Influence of air temperature on drying kinetics and antioxidant potential of olive pomace

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ABSTRACT

This work aims to evaluate the influence of olive pomace drying (a solid by-product of the olive oil industry) on both antioxidant potential and drying kinetics. The two main fractions of olive pomace (pits, PI and pulps+peels, P+P) were characterized by image analysis and density measurement. The drying process was analyzed in experiments carried out at different temperatures (from 50 to 150 °C) and mathematically described from the diffusion and Weibull models. The antioxidant potential of the extracts (ethanol-water 80:20 v/v, 22 ± 1 °C, 170 rpm for 24 h) obtained from the dry product was analyzed by measuring the total phenolic content and antioxidant capacity and the main polyphenols were quantified by HPLC-DAD/MS-MS.

The drying behavior of olive pomace was well described by considering the diffusion in the PI and P+P fractions separately and the influence of temperature on effective moisture diffusivities was quantified by an Arrhenius type equation. The antioxidant potential was only mildly influenced by the drying temperature. However, long drying times at the highest temperature tested (150 °C) significantly ($p<0.05$) increased the antioxidant potential.

Key words: phenolic content; antioxidant capacity; drying kinetics; diffusion; olive pomace

1. Introduction

The olive (*Olea europea*) is an evergreen tree traditionally cultivated for the production of oil and table olives. As regards both wealth and tradition, the olive oil industry is a relevant one, especially in the Mediterranean countries where 97 % of the world's olive production is harvested. Spain is the leading country in terms of the total crop surface and the number of productive trees (Niaounakis & Halvadakis, 2004).

Nowadays, the olive oil industry generates a great environmental impact due to the production of high polluting residues (Baeta-Hall et al., 2005). Several studies have stated the negative effects of these forms of waste on soil's microbial populations (Paredes et al., 1987), aquatic ecosystems (DellaGreca et al., 2001) and even on the air (Rana et al., 2003). However, olive polyphenols, such as oleuropein, verbascoside or hydroxytyrosol, are present not only in olive oil but also in oil waste products, exhibiting among other things, antiviral, antitumoral and antioxidant activities (Della Ragione et al., 2000; Liu et al., 2003; Micol et al., 2005). One of the most problematic olive oil waste products is pomace (the solid byproduct made up from pieces of pit, skin and pulp), also known as cake. Actually, it is used for animal feed, residual oil extraction, energy recovery, soil amendment or the extraction of valuable polyphenols (Roig et al., 2006). A previous dehydration stage reduces the pomace water content to 5-6 % (wet basis), aiming to stabilize the byproduct and so avoiding undesirable degradation during storage. Moreover, in the particular case of bioactive compound extraction, drying avoids the interference of water in the polyphenol release (Soysal & Öztekin, 2001), improving the

extraction yield. For industrial purposes, hot air drying is the most widely used method, since it allows an accurate control of the process variables. Traditionally, low air temperatures are used as a means of better protecting the bioactive compounds from degradation during drying. However, drying at low temperatures constitutes a slow process in which metabolic reactions may be long lasting, leading to quality loss (Fennell et al., 2004). Thereby, certain studies also suggest the use of high temperatures for the industrial drying of olive pomace (Göğüs & Maskan, 2006). High temperatures speed up the drying kinetics, which could be interesting for the purposes of increasing productivity on an industrial scale (Ahmad-Qasem et al., 2013a), but at the same time it could promote the oxidative degradation of polyphenols (Gomes & Caponio, 2001) and requires the use of a great amount of energy. For this reason, the main aim of this work was to assess the influence of the air temperature on the drying kinetics and antioxidant potential of olive pomace, two aspects which have not previously been considered together.

2. Materials and methods

2.1 Raw material

The raw material used in this work was olive pomace from a traditional pressing system for obtaining olive oil, provided by an oil factory located in Altura (Castellón, Spain) The pomace was collected just after the pressing operation and immediately vacuum packaged and stored at 4 °C. The initial moisture content was determined by drying in a vacuum chamber at 70 °C until reaching constant weight (AOAC method nº 934.06, AOAC, 1997).

It could be considered that olive pomace is mainly composed of two main fractions: pits (PI) and pulps+peels (P+P). Homogeneous samples of olive pomace were taken, both fractions were separated by hand and their corresponding mass fraction (X) calculated and characterized by image analysis (Table 1). RGB images were taken (Figures 1a and 1c) and processed using Image J software (Research Service Branch, National Institute of Mental Health, US, available as freeware from http://rsbweb.nih.gov/ij/). Images were converted to the binary system (Figures 1b and 1d) using an automatic threshold. Finally, the particles were counted and their surface (S, mm^2) calculated considering the scale reference. From another set of experiments, the initial moisture content of both fractions was also determined, as already explained for the olive pomace.

The bulk density (ρ) of both the PI and P+P fractions, as well as that of the fresh olive pomace, was determined at 20 ºC by liquid displacement using water, a volumetric standard picnometer (48.89 mL) and an analytical balance (PB 303-S, Mettler Toledo).

2.2 Drying experiments

Drying experiments were conducted in a forced air laboratory drier (FD, Binder, Tuttlingen, Germany), using a horizontal air flow of 0.094 m^3/s and an air velocity of 0.683 m/s. Each run was carried out with an initial mass load of 40 g of olive pomace, uniformly distributed in a monolayer (4 ± 1 mm thick, 0.083 g/cm^2).

Two different sets of experiments were designed. In the first one, the variable to be considered was that of the air temperature in order to determine its influence on both the drying kinetics and antioxidant potential of the extracts obtained from the dried product. For this purpose, the drying experiments were carried out at different air drying temperatures: 50, 70, 90, 120 and 150 °C. During the process, the samples were weighed (XS204, Mettler Toledo, Barcelona, Spain) at pre-set times. The drying experiments finalized when the sample weight loss reached 30 ± 1 %. This fact was established by previous experiments, ensuring that the water activity was below 0.4 and the obtained product was stable.

In the second set of experiments, the variable to be studied was the drying time. For that purpose, drying experiments were carried out at 150 °C and for different drying times: 5, 10, 20, 30 and 60 min. It should be highlighted that, in this set of experiments the effective drying period took place between 5 and 10 min, from which mass transfer could be considered negligible. Therefore, this involves overexposing the olive pomace to a high temperature (150 ºC).

The drying experiments for each experimental condition tested were carried out three times, at least.

2.3 Modeling of hot air drying kinetics

The experimental drying kinetics were determined from the initial sample mass and the weight loss measured during drying. Previous approaches to the modeling of the drying kinetics of olive pomace have been addressed through the use of deep beds, assuming in the modeling that the sample is as thick as

148 the bed is high and that it behaves like an infinite slab (Göğüs & Maskan, 2006).
149 In addition, Vega-Gálvez et al. (2010) molded olive cake into a rectangular form
150 and conducted drying experiments in monolayer at different temperatures in
151 order to identify an effective moisture diffusivity in this particular body. However,
152 the drying of the individual particles of olive pomace has not previously been
153 addressed. This could be considered a complicated issue, since olive pomace
154 is a heterogeneous material made up mainly of pits, peels and pulp pieces,
155 which represents a handicap when using a diffusion model where the samples
156 are assumed to be homogeneous. In this work, therefore, the monolayer drying
157 of this byproduct has been studied in order to identify the drying behavior of
158 olive pomace at particle level, and further studies should be performed to
159 address the drying of the bulk of the olive pomace. For that purpose, two
160 different approaches were considered.

161 On the one hand, a diffusion model for the olive pomace was used by
162 considering the diffusion in both fractions of the olive pomace to be different:
163 Pits (PI) and pulps+peels (P+P). It was assumed that pits could be considered
164 as geometrically spherical particles, while peels+pulps could behave like infinite
165 slabs. Eqs. 1 and 2 show the solution of diffusion models for spheres and
166 infinite slabs, respectively, considering:

167 - Homogenous and isotropic solids.
168 - Constant effective diffusivity.
169 - Negligible shrinkage.
170 - Uniform initial moisture and temperature.
171 - The solid surface at equilibrium with the drying air.
172 - Solid symmetry.

173 $$W_{PI} = W_e + (W_c - W_e)\left[\sum_{n=1}^{\infty} \frac{6}{n^2\pi^2} \exp\left(-\frac{D_e^{PI}}{R^2} n^2\pi^2 t\right)\right] \quad (1)$$

174 $$W_{P+P}(t) = W_e + (W_c - W_e)\left[\sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(-\frac{D_e^{P+P}(2n+1)^2\pi^2 t}{4L^2}\right)\right] \quad (2)$$

175 where W is the average moisture content (dry basis), subscripts c and e refer to
176 the critical and equilibrium states, t (min) the drying time, D_e is the effective
177 moisture diffusivity (m^2/s), which was considered to be different in both PI and
178 P+P fractions. The characteristic diffusion paths, radius (R) and thickness (L),
179 were experimentally determined. The average radius of pit pieces was obtained
180 from image analysis. For that purpose, the radius of individual particles, which
181 was calculated from the measurement of the surface ($S_p = \pi R^2$), was computed
182 and weighed to obtain an average value. Whereas the average particle
183 thickness of the pulp+peel fraction was calculated from the measurement of the
184 total particles surface (S_t), also obtained by image analysis, the mass (M) and
185 the density (ρ) (Eq. 3):

186 $$L = \frac{M}{\rho S_t} \quad (3)$$

187 Considering the diffusion in PI and P+P fractions to be different, the
188 moisture content of olive pomace could be calculated from Eqs. 1 and 2 by
189 using a compositional model (Eq. 4). Similar diffusion models have been used
190 for analyzing mass transfer phenomena in geometrically complex plant tissues,
191 such as grape stalk (García-Pérez et al., 2006) and broccoli (Sanjuán et al.,
192 2001).

193 $$W = X_{PI} W_{PI} + X_{P+P} W_{P+P} \quad (4)$$

where X is the mass fraction of PI and P+P fractions ($X_{PI} + X_{P+P} = 1$).

On the other hand, the Weibull empirical model (Cunha et al., 1998; Simal et al., 2005) was also used for the mathematical description of the drying kinetics of olive pomace. The Weibull model (Eq. 5) is a probability function used to explain the behavior of changeable complex systems (Cunha et al., 1998). Initially, it was used to predict material failures caused by fatigue. In food technology, it has been used for the description of degrading processes, since the degradation of food can be considered as a system fault under certain stress conditions (Blasco, 2003), such as when exposed to hot air. Thus, the Weibull model adapted to a drying process is presented in Eq. 5:

$$\psi(t) = \frac{W(t)-W_e}{W_c-W_e} = \exp\left(-\left(\frac{t}{\beta}\right)^{\alpha}\right) \quad (5)$$

where Ψ represents the dimensionless moisture content, α the dimensionless parameter related to the shape, assimilated to the behavior index of the product during drying, and β (min^{-1}) is the kinetic parameter inversely related (1/β) with the process rate.

The identification of the model parameters (α and β in the Weibull model, and D_e for PI and P+P fractions in the diffusion model) was carried out by minimizing the sum of the squared differences between the experimental and calculated moisture content of olive pomace samples using the Solver tool from Excel™ (Microsoft Corporation, Seattle, USA). For each drying condition tested, the parameter identification was simultaneously carried out with all the replicates. The explained variance (VAR) was computed (Eq. 6) to determine the goodness of the model's fit to experimental data:

$$VAR = 1-\frac{S_{xy}^2}{S_y^2} \quad (6)$$

where S^2_{xy} is the variance of the estimation and S^2_y the variance of the sample. In addition, the mean relative error (MRE) was calculated (Eq. 7) to establish the difference between the experimental (W_{EXPi}) and calculated (W_{CALi}) data:

$$MRE = \frac{100}{N}\left(\sum_{i=1}^{N}\frac{W_{EXPi}-W_{CALi}}{W_{EXPi}}\right) \quad (7)$$

where N is the number of experimental data.

Moreover, in order to evaluate the influence of temperature on the kinetic parameters, an Arrhenius type equation (Meziane, 2011) was used (Eqs. 8 and 9):

$$\frac{1}{\beta} = \frac{1}{\beta_0}\cdot\exp\left(-\frac{E_a}{R\cdot T}\right) \quad (8)$$

$$D_e = D_0\cdot\exp\left(-\frac{E_a}{R\cdot T}\right) \quad (9)$$

where $1/\beta_0$ (min^{-1}) and D_0 (m^2/s) are the pre-exponential factors, E_a (kJ/mol) the activation energy, R (kJ/mol·K) the universal gas constant and T (K) the drying temperature.

2.4 Extraction experiments

Dried olive pomace was milled (Blixer 2, Robot Coupe USA, Inc., Jackson, MS, USA) and sieved (Metallic mesh 0.05 mm, Filtra Vibración, Barcelona, Spain) to obtain particles with a diameter of under 0.05 ± 0.01 mm. The extraction was carried out in sealed containers protected from light and immersed in a thermostatic shaking water bath (SBS40, Stuart, Staffordshire,

239 UK) working at 170 rpm. The solvent used was a solution of ethanol-water
240 (80:20, v/v) and the ratio between the weight of the olive pomace and the
241 solvent volume, 20 g/30 mL. The extraction process was carried out at 22 ± 1
242 °C for 24 h, which was based on previous works (Ahmad-Qasem et al., 2013a
243 and 2013b). In addition, another set of extraction experiments was carried out
244 by varying the extraction times from 5 to 48 hours to monitor the extraction
245 process, which is relevant in the case of industrial operations where a high level
246 of productivity needs to be attained. In this case, extraction experiments were
247 conducted with fresh and dried olive pomace at 50 and 150 °C.

248 Every extract was centrifuged for 10 min at 5000 rpm (Medifriger BL-S,
249 J.P. Selecta, Barcelona, Spain), filtered (nylon filters of 0.45 μm) and stored in
250 opaque vials at 4 °C until analysis. At least 3 replicates were made for each
251 different condition tested.

252

253 *2.5 Total phenolic content (TPC) and antioxidant capacity (AC) measurement*

254 The phenolic content and antioxidant capacity of the extracts obtained
255 from the dried olive pomace were determined by the Folin-Ciocalteu (Singleton
256 et al., 1999) and Ferric-Reducing Ability Power (FRAP) methods, respectively
257 (Benzie & Strain, 1996). These methods are exhaustively described by Ahmad-
258 Qasem et al. (2013a and 2013b).

259 The TPC was expressed as mg of gallic acid (GAE) per g of dry weight of
260 olive pomace (g d.w.), while the AC was expressed as mg of Trolox per g of dry
261 weight of olive pomace (g d.w.).

262

263 *2.6 Identification and quantification of polyphenols by HPLC-DAD/MS-MS*

In order to identify and quantify the main polyphenols, the olive pomace extracts were analyzed using an HPLC instrument (Agilent LC 1100 series; Agilent Technologies, Inc., Palo Alto, CA, USA) controlled by the Chemstation software. The HPLC instrument was coupled to an Esquire 3000+ (Bruker Daltonics, GmbH, Germany) mass spectrometer equipped with an ESI source and ion-trap mass analyzer, and controlled by Esquire control and data analysis software. A Merck Lichrospher 100RP-18 (5 µm, 250 x 4 mm) column was used for analytical purposes.

Separation was carried out through a linear gradient method using 2.5 % acetic acid (A) and acetonitrile (B), starting the sequence with 10 % B and programming the gradient to obtain 20 % B at 10 min, 40 % B at 35 min, 100 % B at 40 min, 100 % B at 45 min, 10 % B at 46 min and 10 % B at 50 min. For the LC-MS pump to perform accurately, 10 % of organic solvent was pre-mixed in the water phase. The flow-rate was 1 mL/min and the chromatograms monitored at 240, 280 and 330 nm. Mass spectrometry operating conditions were optimized in order to achieve maximum sensitivity values. The ESI source was operated in negative mode to generate $[M–H]^-$ ions under the following conditions: desolvation temperature at 365 °C and vaporizer temperature at 400 °C; dry gas (nitrogen) and nebulizer were set at 12 L/min and 4.83 bar, respectively. The MS data were acquired as full scan mass spectra at 50–1100 m/z by using 200 ms for the collection of the ions in the trap.

The olive pomace compounds were identified by HPLC-DAD analysis, comparing the retention time, the UV spectra and the MS/MS data of the peaks. Only the luteoilin-7-O-glucoside was quantified using a commercial standard (Phytolab, Vestenbergsgreuth, Germany). The quantitative evaluation was

289 performed with a calibration curve using methanol solutions of known
290 concentrations. The polyphenol concentration was expressed as mg luteolin-7-
291 O-glucoside per g of dry weight of olive pomace (g d.w.).
292
293 **3. Results and discussion**
294
295 *3.1 Hot air drying kinetics at different temperatures*
296 In order to evaluate the influence of air temperature on drying kinetics,
297 experiments were carried out at temperatures ranging from 50 to 150 °C. In
298 these experiments, the initial moisture content of olive pomace was reduced
299 from 0.33 to 0.05 kg water/kg fresh olive pomace (30 % of the initial weight
300 loss). Despite the fact that olive pomace is a heterogeneous material, an
301 adequate repeatability and a small experimental variability was found in the
302 experimental drying kinetics (Figure 2).
303 As can be observed in Figure 2, the air temperature significantly affected
304 ($p<0.05$) the drying rate: the higher the temperature, the shorter the processing
305 time. Thus, the drying times needed to achieve a 30 % loss of the initial weight
306 ranged from 40 min at 50 °C to 10 min at 150 °C and increasing the drying
307 temperature from 90 to 150 °C shortened the drying time by 50 %. These
308 results agreed with those reported by other authors who studied olive pomace
309 drying by means of different techniques. Thus, Ruiz-Celma et al. (2008), who
310 studied the infrared drying of wet olive husk (pomace), found that a rise in
311 temperature from 80 to 140 °C reduced the drying time by a third.
312 The experimental data showed that, for the air temperatures tested, the
313 drying only took place during the falling rate period. As an example, the drying

rate for two particular temperatures tested (50 and 120 °C) is shown in Figure 3. Therefore, the initial moisture content was assumed to be equal to the critical one. These results agreed with previous works, like those published by Göğüs & Maskan (2006) who studied olive pomace behavior during hot air drying at temperatures ranging between 60 and 80 °C or Ruiz-Celma et al. (2008) working on infrared drying at temperatures from 80 to 140 °C. However, Kadi & Hamlat (2002) found a constant drying period during the hot air drying of olive pomace. These contradictory results could be linked to the sample layer thickness used in each experimental design. Thus, the constant rate period cited by Kadi & Hamlat (2002) could be attributed to a thick sample layer, which leads to air saturation, but not to the behavior of the particle.

Modeling of drying kinetics was addressed from the diffusion and Weibull (Cunha et al., 1998) models, as explained sin section 2.3. The modeling not only aimed to quantify the influence of the temperature on the drying kinetics but also to better characterize the olive pomace drying at particle level. The characterization of PI and P+P fractions is shown in Table 1, while the results of drying kinetics modeling are included in Table 2.

A much higher effective moisture diffusivity (D_e) was found in the PI fraction than in the P+P one (Table 2). Thus, D_e ranged from $1.17 \cdot 10^{-7}$ to $2.92 \cdot 10^{-7}$ m^2/s for the PI fraction and between $3.58 \cdot 10^{-11}$ and $1.60 \cdot 10^{-10}$ m^2/s for the P+P fraction. The temperature was found to have a significant influence on D_e values: the higher the temperature, the higher the D_e. The fact that the D_e figures found in the PI fraction are higher suggests that its structure has a low water retention capacity, which leads to a higher water removal rate than in the P+P fraction. This fact could be explained by taking the lower density of the PI

fraction into account (Table 1) while the low D_e values of the P+P fraction could be ascribed to the water proof capacity of peels, which constitutes a natural protection of olive fruit from dehydration . To our knowledge, there are no references in the literature to the D_e in the PI and P+P fractions since this issue has not been previously addressed. However, the values identified in this work for both fractions are similar to others reported in literature for olive pomace drying in deep beds, thin layers or regular-shaped bodies. Thus, Meziane (2011) in working on fluidized bed drying (thickness 41-33 mm) at 50-80 ºC, reported D_e figures from $0.68 \cdot 10^{-7}$ to $2.15 \cdot 10^{-7}$ m^2/s, which were similar to those reported by Göğüs & Maskan (2006) for tray drying (thickness 6-12 mm) at 60-80 ºC. However, lower D_e figures have also been reported. Thus, in the case of tray drying (thickness 4-12 mm) at 80-110 ºC, Doymaz et al. (2006) found values ranging from $4.89 \cdot 10^{-10}$ to $9.89 \cdot 10^{-10}$ m^2/s while Montero et al. (2011) identified values ranging from $9.1 \cdot 10^{-11}$ m^2/s to $1.4x10^{-10}$ m^2/s for solar drying at 20-50 ºC (thickness 20-40 mm). The great differences found in the literature for the D_e figures of olive pomace could be ascribed not only to the effect of the thickness of the sample being dried but also to the highly heterogeneous nature of this product.

The diffusion model proposed in this work fitted the experimental data closely, providing similar explained variance (VAR) and mean relative errors (MRE) to the Weibull model (Table 2). In overall terms, the VAR and MRE were close to 99 % and 10 %, respectively. The only significant difference between both models was found at 150 ºC (Figure 4), at which temperature the Weibull model fitted the drying kinetic much better than the diffusion (Table 2); the VAR was found to fall from 99.7 to 96.9 %. This could suggest that, at high

364 temperatures, diffusion was less important and other significant mass transport
365 phenomena appeared. In this sense, it was found that the α Weibull parameter,
366 related to product behavior, was not significantly ($p<0.05$) affected by
367 temperature in the range of 50 to 120 °C, reaching an average value of 0.87 ±
368 0.02. However, the value identified at 150 °C (0.99) was significantly ($p<0.05$)
369 higher. Therefore, although it could be stated that the behavior of olive pomace
370 remained stable during drying over the temperature range of 50 to 120 ºC,
371 water removal phenomena seemed to change at 150 ºC.

372 The drying temperature also affected the identified kinetic parameter (β)
373 of the Weibull model. Thus, $1/\beta$ increased when the air drying temperature rose,
374 showing that, over the range studied, the higher the temperature applied, the
375 faster the drying. The influence of temperature on D_e of the PI and P+P
376 fractions and the 1/β parameter was well described from an Arrhenius-type
377 relationship (Figure 5) over the range of 50 to 120 °C. In every case, the value
378 identified at 150 °C departed from the trend observed at the other temperatures,
379 as can be seen in Figure 5. So, excluding the kinetic data at 150 °C, the
380 identified activation energies (E_a) were 20.3 kJ/mol for olive pomace from the
381 1/β Weibull parameter, 21.9 kJ/mol for the P+P fraction and 14.6 kJ/mol for the
382 PI fraction. The E_a figure reported for olive pomace was in the same order of
383 magnitude as that obtained by other authors. Thus, Meziane (2011) reported a
384 value of 36.8 kJ/mol (50-80 ºC), Göğüs & Maskan (2006) 25.7 kJ/mol (60-80 ºC)
385 and Doymaz et al. (2006) 26.71 kJ/mol (80-110 ºC).

386

387 *3.2 Antioxidant potential affected by drying temperature*

Olive pomace is susceptible to spoilage due to the fact that it presents a high level of enzymatic and microbial activity. This must be considered when it is used as a potential source of bioactive compounds. Drying stabilizes the raw material during storage and limits some degradative reactions but, in a certain way, it can influence the bioactive potential of olive pomace. Hence, the total phenolic content (TPC) and the antioxidant capacity (AC) were assessed in the extracts obtained from olive pomace dried at temperatures ranging between 50 and 150 °C and were compared with those obtained from fresh pomace.

As can be observed in Figure 6, once the drying temperature exceeded 70 °C, it was noticeable that there was a slight tendency of the TPC to increase as the temperature rose. This could be attributed to the formation of new phenolic compounds at high temperatures (90-150 °C), due to the fact that non-enzymatic interconversion leads to the availability of precursors of phenolic molecules (Que et al., 2008). However, the statistical analysis highlighted the fact that the influence of temperature on TPC was not significant ($p<0.05$). Moreover, the dried material exhibited a similar TPC to that shown by fresh pomace. Different results have been found in literature when using similar biomaterials. Thus, Khanal et al. (2010) reported that drying temperatures over 60 °C had a negative effect on the phenolic content of grape and blueberry pomace.

As regards the AC of extracts, the drying temperature of pomace had a significant ($p<0.05$) effect on the antioxidant potential. Olive pomace dried at 150 °C provided the extracts with the highest AC (Figure 6), it being 15.5 % higher than the one obtained from pomace dried at 50 °C. Furthermore, compared with fresh pomace, drying at 150 °C increased the AC of extracts by

12.8 %. Samples dried over the range of 50 to 120 °C did not exhibit significant ($p<0.05$) differences compared with the fresh product. Studying the effect of the drying air temperature on the antioxidant capacity of polyphenolic compounds in mulberry leaves, Katsube et al. (2009) also observed an increase in the antioxidant capacity when the air temperature rose from 70 to 110 °C.

The effect of the drying conditions on the antioxidant properties of different byproducts and materials has been evaluated in several research studies. In overall terms, it can be stated that there is great controversy over the most suitable drying conditions. Thus, the use of mild drying temperatures (60 °C) and intermediate drying times is reported as the most suitable for orange peel (Garau et al., 2007) or mulberry (Katsube et al., 2009). On the contrary, Harbourne et al. (2009) found that, over the range of 30-70 °C, the drying air temperature did not influence the phenolic constituents of meadowsweet and willow. Other authors state that the use of high temperatures (90 °C) allows extracts to be obtained with a high antioxidant potential (Vega-Gálvez et al., 2009). These different conclusions concerning the effect of the drying temperature on bioactive properties could probably be ascribed to the different nature of the raw material processed.

In the case of the present study, the highest drying temperature tested, 150 °C, seemed to be the most suitable drying conditions under which to obtain the highest AC of the extracts. It should be remarked that it is not only the temperature but also the length of exposure to heat which can influence the extract properties (Erbay & Icier, 2009), since the short treatments at high temperatures may promote the presence of bioactive compounds in the extracts (García-Pérez et al., 2010). However, since in a certain way drying also

438 involves thermal treatment, the impact of the heating time during drying at high
439 temperatures was further studied and the results are presented in the following
440 section.
441
442 *3.3 Antioxidant potential affected by drying time at high temperatures*
443 A new set of drying experiments at 150 °C was carried out varying the
444 drying time of olive pomace from 5 to 60 min. It should be noticed that after
445 approximately 8 min of drying, see section 3.1, samples could be considered
446 dried (water activity less than 0.4). Thus, longer processing times are
447 unnecessary for water removal and represent an additional overheating due to
448 the product being overexposed to high air temperatures. Once processing
449 finalized, the TPC and AC of the extracts obtained from these dried samples
450 were measured.
451 Although phenolic compounds are considered as heat sensitive
452 antioxidants (Erbay & Icier, 2009), the results showed that there was a
453 significant ($p<0.05$) increase in the TPC as the drying time lengthened . As can
454 be observed in Figure 7, at a drying time of over 10 min the samples exhibited a
455 significantly ($p<0.05$) higher TPC than the fresh material, and the longer the
456 drying time, the higher the TPC of the extracts. In such a way, the highest TPC
457 was obtained after a drying time of 30 min, representing a 39.9 % increase
458 compared to what was observed in the fresh olive pomace extracts. The
459 increase in the drying time, from 30 to 60 min, did not significantly ($p<0.05$)
460 affect the TPC. Thereby, it is not advisable to heat olive pomace longer than 30
461 min, since this would reduce the productivity and increase both the processing
462 costs and the energy consumption. As far as this aspect is concerned, the

463 literature throws up contradictory results. It is widely recognized that
464 polyphenols are heat labile, thus, it is reported that heat treatments cause
465 irreversible chemical changes (Mejía-Meza et al., 2008). In this way, Kyi et al.
466 (2005) highlighted the fact that, when cocoa beans were dried at temperatures
467 over the 40-60 °C range, the concentration of total polyphenols declined
468 drastically when the drying time was extended, additionally observing that the
469 higher the temperature, the lower the residual amount of polyphenols. On the
470 contrary, the positive influence that heating has on the antioxidant capacity has
471 also been observed in microwave treatments. Hence, Hayat et al. (2010) stated
472 that, in mandarin pomace, the sum of the content of the individual phenolic
473 acids in the free fraction significantly increased as the drying time lengthened.

474 As regards the AC measurements, overheating the olive pomace also
475 significantly ($p<0.05$) increased the AC of extracts (Figure 7). For drying times
476 longer than 5 min, the extracts exhibited a significantly ($p<0.05$) higher AC than
477 the extracts obtained from fresh olive pomace; from 5 min of drying onwards,
478 the longer the overheating, the higher the AC. However, it is important to
479 highlight that, as in TPC measurement, no significant ($p<0.05$) differences were
480 found between extracts obtained from pomace treated for 30 and 60 min.
481 Therefore, drying at 150 °C for 30 min seemed to be the best processing
482 conditions under which to obtain the highest AC. It should be remarked upon
483 that, under these conditions (150 ºC and 30 min) and compared with the fresh
484 product, AC increased almost twice as much (78 %) as TPC (40 %).

485 Vashisth et al. (2011) observed that the drying time had no influence on
486 the antioxidant capacity of muscadine pomace at 70 and 80 °C. Considering the
487 fact that long drying times at low air temperatures (30-40 °C) promote a

488 decrease in the antioxidant capacity (Garau et al., 2007) and in view of the
489 results obtained in this work, it could be reasonable to consider that there is a
490 temperature threshold from which point onwards the drying time increases the
491 content of antioxidant compounds. This behavior could be explained by
492 considering that high temperatures promote the inactivation of oxidative
493 enzymes (Sanjuán et al., 2000), avoiding the degradation of antioxidants for
494 later processing, which includes the extraction stage. Furthermore, at high
495 temperatures, the generation and accumulation of Maillard-derived melanoidins
496 with a varying degree of antioxidant activity could also enhance the antioxidant
497 properties of extracts (Que et al., 2008).

498 In order to clarify the effect the overheating had on the increase in
499 antioxidant phenolic compounds, the composition of the extracts was analyzed
500 by HPLC-DAD/MS-MS. The HPLC-DAD profile of the samples was quite
501 complex and a large variety of peaks were detected at UV wavelengths.
502 Nevertheless, the fact that ionization occurred in only a few of them was
503 probably due to the presence of organic polymers in pomace samples, which
504 complicated the identification of the polyphenolic profile of the samples. Among
505 the phenolic compounds identified, minor quantities of secoiridoids, such as
506 oleuropein and ligstroside, were detected. The main polyphenol to be identified
507 and quantified was luteolin, which was selected as a marker to be quantified in
508 the different extracts obtained from samples subjected to different drying times.
509 The drying treatment at 150 ºC led to an increase in the luteolin concentration
510 as compared to fresh material (Figure 8); additionally, the longer the drying
511 time, the higher the luteolin content. Thus, as shown in Figure 8, increasing the
512 drying time from 10 to 60 min led to a rise in the luteolin content of

513 approximately 100 %. Therefore, these results highlighted the relationship
514 between the previously observed enhancement of antioxidant potential and the
515 increase in the content of some individual polyphenols, such as the flavone
516 luteolin.
517
518 *3.4 Monitoring of the extraction process*
519 In experiments carried out to assess how the drying temperature of olive
520 pomace or the drying time at high temperatures affected the antioxidant
521 potential of extracts, an extraction time of 24 h was considered enough to reach
522 equilibrium conditions according to previous studies (Ahmad-Qasem et al.,
523 2013a and 2013b). In order to test the feasibility of using shorter extraction
524 times as a means of improving productivity, which could be relevant for
525 industrial purposes, another set of experiments was performed using the fresh
526 and dried pomace at the lowest (50 °C) and the highest (150 °C) temperatures
527 tested. Thus, separate extraction experiments were conducted, varying the
528 extraction time from 5 to 48 hours, and replicated at least three times.
529 As observed in Figure 9, most of the phenolic compounds were extracted
530 from the solid matrix during the first 5 h of contact with the solvent. Afterwards,
531 some slight variation of TPC was found, which was especially noticeable in the
532 case of fresh material and olive pomace dried at 50 °C. Thus, increasing the
533 extraction time from 5 to 48 h led to an observed rise in the TPC of fresh and
534 dried pomace of 23.4 and 24.8 % at 50 °C, respectively. However, for the
535 material dried at 150 °C, the difference in the TPC at these extraction times was
536 almost negligible. This fact highlights another noticeable benefit of drying at
537 high temperatures (150 °C), which is the degradation of the raw structure which

promotes a sharp rise in the TPC of the solvent. From experimental results, it is also evident that 24 h is a reasonable extraction time after which to evaluate the TPC of olive pomace, since equilibrium is reached. Nevertheless, if further industrial applications are considered, it seems reasonable to choose a short extraction time, like 5 h, in order to increase productivity, thereby generating large volumes of extracts with a high TPC after short treatment times.

4. Conclusions

A compositional diffusion model considering a different effective diffusivity in pit and pulp+peel fractions provided a good description of the drying behavior of olive pomace. Effective diffusivity for the pit fraction was higher than in that of the pulps+peels and increased as the air temperature rose. Although the influence of the drying temperature on the antioxidant potential was only mild, long drying times at the highest temperature tested (150 °C) significantly increased the antioxidant potential.

Further studies should analyze the deep bed drying of olive pomace in order to validate the developed model and confirm the effect of temperature on the antioxidant potential of olive pomace.

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564

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714

Figure captions

Figure 1. RGB images of pulp+peel (P+P, a) and pit (PI, c) fractions of olive pomace and binary conversion (P+P, b and PI, d) using Image J.

Figure 2. Experimental (average ± standard deviation) drying kinetics of olive pomace at different temperatures.

Figure 3. Evolution of drying rate (average ± standard deviation) during drying of olive pomace at 50 and 120 °C.

Figure 4. Experimental and calculated dimensionless moisture content using Weibull and diffusion models. Experiments carried out at 50 (a) and 150 ºC (b).

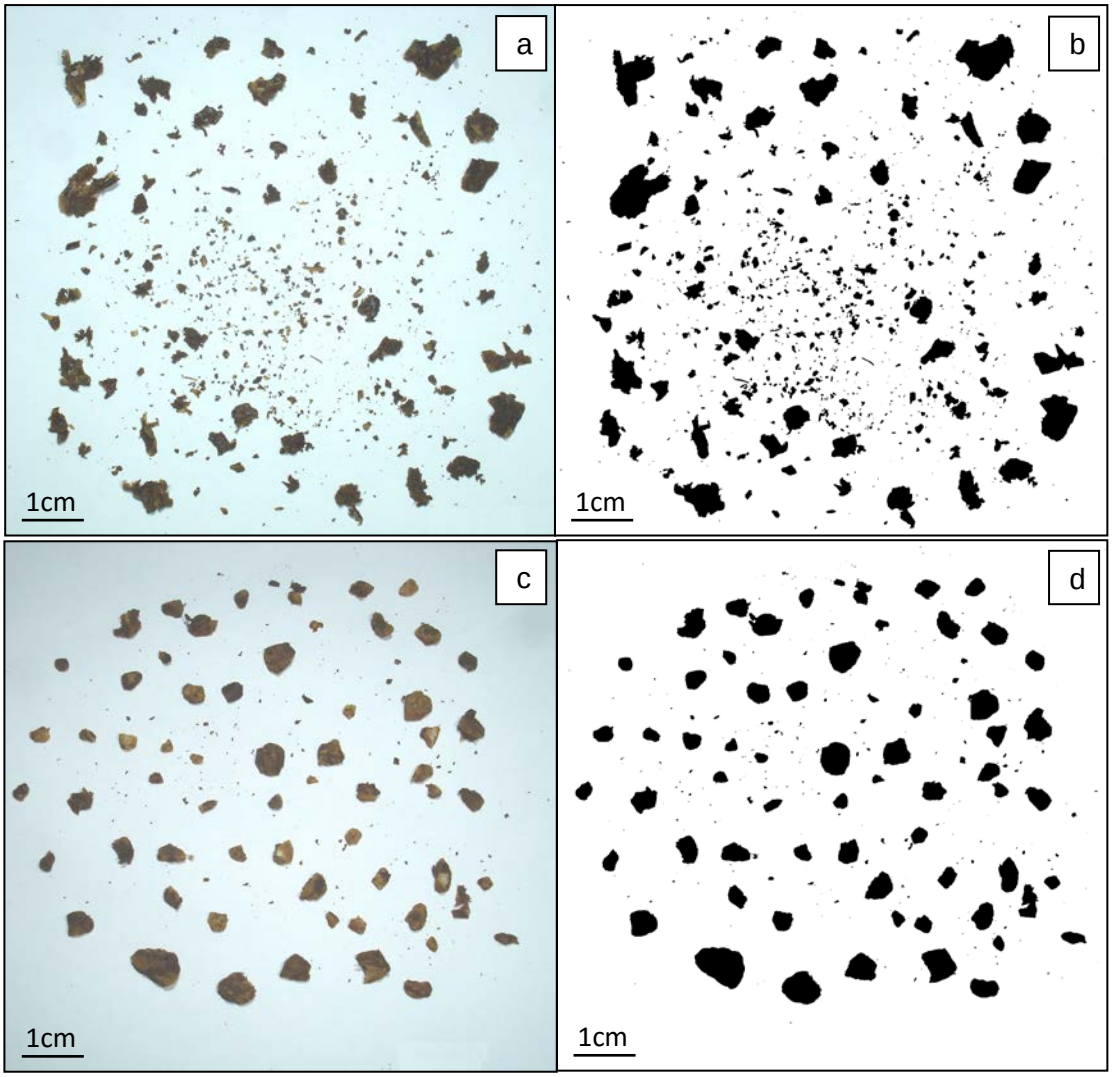
Figure 5. Fit of an Arrhenius type equation to the kinetic parameter of the Weibull model (1/β, a) and effective moisture diffusivities for pit (D_e^{PI}, b) and pulp+peel (D_e^{P+P}, c) fractions.

Figure 6. Experimental TPC and AC (average ± standard deviation) of extracts of olive pomace dried at different temperatures. Superscript letters show homogeneous groups established from Least Significance Difference (LSD) intervals ($p<0.05$).

Figure 7. Experimental TPC and AC (average ± standard deviation) of extracts of olive pomace dried at 150 ºC for different times. Superscript letters show homogeneous groups established from Least Significance Difference (LSD) intervals ($p<0.05$).

Figure 8. Luteolin-7-O-glucoside content (average ± standard deviation) of extracts of olive pomace dried at 150 ºC for different times. Superscript letters show homogeneous groups established from Least Significance Difference (LSD) intervals ($p<0.05$).

Figure 9. TPC of extracts obtained from fresh and dried olive pomace (at 50 and 150 °C) at different extraction times. Average ± standard deviation.



744

745 Figure 1

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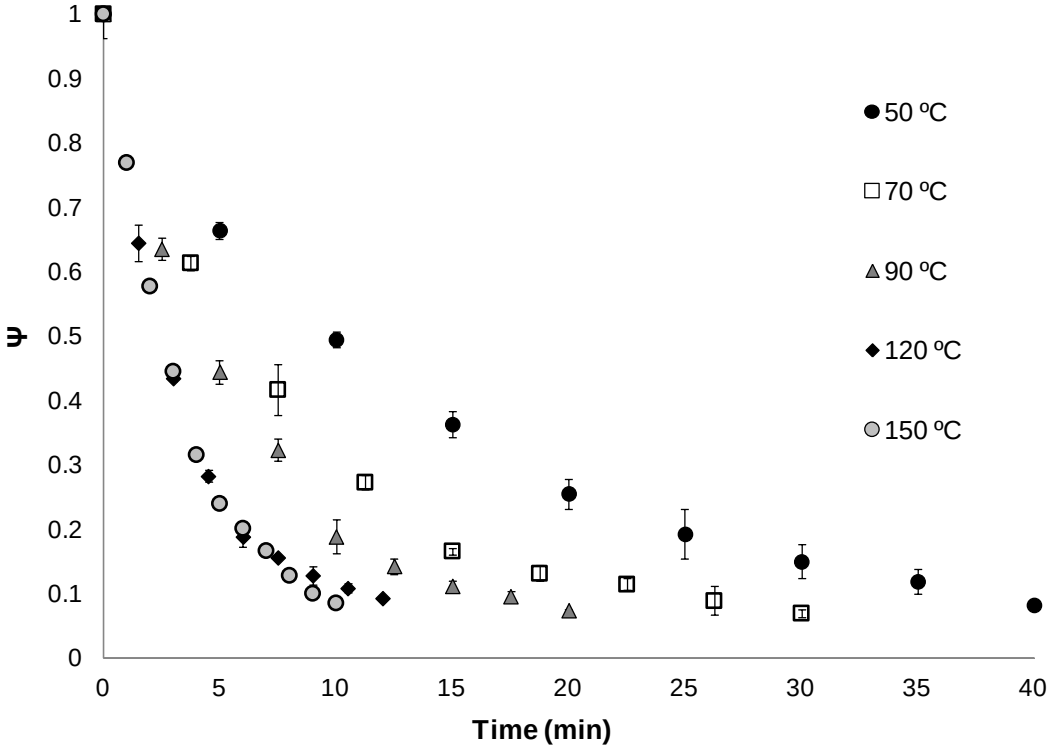

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749 Figure 2

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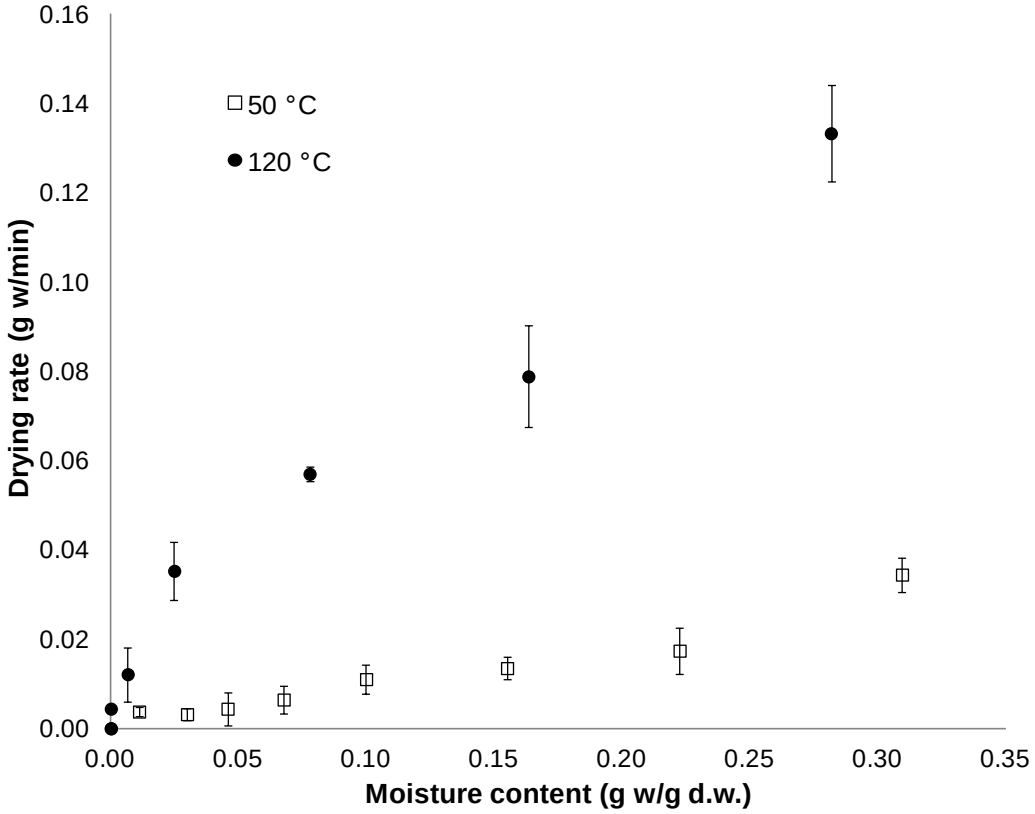

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752 Figure 3

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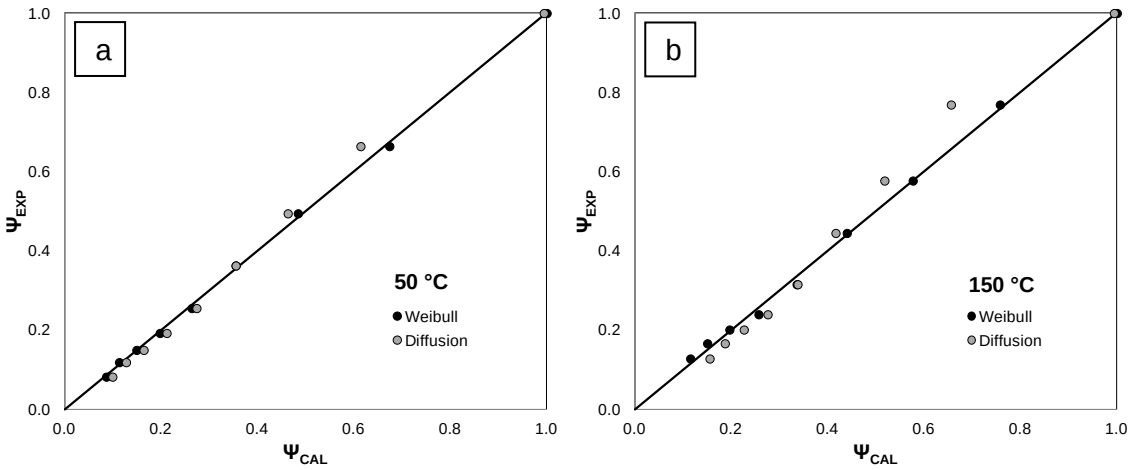

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755 Figure 4

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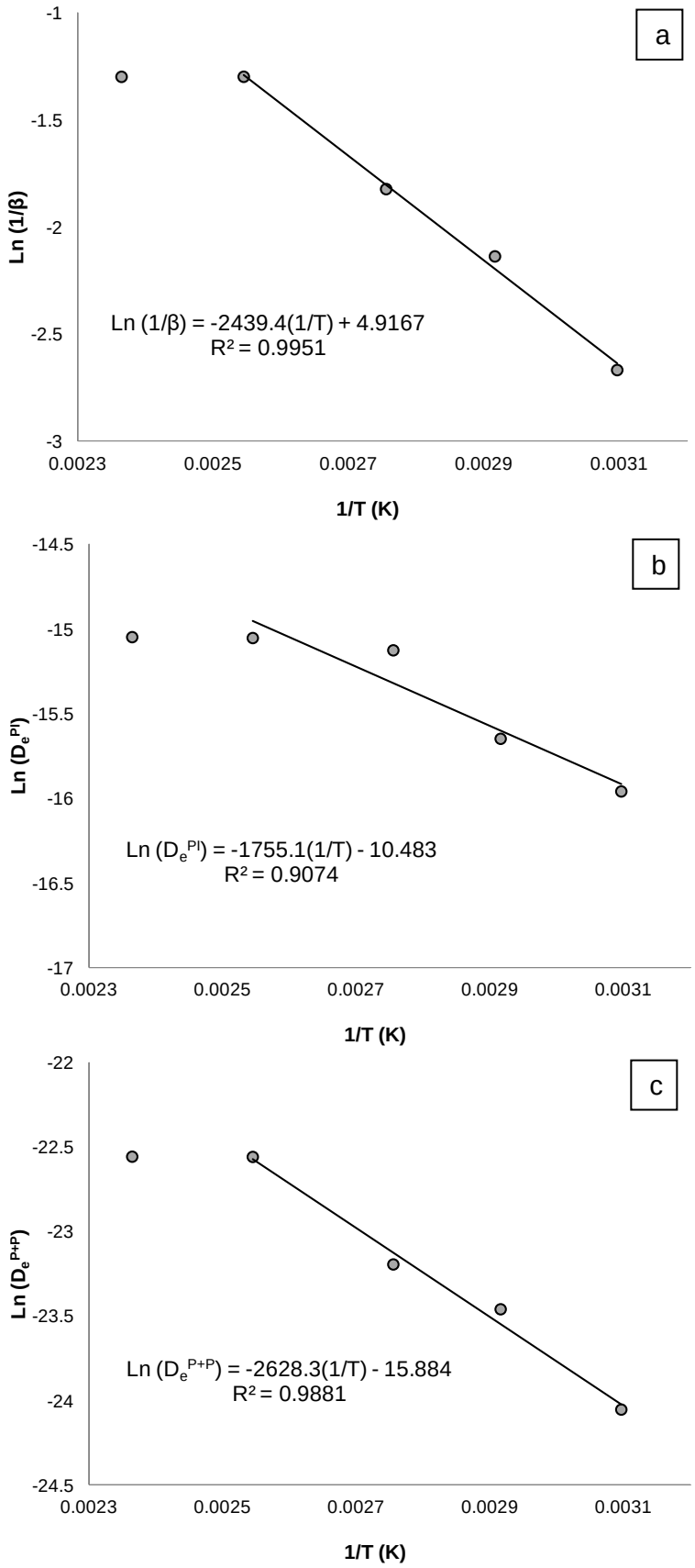

757 Figure 5

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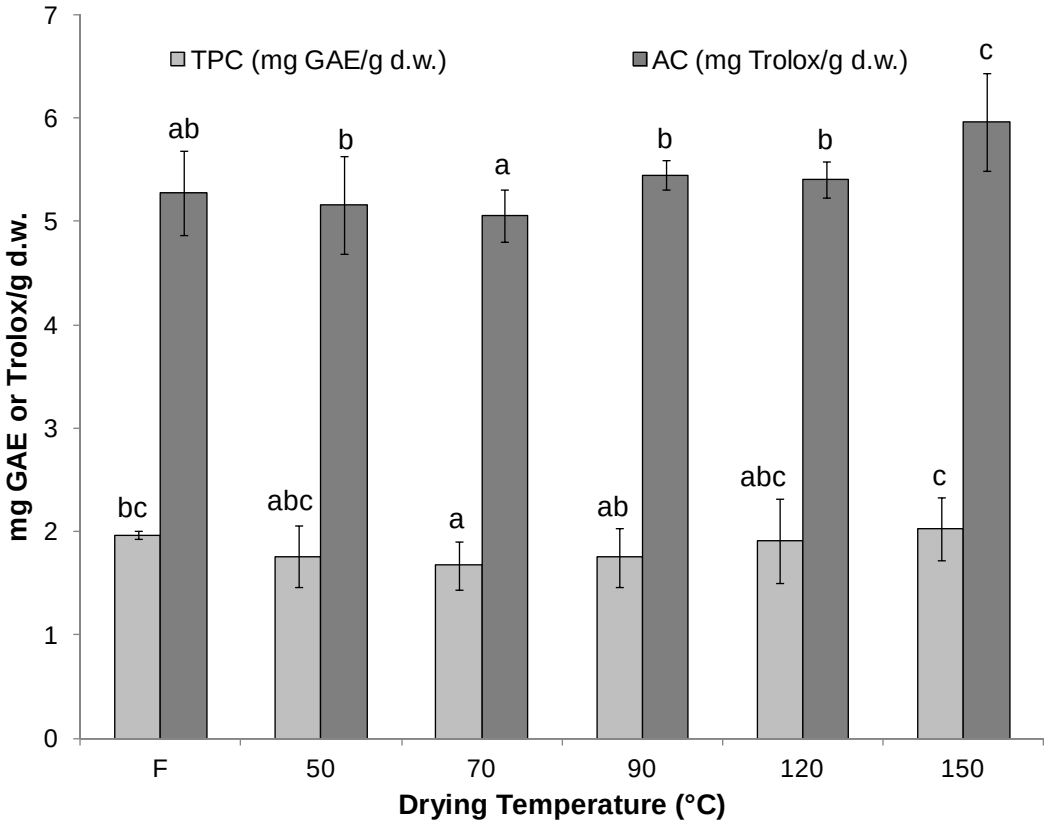

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760 Figure 6

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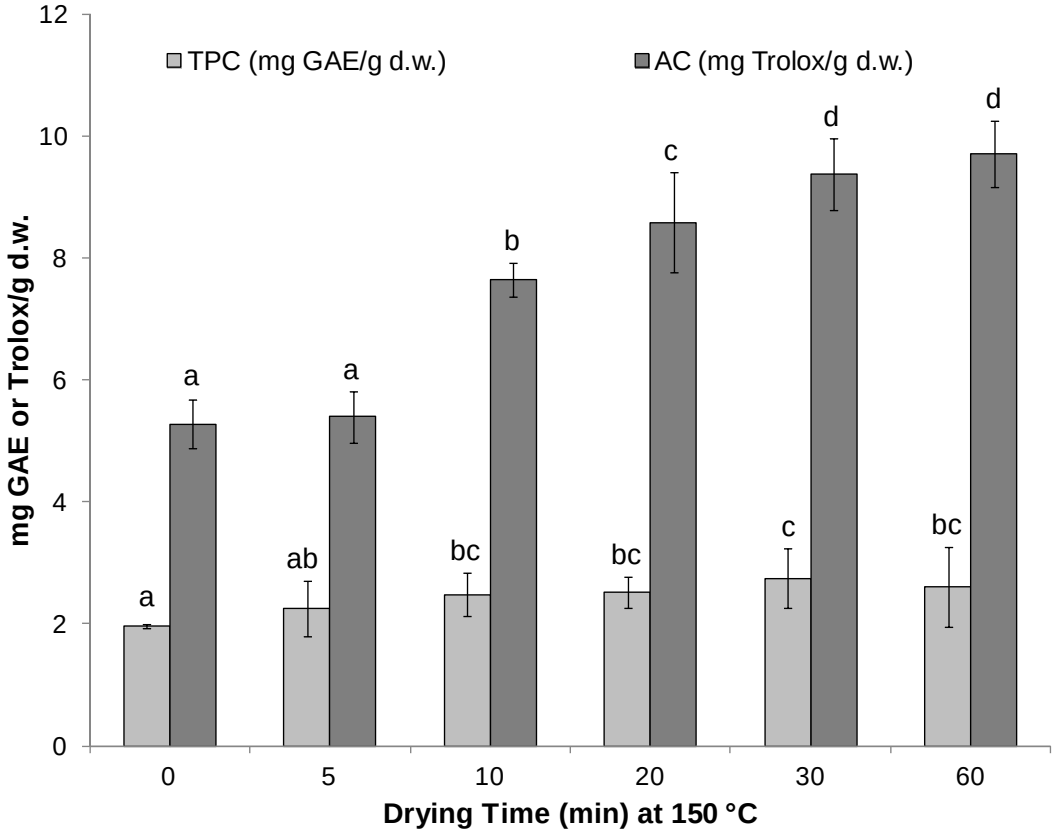

762 Figure 7

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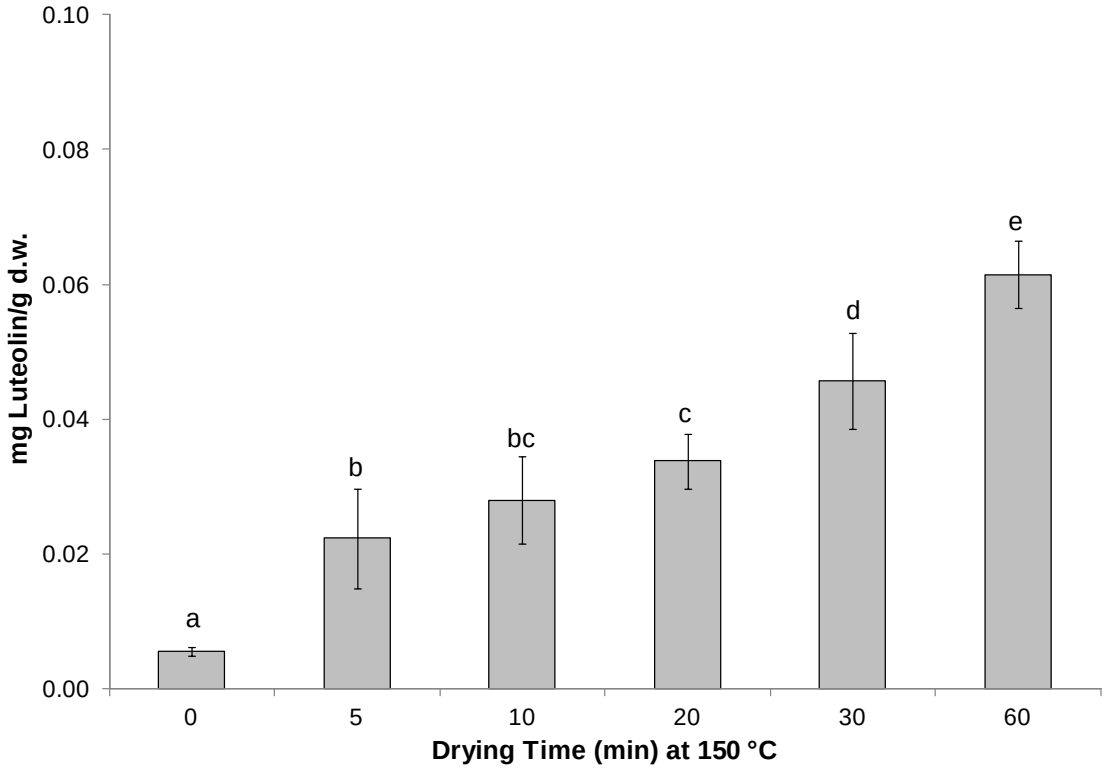

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765 Figure 8

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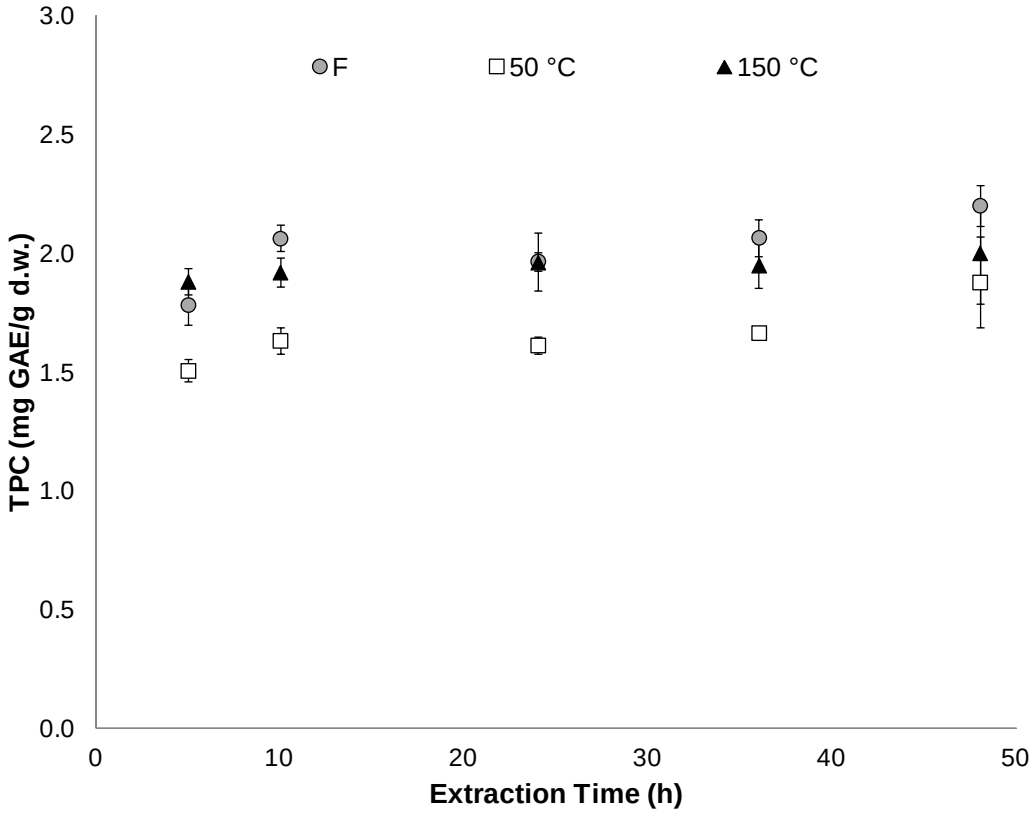

767 Figure 9

768

769 **Table 1.** Characterization of pit (PI) and pulp+peel (P+P) fractions of olive
770 pomace.
771

	PI	P+P
ρ (kg/L)	1.30 ± 0.05	1.5 ± 0.2
W_0 (g w/g d.w)	0.234 ± 0.004	0.66 ± 0.05
X	0.424 ± 0.005	0.576 ± 0.005
r_m (mm)	1.80 ± 0.02	0.311 ± 0.015
Y_1 (S_p > 10 mm^2)	0.584	0.502
Y_2 (1 < S_p < 10 mm^2)	0.381	0.384
Y_3 (0.25 < S_p < 1 mm^2	0.021	0.063
Y_4 (S_p < 0.25 mm^2)	0.015	0.051

772 ρ = density, W_0 =initial moisture content, X = mass fraction, r_m = characteristic dimension
773 (thickness in PI and radius in P+P fraction), Y = sub-fraction of particles with a specific surface
774 (S_p), $Y_1+Y_2+Y_3+Y_4 = 1$)

775

776

777 **Table 2.** Modelling of drying kinetics of olive pomace carried out at different
778 temperatures and identified parameters of Weibull and Diffusion models.
779

		Drying temperature (°C)				
		50	**70**	**90**	**120**	**150**
Weibull	α	0.88	0.85	0.88	0.85	0.99
	β (s)	14.4	8.5	6.2	3.7	3.6
	% VAR	99.4	99.5	99.6	99.4	99.7
	% MRE	9.1	11.0	8.4	10.1	4.6
Diffusion	D_e^{PI} (m^2/s)	$1.17 \cdot 10^{-7}$	$1.60 \cdot 10^{-7}$	$2.69 \cdot 10^{-7}$	$2.90 \cdot 10^{-7}$	$2.92 \cdot 10^{-7}$
	D_e^{P+P} (m^2/s)	$3.58 \cdot 10^{-11}$	$6.48 \cdot 10^{-11}$	$8.45 \cdot 10^{-11}$	$1.59 \cdot 10^{-10}$	$1.60 \cdot 10^{-10}$
	% VAR	98.8	99.1	99.03	98.9	96.9
	% MRE	11.9	10.9	9.5	9.2	11.3

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