FREEZE DRYING - NOTABLE ADVANCEMENTS IN SUBLIMATION - DRYING OF FOODS

Ramona Cotruț 1*

1 Research Center for the Study of Quality Food Products, 59 Mărăști Blvd, District 1, 011464, Bucharest, Romania, Phone: +4021.318.25.64, Fax: +4021.318.25.67

Abstract
Freeze drying is one of the best methods of water removal which results in final product with the highest quality, combining science and controlled process to result in beautifully preserved food. Freeze drying is sublimation of ice fraction where water passes from solid to gaseous state. Suitable parameters of process application allow us to obtain best quality products compared to products dried with traditional methods. Due to very low temperature all the deterioration activity and microbiological activity are stopped and provide better quality to the final product retaining the most nutrients than any other food preservation method, and maintains its color and flavor. Given the fact that food and biotechnological products maintain their physical and chemical properties we can affirm that lyophilization is the best method for drying products. This review focused on the recent advances and its targets in near future, considering also that the market for organic products is increasing and new market demands are emerging that could concern freeze-dried products.

Keywords: food preservation, freeze-dried, lyophilisation, sublimation.

1. INTRODUCTION
Drying from the frozen state is not uncommon in nature. One example of the natural phenomenon is the snow disappearing along the roads without melting, as also the discovering of the freeze-dried mammoths dated according with the science from the past 15,000 years (Shukla, 2011). Freeze drying foods exist from ancient peruvian incas, they were ahead of their time when it came to science. The Incas in the Peruvian high plateau, stored meat in their tambos, that had been dried in the sun at the reduced pressure of the Andes. Also they would place their potatoes and other crops above Machu Picchu where the produce would freeze. The low pressure of the high altitudes vaporized the water in the produce, essentially freeze drying it.

The scientific interest in freeze-drying began at the turn of the twentieth century with a publication by Bordas and d'Arsonval at the French Academy of Sciences (Shukla, 2011). Modern freeze-drying was developed during World War II when the first commercial use was used to dry blood plasma and penicillin.

Traditionally food drying products were made by using the sun energy, now days due to all scientific improvements drying technologies have multiple options: kiln drying, tray drying, spray drying, freeze drying, osmotic drying, microwave drying and refractance window drying (Humberto et al., 2001). However, the quality loss mostly caused by oxidation and the product contamination has led to the development of alternate drying technologies (Bezyma and Kutovoy, 2005). Freeze
drying is known to be the best drying technology which results in final products of the highest quality (Cohen and Yang, 1995; Sagar and Suresh, 2010). Freeze dried products have the most desirable properties with preserved texture of fresh foods without negatively impacting their structure. The freeze-drying consists in freezing the food at first, then in eliminating the ice, leaving only a dry, porous and high-quality food. Lyophilisation or freeze drying is a low temperature dehydration process which involves freezing the product, lowering pressure (< 300 Pa) under a vacuum, then removing the ice by sublimation, were the ice changes from solid to vapour without passing through a liquid phase (Shukla, 2011).

2. PRINCIPLE

The lyophilization (or freeze-drying) process falls into three stages: freezing, the primary drying stage and the secondary drying stage, in which water is frozen, followed by removal of water from the sample, initially by sublimation (primary drying) and then by desorption (secondary drying). According to Liu et. Al., 2008, the process within the three stages, includes the following operations: freezing, sublimation, desorption, vacuum pumping and vapor condensation. The material to be dried is first frozen and then subjected to hot vacuum (by conduction or by radiation or both) so that the frozen liquid sublimates leaving only solid, dry components of the original product. The lyophilization process of removing water from a product by sublimation and desorption is carried out at temperatures and pressure conditions below the triple point (0.00603 atm/4,579 mm Hg and 0,0099º Celsius), to allow sublimation of the ice (Chien and Yiew W. 1981, Lavakumar et al, 2013). Sublimation occurs when the vapor pressure and the temperature of the ice surface are below those of the triple point, as shown in the pressure-temperature phase diagram of pure water (Figure 1).

Figure 1. Phase diagram showing the triple point of water at 0.01°C, 0.00603 atm

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*Corresponding author, E-mail address: ramona_cotrut@yahoo.com
3. THE PROCESS OF LYOPHILIZATION

Freeze-drying stages involves three essential Steps: freezing, the primary drying phase and the secondary drying phase (Welti-Chanes et al., 2004) (Figure 2).

**Freezing** - Freezing is a very important part of lyophilization, since influence on the shape, size and distribution of the ice crystals and thus, on the drying process and the final structure of the freeze-dried product.

To start the freeze-drying process, first of all it is necessary to freeze the raw material. It is important that the structure of the raw material remains unchanged and therefore products are shock frozen directly after harvesting. Freezing is usually done using a freeze-drying machine, and according to Shukla the freezing temperatures should be between −50°C and −80°C (Shukla, 2011). A fast freezing of the product will lead to smaller and irregular ice crystals being formed, making it impossible to achieve a uniform drying. A poorly frozen product will bubble when under vacuum conditions. This indicates the product is not 100% frozen. The temperature for freezing products should be about -20°C, but for products with high sugar, fat or acid contents the freezing temperature should be about -40°C. The optimal way to define the freezing phase for lyophilization is to experimentally determine it for each product.

**Primary drying** - The second step of the process is the extraction of water from the raw material. The individually quickfrozen (IQF) product is placed in a vacuum chamber. Under very low pressure, the frozen water contained in its structure is evacuated in the form of steam. This is called sublimation. To speed up the sublimation process, low temperature heat is used, as low as 35°C. The drying chamber and the condenser area are kept under vacuum in order to support the migration
of water vapour to the condenser where it is deposited in the form of ice, making sure that the vacuum is below the threshold required for sublimation.

**Secondary drying** - After the free ice has been removed by sublimation, the product still contains bounded water that could affect shelf life and quality. During the post-drying the most strongly bounded water inside the product is converted into steam. The fruits used for the process of lyophilization are taken from the freezing chamber and transported to the processing chamber. On the working table in the processing chamber, the deeply frozen fruits are put on the stainless steel plates and equally arranged over the surface (Figure 3).

![Figure 3. From fresh raspberry to frozen fruits until freeze-dried products ready for consume using a lyophilization system with stainless steel plates](image)

Time for performing the process of lyophilization can vary from 30, 40 to 72 hours depending on the quantity, size and the type of the deeply frozen fruits. In the meanwhile, the vacuum, temperature and other values parameters are constantly monitored.

To develop the optimization of a freeze-drying cycle, critical temperature determination is highly important. During primary drying, the drying temperature must not exceed the critical temperature which otherwise results in the phenomenon called "melting" or "collapse" (Rambhatla and Pikal, 2003).

Rindler et al. in 1999, have investigated different pretreatment methods applied before freeze-drying and modification of the freeze-drying process. They were able to show a significant dependence of the recovery rate on the shelf temperature, explaining that if the shelf temperature is too high, the sample can be damaged creating the following possible reactions: recrystallization, diversification, glass transition or collapse.

*Corresponding author, E-mail address: ramona_cotrut@yahoo.com*
4. APPLICATIONS

Today a great variety of foods, pharmaceuticals, etc. are produced by lyophilization. Lyophilization, or freeze-drying is used to preserve the, vaccines, blood samples, purified proteins, DNA, enzymes, antibiotics, bacterial cultures and other biological material; becoming an increasingly popular method for the long-term preservation of various biological materials (Ciurzyńska, 2011). In a recent report on Orbis Freeze-Dry Food Market, it provides a punctual analysis for changing competitive dynamics and a perspective on the various factors that drive or restrict industry growth. The global freeze-dried product market is expected to grow during the forecast period of 2016-2021.

Market segmentation - The freeze-dried product market is segmented by the product type that includes freeze-dried fruits and berries, vegetables, beverages (coffee, tea and other extracts and liquids), meat and sea food, dairy products and prepared meals, milk products, dyes, pharmaceuticals, pigments and enzymes.

Fruits and vegetables are heat sensitive products, which are more liable to loss of vitamins and minerals when exposed to high temperature. Freeze-drying technology preserves necessary vitamins and antioxidants during dehydration, which increases its importance among the drying techniques. Freeze-dried fruits market holds the largest share, followed by vegetables and beverages. Freeze-dried food is the best dehydrated food, due to its superior texture and sensory quality after rehydration. Industrial companies use freeze-dried ingredients (strawberries, banana, etc.) in their breakfast cereal products, giving rise to the freeze-dried ingredient market. This sub-segment is growing at a fast rate due to the excellent nutrition and sensory quality.

ADVANTAGES

Using the process of freeze drying, the contamination of the product is avoided due to the fact that, having 97% of the moisture isolated, the most of the bacteries and mold are not able to survive this process. Freeze-dried food retain all the nutrients, flavors and aroma; the food does not shrink or its texture does not change when it is freeze dried. This makes it a better option than dehydration and conventional food preservation technologies. The ice sublimes, it leaves small pockets in food, all the moisture is removed from the food, its weight decreases making it easier to carry or transport. Easy reconstitution by adding water thus, it has a very long shelf life and can be quickly rehydrate as well. This makes it ideal for backpackers or hikers to carry. Freeze-dried foods can stay edible for up to 25 years if unopened. Fruits or ice creams can be eaten without hydrating them. This makes it a very convenient food option.

DISADVANTAGES

Freeze-drying is facing difficult challenges as the equipment for the process of freeze drying is very complex and it consists of several systems (expensive unit operation/pumps are more expensive); it demands huge electric energy consumption in order to perform this process. Large objects take a few months to freeze-dry. If too much heat is added, the material’s structure could be altered. Freezing damage can occur with labile products such as liposomes, proteins (Shukla, 2011).

The restraining factor for the market is the availability of other drying techniques such as spray drying, and fluid bed drying, which is relatively low-cost than freeze-drying. Freeze-drying equipment is comparatively costlier than other dryers, which is a major drawback for the small and medium scale industries.

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*Corresponding author, E-mail address: ramona_cotrut@yahoo.com
5. CONCLUSIONS
Freeze-drying research began more than 60 years ago in an effort to preserve blood plasma. Today, it is used to preserve a wide variety of products; by freeze-drying we can maintain high-quality dehydrated products. Freeze-dried products have high structural rigidity, high re-hydration capacity, low density, and retain the initial raw material properties such as appearance, shape, taste, flavor, texture, vitamins and proteins. This process is generally used for the dehydration of products of high added value and sensitive to heat treatments, produced by food, pharmaceutical and biotechnological industries (Welti-Chanes et al., 2004).
Lyophilization is a set of stages where the final result is a dry product. However, this dry product will preserve all of the properties of the original product. This is the main difference between lyophilization and other dehydration or drying techniques. Primary factor driving this market is the superior quality of its products when compared to other drying technology products. The final product has an excellent shelf-life without any added preservative. The increased shelf-life makes it a profitable product during its supply chain. Research into the mechanisms of high-quality dehydrated products freeze-drying continues through the present, with more yet to come.

6. REFERENCES