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Sonication of dairy systems improves their properties

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The paper describes the results of recent research in the field of food sonochemistry dairy products which held in universities in Australia, Russia and Estonia. This research relates to technology preparation of mixtures from natural milk, vegetable fat and dry milk products with cavitation treatment using water. She is devoted to obtaining homogeneous dairy semi products, from which later produce dairy products such as cottage cheese or cheese where the bulk of the water is separated in the sera. It is shown that the sonochemical water treatment has a positive effect on the entire process and its outcome.

Keywords: Sonochemistry, water conditioning, dairy semi products.

INTRODUCTION

The dairy industry is one of the leading food industries to use artificial hydration since most ingredients of milk kept in a dry form and to restore if necessary with water. Even though the water in many products from milk is removed during cooking in a serum, but it has an important influence on the quality of the finished product. Water in the milk, as well as in the liquid that produces the living organism has particular characteristics. The water which passes through biological membranes is divided into separate molecules involved in protein synthesis and increases the hydrophilicity of amino acids. The water used in the recovery of dry milk ingredients may be close to a state in which it is found in natural milk, where its energy of hydration with the protein is maximal. The very same hydration as any reversible chemical reaction, in accordance with the law of Le Chatelier-Braun is more intense in the energetically favorable terms. Since hydration - an exothermic process, it occurs when the protein hydration shell is constructed from the individual water molecules are not linked together to the start of the reaction [1].

REVIEW OF THE TECHNICAL AND PATENT LITERATURE

Application of cavitation in the processing of milk is already known. For example, hydrodynamic cavitation has been used for the pasteurization and homogenization of milk. Specialists from the University of Mexico have developed a method of disinfection of milk. It is based on cavitation and does not require heating the entire fluid, but can also replace

pasteurization. Many useful reactions initiated by ultrasound in milk occur due to the effects of cavitation on the supramolecular structure of biopolymers [2]. However, radicals generated by pyrolysis and peroxy compounds generated during acoustic cavitation are undesirable in food processing [3, 4].

At the Institute of Chemical Physics RAS, proton magnetic relaxation measurement in sonicated water is used to evaluate the moisture content in food substances. They observed a spin-spin relaxation with a characteristic time of T_2, obtained after processing a two-component character. The two-component relaxation was observed for 2–3 hours, indicating the appearance of new water phases for a limited time. During the time of relaxation this nonequilibrium state of water shows unusual solubility features. This nonequilibrium state of water can form dense hydration shells around proteins providing thermoresistance to proteins [3].

Homogenization of milk (the dispersion of large fat globules) by the cavitation effect is due to selectivity. Particles of fat globules of different sizes are sheared by the physical forces generated during cavitation – larger particles are affected by the physical forces of ultrasound to a greater extent. The newly generated surfaces (fat particles of smaller size) need to be stabilized by proteins, di- and monoglycerides of fatty acids. In the initial stages of sonication, there is a deficiency of substances that stabilize the fat globules. The proteins move to the fat globule surface from the colloidal aqueous phase of milk generating a little breakdown in the equilibrium of the entire system. The di- and monoglycerides in a balanced dispersed system of milk may not participate in the stabilization process.

It has been found that the forces generated by acoustic cavitation in conventional ultrasonic reactors are about 3 times higher than the hydrostatic pressure [4] leading to the hydrolysis of fat particles. The fatty acid residues formed during the hydrolysis process increase the acidity and reduce the stability of the milk system. In this work, studies were carried out in milk systems produced in a cavitation reactor in the absence of hydrolysis of fat. Control experiments were carried out in the presence of hydrolysis of fat. Relative stability in terms of sedimentation of the samples was measured by photometric method. For this, specimens of samples taken from the top and bottom of the sonication cell and their absorption measured in the green region of the spectrum. It was found that the milk system that underwent hydrolysis showed a higher optical density.

An ultrasound device (patent CA 2111802) has been used in the homogenization of milk and other systems. In this device, it is not possible to control the ratio of hydrostatic and average sound pressure, as the gap in which the process takes place is a small. Due to this problem, the energy required to creating cavitation is very high. Homogenization of milk reported in Ref. 5 includes processing it through recirculation at temperatures up to +85 °C. However, heating the milk is a drawback for its homogenization. Although the threshold of cavitation in liquids decreases with increasing temperature, it is accompanied by a reduction of cavitation intensity [6]. A reduction in the cavitation intensity reduces the formation of substances which stabilize the milk emulsion. A rotor-pulsating device was developed for homogenization [7]. In such a device, a uniform particle size of milk fat could be obtained by cavitation. As mentioned earlier, by increasing the surface area of the oil phase in the process

of homogenization, there a deficiency of substances on the surface of the fat particles for stabilizing milk system. This can later lead to the coalescence of fat. Hence, the resulting milk formula is not stable. To increase the stability of the milk system, it is ideal to add excess proteins necessary to stabilize the newly formed surfaces. It should be noted that the addition of excess protein is not a simple process as the newly added protein needs to be hydrated. The sonication process can also aid the hydration of the proteins prior to them stabilizing the newly generated fat globules [8].

By most of the known methods of hydration of biopolymers the energy of cavitation is not explicitly set. However, the value of acoustic energy which applied to the system is very important. For example, in Ref. 9, wherein water or an aqueous solution before mixing with the biomass is treated with ultrasonic cavitation set only the lower limit of the ratio intensity of ultrasound to square of hydrostatic pressure, what determines only the required power. Time the impact of cavitation, ie the amount of energy for the sonochemical changes in water remains arbitrary. In a patent application WO 2007111524, the amplitude of sound pressure applied in a cavitation reactor was 5.5 times that of static pressure. The energy necessary to destroy the structure of water was controlled by the productivity of reactor and its electrical capacity. The duration of cavitation treatment of water was established by examining the dependence of the dynamic viscosity of water on the length of sonication. It was assumed that the viscosity of water is determined by the ratio of volumes of structured and unstructured components of water and obeys the Einstein-Smoluchowsky law [10]. However, studies carried out at the University of Leiden [11] suggest that the efficiency of the process based on this hypothesis is understated. In practice, this can lead to excessive energy consumption.

Generally, ultrasonic processing of milk systems is an order of magnitude more economical than thermal processing. For example, in pasteurization, where the whole mass of the liquid containing micorbes is heated to a temperature of +70°C and above, held for certain time and then sometimes forcibly cooled. However, with a cavitational process, the mechanical destruction of microbes requires only several cycles of ultrasonic wave. The task here is to find a way to obtain homogeneous and stable milk systems with high-protein without using excessive acoustic energy.

HYPOTHESIS

It is known that cavitation that generates above a certain level of energy can lead to thermodynamically nonequilibrium structures of water. The water possessing such nonequilibrium physical state acquires unusually high hydration ability with respect to proteins [12]. Dense hydration shells, formed on the sulfur containing amino acids of the protein, hinder thermal denaturation of proteins [13]. Hydrated shell formed on milk proteins, leads to κ-casein blocking the β-lactoglobulin from exposure to heat during thermal pasteurization.

In addition, cavitation converts soluble bicarbonates into insoluble carbonate form, effectively reducing the temporary hardness of water. This process assists the efficient rehydration of milk powers. The mechanism involved is based on the cavitation-induced destruction of hydration shells around the bicarbonates, $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. It is

based on a similar phenomenon that destroys the molecular structure of the water, converting the soluble salts into amorphous colloidal form of $CaCO_3$ and $MgCO_3$ [14].

Under natural conditions, proteins in the milk form a supramolecular structure due to the dipole-dipole interactions between amino acids present in the proteins. This structure can be destroyed by hydrodynamic cavitation generated by rotary-pulsational apparatus. Such a process will help in the rehydration process. In addition, it is also necessary to break the structure of water in order to promote the rehydration process. It is known that the best way to destroy the structure of water, in preparation for hydration, is by a sonication process in a cavitation reactor [12]. For efficient rehydration of milk proteins, the dry milk powder should be mixed with sonicated water with a minimum time delay since the nonequilibrium structure of water, created by sonication, is short lived. Hence, there is a need to synchronize the processing speed of the whole mixture in a rotor-pulsating device.

The electrical energy conversion efficiency of cavitation reactors can be evaluated by measuring the yield of hydrogen peroxide [15]. The energy efficiency of ultrasonic reactors can be improved by means of practical optimization. There are some ways to convert electrical energy into the energy of elastic vibrations with different coefficients of performance. In the device reported in the patent application WO 2007111524, a high energy efficiency of 90% has been reported. The specific performance of the device was 0,17 $m^3/KW{\cdot}h$. The reactor, powered by a magnetostrictive transducer (efficiency 50%), used in this work showed a power capacity of 630 watts and a productivity of about 2 dm^3/min.

EXPERIMENTAL CONFIRMATION OF THE HYPOTHESIS

Optimization was carried out using Reactor 1 shown in Figure 1 in recirculation mode consisting of dispersant 2, which used a laboratory pump-emulsifier, mixer 3, filled before each experiment of whole milk by three quarters. The feed rate of water into the mixer was maintained constant using stabilizer 4, consisting of a coaxially placed tanks on one side and choke 5, which was coaxially mounted on the pipe and adjusted to a minimum flow rate. Skim milk powder was introduced by sprinkling in mixer 3. Sonicated water was continuously fed into the internal tank of the stabilizer from the outlet of the reactor through a three-way valve 6. The overall performance was adjusted through the setting on the output of the reactor choke 7. The reactor could run at any given capacity with the water fed at the same rate from the stabilizer into the mixer. Excess water at the filling of the tank flows through the drain pipe 8 mounted on the bottom of the outer container. An agitation impeller 10 was set in the mixer, filled during each experiment to the mark 9 for effective mechanical agitation. The mixing container had a similar appearance to a pasteurizing or fermenting tank used in dairy industry. The experiment was conducted at room temperature.

Five samples of mixtures were prepared with different capacities of the reactor. The viscosities of these samples, taken from the central part of the tanks and stored at +8 °C for 3 days, were measured by a rotational viscometer. The results of these measurements were divided by the viscosity of reconstituted milk prepared without ultrasonic processing and for comparison. Was shown that magnitude of the erosive power (ΔP) of cavitation depends on the static pressure p (Fig. 2).

It has been found that in the rotor with n rectangular openings and in the stator with N apertures through which the stream of processed fluid is flowing, the total number of holes must satisfy $Nn \geq \left\lfloor \frac{\pi R}{a + 0{,}75\delta} \right\rfloor^2$ where: $\lfloor\ \rfloor$ — denotes the lower integer part (floor); a — the width of the hole; R — outer radius of the rotor; δ — the gap between the stator and the rotor. This may be achieved by the highest power of cavitation erosion.

Figure 1. Scheme of the experimental stand, on which was carried out of the practical optimize of the getting mixture: 1 - cavitation reactor; 2 - a dispersant; 3 - mixer; 4 - stabilizer; 5 - choke; 6 - three-way valve; 7 - choke; 8 - drain connection, 9 - a mark, 10 - impeller mixer, 11 - choke, 12 - drain pipe

Figure 2 (from [16]). The dependence of the erosive power of cavitation ΔP rotary supramolecular disintegrator from the static pressure in his chamber p

PRACTICAL IMPLEMENTATIONS OF RESEARCH FINDINGS IN INDUSTRY

Results of this study can be implemented in an industrial scale (Fig. 3) by using a dispersant rotary-pulsational disintegrator (Fig. 4), developed in the homeland of one of the first researchers, Dr J. Hint [16], who developed the mechanical disintegration in rotary apparatus. For example, an industrial processor UIP4000 was developed by Hielscher Systems GmbH [17].

Figure 3. Industrial version of implementation:
1 – rotary dispersant; 6 – metering pump; 7 – a device for the introduction of dry skim milk; 8 – water inlet

The reactor shown in Figure 3 can be used for processing dried whole or skim milk or whey powder or milk protein concentrates. According to patent application WO 2007111524, the rehydration process is effective when 40 wt% of water to that of dry milk protein is added [1].

Thus the mass of water that was subjected to sonication was approximately one third of the volume of the solids [10] reducing the overall energy requirement. The protein that provides stability to the fat globules is well hydrated resulting in a greater wettability and surface activity.

Figure 4.

The dispersant of company *Oil Tech Production OY* with removed lid of working volume (1) and removed rotor (2) from the stator (3)

REFERENCES

1. Kuntz I. D. The physical properties of water bound to biomacromolecules // Water relations of foods / Ed. by R.B. Duckworth.- London: Academic Press, 1975.
2. Ashokkumar M. at al. The ultrasonic processing of dairy products // Dairy Science and Technology, 2010, V.90, pp. 147-168.
3. Shestakov S., Krasulya O. Sonochemical technologies in food industry // Electronic Journal “Technical Acoustics”, http://www.ejta.org, 2010, 10.
4. Shestakov S. Technologies of cavitational disintegration in dairy industry // Dairy industry, 2007, 9, pp. 58-60.
5. Glaznev N. et al. A method of pasteurization and homogenization of the liquid food and the device for its realization // Patent RU 2172107, 2001.
6. Knapp R., Daily J., Hammitt F. Cavitation.- New York: McGraw Book Company, 1970.
7. Volkov G. et al. A method for producing drinking milk and line for its production // Patent RU 2222952, 2004.
8. Shestakov S., Babak V. Mathematical Model of the Spatial Distributing of Density of Erosive Power of Multibubble Cavitation // Applied Physics Research, V.4, 1, 2012, pp. 64-77.
9. Shestakov S. Method hydration of biopolymers and product from the hydrated biomass // Patent RU 2331478, 2008.
10. Rogov I., Shestakov S. Epithermal change the thermodynamic equilibrium of water and aqueous solutions: Delusion and Reality // Storage and Processing of Farm Products, 10, 2004, pp. 9-13.
11. Jinesh K. B., Frenken J. W. M. Experimental evidence for ice formation at room temperature // Physical Review Letters, 2008, 101, 036101.
12. Shestakov S. Food sonochemistry: concept, theoretical aspects and practical applications.- Saarbrücken: LAMBERT Academic Publishing, 2012.
13. Krasulya O. et al. Way to improve the heat resistance of the biologically active components of food and medicinal raw materials of materials plant and animal origin // Patent RU 2444201, 2012.
14. Tikhomirova N. et al. A method for reducing the temporary hardness of water in the flow and cavitational reactor for its realization // Patent RU 2422371, 2011.
15. Shestakov S. D. Basics of cavitational disintegration.- Moscow: EVA press, 2001.
16. Ashokkumar M. et al. A New Look at Cavitation and the Applications of Its Liquid-Phase Effects in the Processing of Food and Fuel // Applied Physics Research, V.4, 1, 2012, pp. 19-29.
17. Zisu B. et al. Ultrasonic processing of dairy systems in large scale reactors // Ultrasonics Sonochemistry, 17, 2010, pp. 1075-1081.