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MECHANISM OF WATER CRYSTALLIZATION AND ICE MELTING IN WILD BERRIES

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Abstract

The fast freezing of fruit and berries and their further storage in frozen state is one of the best ways to keep the quality and the utile properties of initial raw. Freezing will help protect the harvest and process it in longer terms, reduce the seasonality in procession of fruit and berries, because frozen raw materials can be used in production of preserved foodstuffs. We conducted the research with a help of differential scanning calorimetric method that would give a great deal of information about both the state of water inside the cells and the correlation between free and constrained water in researched materials. The received data allowed us defining the temperature intervals for the most efficient freezing of different raw materials from the viewpoint of maximal storage of all the precious biologically active components in raw and keeping the fruit and berries undamaged.

Introduction

The specificity of modern food science (particularly the branch concerning the production of healthy foodstuffs) can be formulated that the object of its activity is the state of human health, the means to increase the quality of human life, and the active and creative longevity.

This is why the food industry nowadays is being transformed into greatly important component of health protection and therefore occupying the outstanding position in the field of intellectual and physical activity of a man.

The wild-growing fruit and berries are the rich source of vitamins, carbohydrates, lipids, proteins, organic acids, aromatics, minerals, and others. As the curative raw and foodstuff component, they are valuable due to the complex of biologically active substances that have the capillary-strengthening, anti-sclerotic, hypotensive, anti-inflammation, and hormonal action.

Many species of wild-growing berries have the high nutritional value, so that they would become the important reserve to create the new poly-functional compounds for enriching the traditional food products. However, the range of such a raw to use in food industry is significantly limited by now. The studies over the biological value of wild plant raw materials are one of the main ways to introduce them into the sphere of food technologies; henceforth, it would allow widening the range of wild-grown plant resources.

The scientific innovation of this work was based on the usage of temperatures below zero (by Celsius) to dehydrate the plant raw material. Now the mentioned technology is the only one that makes possible to keep the whole natural biologically-active complex of all of the necessary substances undamaged. Cryogenous technologies were wide-spread in the developed countries of the world, like the USA, England, Japan, France. Generally, there was established the principally new way to preserve the agricultural raw material, which, according to the scientists, would soon replace the traditional ways (like sterilization, high-temperature drying etc.). Talking about Ukraine, the usage of cryogenous technologies in food industry has just begun developing. That is why each way of work in such a trend fills the knowledge sum about the special features of freezing and sublimation of plant materials.

The **objectives** of this article are to elucidate the mechanism of ice behavior during freezing and thawing the juicy raw materials (particularly cowberries).

Method

Studying the process of water crystallization in any systems by differential scanning calorimetric method (DSC) will give a large amount of information about not only the state of water within cells and intercellular space, but also the researched object as a whole. Thenceforth, in studying the dependence of thermal capacity of its samples on the temperature in phase transition **water – ice**, we obtained the sufficient experimental data about the amount of frozen (free) and non-frozen (constrained) water in all the samples in relation to their initial humidity. Those data became a base for working out a technological regime of sublimation dehydration of different plant materials.

Results and Discussions

Setting up the optimal conditions for berries' freezing, based on the studies of the main processes (overcooling, crystallization's start and finish, intensive crystallization), was visually presented on differential-and-thermal analysis thermograms (Fig. 1 – 2), containing the data obtained for cowberries (See Simakhina, 2009). The thermogram showed the freezing process by upper declination of differential curve (Fig. 1). This process might be characterized with several sharp leaps on the differential curve, which corresponded to the certain phase transitions' temperatures: *overcooling* period that went on within the temperature range of 283…272 K; *crystallization start* within the temperature range of 272…271 K; *intensive crystallization* zone within the temperature range of 271…269 K; *subsequent crystallization* within the temperature range of 269…265 K; *crystallization finish*.

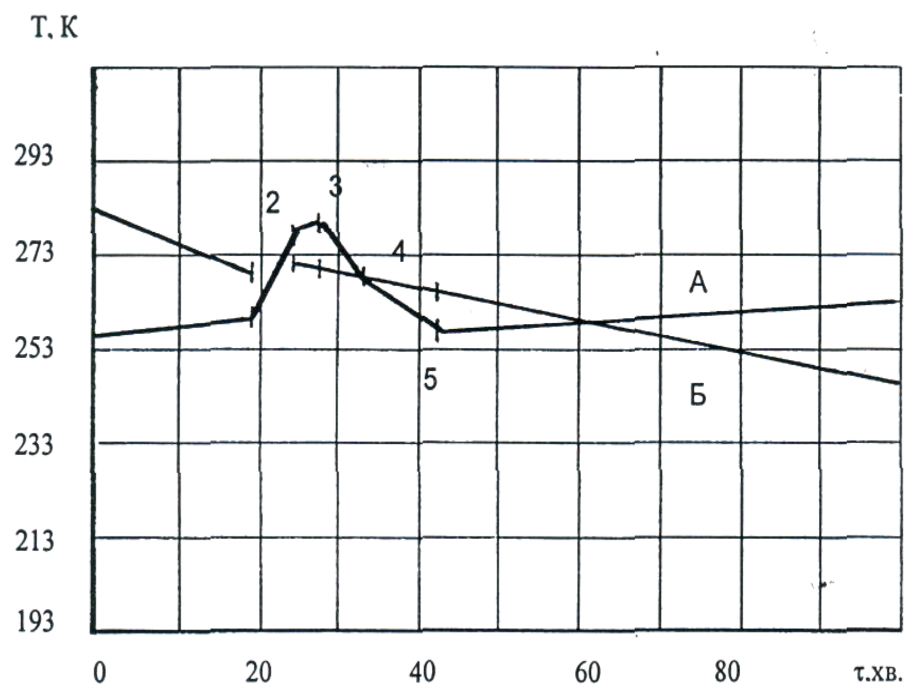

Fig. 1. Thermogram of water freezing in cowberries (A – differential thermal measuring machine indices; B – thermal measuring machine indices)

Water crystallization process should be continued with the studies of its melting process. The analysis of obtained thermograms could wholly visualize the main picture of water's phase transitions. Figure 2 showed that the ice melting got characterized by the fluent start and it could be proved with almost straight shortcut within the temperature range of 240…258 K. Then it got turned from the maximal melting zone to intensive process zone within 258…260 K. Finally, the temperature range of 260…269 K corresponded to the intensive melting zone with 265 K as a peak on the thermographic curve.

The analysis of melting thermographic curve allowed the authors giving some explanations. First of all, the fluent phase transition was a result of low warm conduciveness of the researched object. The initial melting zone expressed the initial stage of dissipation of molecules which were previously concentrated around the crystallization centers. Then, the amount of dissipated molecules grew up, which caused the destruction of thermodynamic stability of water molecules' crystal grate, and hereinafter disturbed the process of transition into intensive melting zone. This zone was characterized by a 265 K peak on the thermographic curve, whose projection onto the curve of indices obtained with a common thermal measuring device corresponded to the temperature that was close to the critical point.

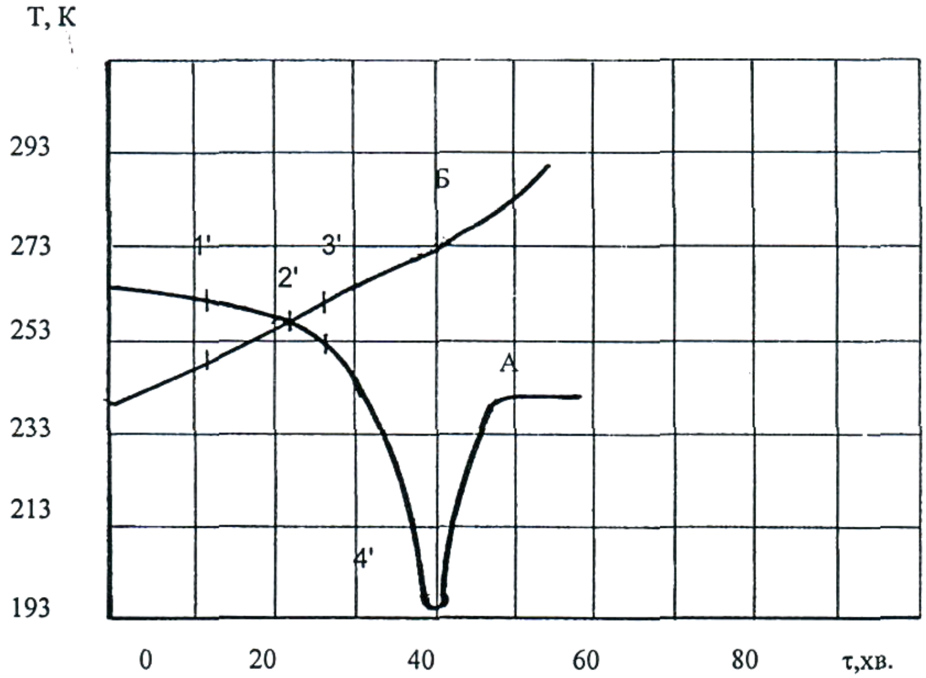

Fig. 2. Thermogram of ice melting in cowberries (A – differential thermal measuring machine indices; B – thermal measuring machine indices)

The thermogram showed that the complete free water crystallization in cowberries went on within the temperature range lower than 250 K, which corresponded to eutectic concentrations.

The temperature of water freezing could be considered the maximal temperature of its getting into solid phase. Achievement of this temperature is a necessary and sufficient condition for plant raw materials' freezing before sublimation.

The choice of optimal freezing temperature was based on the fact that the minimal melting temperature for crystallized water, which could be defined experimentally, was significantly higher than the maximal solid-phase temperature. This could be connected with overcooling the transitive eutectic mixtures during the freezing process, which delayed the subsequent crystallization (See Gordiyenko, 1994), so that the plant raw material was to be cooled to lower temperatures. The index of marginal temperature was determined by the properties of the cooled object and the characteristics of any solid matter which was present at the same environment.

The temperature of water freezing may be examined as the maximal temperature of water's transition to solid phase. The achievement of such an index is a necessary and sufficient condition for plant raw freezing before sublimation.

Selection of optimal freezing temperature should be based on the fact that the minimal melting temperature of crystallized water (note: this index gets obtained by experimental method) is quite higher than the maximal constraining temperature. It is connected with overcooling while freezing the midterm eutectic mixtures, which delays the subsequent crystallization (Silvares, 2005). Therefore, the plant raw should be cooled to the lower temperatures. The index of extreme overcooling temperature is determined with the properties of cooled object and the characteristics of matters that abide at the same environment.

According to our results, and also to the data presented in literary sources (Schwartz, 2003), the extreme overcooling temperature oscillates between 1…10 K. Thenceforth, we should take 240±5 K as the low limit of freezing temperature, and the minimal temperature of ice melting (250±5 K) will serve the high limit.

The analysis of results presented in figures 1 and 2 shows that cellular and tissue water, being influenced by cooling and freezing processes, gets crystallized in different ways due to various states – one part of water remains free, and another one gets strictly fixed by physical and chemical connections with the surface of reactively liable macromolecule groups. Hydrophilic biopolymers are able to keep a certain quantity of free and constrained water, which does not freeze in quite low temperatures, within the cell and in its closest surround.

The low freezing point for water with prevailing constrained faction is connected to its ability to concentrate the great amount of soluble substances (including ions). As a result, the high-viscose protein and mineral mixture gets formed within localized protein components of cytoplasm and membrane structures of a cell.

Based on the results of conducted researches of low-temperature procession of cowberries and on the new scientific notions of quality and ecology of foodstuff, we proved, designed, and realized some of the newest decisions in the technology of production of plant raw materials into sublimed biological additives with high nutritional quality. Those technologies would increase the output of high-quality products; provide the growth of production efficiency; make possible to use the fruit and vegetable raw on the new level as the source of important biocomponents synthesized by nature. Our technologies would allow widening the new generation foodstuff spectrum, and implement some radical changes into Ukrainians' nutrition structure. The mentioned thesis describes the main factor of healthy lifestyle, prevention and medication of different diseases.

Significant decreasing the losses of plant raw materials during harvesting and storage, high quality of final products and their absolute safety for consumer, possibility to widen the range of half-fabricates and final products with increased content of essential and biologically active components through the year, creation of competitive and competition-oriented foodstuff with healthy and preventive destination were the cardinal advantages of using the low temperatures to process and to store fruit and berry raw and the products made of it.

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