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ULTRASONICALLY ENHANCED LOW-TEMPERATURE DRYING OF APPLE: INFLUENCE ON DRYING KINETICS AND ANTIOXIDANT POTENTIAL

J.V. Santacatalina[1], O. Rodríguez[2], S. Simal[2], J.A. Cárcel[1], A. Mulet[1] and J.V. García-Pérez[1]*

[1]ASPA Group, Department of Food Technology, Universitat Politècnica de València, Camí de Vera s/n, E46022, València, Spain.

[2]Department of Chemistry, University of the Balearic Islands, Ctra. Valldemosa, km. 7.5, E07122, Palma de Mallorca, Spain.

*Corresponding author. Tel.: +34 963879376; fax: +34 963879839. E-mail address: jogarpe4@tal.upv.es (J.V. García-Pérez).

Abstract

Low-temperature air drying represents an alternative means to hot air drying of better retaining the sensory, nutritional and functional properties of foods. However, reducing the air temperature to figures below the product's freezing point involves low drying rates, which largely places constraints on any further industrial application. The main aim of this work was to evaluate the feasibility of using power ultrasound to improve the low-temperature drying of apple, considering not only the kinetic effects but also the influence on the antioxidant potential of the dried apple.

For that purpose, apple (*Malus domestica* cv. Granny Smith) cubes (8.8 mm side) were dried (2 m/s and a relative humidity of under 10%) at low temperatures (-10, -5, 0, 5 and 10ºC) with (20.5 kW/m^3) and without ultrasound application. The drying kinetics were modeled by considering the diffusion theory, negligible shrinkage and cubic geometry. In the dried apple, total phenolic and flavonoid contents and antioxidant capacity were measured.

The application of power ultrasound sped up the drying kinetics at every temperature tested, achieving drying time reductions of up to 77%, which was linked to the improvement in diffusion and convective mass transport. In overall terms, ultrasound application involved a greater degradation of polyphenol and flavonoid contents and a reduction of the antioxidant capacity, which was related to the cell disruption caused by the mechanical stress of acoustic waves.

Keywords: Dehydration; Ultrasound; Modeling; Antioxidant capacity

1. Introduction

Food drying is an ancient and widely used preservation method that allows for greater flexibility in the availability of food products, regardless of the season. Nowadays, dried products occupy an important place within the food industry (Vega-Gálvez et al., 2012). Drying involves the reduction of moisture in the product and so, the slowing down of its microbial and chemical deterioration. Moreover, a reduction in the product volume and weight makes the transport and storage easier (Doymaz & Pala, 2003). Nowadays, there is an increasing demand for high-quality dried products whose nutritional and sensory properties have only been minimally altered if compared to the fresh product (Mayor & Sereno, 2004). However, drying provokes a series of changes in materials, such as oxidation, color change, shrinkage or loss of texture and nutritional-functional properties (Vega-Gálvez et al., 2009). These changes are greatly dependent on the drying technique applied or the temperature used (Heras-Ramírez et al., 2012; Vega-Gálvez et al., 2012). In fact, severe drying conditions, like high temperatures, could imply the greatest degradation.

Low-temperature drying may be defined as the water removal process carried out at temperatures below standard room conditions, e.g. below 20ºC. This technique includes a wide range of processing conditions and temperatures both below and above the product's freezing point. The main exponent of low-temperature drying is vacuum freeze drying or lyophilization, in which the total or partial reduction of vapor pressure leads to an increase in the water removal rate and keeps the temperature of the wet product low (Ratti, 2001). Drying below freezing point can also be performed at atmospheric pressure, which consists of blowing low temperature air through the product. In this way, high quality products can also be obtained and continuous processing is feasible (Stawczyk et al., 2007), thus reducing the processing cost compared to vacuum freeze drying. However, working at atmospheric pressure and low temperatures leads to very low drying rates (García-Pérez et al., 2012a). Therefore,

there is a particular interest in intensifying this low-temperature drying process, thereby making its application in the food industry feasible.

Power ultrasound (PU) has been applied to the hot air drying of different products, such as several fruits and vegetables, leading to shorter drying times (Gallego-Juárez et al., 2007; García-Pérez et al., 2007). The mechanical energy introduced by PU into the drying medium could help to reduce both the external and the internal mass transfer resistance without introducing a high amount of thermal energy during drying (Riera et al., 2011). Therefore, the use of PU to dry heat-sensitive materials or in low-temperature drying processes has great potential (Awad et al., 2012) that needs to be investigated. In this sense, ultrasound has been applied during the drying of apple, carrot and eggplant at -14ºC (García-Pérez et al., 2012a) and the drying time was shortened by between 65 and 70%. Therefore, to confirm the potential of applying PU during low-temperature drying, it should be investigated over a wide range of temperatures both above and below the sample freezing point and it should not only be the kinetics that are taken into consideration, but also issues of quality.

Dried apples can either be consumed fresh or used as a raw material in the processing of prepared foods, such as snacks, breakfast cereals and other functional foods (Akpinar et al., 2003). Furthermore, apple constitutes one of the main sources of polyphenols and flavonoids in the western diet (Boyer & Liu, 2004) and the antioxidant activity of apple is among the highest in commonly consumed fruits and vegetables (Lee et al., 2003; Van der Sluis et al., 2002; Vrhovsek et al., 2004). However, it has been observed that processing brings about a large reduction in both the total phenolic content and the antioxidant activity (Tiwari & Cummins, 2013; Van der Sluis et al., 1997 and 2002). Thus, it is important to define the drying conditions under which the characteristics of fresh apples can be better preserved. Nowadays, there are very few studies into the effect of low-temperature drying on the antioxidant activity of dried products, and no references have been found about how ultrasound can influence it. In

this sense, apple is an all-year-round product with a homogeneous solid matrix and for these reasons it has been used in several studies into the influence of different drying process variables (Kaleta & Górnicki, 2010; Li et al., 2008; Stawczyk et al., 2007 and Vega-Gálvez et al., 2012). Therefore, the main aim of this work was to evaluate the feasibility of PU application as a means of improving the low-temperature drying of apple, quantifying its influence on both the drying kinetics and antioxidant potential of the dried product.

2. Materials and methods

2.1. Raw material

Apples (*Malus domestica* cv. Granny Smith) were purchased in a local market (Valencia, Spain). Fruits were selected to obtain a homogeneous batch in terms of ripeness, size and color and held at 5ºC until processing. Cubic samples (8.8 mm side) were obtained from the flesh using a household tool. Samples dried at temperatures of 0ºC or above were immediately processed, while those dried at temperatures below 0ºC were wrapped in plastic film and frozen by placing in a freezing room at -18±1ºC until processing (at least 10 h). The initial moisture content was measured by placing samples in a vacuum oven at 70ºC and 200 mmHg until constant weight was reached, following the standard method 934.06 (AOAC, 1997).

2.2. Drying experiments

Drying experiments were carried out in a convective drier with air recirculation (Figure 1), already described in the literature (García-Pérez et al, 2012a). The drying air temperature and velocity are controlled using a Proportional-Integral-Derivative (PID) algorithm. Air temperature control is achieved by coupling a cooling system and an electric resistance. Thus, a chiller (KAE evo-121, MTA, Italy) feeds a copper tube heat

exchanger (area 13m^2, fin space 9 mm; Frimetal, Spain) with a glycol-water (45% v/v) solution at -22ºC, where the air flow is cooled down. Finally, acting over the electrical resistance, the air drying temperature is set to the desired value. In order to keep the relative humidity low, the air is forced to flow through a tray containing desiccant material, which is periodically regenerated. The drying chamber consists of a vibrating cylinder attached to a piezoelectric transducer (22 kHz). Thus, the walls of the cylinder radiate the ultrasonic energy into the air medium producing a sound pressure level of 154.3 dB (Riera et al., 2011). The samples are placed in a sample holder to be randomly distributed in the drying chamber. The dryer is equipped with an industrial scale (VM6002-W22, Mettler-Toledo, USA) to weigh the samples automatically at preset times.

The drying tests (2±0.1 m/s air velocity and 7±4% relative humidity) were carried out at different temperatures (-10, -5, 0, 5 and 10ºC) with (AIR+US) and without (AIR) ultrasound application. An acoustic power density of 20.5 kW/m^3 was applied in the AIR+US experiments; this energy density is defined as the electric power supplied to the ultrasonic transducer (50 W) divided into the volume of the drying chamber (cylindrical radiator, 2.43 L). For each run, 40 cubic samples were processed and the initial mass load density was 9.5 kg/m^3. The drying experiments were extended until the samples lost 80% of the initial weight. At least four replicates were carried out for each drying condition tested.

2.3. Modeling of drying kinetics

A diffusion model was used to describe the drying kinetics. The governing diffusion equation was obtained by combining Fick's second law and the microscopic mass balance. For cubic geometry, considering the effective moisture diffusivity to be constant, the temperature uniform and the shrinkage negligible, the diffusion equation (Equation 1) is written as follows:

153 $$\frac{\partial W_p(x,y,z,t)}{\partial t} = D_e\left(\frac{\partial^2 W_p(x,y,z,t)}{\partial x^2} + \frac{\partial^2 W_p(x,y,z,t)}{\partial y^2} + \frac{\partial^2 W_p(x,y,z,t)}{\partial z^2}\right) \quad (1)$$

154 where W_p is the local moisture (kg water/kg dry matter, dm), t is the time (s), D_e is the
155 effective moisture diffusivity (m^2/s) and x, y and z represent the characteristic mass
156 transport directions in cubic geometry (m).

157 In order to solve Equation 1, the initial moisture was assumed to be uniform and the
158 symmetry was considered in directions x, y, z. Two different approaches to the
159 boundary condition on the interface were taken into consideration. As a first approach,
160 the external resistance was considered negligible. Therefore, the surface moisture
161 content suddenly reached equilibrium with the drying air, as reflected by Equation 2 for
162 the x coordinate, and mass transfer was entirely controlled by internal diffusion (D
163 model). The model's analytical solution, in terms of the average moisture content, is
164 given by Equation 3 (Simal et al., 2005).

165 $$W_p(L,y,z,t>0) = W_e \quad (2)$$

166 $$W(t) = W_e + (W_0 - W_e)\left[\sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left(-\frac{D_e(2n+1)^2\pi^2 t}{4L^2}\right)\right]^3 \quad (3)$$

167 where W is the average moisture content (kg water/kg dm), L the half-length of the
168 cube side (m) and subscripts 0 and e represent the initial and equilibrium states,
169 respectively. Sorption data at 10ºC reported by Veltchev & Menko (2000) were used to
170 estimate the equilibrium moisture content.

171 In a second approach, the external resistance to mass transfer was also considered.
172 Therefore, the moisture transport was jointly controlled by diffusion and convection
173 (D+C model), this being represented in the model by the boundary condition shown in
174 Equation 4, again for the x coordinate. The D+C model permits the quantification of
175 both the effective diffusivity and the external mass transfer coefficient (k, kg water/m^2s):

176 $$t > 0 \qquad x = L \qquad -D_e \rho_{ds} \frac{\partial W_p(L,y,z,t)}{\partial x} = k(a_w(L,y,z,t) - \varphi_{air}) \qquad (4)$$

177 where ρ_{ds} is the dry solid density (kg dm/m^3) and φ_{air} is the relative humidity of the
178 drying air. As mentioned previously, the water activity on the surface of the material (a_w
179 (L,y,z,t)) was estimated from sorption isotherm data reported in the literature (Veltchev
180 & Menko, 2000).

181 The D+C model was numerically solved by applying an implicit finite difference method
182 (García-Pérez et al., 2012a), for which a computational algorithm in MATLAB 7.9.0
183 (The MathWorks, Inc., USA) was written. The application provided the local moisture
184 distribution inside the solid and the average moisture content of the solid as a function
185 of the drying time.

186

187 *2.4. Model fitting*

188 The D model was fitted to the experimental data in order to identify the effective
189 moisture diffusivity (D_e). For that purpose, an optimization problem was defined. The
190 objective function to be minimized was the sum of the squared differences between the
191 experimental (W_{exp}) and calculated (W_{calc}) average moisture contents. The optimization
192 was conducted by applying the generalized reduced gradient method available in the
193 Solver tool (Microsoft Excel 2007).

194 In the case of the D+C model, kinetic parameters, k and D_e, were jointly identified by
195 minimizing the same objective function as in the D model. In this case, the SIMPLEX
196 method available in fminsearch function (MATLAB) was used for optimization. Both D
197 and D+C models were fitted to each drying run and the kinetic parameters averaged.

198 Finally, the percentage of explained variance (%VAR, Equation 5) was calculated in
199 order to determine the goodness of the fit to the experimental data.

200 $$\%VAR = \left[1 - \frac{S_{xy}^2}{S_y^2}\right] \cdot 100 \quad (5)$$

201 where S_{xy} and S_y are the standard deviation of the estimation and the sample,
202 respectively.

203

204 *2.5. Antioxidant potential*

205 The antioxidant potential content was measured by means of the Total Phenolic
206 Content (TPC), the Flavonoid Content (FC) and Antioxidant Capacity (AC).

207 For that purpose, extracts of dried samples were prepared following the methodology
208 proposed by Eim et al (2013), with some modifications. Samples (1.00±0.02 g) were
209 placed into 20 mL of methanol (MeOH) (Scharlau, Barcelona, Spain) and homogenized
210 at 4ºC using an Ultra-Turrax® (T25 Digital, IKA, Germany), at 13,000 rpm for 1 min.
211 Then the homogenized solution was kept overnight in refrigeration. After that, the
212 mixture was centrifuged at 4,000 rpm for 10 min and filtrated (Ederol filter paper No
213 202, J.C. Binzer, Hatzfeld, Germany); the extract was subsequently kept at 4ºC until
214 analysis.

215 Total polyphenol and flavonoid contents were determined by means of the Folin-
216 Ciocalteu and Aluminum chloride assays (Carbone et al., 2011; Leontowicz et al.,
217 2003), respectively. The antioxidant capacity was determined by ABTS, FRAP,
218 CUPRAC and DPPH assays, which provides a good estimation of the AC in different
219 oxidative reactions. Table 1 briefly summarizes the above-mentioned assays, as well
220 as showing recent references in which the different assays are described in detail. The
221 absorbance measurement was taken at 25°C in a microplate spectrophotometer
222 (MultiSkan® Spectrum, Thermo Scientific, USA).

223 For each drying run, a batch of fresh samples was separately analyzed and used as
224 control to compare with the dried samples. From the standard curves, the absorbance

results were expressed as mg of Gallic acid equivalent (GAE)/g dm and mg of Cathechin equivalent (CE)/g dm for the phenolic and flavonoid contents, respectively, while the AC was expressed as mg of Trolox/g dm. Every analysis was carried out in triplicate and the results were reported as mean ± standard deviation.

The percentage of degradation for each parameter (%Degradation, Equation 6) was used in order to quantify the influence of both the drying temperature and PU application on each specific parameter:

$$\%\text{Degradation} = \frac{(C_0 - C_f)}{C_0} \cdot 100 \quad (6)$$

where C_0 and C_f are the initial (fresh product) and the final concentration (mg/g dm) for each parameter.

2.6. Statistical analysis

In order to evaluate if PU application and air temperature had a significant influence on the kinetic parameters (D_e and k), an analysis of variance (ANOVA) was carried out and the least significant difference (LSD) intervals ($p<0.05$) were estimated using Statgraphics Plus software 5.1. (Statistical Graphics Corp., Rockville, USA). Likewise, the influence of the drying conditions on the antioxidant capacity and the polyphenolic and flavonoid contents of the dried samples were also compared by means of an analysis of variance and LSD intervals.

3. Results and discussion

3.1. Drying experiments

The drying kinetics of apple cubes without ultrasound application (AIR experiments) are shown in Figure 2A. It should be noted that when drying temperatures were above the

249 sample's freezing point (0, 5 and 10ºC), the water was removed from the solid matrix
250 by evaporation, while for temperatures below freezing point (-5 and -10ºC), it was
251 removed by sublimation. In this last case, according to the "uniformly retreating ice
252 front" theory (URIF) (Claussen et al., 2007), sublimation happens in the ice front and
253 the water vapor moves through the dry layer to the sample surface. It can be observed
254 that, at temperatures above freezing point (0, 5 and 10ºC), the lower the temperature
255 used, the longer the drying time (Figure 2A), which is the typical behavior found in
256 foodstuffs drying. Likewise, the drying process at -5ºC was faster than at -10ºC.
257 However, when experiments below and above freezing point are compared, it was
258 found that experiments carried out at -5ºC were faster than those carried out at 0 and
259 5ºC (Figure 2A) and the drying rate of experiments performed at -10ºC was quite
260 similar to at 0ºC. This fact is probably linked to the degradation of the sample's
261 structure produced by the prior freezing of samples dried at -5 and -10ºC, which can
262 make the water removal easier. In this sense, Eshtiaghi et al. (1994) and
263 Dandamrongrak et al. (2003) already reported that prior freezing of the raw material
264 sped-up the drying of green beans, carrots, potatoes and bananas. In addition, the
265 drying rate at 0ºC, and considering the temperature drop ascribed to water
266 evaporation, could be also limited because part of the energy was used for providing
267 the necessary latent heat for water freezing or thawing. A similar effect of the drying
268 temperature was observed in experiments with ultrasound application (AIR+US, Figure
269 2B).

270 Applying PU greatly increased the drying rate of apples at all the temperatures tested.
271 The reduction of the drying time brought about by PU application was similar in the
272 experiments carried out at 10, 5, 0 and -5ºC (around 60%). However, an average
273 drying time reduction of 77% was observed in the experiments performed at -10ºC
274 (Figure 3), shortening the drying time from 43.8 (AIR) to 10.3 h (AIR+US). The drying
275 time reduction may be ascribed to the mechanical effects associated with ultrasonic

waves that cause a reduction of both the internal and external resistances to mass transfer. On the one hand, PU generates alternating expansions and contractions when travelling in a solid medium, this mechanical stress helps to make the water movement towards the product surface easier. In addition, ultrasound may also promote water sublimation since, to a certain extent, the attenuation of the acoustic wave may provide the energy needed for the water to change state (Gallego-Juárez, 2010). On the other hand, the application of ultrasound in solid/gas systems also produces a mechanical stirring of the gas medium caused by the generation of oscillating velocities, micro-streaming and pressure variation on the interfaces, which reduces the boundary layer and, as a consequence, improves the movement of water from the solid surface to the air (Gallego-Juárez et al., 1999).

Schössler et al. (2012) developed a contact ultrasound system for the purpose of improving vacuum freeze-drying. It mainly constituted an ultrasonically activated meshed tray on which the samples were placed and the acoustic energy was directly transmitted from the vibrator to the sample. It is a very different system from the one used in this work, where an air-borne ultrasound application is performed. These authors found that ultrasound treatment led to an 11.5% reduction in the drying time required to reach a final moisture content of 10% (dry basis) when freeze-drying red bell pepper cubes. Bantle & Eikevik (2011) reported a maximum drying time reduction of around 10% when drying green peas at -3ºC using a commercial air-bone ultrasonic radiator (20kHz; DN 20/2000, Sonotronic). Therefore, previous reported attempts at using ultrasound as a means of intensifying low-temperature drying were less satisfactory than the results obtained in this work.

3.2. Modeling of drying kinetics

Among other purposes, modeling aims to quantify the influence of both air temperature and ultrasound application on the drying kinetics of apple. In a first approach, the

303 drying kinetics were modeled considering a pure diffusion model (D model, Table 2).
304 First of all, it should be highlighted that the effective diffusivities identified for drying
305 experiments carried out below and above the freezing point are not easily comparable.
306 At - -10ºC (atmospheric freeze drying) and assuming the URIF theory (Claussen et al.,
307 2007), vapor diffusion is only restricted to the dry layer. As drying progresses, the ice
308 core shrinks and the dry layer is made thicker. In the diffusion model, the characteristic
309 dimension for diffusion is considered constant, and equal to the half-length (L) of the
310 cubic sample; as a consequence, the effective diffusivities identified at -10 and -5ºC
311 are overestimated due to the fact that the real characteristic dimension is always
312 shorter than L. In the literature (García-Pérez et al., 2012a; Li et al., 2008), the general
313 diffusion theory is mostly adopted to mathematically describe atmospheric freeze
314 drying when modeling is not the final goal and the search for accurate diffusion
315 coefficients is not required, such as in this work. Notwithstanding, further research
316 should focus on developing and validating mechanistic models for atmospheric freeze
317 drying. In addition, it should be emphasized that modeling assumed constant cubic
318 shape and volume, which is a more reliable hypothesis in low-temperature than in hot
319 air drying (Mayor & Sereno, 2004; Li et al., 2008).

320 The effective diffusivities obtained for AIR experiments ranged between $4.3 \cdot 10^{-11}$ m^2/s
321 at -10ºC and $10.9 \cdot 10^{-11}$ m^2/s at 10ºC (Table 2). The identified D_e figures are consistent
322 with previous results obtained in literature. Thus, Li et al. (2008) reported effective
323 diffusivities of $1.0 \cdot 10^{-11}$ and $1.1 \cdot 10^{-11}$ m^2/s for apple drying at -8 and -4ºC, respectively.
324 The influence of temperature on D_e can also be observed in Table 2. Thus, in the range
325 from 0 to 10ºC, the higher the temperature used, the greater the identified effective
326 diffusivity. Likewise, for drying temperatures below freezing point, D_e at -5ºC was
327 higher than at -10ºC. However, the values of D_e for the experiments at -5 and -10ºC
328 were similar to those obtained at higher temperatures (5 and 0ºC, respectively) due
329 mainly to the effects of freezing on the product structure.

330 The application of PU during apple drying significantly ($p<0.05$) increased the effective
331 moisture diffusivity at all the temperatures tested (Table 2). The increase in D_e
332 produced by PU application was of the same order at the drying temperatures of 10, 5,
333 0 and -5ºC, around 140%. However, for drying experiments carried out at -10ºC, the
334 increase was found to be much higher (267%). This could be explained by the fact that
335 drying at temperatures below the product's freezing point, where sublimation is the
336 predominant water removal mechanism, converts the material into a highly porous
337 dried matrix, which is more prone to ultrasound application (García-Pérez et al., 2009;
338 2012a; Ozuna et al., 2014). The improvement in D_e found in this work was more
339 marked than others reported in the literature due to the high efficiency of the electric/
340 acoustic energy conversion of the transducer used (Gallego-Juarez, 2010). Thus,
341 Bantle & Eikevik (2011) found an effective diffusivity increase of up to 14.8% in the
342 ultrasonic assisted drying of green peas at -6ºC.

343 In overall terms, D model fitted the AIR experiments well, with percentages of
344 explained variance of over 97.8%. However, the modeling of the AIR+US experiments
345 was always less accurate and the explained variance fell to 94.4 and 92.9% in
346 experiments carried out at -10 and -5ºC, respectively. These low values of %VAR
347 indicate that the assumptions considered in the model formulation were not close to
348 real behavior for these specific conditions, diffusion not being the only significant mass
349 transport mechanism. García-Pérez et al. (2012a) had already observed this fact for
350 apple, carrot and eggplant drying at -14ºC. These authors stated that, under these
351 conditions, ultrasound application can modify the relative importance of convection in
352 mass transport control. This is the reason why the drying kinetics were also modeled,
353 including the external resistance to mass transfer (D+C model). In every case, the D+C
354 model provided an accurate fitting of the drying kinetics, with explained variances of
355 over 99.8% (Table 3). The different accuracy of D and D+C models is illustrated in
356 Figure 4, where it is observed that the calculated moisture contents with D+C model

were much closer to experimental values than those found with the D model. As regards the identified parameters (Table 3), PU application involved a significant ($p<0.05$) increase in the effective moisture diffusivity (D_e) and mass transfer coefficient (k). It was observed that ultrasound application at every temperature led to a greater increase in D_e than in k (Table 3). This fact was particularly noticeable at -5 and -10ºC, which suggests that ultrasound had a greater effect on internal transport than on external. Therefore, ultrasound reduced the role of diffusion in mass transport rate control and lent more significance to convection, which explains the fact that D model provided a poor fit at -5 and -10ºC in AIR+US experiments.

The improvement in D_e and k brought about by PU application in experiments performed at -10ºC (501 and 148%, respectively) was more marked than at -5ºC (263 and 96%); this could in all likelihood be explained by considering the more porous structure of the dried product when drying at -10ºC, because, at this temperature, the water was totally frozen. At -5ºC, however, the water of the apple samples would only be partially frozen since the freezing temperature of apple is around -5±0.3ºC (Cornillon, 2000) taking the ºBrix of fresh apple into account (12.2±0.6ºBrix). Therefore at -5ºC, a combined sublimation/evaporation could be found.

3.3. Antioxidant potential

In order to determine the influence of both PU application and the drying temperature on the antioxidant potential of the final dried product, the polyphenol and flavonoid content and the antioxidant capacity of dried samples were determined.

3.3.1. Polyphenol content

The total polyphenol content of fresh apples was 10.2±1.9 mg GAE/g dm. This value is in the range of those found by Vrhovsek et al. (2004) (7.8±0.5 mg GAE/g dm) and

383 Heras-Ramírez et al. (2012) (11.9±1.0 mg GAE/g dm). AIR drying caused a reduction in
384 the total polyphenol content regardless of the temperature used; thus, the degradation
385 percentages ranged from 26.0±1.7% to 35.1±2.0% (Figure 5A). At temperatures above
386 the freezing point, the higher the temperature used, the higher the degradation
387 percentage observed; the lowest degradation was achieved at 0 and 5ºC. However, the
388 degradation percentages found in the experiments carried out at -5 and - 10ºC were
389 significantly higher ($p<0.05$). This fact could be ascribed to the cell damage caused by
390 freezing, which, among other things, aids the release of oxidative enzymes during
391 thawing and extraction (Ahmad-Qasem et al., 2013). As for PU application during
392 drying (AIR+US experiments), it brought about an average percentage of degradation
393 of the total polyphenol content which was significantly ($p<0.05$) higher (40.8±3.5%) than
394 those found in AIR experiments (30.5±3.6%) at every temperature tested. This fact
395 could be linked to the structural damage of cells brought about by ultrasound (García-
396 Pérez et al., 2012b; Puig et al., 2012). Therefore, the mechanical stress linked to
397 ultrasonic wave propagation could aid the release of oxidative enzymes and intra-
398 cellular compounds into the solvent, contributing to the degradation of polyphenol in a
399 similar way to freezing. It should be noted that the degree of polyphenol degradation
400 found in this work was greater than that reported by Stawczyk et al. (2007), who found
401 an average reduction in the polyphenol content of only 20% in the convective drying of
402 apple cubes (1 cm side) at -8 and -12ºC. The milder polyphenol degradation found by
403 these authors could be explained by the fact that the samples were pre-treated in a 3%
404 citric acid solution before drying. As regards the effect of PU application during drying
405 on TPC, Soria et al. (2010) did not found significant differences between the TPC of
406 carrot samples freeze dried and those dried at 20ºC with PU application.
407
408
409 *3.3.2. Flavonoid content*

410 The total flavonoid content measured in fresh apple was 2.2±0.1 mg CE/g dm, which is
411 in the range of the figures found by other authors, such as Leontowicz et al. (2003)
412 (0.9±0.1 mg CE/g dm) and Heras-Ramírez et al. (2012) (5.3±0.5 mg CE/g dm) working
413 with the Granny Smith variety . The influence of the drying air temperature and PU
414 application on the degradation of the total flavonoid content (Figure 5B) was similar to
415 that observed in the case of polyphenol degradation, since flavonoids are an important
416 part of total polyphenols. Thus, in general terms, the drying process caused a
417 reduction in the total flavonoid content at every drying temperature tested. In AIR
418 experiments, the highest percentage of degradation was found at temperatures of
419 -10ºC (33.9±1.8%) and -5ºC (32.3±1.7%), while the lowest degradation was found at
420 0ºC (24.2±2.1%) and 5ºC (26.3±2.3%). Heras-Ramírez, et al (2012) reported a
421 flavonoid loss in the order of 50% in apple pomace dried at temperatures of 50, 60, 70,
422 and 80ºC. At the different temperatures tested, these authors did not find any
423 significant differences, but they suggested that blanching in a citric/ascorbic acid
424 solution at 86ºC for 4 min before drying prevented degradation. Thus, considering the
425 results of Heras-Ramírez et al. (2012), the low-temperature drying used in this study
426 allowed for a better preservation of the flavonoid content in apples than hot-air drying.
427 It could also be observed that in AIR+US experiments the degradation of the flavonoid
428 content was significantly ($p<0.05$) greater than in AIR experiments (e.g. 44.7±2.1% and
429 34.7±1.5% for AIR+US experiments at -10 and 0ºC, respectively). It is worth
430 mentioning that there are no published studies that relate the effect of PU application
431 during low-temperature drying on the polyphenol and flavonoid content of fruits.
432 However, Rodriguez et al. (2014) have studied the effect of ultrasonically assisted
433 apple drying at 30, 50 and 70ºC on phenolic and flavonoid content. These authors
434 observed that, in overall terms, the US application involved a lower TPC and FC in
435 comparison to air dried apple samples.

436 *3.3.3. Antioxidant capacity*

437 In order to achieve a greater and more thorough understanding of the influence of
438 drying temperature and PU application on bioactive compounds, four different assays
439 of the antioxidant capacity were used in the present study: ABTS, CUPRAC, FRAP
440 and DPPH. The antioxidant capacity measured for fresh apple was 12.9±1.8, 18.3±3.3,
441 8.0±1.7 and 29.2±5.5 mg Trolox/g dm using ABTS, CUPRAC, FRAP and DPPH
442 assays, respectively. In every assay, the measurement is based on a single-electron-
443 transfer, but the antioxidants present in the medium may be hydrophilic or lipophilic in
444 nature and this will aid the reaction to a greater or lesser extent. It should be noted that,
445 due to each assay being based on a different chemical system and/or reaction, the
446 antioxidant activity values clearly varied for each sample extract depending on the
447 method used (Gonzalez-Centeno et al., 2012).

448 The ABTS assay is based on the ability of antioxidants to quench the long-lived radical
449 cation 2,2-azinobis-(3-ethylbenzothiazoline-6-sulphonate). Thus, ABTS allows the most
450 preferably lipophilic fraction of polyphenols to be determined with AC (Buratti et al.,
451 2001). AIR samples dried at -10 and -5ºC showed higher AC degradation figures
452 ($p<0.05$) than those dried at higher temperatures (0, 5 and 10ºC) (Figure 6A). A higher
453 degree of degradation was obtained in samples dried with PU application, a common
454 fact at every temperature tested. However, these differences between both drying
455 techniques (AIR, AIR+US) were not significant ($p<0.05$) at drying temperatures below
456 0ºC.

457 The FRAP assay is based on the reduction of Fe (III)-Fe (II) in the presence of ferrous
458 ion stabilizing ligand (TPTZ) allowing the AC of water-soluble antioxidants to be
459 determined (Benzie & Strain, 1996). From the AC degradation measured by this
460 method (Figure 6B), two observations could be made: the positive effect of the using
461 low temperatures but the negative effect of freezing. Thus, the highest degree of
462 degradation was found at -10ºC (50.2±2.1%) and the lowest at 0ºC (39.0±2.1%),

showing a similar trend to TPC and FC. Significant ($p<0.05$)differences between the FRAP measurements in AIR and AIR+US samples were found only at -5ºC.

The CUPRAC assay is suitable as a means of analyzing biological samples due to the fact that the reaction is carried out at physiological pH (Apak et al., 2007) and it is used for the determination of both hydrophilic and lipophilic antioxidants. This assay (Figure 6C) exhibited the lowest degradation values of the different methods tested for measuring AC. In AIR experiments, a significant ($p<0.05$) influence of the drying temperature was observed and the highest degradation percentage was obtained at -10ºC and the lowest was attained at 0ºC. PU application during drying induced a greater AC degradation than those found in other AC assays. Thus, at every temperature tested, AIR+US samples showed a significantly ($p<0.05$) greater AC degradation than AIR ones. There are no previous data about the effect of PU application on the AC measured by CUPRAC. However, Eim et al., (2013) measured the effect of the drying temperature on the AC of carrots by means of the CUPRAC assay and reported an AC degradation of 70.2% and 45.3% for drying temperatures of 55 and 70ºC, respectively, which are much higher values than the ones found in this work for low-temperature AIR experiments .

The DPPH assay is based on the measurement of the scavenging ability of antioxidants towards the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH). The free radical DPPH is reduced to the corresponding hydrazine when it reacts with hydrogen donors (Sánchez-Moreno, 2002). Comparing all the AC measurements tested, the greatest degradation of the AC was found using the DPPH method (Figure 6D). Once again, it may be observed that the lowest degradation percentage was found at 0ºC (59.8±2.9%). Stawczyk et al., (2007) reported lower figures of AC degradation for apples dried at -4ºC (19.4%) and -8ºC (20.0%) which had been pre-treated in a 3% acid citric solution. This fact could be explained by the fact that these authors only considered a 50% reduction of DPPH radicals, whilst the assay used in our study

considered their total reduction (100%). At every temperature tested, the AIR+US samples presented a greater degradation than the AIR ones, although the differences were only significant ($p<0.05$) at 10ºC. This indicates that PU application has no effect on the AC degradation measured by the DPPH assay, except for experiments carried out at 10ºC.

In overall terms, it should be emphasized that under every experimental condition tested, the drying process caused degradation in the AC of the fresh apple, regardless of the method used (Figure 6), but PU application during drying induced a greater AC degradation. Nevertheless, whether the differences between the AC degradation of the AIR and the AIR+US samples were significant or not depended on both the assay and the drying temperature used.

4. Conclusions

In this work, the feasibility of applying PU to increase the mass transfer rate during low-temperature drying has been demonstrated. Thus, a maximum drying time reduction of 76.5% was achieved by PU application. Water transport followed a clear diffusion pattern for cubic samples, except for experiments with PU application carried out at -5 and -10ºC, because the ultrasonic energy modified the mass transport controlling mechanisms, decreasing the internal mass transfer resistance more than the external. Thus, the effective diffusivity and the mass transfer coefficient were increased by up to 501 and 148%, respectively. As regards antioxidant potential, in overall terms, ultrasound application involved a greater degradation of polyphenol and flavonoid contents and a reduction of antioxidant capacity, which was linked to the cell disruption under acoustic stress. Therefore, PU can be used to speed-up the low-temperature drying processes and further works should focus on determining the energy budget for the scaling-up and elucidating if the time saving is linked to a less energy consumption.

However, it should be taken into account that PU may negatively affect the biological components due to the mechanical stress caused by the acoustic waves.

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677

678 **Figure captions**

679

680 **Figure 1.** Diagram of the ultrasonically assisted convective dryer (García-Pérez et al.,
681 2012a): 1, fan; 2, Pt-100; 3, temperature and relative humidity sensor; 4, anemometer;
682 5, ultrasonic transducer; 6, vibrating cylinder; 7, sample load device; 8, retreating pipe;
683 9, slide actuator; 10, weighing module; 11, heat exchanger; 12, heating elements; 13,
684 desiccant tray chamber; 14, details of the sample load on the trays.

685

686 **Figure 2.** Experimental drying kinetics (10, 5, 0, -5 and -10ºC and 2 m/s) of apple. A:
687 Convectional drying experiments (AIR) and B: Ultrasonically assisted drying
688 experiments (AIR+US; 20.5 kW/m^3).

689

690 **Figure 3.** Experimental drying kinetics (-10ºC and 2 ms^{-1}) of apple. AIR: Convectional
691 drying experiments and AIR+US: Ultrasonically assisted drying experiments (20.5
692 kW/m^3).

693

694 **Figure 4.** Experimental vs calculated moisture content evolution of apple with D and
695 D+C model of an experimental drying kinetic (-5ºC and 2 m/s) assisted by power
696 ultrasound (20.5 kW/m^3).

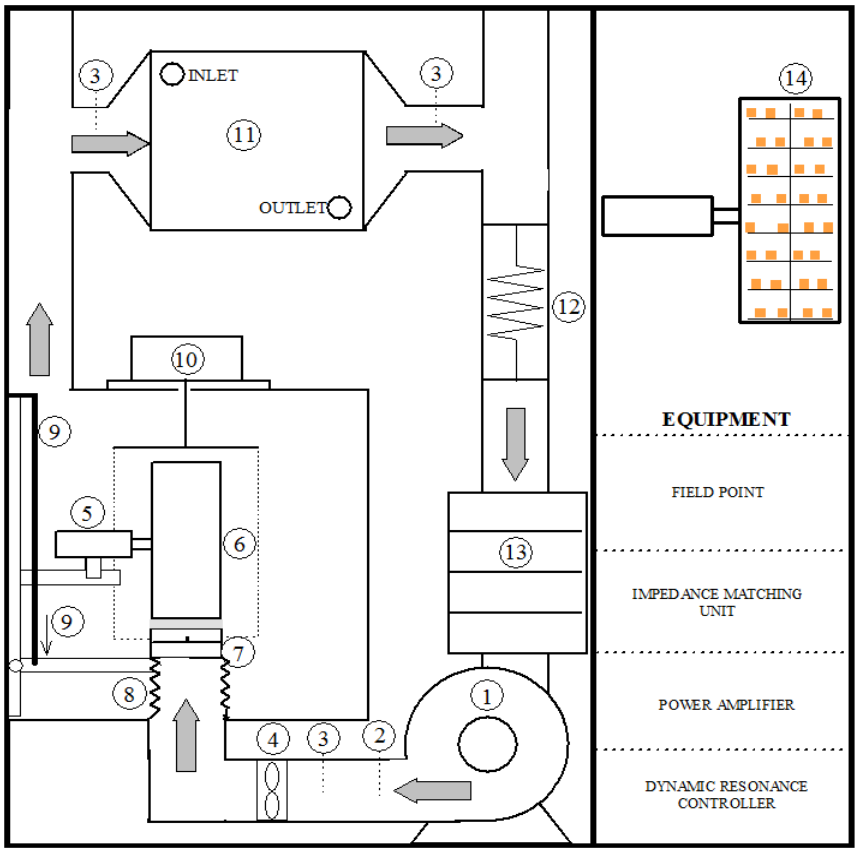
697

698 **Figure 5.** Degradation of total polyphenol (A) and flavonoid (B) content in apples during
699 AIR and AIR+US drying. Different letters show significant differences according to LSD
700 intervals ($p<0.05$).

701

702 **Figure 6.** Degradation of the antioxidant capacity of apples during AIR and AIR+US
703 drying. ABTS (A), FRAP(B), CUPRAC (C), DPPH (D). Different letters show significant
704 differences according to LSD intervals ($p<0.05$).

Figure 1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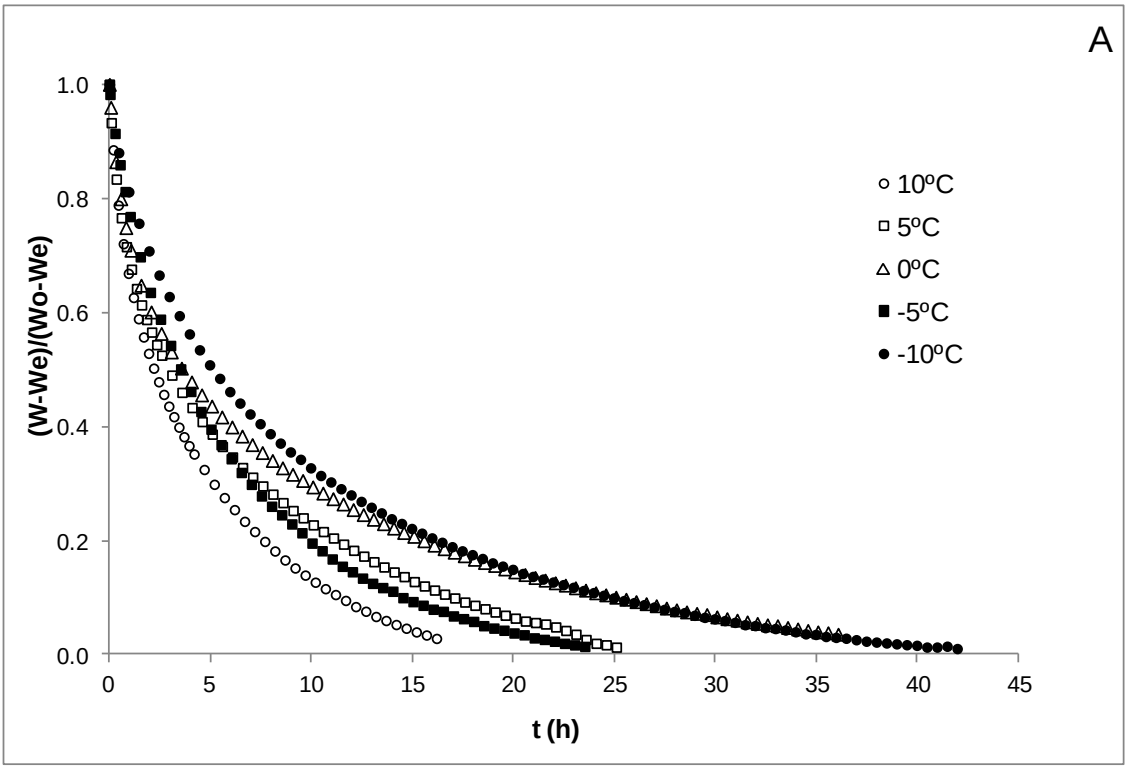
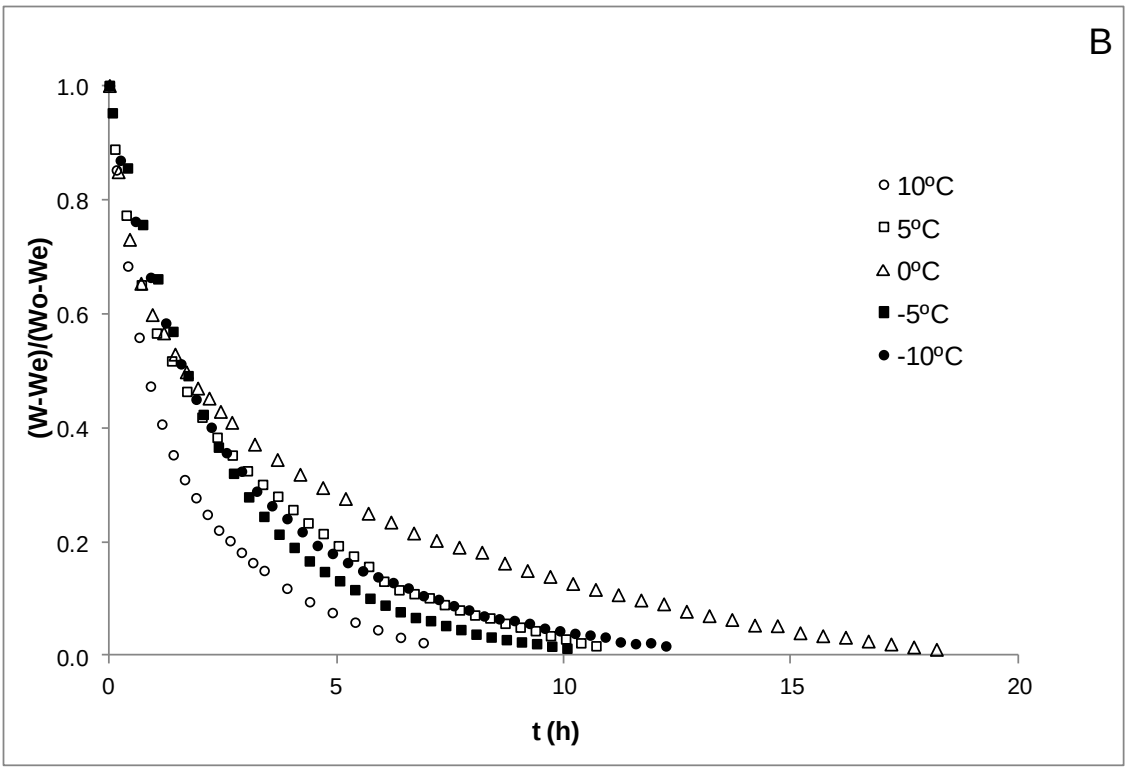
OUTLET
EQUIPMENT
FIELD POINT
IMPEDANCE MATCHING UNIT
POWER AMPLIFIER
DYNAMIC RESONANCE CONTROLLER

Figure 2


A
1.0
0.8
0.6
0.4
0.2
0.0
(W-We)/(Wo-We)
0
5
10
15
20
25
30
35
40
45
t (h)
10ºC
5ºC
0ºC
-5ºC
-10ºC


B
1.0
0.8
0.6
0.4
0.2
0.0
(W-We)/(Wo-We)
0
5
10
15
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t (h)
10ºC
5ºC
0ºC
-5ºC
-10ºC

Figure 3

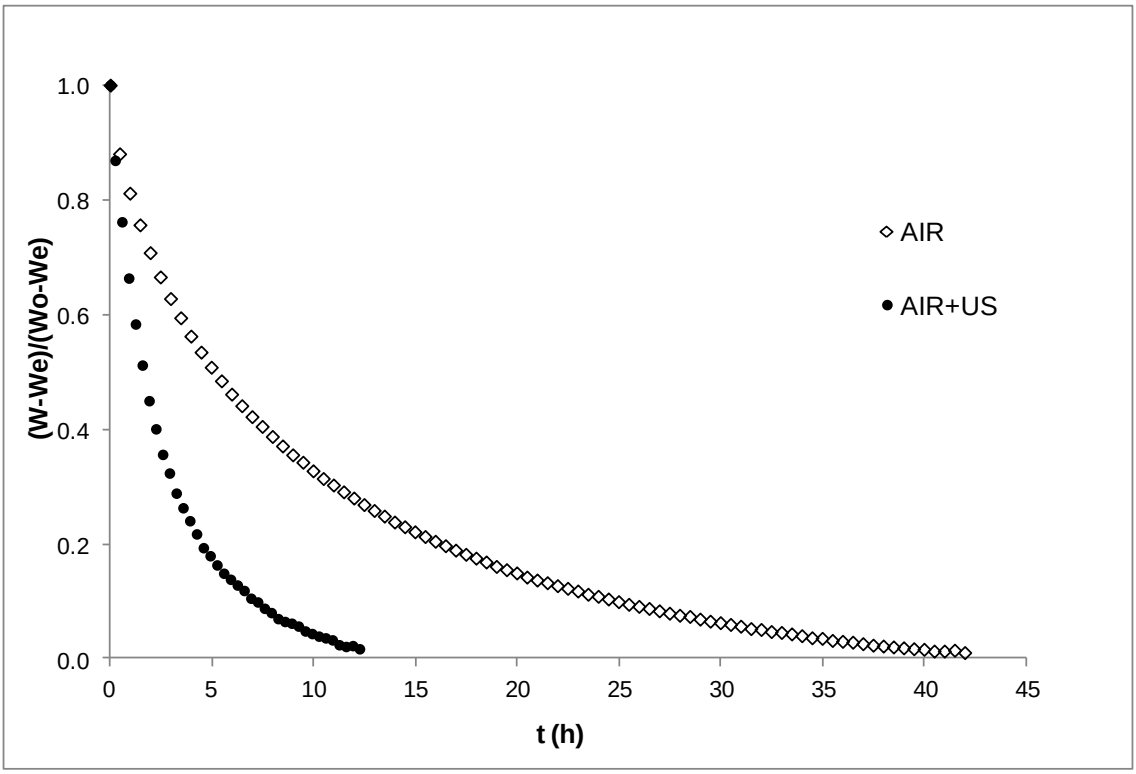

Figure 4

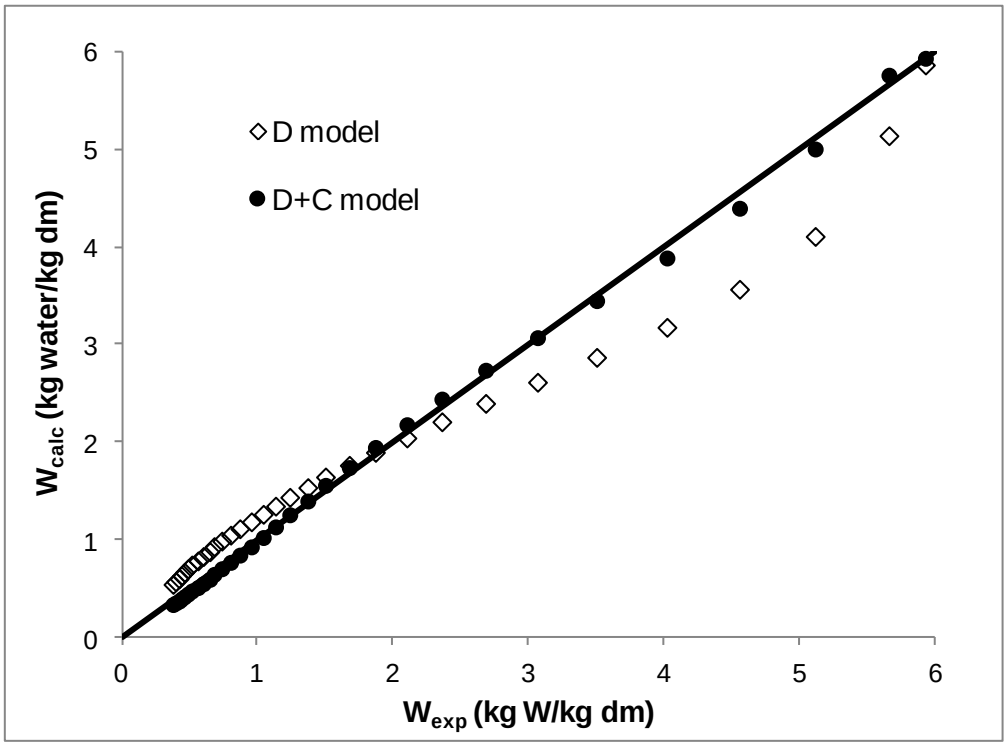

Figure 5

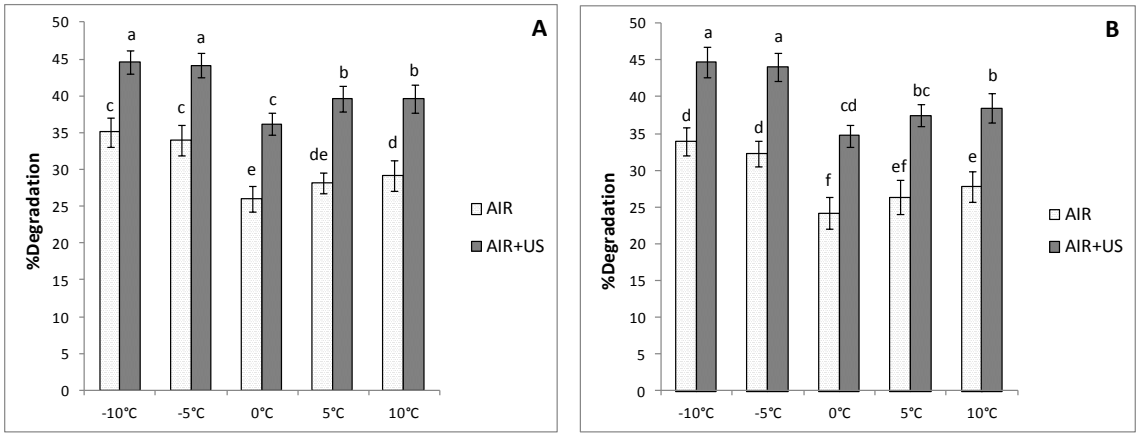
A
%Degradation
50
45
40
35
30
25
20
15
10
5
0
c
a
c
a
e
c
de
b
d
b
-10°C
-5°C
0°C
5°C
10°C
AIR
AIR+US
B
%Degradation
d
a
d
a
f
cd
ef
bc
e
b
-10°C
-5°C
0°C
5°C
10°C
AIR
AIR+US

Figure 6

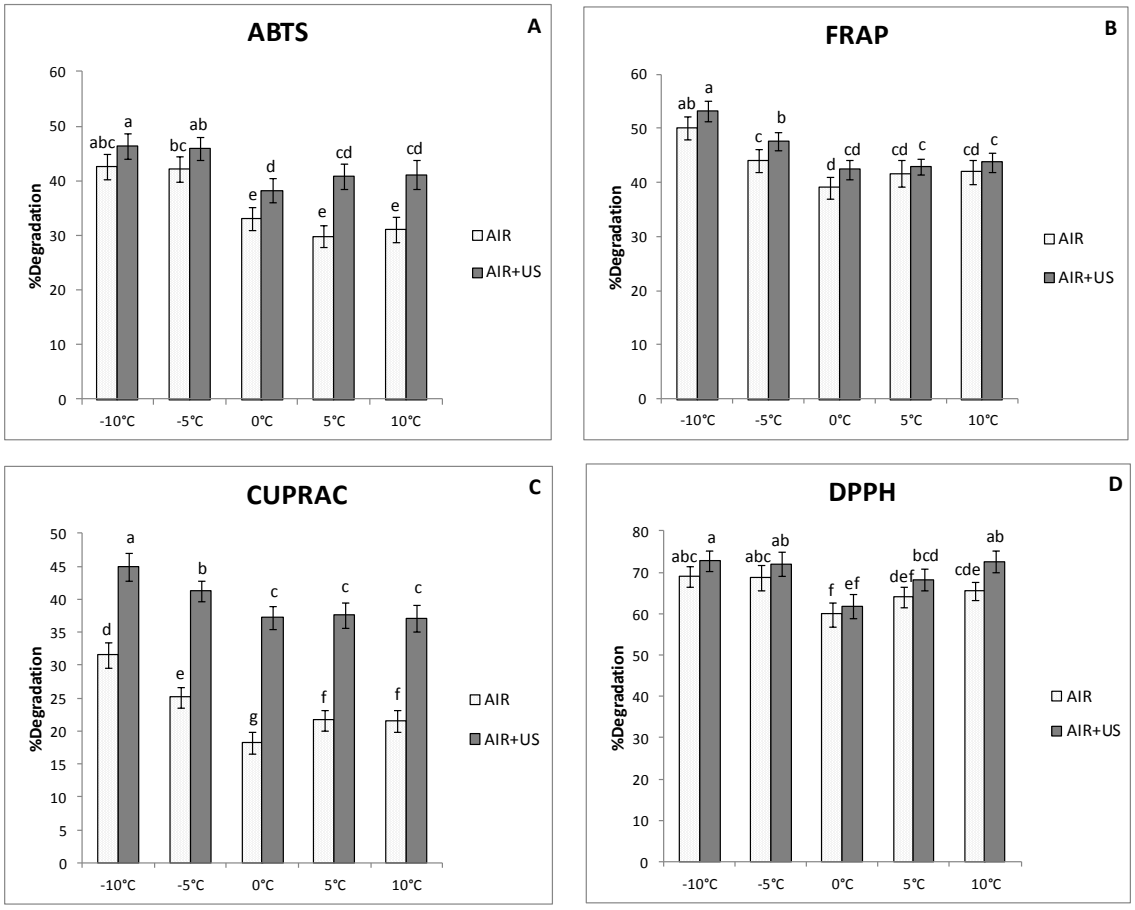
A
ABTS
%Degradation
60
50
40
30
20
10
0
abc
a
bc
ab
e
d
e
cd
e
cd
-10°C
-5°C
0°C
5°C
10°C
AIR
AIR+US
B
FRAP
%Degradation
ab
a
c
b
d
cd
cd
c
cd
c
C
CUPRAC
%Degradation
50
45
40
35
30
25
20
15
10
5
0
d
a
e
b
g
c
f
c
f
c
D
DPPH
%Degradation
80
70
60
50
40
30
20
10
0
abc
a
abc
ab
f
ef
def
bcd
cde
ab

Table 1. Total phenolic content, flavonoid content and antioxidant capacity assays.

Determination	Assay	Reagents	λ (nm)	Reference
Polyphenol content	Folin Ciocalteu	[a]Folin Ciocalteu [e]Na_2CO_3 7.5%	745	(Carbone et al., 2011)
Flavonoid content	Aluminium chloride	[e]$NaNO_2$ 5% [d]$AlCl_3$*$6H_2O$ 10% [f]NaOH 1M	510	(Leontowicz et al., 2003)
Antioxidant capacity	ABTS	[c]ABTS 7 mM [a]$K_2S_2O_8$ 2.45mM	734	(Floegel et al., 2011)
	FRAP	[b]TPTZ 0.01M [a]$FeCl_3$*$6H_2O$ 0.02M [a]Acetate buffer (pH 3.6)	593	(Gonzalez-Centeno et al., 2012)
	CUPRAC	[a]$CuCl_2$*$2H_2O$ 10 mM [d]Neocuprine 7.5 mM [a]NH_4Ac Buffer 1.0 M	450	(Eim et al., 2013)
	DPPH	[d]DPPH 0.2 mM:	517	(Lo Scalzo et al., 2004)

[a]Purchased from Scharlau (Barcelona, Spain).
[b]Purchased from Acros Organics (New Jersey, USA).
[c]Purchased from Biochemica (Darmstadt, Germany).
[d]Purchased from Sigma-Aldrich (Steinheim, Germany).
[e]Purchased from Panreac (Barcelona, Spain).
[f]Purchased from Riedel-de Haën (Seelze, Germany).

Table 2. Results of the modeling of the drying kinetics of apple without (AIR) and with (AIR+US) ultrasound application (20.5 kW/m^3) using the diffusion model (D model). Average values and standard deviation are shown for effective moisture diffusivity (D_e). VAR (%) is the percentage of explained variance. ΔD_e shows (in percentage) the increase in effective moisture diffusivity produced by ultrasonic application.

		-10ºC	-5ºC	0ºC	5ºC	10ºC
AIR	D_e (10^{-11} m^2/s)	4.3±0.5 ^{c}	6.8±0.3 ^{b}	4.7±0.5 ^{c}	6.6±0.4 ^{b}	10.9±1.9 ^{a}
	VAR (%)	98.4	97.8	99.8	99.5	98.8
AIR+US	D_e (10^{-11} m^2/s)	15.6±1.3 ^{y}	16.7±2.9 ^{y}	11.6±2.2 ^{z}	15.9±2.8 ^{y}	25.8±2.7 ^{x}
	VAR (%)	94.4	92.9	99.4	98.6	98.3
	ΔD_e(%)	267	146	148	141	136

Superscript letters (a, b, c) and (x, y, z) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$) for the D_e of AIR and AIR+US experiments, respectively.

Table 3

Table 3. Results of the modeling of the drying kinetics of apple without (AIR) and with (AIR+US) ultrasound application (20.5 kW/m^3) using the diffusion and convection model (D+C model). Average values and standard deviation are shown for kinetic parameters: effective moisture diffusivity (D_e) and mass transfer coefficient (k). VAR (%) is the percentage of explained variance. ΔD_e and Δk (in percentage) the increase in a kinetic parameter produced by ultrasonic application.

		-10ºC	-5ºC	0ºC	5ºC	10ºC
AIR	D_e (10^{-11} m^2/s)	3.5±0.4 ^{c}	6.6±1.0 ^{b}	3.3±0.4 ^{c}	4.8±0.4 ^{c}	8.8±2.0 ^{a}
	k (10^{-4} kg water/m^{2}s)	1.6±0.2 ^{D}	2.0±0.1 ^{D}	2.7±0.1 ^{C}	3.2±0.3 ^{B}	4.4±0.5 ^{A}
	VAR (%)	99.9	99.9	99.9	99.9	99.8
AIR+US	D_e (10^{-11} m^2/s)	20.8±8.8^{xy}	24.0±8.4 ^{x}	8.6±2.1 ^{z}	12.5±2.6^{yz}	22.3±1.5 ^{x}
	k (10^{-4} kg water/m^{2}s)	3.9±0.6 ^{Z}	4.0±0.2 ^{Z}	5.4±1.1 ^{Y}	5.6±0.7 ^{Y}	9.1±1.4 ^{X}
	VAR (%)	99.9	99.8	99.9	99.9	99.9
	ΔD_e (%)	501	263	163	161	153
	Δk (%)	148	96	101	77	107

Superscript letters (a, b, c) and (x, y, z) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$) for the D_e of AIR and AIR+US experiments, respectively.
Superscript letters (A, B, C, D) and (X, Y, Z) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$) for the k of AIR and AIR+US experiments, respectively.