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Comparative Study of Different Process Conditions of Freeze Drying of 'Murtilla' Berry

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Different operating conditions for drying halves of 'Murtilla', a native Chilean berry food species, were studied in atmospheric freeze drying, using dry air through a pulsed fluidized bed, and vacuum freeze drying. Applying a 2^3 experimental design, the effect of the freezing rate, the air temperature, and the application of infrared radiation was studied on the moisture content and the drying time. Fast freezing with infrared (IR) and air at 15°C for the second drying stage allowed achieving final moisture contents similar to vacuum freeze drying in equivalent total drying periods. Drying at the same conditions except with air at 5°C resulted in a larger preservation of antioxidant capacity of the fresh fruit. Also, the texture was adequate for a dry fruit, with a pleasant flavor for direct consumption or mixed with yogurt.

The drying kinetics of the first drying stage was modeled by an equation based on the uniformly retreating ice front model, which gave a reasonable description of the trend for this stage, although it does not include the application of IR radiations or the rate of freezing. The Page equation was an adequate tool to represent the second drying stage (which started after 7 h) for each experimental run, by using specific parameters (n and k) obtained by fitting the experimental data. The parameters exhibited similar values to those cited in the literature for foods.

Keywords Atmospheric freeze dryer; Murtilla; Pulsed fluidized bed; *Ugni molinae* Turcz

INTRODUCTION

Convective drying impairs sensory and functional properties of fruits and vegetables, due to vitamin, aroma, flavor, and protein degradation caused by high temperatures. In addition, the structure of the solid may also be changed considerably, affecting texture and rehydration. Freeze drying is a good alternative for drying foods and other sensitive materials because it does not present the disadvantages mentioned above for convective drying.[1–4] The freeze-drying process consists of three stages: (1) freezing of the matter; (2) a first drying stage, where sublimation of the frozen free water occurs; and (3) a second drying stage, where the bound frozen water is eliminated by desorption. The freeze-drying process is slow and involves high investment and operating costs due to the need for producing and maintaining a high vacuum, because the removal of moisture at low temperatures requires the use of vacuum to increase the mass transfer and the hydraulic gradient between the sublimation front and the drying medium.[4,5] To reduce the costs, one alternative is to use atmospheric freeze drying,[1,6] because the use of expensive vacuum generating equipment could be eliminated,[7] with only a small increase in drying time. The drying time can be reduced by using a fluidized bed, which produces high heat and mass transfer coefficients, and/or by introducing a change in operating conditions.[2,6,8–10] Recently, Huang et al.[11] compared the energy consumption and the quality parameters of apple slices obtained in freeze drying combined with microwave vacuum drying.

'Murtilla', 'mutilla,' or 'murta' (*Ugni molinae* Turcz) is a native Chilean species that produces a small berry fruit of 0.7–1.3 cm in diameter and an exotic taste and aroma, along with a high antioxidant capacity, equal or superior to other commercial berry fruits. Murtilla is consumed raw and in jams, juices, canned products, confectioneries, and liquors.[12]

In the present work, the effect of the freezing rate, air temperature, and type of energy supply on the final moisture, antioxidant activity, and polyphenols content was investigated using a pulsed fluidized bed with atmospheric freeze-drying technology. The mass transfer gradient was maximized by passing the incoming air through a bed of silica gel.

FREEZE-DRYING PROCESS

The overall freeze-drying process, depicted in Fig. 1, starts with a freezing step, followed by the first drying step, in which mainly the frozen water is removed by sublimation. A second drying step follows, in which bound water (nonfrozen) is removed by desorption.[13–15] In both conventional drying and freeze drying, two drying periods are present: the first step is controlled by external heat and mass transfer, and the second step is controlled by internal

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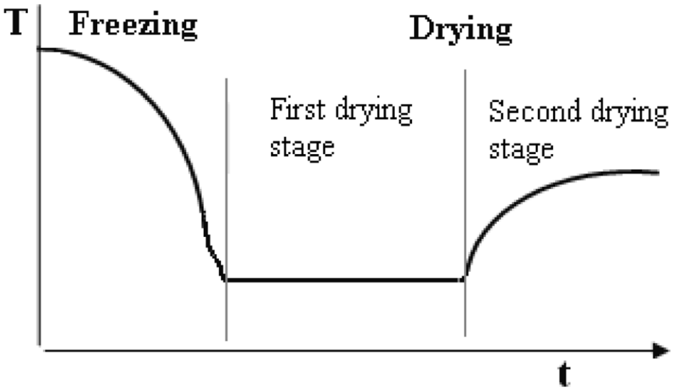


FIG. 1. Stages of the lyophilization process.

heat and mass transfer. The second step in conventional drying starts when the critical moisture content is reached, whereas in freeze drying it starts when there is no more frozen layer (that is, there is no more sublimation interface).

Description of the Stages of the Lyophilization Process

Freezing Stage

Initially, the product is frozen, achieving a solid structure, without any interstices with residual liquid, which avoids collapse of its structure while the drying process takes place by sublimation.

The freezing stage has a great influence on the whole process because it sets the structure of the ice crystals (shape and size), which affects the heat and mass transfer rates and therefore the time taken by the subsequent drying stages.[14,16–19] Hottot et al.[20] modeled the freezing step and concluded that great attention must be devoted to the control of the uniformity of the cooling gas temperature.

Aguilera and Stanley[21] pointed out that just as important or even more so than the shape of the crystals is where they are formed, which is also affected by the freezing rate. Slow cooling (less than 1°C/min) leads to crystal growth in extracellular locations. On the other hand, quick cooling produces small crystals, uniform crystallization, and a product of better quality.

In the first drying stage (sublimation), the ice crystals should be large in order to reduce the drying time, but in the second drying stage, and with the purpose of increasing the specific surface area of the pores, it is desirable to have the smallest possible crystals. This combination of requirements points to the existence of an optimum ice crystal size.[16]

The First Drying (Sublimation) Stage

Sublimation requires a large amount of energy: heating of a frozen material generates a sublimation front that advances gradually inside the frozen solid, and the temperature at this front is practically constant. This temperature is determined by a balance between the heat transfer rate from the outer gas film through the dry layer and the energy required for evaporating water at the sublimation front. Mass transfer occurs by migration of internal vapor through the solid’s dry layer. In summary, sublimation takes place only in this first stage, with the formation of a retreating ice front. The time to complete this stage is between 25 and 45% of the total drying time, depending on the nature of the solid and the drying conditions. Hottot et al.[22] used different experimental procedures to detect sublimation end-points for freeze drying of pharmaceutical proteins.

The Second Drying Stage

This stage involves the removal of the unfrozen water (bound water) by evaporation and it begins when the ice has already been removed by sublimation. The bound water appears in two forms: physically adsorbed and as water of crystallization. The removal of bound water is slower than the first removal of free water, and it markedly affects the overall drying time.

In traditional freeze drying, the bound water may be removed by heating the product under vacuum. The heat supplied in this drying stage should be controlled because the structure of the solid matrix would be modified if the temperature of the product rises, which, in turn, may influence the stability of the product during and/or after drying. The energy delivered to the solid can be supplied by conduction, convection, and/or radiation.

Fitting Drying Curves

Modeling of the First Drying Stage

Wolff and Gibert[7] modeled the atmospheric freeze drying of potato particles in a fluidized bed of adsorbent, using a quasi-steady-state (equality of internal and external heat and mass transfer). This model was based on the uniformly retreating ice front (URIF) equations as described by King[23] and employing the laws of Fick and Fourier to describe mass and heat transfer, respectively. Then, the freeze-drying kinetics can be represented by:

$$m_o \frac{d(1-Y)}{dt} = \frac{S}{\lambda_S}\frac{1}{\left(\frac{1}{h}+\frac{e_S(t)}{k_c}\right)}(T_b - T_{SF}) \qquad (1)$$

$$m_o \frac{d(1-Y)}{dt} = S\frac{1}{\left(\frac{1}{\beta_{ext}}+\frac{R\cdot T\cdot e_S(t)}{D_W\cdot M}\right)}(p'_{SF} - p'_C) \qquad (2)$$

Wolff and Gibert[7] also linked the values for the saturating pressure P'_o and the temperature of the sublimation front T_{SF} by means of the Clausius-Clapeyron law:

$$\frac{dP'_o}{dT} \approx \frac{(P'_o - p'_{SF}}{(T_b - T_{SF})} = \frac{\lambda_S \cdot M \cdot P'_o}{T^2 \cdot R} \qquad (3)$$

A combination of the previous equations results in Eqs. (4), (5), and (6).

$$-\frac{\mathrm{dm}}{\mathrm{dt}} = \mathrm{m}_0 \cdot \frac{\mathrm{d}(1-\mathrm{Y})}{\mathrm{dt}} = \mathrm{S} \cdot \frac{(\mathrm{P}'_\mathrm{o} - \mathrm{P}'_\mathrm{b})}{\mathrm{R}_\mathrm{e} - \mathrm{R}_\mathrm{i} \cdot \mathrm{e}_\mathrm{S}} \tag{4}$$

$$\mathrm{R}_\mathrm{e} = \frac{1}{\beta_\mathrm{ext}} + \frac{1}{\mathrm{h}} \cdot \frac{\lambda_\mathrm{S}^2 \cdot \mathrm{P}'_\mathrm{o} \cdot \mathrm{M}}{\mathrm{T}^2 \cdot \mathrm{R}} \tag{5}$$

$$\mathrm{R}_\mathrm{i} = \frac{\mathrm{R} \cdot \mathrm{T}}{\mathrm{M} \cdot \mathrm{D}_\mathrm{W}} + \frac{1}{\mathrm{k}_\mathrm{c}} \cdot \frac{\lambda_\mathrm{S}^2 \cdot \mathrm{P}'_\mathrm{o} \cdot \mathrm{M}}{\mathrm{T}^2 \cdot \mathrm{R}} \tag{6}$$

In Eq. (4), R_e combines all the external resistances of heat and mass transfer and $\mathrm{R}_\mathrm{i} \cdot \mathrm{e}_\mathrm{S}$ combines the corresponding internal resistances.

For the particular geometry of the particles to be dried in this study (Fig. 2a), the previous equations had to be adapted. The murtilla berries were cut in two halves, which were considered to maintain their semispherical form and size (Fig. 2b) during the whole process, and to be equivalent to a cylinder opened only on one of its faces (due to the hard peel), with the lateral walls (which are semispherical in the real case and cylindrical in the model) and the bottom face considered impermeable to water vapor transport. Thus, the water vapor would only be removed through the open face of the cylindrical particles, whose height is $\mathrm{L} = \mathrm{R}_\mathrm{o}$ (Fig. 2c). On the other hand, the amount of water contained (Y) was related to the amount of sublimed water, as a function of the radius of the particle (R_o) and the thickness of the dry layer (e_S), by means of Eq. (7), considering that the porosity of the particle (ϵ) remains constant and that initially the open spaces are filled with water:

$$\begin{aligned}(1-Y) &= \frac{sub\lim ated \quad water}{initial \quad water} \\ &= \frac{(\varepsilon \cdot V_{particle} - \varepsilon \cdot V_{water}) \cdot \rho_w}{\varepsilon \cdot V_{particle} \cdot \rho_w} \\ &= \frac{V_{particle} - V_{water}}{V_{particle}} \cong \frac{e_S}{R_o}\end{aligned} \tag{7}$$

The introduction of Eq. (7) into Eq. (4) gives:

$$-\frac{dm}{dt} = \frac{m_0}{R_o} \cdot \frac{d\,(e_S)}{dt} = S \cdot \frac{\left(P'_0 - P'_b\right)}{R_e - R_i \cdot e_S(t)} \tag{8}$$

The integration of Eq. (8) gives:

$$R_e \cdot e_S - \frac{R_i}{2} \cdot e_S^2 = \frac{S \cdot R_o\left(P'_0 - P'_b\right)}{m_0} \cdot t \tag{9}$$

or, when Eq. (7) is used,

$$R_e \cdot (1-Y) - \frac{R_i}{2} \cdot (1-Y)^2 \cdot R_o = \frac{S \cdot \left(P'_0 - P'_b\right)}{m_0} \cdot t \tag{10}$$

Equation (10) combines all the external resistances of heat and mass transfers R_e and the corresponding internal resistances, R_i.

Modeling of the Second Drying Stage

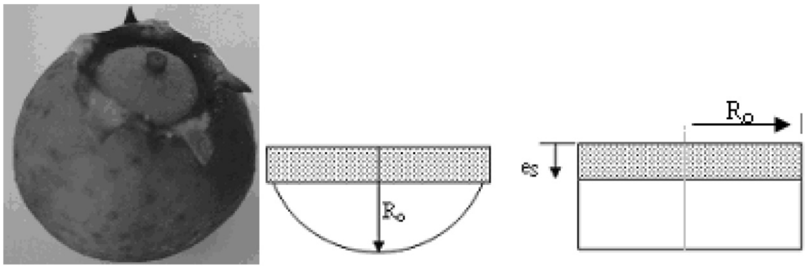
The Page empirical model, Eq. (11), is frequently used to describe the falling rate period of conventional drying of agricultural products,[24] where the mechanism is of diffusive nature. A similar behavior is found in the second drying stage of freeze drying, for the removal of the residual bound water, justifying the use of the Page model.

$$\frac{\mathrm{X}}{\mathrm{X}_\mathrm{o}^*} = \exp(-\mathrm{k} \times \mathrm{t}^\mathrm{n}) \tag{11}$$

where k and n are parameters of the model.

EQUIPMENT, MATERIALS, AND METHODS

Figure 3 shows a scheme of the atmospheric freeze dryer utilized, where air is circulated by a centrifugal blower (A), its temperature is adjusted by a heat exchanger (B), and it is dried in a fixed bed of silica gel (C). Then, the air is passed through a horizontal rotating cylinder with two slots, which generates a pulsating air flow (D),[25] and then through the bed of berries (E). For the experimental runs



(a) (b) (c)

FIG. 2. Murtilla: (a) fruit; (b) model of the semispherical particle of the fruit; (c) cylindrical model of the particle.

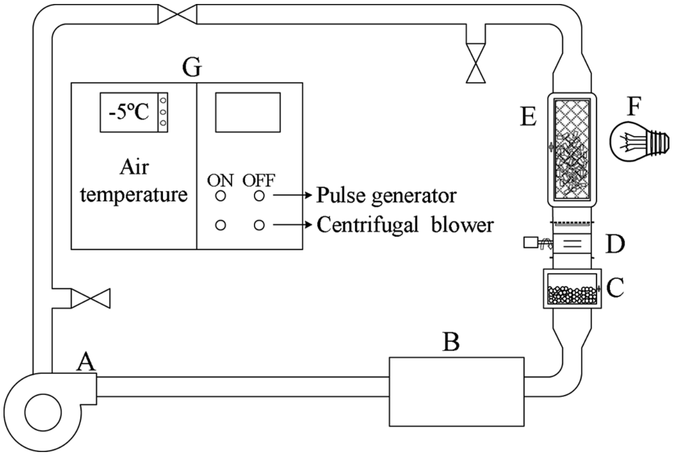


FIG. 3. Atmospheric freeze dryer. A: centrifugal blower, B: heat exchanger, C: silica gel, D: pulse generator, E: freeze drying chamber, F: IR lamp, G: control panel.

that required it, the system was provided with a 250 W infrared (IR) lamp (F) installed 0.3 m away from the drying chamber.

Silica gel (2 kg) was loaded in the compartment (C), the desired temperature value was set on the cooling system (B), and the pulse generator and centrifugal blower were turned on. After the system reached a steady temperature, 250 g of frozen murtilla fruits was loaded into the drying chamber (a 9.5-cm-diameter glass tube, with a perforated plate at the bottom to allow air to pass through), and the initial mass was measured with a Boeco balance (BBL62, Boecktel Co., Hamburg, Germany). After 60 min, the drying chamber was removed from the equipment, weighed, and then put back in the equipment. This procedure was repeated for 13 h of operation. The initial and final moisture contents of the berries were determined in a vacuum oven until constant weight according to AOAC 920.151.[26] To ensure the dryness of the fluidizing air, the silica gel was replaced every 2 h.

Murtilla (*Ungi molinae* Turcz), ecotype 14-4 from the INIA Carrillanca Genetic Bank, was obtained from an experimental station near Puerto Saavedra, Chile. Berry fruits with an average diameter of 10 mm (±2 mm), a density of 1,062 kg/m^3, and an initial moisture content of 79.3% (±1.2%, wet basis) were selected.

Freezing was carried out in a household freezer for 15 h at −18°C (slow freezing) or by immersion in liquid nitrogen for 5 min (quick freezing). In order to increase drying rate, each individual frozen berry was cut into halves using a scalpel and stored in a freezer at −18°C before drying.

Freeze Drying

A temperature program for the drying air was employed: 7 h at −5°C, which was called the *first drying (sublimation) stage*, followed by 6 h at 5°C or 15°C, corresponding to the *second drying stage*.

The experimentation for the first drying stage was carried out applying a 2^2 factorial design (in duplicate), to study the effect of freezing rate and type of energy supply on the dimensionless moisture content at the end of the 7th hour. The second drying stage was studied by means of a 2^3 factorial design, to study the effect of freezing rate, type of energy supply, and air temperature on the dimensionless moisture content at the end of the 13th hour. The statistical analysis, including calculation of the effects values and their significance, was carried out according to standard procedures[27] by means of the software Statgraphics Plus 5.1 (Statistical Graphics Corp., Warrenton, VA), using the operating conditions for each run shown in Table 1.

Additionally, the antioxidant activity and polyphenols content of murtilla fruits were studied at the end of the atmospheric freeze-drying experiments.

Texture

The texture was characterized by a maximum penetration force assay on a texture analyzer (TA-XT2i, Surrey, England) equipped with Texture Expert software (Quimatic, Santiago, Chile), on 18 semispheres of murtilla with a multiple puncture probe, which entered the samples at a constant velocity of 1 mm/s.

Rehydration

The rehydration tests were done by measuring the weight gain of dehydrated samples (ca. 2 g) that were immersed in 200 mL of distilled water at a constant temperature of 25°C. Samples were withdrawn every 5 min, drained, wrapped in absorbent tissue to remove surface

TABLE 1
Set up values of the experimental variables for each run of freeze-drying experiments of murtilla berry fruits

Run	Freezing rate	Air temperature in the first stage (°C)	Air temperature in the second stage[a] (°C)	Type of energy supply
A1	FF (Fast)	−5	15	Convective
A2	FF (Fast)	−5	15	Convective + IR
A3	FF (Fast)	−5	5	Convective
A4	FF (Fast)	−5	5	Convective + IR
B1	SF (Slow)	−5	15	Convective
B2	SF (Slow)	−5	15	Convective + IR
B3	SF (Slow)	−5	5	Convective
B4	SF (Slow)	−5	5	Convective + IR

[a] From 7 h onward.

water, and weighed on an analytical balance until constant weight. The moisture of the rehydrated product was calculated from the sample weight before and after rehydration. The rehydration measurements were made in triplicate for all the samples and average values were reported.

Total Polyphenols Content

The content of total polyphenols was determined spectrophotometrically using the method of Folin-Ciocalteau. To 3.16 mL of distilled water, 40 mL of extract and 200 mL of Folin-Ciocalteau reagent were added. The mixture was left standing in the darkness for 5 min. Then 600 mL of a 20% (w/v) sodium carbonate solution was added and left in the darkness for other 2 h. Finally, absorbance at 765 nm was measured[28] and the results were expressed as milligrams of gallic acid equivalents per liter of extract.

Antioxidant Capacity

The measurement of the antioxidant capacity was based on the free radical sequestering ability of the compounds present in the fruit extracts, using the stable radical 2,2-diphenyl-1-picryhydrazyl (DPPH) according to the procedure described by Atoui et al.,[29] in which 50 mL fruit extracts was mixed with 1.950 mL of DPPH solution (5.6×10^{-5} M in methanol). The decrease in absorbance at 515 nm was continuously recorded spectrophotometrically during 30 min.

The percentage of inhibition of the free radical (% FRI) was calculated according to the following equation:

$$\%\mathrm{FRI} = \frac{a_{(t=0\,\mathrm{min})} - a_{(t=30\,\mathrm{min})}}{a_{(t=0\,\mathrm{min})}} \times 100 \qquad (12)$$

where $a_{(t=0\,\mathrm{min})}$ is the absorbance of the pure DPPH at zero time and $a_{(t=30\,\mathrm{min})}$ is the absorbance of the mixture extract/DPPH, after 30 min reaction.

RESULTS AND DISCUSSION

Preliminary experiments showed that the skin of the murtilla berry was a strong natural barrier to dehydration, making it necessary to employ long drying times, but acceptable drying rates were obtained if the frozen murtilla berries were halved before drying. This last procedure was utilized because the usual treatment by dipping in a warm alkali solution, which is an effective way to peel most other fruits, was completely ineffective. In addition, preliminary work allowed verifying that better drying kinetics results were achieved when two temperature levels were applied during drying: −5°C for the first 7 h and 5°C (or 15°C) during the final 6 h.

Drying Kinetics

Figure 4 shows the evolution of dimensionless moisture content of murtilla berries during freeze drying under different conditions. Statistical analysis of the results of the first drying stage indicates that both freezing rate and type of energy supply were significant effects (under the criterion of the normal probability graph) on the dimensionless moisture content obtained at the end of that stage, with values of −0.054 and −0.0465 (in coded levels), respectively. This latter situation might be due to a larger energy input (provided by IR) and also to a faster transport of water vapor through smaller pores (left by sublimation of smaller ice crystals obtained by fast freezing). From hour 7 onwards, the drying temperature in each run was set either to 5 or 15°C, at the different drying conditions, and Fig. 4 shows that the drying rate increases for all of them, with the largest effect for run A2 at 15°C, fast freezing, and with IR.

Figure 4 also shows the results for a run of freeze drying under vacuum (VFD), whose drying rate is considerably higher than in the atmospheric freeze-drying processes; however, when the moisture content is lower than $X/X_o = 0.1$, the drying rate values for all runs come closer, especially for Run A2, the best one, performed at atmospheric pressure. Another increase in the drying rate is observed when fast freezing is used (liquid nitrogen bath) instead of slow freezing (−18°C freezer), probably due to the generation of smaller crystals in the first case, which favors drying kinetics.

Regarding the moisture content, temperature [*AT*] had the most significant effect on the moisture content reduction, followed by the freezing rate [*FR*]. The lowest moisture content after 13 h of atmospheric freeze drying was obtained when samples subjected to fast freezing were dried at 15°C in the second stage. The moisture content of murtilla fruit as a function of the significant effects (in coded levels), at a 95% confidence level, is the following:

$$\left(\frac{X}{X_o}\right) = 0.24425 - 0.1155 \cdot [FR] - 0.0495 \cdot [AT] \qquad (13)$$

The fact that the application of IR was not statistically significant at a 95% confidence level might have been due to the low energy efficiency of the heating radiation system utilized.

Modeling of the First Drying Stage

Figure 5 shows the evolution of dimensionless moisture content of murtilla berries during atmospheric freeze-drying under different conditions. Until the 7th hour, a constant temperature of −5°C was used. From hour 7 onwards, the drying temperature of the runs was set either to 5 or 15°C. The experimental values are compared with those calculated with Eq. (10), which was adapted from equations developed by Wolff and Gibert,[7] using the properties given in Table 2. Because Eq. (10) does not consider the freezing

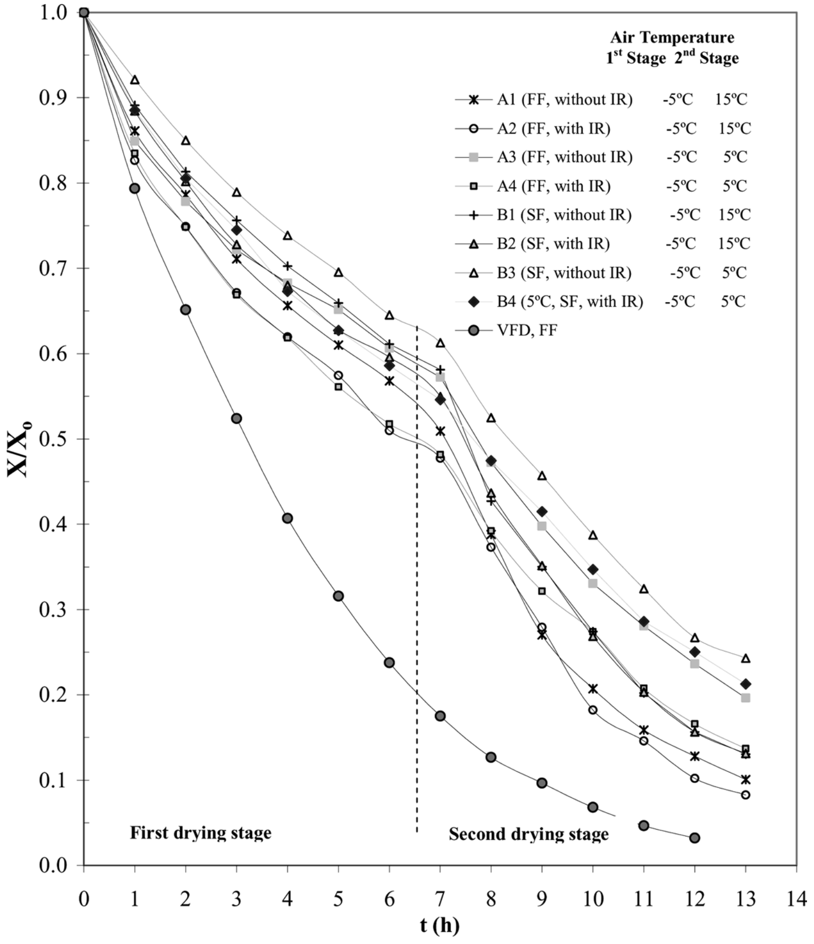


FIG. 4. Effect of freezing rate, drying temperature and infrared light application on the drying kinetics of murtilla berry fruit halves.

rate or the application of IR radiations as variables, one single curve represents all the values for the first stage, with a deviation of ±10% for X/X_o. The best agreement is observed for slow freezing experiments. On the other hand, experiments carried out with fast freezing show higher drying rates than the calculated data, whereas those without application of IR show a lower rate.

Modeling of the Second Drying Stage

For the second drying stage (from hour 7 onwards), the parameters of the empirical Page model, Eq. (11), were adjusted by minimizing the difference between the experimental and calculated values, considering as initial moisture content the value obtained at hour 7 (which was fixed as the origin for the time scale; that is, zero time, for the second drying stage; the time scale in the Fig. 5 denotes total time). Figure 5 shows this fit, and Table 3 shows the initial moisture content of murtilla fruit at the beginning of the second drying stage (hour 7), the resulting parameters for the Page model, and the residual standard error for each run.

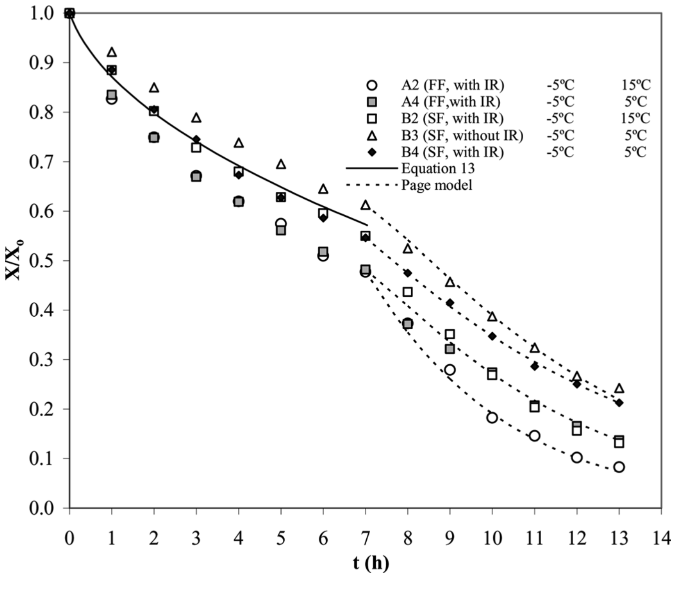


FIG. 5. Comparison between experimental and calculated values of drying kinetics for murtilla berry fruits halves.

TABLE 2
Experimental and literature values used with Eq. (10)

Property	Value
Particle radius, R_o	5 mm
Partial pressure of saturated vapor at the sublimation front, $P'_0(-5°C)$[30]	0.004153 atm
Partial pressure of vapor in the fluidized bed, $p'_c(-5°C)$	0
External mass transfer coefficient, β_{ext}[7]	8×10^{-7} kg/m^{2}s
Heat transfer coefficient, h[7]	170 W/m^{2}K
Vapor diffusivity of the vapor in the dry layer of murtilla (−5°C and thickness of 3 mm), D_W [7]	2.42×10^{-5} m^2/s
Thermal conductivity of the dry layer, k_c[7]	0.4 W/mK
Heat of sublimation, λ_S[30]	46.7 kJ/mol
Air conductivity (−5°C), k_{air}[30]	0.023669 W/mK
Air density (−5°C), ρ_{air}[30]	1.310436 kg/m^3
Air viscosity (−5°C), μ_{air}[30]	1.7105×10^{-5} kg/ms
Air velocity, v	2 m/s

Freeze Drying Under Vacuum

To establish the effect of the application of vacuum on freeze-drying kinetics, some experiments were carried out in a conventional vacuum freeze dryer, with particles that had been subjected either to slow or fast freezing. Figure 6 shows the drying kinetics obtained both under vacuum and at atmospheric pressure. It is observed that the final moisture content tends to become equal at the end of the drying period, especially so for the run performed under optimum conditions (Run A2). Finally, it can be observed that the rate of freezing of the particles did not affect the drying kinetics under vacuum.

TABLE 3
Parameters of the page model

Run	X_o^*	n	k (min^{-1})	SE
A1	1.946	0.8553	0.0106	0.030
A2	1.772	1.0285	0.0044	0.030
A3	1.959	0.9657	0.0036	0.025
A4	1.825	1.1356	0.0016	0.040
B1	2.197	1.1009	0.0023	0.032
B2	2.192	1.0902	0.0025	0.021
B3	2.316	1.1841	0.0010	0.036
B4	2.247	1.0659	0.0018	0.015

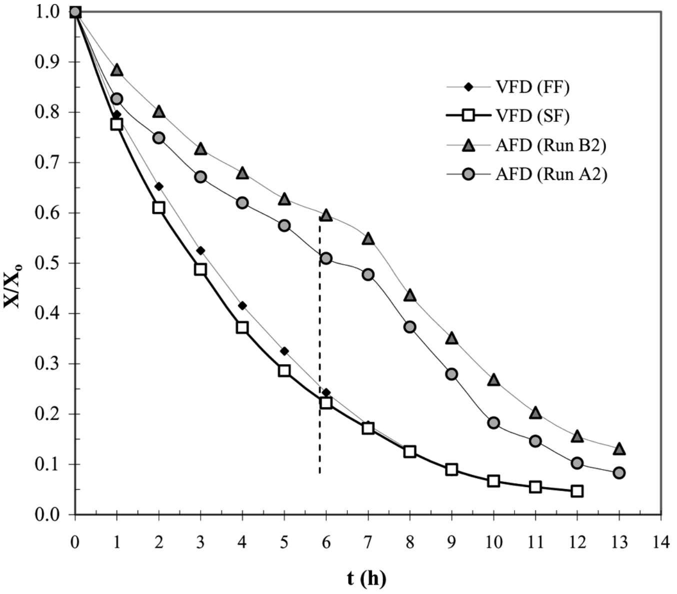


FIG. 6. Comparison of the drying curves for atmospheric and vacuum freeze drying of murtilla berry fruits halves.

Antioxidant Activity and Polyphenols Content of Murtilla

Table 4 shows the polyphenols content and the antioxidant activity of both fresh murtilla fruit and fruit dried under different drying processes. For all the dried products, a decrease in these properties is observed (with respect to their original values).

When comparing Run A2 (15°C) with Run A4 (5°C), both with fast freezing (FF) and IR heating, it can be observed that, by increasing the drying temperature, both the polyphenols content and the antioxidant activity decrease markedly. On the other hand, when comparing Run B4 (with IR) with Run B3 (without IR), both with slow freezing (SF) and the same drying temperature, a lesser decrease in the antioxidant activity is observed (30 and 50% decrease, respectively), indicating that the application of IR helps to preserve the antioxidant activity, which was actually seen throughout this study.

In all cases, FF results in a larger decrease of the polyphenols content than SF. This might be due to a smaller pore size left by FF, which means a larger surface area and consequently a larger exposure of the polyphenols to the drying medium.

A multifactor analysis of variance (ANOVA), carried out on the results of the content of polyphenols and the antioxidant activity of murtilla fruits obtained with vacuum freeze drying and atmospheric freeze drying, indicates that at 95% confidence level (p value <0.05) only the freezing rate had a significant effect on the antioxidant activity. On the other hand, none of the factors had a significant effect on the content of polyphenols. Previous work[12]

TABLE 4
Effect of the drying process conditions on the final polyphenols content and antioxidant activity of murtilla berry fruit halves

Type of drying	Drying process conditions	Polyphenol (mg/100 g dry weight)	Antioxidant activity EC50 (mg/L)
	Fresh fruit	1,460	108
Vacuum freeze drying	Fast rate freezing (FF)	793	72
	Slow rate freezing (SF)	815	35
Atmospheric freeze drying	Run B3 (5°C, SF, without IR)	867	51
	Run B4 (5°C, SF, with IR)	847	68
	Run A2 (15°C, FF, with IR)	583	59
	Run A4 (5°C, FF, with IR)	728	94

demonstrated that there is not a relationship between polyphenols content and antioxidant activity for most murtilla ecotypes. Additionally, Scheuermann et al.[12] demonstrated that thermal treatment (100°C per 20 min) decreased polyphenols content to half the content of the fresh fruits, whereas the antioxidant activity did not suffer any significant change. Therefore, polyphenols content is not a reliable parameter to measure antioxidant activity. In this study it was observed that the best treatment for keeping the antioxidant activity (run A4) was fast freezing (FF) of murtilla fruits and atmospheric freeze drying using IR at 5°C, where antioxidant activity decreased by no more than 13%, whereas polyphenols content decreased by more than 50%, both with respect to fresh fruit.

Rehydration

Figure 7 shows the moisture uptake of dehydrated fruit samples upon rehydration in water at 25°C during 40 min. It is seen that a final moisture content of 70% is achieved, regardless of the operating conditions used in the freeze drying process (as an example, Fig. 7 shows the results only for two runs, although the results were similar for the other runs). The external appearance of the rehydrated product was similar to a frozen fresh fruit that has been defrosted but inside exhibited a gelatinous consistency probably due to the presence of pectin, which has the capacity of gel formation.

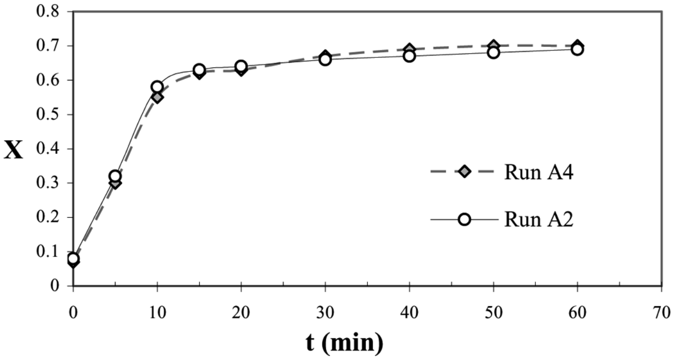


FIG. 7. Rehydration at 25°C for Runs A2 and A4 of dry murtilla berry fruits halves.

Rupture Resistance of the Dried Product

A potential use for dry murtilla berry fruit is to mix it with cereals and yogurt (Muesli) for breakfast food, for which a required structural property would be a higher or lower resistance to rupture, respectively. This resistance was determined from force/time curves (Fig. 8) measured on a texturometer, and the results for the fruit with the highest and with the lowest resistance are shown in Fig. 8. Statgraphics software was then applied to determine the optimum conditions for the generation of dehydrated fruits with an appropriately resistance. This analysis showed that application of IR radiation was the only statistically significant variable, which increases the resistance to rupture probably through the formation of a crust during IR application.

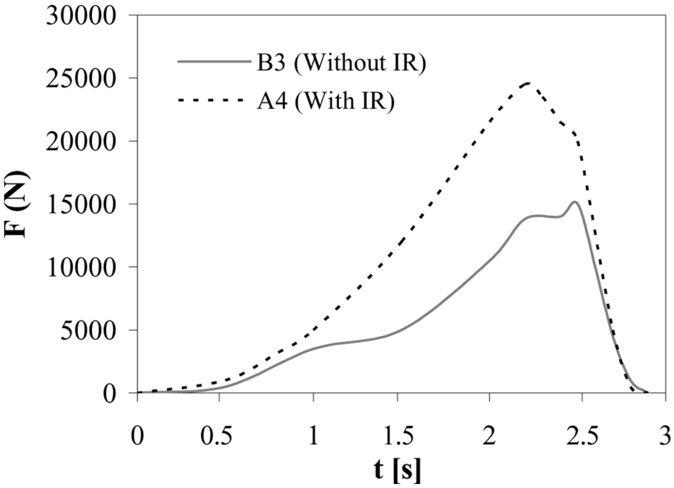


FIG. 8. Force vs. time curves of dry murtilla berry fruits halves: B3 (rupture force = 15,000 N) and Run A4 (rupture force = 25,000 N).

CONCLUSIONS

Murtilla berries, split into semispheres, were adequately dried in a pulsed fluidized bed. The optimal conditions in atmospheric freeze drying by fluidization with dry air (fast freezing with IR and air at 15°C for the second drying stage) allowed achieving final moisture contents similar to vacuum freeze drying and similar sensory attributes, in equivalent total drying periods.

In the first drying stage, only the rate of freezing was a significant variable, which can be attributed to the generation of small ice crystals, which in turn increases the rate of drying by increasing the area of sublimation.

In the second drying stage, the significant effects (at a 95% confidence level) that influenced the drying time were rate of freezing and temperature, with values of 0.231 and 0.1 (in coded levels), respectively. These two variables also had an effect on the polyphenols content and antioxidant capacity but with divergent trends for each of them.

In all cases, slow freezing without application of IR preserves the polyphenols content better than fast freezing, whereas the antioxidant activity shows a lesser decrease with the application of IR. On the other hand, increasing the drying temperature resulted in a lowering of both the polyphenols content and antioxidant activity.

The application of IR radiation generates products with higher resistance to fracture compared to those obtained without IR and also intensifies the red color.

Equation (10) is a reasonable description of the trend for the first drying step, although it does not include the application of IR radiation or the rate of freezing.

The Page equation was an adequate tool to represent the second drying stage (which started after 7 h) for each experimental run, by using specific parameters (n and k) obtained by fitting the experimental data. The parameters exhibited similar values to those cited in the literature for foods.[2,24]

NOMENCLATURE

AT	Air temperature, in coded levels
a	Absorbance
D_W	Vapor diffusivity in the dry layer (m^2/s)
e_s	Dry layer thickness (m)
F	Force (N)
FR	Freeze rate, in coded levels
h	Heat transfer coefficient ($W/m^2 \cdot K$)
k	Parameter of the Page model (min^{-1})
k_c	Thermal conductivity of the dry layer ($W/m \cdot K$)
l	Half-thickness of the sample (m)
m	Mass of water (kg)
N	Number of data points
Nu	Nusselt number
n	Dimensionless parameter of the Page model
P'_o	Saturating pressure of water in the sublimation front (N/m^2)
p'_C	Partial pressure of water vapor in the fluidized bed (N/m^2)
p'_{SF}	Partial pressure of water vapor in the sublimation front (N/m^2)
R	Perfect gas constant (J/°K mol)
R_e	External resistances of heat and mass transfers (N s/kg)
R_i	Internal resistances of heat and mass transfers ($N \cdot s/m$ kg)
R_{MS}	Root mean square (%)
R_o	Radius of particle (m)
S	Exchange surface (m^2)
T_b	Temperature of the bed of particles (K)
T_{SF}	Sublimation front temperature (K)
t	Drying time (s, min, or h)
V	Volume (m^3)
X	Moisture content fraction (dwb)
X_o	Initial moisture content fraction (dwb)
X_o^*	Moisture content fraction at the 7th hour (dwb)
Y	Relative water content in the particles (m/m_o)

Greek Letters

β	External mass transfer coefficient ($kg/N \cdot s$)
ϵ	Porosity
λ_S	Heat of sublimation (J/kg)
ρ	Density (kg/m^3)

Subscripts

ds	Dry solids
eff	Effective
i	Initial
o	Zero time
p	Particle
t	Any time

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