Studying the phase transitions "Water – ice" in plant raw materials

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ABSTRACT

Introduction. For working out the optimal parameters of freezing, it is necessary to determine the temperature intervals of crystallizing water that takes about 90 per cent of raw material mass. The objectives of this paper are studying the phase transitions "water – ice" in different varieties of plant raw during freezing and further ice melting.

Materials and methods. The objects of our studies are wide-spread in Ukraine wild and cultivated berries – black currant, blueberries, eglantine, cranberries, strawberries etc. 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.

Results and discussions. 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

One of the main problems in modern food technologies is the loss of precious biologically active components during raw material procession. Henceforth, it is necessary to work out and realize the new technologies that would allow obtaining new food products whose composition is adequate to the needs of a modern human; these are food products with healthy, preventive, and functional destination.

The experience accumulated in the world can show that the usage of artificial cold in transporting, processing, storing, and realizing the food raw is the most efficient way to solve the mentioned problem. Artificial cold causes the minimal changes in nutritional and biological value of an initial raw and its organoleptic indices. Along with that, freezing as a method of food raw preservation has some great advantages in comparison with thermal processing methods like pasteurization, sterilization, drying etc.

Unfortunately, the assortment of fresh frozen products issued in Ukraine is not enough large by now. Just the private enterprises with low productivity do produce small amounts of it; their production is mostly of low quality and gets spoiled quickly because of the lack of efficient freezing technologies.

So the objective of this article is defined as studying the phase transitions "water – ice" to determine a temperature interval that would be most adaptable to freeze certain varieties of fruit and berry raw material, from the viewpoint of maximal storage of all the precious biologically active components in a frozen semi product.

Materials and methods

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.

The fruit and vegetable raw material had not been investigated enough that way (See *Simakhina 2009, 7*). 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 discussion

The obtained data are presented in tables 1 to 6. These are the average results of three parallel experiments, which were processed with the method of mathematical statistics. According to the table figures, crystallization of free water during researched samples' freezing began at the significant overcooling, and its initial temperature got lower along with samples' initial humidity decrease.

The comparative analysis of the tables showed that the adaptability to overcooling depended on the kind of a material, the grade of its maturity, its chemical composition, and initial humidity. High-molecular compositions and hydrophilic colloids, which are inclined to swelling and water constraining, play the significant role in this process.

There is well-known (See *Kaatze 2004*) that the presence of stable embryos is necessary for development of crystallization process in the solution. Embryos got created in the certain grade of overcooling in the system; as in our experiments, this grade varied from –7 ºC to –32 ºC (particularly, for black currant this index was 14ºC below zero).

The subsequent growing of ice crystals depended not on temperature, but on time; ice "grew" in the entire volume of liquid. As it was seen from the tables, the temperature of stable germs' growing depends on initial relative humidity of the samples, *ceteris paribus*; further both of these indices grow lower.

Analyzing the results obtained on the base of DSC curves, we are to witness the more or less lasting temperature interval of water crystallization for each of the carbohydrate-containing raw samples in our studies.

Dissolved substances, as a rule, would decrease the water freezing temperature. They provide the osmotic pressure in a solution. One gram-molecule of an ideal non-dissociative and non-associative substance, being dissolved in 1,000 grams of water with pressure of 760 mmHg, lowers the temperature of its freezing on 1.86 Celsius degrees.

Table 1

Experimental data of crystallization / melting of apple water

Relative humidity	Freezing water	Non-freezing water, % to the main mass	Starting crystallization temperature, °C	Starting melting temperature, °C	Maximal melting temperature, °C
80.77	76.74	23.26	-23.0	-6.5	-2.5
80.28	80.28	74.05	-23.0	-11.5	-2.0
77.32	70.67	29.33	-26.5	-13.5	-3.5
76.79	65.22	34.78	-24.5	-12.5	-6.5
68.82	62.12	37.88	-26.5	-9.5	-4.5
62.28	54.23	44.60	-26.5	-11.5	-7.5
58.07	46.17	53.83	-26.5	-8.5	-9.5
57.09	40.99	59.01	-26.5	-11.5	-9.5
54.58	35.33	64.67	-26.5	-17.5	-11.5
38.44	-	100.00	-	-	-

Table 2

Experimental data of crystallization / melting of eglantine water

Relative humidity	Freezing water	Non-freezing water (% to the main mass)	Starting crystallization temperature, °C	Starting melting temperature, °C	Maximal melting temperature, °C
73.20	69.98	30.02	-8.0	-20.0	-1.0
67.25	60.65	39.35	-9.2	-13.0	-0.5
57.91	56.48	43.52	-11.0	-14.0	-2.0
56.89	64.84	35.16	-10.0	-20.2	-1.0
39.94	35.60	64.40	-12.0	-18.0	-2.0
39.39	38.64	61.36	-13.5	-20.0	-2.5
38.17	26.81	73.19	-16.0	-18.8	-2.0
34.15	26.91	73.09	-16.0	-20.0	0
24.43	2.01	97.99	-18.6	-19.0	+ 1.0
22.61	-	100.00	-	-	-

Table 3

Experimental data of crystallization / melting of blueberry water

Relative humidity	Freezing water	Non-freezing water (% to the main mass)	Starting crystallization temperature, °C	Starting melting temperature, °C	Maximal melting temperature, °C
94.51	92.71	7.29	- 9.8	-12.5	-0.5
94.40	91.71	8.29	- 6.5	-12.5	-2.5
93.44	85.71	14.29	-11.7	-14.5	-1.5
86.49	75.68	24.32	- 7.9	-19.5	-2.5
75.34	70.91	29.09	-12.8	-20.5	-1.8
72.64	72.00	28.00	-19.5	-32.0	-0.2
62.50	53.92	41.08	-19.1	-27.5	-4.2
61.11	47.59	42.41	-21.8	-30.5	-4.7
39.37	36.50	63.50	-29.5	-31.5	-12.0
33.42.	-	100.00	-	-	-

Table 4

Experimental data of crystallization / melting of black currant water

Relative humidity	Freezing water	Non-freezing water (% to the main mass)	Starting crystallization temperature, °C	Starting melting temperature, °C	Maximal melting temperature, °C
84.45	71.15	28.85	-14.0	-21.5	-2.0
84.03	61.09	38.91	-14.5	-20.0	-2.0
83.64	75.90	24.10	-16.0	-26.0	-2.0
62.37	82.96	17.04	-	-22.0	+2.0
78.61	70.28	29.72	-16.0	-29.0	-3.0
77.42	77.17	22.83	-13.0	-21.0	+1.0
71.93	71.56	28.44	-16.0	-31.0	-3.0
67.83	52.23	47.77	-21.5	-29.0	-6.0
61.08	48.87	51.13	-21.0	-31.0	-8.0
50.94	33.86	66.14	-27.0	-29.0	-13.0
49.11	41.68	58.32	-19.0	-28.0	-8.0
38.18	-	100.00	-	-	-

Table 5

Experimental data of crystallization / melting of raspberry water

Relative humidity	Freezing water	Non-freezing water (% to the main mass)	Starting crystallization temperature, °C	Starting melting temperature, °C	Maximal melting temperature, °C
89.86	68.01	31.99	-12.0	-23.0	-2.0
88.36	79.26	20.74	-15.0	-21.0	-1.0
87.54	82.12	17.88	-12.0	-18.0	-2.0
87.48	78.21	21.79	-11.0	-20.0	-4.0
87.33	76.54	23.46	-12.0	-18.0	-2.0
87.14	75.65	34.35	- 9.0	-20.0	-2.0
86.85	72.71	27.29	-11.0	-15.0	-1.0
85.12	75.38	24.62	- 8.0	-20.0	-1.0
82.00	69.15	30.85	-13.0	-25.0	-2.5
80.56	71.07	28.93	-12.0	-22.0	-2.0
80.07	71.86	28.14	-10.0	-21.0	-1.0
79.13	59.71	40.29	-	-	-2.0
72.48	62.17	37.83	-13.0	-27.0	-2.0
67.32	55.73	44.27	-16.0	-26.0	-4.5

As the behavior of real water solutions significantly differs from those ideal, the sufficient approximation to this index is observed only in infinite dissolution, i.e. extrapolation to zero concentration of the solved substance.

All mentioned above is an explanation to the fact that water from strawberry with a content of dry substances equal to 11.16 per cent (See Table 6) starts crystallization in –9.0 Celsius degrees; if the amount of dry substances reaches 46.01 per cent, then the temperature of crystallization start should be lowered to 32 Celsius degrees below zero.

Table 6

Experimental data of crystallization / melting of strawberry water

Relative humidity	Freezing water	Non-freezing water (% to the main mass)	Starting crystallization temperature, °C	Starting melting temperature, °C	Maximal melting temperature, °C
14.39	-	100	-	-	-
16.83	-	100	-	-	-
53.99	51.14	48.86	-32	-28	-10.7
56.71	48.23	51.77	-17	-28	-8
57.99	55.78	44.22	-24	-40	-1.5
68.68	64.20	35.80	-15	-28	-5
76.86	71.84	28.16	-9	-27.5	-3
77.97	69.57	30.43	-21	-25	-3.5
85.71	78.52	21.48	-13	-20	-1.8
88.84	82.02	17.98	-9	-20	-0.7
89.95	74.86	25.14	-19.5	-13	0.6

In thawing the samples with velocity of 4.0 Celsius degrees per minute, starting melting temperature of crystallized water got also decreased. The consequence in temperature changes got observed in the moment of endothermic peak. The absence of first-grade phase transition on the thermograms of samples with low initial humidity was evidence that all water contained by the researched object was constrained.

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, 585*). 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, 363*), 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 tables 1 to 6 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.

Table 7 represents the calculation of constrained water content in some plant objects. According to these data, various samples of raw contain 7.0 to 70 percent of the entire content of water. Such index, first of all, depends on raw's initial humidity – the fresher is raw, the lower is the content of constrained water in it, and thus this kind of raw is more adaptable to freezing and further sublimation. It is also evident that, upon the similar initial humidity, the amount of constrained water depends on the modification of raw, i.e. on its chemical content.

Table 7

The mass part of constrained water in plant raw materials

Material	General humidity, %	Constrained water, % to general amount
Eglantine	74,21	30,62
	55,83	36,46
	42,65	61,53
Amaranth	18,40	72,84
	14,48	97,80
Apples	80,74	23,36
	68,82	37,88
	57,09	59,01
Blueberry	84,51	7,29
	86,49	24,32
	72,64	28,00
	61,11	52,41
	39,37	63,50
Black currant	84,45	28,85
	78,61	29,72
	67,83	48,77
	50,94	66,14

Conclusions

1. Freezing any biological objects, including fruit and vegetable raw, gets accomplished with a help of low temperatures in the interval from 0 to 273 Celsius degrees below zero.
2. The stable germs are being formed in the conditions of certain overcooling in the system. Talking about our experiments, this condition is a temperature interval from 7 to 32 degrees below zero for different plant objects. The further growing of ice crystal is a question of time but not of temperature.
3. Freezing the many-component solution that is proper for fruit and berry raw is passing two stages. First one is a prime crystallization (only water gets crystallized); second one is secondary crystallization (this process involves the solver and dissolved biocomponents in it).

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