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RESEARCH OF HEAT TREATMENT INFLUENCE OF MILK ON QUALITY AND SAFETY OF HARD CHEESES

Об'єктом дослідження є молоко-сировина, що використовується для виробництва твердих сирів молокопереробними підприємствами України. Якість молока-сировини є особливо важливим, ключовим фактором, який визначає ефективність молокопереробної галузі. Без молока, яке відповідає певним вимогам, неможливо організувати виробництво високоякісної продукції. Особливі вимоги висуваються до якості молока-сировини, призначеного для виробництва сирів. Одним з найбільш проблемних місць є підвищення якості і сиропридатності молока-сировини та удосконалення технологічного процесу виробництва натуральних твердих сирів.

У ході дослідження при проведенні визначень якісних показників молока-сировини та готової продукції, а також їх мікробної забрудненості застосовувались лабораторні (біохімічні та мікробіологічні) методи досліджень. А для обробки результатів дослідження застосовувались методи математичної статистики.

В роботі показано, що бактеріальне забруднення молока-сировини, яке перевищує нормативно встановлені граничні значення, являє загрозу як для технологічного процесу виготовлення сирів, так і для якості готової продукції. Запропоновано способи запобігання зниження виходу сиру і погіршення його якості внаслідок тривалого зберігання молока при низьких температурах. Доведено, що найкращі результати отримують при ультрависокотемпературній обробці молока з витримкою 2–4 с. А також, що високотемпературна і, особливо, ультра високотемпературна (УВТ-обробка) є дуже ефективним способом знищення бактеріальної мікрофлори і підвищення якості сирого молока за таким показником, як «бак забруднення». Це дозволяє підвищити сиропридатність молока-сировини. Високі температури теплової обробки молока призводять до змін у сольовому і білковому складі молока. Ці зміни мають як негативні наслідки – погіршення сичужного згортання молока і синергетичних властивостей згустку, так і позитивний результат, що полягає в збільшенні переходу сухих речовин молока, передусім сироваткових білків, у згусток і сир.

Ключові слова: *молоко-сировина, сиропридатність молока, бактеріальне забруднення, високотемпературна обробка, ультрависокотемпературна обробка.*

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1. Introduction

Providing the population with benign food is the most important national economic and social problem. The leading role in the implementation belongs to the dairy industry, including the cheese-making industry.

The total cheese production in the world is constantly growing and, along with dairy products, is becoming one of the main ways of milk processing. The market economy of Ukraine needs to increase the production of natural hard cheeses, improve their quality, expand the range. Among a wide variety of cheeses, a special place is occupied by natural hard rennet cheeses with high-temperature processing of milk, the demand for which is constantly growing.

The production of hard rennet cheese is a complex multifunctional process in which changing the influence of even one of the technological factors can change the dynamics of the biochemical, microbiological and physico-chemical transformations of the cheese mass. This is reflected not only in the organoleptic properties and biological value of the final product, but also in its safety.

The quality of raw milk in a market economy is becoming especially important, and sometimes even a key factor, determining the effectiveness of the milk processing industry. Without milk, which meets certain requirements, it is impossible to organize the production of high-quality products. Special requirements are placed on the quality of raw milk intended for the production of cheese.

The works of many scientists are devoted to the problems of researching the milk and cheese market. So, in [1], the milk market in Ukraine and prospects for various categories of farms are studied. In [2], problems of the development of effective milk production and its industrial processing in Ukraine are considered. The quality of milk and its compliance with European requirements are the subject of works [3–5]. The problems associated with improving the quality and cheese suitability of raw milk and improving the technological process for the production of natural hard cheeses are among the most important. The solution to these problems will expand the range of hard natural cheeses and increase their production volumes.

Therefore, today the urgent issue is the study of the quality of raw milk used in the production of dairy products.

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This is extremely important for the production of hard cheeses, because it is a consumer product, for the production of which only high-quality milk is needed.

Thus, *the object of research* is the raw milk used for the production of hard cheeses by milk processing enterprises of Ukraine. And *the aim of research* is determination the cheese suitability indicators of raw milk according to bacteriological indicators.

2. Methods of research

In the research, the following scientific methods are used:

– analysis and synthesis method – in the study of sources of scientific literature on research topics;
– methods of laboratory (biochemical and microbiological) studies – when determining the quality indicators of raw milk and finished products, their microbial contamination;
– methods of mathematical statistics – for processing research results.

3. Research results and discussion

Bacterial contamination of raw milk, which exceeds the regulatory limits, poses a threat to both the cheese manufacturing process and the quality of the finished product.

The author of [6] believes that, under the conditions of other criteria meeting the requirements for cheese suitability, a high-quality product can be obtained from milk with bacterial contamination of up to 4000 CFU/g. The author evaluated the value of the total bacterial contamination of raw milk from the point of view of safety quality cheese. Ukrainian cheese production allows the use of raw milk with a total bacterial contamination according to NMAOAnM (the number of mesophilic aerobic and optional anaerobic microorganisms) up to $4 \cdot 10^6$ CFU/g (colony forming units). This is the limiting feature of the number of bacteria in milk of class II by reductase breakdown. However, in the USA and most European countries, similar indicators for raw milk do not exceed 10^2 CFU/g.

Describing the state of affairs related to the quality of raw milk is procured for the dairy industry, in most cases it does not meet the requirements of DSTU 3662-97, especially with respect to microbiological and safety indicators. The main reason is that manufacturers, as well as private households, do not comply with sanitary and hygienic requirements when receiving milk. As a result of this, a significant amount of milk with bacterial contamination, which is not only at the ultimate level, but even sometimes exceeds these indicators, enters the ceese production companies.

Bacterial contamination of raw milk is a significant problem in the production of cheese. In Ukraine, the regulated NMAOAnM is from $3.0 \cdot 10^5$ to $4.0 \cdot 10^6$ CFU/cm^3, which corresponds to milk of I and II class. Almost 80 % of Ukrainian milk belongs to the second class [7]. The requirements of the European Union limit the content of NMAOAnM in raw milk to $1.0 \cdot 10^5$, and, on the recommendation of the World Health Organization (WHO), to $1.0 \cdot 10^3$ CFU/cm^3 [8, 9].

Experts believe that in raw milk, the risk line for changing the quality of milk and products made from it should be considered: the content of lactic acid lactococci – at the level of $1 \cdot 10^7$ in 1 cm^3, psychrotrophic microbes – at the level of $1 \cdot 10^6$ in 1 cm^3 [10, 11].

Reducing the yield of cheese and the deterioration of its quality due to long-term storage of milk at low temperatures can be prevented using the following proposed methods:

– carry out preliminary pasteurization of milk before cooling and storage;
– conduct the milk thermalization at a temperature not exceeding 65 °C;
– add lactic acid bacteria to milk before storage;
– add calcium chloride to milk before coagulation;
– mix milk with long-term storage with fresh milk.

The main type of heat treatment of raw milk in the cheese production industry is pasteurization, which results in a reduction in the content of pathogenic and technically harmful microorganisms in raw materials to a safe level.

Modes of pasteurization of raw milk, which are used in the production of hard rennet cheese, do not destroy the entire microflora. Even pasteurization of milk at a temperature of 75...76 °C for 20–25 s, which corresponds to the upper limit of the heat treatment of raw milk in the production of hard rennet cheese, ensures the efficiency of neutralization of heat-resistant bacteria by only 94.6 %. This is later confirmed by the results of studies [12].

The accepted modes of short-term pasteurization for most rennet cheeses at the level of 72...76 °C with a shutter speed of 20–25 s make it possible to achieve a residual amount of bacterial contamination of milk with a pasteurization mode of 72 °C – 3.2 %, with a pasteurization mode of 76 °C – 0.7 %.

Usually, most vegetative cells of pathogenic microorganisms are destroyed as a result of short-term pasteurization of milk at 72...76 °C, but their individual cells can withstand such heat treatment. So, it is found that even after pasteurization at 74...75 °C for 16 s, bacteria of the Escherichia coli group are present in milk.

In unpasteurized milk, a heat-resistant microflora is found that can withstand heat up to 80 °C. Experiments [13] establish the presence in the milk of heat-resistant lactic acid sticks hazardous to the quality of milk products, which can withstand short-term heating to a temperature of 85...95 °C and cause such milk deficiencies like ductility and unpleasant taste of the product.

At pasteurization temperatures of 72, 75, 80, and 85 °C with an exposure of 21 s, 80, 30, 20, and 8 % of heat-resistant bacteria, respectively, remain in milk. An increase in the duration of milk exposure at these temperatures from 21 to 49 s and even 59 s did not significantly affect the degree of contamination of milk with bacteria.

Assessing the influence of pasteurization modes on the bacterial contamination of milk, it is concluded [14] that the pasteurization modes of milk that are used in cheese making (temperature 72...76 °C with an exposure of 15–30 s) do not provide guaranteed bacterial neutralization of milk microflora.

Short-term heating of milk during the production of natural cheeses to temperatures exceeding 76 °C is considered high-temperature (HT) processing or pasteurization, and heating above 100 °C is considered ultra-high temperature (UHT) processing.

The best results are obtained with UHT processing of milk with an exposure of 2–4 s. The possibility of using short-term high temperatures is explained by the fact that living cells of microorganisms respond faster to high temperatures than the constituent parts of milk. In other words, the rate of destruction of microorganisms under short-term exposure to high temperatures is higher than the rate of chemical reactions and the destruction of the constituent components of milk over this period of time.

It can be concluded that high-temperature and, especially, UHT treatment is a very effective way to destroy bacterial microflora and improve the quality of raw milk by such an indicator as a «pollution tank», which makes it possible to increase the cheese suitability of raw milk. However, it should be noted that under the influence of high pasteurization temperatures, changes occur in the salt composition of raw milk, as well as in the structure and properties of proteins [15].

The use of high temperatures for pasteurization of milk in cheese making is mainly limited by soft cheese technologies and is hardly used in the production of hard cheeses. This leads to a deterioration of rennet coagulation of milk and dehydration of cheese grains.

Any thermal effect affects the constituent components of milk and its physico-chemical properties. The degree of influence depends mainly on the temperature regime and duration of exposure to temperature. The protein system has high heat resistance due to casein, which refers to heat-resistant proteins. Without coagulation, it withstands heating at a temperature of 140 °C for 10–20 minutes.

The main mineral components involved in rennet coagulation of milk, as well as in the formation of the structure and texture of cheese, are calcium and phosphorus. The latter are found in milk both in true solution and in colloidal form. In fresh raw milk, the true solution accounts for about 33 % calcium and 53 % phosphorus. During heat treatment of milk, a significant part of the soluble forms of phosphorus and especially calcium goes into a colloidal state.

During heat treatment, the salt composition of milk changes, and, first of all, the composition of calcium salts. These changes are associated with the transition of a part of calcium phosphate and dehydrogen phosphate from a monomolecular form to poorly soluble calcium phosphate, which is aggregated and precipitated in the form of a colloid on casein micelles. In this case, irreversible mineralization of the caseinate-calcium phosphate complex occurs, causing a violation of the structure of micelles and a decrease in the heat resistance of milk. Part of the calcium phosphate together with the denatured plasma proteins forms milk stone.

Ionized calcium makes up about one third of the soluble forms of calcium. The rennet coagulation rate, clot strength, structure and consistency of cheese dough largely depend on its content. The normal concentration of ionized calcium is considered to be 11 mg/100 g. When the amount of ionized calcium is reduced to 8 mg/100 g, milk becomes «rennet-slow».

The influence of heat treatment on the content of ionized calcium in milk was studied by Lithuanian researchers in [16]. According to them, after heating raw milk to a temperature of 74, 88 and 125 °C, the mass fraction of ionized calcium decreases and is, respectively, 84.76; 77.68 and 73.42 % of the initial amount of calcium.

Due to the fact that the content of ionized calcium in milk after heat treatment is reduced, this loss in the production of cheese is compensated by the addition of calcium chloride at the rate of 10 to 40 g of anhydrous salt per 100 kg of pasteurized milk. It should be noted that a simple correlation of the composition of milk by adding calcium chloride to it is not always able to give the properties rennet-slow milk necessary for the production of cheese. When using rennet-slow milk, a feature of the process is associated with the following phenomena:

– higher costs of milk-forming enzyme;
– long process of clot formation;
– underestimated rheological parameters of the clot;
– weak whey syneresis;
– long-term processing of cheese grain;
– slow pH increase during the manufacturing process;
– low yield and low quality cheese.

It is known that poor coagulability of milk by rennet is due to violations in the casein-salt of milk system.

The heat treatment of milk leads not only to the transition of some of the soluble forms of non-protein calcium and phosphorus to the colloidal state, but also to structural changes in whey proteins. The total content of the latter in cow's milk averages 0.6 %.

In terms of stability with respect to thermal denaturation, whey proteins are arranged in increasing order in the following sequence: immunoglobulins, whey albumin, β-lactoglobulin.

Whey protein denaturation increases with increasing heating temperature. So, at a temperature of 165 °C with a holding time of 2 s and 72–74 °C with a holding time of 20 s, the total denaturation of the protein components of the whey is 90.0 % and 8.8 %, respectively.

The denaturation degree of whey proteins depending on the heat treatment mode is:

– at a pasteurization temperature of 72–74 °C for 15–20 s – 9 %;
– at 85 °C for 15–20 s – 22–30 %;
– at 140–150 °C for 1 s – 40–80 %.

It is also noted that whey proteins due to their high hydrophilic properties increase the water-holding capacity of casein and slow down the separation of whey from casein clot.

It should be noted that the amount of denatured proteins depends on the duration of heat treatment of milk.

The most important protein in whey is β-lactoglobulin, since it accounts for about half of all whey proteins and is characterized by a high content of essential amino acids. It refers to heat-labile whey proteins. Denaturation of β-lactoglobulin ends already when milk is heated to 85 °C and held at this temperature for 30 minutes.

At high heat treatment temperatures, β-lactoglobulin is complexed with α-lactalbumin and casein micelles with χ-casein. When milk is heated to 125–138 °C with a holding time of 2 s, the average diameter of casein particles increases from 66.7 to 85 microns. It should be noted that casein is a heat-resistant protein and only with prolonged exposure to high temperatures does its composition and structure change. As for milk fat, the triglycerides are almost unchanged in pasteurization in chemical composition.

The action of high temperatures on the thermolabile components of milk leads to a deterioration in the rennet coagulation of milk and the synergistic properties of the clot. A study of rennet coagulation of milk that has undergone heat treatment through the wall at 85 °C has

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shown that the duration of milk coagulation increases by more than 3 times, and after heating through the wall at a temperature of 125, 135 and 145 °C, milk almost completely loses its coagulation ability.

The use of the steam-contact method of UHT treatment at the same temperatures showed a significantly lesser degree of influence on the ability of milk to rennet coagulation. Moreover, the duration of the formation of rennet increases by almost 5 times.

The results of determining the synergistic properties of rennet clots obtained from milk, which has undergone heat treatment from 74 to 135 °C, show that increasing the pasteurization temperature reduces the excretion of whey. Some researchers interpret the phenomenon of the transition of denatured whey proteins into a casein clot as a progressive process. The transition of whey proteins is determined by the solids content, namely: at a pasteurization temperature of milk 74 °C, the solids content increased by 0.05 %, at 88 °C – 0.40 % and at 135 °C – 0.63 %.

It is known that the main component of milk in the production of cheese is proteins. The yield of cheese depends primarily on their content in milk. With an increase in the content of casein in milk by even 0.1 %, the yield of cheese increases by 2.3 %, while an increase in fat content by 0.1 % increases the yield of the finished product by only 1 %.

One of the main problems associated with the economy in the field of synergy is the more complete use of milk constituents. Thermal processing of milk contributes significantly to the improvement of the use of milk proteins in the production of cheese. A technology is developed for the use of high-temperature milk processing in the production of soft cheeses. Temperature conditions are divided into three groups: in the first – 74–76 °C; in the second – 80–90 °C; in the third – 93–95 °C. Elevated pasteurization temperatures show a more effective destruction of the microflora of raw milk, which allows to achieve a process efficiency of 99.99 %. But the higher the temperature of the heat treatment, the more profound changes occur with the components of milk. The most sensitive are whey proteins.

The yield of finished products to a certain extent depends on the pasteurization regime, since this affects the degree of use of the constituent components of milk. It is established that with increasing temperature from 72...74 °C to 85...90 °C during the production of Lori cheese, a significant increase in the yield of the finished product is observed, raw material costs are reduced by 2.4 % with a mass fraction of fat in the mixture 3.4 % This reduction in milk consumption occurs due to a decrease in protein and fat loss with whey. A study of the chemical composition of cheese whey obtained in the manufacture of experimental and control cheese samples show that the total protein content is, respectively, 0.59 and 0.70 %, casein – 0.25 and 3.0 %, fat – 0.32 and 0.41 %.

In order to obtain high-quality cheese in the processing of milk with bacterial contamination above 10^6 CFU/cm^3, experts consider it appropriate to use elevated pasteurization temperatures. To improve the cheese suitability of pasteurized milk at high temperatures, the authors recommend that it be ripened with sourdough.

It is established that in the production of cheese it is necessary to apply the ripening of milk, the activation of bacterial sourdough and an increase in the amount of milk up to 2–3 %. If do not use these technological methods, the application of pasteurization temperatures above 75...76 °C leads to a deterioration in the ability of milk to rennet to curl.

Significant influence on the course of the technological process of cheese production has UHT milk processing.

Specialists in [17, 18] proposed a method of preparing milk for rennet coagulation, which consists in the heat treatment of milk at a temperature of 110...120 °C with a holding time of 7–12 s and cooling to a temperature of 65...72 °C for 5–10 seconds. One of the main advantages of this method is that it allows to increase the yield of cheese.

Cheeses made from milk that has undergone UHT treatment should have an overly sour taste and a greasy consistency. However, the negative impact of UHT processing on cheese yield can be eliminated.

It is found that in the case of the use of UHT treatment, the greatest influence on the kinetics of the formation and improvement of rennet has an increase in the acidity of milk. In [16], the possibility of increasing the yield and improving the quality of Lithuanian cheese during its production from milk, which underwent UHT processing and prepared by combining aging with cold fermentation, was proved. The latter is carried out by holding for 10–20 hours. Milk cools to 6...12 °C with added bacterial yeast in an amount of 0.3 % and an aqueous solution of calcium chloride – 0.04 %. This method allows to use for the production of cheese up to 30 % of milk that has passed UHT processing, in a mixture with milk pasteurized at 74 °C.

However, this method of preparing milk is not rational enough. One of its shortcomings is that it provides for UHT treatment of only a portion of milk intended for the production of cheese. In addition, it significantly increases the duration of milk processing and requires additional containers for ripening and fermentation of milk.

A promising way to realize the advantages of HT and UHT milk processing in cheese making is development of new types of cheese with a high moisture content.

4. Conclusions

It is found that the rate of destruction of microorganisms with short-term exposure to high temperatures is higher than the rate of chemical reactions and the destruction of the constituent components of milk for this period of time. It is shown that high temperature and, especially, UHT treatment is a very effective way to destroy bacterial microflora and improve the quality of raw milk by such an indicator as a «pollution tank». This allows to increase the cheese suitability of raw milk.

It is also found that the effect of high temperatures on the thermolabile components of milk leads to a deterioration in the rennet coagulation of milk and the synergistic properties of the clot. The study of rennet coagulation of milk that has undergone heat treatment through the wall at 85 °C shows that the duration of coagulation of milk increases by more than 3 times. And after heating through the wall at a temperature of 125, 135 and 145 °C milk almost completely loses its ability to clot. The use of the steam-contact method of UHT treatment at the same temperatures shows a significantly lesser degree of influence on the ability of milk to rennet coagulation. Moreover, the duration of the formation of rennet increases by almost 5 times. The results of determining the synergistic properties of rennet clots obtained from milk that underwent heat treatment from 74 to 135 °C show that an increase in pasteurization temperature reduces the whey excretion. The transition of whey proteins was determined by the solids content, namely: at a pasteurization temperature of milk 74 °C, the solids content increases by 0.05 %, at 88 °C – 0.40 % and at 135 °C – 0.63 %.

A technology is developed for the use of high-temperature milk processing in the production of soft cheeses. The yield of finished products to a certain extent depends on the pasteurization regime, since this affects the degree of use of the constituent components of milk. It is found that with increasing temperature from 72...74 °C to 85...90 °C, a significant increase in the yield of the finished product is observed, the raw material costs are reduced by 2.4 % with a mass fraction of fat in the mixture of 3.4 %. And also, in the production of cheese, it is necessary to apply the ripening of milk, the activation of bacterial sourdough and an increase in the amount of milk to 2–3 %.

The research results will be useful to technologists and scientists who are researching the quality and safety of milk and dairy products will also be interesting.

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