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THEORETICAL RESEARCH ON FOREST FRUIT CONSERVATION BY LYOPHILIZATION

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Abstract: *The paper presents several theoretical aspects related to the technological process of forest-fruit conservation by lyophilization. Lyophilization has proved to be particularly effective, because it ensures product conservation for long periods, without significant loss of physico-chemical properties. It proves that the use of lyophilization in the plant-origin food industry constantly extends, this method offering superior results compared to other conservation methods.*

Key words: *forest fruits, conservation, lyophilization.*

1. Introduction

Lyophilization (freeze drying) is a conservation method based on the removal of water from food by vacuum sublimation, thus inhibiting the development of bacterial flora [3]. Lyophilization is achieved by food freezing, followed by virtually eliminating water, by sublimation (water tums directly into vapour) under vacuum conditions, with controlled heat intake [5].

In the case of forest fruits, by lyophilization, they are frozen; then, at high pressure, the water is extracted, thus obtaining a fruit “squeezed” of water, but with all nutritional values intact [6].

Lyophilization causes food to dehydrate, without losing, or perhaps only to a small extent, its nutritional qualities, but preserving its aroma. In the case of nutritional substances, the vitamins A, C and E are the most affected, although they suffer only moderate losses. Fibers, antioxidants and phytonutrients remain at unchanged levels after lyophilization.

This dehydration process was developed in the Second World War, in order to easily transport the medicines which required storage at low temperatures. Since then, this dehydration has been extended to other products, including food.

According to the American Institute for Research on Oncology, lyophilized food is a way to supplement the intake of phytonutrients and antioxidants from freshly consumed food. The same institute supports the research conducted at Ohio State University, which shows how the phytonutrients from lyophilized forest fruits can protect the body against colon and oesophagus cancers [2].

Also known as cryosublimation or “freeze drying”, lyophilization is a

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dehydration process by cold: water freezes faster than the other components and is eliminated as ice. This technique allows food conservation in good conditions, while preserving the colour, flavour and essential nutritional values (vitamins, enzymes) [4].

Lyophilized fruits are superior to:

- candied fruits, as they do not contain excess sugar, they are not rich in carbo-hydrates, and they do not have high calories;
- dried fruits, as their nutritional values are not lost, they do not contain dyes and additives to improve the aspect of the fruit;
- frozen fruits, as they do not contain excess water and they can be kept anywhere (not only in the freezer) [6].

Lyophilized products do not require low temperatures for storage and transport. By lyophilization, the product weight decreases at 1/4….1/10 of the initial value, a phenomenon accompanied by a reduction in volume.

2. Material and Method

2.1. Technique of Lyophilization

The lyophilization process is based on biology and physics principles, namely: anabiosis, freezing and sublimation in vacuo, which are analysed below:

a) *anabiosis:*

- after lyophilization, organic substances are transformed into dry substances;
- in this case, the vital changes from the lyophilized cells are very much reduced, or cease to exist altogether, a phenomenon known as *anabiosis*;
- organic substances thus transformed keep all their characteristics unchanged for a long time.

b) *freezing and drying in vacuo:*

- the use of lyophilization for product
- drying stood out, due to its keeping most of their characteristics intact, stopping any fermentation, any enzymatic action, hence making products keep their physiological state they had at the time of freezing;
- the way in which lyophilization is
- performed has a great importance on the success of fruit conservation.

The most important lyophilization procedures are the following:

- *slow lyophilization*, which targets the gradual loss of latent heat, so that the temperature of the material drops with 0,5...1°C/minute. During the freezing, ice crystals are formed, whose size depends on the freezing speed. In the case of slow freezing, these crystals have a size of several microns, and in the case of extremely slow freezing, the crystals reach a size of a few millimeters.
- *rapid lyophilization,* which targets the heat loss from the material to be frozen. In this case, the temperature drops from +20°C to -170°C in 0,5 ... 1 seconds.

  Rapid freezing has the advantage of giving the product a higher porosity, by multiplying small-sized ice crystals. The rehydration of the product lyophilized in this way is made in better conditions.

c) lyophilization in protective substances, which supposes the material to be frozen to undergo, before freezing, the protective action of a colloidal substance.

The drying which occurs in the case of lyophilization differs from evaporation, hence from distillation, in that the water loss is made by sublimation of the vapour from the solid matter, whereas for the distillation, the substance must be in liquid form.

The basic feature of lyophilization is the direct passage of water from solid form (ice) into the form of water, hence sublimation accompanied by the elimination of the formed vapours [1].

2.2. Influence of Lyophilization on Forest Fruits

The influence of lyophilization on forest fruits is manifested by physical, chemical and biochemical changes.

- **Physical changes**

Depending on the product, on the freezing modality and on the parameters of the lyophilization process, cryodesiccation leads to a volume lessening by 2…10% compared to the fresh product; at the same time, the weight reduces to 50…90% of the initial value.

Lyophilization can cause changes in the product colour, which are due to water removal, and to chemical and biochemical reactions, which may also occur because of the deficiencies in the technological process of lyophilization. Most often, the darker colour of the lyophilized products does not influence the product quality.

After rehydration, the product texture changes from the initial situation; basically, the slower the freezing, the more the rehydrated product will have a softer texture, which can be accentuated in case of over-rehydration. As for liquid products, their viscosity decreases after rehydration.

After the rehydration of the product, changes in taste and smell, from the initial situation, may also occur.

- **Chemical and biochemical changes**

Chemical and biochemical modifications result from reactions of substitution, oxidation etc., which make some of the original constituents disappear during rehydration, and new constituents appear instead. Ultraviolet radiations can catalyse some reactions.

- **Changes in nutritional value**

The preservation of the nutritional value of lyophilized products, after rehydration, depends on the product type and process parameters. Thus, a lower freezing speed will entail destruction of cell walls; as a result, the active principles are freed, and reactions occur which diminish the nutritional value.

2.3. Stages of the lyophilization process

The stages of the lyophilization process for forest fruits are shown in Fig. 1.

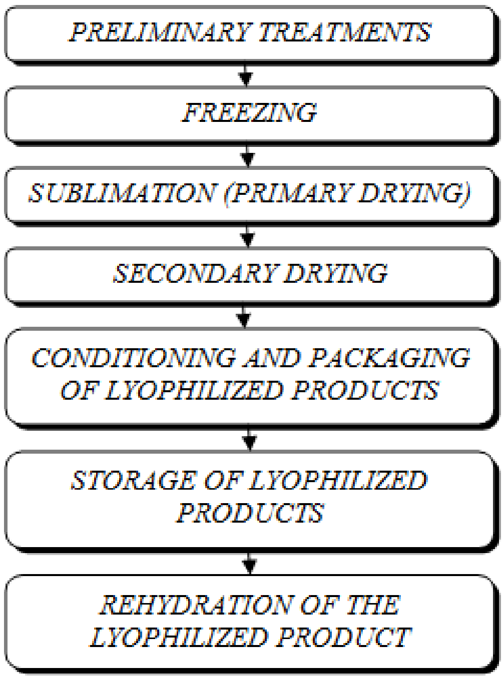

Fig.1. *Stages of the lyophilization process for forest fruits*

The scheme of the lyophilization process for forest fruits is shown in Fig. 2.

The most important aspects targeted at each of the stages specified in Fig. 1 are developed below.

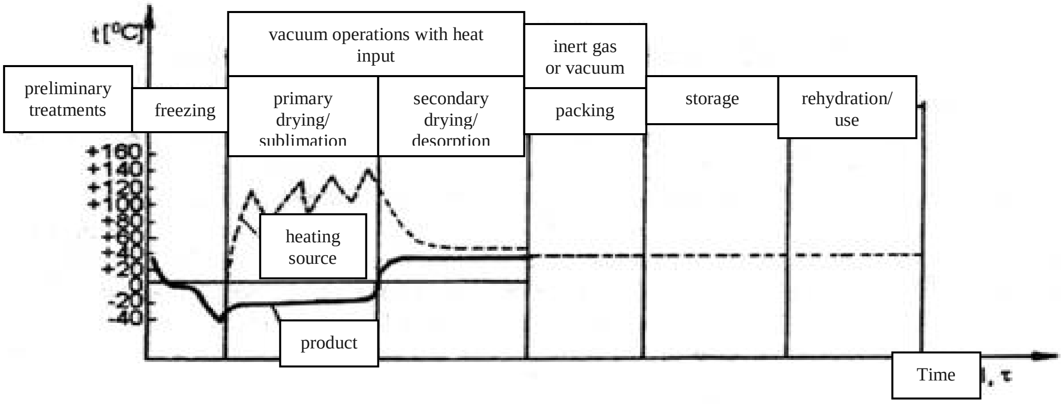

Fig. 2. *Diagram of the lyophilization process*

2.3.1. Preliminary treatments

Any product to be lyophilized must be of superior quality, must have a high content of dry matter, and a low content of fats and bound water.

The product must have a surface/volume ratio as high as possible, for the sublimation to be favoured. In products with low thickness and large surface area, the sublimation front will advance faster towards the centre and therefore the sublimation duration will be shorter; In products with high thickness, as the sublimation front advances, the vapours inside will take more time leaving the product.

The products must be distributed as evenly as possible in the place where the sublimation occurs, for the sublimation process to take place as far as possible identically for each product.

Depending on the nature of the product, it may undergo preliminary treatments before lyophilization; these treatments may be:

– of mechanical nature (milling, grinding, chopping, mincing etc.);
– of physical nature (boiling/ blanching);
– of chemical nature (adding substances with a view to protecting the product or to obtaining specific qualities).

2.3.2. Freezing

Freezing produces mechanical and physical effects: the mechanical effects refer to cell breaks, tissue tears, cell-wall perforation; the chemical effects are caused by the concentration of the solutions within the product, due to water solidification. The diminution of these effects is enabled by the fastest freezing possible of the products to be lyophilized. High freezing speeds lead to evenly distributed small-sized ice-crystal formation, and the solution-concentration phenomenon takes too little time to affect the product quality.

The final temperature of the product, after freezing, must be low enough for the whole water quantity to be solidified; the final temperatures recommended can reach values of -40…-60^{0}C.

2.3.3. Sublimation (primary drying)

In the primary-drying phase, the free water and constitutive water are eliminated from the product. In order to achieve the sublimation, the product is introduced into chamber 1 (Fig. 3) which is hermetically closed; by a vacuum pump 5, the pressure in the chamber is reduced to values of 0,3…1 mm Hg. The pressure is lower than the one corresponding to the triple point of water, as the water contained by food products is not chemically pure.

With a view to sublimating ice, the shelves 2 on which the products are placed, can be heated in a controlled way, by means of heating plates; by increasing temperature, the process of transformation from the solid to the liquid state occurs. The heat flow must be permanently controlled in order to avoid the partial defrosting of the products.

For the sublimation to take place continuously, it is necessary to evacuate the vapour from the enclosure. Given that the large volume of resulting vapour cannot be evacuated by the vacuum pump, the water vapours resulted from the sublimation are condensed on the cold surface of the vaporizer 3, located in the condensation chamber 6. The installation further includes the set 4 which consists of a compressor and a condenser.

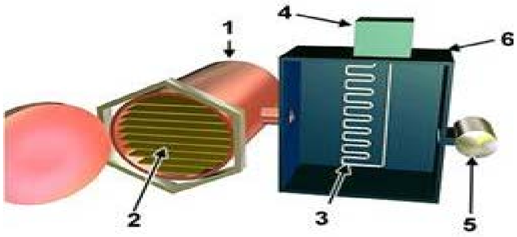

Fig. 3. *Schematic diagram of the installation for cryodesiccation*

During this process, the temperature of the heating plates reaches 120…140^{0}C, and the temperature of the products is -25…0^{0}C (Fig. 4).

In the late primary-drying phase, the product also contains 10…30% water, which is in adsorbed liquid form, and in vapour state. This quantity of water has negative effects on the product behaviour during the storage phase. In order to eliminate this quantity of water, the secondary drying phase is applied.

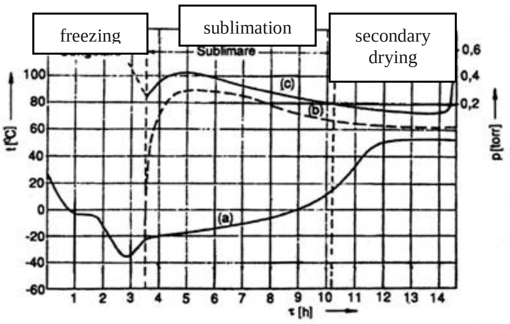

Fig. 4. *Evolution of the parameters of the cryodesiccation process*

2.3.4. Secondary drying

This phase aims at eliminating the water remaining from the previous phase; in the late secondary-drying phase, the quantity of water in the water drops below 6% possibly reaching 2…3%, depending on the type of product.

In order to eliminate the water, the chamber pressure must be below 1 mm Hg; the product surface temperature rises to 20…40^{0}C for sensitive products, such as forest fruits (Fig. 4). The passage from the sublimation temperature to the adequate temperature for water desorption is made faster or slower, the duration of the secondary drying ranging between 1-6 hours. Primary and secondary drying can last 6-20 hours in total.

After the completion of the secondary drying, the drying chamber is pressurized (usually with a neuter gas-argon or carbon dioxide) up to a slightly superior value to the barometric pressure. This prevents the air outside to enter, upon opening the drying chamber door.

In Fig. 4, the notations have the following meanings: a-product temperature; b-temperature of heating plates; c-pressure in the drying chamber [5].

Fruits are products frequently conserved by lyophilization. By fruit dehydration, as a result of the previously described lyophilization process, the fruit nutrients (sugars, antioxidants, mineral salts, fibres) are very well kept. Due to the presence of sugars in lyophilized fruits, they have a high energy value [1].

2.3.5. Conditioning and packaging of lyophilized products

Following the two drying phases, the lyophilized product is porous and hygroscopic; the contact with the water vapours in the air may lead to the rapid imbibition of the pores with water vapours, a phenomenon which cancels the effect of secondary drying. A residual moisture content higher than 2…6% will have negative effects on fruit quality (enzymatic reactions occur, microbial flora develops, the product discolours etc.). For this reason, it is recommended, immediately after removing the fruits from the chamber where the lyophilization occurred, to store them for 2…3 days in vacuum containers of large capacities, in order to homogenize the residual moisture content. After this stage, definitive conditioning is made in small-sized packages. Lyophilized products are conditioned and packed, with a view to minimizing the causes that determine changes in product quality during storage. Lyophilized products are packed in vacuo or in controlled atmosphere (azote, carbon dioxide or dry air for the less sensitive products). Packaging materials must be impermeable to fats, gases, water vapours, and the packages must be sealed.

Lyophilized products are packaged in:

- aluminium or steel sheet boxes, with a closure system allowing packaging in vacuo or in controlled atmosphere;
- glass packaging, rarely used, because of greater curb weights, or the difficulty in ensuring their tightness and transparency;
- multilayer packaging, consisting in plastic and metallic foils.

2.3.6. Storage of lyophilized products

The storage temperature influences the preservation life of lyophilized products; most products can be stored at temperatures up to 30^0C without negative effects. The maximum duration of preservation varies between 1-5 years [5].

2.3.7. Rehydration of the lyophilized product

Lyophilized forest fruits are rapidly and totally rehydrated, by adding water.

2.4. Way of working

The saturation curve diagram for water (Fig. 5) shows that water sublimation (the passage from the solid into the vapour state) occurs only if the pressure is below the one corresponding to the triple point (PT), this being lower than 4,579 mm Hg (0,006 bar); from figure 4, it also follows that, at constant pressure, the sublimation occurs by increasing temperature, hence with heat intake. The definition of lyophilization as a process of sublimation in vacuo (much lower pressure than normal atmospheric pressure), with heat intake (in order to raise the product temperature) is thereby justified. It should be noted that the ice sublimation process also occurs at normal atmospheric pressure: at a temperature of -5^0C and a relative humidity of 20%, the partial pressure of the water vapours in air is 0,6 mm Hg (being thus lower than the pressure of the triple point), the ice sublimating up to the vapour saturation of the surrounding environment.

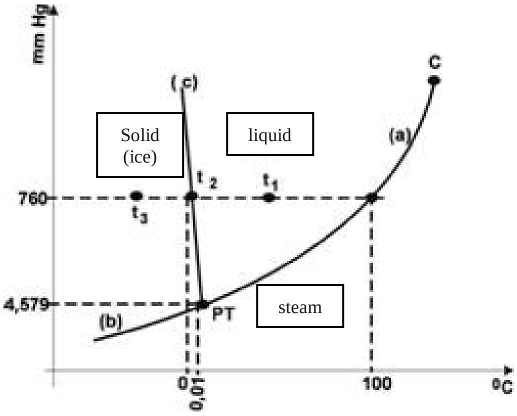

Fig. 5. *Saturation curve diagram for water*

3. Results and Discussions

The forest-fruit lyophilization technique differs from the one of drying all the other products of plant origin, as they are different in chemical, histological, physiological terms.

Forest fruits have a very high-water content, of approximately 88%, they contain hydrocarbonated substances, organic acids of malic, tartaric or citric type, essential oils, phenolic compounds, etc.

By lyophilization, most of the inconveniences of the preservation by freezing, or drying by heat, such as: loss of taste, smell, aspect are removed [1].

The nutritional values before and after the lyophilization process of some forest fruits are shown in Table 1.

Nutritional values of fresh, respectively lyophilized forest fruits [3], [6], [7], [8], [9] Table 1

Nutritional values FRESH fruit	Fruit assortment	Nutritional values LYOPHILIZED fruit
Nutritional values **per 100g** Water 84,5g Energy value 41 kcal (172 kj) Proteins 1,8g Sugars 8,1g	Cranberries 	**Nutritional values** **per 100g** Energy value 212 kcal (1157 kj) Proteins 3,8g Sugars 14,5g Fibres 15g
Nutritional values **per 100g** Water 90g Energy value 41 kcal (172 kj) Proteins 1,0g Sugars 9,0g	Strawberries 	**Nutritional values** **per 100g** Energy value 289 kcal (1229 kj) Proteins 7,2g Sugars 18,6g Fibres 15g
Nutritional values **per 100g** Water 86,5g Energy value 46 kcal (192 kj) Proteins 0,4g Sugars 11,3g	Red currants 	**Nutritional values** **per 100g** Energy value 355 kcal (1480 kj) Proteins 2,6g Sugars 0g Fibres 34g
Nutritional values **per 100g** Water 85g Energy value 40 kcal (167 kj) Proteins 1,0g Sugars 8,0g	Black currants 	**Nutritional values** **per 100g** Energy value 190 kcal (810 kj) Proteins 7,1g Sugars 3,8g Fibres 42,9g
Nutritional values **per 100g** Water 87g Energy value 41 kcal (172 kj) Proteins 0,8g Sugars 9,0g	Raspberries 	**Nutritional values** **per 100g** Energy value 192 kcal (814 kj) Proteins 8,6g Sugars 6,6g Fibres 44,1g

4. Conclusions

The first condition for obtaining high-quality lyophilized forest fruit, is to use the best-quality raw material, their correct processing before lyophilization, and especially throughout the lyophilization process.

Forest fruits are generally more difficult to treat, both by means of freezing and preserving by heat, due to the change in the organoleptic characteristics, such as: loss of their initial aspect, form, taste and aroma, their emaciation and even caramelization, destruction of vitamins, etc., however by lyophilization, all these inconveniences are much improved or even completely removed.

Advantages of using lyophilization:

- Lyophilized foods keep much of their nutritional value, having withal a longer period of validity, they can be hydrated and used at will [2];
- Lyophilized foods can be easily transported, at normal temperatures, and they can be consumed with a minimum preparation effort;
- Lyophilized fruits offer a great advantage to the persons who want to lose weight, inasmuch as they give the persons who eat even a small amount of fruit, a feeling of satiety;
- Lyophilized fruits present a low weight, the absence of water, they do not allow microbial development, the aroma and nutrients of fruits are kept unaltered, they can be stored without refrigeration, they can be easily rehydrated etc.
- Lyophilized fruits can be consumed in breakfast cereals or even as a simple snack.

Disadvantages of using lyophilization:

- High costs of the investments, as the installations are three times more expensive than in case of other methods;
- The relatively complicated working technique and lengthy process (approximately 24 hours);
- High energy consumptions.

Due to the success of lyophilization in the case of forest fruits, the sphere of action of lyophilization was subsequently extended over other products [1].

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