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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<sup>-1</sup>) 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-Ciocalteu 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, Rodríguez-Corral, Gálvez-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 remain 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  $4\pm 1^\circ\text{C}$  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 ( $\text{Na}_2\text{S}_2\text{O}_5$ , 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  $\text{ms}^{-1}$  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

carried out on 8.8 mm side cubes.

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

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

Additional tests were carried out for the purposes of studying the influence of ultrasound application on the evolution of the sample temperature during drying. For this purpose, small and large cubes were dried together at 0,  $10.3\text{ kW m}^{-3}$  and  $20.5\text{ kW m}^{-3}$ . Five K-type thermocouples (TC1 to TC5) were fixed to the sample holder. For each run, as shown in Figure 2, TC1 and TC2 were placed in the centre of one of the small-sized cubes and of one of the large-sized ones, respectively, both at the same height in the holder in order to ensure exactly the same drying conditions. At a different height, two other thermocouples, namely TC3 and TC3, were placed in two other cubes (one of each size). Some more cubes, of both sizes, were added to reach the mass load of  $14 \pm 1\text{ g}$ . TC5 was used to measure the temperature inside the drying chamber. Temperature measurements were recorded every five minutes by a data logger placed outside the drying chamber. The experiments were also carried out with the large-sized cubes, but completely dry, just to record the increase in temperature due to the ultrasound application. Every test was repeated to ensure the reproducibility of the results.

## *2.2. Quality assessment procedure*

Ethanol (PanReac química S.A., 96% v/v) was used to extract the components of interest from the dried samples (Santacatalina et al., 2016a). Extractions were carried out at room temperature ( $20^{\circ}\text{C}$ ) to prevent any thermal damage to the compounds considered. Lower 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  $4\pm 1^\circ\text{C}$  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-Ciocalteu 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  $4\pm 1^\circ\text{C}$ . 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-Ciocalteu 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  $1\text{-}15\text{ mg}_{\text{AA}}\text{ L}^{-1}$ . The results are reported as milligrams of ascorbic acid ( $\text{mg}_{\text{AA}}$ ) per 100 grams of dried matter, and as the percentage of degradation with respect to the concentration measured in the fresh product ( $c_0$ ):

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

### 2.2.2. Total Phenolic Content (TPC)

The total phenolic content was determined by means of the Folin-Ciocalteu method, as reported by Gao, Ohlander, Jeppson, Bjork, & Trajkovski (2000), with few modifications (Ahmad-Qasem, Barrajon-Catalan, Micol, Mulet, & Garcia-Perez, 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-Ciocalteu 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<sub>GA</sub> L<sup>-1</sup>. The resulting concentration of phenolic compounds is reported as milligrams of gallic acid (mg<sub>GA</sub>) 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<sub>T</sub>L<sup>-1</sup>. The results were reported as milligrams of Trolox (mg<sub>T</sub>) 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<sup>TM</sup> 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<sub>AA</sub> 100 g<sub>dm</sub><sup>-1</sup>, 52.5 mg<sub>GA</sub> 100 g<sub>dm</sub><sup>-1</sup>, and 376.2 mg<sub>Trolox</sub> 100 g<sub>dm</sub><sup>-1</sup> 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 -10°C to 57.9% at -7.5°C and, finally, to 68.8 % at -5°C. In a similar way, the mean value of degradation of TPC increased from 48.9% at -10°C to 60.3% at -7.5°C and, finally, to 73.3% at -5°C. 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 -5°C, 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

temperatures below 0 °C, the degradation of antioxidant capacity was greater the lower the temperature used. The residual enzyme activity present in the unfrozen rubbery-state water fraction of frozen apple samples can produce enzymatic reactions (Blanda, Cerretani, Cardinali, Bendini, & Lercker, 2008) during drying. Thus, the longer drying time needed at lower temperatures increased the oxidant reactions (Ahmad-Qasem et al., 2015). However, in the present paper, the pre-treatment of eggplant samples with sodium metabisulfite solution can prevent these enzymatic reactions. Therefore, the degradation of antioxidant properties can only be attributed to their own drying process and the influence of the process variables. Thus, the drying was more aggressive with antioxidant properties as higher the drying temperature.

### *3.2. Influence of the air-drying velocity on the antioxidant potential*

The degradation of the antioxidant potential was slightly enhanced by an increase in air velocity (Figure 4). Thus, in the case of drying processes carried out at -10°C and without ultrasound application, the mean value of AA degradation moved from 41.1% to 58.1% when the air velocity increased from 2 to 5 m s<sup>-1</sup>. For TPC, the degradation was 20.6% and 58.1% for 2 and 5 m s<sup>-1</sup>, respectively, and 48.9% and 59% in the case of AC. The statistical analysis confirmed the significance ( $p < 0.05$ ) of these differences in the case of AC and AA degradation (Table 1). On the contrary, no significant differences were found in the average TPC degradation between the two air velocities tested. The increase in air velocity produces turbulences in the air-solid interphase that reduce the boundary layer and, thus, may improve mass transport and, finally, the drying rate. This can contribute to a better oxygen transfer from the drying air to the sample, increasing oxidation reactions, which can affect both the AA and the AC (Moreno, Brines, Mulet, Rosselló, & Cárcel, 2017). On the contrary, the natural variability of the raw matter may be the reason for the non-significant effect of air velocity on the TPC.

### *3.3. Influence of the ultrasonic power applied on the antioxidant potential*

Ultrasound application slightly influenced the degradation of the antioxidant properties studied. As can be observed in Figure 5, a mild increase in the percentage of degradation of the AA, TPC and AC of the samples dried at -10 °C and 2 m s<sup>-1</sup> may be noticed when ultrasound is applied, with no differences between the two ultrasonic power levels tested. 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 °C) 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  $-8\text{ }^{\circ}\text{C}$ ). 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  $0^{\circ}\text{C}$  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

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

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

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## List of references

- Ahmad-Qasem, M. H., Barrajon-Catalan, E., Micol, V., Mulet, A. & Garcia-Perez, J.V. (2013). Influence of freezing and dehydration of olive leaves (var. Serrana) on extract composition and antioxidant potential. *Food Research International*, 50, 189-196.
- Ahmad-Qasem, M. H., Santacatalina, J. V., Barrajon-Catalan, E., Micol, V., Carcel, J. A., & Garcia-Perez, J. V. (2015). Influence of drying on the retention of olive leaf polyphenols infused into dried apple. *Food and Bioprocess Technology*, 8, 120-133.
- Akyildiz, A., Aksay, S., Benli, H., Kiroglu, F. & Fenercioglu, H. (2004). Determination of changes in some characteristics of persimmon during dehydration at different temperature. *Journal of Food Engineering*, 65, 95-99.
- Awad, T. S., Moharram, H. A., Shaltout, O. E., Arker, D., & Youssef, M. M. (2012). Applications of ultrasound in analysis, processing and quality control of food: A review. *Food Research International*, 48, 410-427.
- Barbagallo, R. N., Chisari, M. & Patanè, C. (2012). Use *in vivo* of natural anti-browning agents against polyphenol oxidase activity in minimally processed eggplants. *Chemical Engineering Transactions*, 27, 49-54.
- Benzie, I. F. F. & Strain, J. J. (1996). The ferric reducing ability of plasma (FRAP) as a measure of "antioxidant power": the FRAP assay. *Analytical Biochemistry*, 239, 70-76.
- Blanda, G., Cerretani, L., Cardinali, A., Bendini, A., & Lercker, G. (2008). Effect of frozen storage on the phenolic content of vacuum impregnated Granny Smith and Stark Delicious apple cvv. *European Food Research and Technology*, 227, 961-964.
- Boonprakob, U., Kriengsak, T., Crosby, K., Cisneros-Zevallos, L., & Byrne, D. H. (2006). Comparison of ABTS, DPPH, FRAP and ORAC assays for estimating antioxidant activity from guava fruit extracts. *Journal of Food Composition and Analysis*, 19, 669-675.
- Carcel, J.A., Benedito, J., Bon, J. & Mulet, A. (2007). High intensity ultrasound effects on meat brining. *Meat Science*, 76, 611-619.
- Carcel, J.A., Garcia-Perez, J.V., Benedito, J. & Mulet, A. (2012). Food process

innovation through new technology: Use of ultrasound. *Journal of Food Engineering*, 110, 200-207.

- Colucci, D., Fissore, D., Mulet, A. & Carcel, J.A. (2017). On the investigation into the kinetics of the ultrasound assisted atmospheric freeze drying of eggplant. *Drying Technology*, 35, 1818-1831.
- De la Fuente, S., Riera, E., Acosta, V., Blanco, A., & Gallego-Juarez J. A. (2006). Food drying process by power ultrasound. *Ultrasonics*, 44, e523-e527.
- Do Nascimento, E. M. G. C., Mulet, A., Ramirez-Ascheri, J. L., De Carvalho, C. W. P., & Carcel, J. A. (2016). Effects of high-intensity ultrasound on drying kinetics and antioxidant properties of passion fruit peel. *Journal of Food Engineering*, 170, 108-118.
- Frias, J., Peñas, E., Ullate, M., & Vidal-Valverde. C. (2010) Influence of drying by convective air dryer or power ultrasound on the vitamin C and  $\beta$ -carotene content of carrots. *Journal of the Agriculture and Food Chemistry*, 58, 10539-10544.
- Gallego-Juarez, J. A., Rodriguez-Corral, G., Galvez-Moraleda, J. C. & Yang, T. (1999). A new high-intensity ultrasonic technology for food dehydration. *Drying Technology*, 17, 597-608.
- Gamboa-Santos, J., Montilla, A., Soria, A., Cárcel, J. A., & Garcia-Perez, J. V. (2014) Impact of power ultrasound on chemical and physicochemical quality indicators of strawberries dried by convection. *Food Chemistry*, 161, 40-46.
- Gao, X., Ohlander, M., Jeppson, N., Bjork, L. & Trajkovski, V. (2000). Changes in antioxidant effects and their relationship to phytonutrients in fruits of sea buckthorn (*Hippophae Rhamnoides L.*) during maturation. *Journal of Agricultural and Food Chemistry*. 48, 1485-1490.
- Garcia-Perez, J. V., Carcel, J. A., Rossello, C., Riera, E. & Mulet, A. (2012). Intensification of low-temperature drying by using ultrasound. *Drying Technology*, 30, 1199–1208.
- Garcia-Perez, J. V., Carcel, J. A., Mulet, A., Riera, E. & Gallego-Juarez, J. (2015). Power ultrasonics: Application of high-intensity ultrasounds. In: Gallego-Juarez, J. A., Graff, K.F. (eds.), *Ultrasonic Drying for Food Preservation* (pp. 875-910). Cambridge: Elsevier.

- García-Salas, P., Gomez-Caravaca, A. M., Morales-Soto, A., Segura-Carretero, A. & Fernández-Gutiérrez, A. (2014). Identification and quantification of phenolic compounds in diverse cultivars of eggplant grown in different seasons by high-performance liquid chromatography coupled to diode array detector and electrospray-quadrupole-time of flight-mass spectrometry. *Food Research International*, 57, 114-122.
- Halliwell, B. (2007). Oxidative stress and cancer: have we moved forward? *Biochemical Journal*, 401, 1-11.
- Hossain, M. A. & Shah, M. D. (2011). A study on the total phenols content and antioxidant activity of essential oil and different solvent extracts of endemic plant *Merremia borneensis*. *Arabian Journal of Chemistry*, 8, 66-71.
- Jagota, S. K. & Dani, H. M. (1982). A new colorimetric technique for the estimation of vitamin C using Folin phenol reagent. *Analytical Biochemistry*, 127, 178-182.
- Legay, M., Gondrexon, N., Le Person, S., Boldo, P. & Bontemps, A. (2011). Enhancement of heat transfer by ultrasound: review and recent advantages. *International Journal of Chemical Engineering*, Article ID 670108, 17 pages.
- Li, F., Bo-Tao, X., Xiang-Rong, X., Xin-Sheng, Q., Ren-You, G. & Hua-Bin, L. (2010). Antioxidant capacities and total phenolic contents of 56 wild fruits from south China. *Molecules*, 15, 8602-8617.
- Liang, H. (1993). Modelling of Ultrasound Assisted and Osmotically Induced Diffusion in Plant Tissue. PhD Thesis, Purdue University.
- Meryman, H. T., 1959. Sublimation: Freeze drying without vacuum. *Science*. 130, 628-629.
- Moneim, A. E. A. (2015). Oxidant/Antioxidant imbalance and the risk of Alzheimer's disease. *Current Alzheimer Research*, 12, 335-349.
- Montgomery, D. C. (2001). Design and Analysis of Experiments. (5th ed). New York: John Wiley and Sons.
- Morales-Soto, A., García-Salas, P., Rodríguez-Pérez, C., Jiménez-Sánchez, C., Cádiz-Gurrea, M., Segura-Carretero, A. & Fernández-Gutiérrez, A. (2014). Antioxidant capacity of 44 cultivars of fruit and vegetables grown in Andalusia (Spain). *Food Research International*, 58, 35-46.
- Moreno, C., Brines, C., Mulet, A., Rosselló, C., & Cárcel, J. A. (2017). Antioxidant potential of atmospheric freeze-dried apples as affected by ultrasound application

- and sample surface. *Drying Technology*, 35, 957-968.
- Oroian, M. & Escriche, I. (2015). Antioxidants: Characterization, natural sources, extraction and analysis. *Food Research International*, 74, 10-36.
- Pereira, R.N. & Vicente, A. A. (2009). Environmental impact of novel thermal and non-thermal technologies in food processing. *Food Research International*, 43, 1936-1943.
- Porter, Y. (2012). Antioxidant properties of green broccoli and purple-sprouting broccoli under different cooking conditions. *Bioscience Horizons*, 5, 1-11.
- Puig, A., Pérez-Munuera, I., Cárcel, J. A., Hernando, I., & García-Pérez, J. V. (2012). Moisture loss kinetics and microstructural changes in eggplant (*Solanum melongena* L.) during conventional and ultrasonically assisted convective drying. *Food and Bioprocess Processing*, 90, 624-632.
- Raso, J., Mañas, P., Pagán, R. & Sala, F. J. (1999). Influence of different factors on the output power transferred into medium by ultrasound. *Ultrasonics Sonochemistry*, 5, 157-162.
- Ricce, C., Rojas, M. L., Miano, A. C., Siche, R. & Augusto, P. E. D. (2016). Ultrasound pre-treatment enhances the carrot drying and rehydration. *Food Research International*, 89, 701-708.
- Riera, E., García-Pérez, J. V., Acosta, V. M., Carcel, J. A., & Gallego-Juárez, J. A. (2011). A computational study of ultrasound-assisted drying of food materials. In K. Knoerzer, P. Juliano, P. Roupas, & C. Versteeg (Eds.), *Multiphysics Simulation of Emerging Food Processing Technologies* (pp. 265-302). John Wiley and Sons, Ltd.
- Santacatalina, J. V. (2015). Contribucion al estudio de la aplicacion de ultrasonidos de alta intensidad en procesos de secado a baja temperatura. Ph.D. Thesis, Univesitat Politecnica de Valencia.
- Santacatalina, J. V., Rodriguez, O., Simal, S., Cárcel J. A., Mulet A. & Garcia-Perez, J. V. (2014). Ultrasonically enhanced low-temperature drying of apple: Influence on drying kinetics and antioxidant potential. *Journal of Food Engineering*, 138, 35-44.
- Santacatalina, J. V., Fissore, D., Cárcel, J. A., Mulet, A. & Garcia-Perez, J. V. (2015). Model-based investigation into atmospheric freeze drying assisted by power ultrasound. *Journal of Food Engineering*, 151, 7-15.
- Santacatalina, J. V., Contreras, M., Simal, S., Cárcel, J. A. & Garcia-Perez, J. V. (2016a). Impact of applied ultrasonic power on the low temperature drying of apple.

*Ultrasonics Sonochemistry*, 28, 100-109.

Santacatalina, J. V., Guerrero, M. E., Garcia-Perez, J. V., Mulet, A. & Cárcel, J.A., (2016b). Ultrasonically assisted Low-temperature drying of desalted codfish. *LWT - Food Science Technology*, 65, 444-450.

Stawczyk, J., Li, S., Witriwa-Rojchert, D. & Fabisiak, A. (2007). Kinetics of atmospheric freeze-drying of apple. *Transport in Porous Media*, 66, 159-172.

Wolff, E. & Gibert, H. (1990). Atmospheric freeze drying, Part 1: Design, experimental investigation and energy saving advantages. *Drying Technology*, 8, 385-404.

## List of Tables

**Table 1.** P-value and level of significance for Ascorbic Acid, Total Phenolic Content and Antioxidant Capacity for all the tests carried out on 8.8 mm side cube.

**Table 2.** P-value and level of significance for Ascorbic Acid, Total Phenolic Content and Antioxidant Capacity for the tests carried out on the sample processed at an air temperature of  $-10\text{ }^{\circ}\text{C}$ , an air velocity of  $2\text{ m s}^{-1}$  and both sample sizes (8.8 and 17.6 mm).

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

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

**Figure 3.** Effect of the different air temperature values on the percentage of degradation of the antioxidant properties of eggplant (8.8 mm side cube samples) dried at  $2 \text{ ms}^{-1}$  and without ultrasound application. Average values and standard deviation.

(■: Ascorbic acid, □: Total phenolic content, ▣: Antioxidant capacity).

**Figure 4.** Effect of the air velocity on the percentage of degradation of the antioxidant properties of eggplant dried at  $-10 \text{ °C}$  without ultrasound application. Average values and standard deviation.

(■: Ascorbic acid, □: Total phenolic content, ▣: Antioxidant capacity).

**Figure 5.** Effect of different US power applied on the degradation of the antioxidant properties of eggplant (8.8 mm side cube samples) dried at  $-10 \text{ °C}$  and  $2 \text{ ms}^{-1}$ . Average values and standard deviation.

(■: Ascorbic acid, □: Total phenolic content, ▣: Antioxidant capacity).

**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<sup>-1</sup>. 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).

*Table 1*

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

Table 2

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

Figure 1

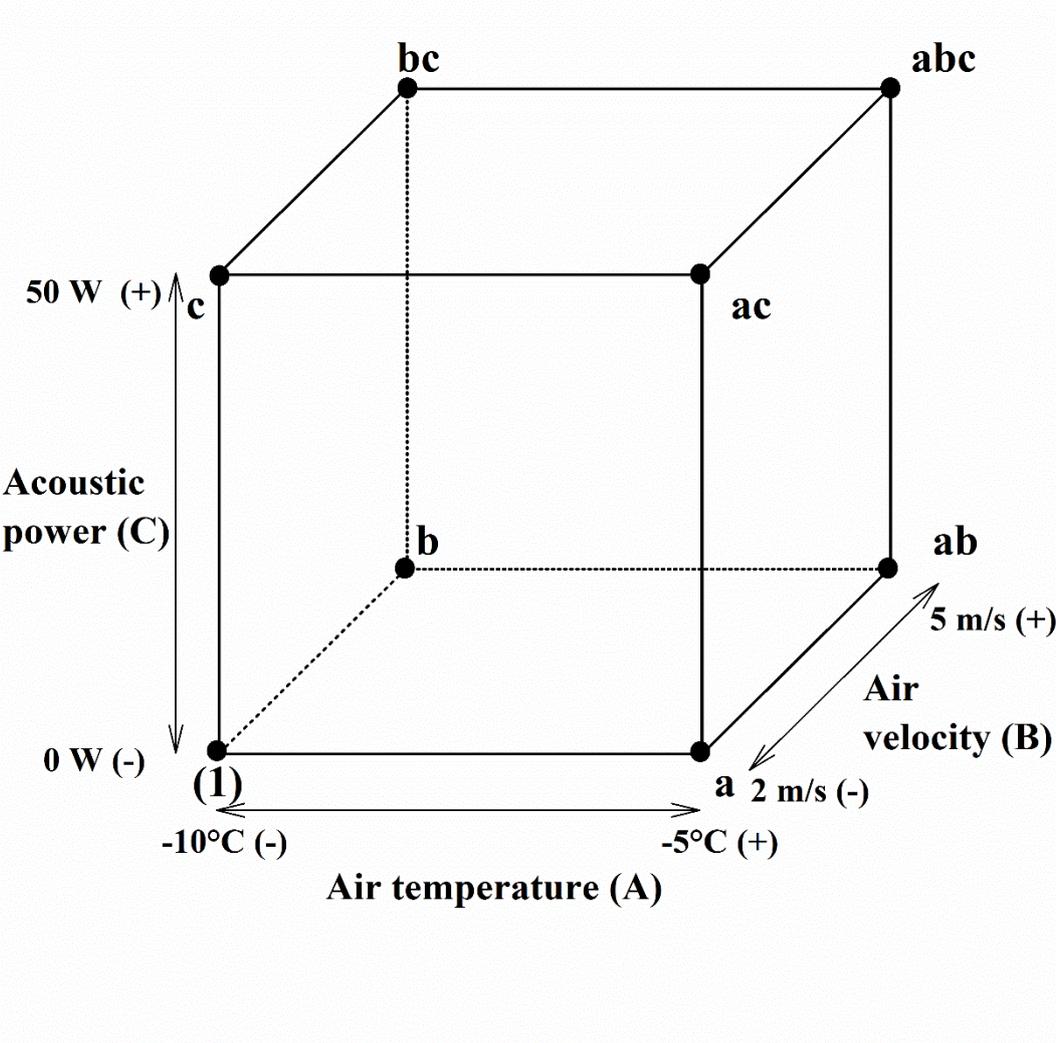


Figure 2

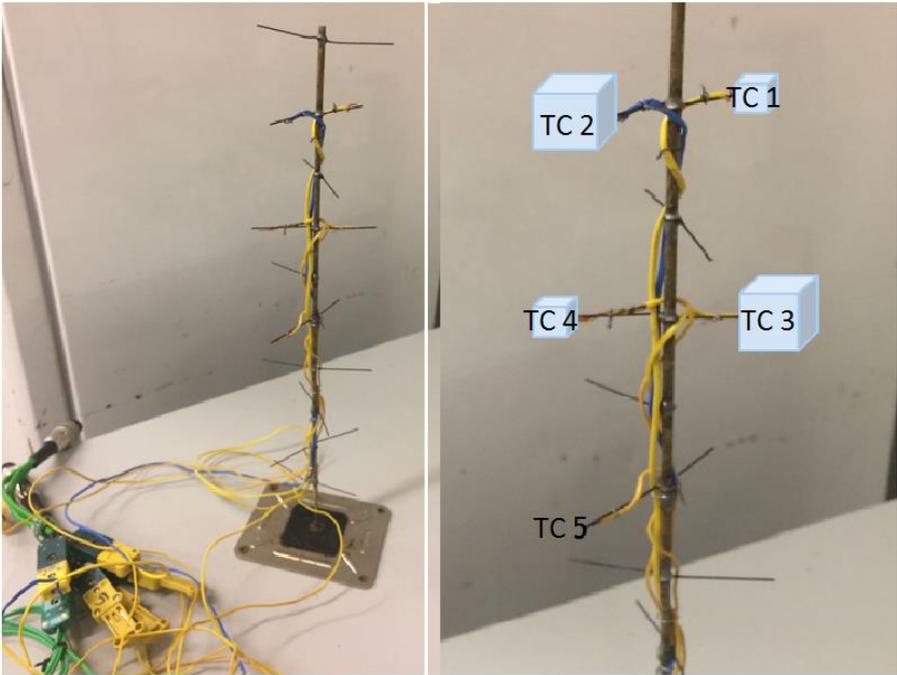


Figure 3

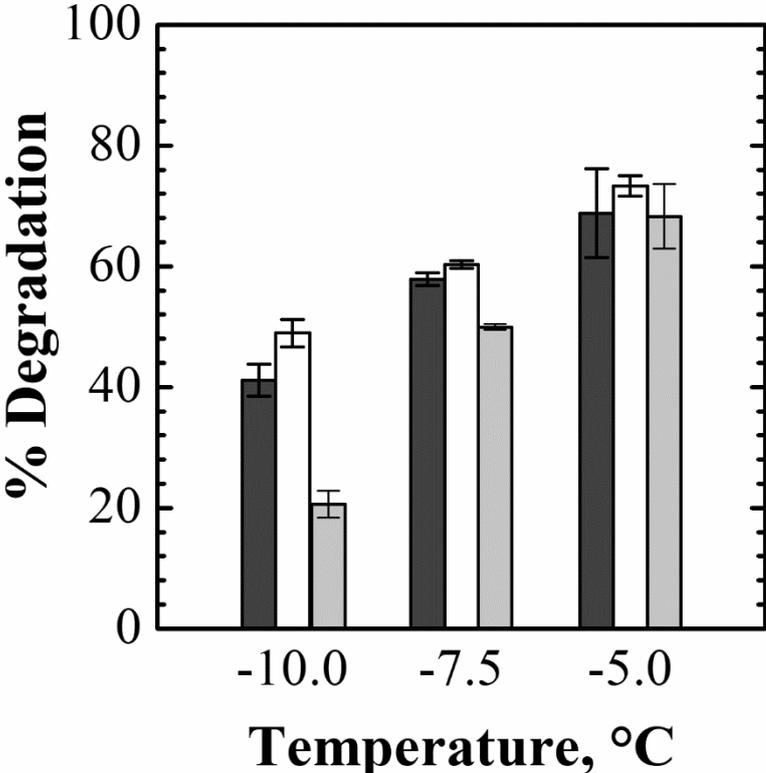


Figure 4

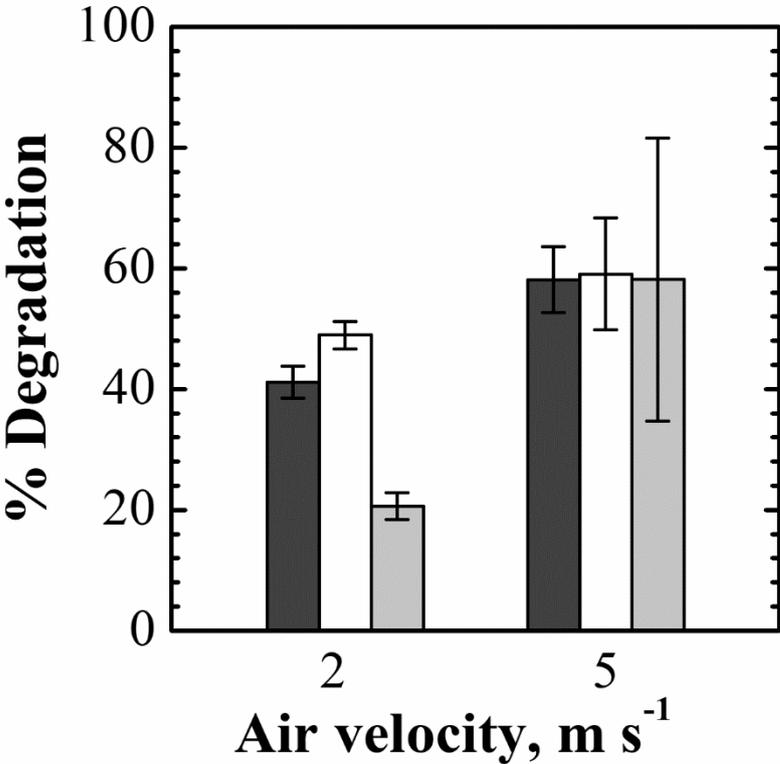


Figure 5

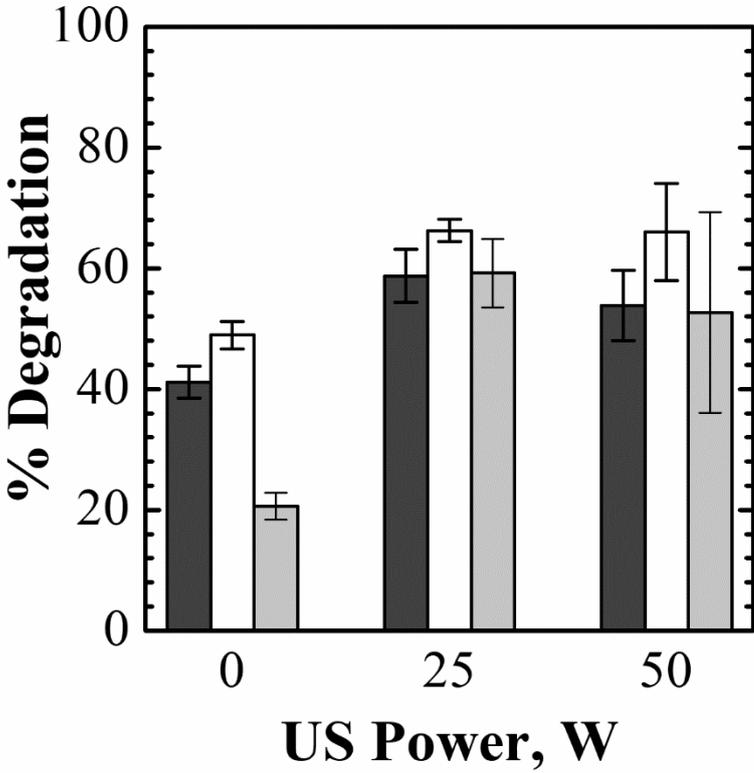


Figure 6

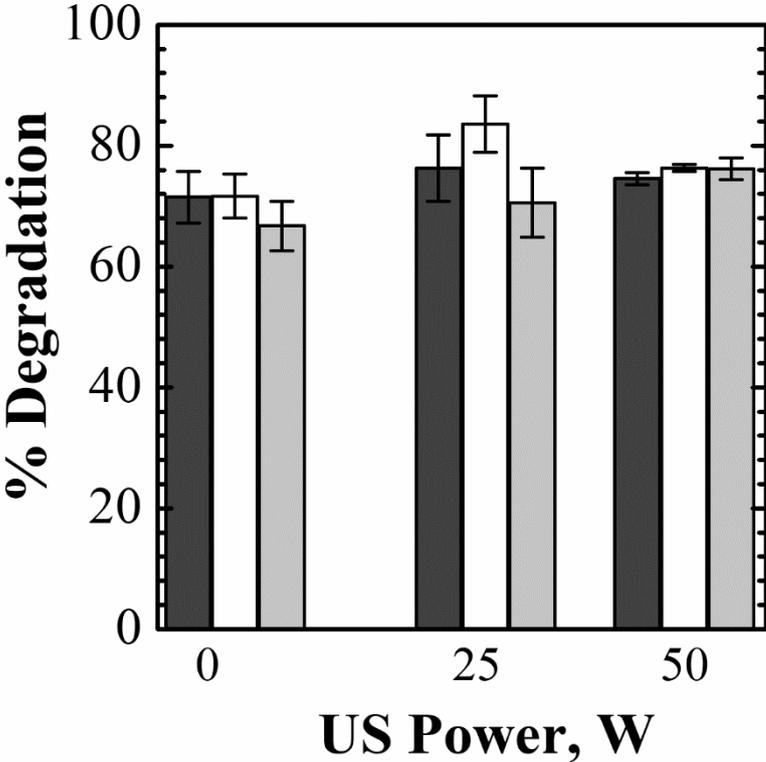


Figure 7

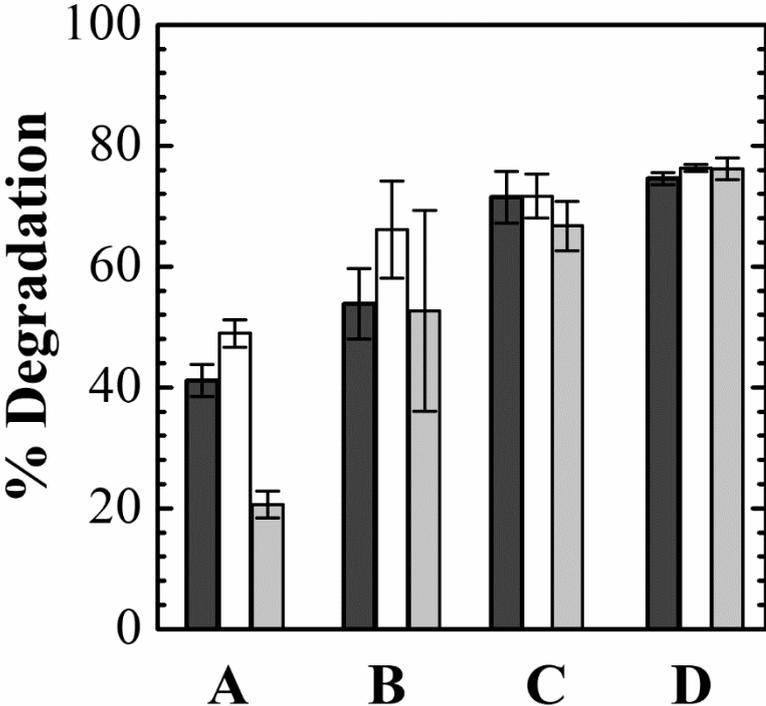


Figure 8

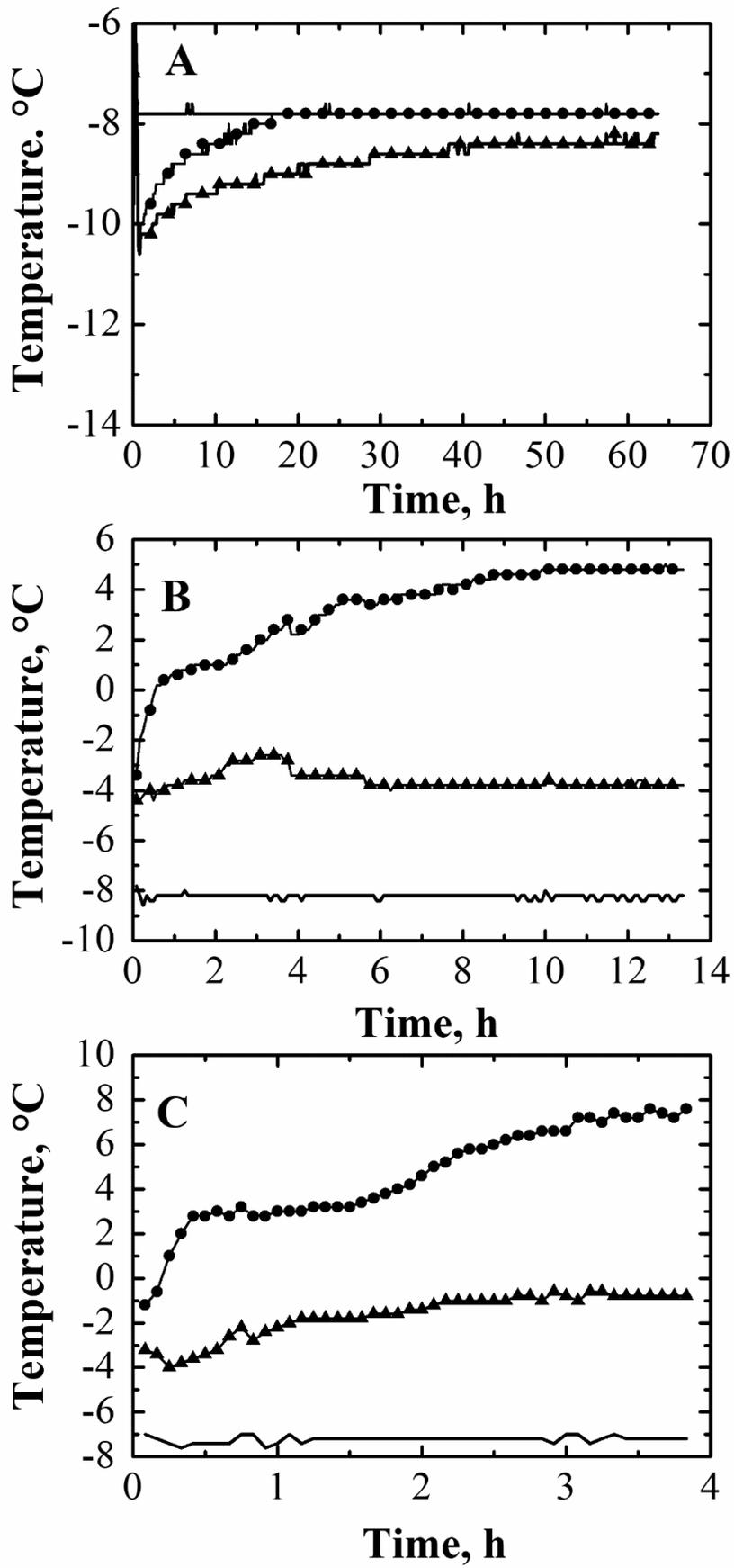


Figure 9

