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Effect of ultrasonic treatment on the dissolution of milk solids during the reconstitution of skim milk powder

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Abstract. The producing reconstituted milk products that retain the same sensory properties as those of raw milk products is of high interest to the food industry In the technology of producing reconstituted milk processing products, the most significant factor that determines the component transition degree and the usefulness of the product being produced is the recombination process. It determines the possibility of bringing the organoleptic characteristics of reconstituted milk to the properties of the genuine one. One promising method to improve the process of milk powder recombination is ultrasonic exposure. The aim of the present study is to improve the process of milk powder recombination using ultrasonic exposure. The results of the conducted studies show that the ultrasonic treatment eliminates the agglomerates of dried milk particles in water and provides more accessible interaction between the particles and water, and as a result, improves the recombination process. The application of ultrasonic treatment during the reconstitution of the skim milk powder improved the dissolution of milk solids, as evidenced by around a 75% reduction in the amount of centrifuged insoluble sediment. The mass fractions of protein and lactose have increased by 4.8 and 6.5%, respectively.

Key words: reconstituted milk products, ultrasonic exposure, skim milk powder.

INTRODUCTION

The food and pharmaceutical processing industry is an important, system-forming sphere of the national economy, forming the agro-food market and the food and economic security of Russia. The modern dairy industry is characterized by significant changes towards smoothing the seasonality of the dairy production and the activation of the processes of creating large dairy farms implementing modern technological solutions for fodder preparation, feeding, handling and milking.

Currently, Russian dairy market is in a difficult situation. There are many problems, such as ireduction in the number of cows, significant proportion of semi-subsidence households in the production of raw milk, significant increase in the cost of milk production and processing, poor development of the raw material base, increase in the proportion of falsified dairy products in the diary market. All these factors restrain the ramp-up of the dairy production, do not allow modernizing the production and increase its efficiency, impede imports phase-out in the Russian dairy market.

At the same time, increased production of dried milk. Taking into account a large share of both domestic and imported dried milk in the production of milk products, the modernization of the technology for the production of dairy products based on or using dried milk remains an important issue (Andersson et al., 2018).

In the technology of producing reconstituted milk processing products, the most significant factor that determines the component transition degree and the usefulness of the product being produced is the recombination process. It determines the possibility of bringing the organoleptic characteristics of reconstituted milk to the properties of the genuine one.

The recombination process is a heterogeneous chemical reaction between a solid substance and a liquid and is accompanied by a transition of the substance to the solution.

The essence of the dissolution process lies in the interaction of dried milk products with water and includes several stages: dissolution of lactose and mineral substances, distribution of protein and fat in the solution, hydration of the dispersed phase, separation of excess air from the product. The intensity of the process and its effectiveness are determined by the properties of both dried milk and water.

The water that is a part of milk and dairy products is heterogeneous in its physicochemical properties, and its role is unequal. Most of the milk water (84.5–85%) is in a free state, i.e, it can participate in biochemical reactions. Free milk water is a solution of various organic and inorganic substances (sugar, salts, etc.). It can be easily turned into ice when milk is frozen or removed during thickening and drying.

A smaller portion (3–3.5%) of the water is in the bound state: the adsorption-bound water is retained by molecular forces at the surface of colloidal particles (proteins, phospholipids, polysaccharides). The stability of protein particles, as well as milk fat globules, depends on the properties of the hydrated shells. The subsequent layers of the water molecules are bound to protein by less strong bonds, and its properties do not differ from those of free water; chemically bound water is the water of crystalline hydrates, or crystallization water. In milk, the crystallization water is bound to the crystals of milk sugar. Bound water does not freeze at low temperatures (below –40 °C), does not dissolve salts and sugar. Bound water cannot be removed from milk during drying. The amount of bound water is usually used to judge on the hydrophility of proteins, i.e. the ability to bind the entire moisture (moisture of the first and subsequent layers).The forms of water bonds and the hydrophility of proteins determine the quality of reconstituted milk processing products.

The main processes that determine the recombination quality are the dissolution of lactose and mineral substances accompanied by the transition of fat and protein to the emulsion-colloidal state. As a result, a dispersion medium is formed, while the dispersity of proteins and fat should correspond to their dispersity in genuine milk. During the whole recombination process, excess air is released from the product particles, and the gas release rate influences the intensity of the course of other recombination stages (Chandan & Kilara 2011; Chalupa-Krebzdak et al., 2018).

Retrieved from www.scopus.comAt the first stage, when contacting water, lactose, mineral substances and whey proteins leach from the surface of the dried milk particle, then, water penetrates into the cracks and capillaries of the particle, displaces the air and leaches lactose and mineral substances from the inside of the dry matter. All these lead to the decay of the particle, and the insoluble components - fat and protein - are dispersed in the solution. However, particles in dried milk can be not only individual, but also in the form of agglomerates, which are not dissolved for a long time. It has been established that when the agglomerates contact water, a liquid layer having a high concentration and viscosity is formed on their surface. This layer forms a shell that prevents penetration of water inside the agglomerate. Lactose and protein also determine the wetting properties of the dried milk particles: lactose is less subject to physical and chemical changes in production, so when reconstituted, it is well wetted with water and does not impede water impregnation of the milk powder layer. The wetting properties of protein depend on the degree of its denaturation: the less denatured the protein is, the worse it is wetted, however it has a high dissolution rate. Milk generally contains about 3.2% of proteins, the fluctuations range from 2.9% to 3.5%. These include casein, whey proteins and proteins of fat globule membranes (Liu et al., 2018).

Casein is actually a food protein that performs a new structure function in an organism. In addition, casein conveys calcium, phosphorus and magnesium in the composition of its particles. In milk, casein is in the form of specific particles, or micelles, which are complex aggregates of casein fractions with colloidal calcium phosphate (McCarthy et al., 2017; Lucey & Horne, 2018). The hydrophilic properties of casein depend on the structure, the charge value of the protein molecule, the pH of the medium, the concentration of salts and other factors. The stability of casein micelles in milk depends on the hydrophilic properties of casein. The hydrophilic properties of casein influence the ability of the acid and acid-rennet clot to retain and release moisture. Milk casein is contained in the form of a complex aggregate of calcium caseinate with colloidal calcium phosphate, the so-called caseinate calcium phosphate complex (CCPhC). The CCPhC also contains a small amount of citric acid, magnesium, potassium and sodium.

Whey proteins make up about 0.6% of proteins, they consist of |β-lactoglobulin, α-lactalbumin, immunoglobulins, serum albumin, lactoferrin.

Proteins of fat globule membranes are proteins, which are structural elements of fat globule membranes and contribute to their stability during processing.

To accelerate the recombination process, it is necessary to increase the penetrating ability of water, it can be done by mechanical and hydrodynamic methods. To intensify the agglomerate dissolution process, it is expedient to maintain a high viscosity of the dispersion medium. With an increase in the mixing process intensity, the efficiency of the dissolution process increases (Matignon et al., 2015; Hettiarachchi et al., 2018; Mercan et al., 2018; Liu et al., 2019; Wu et al., 2019).

The aim of the present study is to improve the process of milk powder reconstitution using ultrasonic exposure.

The improvement process based on ultrasonic cavitation energy takes place during implementation of mechanisms belonging to high-energy chemistry and is epithermal. Shestakov et al proved that epithermal cavitation treatment of water may destroy its intermolecular hydrogen bonds of cluster structure (thus causing declusterization of water) and may increase its solvency and capacity for dissociation (Shestakov et al., 2010).

Ultrasonic exposure is characterized by the presence of elastic vibrations and waves with the frequency above 15–20 kHz, which determine its specific features in various media. The most important nonlinear effect in the ultrasonic field is cavitation - the appearance of a mass of pulsating bubbles filled with steam, gas or their mixture in the liquid. The movement of bubbles in different directions, their collapse, merging with each other, etc. generate compression pulses (micro-shock waves) and microflows in the liquid, which contributes to local heating of the medium and the appearance of ionization. As the result of these effects, solid bodies in the liquid are destroyed (cavitation erosion), the liquid is mixed, various physical and chemical processes are initiated or accelerated. The degree and depth of the cavitation processes are determined by the ultrasonic exposure conditions (Gogate, 2011).

The aim of the present study is to improve the process of milk powder reconstitution using ultrasonic exposure.

MATERIALS AND METHODS

Model samples of raw milk were reconstructed by traditional technology and using ultrasound treatment.

Traditional recovery technology: powdered milk is introduced into water at a temperature of 38–45 °C in the ratio of 1:10, actively mixed and aged for 3 hours.

Dry milk samples had the following characteristics: mass fraction of moisture - 2.85 ± 0.02%, fat – 1.1 ± 0.02%, protein – 37.4 ± 0.1%, lactose – 50 ± 0.1%.

Ultrasonic exposure on the sample was performed taking into account the variations in power and duration (120, 180 and 240 W for 1, 3 and 5 minutes) at various stages: 1) treatment of water (before adding dried milk); 2) jointly dried milk and water, and 3) two-stage treatment (first water and then jointly water and milk powder) (Fig. 1). After adding dry milk to the water treated with ultrasound (option 1), it has been mixing actively for 1 minute. Additional mixing of samples 2 and 3 was not carried out, since ultrasound, when exposed to a mixture of dry milk and water, also contributed to their dispersion.

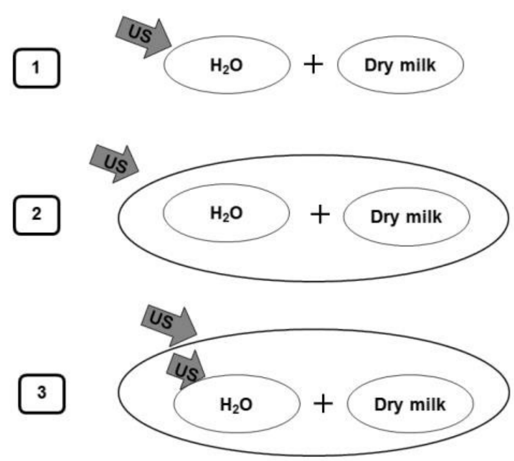

Figure 1. Experiment model of milk powder reconstitution.

To process the studied samples based on ultrasonic exposure, Volna-M ultrasonic technological device (model UZTA-04/22-OM) with the following characteristics was used:

frequency of mechanical oscillations – 22 ± 1.65 kHz;

power – 400 VA;

ultrasonic exposure intensity, no less than 10 W cm^{-2}

radiating surface diameter – 25 mm.

The ultrasonic oscillatory system is built on piezoelectric ring elements and is made of VT5 titanium alloy. The engineering solutions used are protected by the RF patent No. 2141386.

The insolubility indices were determined in a graduated tube after holding the reconstituted sample and centrifuging it for 5 minutes. It is characterized by the amount of insoluble sediment in the reconstituted dry milk product sample.

Thermogravimetric analysis was performed by mass spectrometry analysis of volatile products of thermal decomposition of liquid materials using NetzchSTA 449 'Jupiter' at temperatures from 20 °C to 400 °C. The method is based on recording the thermal effects of transformations occurring under the conditions of a programmed exposure to temperature, and makes it possible to follow the course of the transformation of a substance during the heating process (Duckworth, 1980; Nilova et al., 2017).

Ratio of free and bound water in the samples of recombined raw milk, % was determined by thermogravimetric method, based on the change in mass of the sample of the analyzed products under the influence of temperature 125 ± 2 °C.

The mass fraction of lactose was determined by the refractometric method, based on the determination of the refractive index of protein-free whey.

The mass fraction of skim solids was defined as the difference between the mass fractions of solids and fat. The mass fraction of solids was determined by drying the analyzed sample at a temperature of (102 ± 2) °C. The method of determining the mass fraction of fat is based on the selection of fat from a milk drink under the action of concentrated sulfuric acid and isoamyl alcohol, followed by centrifugation and measuring the amount of released fat in the graduated part of the fat meter.

The mass fraction of protein was determined by the method based on the burning of the organic components of the milk sample in the Kjeldahl flask in the presence of sulfuric acid and catalysts (GOST R 53951-2010).

The statistically significant differences amongst the groups were established using the Kruskal-Wallis criteria. In order to be able to detect statistically significant differences between the two compared groups, the Manna-Whitney criteria (U) were used. The differences were deemed significant where $p < 0.05$. The statistical interconnections were studied using a non-parametric correlational analysis calculating the coefficients of the correlation of rankings according to Spearman (Rs).

RESULTS AND DISCUSSION

The results of evaluating the ratio of free and bound water in reconstituted raw milk (Fig. 2) showed a large proportion of water in the free state (38.01%) in the control sample (produced using the traditional dried milk recombination technology), which in turn is preconditioned by the processes of the ability of the dried milk particles to interact with clusters of water, and protein substances - to the hydration processes. Ultrasonic cavitation through internal explosions improves the separation of water clusters into individual molecules and agglomerates of dried milk into individual particles, which determines the increase in the ability of individual particles to interact with water molecules, promoting their swelling. This fact is illustrated by the data in Fig. 2, which indicates a smaller amount of free water in the raw milk sample processed by ultrasound at the stage of a mechanical mixture of dried fat-free milk and water – 30.9%, which is 18.7% less than the control sample obtained using the traditional technology. Water treatment before adding dried milk allows separating water clusters, however, the agglomerates of dried milk particles that are not broken into individual particles are probably less accessible to interaction, which increases the free water content in the sample obtained on the water exposed to ultrasonic trratment, to 32.1%.

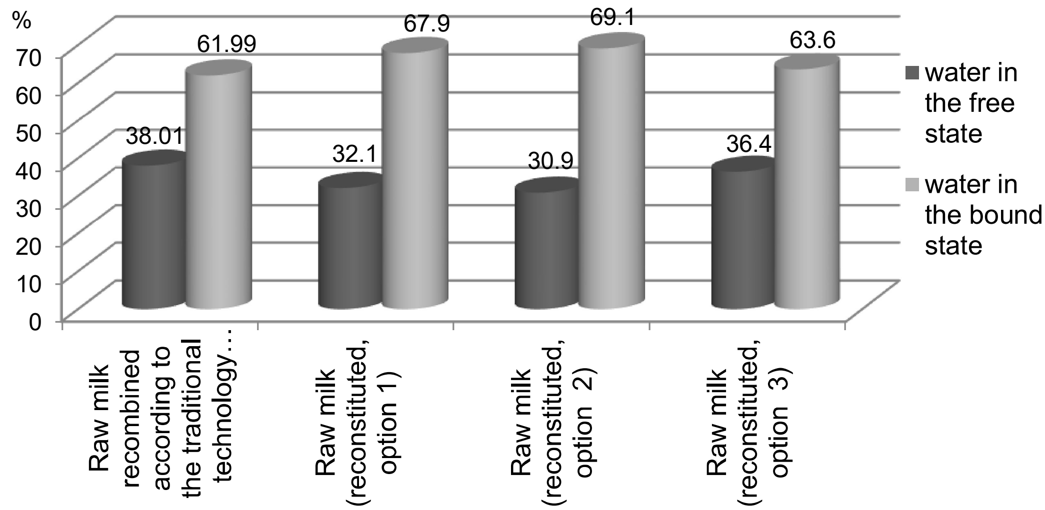

Figure 2. Ratio of free and bound water in the samples of reconstituted raw milk, %.

The state and forms of water bonds in the structure predetermine the uniformity of the composition, resistance of the milk system to various impacts (temperature drops, mechanical treatment, processing with a simultaneous exposure to several factors, etc.). Digestibility and other properties of milk are also characterized, as it has already been noted, by the state and forms of the water bond in the structure. Water in the bound state determines the degree of protein hydration and, as a consequence, its nutritional value (Tsirulnichenko & Popova, 2016).

The aforesaid was confirmed in the subsequent evaluation of the mass fraction of protein in the test samples.

The results of evaluating protein and lactose mass fractions, skim solids of milk drinks made according to the processing schemes modified by ultrasonic exposure, versus the control sample are shown in Fig. 3.

The protein content of the milk produced on the raw milk (control) recombined according to the traditional scheme was 2.69%, which does not meet the requirements of the standard, and one of the reasons for this may be a low reconstitution rate.

The ultrasonic treatment of the mixture of dried fat-free milk and water confirms the previous conclusions on the positive tendencies in the destruction of agglomerates of dried milk particles and water dissociates, which makes them more accessible for the interaction, and as a result, intensifies the reconstitution process (the volume of the insoluble precipitate twice decreased), and confirms the data on increasing water-bearing capacity of the protein fraction (Fatkullin et al., 2017; Silva et al., 2018).

The most intense changes covered the mass fractions of protein and lactose in the milk sample made from raw milk reconstituted according to version 2 (joint ultrasonic treatment of the mixture of fat-free milk and water) by 4.8 and 6.5%, respectively. This eventually led to an increase in the mass fraction of skim solids by 11.6%.

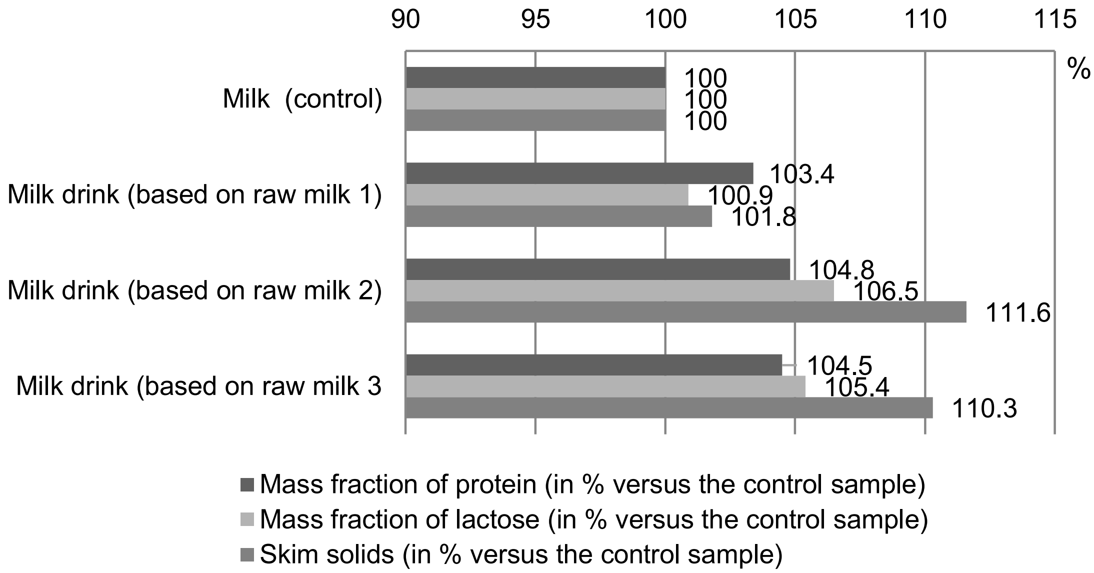

Figure 3. Results of evaluating the mass fraction of protein, lactose, skim solids versus the control sample in test samples, %.

Table 1. Results of evaluating the mass fraction of protein, lactose, skim solids in milk drink samples, % ($P < 0.05$)

	Mass fraction of protein, %	Mass fraction of lactose, %	Skim solids, %
Milk drink (control)	2.69 ± 0.03	3.52 ± 0.03	7.79 ± 0.03
Milk drink (based on raw milk 1)	2.78 ± 0.03	3.55 ± 0.03	7.93 ± 0.03
Milk drink (based on raw milk 2)	2.82 ± 0.03	3.75 ± 0.03	8.69 ± 0.03
Milk drink (based on raw milk 3)	2.81 ± 0.03	3.71 ± 0.03	8.59 ± 0.03

When processing the mechanical mixture of dried fat-free milk and water at the recombination phase, the mass fraction of protein in the milk drink was 2.82 ± 0.03% (see Table 1). The physical essence of the ultrasonic effect, namely the formation of cavitation bubbles, the rupture of which leads to the development of enormous pressures, is a source of a powerful impact and intensification of physicochemical processes.

Water treatment before adding dried fat-free milk thereto, as well as the two-stage ultrasonic treatment, also yield positive results, intensifying the process of milk powder recombination, which is reflected in the content of the protein fraction in the milk drink – 2.78 ± 0.03% and 2.81 ± 0,03% respectively.

The difference in the mass fractions of protein and lactose in samples 2 and 3 is statistically insignificant, fits into the range of experimental error.

The difference in values between skim solids and the sum of mass fractions of protein and lactose may be due to the better recovery of carbohydrates during ultrasound exposure. As it is known, milk contains monoses (glucose, galactose, fructose, etc.), deoxysugar, aminosugar, phosphosugar. The share of mineral substances increases as well (Popova et al., 2014; Potoroko et al., 2018).

The results of increasing the mass fraction of protein in the milk drink samples correlate with the results of decreasing the insolubility index in raw milk (Fig. 4).

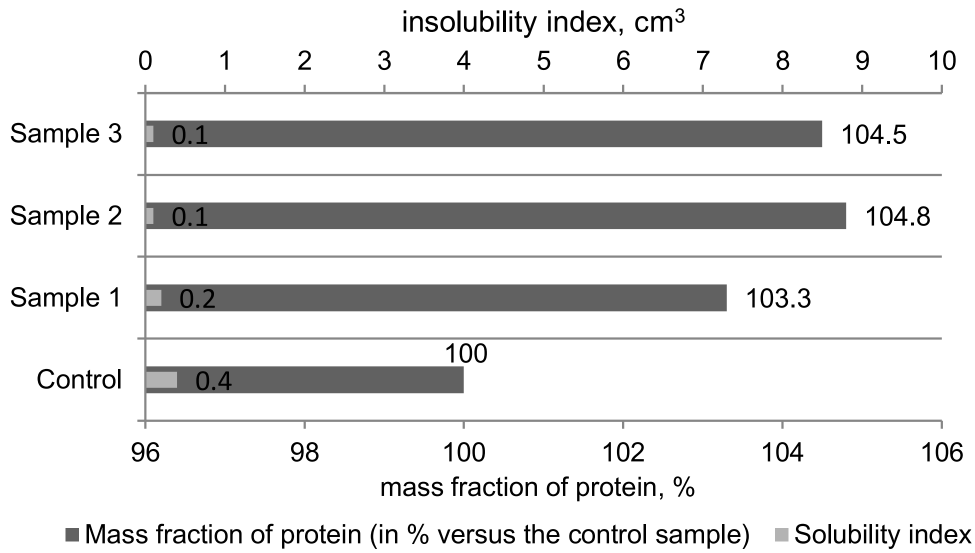

Figure 4. Insolubility indices and relative change in the mass fraction of protein in the samples obtained under different conditions, %.

The correlation coefficient is –0.97, which characterizes a strong feedback. The figure shows that when ultrasonic treatment is introduced into the dried milk reconstitution technology, the insolubility index decreases within the range of 62.5–75% versus the control sample, while the increase in the mass fraction of protein is from 3.3 to 4.8%.

The data on the change in the protein mass fraction content in the samples are correlated with the results of determining the mass fraction of lactose. During reconstitution water leaches the main components from the surface of the dried milk particles in the following sequence: lactose → mineral substances → whey proteins. Then, it penetrates into the agglomerates and leaches these components from the inside of the dry matter. Ultrasonic exposure of dried milk and water in addition to the rupture of the hydrogen bonds in the water also destroys the agglomerates of the particles, which accelerates the interaction of water with individual particles and facilitates the lactose release process. Therefore, the treatment at the stage of the mechanical mixture of dried fat-free milk and water gives a better lactose reconstitution effect (3.75 ± 0.02%).

Water treatment before the reconstitution of dried fat-free milk due to the rupture of the hydrogen bonds and the occurrence of cavitation processes tends to intensify the process of lactose leaching from the particles surface, which increases the lactose content in the milk drink to 3.55 ± 0.03%.

This index also correlates with the insolubility index -0.8. The increase in the mass fraction of lactose during the ultrasonic treatment is 0.9–6.5% on average, depending on the ultrasonic treatment conditions.

CONCLUSIONS

The application of ultrasonic treatment during the reconstitution of the skim milk powder improved the dissolution of milk solids, as evidenced by around a 75% reduction in the amount of centrifuged insoluble sediment.

The mass fractions of protein and lactose increased by 4.8 and 6.5%, respectively. This eventually led to an increase in the mass fraction of skim solids by 11.6%.

Thus, the results of the conducted studies show for the influence of the ultrasonic treatment, taking into account the exposure stage, on the quality indicators of reconstituted raw milk and its technological characteristics, which are further reflected in the improvement of the quality of milk products including fermented milk products.

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