



Influence of process temperature on drying kinetics, physicochemical properties and antioxidant capacity of the olive-waste cake



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ABSTRACT

The objective of this study was to determine the effect of drying temperature on the drying kinetics, proximal analysis, energy consumption and the antioxidant capacity of the olive-waste cake “Picual” variety from 40 to 90 °C. Evaluation of proximal analysis evidenced the influence of temperature on the waste parameters. Values of effective moisture coefficients were in the range of $1.97\text{--}6.05 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ under the studied conditions. Activation energy was found to be $28.24 \text{ kJ mol}^{-1}$. The Weibull model was successfully applied ($r^2 > 0.973$). Specific energy consumption decreased as temperature increased, showing the effect of drying times over temperature. Although dehydrated samples decreased the initial total phenolic content, significant differences were not detected. Effects of drying temperatures did not present significant differences on antioxidant capacity (ORAC and DPPH) when compared to fresh samples. The oleic acid (main fatty acid in fresh samples) presented a maximum increased at 90 °C.

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1. Introduction

By-products of plant food processing, like the olive-waste cakes, represent a major disposal problem for industry concern. However, they are a very promising source of value-added substances because they contain a high amount of bioactive compounds (Vega-Gálvez et al., 2010). Chile, favoured by appropriate climatic conditions in its central regions, has steadily increased its olive oil production (ODEPA, 2008) to join Spain, Italy, Greece, Turkey and Tunisia, large producers that have together marketed 97% of the world olive oil production. Thus, the amount of bio-wastes produced by the olive oil industry is increasing.

The cake needs to be dried prior to further processing due to its high water content, which makes it susceptible to modification by micro-organisms (Aboulkas, El Harfi, & El Bouadilli, 2008). Conventional air drying is one of the most frequently used operations for by-product treatments (Doymaz, Gorel, & Akgun, 2004; Krokida, Maroulis, & Kremalis, 2002). The drying process generally involves high energy costs, and the use of proper operating conditions is crucial not only to warrant quality of final products but also low environmental impact (Liébanes, Aragón, & Palancar, 2008). Drying

temperature is well known to alter initial product characteristics when they are exposed to hot air drying, leading to changes in the quality and safety of food materials (Di Scala & Crapiste, 2008).

Recently, there is a rising interest in natural antioxidants as currently used synthetic antioxidants have been suspected to cause or promote undesirable effects on human health. Phenolic compounds are of considerable interest due to their antioxidant properties (Balasundram, Sundram, & Samman, 2006). Olive-waste cake is an excellent source of phenolic compounds and can reach up to 30% of olive oil manufacturing (Lafka, Lazou, Sinanoglou, & Lazos, 2011; Suárez, Romero, & Motilva, 2010). Indeed, during olive oil processing, fruit phenols shift from paste (crushed fruits) to oil and resulting by-products (wastewater and pomace), depend on the relative polarities of phenols, the presence of surfactants, temperature, and the composition and relative amounts of resulting phases (Klen & Vodopivec, 2012). Moreover, the measured antioxidant capacity (AC) of a sample depends on technology and free radical generator or oxidant is used in the measurement. Consequently, comparison of different analytical methods for determining AC is a key factor in helping investigators to choose a method and to understand the result obtained (Zulueta, Esteve, & Frígola, 2009).

The aims of this study were to evaluate the effect of air temperature on physicochemical properties, drying kinetics,

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moisture diffusion coefficients, energy consumption and fatty acids profile during convective dehydration of the olive-waste cake of “Picual” variety. Moreover, evaluations of total phenolic content as well as antioxidant capacity by means of DPPH and ORAC as affected by air drying temperature were also investigated.

2. Materials and methods

2.1. Raw material

The olive cake was supplied by an agro-food company (Agronoble S.A.) from Ovalle, Chile. The waste resulted from a continuous cold process of the olive oil production. The olive variety used in this investigation was Picual, harvested at optimum ripeness and pressed without delay. The samples used for analysis were packed in polyethylene bags and kept in a freezer at -20°C . Before drying, olive cake samples were thawed during 24 h under refrigeration conditions at 5°C .

2.2. Physicochemical analysis

The crude protein content was determined using the Kjeldahl method with a conversion factor of 6.25. The lipid content was obtained gravimetrically following Soxhlet extraction, using petroleum ether (Merck, p.a.) as solvent according to method described in AOAC method No. 920.39 (AOAC, 1990). The crude fibre content was estimated by Weende method through an acid/alkaline hydrolysis of insoluble residues as described in AOAC method No. 962.09 (AOAC, 1990). The crude ash content was estimated by incineration in a muffle furnace (Felisa, FE-341, Jalisco, Mexico) at 550°C . All methodologies followed the recommendations of the Official Methods of Analysis (AOAC, 1990). The available carbohydrate was estimated by difference. The moisture level was determined by means of AOAC method No. 934.06 (AOAC, 1990). All measurements were done in triplicate.

2.3. Sorption behaviour of olive cake

The desorption isotherm of olive waste was determined following the methodology recommended by project COST 90 (Spiess & Wolf, 1983), where a known mass of sample, prepared in triplicate, was allowed to come into equilibrium with an atmosphere produced from a saturated salt solution having a known water activity including LiCl, $\text{KC}_2\text{H}_3\text{O}_2$, MgCl_2 , K_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, KI, NaCl, KCl and KNO_2 . The sample and the salt solution were kept separated within a sealed container, and the sample weight was taken every 15 days from the initiation of the test until it reached equilibrium (constant weight). Salt solutions, samples and thymol tiny Petri dishes were placed into sealed containers; the latter ones were used to prevent microbial growth, when relative humidity was over 75%. The equilibrium moisture content was determined by means of AOAC method No. 934.06 (AOAC, 1990). All measurements were done in triplicate. The equation for modelling the isotherms was the Guggenheim, Anderson and de Boer, commonly known as GAB (Eq. (1)). This model is usually used with foods since it is considered to have parameters based on physicochemical phenomena, such as monolayer moisture content (X_m), and the constants C and k (Liébanes et al., 2008).

$$X_{we} = \frac{X_m \cdot C \cdot k \cdot a_w}{(1 - k \cdot a_w) \cdot (1 + (C - 1) \cdot k \cdot a_w)} \quad (1)$$

where X_{we} is the equilibrium moisture content (g water g^{-1} dry matter (d.m.)), X_m is the monolayer moisture content (g water g^{-1} d.m.) and a_w is the water activity (dimensionless).

2.4. Drying process and modelling of drying kinetics

Drying process was carried out at six different air temperatures ($40, 50, 60, 70, 80$ and 90°C) in a convective dryer, built at the Department of Food Engineering of Universidad de La Serena, at a constant air flow rate of $2.0 \pm 0.2 \text{ m s}^{-1}$. The load density was 4 kg m^{-2} . The dehydrated samples were packed and kept in the dark in polyethylene bags until analysis. All experiments were done in triplicate. To predict drying process behaviour that takes place during the falling rate period, during which water is transported to the surface material by diffusion transport phenomena is necessary to use Fick's second diffusion law (Eq. (2)) (Di Scala & Crapiste, 2008). In this model the dependent variable is the moisture ratio (MR) which relates the gradient of the sample moisture content in real time to both initial and equilibrium moisture content (Eq. (3)).

$$\frac{\partial \text{MR}}{\partial t} = D_{\text{eff}} \frac{\partial^2 \text{MR}}{\partial x^2} \quad (2)$$

$$\text{MR} = \frac{X_{wt} - X_{we}}{X_{wo} - X_{we}} \quad (3)$$

where X_{wt} is the moisture content (g water g^{-1} d.m.), X_{wo} is the initial moisture content (g water g^{-1} d.m.), X_{we} is the equilibrium moisture content (g water g^{-1} d.m.) obtained from Eq. (1), D_{eff} is the effective moisture diffusivity ($\text{m}^2 \text{ s}^{-1}$), t is the drying time (s) and x is the spatial dimension (m).

The mathematical solution of Eq. (2), when internal mass transfer is the controlling mechanism and one-dimensional transport in an infinite slab is assumed, and is given by Eq. (4). For sufficiently long drying times, the first term in the series expansion gives a good estimate of the solution (Di Scala & Crapiste, 2008), Eq. (5)

$$\text{MR} = \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp \left[\frac{-(2i+1)^2 D_{\text{eff}} \pi^2 t}{4L^2} \right] \quad (4)$$

$$\text{MR} = \frac{8}{\pi^2} \exp \left[\frac{D_{\text{eff}} \pi^2 t}{4L^2} \right] \quad (5)$$

where L is the half-thickness of the slab (m). In practice, the effective moisture diffusivity for each temperature was calculated by plotting experimental drying data in terms of $\ln(\text{MR})$ versus drying time and the D_{eff} value obtained from the straight line's slope.

The standardised Weibull model (Eq. (6)) has been successfully applied to describe kinetics of chemical, enzymatic and microbiological degradation processes as well as in the dehydration process of several foods (Corzo, Bracho, Pereira, & Vásquez, 2008).

$$\text{MR} = \exp \left[- \left(\frac{t}{\beta} \right)^{\alpha} \right] \quad (6)$$

The temperature dependence of the effective diffusivity can be represented by an Arrhenius relationship (Akgun & Doymaz, 2005). Both kinetic parameters (E_a and D_o) can be estimated from the slope and intercept of the plot $\ln D_{\text{eff}}$ versus $1/T$ (Vega-Gálvez et al., 2010).

$$D_{\text{eff}} = D_o \exp \left(\frac{-E_a}{RT} \right) \quad (7)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), E_a is the activation energy (kJ mol^{-1}), D_o the Arrhenius factor ($\text{m}^2 \text{ s}^{-1}$) and T is the absolute temperature (K).

2.5. Energy consumption in hot-air convection drying

During the test, dryer specific energy consumption required for drying a kilogram of olive-waste cake is calculated using Eq. (8)

according to the work of Motevali, Minaei, and Khoshtagaza (2011):

$$E_t = \frac{v \rho_a C_a \Delta T t}{d \Delta X} \quad (8)$$

where E_t is total energy consumption in each drying condition (kJ kg^{-1}), d : is the load density (kg m^{-2}), v : air velocity (m s^{-1}), ρ_a is the air density (kg m^{-3}), t is the total drying time of each sample (h), ΔT is the temperature difference ($^{\circ}\text{C}$), C_a is the specific heat ($\text{kJ kg}^{-1} ^{\circ}\text{C}^{-1}$) and ΔX is moisture content difference (kg kg^{-1}).

2.6. Determination of total phenolic content

Total phenolic content (TPC) was determined colorimetrically using Folin–Ciocalteu reagent (FC) according to Chuah et al. (2008) with modifications. Extract was obtained using 3–5 g dried and finely crushed sample, to which 40 ml of methanol were added. Mixture was homogenised for 24 h on an orbital shaker, before filtering through a Whatman filter No. 1. The filter cake was washed twice with 40 ml of methanol and the filtrate was evaporated under reduced pressure at 40°C on a rotary evaporator (Büchi RE 121, Switzerland). Extract was then dissolved in 50 ml methanol and kept refrigerated until further analysis.

0.5 ml aliquot of the olive cake extract was transferred to a glass tube; 0.5 ml of reactive FC was added after 5 min followed by 2 ml of Na_2CO_3 solution (200 mg ml^{-1}). The sample was then mixed on a vortex mixer and the reaction proceeded for 15 min at ambient temperature. Ten ml of ultra-pure water were then added and the precipitate formed was removed by centrifugation for 5 min at 5000 rpm. Finally, absorbance was measured at 725 nm in a spectrophotometer (Spectronic™ 20 Genesys™131, Illinois, USA) and compared to a gallic acid (GA) calibration curve. Results were expressed as $\text{mg GA } 100 \text{ g}^{-1} \text{ d.m.}$ All reagents were purchased from Merck (Merck KGaA, Darmstadt, Germany) and all measurements were done in triplicate.

2.7. Determination of antioxidant activity: Oxygen Radical Absorbance Capacity Assay (ORAC)

The ORAC assay was performed as described by Guorong, Mingjun, Fengwang, and Dong (2009). Briefly, the 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH) was dissolved in 10 ml of 75 mM phosphate buffer (pH 7.4) to a final concentration of 360 mM. A fluorescein stock solution (1.20 mM) was made in 75 mM phosphate buffer (pH 4) and stored; before addition the stock solution was diluted with buffer phosphate to 100 nM. 200 μl of this working sodium fluorescein solution (100 nM) was added to each microwell and 40 μl of a diluted sample solution, standards (solutions of 0–200 μM Trolox) and blank (phosphate buffer pH 7.4) were added to the respective microwells. The microplate was incubated 20 min at 35°C under shaking. After this timereactions were initiated by the addition of 35 μl of 2,2'-azobis-2-methyl-propanimidamide, dihydrochloride (AAPH) diluted in 75 mM phosphate buffer (pH 7.4) to 360 mM to all the wells. A Multimode Plate Reader, Victor TM X 3, (Perkin Elmer, Singapore) was used at 485 nm excitation and 535 nm emission. ORAC values were calculated and the AUC and the Net AUC of the standards and samples were determined using Eqs. (9) and (10), respectively. Results were expressed as $\mu\text{mol Trolox equivalents (TE)}$ per milligram of tested dry samples.

$$\text{AUC} = 0.5 + (R2/R1) + (R3/R1) + (R4/R1) + \dots + 0.5(Rn/R1) \quad (9)$$

$$\text{Net AUC} = \text{AUC}_{\text{sample}} - \text{AUC}_{\text{blank}} \quad (10)$$

where $R1$ is the fluorescence reading at the initiation of the reaction and Rn is the last measurement.

2.8. Determination of DPPH free radical scavenging activity

Free radical scavenging activity of the samples was determined using the 2,2-diphenyl-2-picryl-hydrazyl (DPPH) method (Lafka et al., 2011) with some modifications. Different dilutions of the extracts were prepared in triplicate. An aliquot of 3.9 ml of 0.51 mM DPPH radical in methanol was added to a test tube with 20 μl of the sample extract and 80 μl of methanol. The reaction mixture was vortex-mixed for 30 s and left to stand at room temperature in the dark for 30 min. The absorbance was measured at 515 nm, using a spectrophotometer (Spectronic 20 Genesys™, IL, USA). Trolox (0.1–1.0 mM) was used as the standard for the calibration curve, and the DPPH radical-scavenging activities were expressed as $\mu\text{mol Trolox equivalents (TE)}$ per milligram of tested dry samples. Methanol was used to calibrate the spectrophotometer.

2.9. Determination of fatty acids

The fatty acid composition was determined by gas chromatography. Fatty acid methyl esters (FAME) were prepared by UNE-EN ISO 5509, with 0.5 M NaOH used for saponification, isooctane as solvent and $\text{BF}_3\text{--CH}_3\text{OH}$ as esterifying agent. The fatty acid methyl esters (FAME) were analysed using Perkin Elmer gas chromatograph fitted with SGE capillary column, BPX70 bonded phase in fused silica 60 m length, 0.25 mm internal diameter and 0.25 mm film thickness with flame ionisation detector (FID). The injection and detector temperatures were set at 250°C and the carrier gas was Helium at 1.0 ml min^{-1} constant flow. The initial oven temperature was 160°C and then increased to 190°C at a rate of $3^{\circ}\text{C per minute}$ and held for 10 min, again increased to 220°C at rate of $1^{\circ}\text{C per minute}$ for a final time of 10 min. The injection volume was 0.5 μl . Peaks were identified by comparison with their retention times with appropriate FAME standards (Sigma). The standard fatty acid methyl esters were run under the same conditions and the subsequent retention times were used to identify the fatty acids. The fatty acids were expressed as $\text{g } 100^{-1} \text{ g d.m.}$

2.10. Statistical analysis

The effect of air-drying temperature on parameters was estimated using Statgraphics® Plus 5.0 (Statistical Graphics Corp., Herndon, VA, USA). One-way ANOVA with five levels and three replicates was performed. Differences among the media were analysed using the least significant difference (LSD) test with a significance level of $\alpha = 0.05$ and a confidence interval of 95%. In addition, the multiple range test (MRT) included in the statistical program was used to demonstrate the existence of homogeneous groups within each of the parameters.

3. Results and discussion

3.1. Physicochemical analysis

Table 1 shows the mean values and standard deviations of proximate analysis of both fresh and dehydrated samples, including moisture, crude protein, fat, crude fibre and ash contents. Carbohydrate content can be calculated by difference. Water activity is also presented in Table 1. Proximate analysis of fresh and dehydrated samples showed that drying process influenced the overall composition of the olive-waste cake. Significant differences on the contents in fresh and dehydrated samples were obtained ($p < 0.05$). The values of the proximate analysis of the fresh olive cake differed

Table 1Proximate analysis of fresh and dehydrated samples of olive-waste cake “Picual” (g 100 g⁻¹ dry matter).

Parameters	Fresh	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
Moisture	208.53 ± 4.17 ^a	3.78 ± 0.03 ^b	3.21 ± 0.07 ^c	2.37 ± 0.11 ^d	2.97 ± 0.04 ^e	1.39 ± 0.08 ^f	1.50 ± 0.07 ^f
Fat	8.70 ± 0.26 ^a	10.31 ± 0.05 ^b	10.75 ± 0.27 ^c	9.80 ± 0.16 ^d	9.28 ± 0.08 ^e	10.96 ± 0.14 ^c	11.64 ± 0.25 ^f
Ash	5.15 ± 0.12 ^a	5.18 ± 0.39 ^a	6.14 ± 0.18 ^b	6.54 ± 0.05 ^c	5.92 ± 0.31 ^{c,e}	6.46 ± 0.10 ^c	6.29 ± 0.23 ^c
Protein	6.48 ± 0.16 ^a	7.64 ± 0.48 ^{c,d}	7.77 ± 0.08 ^{c,d}	7.24 ± 0.09 ^{b,c}	6.76 ± 0.28 ^{a,b}	7.94 ± 0.42 ^d	7.82 ± 0.37 ^d
Crude fibre	34.14 ± 4.77 ^a	21.88 ± 0.58 ^b	21.98 ± 0.50 ^b	24.31 ± 1.21 ^b	24.66 ± 2.24 ^b	23.83 ± 1.27 ^b	22.66 ± 0.95 ^b
Carbohydrates	12.08 ± 0.76 ^a	73.24 ± 0.79 ^b	72.22 ± 0.05 ^c	74.10 ± 0.21 ^d	75.15 ± 0.23 ^e	73.27 ± 0.47 ^b	72.77 ± 0.23 ^{b,c}
Water activity	0.928 ± 0.00 ^a	0.102 ± 0.004 ^b	0.098 ± 0.004 ^b	0.069 ± 0.002 ^c	0.085 ± 0.003 ^d	0.052 ± 0.002 ^e	0.051 ± 0.001 ^e

^{a,b,c,d,e,f} Different letters in the same row indicate significant difference (*p*-value < 0.05). (Data are expressed as average ± standard deviation in three replicates).

from those reported in previous works (Molina-Alcaide, & Yáñez-Ruiz, 2008; Sellami, Jarboui, Hachicha, Medhioub, & Ammar, 2008). The moisture content of fresh olive cake used in drying experiments was 208.53 ± 4.17 g 100 g⁻¹ d.m. The crude protein content of the fresh olive cake was also similar to those reported by other authors (Alburquerque, González, García, & Cegarra, 2004; Molina-Alcaide, & Yáñez-Ruiz 2008). The main component of fresh olive cake was crude fibre with a mean value of 34.14 ± 4.77 g 100 g⁻¹ d.m. showing that high percentage of crude fibre is typical to olive cake, which is comparable to results presented by Chiofalo, Liotta, Zumbo, and Chiofalo (2004). This high fibre content, associated with the presence of skin and pulp is an important quality attribute of olive cake. As a by-product of the olive oil industry, it would be a good source of animal feeding (Chiofalo et al., 2004; Weinberg, Chen, & Weinberg 2008). It could even be a potential source of dietary fibre, which is known for its health-promoting properties (Garau, Simal, Roselló, & Femenia, 2007). The crude fibre contents of the dehydrated olive cake were also significantly different to that of the fresh sample (*p* < 0.05). A decrease in dehydrated samples was observed, the minimum loss was at 40 °C where a decrease of 36% is evidenced, however, significant differences were not shown.

The proximate analysis also showed significant differences between the ash content of fresh and dehydrated samples from 50 to 90 °C (*p* > 0.05). Protein content also increased with temperature, but significant differences were not found (*p* > 0.05). Regarding to fat, an increase in fat content can be observed in Table 1, presenting significance differences with the fresh sample (*p* < 0.05).

3.2. Desorption isotherms

The experimental desorption isotherms were obtained at 40, 60 and 80 °C. The sorption data were modelled by using GAB equation. The GAB model gave a closest fit to the experimental data (*r*² > 0.952). The value of the monolayer (*X_m*) is of particular importance as it indicates the amount of water that is strongly adsorbed to specific sites and is considered as the value at which a food reaches its highest stability. The estimated monolayer moisture content values ranged from 0.0916 to 0.294 g water g⁻¹ d.m. It was observed that *X_m* decreased as temperature increased since the adsorbed molecules gain kinetic energy (Liébanes et al., 2008). Values of parameter *K* were near 1.0 indicating high sugar solubility (Table 1). The *K* value represents the interaction energies between multilayer properties with respect to bulk liquid (Vega-Gálvez et al., 2010).

3.3. Drying kinetics modelling

The experimental drying curves during drying of olive-waste cake “Picual” variety at different air-drying temperatures are shown in Fig. 1. It can be seen that moisture ratio decreases with temperature leading to shorter times at higher temperatures. All drying curves showed an exponential tendency. Similar effects of

temperature on drying kinetics were reported in previous investigations about dehydration of olive cakes (Doymaz et al., 2004; Freire, Figueiredo, & Ferrao, 2001; Göğüş, & Maskan, 2006; Krokida et al., 2002 and Akgun, & Doymaz, 2005).

To estimate the effective moisture diffusivity (*D_{eff}*), Eq. (5) was applied to each set of experimental drying data at different air-drying temperatures. Thus, effective moisture diffusivity values for waste samples were calculated from drying curves, giving *D_{eff}* = 1.967 ± 0.098 × 10⁻⁹ m² s⁻¹ at 40 °C; *D_{eff}* = 2.534 ± 0.127 × 10⁻⁹ m² s⁻¹ at 50 °C; *D_{eff}* = 3.987 ± 0.199 × 10⁻⁹ m² s⁻¹ at 60 °C; *D_{eff}* = 4.317 ± 0.216 × 10⁻⁹ m² s⁻¹ at 70 °C; *D_{eff}* = 5.379 ± 0.269 × 10⁻⁹ m² s⁻¹ at 80 °C; and *D_{eff}* = 6.052 ± 0.303 × 10⁻⁹ m² s⁻¹ at 90 °C, as a result. These results are comparable to those reported in previous works. Doymaz et al. (2004) reported values between 4.89 and 9.98 × 10⁻¹⁰ m² s⁻¹ during drying of olive cake in the range of 80–110 °C; Freire et al. (2001) obtained values of 1.5–2.2 × 10⁻⁹ m² s⁻¹ for olive bagasse at 125 °C. Göğüş, & Maskan (2006) found diffusivities in the range of 1.84 × 10⁻⁷–3.94 × 10⁻⁷ m² s⁻¹ for olive pomace between 60 and 80 °C and Milczarek, Dai, Otonic, and McHugh (2011) found values ranging from 6.57 × 10⁻¹⁰ to 1.39 × 10⁻⁹ m² s⁻¹ for dry olive cake at 40 and 70 °C.

From the results of ANOVA carried out to the diffusivities using the StatGraphics Plus 5.1 software, for a confidence level of 95%, where *p* < 0.05 was obtained, it could be suggested that LSD there are differences among the diffusivities for all the temperatures used. This computer software also delivered a multiple range test (MRT) to determine the significant means among the temperatures, showing that differences were meaningless between 60 °C and 70 °C, resulting in five homogeneous groups: 40 °C, 50 °C, 60–70 °C, 80 °C and 90 °C.

Then, the natural logarithm of *D_{eff}* as a function of the reciprocal of absolute temperature was plotted resulting in a linear relationship due to the Arrhenius type dependence (*r*² = 0.963). From the slope of this line, an activation energy value of 28.24 kJ mol⁻¹

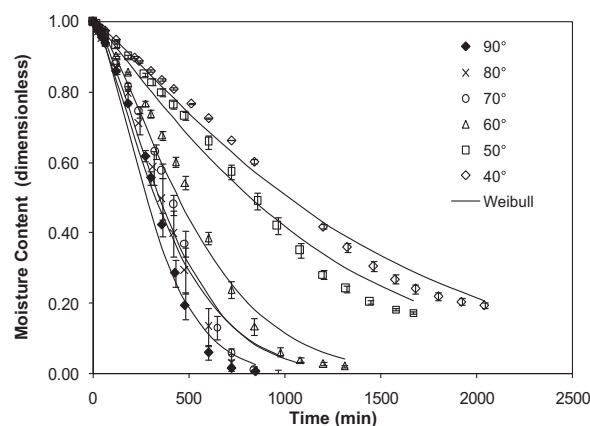


Fig. 1. Experimental and simulated drying curves of olive-waste cake “Picual” variety. Values are mean ± s.d. (*n* = 3).

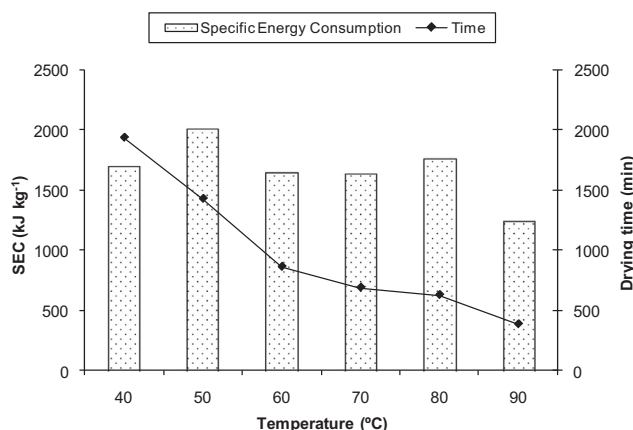


Fig. 2. Effect of drying temperature on specific energy consumption and drying time of olive-waste cake (MR = 0.1).

was determined. This value is similar to those reported in previous investigations on dried olive cake (Doymaz et al., 2004; Akgun & Doymaz, 2005; Gögüs & Maskan, 2006; Milczarek et al., 2011).

Due to the exponential tendency of experimental drying kinetics data, the Weibull model was selected to simulate the drying curves. Satisfactory results were obtained ($r^2 > 0.973$) as can be observed in Fig. 1. The values of scale (β) and shape (α) parameters of standardised Weibull model for fractional amount of moisture content Eq. (6) at different drying air temperatures were obtained. B values ranged from 360.46 ± 0.228 to $1310.133 \pm 0.115 \text{ min}^{-1}$ and α values ranged from 0.817 ± 0.064 to 0.944 ± 0.093 . The shape parameter is related to the velocity of the mass transfer at the beginning, e.g. the lower the α value is, the faster the drying rate is on the onset (Corzo et al., 2008). The parameter β can be interpreted as a kinetic reaction constant and represents the time when concentration, in this case, $X_{wt}-X_{we}$ attains a value corresponding to 36.8% of $X_{wo}-X_{we}$. The influence of temperature was evidenced only for β parameter since an increase of this variable led to a decrease of this parameter (Corzo et al., 2008).

3.4. Energy consumption

Fig. 2 shows the influence of temperature on the specific energy consumption (SEC) during convection drying of olive-waste cake. SEC ranged from 333.55 to $549.87 \text{ kJ kg}^{-1}$. It can be observed that SEC decreases as air temperature increases. By increasing the process temperature, drying time to reach a final MR = 0.1 has been reduced. Similar results were reported by previous investigation working with cherry fruits (Koyuncu, Tosun, & Pinar, 2007); berberis fruit (Aghbashlo, Kianmehr, & Samimi-Akhijahani, 2008) and pomegranate (Motevali et al., 2011). In addition, Hepbasli, Akdeniz, Vardar-Sukan, and Oktay (2003) had already established the olive cake as an excellent source of energy.

3.5. Total phenolic content

Total phenolic content (TPC) in the fresh olive cake was $4226.23 \text{ mg GA } 100 \text{ g}^{-1} \text{ d.m.}$, which was greater than those values reported by previous works for different food residues (Aludatt et al., 2010; Cabral de Oliveira et al., 2009). The influence of drying temperature on TPC for dehydrated olive-waste cakes can be observed in Fig. 3 ($p < 0.05$). Although drying temperature decreased the TPC of dehydrated samples, significant differences were not detected in the whole range of temperature under study ($p < 0.05$). A lower TPC retention was shown at 50°C (66%). These results are in agreement with those of other researchers, who suggested that polyphenolics are heat labile and prolonged heat treatment causes

irreversible chemical changes to such compounds, like in muscadine pomace (Vashisth, Singh, & Pegg, 2011). Nevertheless, some authors have reported that high temperatures required shorter drying times than mild temperatures to achieve the same final moisture content, while providing more bioactive compounds. These contradictory conclusions about the effect of the drying temperature on bioactive properties could probably be ascribed to the different structure and properties of the plant materials and the nature of the bioactive compounds. Therefore, an optimum combination of drying time/temperature should be established for each product's polyphenolic profile to minimise the degradation of these bioactive compounds during the dehydration leading to phenolic compound recovery. Moreover, the utilisation of the phenolic recovery has three limiting factors: the effectiveness of recovery and extraction, the marketability of resulting extracts and the practical suitability for the food, cosmetic or pharmaceutical products (Peschel et al., 2006).

3.6. Antioxidant capacity (ORAC and DPPH)

Fig. 4 presents the antioxidant capacity of olive waste cake by means of the ORAC and DPPH analysis. The ORAC value for fresh sample was $931.15 \mu\text{mol TE g}^{-1} \text{ d.m.}$ The dehydrated samples presented values in the range of 659.11 – $706.04 \mu\text{mol TE g}^{-1} \text{ d.m.}$

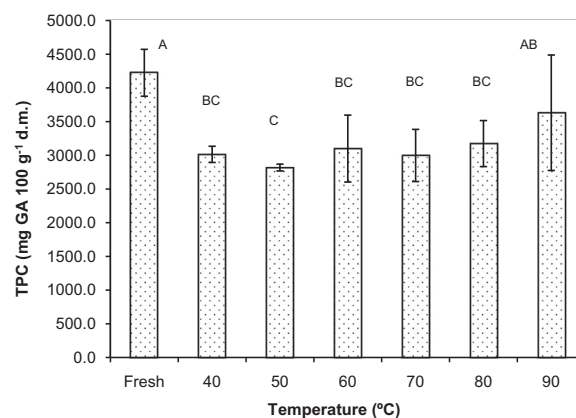


Fig. 3. Total phenolic content of olive-waste cake "Picual" variety as affected by drying temperature. Values are mean \pm s.d. ($n = 3$).

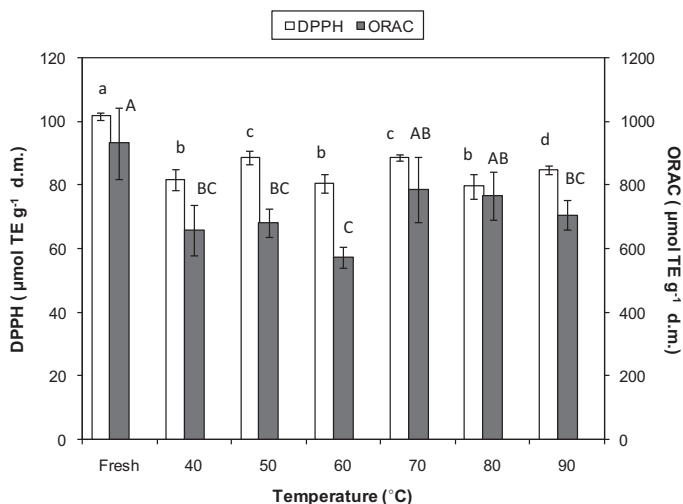


Fig. 4. Antioxidant activity by means of ORAC and DPPH methods of olive-waste cake "Picual" variety. Values are mean \pm s.d. ($n = 3$).

Table 2Fatty acids of olive-waste cake “Picual” variety as affected by drying temperature. Results expressed in g 100 g⁻¹ m.s.

Fatty acids	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C	Fresh
Palmitic	1.304 ± 0.015 ^b	1.422 ± 0.069 ^c	1.395 ± 0.056 ^c	1.179 ± 0.047 ^a	1.463 ± 0.052 ^c	1.406 ± 0.057 ^c	1.143 ± 0.038 ^a
Palmitoleic	0.322 ± 0.010 ^{a,b,c}	0.305 ± 0.041 ^{a,b}	0.267 ± 0.054 ^a	0.325 ± 0.007 ^{a,b,c}	0.385 ± 0.045 ^{c,d}	0.437 ± 0.059 ^d	0.375 ± 0.038 ^{b,c,d}
Stearic	0.481 ± 0.045 ^{a,b}	0.466 ± 0.041 ^d	0.452 ± 0.118 ^{a,b}	0.410 ± 0.033 ^{a,b}	0.412 ± 0.037 ^d	0.492 ± 0.023 ^e	0.387 ± 0.049 ^a
Oleic	7.013 ± 0.063 ^c	7.304 ± 0.153 ^d	6.548 ± 0.095 ^b	6.371 ± 0.080 ^{a,b}	7.489 ± 0.054 ^d	8.092 ± 0.213 ^e	6.272 ± 0.201 ^a
Linoleic	0.938 ± 0.095 ^b	1.028 ± 0.106 ^b	0.976 ± 0.050 ^b	0.788 ± 0.030 ^a	1.014 ± 0.050 ^b	0.985 ± 0.049 ^b	0.763 ± 0.029 ^a
Linolenic	0.194 ± 0.022 ^d	0.179 ± 0.027 ^{c,d}	0.123 ± 0.036 ^a	0.176 ± 0.008 ^{b,c,d}	0.126 ± 0.019 ^{a,b}	0.181 ± 0.026 ^{c,d}	0.133 ± 0.049 ^{a,b,c}
Arachidonic	0.050 ± 0.018 ^{b,c}	0.042 ± 0.009 ^{a,b}	0.030 ± 0.006 ^a	0.025 ± 0.007 ^a	0.065 ± 0.013 ^c	0.040 ± 0.009 ^{a,b}	0.030 ± 0.004 ^a
Eicosanoic	0.007 ± 0.002 ^a	0.007 ± 0.003 ^a	0.006 ± 0.000 ^a	0.004 ± 0.001 ^a	0.004 ± 0.003 ^a	0.007 ± 0.002 ^a	0.005 ± 0.001 ^a

^{a,b,c,d} Different letters in the same row indicate significant difference (p -value < 0.05). (Data are expressed as average ± standard deviation in three replicates).

($p > 0.05$). ORAC assay measures the relative potencies of antioxidants to prevent biological molecules from free radical attacks and a high ORAC value is an indication of high antioxidant capacity in a sample extract (Li, Pickard, & Beta, 2007). A higher ORAC value, which corresponds to the fresh sample, indicates a stronger oxygen radical absorbance capacity of untreated samples. Although drying temperature decreased the initial ORAC value, dehydrated samples did not present significant differences ($p > 0.05$). This result was an indication that antioxidant capacity of olive-waste cake was not adversely affected under the conditions used in this investigation. Comparable results were obtained by previous authors (Li et al., 2007).

In the same figure (Fig. 4) the radical scavenging activity based on air drying temperature was investigated. As it was shown all treatments reduced the initial antioxidant capacity of the samples (47.45 μmol TE mg⁻¹ d.m.), however, significant differences were not evidenced ($p < 0.05$). DPPH radical scavenging activity is influenced by the polarity of the reaction medium, chemical structure of the radical scavenger, and the pH of the reaction mixture (Sharma & Bhat, 2009). Consequently, comparison against different analytical methods to determine total antioxidant capacity is a key factor to help investigators choose a method and understand the result obtained (Zulueta et al., 2009).

To explore the influence of the TPC on antioxidant capacity in olive-waste cake extracts, correlation between the antioxidant capacity and TPC was determined. Results of the ORAC and DPPH assay were positive but weakly correlated to the TPC ($r = 0.462$ and $r = 0.453$), respectively. A correlation was found between the ORAC and DPPH ($r = 0.632$). Therefore, a detailed quality analysis of phenolic compounds (complete acids profile) occurring in the waste is required to elucidate the question of the compounds responsible for the high antioxidant activity in fresh and dried samples.

3.7. Fatty acids

Analysis of some of the most abundant fatty acids revealed that during olive-waste cake dehydration, changes in these individual fatty acids occurred as can be observed in Table 2. The main fatty acids present in fresh waste were the unsaturated acids oleic (18:1) (6.272 g 100 g⁻¹ d.m.), the palmitic (C16:0) (1.143 g 100 g⁻¹ d.m.) together with the linoleic (18:2) (0.763 g 100 g⁻¹ d.m.). The extent of degradation of some of them was dependent on the drying time and process temperature ($p < 0.05$) (Stewart, Raghavan, Orsat, & Golden, 2003). Although the mentioned acids did not present a clear pattern of degradation, the saturated acid (oleic) presented a maximum increased at 90 °C showing significance differences when comparing the fresh to the dried samples ($p < 0.05$). Palmitic acid content increased specially at 80 °C. However, at 40 °C the linoleic acid presented the maximum value. Resistance of polyunsaturated oils (linoleic, linolenic and arachidonic) to oxidation depends on factors such as exposure to oxygen, exposure to light, the presence of pigments and heavy metals as

well as saturation degree (Gutierrez, Ratti, & Belkacemi, 2008; Stewart et al., 2003). The oxidative stability of unsaturated fatty acids decreases when increasing unsaturation degree because unsaturated sites are the most susceptible sites for heat induced and radical-based fat oxidation. When oxygen is present, unsaturated fatty acid decomposition occurs more readily. The products formed are similar to those of auto oxidation but the amounts formed vary with temperature even within low temperature ranges of 25–80 °C (Stewart et al., 2003).

4. Conclusions

Effects of air drying temperature on drying characteristics as well as antioxidants activity during dehydration from 40 to 90 °C of the olive-waste cake were investigated. Sorption experimental isotherms were satisfactorily modelled by means of the GAB equation ($r^2 > 0.952$). Moisture diffusion coefficient increased with temperature. Based on an Arrhenius plot, 28.24 kJ mol⁻¹ as an activation energy of was estimated. The Weibull model was satisfactorily applied to simulate the drying kinetics of the cake ($r^2 > 0.973$). Proximate analysis of fresh and dehydrated olive cakes showed that drying within the given temperature range did cause some changes in overall composition ($p < 0.05$). The high content of crude fibre showed to be typical in olive cake, rendered it a potential source of dietary fibre and useful in animal nutrition. The minimum specific energy consumption as well as the minimum drying time was achieved at 90 °C. Although temperature decreased the TPC of dehydrated samples, significant differences were not detected in the whole range of temperature under study indicating that the dehydrated olive cake could be an excellent source of these compounds. Moreover, the antioxidant capacity of olive-waste cake was not adversely affected under the conditions used in this investigation. Analysis of some of the most abundant fatty acids revealed that during olive-waste cake dehydration, changes in these individual fatty acids occurred during the process. Therefore, optimisation of drying conditions (time/temperature) are required to minimise detrimental changes of olive-waste cake during processing.

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