration of residue added to the brick have been investigated in order to meet the current standards for ceramics materials as structural construction bricks.

2. Material and methods

2.1. Raw materials

The raw materials used in this study are red, black, and yellow clay, wet pomace, and water. The three different types of clay were supplied by a clay-pit located in Bailen, Jaen, and Spain. The wet pomace is collected at the olive oil production plant and transported to the laboratory.

The clay has a very heterogeneous grain size and in the laboratory is subjected to a grinding treatment in a hammer mill. To obtain uniform particle size, the clay was crushed and ground to yield a powder with a particle size suitable to pass through a 0.5 mm sieve, to obtain a fine and homogeneous dust. The control of the particle size have a very direct influence on the physical and mechanical characteristics of the final product. The wet pomace is dried in an oven at 90°C for 24 h to reduce their high initial humidity and then subjected to molturation in the hammer mill.

2.2. Preparation of the samples

To determine the effect of the incorporation of the dried pomace in the production of the ceramic bricks, different amounts of pomace were added to the clay, in between 0 and 10 wt.%. After weighing the raw materials, we proceed to mixing to obtain a good homogenization.

Then, samples were shaped using an extruder. Water is added during this process (25% in weight), to obtain the right plasticity in order to avoid defects in the compression stage, or defects during the sintering process like the formation of cracks.

Once the pieces have been shaped, measured, and weighed, they are dried at 110°C for 48 h to reduce their moisture content. The drying is a surface phenomenon. The water should migrate to the surface to evaporate. As the drying progresses, the particles come closer together and the contraction force increases [29]. The water loss is not linear and occurs in three stages. The first as water loss from the pores, second as loss of the residual water, and third in loss of the absorbed water.

To acquire final resistance and cohesion of the samples , the dried pieces were subjected to a firing process in a kiln. This process consist in obtain the sintering of the grains, increases its density, and change in porosity. This procedure generates new contraction in the volume of the pieces. Therefore, to control this effect, the dry samples are heated in a laboratory kiln and subjected to a temperature ramp (4°C/min up to 400°C, 2°C/min up to 700°C, 1°C/min to maximum temperature, 950°C, maintaining this temperature 180 min and turn off the oven for cooling by natural convection) until they reach 950°C, temperature most frequently used in the structural ceramics industry.

2.3. Characterization of raw materials

The raw materials were tested to determine their physical and chemical characteristics, which are listed in the following.

The chemical composition of the clay and wet pomace after firing at 950°C were determined by X-ray fluorescence (XRF) in a Philips Magix Pro (PW-2440).

The elemental composition of wet pomace was determined by combustion of samples in O_2 atmosphere using Thermo Finnigan Elementary Analyzer Flash EA 1112.

The moisture content of wet pomace was determined by the difference in weight of sample dried in an oven at 90˚C for 24 h.

pH of wet pomace was determined using a laboratory pH-meter model Crison micro pH 2,000.

Loss of ignition at 950˚C was determined by the difference in weight of the sample fired in the laboratory kiln at 950˚C. The results are calculated as a percentage.

The thermal behavior was determined by thermogravimetric and differential thermal analysis (TGA-DTA) with a Mettler Toledo 851e device in oxygen. Samples of 40–60 mg were placed in a platinum crucible and heated at a rate of 10˚C/min from room temperature to 1,000˚C. The data show the percentage weight losses based on temperature and the DTA diagram simultaneously.

2.4. Characterization of the samples

In order to determine whether the products manufactured fulfilled the legislation in effect for use as construction materials, their physical and mechanical properties were studied.

Weight loss from sintering was obtained by weighing the shaped piece after the stage of firing at 950˚C.

Absorption is a measure of moistening when the brick is submerged completely in water for a long period of time. The test was performed following standard UNE 67-027 [30].

The suction of a brick is the quantity of water absorbed during partial immersion for a short time. The test provides the initial capacity for inhibiting absorption through capillary action. To perform this test, the standard UNE 67-031 was followed [31].

The capacity of compression for a brick is the apparent unit load to breaking under an axial compressive force. This test is very important, since the function of the brick is essential to support the force of compression. For this test, a series of 15 fired samples of each sample were used. The test of compressive strength was performed following the standard UNE-EN 772-1:2011 [32] in a laboratory press.

3. Results and discussion

3.1. Raw materials

The FRX analysis of clays and wet pomace in Table 1 show that the chemical composition of the red clay, with low carbonate content, high iron content, Al_2O_3, and K_2O, is a characteristic of Triassic red clay from the Iberian Massif.

Yellow and black clay contains high carbonate content, characteristic of the Neogene clay from Guadalquivir Basin.

Wet pomace contains silica, potassium, and aluminum oxides. A high potassium content can encourage the process of fusion from the ceramic paste during the sintering process. The amount of CNH-S is shown in Table 2. The carbon and hydrogen

Table 1
Chemical composition of the clays and wet pomace ash by XRF

Oxide content (mass %)	LOI	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	ZrO_2	SO_3
Yellow clay	0.255	43.310	10.400	4.697	0.040	2.870	17.020	0.397	2.640	0.647	0.150	0.039	0.148
Red clay	0.264	44.770	14.190	8.020	0.085	2.710	2.090	0.100	5.240	0.789	0.130	0.023	0.139
Black clay	0.250	43.070	10.900	5.003	0.035	2.440	13.060	0.395	2.670	0.660	0.150	0.038	2.650
Wet pomace ash	0.398	27.380	4.930	3.605	0.074	7.273	25.740	0.605	13.160	0.334	4.230	0.016	1.280

Table 2
Physical and chemical properties

Property	Elemental composition (%)				Moisture Content (%)	pH
	C	N	H	S		
Wet pomace	1.6740 ± 0.0418	5.9596 ± 0.3585	7.6894 ± 0.2601	–	70.76 ± 0.11	5.7

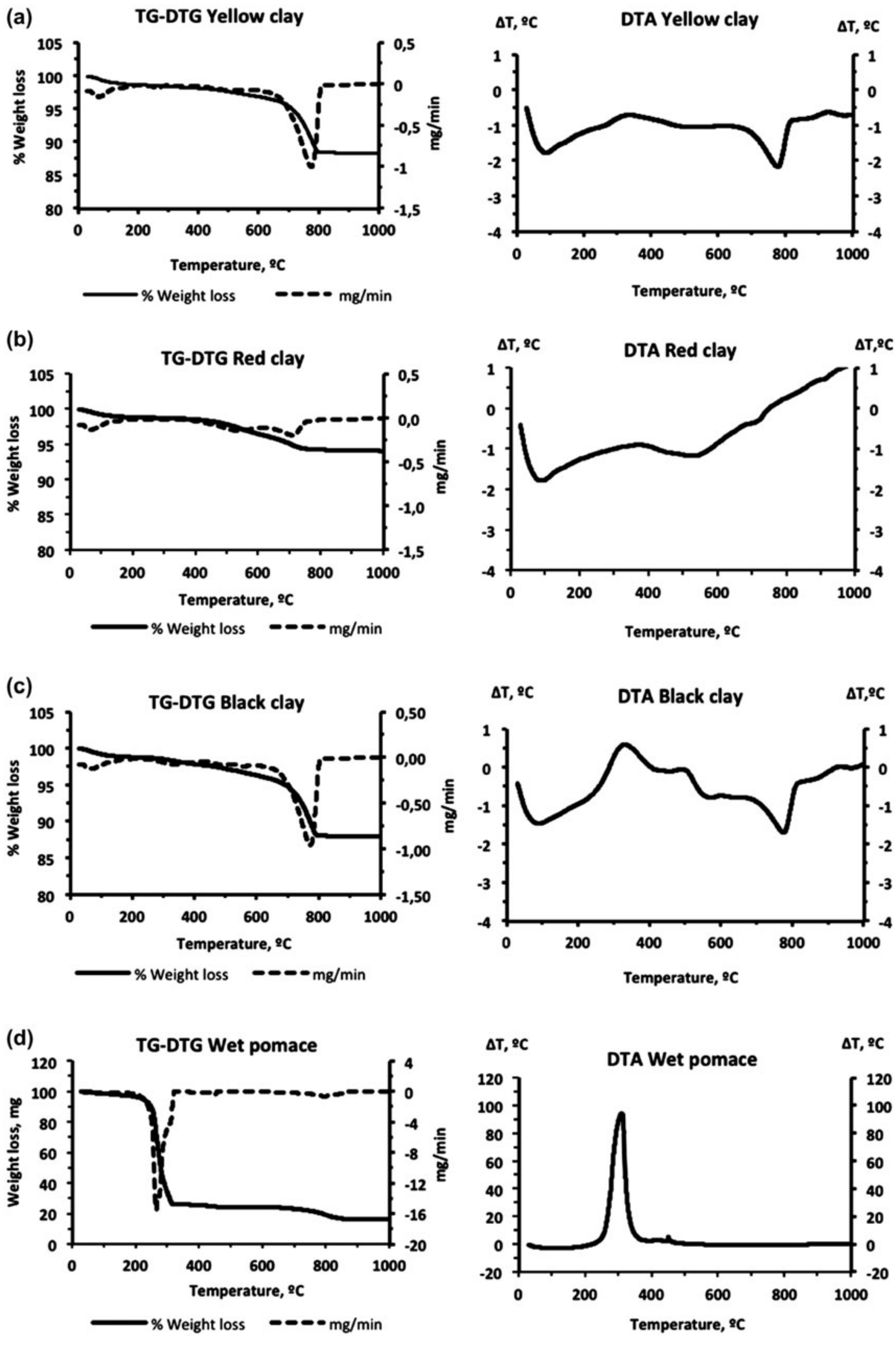

Fig. 1. TG-DTG and DTA of (a) yellow clay; (b) red clay; (c) black clay; (d) wet pomace.

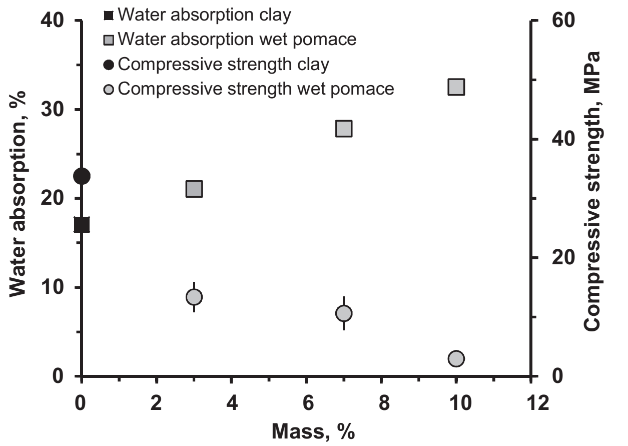

Fig. 2. Water absorption of the clay and samples with wet pomace.

Table 3
Weight loss of samples with wet pomace

Mass wet pomace (%)	Weight loss (%)
0	10.11 ± 0.06
3	14.84 ± 0.33
7	17.45 ± 0.11
10	23.92 ± 0.27

found are in accordance with the organic nature of wet pomace, therefore the nature of the pH is acidic.

The TGA-DTA curves of clays and wet pomace are shown in Fig. 1.

In the case of the yellow, black, and red clay (Fig. 1(a)–(c)) from room temperature to 60˚C, an endothermic peak can be observed. This peak is associated with moisture loss, indicating a weight loss of 1.2–1.5%. From 250 to 550˚C, the weight loss may be attributed to the combustion of organic material associated with an exothermic process. From 450 to 630˚C, dehydroxylation of the minerals in the clay occurs, as well as decomposition of the kaolinite and structural water of the illite, the DTA curve shows an endothermic peak centered around 565˚C. After 600˚C, for yellow and black clay, the decomposition of the calcium carbonate releasing CO_2 can be observed. This process is associated with the endothermic effect centered around 780˚C producing a weight loss in this phase. This peak is less pronounced for the red clay due to its lower carbonate content.

The TGA-DTA curve of wet pomace is typical from a solid fuel, showing a high weight loss. The residue can be totally combusted at low temperatures in the range of 200–500˚C. One exothermic peak and weight loss are observed, due to combustion of organic matter. The total loss of weight is 82.21 wt.%.

3.2. Sintered samples

The weight loss of clay after sintering at 950˚C reached 10.11% and it may be attributed to the elimination of organic matter by combustion, represented by the elimination of water due to dihydroxylation reactions and the decomposition of carbonates.

The addition of different wet pomace percentages increases the weight loss after sintering (Table 2). The weight loss reached its maximum of 23.92% in samples with 10 wt.% of wet pomace. As indicated by thermal analysis, the wet pomace burned almost completely without leaving a residue, with a weight loss of 80% or more.

Water absorption indicates the open porosity of the bricks as a quality parameter. As it absorbs less water, higher will be the life of the ceramic piece and it will have a better resistance to climatic conditions. The incorporation of wet pomace increased the water absorption (Fig. 2). The increase in water absorption with the addition of increasing amounts of pomace is due to weight loss, which is confirmed in the TG-DTG and DTA analysis. These results may be due to the lightening of the residue, due to its high content of organic matter, which is consumed during combustion, generating a porous structure (Table 3).

Fig. 3 shows the results of suction water. There is a slight increase in the water suction after sintering related at the same time with the increasing amounts of wet pomace. These results were as expected, since pieces subjected to these temperatures cause an increase in the interconnected surface porosity and a

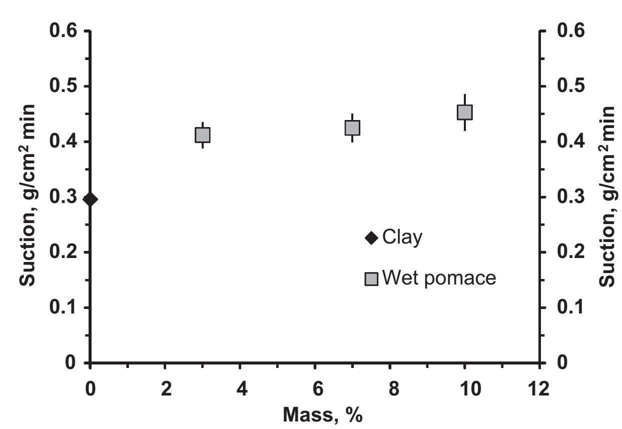

Fig. 3. Suction (g/cm^2 min) of the clay and samples with wet pomace.

tendency to increase the water suction in the samples. This property defines the final quality of the material, as well as its durability. Samples with a high content of wet pomace may have defects and the sepieces could be presented high values of suction of water. Therefore samples with a higher content of wet pomace will be less durable in comparison with samples without residue.

To determine the mechanical properties, very important with those materials, compression tests according to the UNE standard were performed [32]. Fig. 2, shows a high decrease in the compressive strength compared with samples containing only clay, also the relationship between the increase of water absorption with the decrease of compressive strength. A clear downward trend can be observed with an increase in the wet pomace percentage. Due to the higher porosity, reduction occurs in the mechanical strength, according to water absorption values. Samples containing wet pomace above 2.5 wt.% do not meet the standards for structural building materials.

4. Conclusions

This study considered the possibility of using wet pomace as an additive in fabrication of ceramic materials. The chemical and thermal characterization of wet pomace provides data to predict and evaluate its performance for energy purposes. According to its chemical composition and its thermal characterization, the solid olive residue can be used as additive in the manufacture of ceramic bricks, providing added value in their technological properties and reducing the costs of energy production. In addition, due to the nature of this type of organic waste, ceramic bricks with wet pomace may present a more porous microstructure, which reduces its weight and improves their thermal and acoustic insulation properties. The addition of increasing amounts of residue reduces the compressive strength. Addition of residue higher than 2.5 wt.% produced negative effects on mechanical properties of the samples that do not comply with the requirements of the legislation.

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