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On the effect of ultrasound-assisted atmospheric freeze-drying on the antioxidant properties of eggplant

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Abstract

The low operating temperatures employed in atmospheric freeze-drying permits an effective drying of heat sensitive products, without any impairment of their quality attributes. When using power ultrasound, the drying rate can be increased, thus reducing the process duration. However, ultrasound can also affect the product quality. The aim of this study was to evaluate the effect of various drying process variables, namely air temperature and velocity, ultrasound power and sample size, on the antioxidant properties of eggplant (*Solanum Melongena L.*) samples. For this reason, drying experiments were carried out at different drying temperatures (-5, -7.5, -10 °C), power ultrasound levels (0, 25, 50 W; 21.9 kHz) and air velocities (2, 5 m s^{-1}) using different sample sizes (8.8 mm and 17.6 mm cube side). The ascorbic acid content (Jagota and Dani method), total phenolic content (Folin-Ciocalteau method), and the antioxidant capacity (FRAP method) of the dried products were considered as quality indicators of the dried samples. The increase in air velocity and temperature, as well as the sample size, significantly reduced the antioxidant potential of the dried samples (p-value < 0.05). For a given sample size, the application of ultrasound, at the acoustic power levels tested, did not produce significant effects on the antioxidant indicators considered. Temperature measurements inside the drying sample showed a non-negligible temperature rise when acoustic power was applied.

Keywords

Atmospheric freeze-drying, ultrasound, antioxidant properties, phenolic compound, vitamin.

1. Introduction

Freeze-drying is a low temperature drying process widely used for the purposes of obtaining high quality products. The main difference with respect to hot air drying is that water is not removed by evaporation but by sublimation from a completely frozen product. Meryman (1959) showed that it is the difference in water vapor partial pressure between the interface of sublimation of the product and the surrounding environment, and not the absolute pressure, which is the driving force behind water sublimation. This means that it is possible to freeze-dry a product not only under vacuum conditions, as in the conventional vacuum freeze-drying process, but also at atmospheric pressure, as long as a gradient of water partial pressure is established and maintained. In this sense, Atmospheric Freeze-Drying (AFD) is the convective drying of a completely frozen product using a stream of dried cold air for both water removal and heat supply. This process can provide high quality products, as evidenced, among others, by Stawczyk, Li, Witriwa-Rojchert, & Fabisiak, (2007), who proved that apple cubes freeze-dried at atmospheric pressure exhibited a similar quality to those obtained by vacuum freeze-drying. As regards energy consumption, AFD can provide an energy saving of 35% (Wolff & Gibert, 1990) compared to vacuum freeze-drying. However, its main disadvantage is that the mass transfer inside the dried layer becomes rate controlling, and longer process times are required.

The main strategy for intensifying the AFD, saving time and energy without impairing product quality, is the enhancement of the heat and mass transfer rates. To achieve this goal, some additional energy should be supplied to the product. Power ultrasound proved to be an effective, non-toxic and environmentally friendly way to speed up not only the hot air-drying process (De la Fuente, Riera, Acosta, Blanco, & Gallego-Juarez, 2006; Do Nascimento, Mulet, Ramirez-Ascheri, De Carvalho, & Carcel, 2016; Puig, Perez-Munuera, Carcel, Hernando, Garcia-Perez, 2012) but also the AFD process (Garcia-Perez, Carcel, Rossello, Riera, & Mulet, 2012). The acoustic waves create a cycle of periodically repeated mechanical stresses of compression and expansion, which produce different effects depending on the nature of the system (Garcia-Perez, Carcel, Mulet, Riera, & Gallego-Juarez, 2015; Legay, Gondrexon, Le Person, Boldo, & Bontemps, 2011). In solid products, the series of compressions and expansions of the sample generate an effect similar to what happens to a sponge when quickly squeezed

and released (Liang, 1993). This helps water to flow out of the dried cake through both the natural channels and other micro-pathways created by the ultrasonic stresses (Awad, Moharram, Shaltout, Arker, & Youssef, 2010; Ricce, Rojas, Miano, Siche, & Augusto, 2016; Santacatalina, 2015). Ultrasound can also generate a micro-stirring at the solid-fluid interface that contributes to reducing the external mass transfer resistance. Furthermore, Gallego-Juarez, Rodrìguez-Corral, Gàlvez-Moraleda, & Yang (1999) claimed that the application of power ultrasound only exerts a mild heating effect, thus increasing interest in the ultrasound-assisted freeze-drying of thermally sensitive products (Pereira &Vincente, 2009). Finally, it has to be highlighted that samples remains frozen during the atmospheric freeze-drying process. This is a relevant issue as ultrasound is known to induce cavitation in liquids, and during cavitation, hydrogen and hydroxide radicals can be formed, which may lead to oxidation, thus affecting product characteristics. However, this is not a concern in the AFD process as the water is in frozen state when ultrasounds are applied.

When dealing with food drying, care must be taken with the effect of the drying process on food's physical (rehydration capacity, color, texture, etc) and nutritional (e.g. vitamins, proteins, etc.) properties. Natural antioxidants are particularly important, especially in fruit and vegetables, because of their proven ability to prevent the effects of oxidative stress. Disturbances in the organism redox equilibrium can lead to serious damage to tissues, proteins, enzymes and genetic material, such as DNA and RNA (Halliwell, 2007; Moneim, 2015). The antioxidant ability of food is related with vitamins or phenolic compounds (Boonprakob, Kriengsak, Crosby, Cisneros-Zevallos, & Byrne, 2006; Oroian & Escriche, 2015). Vitamins are particularly important because they play an important role in many important reactions and any vitamin shortage may result in serious diseases (Porter, 2012). Another group of molecules of relevant interest is that of the phenolic compounds, whose concentration is closely correlated with the antioxidant capacity of many fruits and vegetables (Hossain & Shah, 2011; Li et al., 2010). Morales-Soto et al. (2014) found that eggplants are one of the vegetables that exhibit the highest antioxidant capacity, although this is heavily dependent on the kind of cultivars and the harvesting season (García-Salas, Gomez-Caravaca, Morales-Soto, Segura-Carretero, & Fernández-Gutiérrez, 2014).

Ultrasound application during drying has been reported to affect some nutritional properties and the quality of the final product, both when drying at high temperatures

(Gamboa-Santos, Montilla, Soria, Cárcel, & Garcia-Perez, 2014) and also at low ones (Santacatalina et al., 2014). This effect appears to be closely related to the porosity of the solid, which determines how the waves propagate inside the product. Although the nutritional properties can be impaired by the acoustic power applied (Santacatalina, Contreras, Simal, Cárcel, & Garcia-Perez, 2016a), in particular for those samples having a less porous matrix, hardness, rehydration rate or whiteness can be improved when the drying rate is enhanced by ultrasound application (Santacatalina, Guerrero, Garcia-Perez, Mulet, & Cárcel, 2016b).

The sample size, namely the surface to volume ratio, may also have a great influence on the drying process: the drying time shortens enormously as the size is reduced, which encourages the processing of small-sized products, when feasible. Besides, the acoustic energy can speed up the drying rate (Colucci, Fissore, Mulet, & Carcel, 2017) with only mild effects on product quality (Santacatalina, Fissore, Cárcel, Mulet, & Garcia-Perez, 2015).

The aim of this study was to evaluate the effect of various operating variables, namely air temperature and velocity, ultrasound power and sample dimension on some antioxidant properties, (vitamin C content, total phenolic content and antioxidant capacity) of eggplant (*Solanum Melongena L.*) samples during the ultrasonically-assisted atmospheric freeze-drying process. The paper is thus organized as follows: firstly, details are given about the experimental approach to the drying, with the design of the experiments used for this purpose. Then, the experimental methods are presented, with the methodology used for the measurement of the antioxidant potential of the samples and the temperature profile during drying. Finally, the results of the experimental investigation and quality assessment analysis are presented and discussed.

2. Materials and methods

Eggplant (*Solanum Melongena*), freshly purchased in a local market (Valencia, Spain), was stored at 4±1°C for no more than two days before being dried. Cubic samples of two different sizes (8.8 and 17.6 mm side respectively) were obtained from the core of the vegetable (all the samples of one batch were obtained from the same vegetable) using a household tool.

Due to the high content of chlorogenic acid, eggplant is more prone to browning

and to enzymatic oxidation than other *Solonaceae* (Barbagallo, Chisari, & Patanè, 2012). In order to avoid any loss of antioxidant compounds not related with the drying process, a widely-used method is to treat the samples with a sodium metabisulfite solution. Therefore, all samples were treated with a 2% w/w ($Na_2S_2O_5$, Probus S.A., 97% purity) solution for five minutes (Akyildiz, Aksay, Benli, Kiroglu, & Fenercioglu, 2004).

The convective dryer has already been presented in literature (Garcia-Perez, Carcel, Rosselló, Riera, & Mulet (2012). It basically consists of a cylindrical drying chamber directly connected to the piezoelectric transducer, whose wall acts as the ultrasound radiator. Air flow is driven by a medium pressure fan, and air velocity is controlled acting over the fan speed. The process air is cooled down by a heat exchanger, using a glycol-water solution (45% v/v), and its temperature is controlled by an electric resistance. In order to keep the relative humidity as low as possible, the air flow is forced to pass through two trays full of water absorbent material, which is regenerated (at 250°C for 7 h) and replaced before each test. To determine the drying kinetics, samples were weighed at pre-set times using an industrial weighing module. For this purpose, the fan is stopped, and the samples are taken out of the drying cylinder before measuring in order to avoid any disturbance in the weight measurement.

2.1.Design of experiments

With the aim of evaluating the effects of the process variables on product quality, and identifying those which play a major role, a proper experimental design was used. The independent variables considered were: air velocity, air temperature and ultrasound (US) power applied. The ascorbic acid content (AA), total phenolic content (TPC), and the antioxidant capacity (AC) of the dried sample were chosen as the dependent variables.

The three factors, temperature (A), air velocity (B), and US power (C), were studied with a classical factorial 2^3 design (Montgomery, 2001). Every factor was tested at two levels, high (+) and low (-): temperature at -10 and -5°C, air velocity at 2 and 5 ms^{-1} and acoustic power at 0 and 50 W. This experimental design is graphically represented in Figure 1.

A second set of experiments was performed in order to examine the effect of temperature and ultrasound application in depth. In this case, a 3^2 factorial design (two parameters, studied at three different values) was used. A temperature value of -7.5°C and an acoustic power of 25 W were added to those previously tested. All the tests were

178 carried out on 8.8 mm side cubes.

179 In order to investigate the effects of the sample size, the experiments at -10 °C, 2
180 m s^{-1}, with and without ultrasound (0, 25 and 50 W), were also carried out using 17.6 mm
181 side cubes. It is worth clarifying that the values of acoustic power applied shown in this
182 paper are just the electric power applied to the ultrasonic transducer. Taking into account
183 the volume of the drying chamber ($2.4 \cdot 10^{-3}$ m^3), these values represent a density of energy
184 applied of 10.3 kW m^{-3} and 20.5 kW m^{-3}, for the power of 25 W and 50 W respectively.
185 The actual acoustic field produced by this kind of transducer was previously measured
186 and reported (Riera, García-Pérez, Acosta, Carcel, & Gallego-Juárez, 2011).

187 In this study, the same mass load was used for every test: 14±1 g, corresponding
188 to forty 8.8 mm cubes or five 17.6 mm cubes. The ultrasonic frequency was set at 21.9
189 kHz. Every drying condition was tested three times in order to ensure the statistical
190 significance of the results.

191 Additional tests were carried out for the purposes of studying the influence of
192 ultrasound application on the evolution of the sample temperature during drying. For this
193 purpose, small and large cubes were dried together at 0, 10.3 kW m^{-3} and 20.5 kW m^{-3}.
194 Five K-type thermocouples (TC1 to TC5) were fixed to the sample holder. For each
195 run, as shown in Figure 2, TC1 and TC2 were placed in the centre of one of the small-
196 sized cubes and of one of the large-sized ones, respectively, both at the same height in
197 the holder in order to ensure exactly the same drying conditions. At a different height,
198 two other thermocouples, namely TC3 and TC3, were placed in two other cubes (one of
199 each size). Some more cubes, of both sizes, were added to reach the mass load of 14±1 g.
200 TC5 was used to measure the temperature inside the drying chamber. Temperature
201 measurements were recorded every five minutes by a data logger placed outside the
202 drying chamber. The experiments were also carried out with the large-sized cubes, but
203 completely dry, just to record the increase in temperature due to the ultrasound
204 application. Every test was repeated to ensure the reproducibility of the results.
205
206 *2.2.Quality assessment procedure*
207 Ethanol (PanReac quimica S.A., 96% v/v) was used to extract the components of interest
208 from the dried samples (Santacatalina et al., 2016a). Extractions were carried out at room
209 temperature (20ºC) to prevent any thermal damage to the compounds considered. Lower
210 temperatures (with longer contact times) were also tested, but no evidence of substantial

improvement was observed in the extract. For the extraction, the dried samples were ground using a domestic blender. Then, 20 ml of ethanol were added, and the mixture was homogenized using an ultra-turrax (IKA T-25 ultra-homogenizer, 9500 rpm) for three minutes. Afterwards, the solution was put into a magnetic stirrer for twenty minutes. The solvent was finally filtered under a light vacuum. The flask was covered with aluminum foil, as protection from the light, and stored at 4±1°C until the quality parameters were measured.

2.2.1. Ascorbic Acid content (AA)

The amount of Vitamin C was determined by means of a test, using Folin-Ciocalteau reagent, derived from what was firstly proposed by Jagota & Dani (1982). The reactants used are the followings:

- Folin-Ciocalteu (Sigma-Aldrich, 2 M) reagent, diluted in distilled water (1:10 v/v);
- Trichloroacetic acid, at 7.5 % by volume.

The procedure for the analysis was the following: 1 ml of the sample extract and 1 ml of trichloroacetic acid were mixed in a tube and, after shaking, were left to rest for 5 minutes at 4±1°C. After that, the solution was filtered, and 0.2 ml were placed in a 4.5 ml spectrophotometer cuvette with 0.2 ml of Folin-Ciocalteau reagent and 2 ml of water. Finally, after 10 minutes rest in darkness at room temperature, the absorbance at 760 nm was read.

The amount of Vitamin C was quantified by means of a calibration curve, previously determined using known solutions of ascorbic acid and ethanol in the range of 1-15 mg_{AA} L^{-1}. The results are reported as milligrams of ascorbic acid (mg_{AA}) per 100 grams of dried matter, and as the percentage of degradation with respect to the concentration measured in the fresh product (c_o):

$$\%Degradation = \frac{c_0 - c_f}{c_0} \cdot 100 \quad (1)$$

2.2.2. Total Phenolic Content (TPC)

The total phenolic content was determined by means of the Folin-Ciocalteau method, as reported by Gao, Ohlander, Jeppson, Bjork, & Trajkovski (2000), with few modifications (Ahmad-Qasem, Barrajón-Catalan, Micol, Mulet, & García-Pérez, 2013). The reactants

used are the followings:

- Folin-Ciocalteu (Sigma-Aldrich, 2 M) reagent, diluted in distilled water (1:10 v/v);
- Sodium carbonate, at 20% v/v.

The procedure for the analysis was the following. The extract was diluted (2 ml of the solvent were added to 1 ml of the previously obtained extract). Then, 0.1 ml of the diluted extract was mixed in a 4.5 ml spectrophotometer cuvette, with 0.2 ml of Folin-Ciocalteau reagent and 2 ml of water. After 3 minutes rest in darkness at room temperature, 1 ml of sodium carbonate solution was added and, after 1 hour of incubation, again in the dark at room temperature, the absorbance at 765 nm was read.

The amount of phenols was quantified using a calibration curve previously obtained using a solution of gallic acid in ethanol in the range of 1-10 $mg_{GA}\ L^{-1}$. The resulting concentration of phenolic compounds is reported as milligrams of gallic acid (mg_{GA}) per 100 grams of dried matter and as the percentage of degradation with respect to the concentration measured in the fresh product (Equation 1).

2.2.3. Antioxidant Capacity (AC)

The Ferric Reducing Antioxidant Power (FRAP) assay was used to determine the antioxidant capacity of extracts (Benzie & Strain, 1996). The reactants used were the following:

- Hexahydrate ferric chloride (LabChem 99%);
- Glacial acetic acid (Panreac quimica S.A.);
- Sodium acetate (Panreac quimica S.A., 99%);
- 2,4,6-Tris(2-pyridyl)-s-triazine (TPTZ) (Sigma-Aldrich, 99%);
- HCl (Sigma-Aldrich, 37%).

The reactive is a mixture of three different reactants: an acetate buffer 0.3 M (pH 3.6), prepared dissolving 0.155 g of sodium acetate and 0.8 ml of acid in distilled water; a 20 mmol/L aqueous solution of ferric chloride (0.27165 g in 50 ml of distilled water) and a solution of 0.064 g of TPTZ in 20 ml of HCl 40 mM (obtained from the dilution of 37% HCl). These three reactants were prepared every day before the test and stored, protected from the light, at 4±1°C. In a 1.5 ml cuvette 30 µl of distilled water, 30 µl of sample and 900 µl of FRAP mixture were mixed and, after 30 minutes at 37°C, the absorbance at 595 nm was read.

The total antioxidant power was quantified using a calibration curve previously determined using a solution of Trolox in ethanol in the range of 20-70 $mg_T\,L^{-1}$. The results were reported as milligrams of Trolox (mg_T) per 100 grams of dried matter and as the percentage of degradation with respect to the concentration measured in the fresh product (Equation 1).

The significance of the difference between the AA, TPC and AC of the samples dried under the different conditions tested was evaluated by the analysis of variance (ANOVA) method. The Statgraphics™ software was used for this purpose, and two levels of confidence value were considered: p-value lower than 0.05 and p-value lower than 0.01.

3. Results and discussion

The ascorbic acid content, the total phenolic content and the antioxidant capacity of the fresh eggplant used in this study were the following: 48.6 mg_{AA} 100 g_{dm}^{-1}, 52.5 mg_{GA} 100 g_{dm}^{-1}, and 376.2 mg_{Trolox} 100 g_{dm}^{-1} respectively. The concentration of all these compounds was affected by the AFD process, and every drying condition tested produced a percentage of degradation higher than 20%, as discussed in the following sub-sections.

3.1.Influence of the drying temperature on the antioxidant potential

As a general trend, the increase in drying temperature produced an increase in the degradation of the antioxidant potential of eggplant samples. From Figure 3, it can be observed that the mean value of degradation of AA moves from 41.1% at -10ºC to 57.9% at -7.5ºC and, finally, to 68.8 % at -5ºC. In a similar way, the mean value of degradation of TPC increased from 48.9% at -10ºC to 60.3% at -7.5ºC and, finally, to 73.3% at -5ºC. A much more pronounced temperature influence was observed for the AC, whose mean degradation values were 20.6%, 49.9% and 68.3% at -10, -7.5 and -5ºC, respectively. Table 1 shows the results obtained from the ANOVA analysis of every drying experiment carried out with the 8.8 mm side eggplant cubes. As can be observed, the effect of air temperature was significant for the three independent variables, with a confidence level of 95 % in the case of the TPC and the AC, and of 99% for the AA.

These results differ from those reported by Santacatalina et al. (2014) during the low-temperature drying of apple. These authors found that, in the case of using drying

309 temperatures below 0 ºC, the degradation of antioxidant capacity was greater the lower
310 the temperature used. The residual enzyme activity present in the unfrozen rubbery-state
311 water fraction of frozen apple samples can produce enzymatic reactions (Blanda,
312 Cerretani, Cardinali, Bendini, & Lercker, 2008) during drying. Thus, the longer drying
313 time needed at lower temperatures increased the oxidant reactions (Ahmad-Qasem et al.,
314 2015). However, in the present paper, the pre-treatment of eggplant samples with sodium
315 metabisulfite solution can prevent these enzymatic reactions. Therefore, the degradation
316 of antioxidant properties can only be attributed to their own drying process and the
317 influence of the process variables. Thus, the drying was more aggressive with antioxidant
318 properties as higher the drying temperature.
319
320 *3.2.Influence of the air-drying velocity on the antioxidant potential*
321 The degradation of the antioxidant potential was slightly enhanced by an increase in air
322 velocity (Figure 4). Thus, in the case of drying processes carried out at -10ºC and without
323 ultrasound application, the mean value of AA degradation moved from 41.1% to 58.1%
324 when the air velocity increased from 2 to 5 m s^{-1}. For TPC, the degradation was 20.6%
325 and 58.1% for 2 and 5 m s^{-1}, respectively, and 48.9% and 59% in the case of AC. The
326 statistical analysis confirmed the significance ($p < 0.05$) of these differences in the case
327 of AC and AA degradation (Table 1). On the contrary, no significant differences were
328 found in the average TPC degradation between the two air velocities tested. The increase
329 in air velocity produces turbulences in the air-solid interphase that reduce the boundary
330 layer and, thus, may improve mass transport and, finally, the drying rate. This can
331 contribute to a better oxygen transfer from the drying air to the sample, increasing
332 oxidation reactions, which can affect both the AA and the AC (Moreno, Brines, Mulet,
333 Rosselló, & Cárcel, 2017). On the contrary, the natural variability of the raw matter may
334 be the reason for the non-significant effect of air velocity on the TPC.
335
336 *3.3.Influence of the ultrasonic power applied on the antioxidant potential*
337 Ultrasound application slightly influenced the degradation of the antioxidant properties
338 studied. As can be observed in Figure 5, a mild increase in the percentage of degradation
339 of the AA, TPC and AC of the samples dried at -10 °C and 2 m s^{-1} may be noticed when
340 ultrasound is applied, with no differences between the two ultrasonic power levels tested.
341 Thus, the average degradation of AA moved from 41.1% in the drying process carried

out without ultrasound to 58.7% and 53.2% in the experiments carried out at 25 and 50 W, respectively. For TPC, the degradation in samples dried without ultrasound application was 48.9%, while it was 66.2% at 25 W and 66.0% at 50 W. In the case of AC, the influence was more important, moving from 20.6% in the experiments without ultrasound to 59.2% and 52.7% at 25 W and 50 W respectively. Other authors found a similar effect of ultrasound application during low-temperature drying in the antioxidant properties of products (Moreno et al., 2017; Santacatalina et al. 2014; 2016a). In general, the effects produced by ultrasound on product structure could promote other oxidation reactions that affect the antioxidant potential of samples. However, the ANOVA analysis showed that these differences between eggplant samples dried with and without ultrasound were not significant (Table 1). The greater influence of ultrasound on drying rate (Colucci et al., 2017), which significantly contributes to the reduction in the contact time between the samples and the air, can make the extent of the oxidation reactions potentially enhanced by the ultrasound non-significant. This fact has also been observed during the drying of food products at moderate (20-40 ºC) temperatures (Frias, Peñas, Ullate, & Vidal-Valverde, 2010; Gamboa-Santos, Montilla, Soria, Cárcel, & Garcia-Perez, 2014). In any case, the results showed that it is possible to carry out the drying process at the highest ultrasonic power tested reducing the processing time by more than 80% (Colucci et al., 2017) and without significantly (p-value > 0.05) affecting the quality of the dried eggplant.

3.4.Influence of the sample size on the antioxidant potential

The size of the samples influenced the percentage of the antioxidant potential degradation of dried eggplant. Thus, the degradation of AA increased from 41.1% in the case of the 8.8 mm side cubes (Figure 5) to 71.5% in that of the 17.6 mm side cubes (Figure 6), both dried without ultrasound application. For TPC, the increase in sample size leads to the percentage of degradation rising from 48.9% to 71.6%, and from 20.6% to 66.7% in the case of AC. This can be jointly attributed to the high porosity of the eggplant and the different time needed to dry the samples, three times higher in the large-sized samples than in the smaller ones (Colucci et al., 2017). On the contrary, drying apples samples of different size and geometry, Moreno et al. (2017) found milder antioxidant properties degradation in the samples with lower external surface/mass ratio, which were larger samples. However, the porosity of apple is significantly lower than eggplant. This means

that the actual surface/mass ratio for eggplant, which is in contact with the oxygen present in the air, is higher than the external surface/mass ratio. Therefore, the longer exposure to the process air can increase the extent of the oxidation reactions, and, so, the percentage of degradation of AA, TPC and AC.

As regards the application of ultrasound, no significant effect was found on the three antioxidant properties studied in the 17.6 mm side cube samples, either at 25 W or at 50 W. In fact, the percentage of degradation was similar for both acoustic power levels, as shown in Figure 6, and not significantly different from non-ultrasonically assisted dried samples. However, as shown previously, the drying time was significantly shortened when the ultrasonic power level applied increased. Similar conclusions may be drawn when considering the 8.8 mm side cube samples, as shown in Figure 5.

The effect of the sample size on the results could indicate that the absorption of ultrasonic energy may be dependent on this variable. In fact, as Figure 7 shows, the 8.8 mm side eggplant cubes dried with the application of an ultrasonic power of 50 W exhibited a lower antioxidant potential degradation than the 17.6 mm side ones dried under the same conditions, even if the drying time was only slightly shorter (2.8 h vs 3.7 h, Colucci et al. 2017). This conclusion is supported by the statistical analysis presented in Table 2, pointing out that the effect of both independent factors, sample size and acoustic power, were significant (p-value < 0.05). An explanation for these results could be a greater ultrasonic absorption in the larger sample size. This can induce a rise in the temperature that leads to product thawing, causing drying to take place by evaporation instead of by sublimation.

3.5.Sample temperature evolution during drying

The effects of ultrasound are mainly mechanical. However, the vibration of product structure caused by ultrasound application can convert this mechanical energy into heat by friction. In fact, in the liquid media application of ultrasound, calorimetry is one of the most widely used methods to determine the acoustic energy applied (Carcel Benedito, Bon, & Mulet, 2007; Raso, Mañas, Pagán, & Sala, 1999). In convective drying processes, like AFD, the application of ultrasound can also produce an increase in the temperature of the material (Carcel, García-Pérez, J.V., Benedito, & Mulet, 2012). This temperature rise could then be a measurement of the acoustic energy absorbed by the solid being dried.

To check the effect of the ultrasound application on the AFD process on the sample temperature, an additional set of experiments was carried out. In this case, the evolution of the temperature inside the samples was measured over a whole drying process (air temperature of -8 ºC). Although the test was carried out twice, and four temperature profiles were obtained for every test, for the sake of simplicity, only the temperature profiles obtained by 3 thermocouples (TC1, TC2 and TC5) are reported in Figure 8. The sample temperature evolution during drying when no acoustic power was applied (Figure 8A) was as expected. At the beginning of the drying, the temperature of the samples was lower than that of the air as the ice sublimation is an endothermic process. When the product was completely dried, the temperature inside the product reached thermal equilibrium with the external air. The temperature inside the 17.6 mm side cube samples was a little bit higher than that of the 8.8 mm side cube samples, but always lower than that of the air.

When drying was carried out with US application, samples of both sizes showed a temperature higher than that of the air inside the drying chamber at every moment. The temperature of the smaller samples was always lower than that measured in the larger one, for both ultrasonic powers applied, 25 W (Figure 8B) and 50 W (Figure 8C). The temperature of the 8.8 mm side cube samples was below the melting point: so, these samples remained frozen during drying. Therefore, in this case, the product was dried following a proper freeze-drying process. On the contrary, the temperature in the 17.6 mm side cube samples reached values greater than 0°C and, therefore, the water elimination took place by evaporation and not by sublimation.

The varying increases in sample temperature in the samples of different sizes can indicate that the amount of acoustic energy absorbed was also different and related with the volume of the product. This could explain the more marked effect of ultrasound application on 17.6 mm side cubes: a greater rise in temperature will indicate a greater absorption of acoustic energy and so more intense ultrasonic effects. In fact, when drying was carried out without ultrasound, the drying time needed by 17.6 mm side cube samples (45 h) was almost three times that needed by 8.8 mm side cube samples (15.3 h) (Colucci et al., 2017). However, when the drying included the application of an ultrasonic power of 50 W, the drying time was similarly reduced for both sample sizes (3.7 h and 2.8 h for 17.6 and 8.8 mm side samples, respectively). On the other hand, the thermal energy provided by the conversion of acoustic energy into heat is partially dissipated by the

process air, which is cooling down the product. The lower surface-to-volume ratio can also help to explain the difference in the temperature profiles, the thermal source being volumetric and the effectiveness of the air cooling proportional to the sample surface. The relevant increase in the drying rate can hardly be explained simply by the relatively low increase in sample temperature, and the different magnitude of the ultrasonic effect on both sample sizes was probably due to a higher ultrasonic energy absorbance. The higher temperature and the greater ultrasonic energy absorption that, in some cases, may result in ice melting, can also explain the high degradation percentage obtained for every antioxidant capacity assay.

Finally, for the purposes of proving that these thermal effects are independent of vapor flow and ice sublimation, one additional test was carried out. In this case, the drying process with power ultrasound was extended to assure the complete drying of samples. Then, when samples were undoubtedly completely dried, the ultrasound was shut down for a certain time and then turned on again. The sample temperature evolution was recorded during the whole experiment. As is shown in Figure 9, when ultrasound was applied, the sample temperature increased until it reached a constant value. When ultrasound application was stopped, the sample temperature decreased to the temperature of the air. When the acoustic power was applied again, the temperature suddenly reached the value observed before ultrasound was shut down. This can indicate that the increase in the measured sample temperature is just due to ultrasonic vibration, disappearing when ultrasound is not applied. This must be clarified by testing the behaviour of other products.

4. Conclusions

Both the drying temperature and the air velocity can reduce the ascorbic acid content, the total phenolic content and the antioxidant capacity of atmospheric freeze-dried eggplant samples. On the contrary, the application of power ultrasound proved to be effective at shortening the drying time and, at the ultrasonic power level tested, did not significantly affect the eggplant antioxidant content. The antioxidant potential degradation was greater when processing larger samples.

The sample temperature rose when ultrasound was applied; this increase was more marked in the largest samples tested, where ultrasound shortened the drying time more

474 significantly. In the case of the large samples, it can lead to ice melting, and the presence
475 of liquid water can jeopardize the final product quality. The increase in temperature
476 indicates the different amount of acoustic energy absorbed by the sample and the
477 effectiveness of ultrasound application. More detailed investigation is required into the
478 physics of converting acoustic power into heat and the behaviour of different sample
479 textures

480 It can be concluded that power ultrasound is a promising technology for
481 accelerating the AFD process, but attention must be paid to the optimization of the
482 operating conditions in order to limit the thermal effects of acoustic energy and to ensure
483 the preservation of the nutritional properties of the samples. In this sense, ultrasonically-
484 assisted AFD also needs to be studied from both an economic point of view and also from
485 the perspective of energy consumption.

486

487 **Acknowledgements**

488

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644 **Figure 1.** Graphical representation of the 2^3 factorial design used to investigate the effect
645 of the main operating parameters of the process.

646

647 **Figure 2.** Diagram of the ultrasonically-assisted low temperature dryer: A, fan; B, Pt-
648 100; C, temperature and relative humidity sensor; D, anemometer; E, ultrasonic
649 transducer; F, vibrating cylinder; G, sample load device; H, retreating pipe; I,
650 slide actuator; J, weighing module; K, heat exchanger; L, heating elements; M,
651 desiccant tray chamber; N, computer; O, amplifier; P, resonance dynamic
652 controller (from Garcia-Pérez et al. 2012). Detail of the modified sample holder
653 used for temperature measurement: TC1 and TC3 are thermocouples attached
654 to 8.8 mm side cube samples, TC2 and TC4 are thermocouples attached to 17.6
655 mm side cube samples, TC5 thermocouple measured the air temperature inside
656 the drying chamber.

657

658 **Figure 3.** Effect of the different air temperature values on the percentage of degradation
659 of the antioxidant properties of eggplant (8.8 mm side cube samples) dried at
660 2 ms^{-1} and without ultrasound application. Average values and standard
661 deviation.
662 (▬: Ascorbic acid, ▭: Total phenolic content, ▭ Antioxidant capacity).

663

664 **Figure 4.** Effect of the air velocity on the percentage of degradation of the antioxidant
665 properties of eggplant dried at -10 °C without ultrasound application. Average
666 values and standard deviation.
667 (▬ : Ascorbic acid, ▭: Total phenolic content, ▭: Antioxidant capacity).

668

669 **Figure 5.** Effect of different US power applied on the degradation of the antioxidant
670 properties of eggplant (8.8 mm side cube samples) dried at -10 °C and 2 ms^{-1}.
671 Average values and standard deviation.
672 (▬ : Ascorbic acid, ▭: Total phenolic content, ▭: Antioxidant capacity).

673

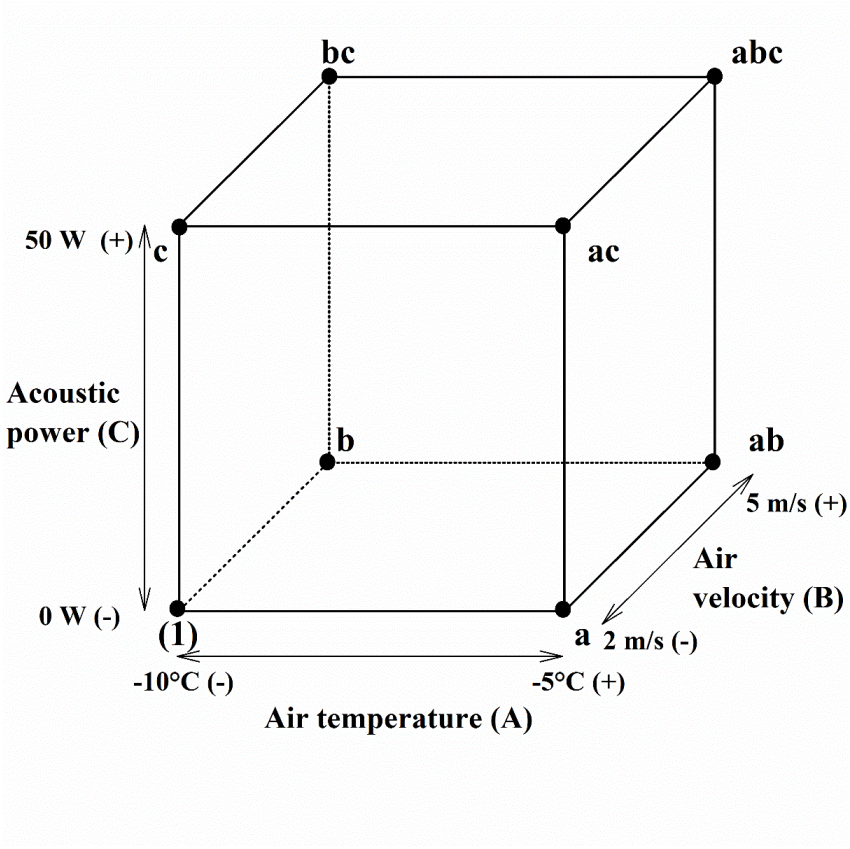
674 **Figure 6.** Effect of different US power applied on the degradation of the antioxidant

properties of eggplant (17.6 mm side cube samples) dried at -10 °C and 2 ms^{-1}. Average values and standard deviation.
(■: Ascorbic acid, □: Total phenolic content, ▭: Antioxidant capacity).

Figure 7. Effect of ultrasound power (cases A and C: no US, cases B and D: 50 W) and sample geometry (cases A and B: 8.8 mm and cases C and D: 17.6 mm) on the degradation of the antioxidant properties.
(■: Ascorbic acid, □ : Total phenolic content, ▭ Antioxidant capacity).

Figure 8. Product temperature measured in the eggplant sample of various sizes (▲: 8.8 mm, ●: 17.6 mm, solid line: chamber temperature) during a drying test at different acoustic powers applied (case A: 0 W, case B: 25 W, case C: 50 W).

Figure 9. Final assessment of power ultrasound thermal effects. Temperature measurement (▲: 8.8 mm side cube sample, ●: 17.6 mm side cube sample, solid line: chamber temperature) during a drying test at different acoustic powers applied (case A: 25 W, case B: 50 W).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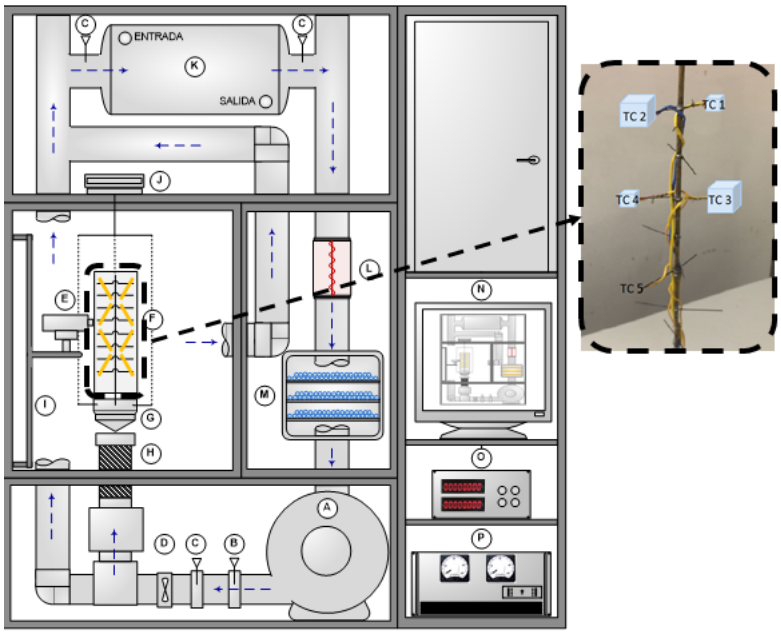

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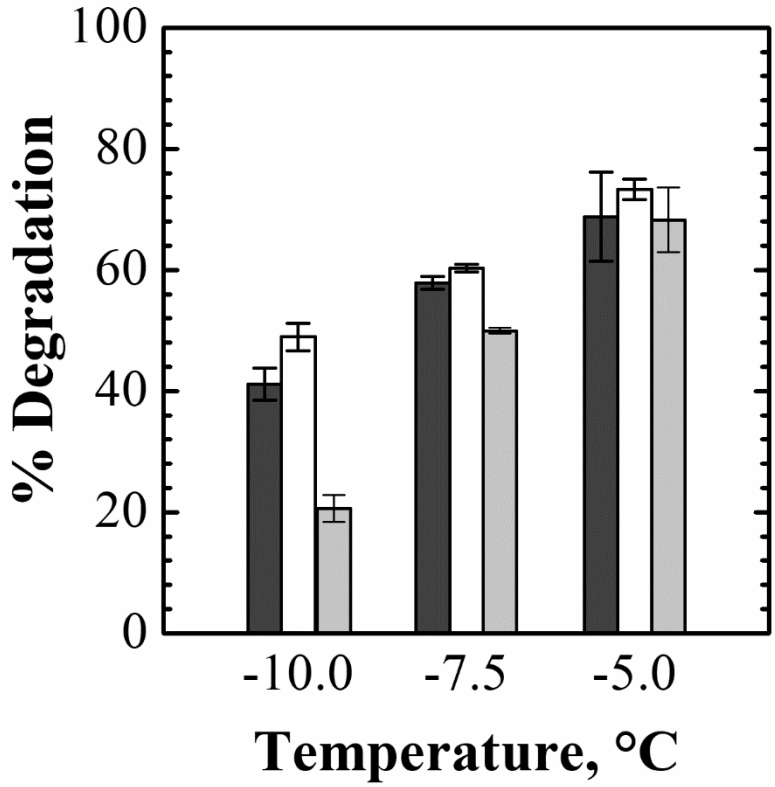

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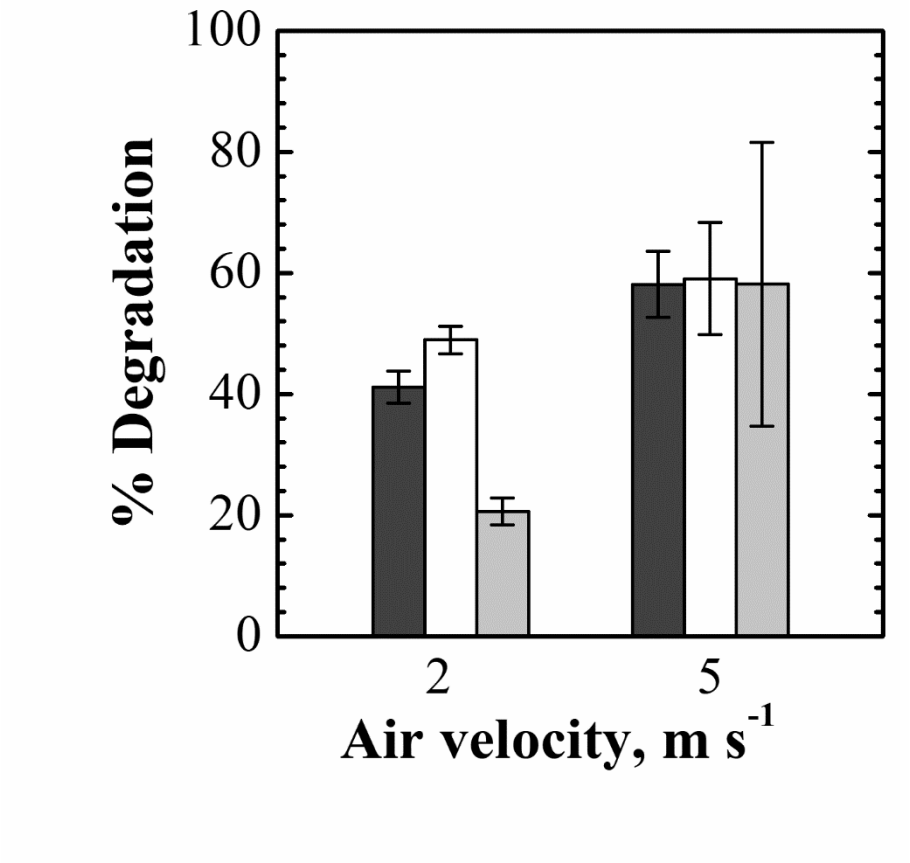

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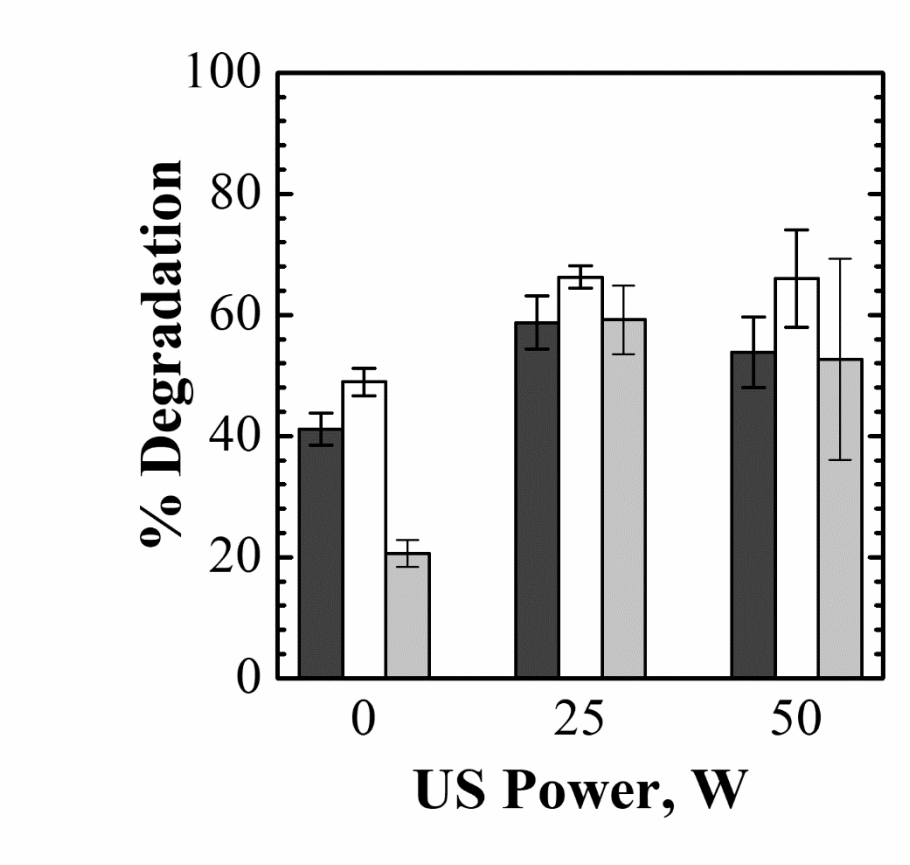

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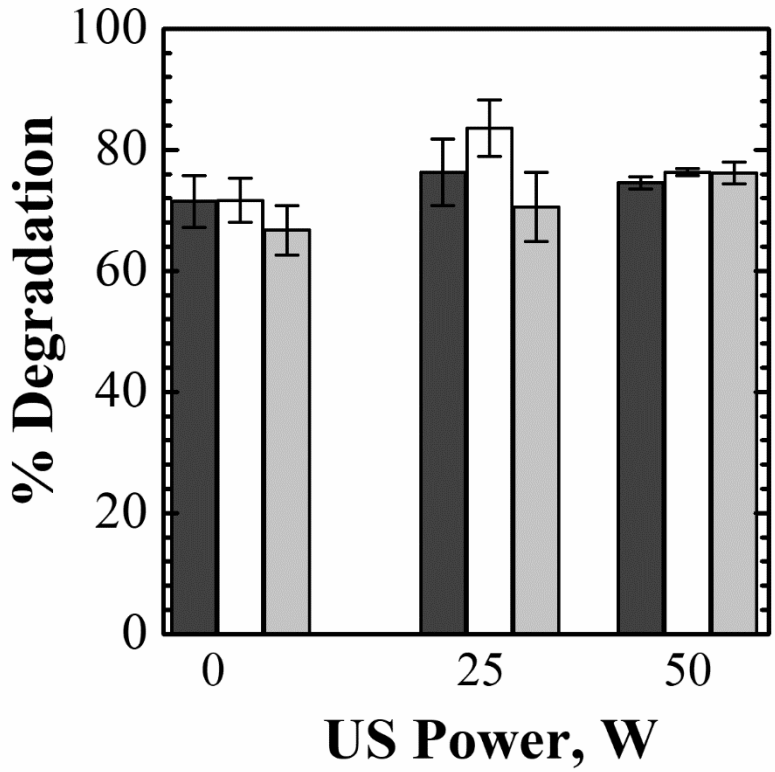

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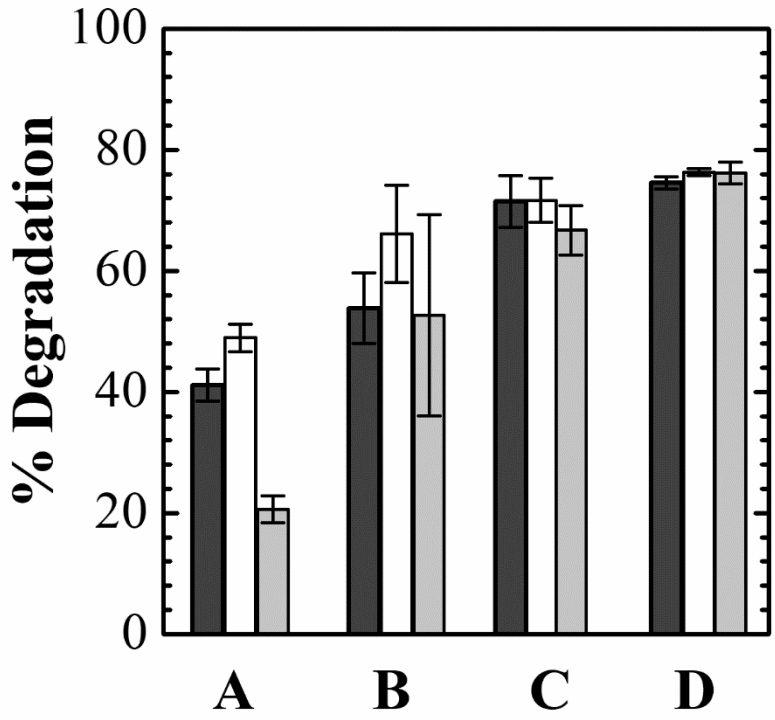

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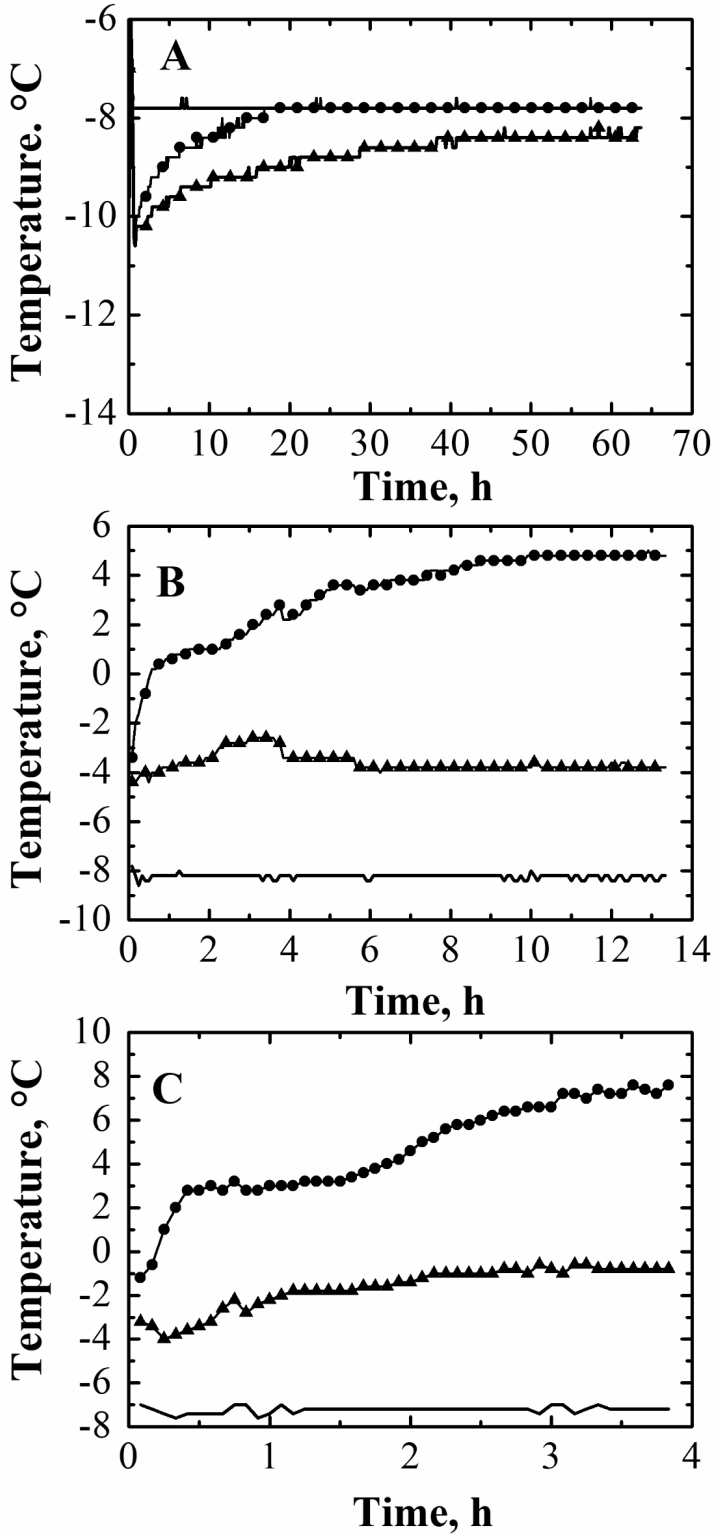
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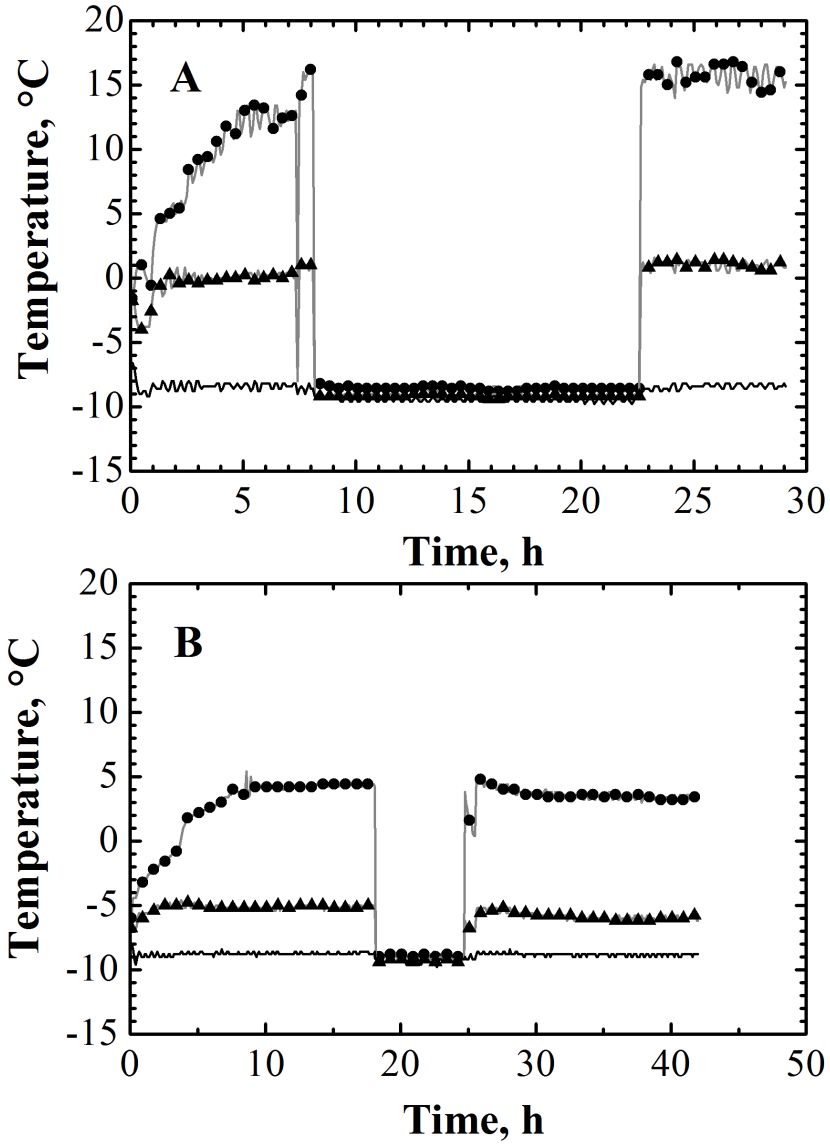

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721 *Table 1*

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Factor	AA		TPC		AC	
	p-value	Confidence Level	p-value	Confidence Level	p-value	Confidence Level
Temperature	0.01	99 %	0.05	95 %	0.05	95 %
Air velocity	0.05	95 %	0.72	NS	0.03	95 %
Ultrasound power	0.45	NS	0.30	NS	0.07	NS

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728 *Table 2*

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Factor	AA		TPC		AC	
	p-value	Confidence Level	p-value	Confidence Level	p-value	Confidence Level
Ultrasound power	0.02	95 %	0.03	95 %	0.01	99 %
Size	0.00	99 %	0.00	99 %	0.00	99 %
Second order size / US power	0.09	NS	0.15	NS	0.24	NS

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