

Review

Structural, physical, functional and nutraceutical changes of freeze-dried fruit

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This review examines the structural, physical, functional and nutraceutical changes of lyophilized fruits. Collapse, porosity, color, glass transition temperature, rehydration capacity, ability to retain water, volatile compounds, phenolic compounds, ascorbic acid, and beta-carotene, were defined, and the causes of changes in these parameters, during freeze-drying, were analyzed. Advantages and limitations of the freeze-drying, were shown, and strategies to reduce the costs associated with its use were proposed. It was concluded that lyophilized fruit retained to a greater proportion characteristics of fresh fruits, compared with other methods of dehydration. The effects of freeze-drying on physical and chemical properties vary in accordance with factors intrinsic to the fruit, and with extrinsic properties inherent to process. Most fruits maintain their color using freeze-drying. The porosity of freeze-dried fruit depends on the freezing speed. The glass transition temperature of dry solid would be an important optimization parameter for the freezing-drying process. The majority of phenolic acids and volatile compounds were conserved in freeze-drying. Freeze-drying increases the rehydration capacity of dried fruits, to a greater extent the hydrophilic groups which are responsible for interaction with water. However, dried fruits by freeze-drying can show structural collapse. The long processing time and energy costs are limiting the application of technology. The researchers recommend using combined to potentiate the benefits of freeze-drying and to lessen their limiting technologies.

Key words: Freeze-drying, fruit, dehydration.

INTRODUCTION

Fruits are necessary in the human diet because of their vitamin, mineral and antioxidant content; they are remarkable for their exuberant flavors, colors and smells. These properties ought to be preserved in agro-industrial processing (Kirmaci et al., 2008). The World Health Organization (WHO) promotes the consumption of 400 g

of fruit per day (Montenegro et al., 2009; Orrego et al., 2009; Shofian et al., 2011). However, the perishability and seasonal availability of many fruits means that they are not always available to consumers. To combat this problem, the industry often offers processed fruits that have partially or completely lost their physical, nutraceutical

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and nutritional properties (Sijtsema et al., 2012).

Dehydrated fruits are excellent alternative, making year-round availability more feasible and extending the shelf life of fruits (Marques et al., 2007). The methods of fruit dehydration include drying in hot air (Giraldo et al., 2010), refraction window (Ocoro and Ayala, 2012), osmotic dehydration (Ayala et al., 2010), frying (Villamizar and Giraldo, 2010), drying by microwave (Duan et al., 2010; Jiang et al., 2010) and freeze-drying (Ayala et al., 2010; Ceballos et al., 2012). These methods diminish water activity and therefore reduce the number of enzymatic, chemical and microbiological reactions that take place (Hincapié et al., 2010). Dehydration methods should minimize the loss of nutrient and antioxidant contents (Santos and Silva, 2008); however, because some antioxidant compounds are weakly bonded to water in the fruit, some nutritional content will be lost in the dehydration process. Generally, fruits with the greatest initial water content lose a greater portion of soluble solids during dehydration (Ceballos et al., 2012).

Freeze-drying is the removal of water from a product through sublimation (Rothmayr, 1975). Sublimation is the conversion from ice directly to vapor without passing through a liquid state. In water, sublimation occurs when the vapor pressure and the temperature of the ice's surface are below the triple point [4.58 mm Hg (610 Pascal), 0°C] (Jennings, 2002). The process of freeze-drying has three essential steps: freezing, primary drying and secondary drying. Approximately 90% of the water is removed from fruits in the first drying phase (Welti et al., 2005). This article reviews the structural, physical, nutraceutical and functional changes of freeze-dried fruit. Advantages and limitations of the freeze-drying process as well as strategies for improvement are discussed.

STRUCTURAL CHANGES THAT CAN OCCUR IN THE FREEZE-DRYING PROCESS

The sought-after freeze-drying products are porous fruits that maintain their volume, can have fast and nearly complete rehydration when water is added and do not shrink (Duan et al., 2010). However, some freeze-dried products undergo undesirable structural changes. Microscopy can be used to study structural changes in freeze-dried fruits and to find a relationship to some physical properties (Yeom and Song, 2010). Table 1 presents a variety of fruits, processing variables, physical changes and the structural and nutraceutical effects of freeze-drying.

Collapse

Collapse and contraction are terms used to describe the loss of structure. A collapsed product may show reduced pore size and volumetric contraction (Khalloufi et al., 2010;

Madiouli et al., 2012). According to Harnkarnsujarit and Charoenrein (2011), collapse is the viscous flow that occurs when the viscosity diminishes beyond the glass transition temperature (T_g). Loss of structure occurs when the material is incapable of supporting its own weight. If the temperature of a porous product is above the glass transition temperature, the viscosity of the solid material may not be able to support the structure, causing collapse and contraction (de Oliveira et al., 2010). Collapse is alternatively defined as a decrease in volume or an increase in apparent specific density (Cui et al., 2008).

Collapse is noted by the shrinkage of the dried product. These structures are sensitive to physical, chemical and microbiological changes, which reduce the shelf life and stability of the product (Queiroz et al., 2008). Several studies have shown that collapse slows some chemical reactions, such as oxidation (Prado et al., 2006) as well as the liberation of trapped volatile compounds (Levi and Karel, 1995).

The primary drying temperature can be manipulated to control collapse. A high freeze-drying temperature negatively affects the humidity of the final product, which can lead to structural loss or collapse. Collapsed products are tougher, are have less aroma, and have less rehydration capacity (Harnkarnsujarit and Charoenrein, 2011).

The structural collapse of fruit can be physically controlled, by modifying the product structures before freeze-drying, and can be chemically controlled, through the addition of compounds that modify the collapse temperature. Products with high sugar content, such as fruit juice, have low collapse temperatures (de Oliveira et al., 2010). Collapse can be decreased, by controlling variables in the process such as the freezing speed and temperature (Ceballos et al., 2012). Ayala et al. (2010) describe collapse (19.15% volume loss) during the osmotic dehydration of yellow pitahaya. Evidence of this collapse can be observed in the deformation of cell walls and diminished cell turgor. Freeze-dried pitahaya, even without pre-treatment, did not collapse, losing only 2.6% of the original volume. Similarly, freeze-dried papaya did not present collapse (Marques et al., 2009).

Collapse is related to product porosity and rehydration. When collapse is not visually obvious, collapse can be evaluated through rehydration because structural collapse is known to diminish rehydration capacity (Marques et al., 2009).

Freeze-drying tropical fruits such as pineapple, guayaba, mango and Barbados cherries does not produce signs of collapse (Marques et al., 2006). The same is true for acerola pulp, which does not show visible signs of collapse (Marques et al., 2007). However, acerola and guayaba have a low rehydration capacity, which can be described as collapse. Mango, papaya and pineapple are readily rehydrated and are not thought to collapse in the freeze-drying process (Marques et al., 2009). de Oliveira et al. (2010) describe the freeze-drying of peki, a Brazilian fruit. The pulp was pretreated with sucrose and ethanol, which

Table 1. Process variables and physical, structural and nutraceutical changes in freeze-dried fruit.

Fruit	Processing variables	Physical and structural changes	Nutraceutical changes		Citation
			Fresh fruit	Freeze-dried fruit	
Acerola (<i>Malpighia glabra</i> L.)	Rapid freezing (-100°C). Liquid nitrogen. Primary drying (-32.1°C). Secondary drying (35°C)	Minimal collapse. Low Tg (-32.1°C). High rehydration capacity (10.1 kg/kg).	Vitamin C 1021 mg/100 g	Vitamin C 153.4 mg/100 g.	Marques et al. (2007)
Strawberry	Rapid freezing (-80°C for 24 h). Freeze-drying time (24 h).	Color: L*57, a*24, b*26, changed to L*58 a*23 b*26.	Vitamin C 50.7 mg/100 g Firmness 0.1 Newton	Vitamin C was conserved. Firmness 0.56 Newton Phenolic acids and aromatic substances were conserved. Anthocyanin was diminished	Yurdugül (2008)
Yellow pitahaya (<i>Selenicereus megalanthus</i>)	Freezing (-35°C). Sublimation: 8 Pa vacuum pressure Drying from -35 to 35°C	Freeze-dried fruit: Aw: 0.382 Porosity: 48.17 Rehydratability: 1,982 Kg water/Kg mass Freeze-dried fruit: Volume was preserved in sliced fruit. Aw: 0.364 Porosity: 84.52 Rehydratability: 2.614 Kg water/Kg dry mass			Ayala et al. (2010).
Peki (<i>Caryocar brasiliense</i> Camb.)	Sublimation: (0.0998 kPa, -40°C), 72 h. Secondary drying (35°C).	Particulates smaller than 1.20 mm. Aw: 0.06 – 0.25 Collapse.			de Oliveira et al. (2010).
Carambola			TPC (181.71 mg/100 g) Vitamin C (4.99 mg/100 g) Beta-carotene (30.79 mg/100 g)	TPC (137.95 mg/100 g) Vitamin C (4.67 mg/100 g) Beta-carotene (25.94 mg/100 g)	
Mango	Freezing (-20°C), 24 h Vacuum drying (-50°C), 3 days.		TPC (99.69 mg/100 g) Vitamin C (8.36 mg/100 g) Beta-carotene (660.27 mg/100 g)	TPC (76.57 mg/100 g) Vitamin C (8.34 mg/100 g) -Beta-carotene (487.34 mg/100 g)	Shofian et al. (2011)
Melon			TPC (16.71 mg/100 g) Vitamin C (2.24 mg/100 g) Beta-carotene (508.18 mg/100 g)	TPC (14.97 mg/100 g) Vitamin C (2.75 mg/100 g) Beta-carotene (523.26 mg/100 g)	

accelerates the freeze-drying process. This pretreatment protected the structure from collapse.

There are reports that freeze-dried apple and carrot also undergo collapse; however, compared with those dried by hot air or microwave, these freeze-dried products lose substantially less volume than their counterparts (Cui et al., 2008).

Variation in porosity

Using scanning electron microscopy (SEM), changes in a model system's microstructure can be studied, and the pore size of freeze-dried fruit can be measured. Similarly, SEM can be used to determine the size and shape of the particulates in pulverized fruits (Yeom and Song, 2010).

Porosity is defined as the relationship between fractional pore volume and the total food volume (Rahman et al., 2005). Porosity affects the texture and quality of dry foods and foods with moderate moisture levels. This characteristic is more important in freeze-dried foods than in microwaved or air-dried foods (Purnama et al., 2010).

The pores of dried products are composed of the small or large spaces formed by ice crystals during the freezing process. These spaces facilitate the diffusion of water vapor during the drying process. The porosity of freeze-dried fruit depends on the freezing speed, which, when slowed or augmented, can cause the ice to form smaller or larger pores, respectively (Voda et al., 2012). Slow freezing leads to the formation of voluminous crystals and pores that facilitate dehydration and subsequent rehydration (Jennings, 2002). Pore size has a small effect on vapor flow (Pardo and Niranjana, 2006).

Information about the characteristics of individual pores and structural characteristics of dried fruit can be used to design processes, determine product quality and estimate other properties such as thermal conductivity, density, water diffusivity and characteristics related to the extraction of bioactive components (Rahman and Sablani, 2003; Madiouli et al., 2012).

Porosity in fresh and freeze-dried fruit can be measured by comparing the apparent (ρ_u) and true density (ρ_r). Pore thickness can be measured using a method proposed by Madiouli et al. (2012) that includes open and closed pores. Direct experimental methods do not permit measurement of the formation of closed pores.

Freeze-dried ginseng has a total porosity of $77.15 \pm 0.93\%$. Freeze-dried pineapple, cherry, guayaba, papaya and mango all have porosity values between 84 and 93% (Marques et al., 2006).

Freeze-dried guanabana has medium-sized pores on the dry outer layer that are associated with rapid freezing (2.4 and 3.1°C/min), which causes the formation of smaller ice crystals. Medium-sized pores on the dry layer make sublimation more difficult and therefore increase the moisture level of the freeze-dried product (Ceballos et al., 2012).

Yellow pitahaya porosity is high (84.52%) compared to the porosity of fresh pitahaya (2.12%) and osmotically dehydrated pitahaya (48.17%) (Ayala et al., 2010). Freeze-dried papaya is less porous than freeze-dried guayaba and has a pore diameter less than 0.003 mm (Hawladar et al., 2006).

PHYSICAL CHANGES TO FRUIT DURING THE FREEZE-DRYING PROCESS

Color

The conservation of color is considered an indication of quality in dried fruits given that non-enzymatic browning processes develop during the drying process (Ceballos et al., 2012). Freeze-dried fruits better maintain red and yellow colors than fruits dried using traditional methods (Shishegarha et al., 2002). However, kinetic color analyses of freeze-dried fruit show some deterioration of reds and yellows (Guiné and Barroca, 2012).

Strawberries that are freeze-dried at temperatures below -50°C retain their color better than strawberries freeze-dried at temperatures above -50°C. This effect is due to a higher concentration of solutes (reduction of water) and the effects of pH on anthocyanin (Shishegarha et al., 2002). Fresh alpine strawberries maintained their color after freeze-drying; color values for freeze-dried strawberries were $L^* = 58$, $a^* = 23$, and $b^* = 26$, while these values were $L^* = 57$, $a^* = 23$ and $b^* = 26$ for fresh strawberries (Yurdugül, 2008).

Color variation in freeze-dried Granny Smith apples was lower ($3,537 \pm 1,717$) than the variation after convective drying [$5,279 \pm 0.989$], convective drying in a vacuum ($11,308 \pm 1,729$) and microwave drying ($5,958 \pm 0,580$) (Valencia et al., 2011).

Moßhammer et al. (2006) found that freeze-drying drastically affected the color of nopal, a change that can be attributed to the formation of soluble melanoidins. Pulverized nopal does not exhibit the same color change.

Sliced carrots maintain their color throughout the freeze-drying process. Sliced apples exhibit minor color variation (Cui et al., 2008). The loss of color in freeze-dried green peppers is minor compared to the color loss in air-dried peppers. However, comparing the color values L^* , a^* and b^* of fresh peppers (37.22 -14.11 and 22.52, respectively) and freeze-dried peppers (44.12 - 12.11 and 19.59, respectively), green color loss is noted, due to the decomposition of chlorophyll (Guiné and Barroca, 2012).

Guiné and Barroca (2012) reported that freeze-dried squash had L^* , a^* and b^* values of 77.70, 15.25 and 41.43, respectively, exhibiting color losses in red and yellow compared to fresh squash (68.97, 18.21 and 49.82).

Rapid freezing of guanabana (from 1.1 to 3.1°C/min) produced a more intense white value ($L^* = 85.10$ to 88.92).

This higher color intensity can be explained by small pores, (an effect of rapid freezing), due to, the small pores dispersing more light than large pores (an effect of slow freezing) (Ceballos et al., 2012). Freeze-dried papaya was more luminescent, and freeze-dried guayaba maintained better color than the same fruits dehydrated in a vacuum (Hawladar et al., 2006).

Glass transition

The glass transition temperature (T_g) is a key physical parameter that explains the chemical and physical behavior of a food system. Freeze-dried foods must have stable moisture levels and good packaging during storage. Absorption of additional moisture can lead to a state of amorphous disequilibrium, which brings with it a transformation from a glass solid state to a plastic fluid state when the glass transition temperature is reached (Duan et al., 2013). The glass transition temperature of dry solid would be an important optimization parameter for the freezing-drying process. This parameter can be used as useful tool for the choice of the most appropriate materials to be freezing-dried (Ratti, 2001).

Freeze-dried cubed apples were analyzed by differential scanning calorimetry (DSC). The T_g was below -30°C (Duan et al., 2013). The T_g of freeze-dried tomatoes was determined using DSC. The thermogram revealed the existence of two similar but distinct T_g values, which generated a water plasticization effect in hygroscopic regions of the product ($T_g = -50^\circ\text{C}$) (Telis and Sobral, 2002). Guizani et al. (2010) studied freeze-dried Deglet Nour palm dates using DSC. The thermograms generated showed a diminishing glass transition temperature (-13.8 to -48.7°C). However, the T_g rose with an increase of the solid content of the fruit. The T_g of the common mushroom (*Agaricus bisporus*) was as low as -77.9°C after freeze-drying (Shi et al., 2012). Freeze-dried kiwi [*Grosella espinosa* China] had a T_g of -57.2°C for optimal freezing-concentration conditions (Wang et al., 2008).

FUNCTIONAL CHANGES DURING THE FREEZE-DRYING PROCESS

Rehydration capacity and water retention

Rehydration capacity (RC) is the ability to reabsorb water relative to the water lost during dehydration, while water retention capacity (WRC) is defined as the ability to absorb and retain water relative to mechanical force. These indicators are related to the structure, the tissue and the capacity to retain absorbed water. Increases or decreases in these indicators can be attributed to the denaturation and/or aggregation of proteins due to heat, salt concentration, desorption of water and destruction of pectins in the cell membrane (Sanjuán et al., 2001). As

mentioned above, porosity also influences the rehydration capacity of freeze-dried fruits. The formation of large water crystals facilitates large pore formation, which in turn facilitates rehydration (Jennings, 2002).

The quality of a freeze-dried product is marked by the speed and ease of reconstitution or rehydration. Rehydration capacity is a key characteristic of freeze-dried fruit and is dependent on the size, geometry, composition, water content and porosity of the fruit (Sanjuán et al., 2001). Rehydratability is also affected by the method of rehydration utilized and the temperature, time and conditions of agitation (Arriola et al., 2006), as well as pre-treatment factors. Sliced yellow pitahaya, for example, has 24% less rehydration capacity when osmotically dehydrated prior to freeze-drying (Ayala et al., 2010). In avocado, the speed and capacity of rehydration are independent of immersion temperature (Arriola et al., 2006).

The rehydration capacities of freeze-dried carrots and apple chips (3.94 and 5.61, respectively) were similar to the values obtained by combined methods (microwave-freeze-drying) (3.95 and 5.22, respectively). Porosity was similar in both of these foods (Cui et al., 2008). Freeze-dried Chilean guava has an external appearance similar to that of the fresh fruit, although the freeze-dried product is gelatinous inside (Reyes et al., 2010).

The rehydration capacity of freeze-dried acerola is high (10.1 kg/kg) when it is frozen with liquid nitrogen at $73.6^\circ\text{C}/\text{min}$, which does not cause cell rupture in the samples (Marques et al., 2007). The rehydration capacity of freeze-dried yellow pitahaya is high, reaching a moisture content nearly equal to that of the fresh fruit (3.393 kg water/kg m.s) (Ayala et al., 2010).

CHANGES IN VOLATILE COMPOUND CONTENT IN FRUIT DURING THE PROCESS OF FREEZE-DRYING

Fruit aromas and flavors are transmitted by volatile compounds, such as esters, alcohols, terpenes (derived from the metabolism of mevalonic acid), aldehydes, carbonyl compounds, acids, brass, phenols, hydrocarbons, arylpropanoids (derived from the shikimic acid metabolic pathway), sulfur compounds and glucosinolates (derived from the amino acid metabolic pathway), among others (Wang et al., 2007; De Torres et al., 2010). Volatile compound content changes as fruit ripens. Ripe cocona, for example, has an increased concentration of esters and alcohols, decreased concentration of carbonyl compounds and high concentrations of methyl salicylate and α -terpineol, as well as (Z)-3-hexenol, though in lesser proportion. The concentrations of the aldehydes (Z)-3-hexenal, (Z)-2-hexenal and (E)-2-hexenal diminish as the fruit ripens (Quijano and Pino, 2006).

The volatile compounds in freeze-dried fruits are retained by entrapment in microregions of dry material. Loss of volatile compounds is due to adsorption of water

by the dry product, which increases the permeability of these dry regions and therefore, the loss of these compounds. Carbohydrate-carbohydrate bonds are replaced by carbohydrate-water bonds. However, for the critical water content, X_c , microregions remain sealed and cease to lose volatile compounds. X_c is defined as the water content at the transition point between the primary and secondary drying phases (Jennings, 2002).

Wang et al. (2007) demonstrated that freeze-dried plantains maintain their ester content. Esters are the most important volatile compound in plantains, though unlike enols, which are lost, esters have little influence on the aromatic profile of the plantains. Coffee that is freeze-dried under conditions with slow freezing and rapid drying retains aromatic compounds (Sagara et al., 2005). Grape peels in freeze-dried grapes retain terpenes, sesquiterpenes norisoprenoids, aldehydes and esters, among other compounds, which ensure wine quality (De Torres et al., 2010).

Analysis of apples by mass spectrometry and gas chromatography [GC/MS] showed that the volatile compounds most common in apples-ethyl acetate, ethyl butyrate and methyl anthranilate-were retained during the freeze-drying process (Krokida and Philippopoulos, 2006).

The chalarina (white zapote), a Peruvian fruit, retained a larger proportion of volatile and thermosensitive compounds, such as vitamin C, when dehydrated via freeze-drying (Castañeda et al., 2010). The majority of phenolic acids and volatile compounds were conserved in freeze-dried strawberries (Yurdugül, 2008).

CHANGES IN THE NUTRACEUTICAL CONTENT OF FREEZE-DRIED FRUIT

Total phenolic compounds (TPC)

Phenolic compounds are a large group of antioxidants that are present in nearly all plant-based foods. The measured total phenolic compound content depends on the type of fruit, ripeness, agricultural and climatic factors, post-harvest storage conditions and method of anti-oxidant extraction (Shofian et al., 2011).

Freeze-drying fruit can diminish the phenolic compound content because ice crystals formed during freezing can cause cell wall rupture and the subsequent release of oxidative and hydrolytic enzymes that degrade phenolic compounds (Chang et al., 2006). However, there are fruits, such as tomatoes and blueberries that have significantly higher levels of phenol compounds after freeze-drying. This effect is due to the liberation of phenolic compounds that had been trapped in the cell wall (Reyes et al., 2011).

The antioxidant content of freeze-dried açai was 255.1 mg/100 g of freeze-dried fruit for cyanidin-3-glucoside and 25 mg/100 g of freeze-dried fruit for ferulic acid

(Rojano et al., 2011). The polyphenol content in fresh Chilean guava is 1460 mg/100 g (dry mass), a value that drops at least 40% after freeze-drying. Freezing speed affects polyphenol content; rapid freezing led to a polyphenol content of 793 mg/100 g (dry mass), and slow freezing produced 815 mg/100 g (dry mass) (Reyes et al., 2010).

In watermelon, papaya, carambola, mango and melon, the levels of phenolic compounds decreased by 48.23, 39.73, 24.08, 23.19 and 10.41%, respectively, during the freeze-drying process (Shofian et al., 2011). The phenolic compounds found in strawberries, esters, terpenoids, carbonyl compounds and various alcohols and acids, do not change during the freeze-drying process (Yurdugül, 2008).

Reyes et al. (2011) demonstrated that freeze-drying diminished the phenolic compound content of blueberries from 832.9 mg/100 g to 769.2 mg/100 g (dry mass); however, this loss was insignificant compared to other dehydration methods. Freeze-dried Chilean guava lost 33.3 and 67.5% of the original total antioxidants after rapid and slow freezing, respectively (Reyes et al., 2010).

Ascorbic acid

Ascorbic acid content can decrease in high-temperature treatments, with this compound degrading when oxidized to dehydroascorbic acid and hydrolyzed to 2,3-diketogulonic acid. The latter can further polymerize to form other nutritionally inactive products (Chang et al., 2006). Some studies have indicated that freeze-drying allows the retention of ascorbic acid when the freeze-drying is conducted at low temperatures, minimizing deterioration of this water-soluble vitamin (Shofian et al., 2011).

Chang et al. (2006) compared the ascorbic acid content of fresh, freeze-dried and hot-air dried tomatoes and found that freeze-drying reduces the loss (8.2%) compared to hot-air drying (56-61%). The losses of vitamin C in the pulp of cherries, papaya, pineapple, mango and guava due to freeze-drying were 3.59, 24.2, 26.92 and 37%, respectively (Marques et al., 2006). Vitamin C loss was 10% in freeze-dried nopal and 50-55% in spray-dried nopal (Moßhammer et al., 2006).

Freeze-dried apples retain a larger proportion of vitamin C (97.0%) than microwave-dried (89%), air dried (63.7) or microwaved and freeze-dried (91.8%) apples (Cui et al., 2008). Chalarina (white zapote) lost 22.55% of its fresh ascorbic acid content when dried (29.75 mg/100 g) (Castañeda et al., 2010).

The original ascorbic acid content was preserved in freeze-dried carambola, mango, papaya, melon and watermelon. This study concluded that freeze-drying maximizes ascorbic acid retention and that freezing had a minimal degradation effect on vitamin C (Shofian et al., 2011). The ascorbic acid content of freeze-dried guanabana

declined from 81 mg/100 g to 40.57 mg/100 g under rapid freezing conditions (3.1°C/min), and from 81 mg/100 g to 53.76 mg/100 g under slow freezing conditions (1.1°C/min) (Ceballos et al., 2012).

The acerola is a Brazilian fruit with a high vitamin C content that varies according to maturity. The green fruit has 179.7 mg/100 g, the red-yellow fruit has 176.4 mg/100 g, and the red fruit has 149 mg/100 g. The vitamin C content declines significantly during the freeze-drying process, to values as low as 55.1 and 72.1 mg/100 g in green and red fruits, respectively. In the yellow-red fruit, vitamin C loss was 13% (Marques et al., 2007). Freeze-dried blueberries lose 60.43% of their initial vitamin C content (151.9 mg/100 g dry mass) during drying (Reyes et al., 2011).

β-Carotene content

β-Carotenes are compounds found in the lipid membranes or vacuoles of leafy green vegetables and yellow to orange fruits and vegetables. The degradation of phenolic compounds can lead to the degradation of β-carotenes (Shofian et al., 2011). Freeze-dried carrots retain 95.4% of their initial β-carotene; this value is a larger proportion than that obtained through other dehydration methods, including microwave and hot air dehydration (Cui et al., 2008). In the process of freeze-drying watermelon, mango, carambola and papaya, 43.1, 26.19, 15.75 and 8.16% of their initial β-carotene was lost, respectively (Shofian et al., 2011).

ADVANTAGES AND LIMITATIONS OF FREEZE-DRYING FRUIT

As has been demonstrated in the studies described, the effects of freeze-drying on physical and chemical properties vary in accordance with factors intrinsic to the fruit and extrinsic properties inherent to the process. Regardless, general advantages and limitations can be identified.

Among the advantages of freeze-drying are enhanced stability, rapid and easy solubility, prolonged shelf life, and increased availability and permanent access to fruit. Freeze-drying guarantees high-quality products with superior sensory and nutritional properties.

As with traditional dehydration methods, freeze-drying is not completely reversible by rehydration; however, damage to the hydrophilic groups responsible for the interaction with water is lower than that of other methods. Freeze-dried products rapidly rehydrate and regain water content and organoleptic properties similar to those of the fresh product (Jiang et al., 2010).

In comparison to products obtained through other dehydration methods, freeze-dried fruits have a more porous structure as well as superior flavor and aroma retention (Ceballos et al., 2012). High porosity facilitates

rehydration with water or other adequate solvents, and greater porosity is directly related to a greater rehydration capacity and is an indicator of product quality (Ayala et al., 2010). The reduction of volume during freeze-drying is minimal (Shishegarha et al., 2002). The temperatures reached in the freeze-drying process are outside of the range of temperatures that induce chemical changes in fruit. There is minimal loss of volatile compounds at freeze-drying temperatures (Yurdugül, 2008).

Freeze-dried fruits have a very low moisture content, which allows them to be stored for long periods; freeze-dried goods are highly stable products (Shishegarha et al., 2002). Freeze-dried fruits can be used as antioxidants and colorants in natural foods (Yurdugül, 2008). Freeze-drying allows the production of powdered fruit that can be used as base materials in the food and pharmaceutical industries. Freeze-drying is an ideal technology for consumers without access to fresh produce, such as astronauts (Aguilera and Stanley, 1999).

Among the limitations of freeze-drying is the cost. Freeze-drying requires long processing times and consumes large amounts of energy to freeze the fruit, sublimate the ice, dry the product and condense the vapor while maintaining vacuum conditions (Sadikoglu et al., 2006; Benloch et al., 2012). The vacuum pump and sublimation account for 26 to 45% of the total energy consumed in the process (Menlik et al., 2010). Equally important to energy costs are general operating conditions, such as the chamber pressure and heating and freezing speeds (Arriola et al., 2006). Structural collapse is a limiting factor for some fruits for which freeze-drying causes a wrinkled and compromised structure that cannot be reversed (Lee et al., 2006).

A final limitation, closely linked to freeze-dried product stability, is hygroscopicity. Freeze-dried products are highly hygroscopic, and further extension of the shelf life can be gained with the addition of solutes such as Arabic gum, tricalcium phosphate and maltodextrin that can increase product stability and act as a barrier to water absorption (Kaushik and Roos, 2007; de Oliveira et al., 2010; Fabra et al., 2011; Benloch et al., 2012; Ceballos et al., 2012; Mosquera et al., 2012).

In an effort to reduce energy costs when maintaining a high-quality product, investigators have sought to combine technologies such as microwave (Cui et al., 2008), hot air (Giraldo et al., 2010) and osmotic dehydration (Ayala et al., 2010) to eliminate a portion of the water before freeze-drying (Zhang et al., 2006). Table 2 outlines the investigations of combined dehydration technologies as a cost-saving measure.

CONCLUSIONS

The structural, physical, functional and nutraceutical effects of freeze-drying produce are dependent on intrinsic factors that are inherent to the fruit and to extrinsic factors that are inherent to the process. Freeze-drying

Table 2. Combining methods to reduce freeze-drying costs.

Fruit	Pre-treatment	Results	Citation
Chalarina (<i>Casimiroa edulis</i>)	Osmotic dehydration 63.57°Brix, 679.06 mmHg and 45.3°C.	4.87% of the total Vitamin C was lost during osmotic dehydration. When osmotic dehydration was combined with freeze-drying, the Vitamin C loss was 49.63%.	Castañeda et al. (2010)
Carrot	Microwave dehydration in a vacuum (MWV)	MWV carrots retained 94.7% of their original carotenoids MWV+freeze-dried carrots retained 94.9% of their original carotenoids.	Cui et al. (2008)
Apple	MWV dehydration	MWV apples retained 89% of their original Vitamin C MWV+freeze-dried apples retained 91.8% of their original Vitamin C.	Cui et al. (2008)

technology offers advantages and has limitations. Freeze-drying is an ideal method for heat-sensitive fruits that require special care during processing. In many fruits, properties such as shape, dimension, appearance, flavor, color, texture and nutraceutical ingredients are retained after freeze-drying, adding value of approximately 120%. The technology is equally valuable when a high rehydration capacity is required, as is the case for powdered freeze-dried fruit. Limitations to the application of this technology include the prolonged processing time, high-energy costs, high product hygroscopicity and undesirable physical changes such as collapse. Investigators have sought to lower freeze-drying costs through the use of pretreatments and the combination of freeze-drying with other dehydration technologies, such as hot air, microwave and osmotic dehydration.

Conflict of interests

The author(s) did not declare any conflict of interest.

REFERENCES

Aguilera J, Stanley D (1999). Microstructural principles of food processing and engineering. 2nd ed. Maryland, Aspen Publisher, Inc.

- Arriola E, García T, Guatemala G, Nungaray J, González O, Ruíz, J. (2006). The behavior of freeze-dried hass avocado during the rehydration process. *Revista mexicana de ingeniería química* 5(1):51-56.
- Ayala A, Giraldo C, Serna L (2010). Kinetics of osmotic dehydration of yellow pitahaya fruit (*Selenicereus megalanthus*). *Revista Interciencia* 35(7):539-554.
- Ayala A, Serna L, Mosquera E (2010). Freeze-drying in yellow pitahaya (*Selenicereus megalanthus*). *Vitae* 17(2):121-27.
- Benlloch M, Moraga G, del Mar M, Martínez N (2012). Combined Drying Technologies for High-Quality Kiwifruit Powder Production. *Food bioprocess Technol.* 6(12):3544-53.
- Castañeda J, Arteaga H, Siche R, Rodríguez G (2010). Comparative study of the loss of vitamin C in chalarina (*Casimiroa edulis*) by four methods of dehydration. *Scientia Agropecuaria* 1:75-80.
- Ceballos A, Giraldo G, Orrego C (2012). Effect of freezing rate on quality parameters of freeze-dried soursop fruit pulp. *J. Food Eng.* 111(2):360-365.
- Chang C, Lin H, Chang C, Liu Y (2006). Comparisons on the antioxidant properties of fresh, freeze-dried and hot-air-dried tomatoes. *J. Food Eng.* 77(3):478-485.
- Cui Z, Li C, Song C, Song Y (2008). Combined microwave-vacuum and freeze-drying of carrot and apple chips. *Drying Technol.* 26(12):1517-1523.
- De Oliveira C, de Resende J, Prado M, Cruvinel, R (2010). The effects of added sugars and alcohols on the induction of crystallization and the stability of the freeze-dried peki (*Caryocar brasiliense* Camb.) fruit pulps. *LWT Food Sci. Technol.* 43(6): 934-941.
- De Torres C, Díaz M, Hermosín I, Pérez M (2010). Effect of freeze-drying and oven-drying on volatiles and phenolics composition of grape skin. *Anal. Chim. Acta* 660(1):177-182.
- Duan X, Ding L, Liu L, Kong Q (2013). The drying strategy of atmospheric freeze-drying apple cubes based on glass transition. *Food Bioprocess Process.* 91(4):534-538.
- Duan X, Zhang M, Mujumdar A, Wang R (2010). Trends in microwave-assisted freeze-drying of foods. *Drying Technol.* 28(4):444-453.
- Fabra M, Márquez E, Castro D, Chiralt A (2011). Effect of maltodextrins in the water-content–water activity–glass transition relationships of noni (*Morinda citrifolia* L.) pulp powder. *J. Food Eng.* 103(1):47-51.
- Giraldo, A, Arévalo, A, Silva, A, Silva, P, Valdes, J, Pavlak, M, (2010). Kinetic drying experimental data and mathematical model for cupuaçu pulp (*Theobroma grandiflora*) slices. *Food Sci. Technol. (Campinas).* 30(1):179-82.
- Guiné R, Barroca M (2012). Effect of drying treatments on texture and color of vegetables (pumpkin and green pepper). *Food Bioprocess Process.* 90(1):58-63.
- Guizani N, Al-Saidi G, Rahman M, Bornaz S, Al-Alawi A (2010). State diagram of dates: Glass transition, freezing curve and maximal-freeze-concentration condition. *J. Food Eng.* 99(1):92-97.
- Harnkarnsujarit N, Charoenrein S (2011). Influence of collapsed structure on stability of β -carotene in freeze-dried mangoes. *Food Res. Int.* 44(1):3188-94.
- Hawladar M, Perera C, Tian M, Yeo K (2006). Drying of guava and papaya: impact of different drying methods. *Drying Technol.* 24(1): 77-87.
- Hincapié G, Omaña M, Hincapié C, Arias Z, Vélez L, (2010). Effect of the drying temperature on the functional properties of the dietary fiber contained in citropulp. *Rev. Lasallista Investig.* 7(2):85-93.
- Jennings T (2010). Lyophilization: introduction and basic principles. Florida. Interpharm.
- Jiang H, Zhang, M Mujumdar A (2010). Microwave freeze-drying characteristics of banana crisps. *Drying Technol.* 28(12):1377-1384.
- Kaushik V, Roos Y (2007). Limonene encapsulation in freeze-drying of gum Arabic-sucrosa-gelatin systems. *LWT Food*

- Sci. Technol. 40: 1381-1391.
- Khalloufi S, Almeida C, Bongers P (2010). A fundamental approach and its experimental validation to simulate density as a function of moisture content during drying processes. *J. Food Eng.* 97(2):177-187.
- Kirmaci V, Usta H, Menlik T (2008). An experimental study on freeze-drying behavior of strawberries. *Drying Technol.* 26(1):1570-1576.
- Krokida M, Philippopoulos C (2006). Volatility of apples during air and freeze-drying. *J. Food Eng.* 73(2):135-141.
- Lee K, Farid M, Nguang S (2006). The mathematical modelling of the rehydration characteristics of fruits. *J. Food Eng.* 72(1):16-23.
- Levi G, Karel M (1995). Volumetric shrinkage (collapse) in freeze-dried carbohydrates above their glass transition temperature. *Food Res. Int.* 28(2):145-151.
- Madiouli J, Sghaier J, Lecomte D, Sammouda H (2012). Determination of porosity change from shrinkage curves during drying of food material. *Food Bioprocess Technol.* 90(1):43-51.
- Marques L, Ferreira M, Freire J (2007). Freeze-drying of acerola (*Malpighia glabra* L.). *Chem. Eng. Process.* 46(4):451-457.
- Marques L, Prado M, Freire J (2009). Rehydration characteristics of freeze-dried tropical fruits. *LWT Food Sci. Technol.* 42(7):1232-1237.
- Marques L, Silveira A, Freire J (2006). Freeze-drying characteristics of tropical fruits. *Drying technology.* 24(4): 457-463.
- Menlik T, Ozdemir M, Kirmaci V (2010). Determination of freeze-drying behaviours of apples by artificial neural network. *Expert Syst. Appl.* 37(12):7669-7677.
- Montenegro G, Doak C, Solomons N (2009). Fruit and vegetable intake of schoolchildren on Quetzaltenango, Guatemala. *Rev. Panam. Salud Pública* 25(2):146-56.
- Mosquera L, Moraga G, Martínez N (2012). Critical water activity and critical water content of freeze-dried strawberry powder as affected by maltodextrin and arabic gum. *Food Res. Int.* 47(2):201-06.
- Moßhammer M, Stintzing F, Carle R (2006). Evaluation of different methods for the production of juice concentrates and fruit powders from cactus pear. *Innov. Food Sci. Emerg. Technol.* 7(4):275-87.
- Ocoro M, Ayala A (2012). Evaluation of the refractance window™ technique on drying of papaya (*Carica papaya* L.) purée. *Vitae* 19(1): 72-74.
- Orrego C, Pamplona F, Perez V (2009). Low pressure water diffusivity measurements of freeze-dried tomato tree (*Cyphomandra Betacea* (Cav) Send) juice. *Ireche* 1(5):1-8.
- Pardo M, Niranjan K (2006). Modeling of the relationship between freezing kinetics and sublimation kinetics in coffee brews. *Revista Ingeniería y competitividad* 8(2):25-33.
- Prado S, Buera M, Elizalde B (2006). Structural Collapse Prevents β -Carotene Loss in a Supercooled Polymeric Matrix. *J. Agric. Food Chem.* 54(1):79-85.
- Purnama M, Yaghmaee P, Durance T, Kitts D (2010). Porosity Changes and Retention of Ginsenosides in North American Ginseng Root Using Different Dehydration Processes. *J. Food Sci.* 75(7):E487-92.
- Queiroz V, Berbert P, Molina M, Gravina G, Queiroz R, Sliva J (2008). Qualidade nutricional de goiabas submetidas aos processos de desidratação por imersão-impregnação e secagem complementar por convecção. *Ciencia e tecnologia de alimentos* 28(2):329-340.
- Quijano C, Pino J (2006). Changes in volatile constituents during the ripening of cocona (*Solanum sessiliflorum* Dunal) fruit. *Revista CENIC Ciencias Químicas* 37(3):133-136.
- Rahman M, Al-Zakwani I, Guizani N (2005). Pore formation in apple during air-drying as a function of temperature: porosity and pore-size distribution. *J. Sci. Food Agric.* 85(6):979-89.
- Rahman M, Sablani S (2003). Structural characteristics of freeze-dried abalone: porosimetry and puncture test. *Food Bioprocess Technol.* 81(4):309-315.
- Ratti C (2001). Hot air and freeze-drying of high-value foods: a review. *J. Food Eng.* 49:311-319.
- Reyes A, Bubnovich V, Bustos R, Vásquez M, Vega R, Scheuermann E (2010). Comparative study of different process conditions of freeze-drying of 'Murtilla' Berry. *Drying Technol.* 28(12):1416-1425.
- Reyes A, Evseev A, Mahn A, Bubnovich V, Bustos R, Scheuermann (2011). Effect of operating conditions in freeze-drying on the nutritional properties of blueberries. *Int. J. Food Sci. Nutr.* 3(62):303-306.
- Rojano B, Vahos I, Arbeláez A, Martínez A, Correa F, Carvajal L (2011). Polyphenols and antioxidant activity of the freeze-dried palm naidi (Colombian Açai) (*Euterpe oleracea* Mart). *Revista Facultad Nacional de Agronomía* 64(2):6213-20.
- Rothmayr W (1975). Basic knowledge of freeze-drying. *Freeze-Drying and Advanced Food Technology.*
- Sadikoglu H, Ozdemir M, Seker M (2006). Freeze-drying of pharmaceutical products: Research and development needs. *Drying Technol.* 24(7):849-861.
- Sagara Y, Kaminishi K, Goto E, Watanabe T, Imayoshi Y, Iwabuchi H (2005). Characteristic evaluation for volatile components of soluble coffee depending on freeze-drying conditions. *Drying Technol.* 23(9-11):2185-2196.
- Sanjuán N, Cárcel J, Clemente G, Mulet A (2001). Modeling of the rehydration process of broccoli florets. *Eur. Food Res. Technol.* 212(4):449-453.
- Santos P, Silva M (2008). Retention of vitamin C in drying processes of fruits and vegetables - A review. *Drying Technol.* 26(12):1421-1437.
- Shi Q, Wang X, Zhao Y, Fang Z (2012). Glass transition and state diagram for freeze-dried *Agaricus bisporus*. *J. Food Eng.* 111(4): 667-674.
- Shishegarha F, Makhlof J, Ratti C (2002). Freeze-drying characteristics of strawberries. *Drying Technol.* 20(1):131-45.
- Shofian N, Hamid A, Osman A, Saari N, Anwar F, Pak Dek M, Hairuddin M (2011). Effect of Freeze-Drying on the Antioxidant Compounds and Antioxidant Activity of Selected Tropical Fruits. *Int. J. Mol. Sci.* 12(7):4678-4692.
- Sijtsema S, Zimmermann K, Cvetkovic M, Stojanovic Z, Spiroski I, Milosevic J, Mora C, Butigan R, Mugosa R, Esteve M, Pohar J (2012). Consumption and perception of processed fruits in the Western Balkan region. *LWT Food Sci. Technol.* 49(2):283-297.
- Telis V, Sobral P (2002). Glass transitions for freeze-dried and air-dried tomato. *Food Res. Int.* 35(5):435-443.
- Valencia C, Rodríguez H, Giraldo P (2011). Drying kinetics and oxidation control in Granny smith apples, through different drying methods. *Revista Tumbaga* 6(7):7-16.
- Villamizar R, Giraldo G (2010). Obtaining and characterization of a chip from a base of mango pulp through immersion frying. *Revista Tumbaga* 5:149-164.
- Voda A, Homan N, Witek M, Duijster A, van Dalen G, van del Sman R, Nijse J, van Vliet L, Van As H, van Duynhoven J (2012). The impact of freeze-drying on microstructure and rehydration properties of carrot. *Food Res. Int.* 49(2):687-693.
- Wang J, Li Y, Chen R, Bao J, Yang G (2007). Comparison of volatiles of banana powder dehydrated by vacuum belt drying, freeze-drying and air-drying. *Food Chem.* 104(4): 1516-1521.
- Wang, H, Zhang S, Chen G (2008). Glass transition and state diagram for fresh and freeze-dried Chinese gooseberry. *J. Food Eng.* 84(2): 307-312.
- Welti J, Vergara F, Pérez E, Reyes A (2005). Fundamentals and new tendencies of freeze-drying of foods. Universidad de las Américas. Segundo Simposio Internacional de Innovación y Desarrollo de Alimentos.
- Yeom G, Song C (2010). Experimental and numerical investigation of the characteristics of spray-freeze drying for various parameters: Effects of product height, heating plate temperature, and wall temperature. *Drying Technol.* 28(2):165-179.
- Yurdugül S (2008). An evaluation of the retention of quality characteristics in fresh and freeze-dried alpine strawberries. *Int. J. Food Sci. Technol.* 43(5):865-870.
- Zhang S, Tang J, Mujumdar A, Wang S (2006). Trends in microwave related drying of fruits and vegetables. *Trends Food Sci. Technol.* 17(10):524-534.