Application of the Calorimetric Methods to the Characteristics of Seeds from Olives†

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Abstract: The olive oil industry represents an important productive sector in the Mediterranean basin countries. Olive stone is an essential by-product generated in the olive oil extraction industries and it represents roughly 10% by weight of olive fruit. The seeds of pickled olives are also a significant waste product. In the present study we have investigated the possibility of use of differential scanning calorimetry for thermal characterization of seeds from green and black pickled olives from Croatia. The differential scanning calorimeter (DSC) with a normal pressure cell equipped with a cooling system was used to determine thermal properties of seeds from olives. The following analyses were also performed: determination of calorific values in a pressure bomb calorimeter, determination of initial water content, determination of changes of water content during drying at the temperatures of 30 °C, 50 °C and 80 °C, determination of a percentage content of seeds mass to the mass of the whole olives, determination of ash content. Seeds from olives are characterized by very good parameters as a biomass. The analysed olive seeds were characterised by low water content, low ash content, and a relatively high caloric value.

Keywords: olive seeds; differential scanning calorimeter (DSC); pressure bomb calorimeter; biomass; waste product

1. Introduction

Olive oil is one of the most traditional agricultural products of Mediterranean countries. In the last few decades, the interest in olive oil, due to its health properties, has increased significantly, and the cultivation of olive trees has spread throughout the world. According to the Food and Agriculture Organization of the United Nations, in 2018, 10.7 million hectares of olive trees were grown in 41 different countries. The total global olive production in 2018 was 21.6 million tonnes [1] An increase in olive oil production means a proportional increase in olive mill waste.

As a result of such an uptrend, olive oil producers face serious environmental problems due to the lack of cost-effective solutions for the management of olive mill waste. Therefore, it is necessary to pay special attention to the correct management of olive mill waste in order to minimize environmental pollution [2]. The seeds of pickled olives are also a significant waste product. As many

authors have shown in their research, now waste management is of great importance. The use of waste is inevitable due to the rapid depletion of natural resources [3].

The industrial processing of olive fruits to obtain olive oil produces large amounts of by-products including flesh, skin and seed, so in addition to the main product—olive oil, the biomass is also produced. Biomass is the term used to describe all biologically produced matter. Wood, energy crops, as well as agricultural and forest residues, which are the main renewable energy sources, are typical examples of biomass [4,5]. Intensive research is currently underway on alternative uses of olive biomass, taking into account their chemical composition and the possibility of producing renewable energy, fuels and compounds from this biomass. Energy is one of the easiest ways to make full use of olive biomass. In addition to direct combustion, there are several indirect ways to use olive biomass as a bioenergy source [6]. One type of biomass from the processing of olives is seeds. Structurally, olive fruits can be divided into the following three parts: the skin, called epicarp (1.0–3.0% of the fruit), which contains chlorophyll, carotenoids and anthocyanins responsible for the color; the flesh, called the mesocarp (70–80% of the fruit), makes up the greater part of the olive and is the reserve of all ingredients; and stone, known as the woody endocarp (18–22% of the fruit), which contains seeds [7].

In order to be used as biomass, olive stones should be characterized in terms of their calorific value, water content and compounds that are formed during their thermal decomposition. 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. Thermal analysis is convenient, reproducible, and is a useful method for characterizing heterogeneous organic materials [5]. One of the promising thermal techniques for biomass characterization is Differential Scanning Calorimetry (DSC) because DSC is sensitive, cheaper and faster, which means that it does not require time-consuming processing of test samples [5,8].

In the present study we have investigated the possibility of using differential scanning calorimetry for a thermal characterization of seeds from green and black pickled olives from Croatia.

2. Materials and Methods

2.1. Materials

Olive seeds extracted by hand from pickled green and dark olives from Croatia (OPG Bagić Zdravko) were analyzed. Determination of a percentage content of seeds mass to the mass of the whole fruit was carried out. Differential scanning calorimeter and pressure bomb calorimeter were used for characterization of olive seeds. The ash content was also determined and the water content at the beginning and during drying at different temperatures. All experiments and analyses were carried out in duplicate (n = 2) for each sample and the analytical data were used for statistical comparisons.

2.2. The drying experiments

The drying study of olive seeds included determination of initial water content (u) by oven-drying method and its change during drying process. Water content (u) of olive seeds was determined using the gravimetric method in a laboratory dryer at 105 °C for 24 h The change of water content during entire drying process were determined of olive seeds in a convective dryer at the temperature of 30 °C, 50 °C and 80 °C, without the flow of drying agent. The weight change of the samples was measured every half hour up to the moment, when mass replicated three times. On the basis of outcomes of carried out experiments the drying curves were drawn up.

2.3. Ash content determination

Ash content in the olive seeds was determined by combusting the material in the muffle furnace. The analysis consisted in taking a known amount of sample, placing the weighed sample in a dried

and weighed porcelain crucible, burning away the sample in an air atmosphere at temperatures above 500 °C, and weighing the crucible after cooling to room temperature in the desiccator.

2.4. Calorific value determination in a pressure bomb calorimeter

The heat of combustion (gross calorific value) was determined by using bomb calorimetry method. For this purpose about 1 g of the sample after grinding and creating pellet was electrically ignited to burn with the presence of pure oxygen. Heat of combustion of a sample was obtained based on the changes in temperature of water surrounding the bomb and exact weight of the sample. The result was automatically calculated by a calorimeter software.

2.5. Differential scanning calorimeter (DSC) measurements

The differential scanning calorimeter (TA Instruments Q 200) with a normal pressure DSC cell equipped with a cooling system was used to determine thermal properties of olive seeds. An approximately 10-15 mg of samples of olive seeds after grinding was heated up to 500°C with a heating rate of 5°C/min in a covered aluminium pan in an inert atmosphere with a flow of N_2 of 50 mL/min. Nitrogen is used as a carrier gas to ensure an inert atmosphere in the heating, which will not react with the samples.

2.6. Statistical analysis

The results are expressed as the mean value with the standard deviation. Relative standard deviation was calculated, where appropriate, for all data collected using Microsoft Excel Software. One-way analysis of variance ANOVA was performed using the Statgraphics Plus. The value of $p \leq 0.05$ was set as a statistical significance limit. Differences were considered to be significant at a p-value of 0.05, according to Tukey's Multiple Range Test.

2. Results and Discussion

Olive stones are not a desirable product in the food industry and constitute production waste in the processing industry and catering. Table 1 shows the basic properties of olive stones. The obtained results indicate that the share of the stone in the weight of the whole fruit is significant and amounts to 17.1% for green olives and 16.5% for dark olives, which is a significant value compared to e.g., cherry stones, where the share of the stone in the fruit is 9.9% [9].

Table 1. Basic properties of olive stones.

| Kinde of olive seeds	The seeds share in the total mass of the olives %	Water content u kg of H_2O /kg D.S.	Moisture %	Ash content %	Calorific value kJ/g
green olives seeds	17.1	0.53	34.7	2.18	20.64
dark olives seeds	16.5	0.55	35.4	2.69	20.07

Olive stones are a waste material and their management can be problematic. However, such a waste material can certainly be utilized for energy purposes. Olive seeds are characterized by a relatively low water content, which is 0.53 kg of H_2O/kg D.S. for green olive stones and 0.55 kg of H_2O/kg D.S. for a dark olive stone (i.e., about 35% moisture). However, in order to use the olives stones for burning or to process them into pellets, they should be dried to a humidity of about 12%, which during drying at 30 °C takes about 36 h for both types of stones tested (Figure 1a). This time can be significantly shortened by increasing the drying temperature to 50 °C, at which the required humidity was achieved after 12 h of the drying process (Figure 1b). In order to achieve the desired moisture content in the shortest time, the stones of the olives should be dried at a temperature of 80 °C. Drying at this temperature to achieve the desired humidity took 4 h (Figure 1c). No significant influence of the type of olive stone on the drying process was observed for the examined green and dark olive stones (Figure 1d).

The ash content of the green olive seeds (Table 1) under investigation was 2.18% and 2.69% of the black olive, which is a relatively high value compared to cherry pits, which contain about 0.25% ash [9], or to nut shells: peanuts, hazelnuts, walnuts, pistachios, which contained respectively: 2.00%; 0.74%; 1.38%; 1.42% of ash (2). The heat of combustion of the tested olive seeds is comparable to other biological materials and was 20.64 kJ/g for green olive seeds and 20.07 kJ/g for dark olive seeds. The results obtained by Mediavilla et al. [11] confirm that olive stones show a good characteristics for being used as a fuel, with low ash content (0.7%), high net calorific value (16.9 MJ/kg).
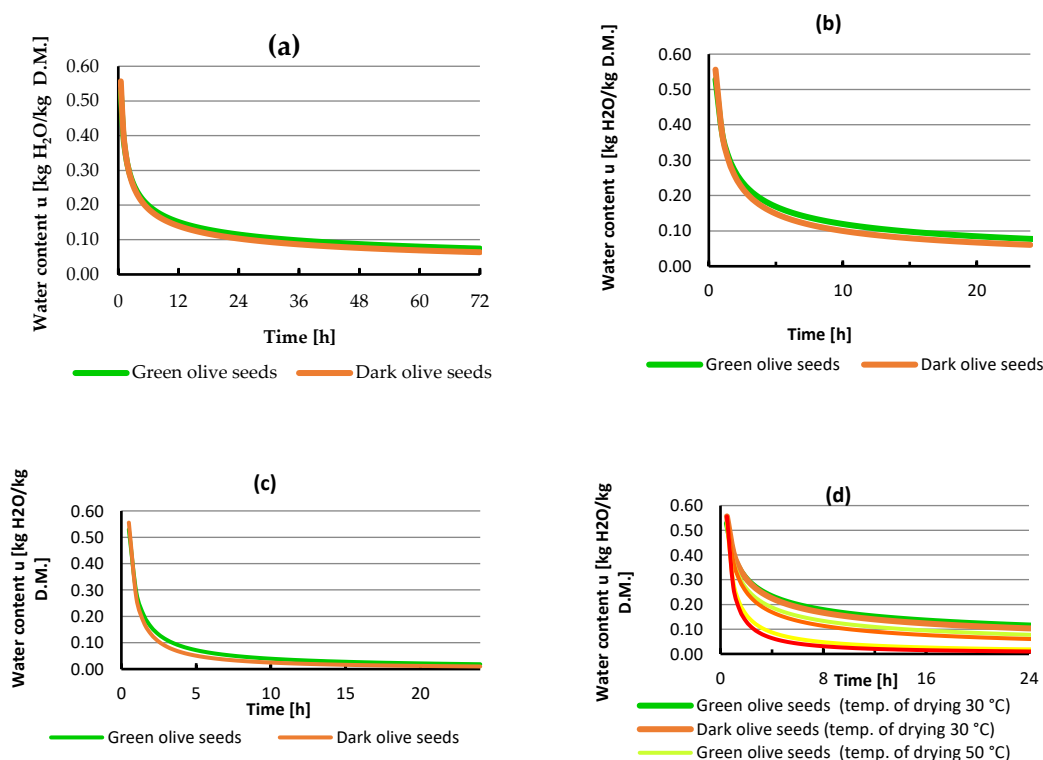
Figure 1. The drying curves for the olive stones dried at the temperature of 30 °C (a); 50 °C (b); 80 °C (c). Comparison of drying curves at different temperatures (d).

Considering olives seeds as a potential energy source, we also have to take into account the chemical composition of this material and its thermal properties. Research has shown that stones of olives mainly contain cellulose, hemicellulose and lignin, respectively 20.9, 26 and 35.6 % [1]. Thermal analysis is a useful, convenient and repeatable method for characterizing heterogeneous organic materials [12]. Differential Scanning Calorimetry (DSC) along with Differential Thermal Analysis (DTA) and Thermogravimetry (TG) are nowadays often used to analyze biological materials [5,12–13]. The DSC with a normal pressure cell equipped with a cooling system was used to determine thermal properties of seeds from olives. Literature data indicate that thermal degradation of hemicellulose begins at about 180 °C and ends at about 350 °C. Cellulose is relatively more stable than hemicellulose, its decomposition temperature ranges from 200 °C to 375 °C, while lignin behaves differently [5,14]. Lignin decomposition is in the range from 180 °C up to 900 °C with an undefined maximum mass loss. As was reported in [15] thermal decomposition regions for cellulose are in ranges of around 315–400 °C with maximum mass losses at and 355 °C and for hemicellulose are in ranges of around 220–315 °C, with maximum mass losses at 268 °C. When analysing the DSC curves for olive seeds, it can be seen that in temperatures ranging between 225–315 °C, characteristic for hemicelluloses, the largest exotherm has dark olive stones and the smallest has green olive stones (Figure 2).
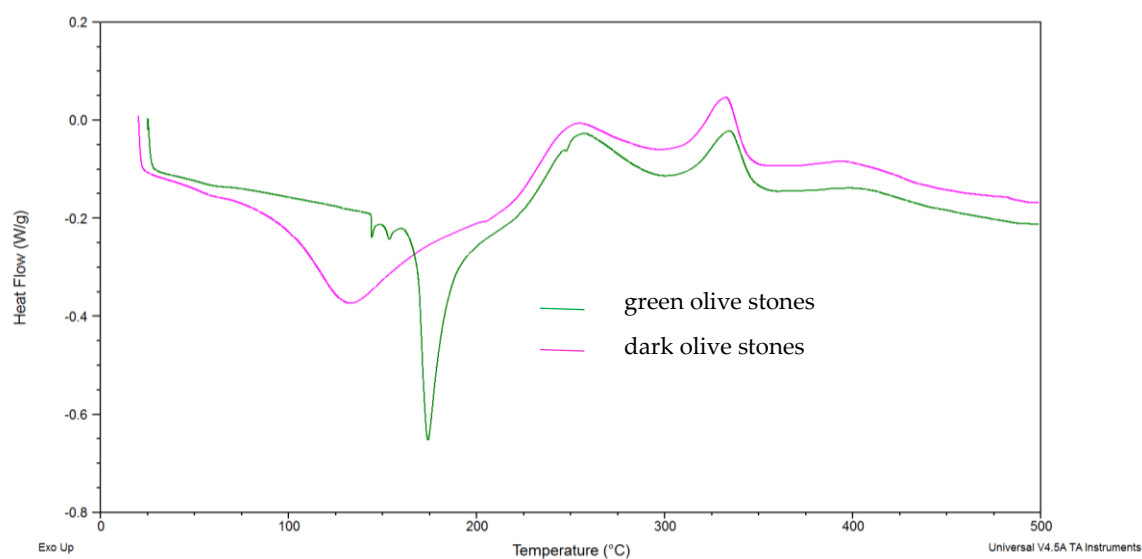
Figure 2. DSC curves of olive seeds.

In temperatures ranging between 315–360 °C, characteristic for celluloses, the largest exotherm for dark olive stones and the smallest green olive stones were observed. The proportion of each olive seed component varies depending on the kind of olives. Therefore, it is expected that the DSC curves are different depending on the type of olive seeds. These results suggest that the curves obtained by differential scanning calorimetry (DSC) can be used as a discriminant characteristic.

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