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CHANGING OF MILK FREEZING TEMPERATURE AFTER INTRODUCTION OF NEW REQUIREMENTS TO ITS ACIDITY

The article deals with some consequences of changing requirements to the level of cow milk acidity under different thermal treatment. The factors, which affect the normalized acidity values of raw milk, are under consideration. The interconnection of cryoscopic temperature and titratable acidity of the product is shown.

The general dynamics of freezing temperature changes of heat-treated milk has been traced by the example of three finished products from well-known Belarusian producers for a few last years.

It is shown the decrease of freezing point for milk products after introduction of more stringent requirements to acidity of the raw material.

Introduction. Milk is a biologically valuable food for people of all ages, as well as one of the most frequently adulterated products. Intentional dilution of milk with water is the simplest way of it adulteration. Aerometric and cryoscopic methods of analysis and a variety of instruments are used for detecting watering [1–6].

The freshness of milk in the dairy industry is usually judged by its acidity. The adulteration by its watering is determined, including freezing temperature [7, 8].

When purchased, norm for titratable acidity of prime quality and above in cow milk is from 16 to 18°T [8–10], and the freezing point of milk of any sort is not over –0,520°C. If there are no conditions for the determination of the freezing point of raw milk, then the index of density is to be defined [8].

Titratable acidity of fresh milk could be out of 16–18°T that depends on the age, breed of animal, diet feeding, maintenance, lactation, health status, as well as on the individual characteristics of the animal. The cows of Red Steppe and Simmental breeds have reduced acidity due to diseases, in the last days of lactation, with age, with the prevalence in feed of triple-substituted phosphates. But it is increased referring to the cows of Red Gorbatovskaya and Kostromskaya breeds in the first days after calving, when the content in the feed monosubstituted phosphates, calcium-poor diet [7].

Since fresh raw milk doesn't have lactic acid, the acidity is caused by proteins, accounting for 4–5°T, acidic salts – about 11°T, carbon dioxide and other titratable chemicals – about 1–2°T.

The freezing point of raw milk varies from –0.570 to –0.510°C. The average currently accepted freezing point of normal milk is –0.540°C [9]. It depends on the chemical composition of milk, so it changes during the lactation period, with the animal disease, as well as when introducing additives to adulterate raw material [10].

At the beginning of the lactation period, milk freezes at temperature up to –0.564°C in the middle of it the point ups to –0.550°C, and at the end of lactation it could as law as –0.581°C [7, 9].

Under a disease of a cow cryoscopic temperature drops and it can be up to –0.900°C in the colostrum of sick cows.

When diluting milk with water, its cryoscopic temperature rises. Introducing dry additives like soda, salt, borax, chalk and other organic and inorganic substances causes decrease of temperature.

Therefore, double "compensating" adulteration is possible. Application of very dilute solutions will be therefore detected as watering, and the establishment of additives will be masked i. e. the received data will demonstrate compensation by additive components of the complementary effect [12].

Lactic microflora develops during storage of raw milk. It brews lactose and produces more and more lactic acid. The subsequent increase in acidity for each Trner degree corresponds 0.009 g lactic acid in 100 cm^3 of raw milk [13–15].

Thermal stability of proteins reduces with increasing of the lactic acid in milk that leads to coagulation of milk during thermal processing.

According to the change in standard from 01.07.2012 [16] the acidity of drinking milk as finished product should not exceed 19°T, which is 2°T lower than the previous norms.

Earlier [17, 18] we described the influence of the heat-treated milk souring on its freezing temperature. The composition of used ferment is also important whereas there are strictly close limits of freezing points for different fermented milk products [19-21].

Some authors propose to accept the value of 17.5°T as the normal milk acidity and correct the measured value of milk freezing point up to 0.0025°C for each Turner degree to obtain more reliable assessments [22, 23].

Accordingly, the change in the requirements for the acidity of the final product [16] may alter its freezing point as well. This should be taken into account in the quality control of milk by cryoscopic method.

Published data on the effect of regulatory tightened requirements to the acidity of drinking heat-treated milk on a freezing temperature as well as their dynamics for several years are too fractional and will be improved by hereinafter given results.

Main part. The samples of drinking, pasteurized (without additives), baked milk, sterilized and ultra-pasteurized milk of domestic producers were selected as the objects of study.

State standard [16] does not apply to drinking milk, so it is produced according to the specifications of enterprises. Therefore, the acidity of the final product may be differ from the prescribed by the standard.

We did not take into account fat and protein content of milk due to their negligible influence [7, 9–11, 13–15].

The lack of data on the freezing temperature of the majority of dairy products in the first half of 2012 refers to the absence of these products in the field of sales because of the crisis phenomena and / or the presence of additives included in it, such as calcium.

Measurements of freezing temperatures were conducted by a thermoelectric MT-5-01 milliosmometer-cryoscope (St. Petersburg). The measurement accuracy is ±0.004°C in the determination of the freezing temperature. We provided ±0,5°T accuracy when measured titratable acidity [24].

It was found that titratable acidity of the selected milk samples, regardless of heat treatment meets the requirements of the standards.

Cryoscopic temperature of heat-treated milk is considerably higher than that of raw milk. Increasing the temperature and processing time of milk lead to a lowering the freezing point.

The degree of reduction of cryoscopic temperature of pasteurized and baked milk is different compared to other heat-treated products. The reasons for this seem to be associated with changes in physical-chemical properties of milk due to:

– there is some mineral residue due to transition of soluble salts of calcium and phosphorus to an insoluble state when the amount of molecules and ions decreased;

– removing volatile substances and gases in milk [7, 9–11, 13–15].

During prolonged high temperature pasteurization lactose interacts with proteins and free amino acids (Maillard reaction or the reaction of melanoidins creation) that leads to differences in freezing temperatures of pasteurized and sterilized milk.

Milk sterilization causes the dissolution of lactose and forming carbon dioxide and acids, which increase the titrable acidity of milk by 2–3°T noticeable decrease of the freezing temperature in sterilized and ultra-pasteurized milk [15].

Results of the study are illustrated by Fig. 1–3 and show a general trend to lower of freezing point of heat-treated drinking milk.

Therefore, stricter requirements for the acidity level of the finished products lead to lowering of the considering indicator. Obviously, this is due to the conservation of all native nutrients of milk since the moment of incoming of raw materials to the factory and before its processing and making of the final food product. No doubt, this resulted in the quality of drinking milk enhancement in general.

One could see (Fig. 2) increasing the freezing temperature for all types of milk in 2011. This is probably due to the crisis in the livestock farming, and therefore changing for the worse of stock keeping.

Measurement inaccuracy for freezing temperature of heat-treated milk in all experiments did not twice exceed the size of the instrumental error. Three-fold size of the tool's inaccuracy is observed for all the measurements obtained in sterilized milk and the rest of the tested products in 2010 and 2013. The reason is large variability of the freezing point of milk products among all producers due to the different conditions of milk heat treatment at the plants; and the quality of raw milk overall territory of the country.

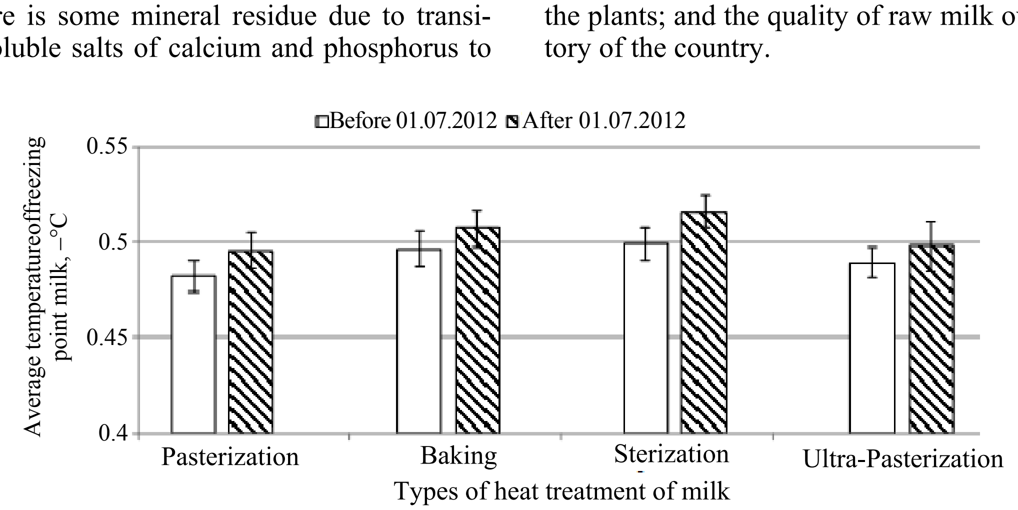

Fig. 1. Changes in the average freezing temperature of heat-treated milk due to new requirements of the standard to its acidity

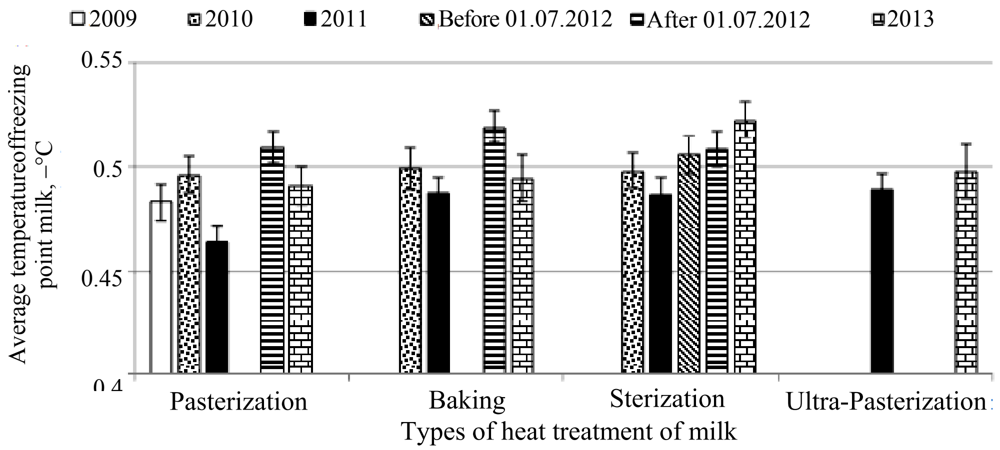

Fig. 2. Changes in the average freezing temperature of heat-treated milk in 2009–2013

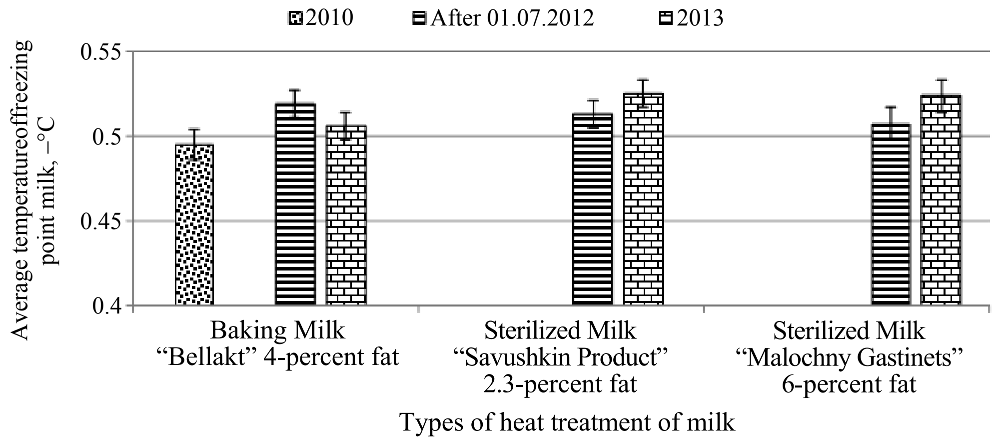

Fig. 3. Changes in the average freezing temperature of heat-treated milk by different manufacturers in 2010–2013

Products of high temperature treatment during the period in question consistently lower their freezing point, which may indicate a high quality source of raw milk production and careful manufacturing regarding to quality and maximum preservation of native nutrients in the finished product.

In general, there is a decrease cryotemperature of pasteurized and boiled milk after the tightening of requirements for the acidity of the finished food product. Some increase of cryoscopic temperature in 2013 is due to the large variability in the temperature of freezing for different manufacturers. All manufacturers have lowered values of this indicator to a variable extent.

One of the two manufacturers of ultra- pasteurized milk shows a general downtrend of researched index. It should be noted that the products are manufactured according to the specifications of the enterprise because of the absence of this type of heat treatment in the standard [16]. Another manufacturer provides the production of ultra-pasteurized milk with the average freezing temperature in the range from –0.481 to –0,475°C. The first manufacturer shows the spread of the mean values of the cryotemperature comes to 0,030°C, and the lowest value of the index reaches –0,533°C that is probably due to the raw material used and the high-temperature short-term treatment regimes.

Comparing the freezing temperature of the finished drinking milk for any extended period is quite difficult, because consumer needs may change with time and the products can be removed from the market or replaced by better ones.

Therefore, we selected the last two years to compare the two types of drinking sterilized milk of different domestic producers widely represented in the trade. Outward package, fat content and composition of baked milk produced by Volkovysk JSC "Bellakt" remains unchanged for a long period. However, in 2011 and 2012 measurements were not carried out because of the acute shortage of this type of product in the trading network.

Fig. 3 shows the previously described basic tendency of lowering freezing temperature for sterilized milk.

Probably, the reason for some increasing of a cryoscopic temperature is connected particularly with the quality of raw milk with low content of lactose [22, 23]. Thus, there is an inverse relationship between the content of the lactose and the chlorides in the milk: lactose increasing brings reduce of the amount of chloride, and vice versa. It is believed, that with the increase of chloride content at 0.01%, the amount of lactose reduces to 0.17% [23].

Conclusion. Stricter requirements to the level of acidity of the finished product has led to a lowering of the freezing point of milk, although to varying degrees for different types of products.

A general dynamic of changes in milk cryoscopic temperature under different heat treatment in the past few years has been found.

Under fierce competition in the domestic and international markets of dairy products the goods of higher quality due to fulfilment of new requirements of the State standard are expected to have god advantages among traditional analogs.

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