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THE OPTIMAL FREEZING TEMPERATURE OF COW MILK AND CAMEL MILK

Abstract. In the freezing process of cow milk and camel milk, three areas of temperature variations were identified. Specifically, on the first period, both types of milk cooled, then supercooled and further the formation process of ice crystals a taken place. On the second area, it was observed the isothermal area and the phase transformation of water into ice was present. On the third stage, the weakly bound water contained in cow milk and camel milk completely transited into ice. Based on a study of the pattern of changes in the amount of frozen moisture, it was found that, at the minis temperature of t=-15 °C, more than 95% of the water consisted in both types of milk are frozen, and further reducing of temperature had monotonously insignificantly increasing behaviour of the freezing. Therefore, from the point of view of energy savings and maximum preservation of the initial qualities during the shelf-life of cow milk and camel milk, the optimal freezing temperature range is recommended.

Key words: freezing, milk, frozen moisture, isothermal process, free and bound water.

Introduction

One of the most consumed groups of products in Kazakhstan households and abroad is milk and dairy products [6]. However, storage of raw milk by energy saving benefits with a prolonged shelf-life is actual problem for the dairy technology specialists.

There are several advantages of using freeze-drying instead of conventional sensory characteristics within the food product. These advantages make freeze-drying an adequate technology among the new trends of functional and nutraceutical products in the food industry [4].

Freeze drying method is used for the increasing a shelf-life of dried milk as one of the significant parameters and to maximize the amount of preserved nutrients [10, 14].

Review of the available literature shows that currently among researchers engaged in the field of vacuum freeze-drying of the food products, there is no consensus regarding of a selection of the freeze-drying temperature of milk [3]. For example, according to the authors' opinion [8], for the maintenance of the original quality during of the freeze-drying of the product, a lower value of the freezing temperature is sufficiently within t= -45 °C. However, the authors [12] consider that the initial quality of the dried milk can be achieved at the temperature range: t= -10...- 13 °C, where until 90-92% of water in milk are frozen, residual water content is not available for the spoilage of food. (in remain, it will be 8% of water that has an insignificantly value)

As a result of freezing of mare and camel milk, powder remains, which when re-diluted with water retain practically all the beneficial properties of milk [9].

On average camel milk contains 81.4-87% water, 10.4% dry matter, 1.2-6.4% milk fat, 2.15-4.90% protein, 1.63-2.76% casein, 0.65-0.80% whey protein, 2.90-5.80% lactose and 0.60-0.90% ash [1].

The fat content in camel milk varies in a fairly wide range, which depends on the species, season, forage, individual and other factors [13].

Water of cow milk and camel milk is a weakly bound and with its dry framework, besides the forms and energy of bond of this moisture are various [8].

Within a temperature dropping below $T=0^0C$, i.e. below the cryoscopic temperature, a part of water of cow milk and camel milk is frozen [5]. In the refrigeration technology, water that has turned into a solid state is called frozen. The amount of frozen water is presented as a fraction of its total mass in the product [11].

In accordance with the existing classification of the food products there are available a free and bound water [3]. At the freezing of camel milk a tightly bound water is not involved in phase transformations.

It is known that at a temperature below of cryoscopic value, free water is gradually transformed into ice. At the vacuum freeze-drying, in the initial drying period, firstly a frozen part of the free moisture and then the associated part of the water are outlets. In our opinion, on the base of the foregoing statement, by using the parameter of frozen water amount, as a parameter that describes the state of water in the drying process and reveals qualitative changes when camel milk is frozen. Objectively, it is possible to set a lower limit temperature during a vacuum freeze-drying of camel milk [12].

The purpose of this work is a determination of the lower limit of the freeze-drying temperature by amount of frozen water in cow milk and camel milk.

Materials and methods

As the study objects, cow milk and camel milk of the "Gulmaira" farm (Turkestan region, Kazakhstan) were used.

To study of the physico-chemical properties of cow milk and camel milk, the following analytical devices were applied:

- Water content in milk was determined by the standard method of drying at a temperature of 105 °C.
- pH was measured by the ionomer SCHOTT Instrument Lab 850 (Germany) device.
- For the determination of density, proteins and fats content the Lactan-4 of "Sibagropribor NPP" (Russia) device was used.

Both milks were frozen in the freezer device at a temperature of -18 ° C in the form of a cylinder: diameter 30 mm, height 50 mm. Previously, a thermometer sensor was installed in the center of the cylinder, fixed on all sides, and then placed in a refrigerator/

The electronic LCD thermometer TE-850 brand was used for the measuring a temperature.

The amount of water in milk was determined by the standard method of drying in the ALTO SHAAM VECTOR VMC-H2 3F convection multifunctional oven, according to the GOST 3626-73, until constant weight at the temperature of 105 ° C.

A quantity of frozen water in the milk was determined by the formula of G.B.Chizhov [2] that is widely used in practice:

$$\omega = 1 - \frac{t_{cryos}}{t}$$

where ω – a quantity of frozen water at cryoscopic temperature t_{cryos}; t – start temperature, °C.

Results and discussion

Physico-chemical properties

The quality of milk depends on its chemical composition, i.e. protein, lipids, lactose, etc. In this regard, the studies were carried out on the physicochemical properties of cow milk and camel milk. The results of the physico-chemical properties are shown in Table 1.

Table 1 - Physico-chemical properties of cow milk and camel milk

№	Indicator	Cow milk	Camel milk
1	Mass fraction, %: - dry matter	8,5	12,6

	- fats - proteins - lactose	3,00 3,10 4,50	4,38 4,25 4,32
2	Density, kg/m^3	1027	1029
3	pH	6,70	6,80

The obtained results meet the standards for raw milk. The value of dry matter of camel milk is more than for cow milk. The contents of protein, lipids and lactose in camel milk are high then in cow milk. The values of density and pH are equal for both milks.

Studyoftheprocessoffreezing cow and camel milk

It was experimentallyfound that a water content in camel milk W = 84.7%, and in cow milk W = 87.0%. Water in both milks can be represented as a medium in that other components are dissolved. Lactic acid and it salts that contained in water basically form true solutions; proteins and other high-molecular compounds transform to the colloidal solutions in water. Fats and other poorly soluble compounds form emulsions when dispersed with water [8]. Based on the above mentioned, it can be concluded that the composition of cow milk and camel milk have a complex colloidal solution.

The results of the study of the freeze-drying process of cow milk and camel milk are presented in Figure 1.

Thermogram's analysis shows that in the freeze-drying process of the cow milk and camel milk there are three areas of temperature variations. On the first section, both types of milk are not only cooled, but also supercooled till a cryoscopic temperature. The duration of this period for camel milk is 46 minutes, and for cow milk is 72 minutes. Further it was observed the isothermal area that has a long duration, particularly the phase transformation of water into ice. The duration of this second area for camel milk is 70 minutes or in the range from 46 minutes to 116 minutes, and for cow milk is 44 minutes or in the range from 72 minutes to 116 minutes. As known from the refrigeration technology, the freezing process is considered as a complete when the centre frozen product temperature reached T=-8°C. In this regard the third area is a short, and on this stage water containing in camel and cow milk transforms into ice. The duration of this area for both types of milk is 15 minutes, or in the range from 116 minutes to 135 minutes.

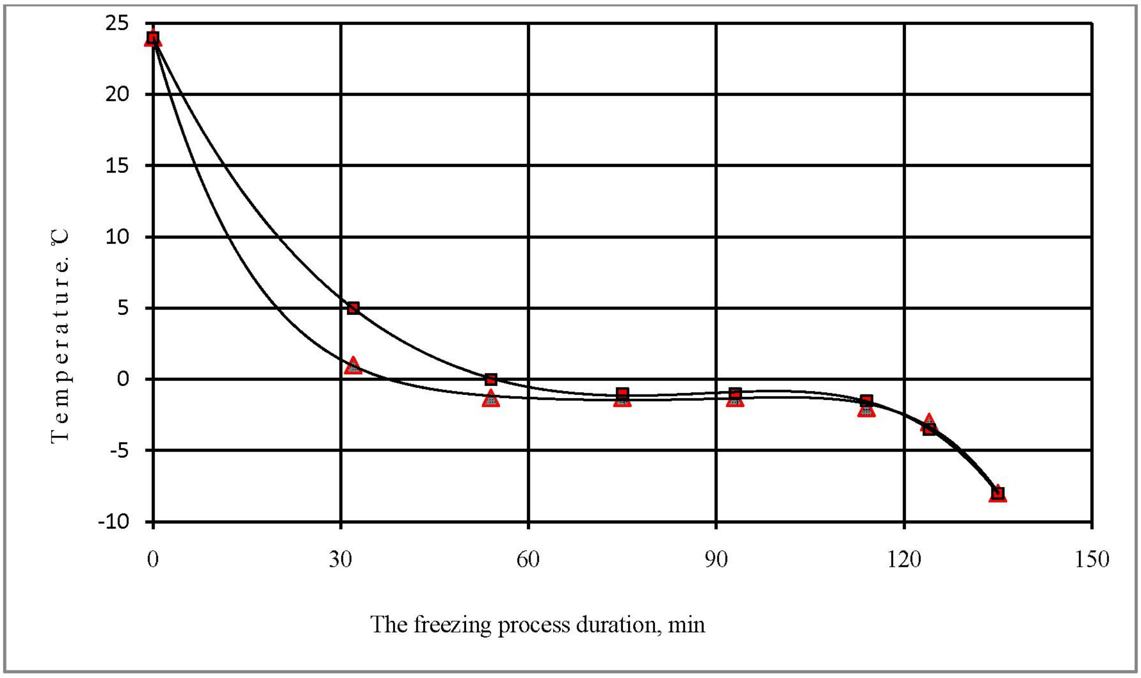

Figure 1 - Thermograms of the freezing of cow milk (□) and camel milk (Δ)

The kinetics dependence of the freezing process of cow milk and camel milk

For a more detailed analysis of the phase transition process of water contained in cow milk and camel milk, its freezing thermograms (Figure 1) were differentiated by time, and the dependence of cooling rate of both milks by time were obtained. The kinetics dependence of the freeze-drying process of cow milk and camel milk are presented in Figure 2.

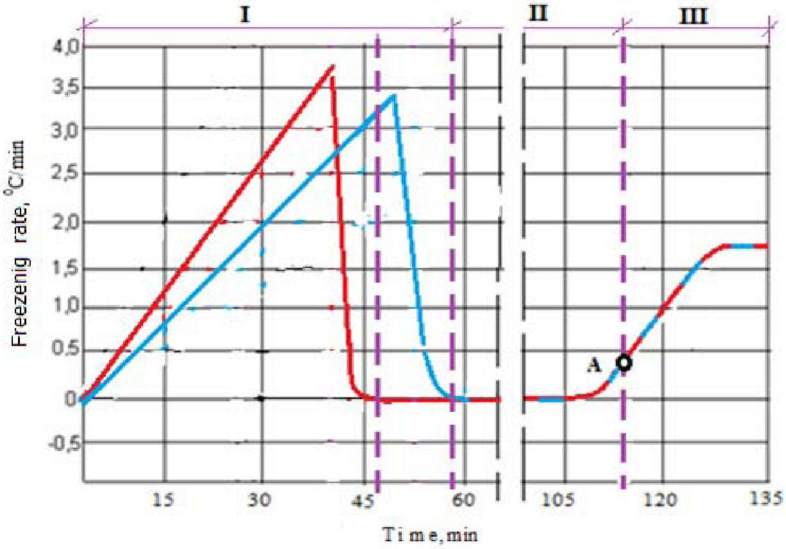

Figure 2 – Kinetics dependence of the freezing process of cow milk (a red curve) and camel milk (a blue curve)
I – cooled and supercooled phase, II - isothermal area and a phase transformation of water into ice,
III – ice forming phase

Figure 2 shows availability of an area with a zero cooling rate that corresponding to the isothermal field of moisture crystallization beginning in cow milk and camel milk. In addition, it can be determined the end point of the crystallization process of free and bound moisture: it corresponds to the inflection point on the cooling rate curve (point A) or t=-3^{0}C.

Study of the amount of frozen water in cow milk and camel milk

The following step in our study was a research of the amount of frozen water in cow milk and camel milk. The obtained results are presented in Figure 3.

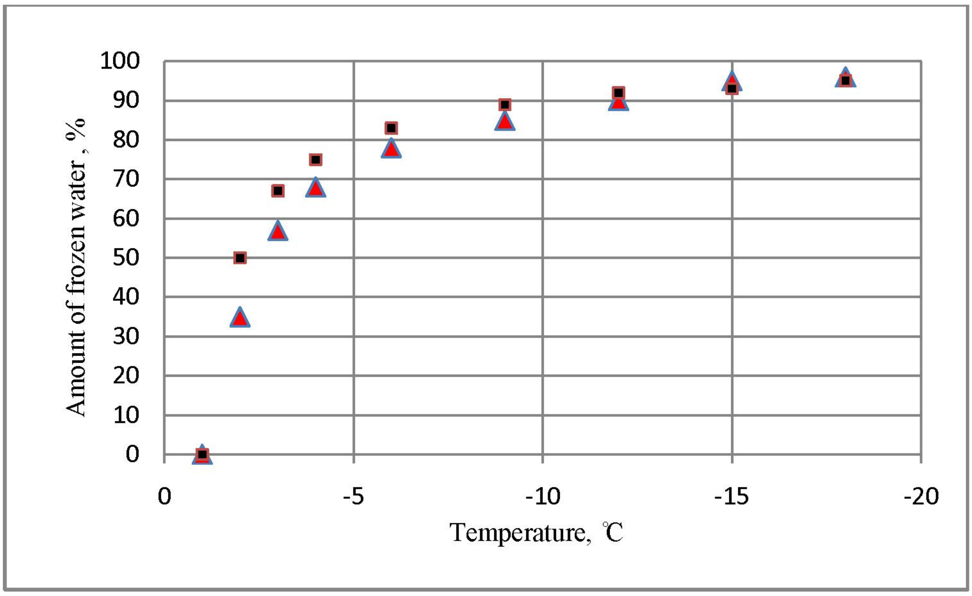

Figure 3 - The amount of frozen water in cow milk (□) and camel milk (Δ)

Analysis of Figure 3 shows that in the range from the cryoscopic temperature till -5 °C in the composition of camel milk, over 70% of the moisture freezes. However, over 80 % of water is frozen in cow milk. At the subsequent temperature decreasing a dependence on the amount of frozen water by a temperature for both types of milks have a monotonously increasing behaviour.

For example, in camel milk, at the temperature range from -5 °C till -10 °C 88% of water is frozen, then at the temperature range from-10 °C till -15 °C, up to 95% of moisture is frozen, and at temperature -20 °C 96% of water is frozen. In cow milk at the temperature range from -5 °C till -10 °C freezes 91 % of moisture, then at the temperature range from -10 °C till -15 °C freezes like in camel milk up to 95% moisture, and at temperature -20 °C 96% of water is frozen.

Based on the above mentioned, it can be concluded that from the point of view of energy savings, lowering the minus temperature below t=-15 °C is economically unprofitable. Because if it is considered a refrigeration machine, where a cold is produced, for the lowering of the temperature in one ^{0}C, the power consumption for the production of cold increases for 4,5%.

Conclusion

In the freeze-drying process of cow milk and camel milk, three areas of temperature variations were identified. The first freezing period for camel milk duration is 46 minutes, and for cow milk is 72 minutes. At the second area the phase transformation of water contained in cow milk and camel milk into ice is present. For cow milk duration is 44 minutes, i.e. from 72 minutes to 116 minutes, and for camel milk is 70 minutes, i.e. from 46 minutes to 116 minutes. The third area has a comparably short time for both milks, and the weakly bound water completely transforms into ice. The duration of this area for both types of milk is 15 minutes, i.e. from 116 minutes to 135 minutes.

The kinetics dependence of the freeze-drying process indicates the inflection point of the cooling rate at the temperature t=-0,5^{0}C. The study of patterns of the freeze-drying process shows the major part of the water contained in the cow milk and camel milk, frozen till a temperature of t=-10 °C. From the point of view of energy savings, lowering the minus temperature below t=-15 °C is economically disadvantageous. Therefore, in the case of using of vacuum - freeze drying process of cow milk and camel milk, the lower limit of the sublimation temperature, a temperature of -13 °C ...- 15 °C is recommended.

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СИЫР МЕН ТҮЙЕ СҮТІНІҢ МҰЗДАТУНЫҢ ОҢТАЙЛЫ ТЕМПЕРАТУРАСЫ

Аннотация. Сиыр сүті мен түйе сүтін мұздату кезінде температураның өзгеруінің үш аймағы анықталды. Атап айтқанда, бірінші кезеңде сүттің екі түрі де салқындатылады, содан кейін аса салқындатылады және одан әрі мұз кристалдарының пайда болу процесі жүреді. Екінші учаскеде изотермиялық аймақ байқалып, судың мұзға фазалық айналуы байқалды. Үшінші кезеңде сиыр және түйе сүтіндегі әлсіз байланысқан су толығымен мұзға өтті. Қатып қалған ылғал мөлшерінің өзгеру сипатын зерттеу негізінде минус T=-15°C температурада сүттің екі түрлерінде болатын судың 95% - дан астамы мұздатылады және температураның одан әрі төмендеуі бірқалыпты азырақ өсіп келе жатқан сипатқа ие болды. Демек, сиыр сүті мен түйе сүтін мұздату кезінде энергияны үнемдеу және бастапқы қасиеттерін барынша сақтау тұрғысынан сублимация температурасының оңтайлы диапазоны ұсынылды.

Кілт сөздер: сүт, мұздатылған ылғал, изотермиялық процесс, еркін және байланысқан су.

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ОПТИМАЛЬНАЯ ТЕМПЕРАТУРА ЗАМОРАЖИВАНИЯ КОРОВЬЕГО МОЛОКА И ВЕРБЛЮЖЬЕГО МОЛОКА

Аннотация. В процессе замораживания коровьего молока и верблюжьего молока были выявлены три области изменения температуры. В частности, в первый период оба типа молока охлаждаются, затем переохлаждаются и далее происходит процесс образования кристаллов льда. На втором участке наблюдалась изотермическая область, и присутствовало фазовое превращение воды в лед. На третьем этапе слабосвязанная вода, содержащаяся в коровьем молоке и верблюжьем молоке, полностью переходила в лед. На основании изучения характера изменений количества замерзшей влаги было установлено, что при температуре минус T=-15°C более 95% воды, содержащейся в обоих типах молока, замораживается, и дальнейшее снижение температуры имело монотонно незначительно возрастающее поведение. Следовательно, с точки зрения экономии энергии и максимального сохранения первоначальных качеств, при замораживании коровьего молока и верблюжьего молока, рекомендуется оптимальный диапазон температур сублимации.

Ключевые слова: молоко, замороженная влага, изотермический процесс, свободная и связанная вода

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REFERENCES

[1] Brezovečki A., Čagalj M., Dermit Z.F., Mikulec N., Ljoljić D. B., Antunac N. (2015).Camel milk and milk products. Mljekarstvo/Dairy, 65(2), 81-90 http://dx.doi.org/10.15567/mljekarstvo.2015.0202

[2] Chizhov G. B. (1979). Teplofizicheskie process v holodil'nojtehnologiipishhevuhproduktov[Thermophysical processes in refrigeration technology of food products]. Moscow, 1979, 271 (in Russian)

[3] Chomanov U.Ch., Shingisov A.U. (2016). Sovershenstvovanijatehnologiivakuum-sublimacionnojsushkikumysaishubata (Improving of the vacuum freeze-drying technology of koumiss and shubat). Monography, Almaty: TOO «378», 272 (in Russian)

[4] Garcia-Amezquita LE, Welti-Chanes J, Vergara-Balderas FT, Bermúdez-Aguirre D. (2016). Freeze-drying: the Basic Process. Reference Module in Food Science from Encyclopedia of Food and Health, Academic Press Oxford, 104-109 http://dx.doi.org/10.1016/B978-0-12-384947-2.00328-7

[5] Kamerbaev A.J. (2001). The role of water in food products and its function. Almaty, 203 (in Russian)

[6] Orymbetova G.E., Conficoni D., Kassymova M.K., Kobzhasarova Z.I., Orymbetov E.M., Shambulova G.D.(2018) Risk assessment of lead in milk and dairy products. News of the National Academy of Sciences of the Republic of Kazakhstan-Series Chemistry and Technology, 6(432), 23-28https://doi.org/10.32014/2018.2518-1491.22

[7] SemenovG.V., KasianovG.I. (2002). Sushkasyr'ja: mjaso, ryba, ovoshhi, frukty, moloko. (Drying of raw: meat, fish, vegetables, fruits, milk). Rostov-on-Don: TOO «MarT», 112 (in Russian)

[8] Semenov G.V., Krasnova I.S. (2013).Vakuumnajasublimacionnajasushka (Vacuum freeze-drying). Moscow: DeLipljus, 264 (in Russian)

[9] Kantureeva G.O., Defrancesco E, Alibekov R.S., Urazbayeva K.A., Efimova I.E. (2018). New trends in the identification of the traditional food products of Kazakhstan. News of the National Academy of Sciences of the Republic of Kazakhstan-Series Chemistry and Technology, 5(431), 6-12 http://dx.doi.org/10.32014/2018. 2518-1491.1

[10] Myrkalykov B., Shingisov A., Ospanov A., Simov Z., Latif A., Aripbaeva A. (2018). Freeze Drying of Sheep Milk: Calculating Process Duration. European Online Journal of Natural and Social Sciences; 7(2), 460-470 http://european-science.com/eojnss/article/view/5281

[11] Olenev Y.A. (1983). Energy outage moisture during the hardening ice cream. Refrigeration technics, 1(5), 41-42 (in Russian)

[12] Shingisov A.U., Alibekov R. S. (2017). Analysis of the moisture evaporation process during vacuum freeze-drying of koumiss and shubat. Heat and Mass Transfer, 53(5), 1571-1578 http://dx.doi.org/10.1007/s00231-016-1920-4

[13] Shingisov A., Alibekov R., Nurseitova Z., Orymbetova G., Kantureeva G., Mailybaeva E. (2015). Desorption isotherms of the koumiss and shubat clots enriched by various additives. Modern Applied Science, 9(8), 409 http://dx.doi.org/10.5539/mas.v9n8p409

[14] Sulieman A.M.E., Elamin O. M., Elkhalifa E. A., Laleye L.A. (2018). Comparative Study of Physicochemical Properties of Freeze-dried Camel's Milk and Cow's Milk Powder.Discourse Journal of Agriculture and Food Sciences, 6(2), 11-16 http://www.resjournals.org/JAFS/PDF/2018/March/Sulieman%20et%20al.pdf