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Д.В. Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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NEWS

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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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**BAROMEMBRANE TECHNOLOGIES AS A PROSPECTIVE
ALTERNATIVE TO VACUUM EVAPORATION
IN THE DRY MILK PRODUCTION**

Abstract. In the dairy industry, in recent years, baromembrane technologies (microfiltration, ultrafiltration, nanofiltration, reverse osmosis) have become increasingly widespread, which make it possible to obtain milk raw materials that are safe from a microbiological point of view and to standardize the protein mass fraction, concentration and fractionation of milk constituents. These filtration methods are definitely an alternative to traditional manufacturing processes. They are integrated into many production steps for a wide range of whole milk products, cottage cheese, cheese, etc.

Among dry dairy products, milk powder occupies a leading position in terms of use for processing in powdered or reconstituted form in almost all sectors of the food industry due to its high nutritional value, transportability, long shelf life, etc. In this regard, from quality and safety, and also the technological properties of milk powder certainly depend on the final product quality. Improving the organoleptic, physicochemical, sanitary and hygienic indicators of milk powder and directionally forming its basic technological properties (thermal stability, cheese suitability, solubility), it is possible to design its food and functional technological profile, using baromembrane installations in the process of obtaining milk powder.

Based on the study of specialized scientific and technical literature, the article presents an analysis and systematization of information on the influence of baromembrane methods, integrated into the technological chain of obtaining milk powder, on its quality and functional and technological properties.

Key words: membrane technologies, baromembrane methods, milk powder, quality, cheese suitability, heat resistance, solubility.

Introduction. In the last decade, membrane technologies have found increasing application in the dairy industry, due to a huge range of technical and technological advantages and undoubtedly have the prospect of use and development. In terms of their prevalence in the dairy industry, they rank second in comparison with their use in water purification technologies and are certainly an alternative to the traditional technology stages (fractionation, concentration, etc.) in the production of a large range of dairy products, such as drinking milk, dairy products, cottage cheese, cheese, etc., and also constitute an integral part of the caseinates production process, whey protein concentrates, demineralized whey, etc. [1-4].

The methods of baromembrane filtration are based on the processes occurring under the action of a pressure difference when passing liquid media through special semi-permeable filters (membranes) made of various materials (polymer, ceramic, etc.), which leads to the macro- and microcomponents separation of the feed stream, depending on the particles and pores size of membranes [2,5].

Due to its physical and chemical composition, milk is considered a complete food product and is an ideal liquid for pressure-membrane filtration.

Depending on the membrane's selectivity, as well as the working pressure, the baromembrane filtration methods are divided into:

- microfiltration (MF) - the process is carried out at a low pressure of 0.1-0.8 MPa, using membranes with a pore diameter of 0.05-10.0 microns, which allows milk bacterial purification and skimming, as well as casein and whey proteins fractionation;

- ultrafiltration (UF) - carried out at an average pressure of 0.4-1.3 MPa, using membranes that trap colloidal particles and high-molecular substances with a size of 0.005-0.1 microns (whey proteins, non-protein nitrogenous compounds), providing an increase in protein concentration and a decrease in the lactose content in milk, which increases the yield of the finished product;

- nanofiltration (NF) - is carried out at an average or high pressure of 0.7-4.0 MPa, operating membranes with a pore diameter of 0.001-0.005 microns, trapping most divalent ions and passing monovalent ions, which, for example, makes it possible to concentrate and/or partially demineralize whey;

- reverse osmosis (RO) - is carried out at a high pressure of 2.7-7.0 MPa, using high-density membranes with pore sizes that are minimal in relation to other filtration methods (less than 0.001 microns), allowing only water molecules and some ions to pass through. This method is used for pre-thickening in the production of concentrated and dry milk products.

It should be noted that the indicated baromembrane methods are effective in operation under sufficiently gentle thermal conditions (4-50 °C), which have a minimal denaturing effect on the milk protein fractions and changes in its sensory properties [2,4-6].

Among dry dairy products, spray-dried milk powder (MP) occupies a leading position in use terms for processing in dry or reconstituted form in almost all branches of the food industry due to its high nutritional value, transportability, long shelf life, etc. The quality and safety, as well as the technological properties of the MP, undoubtedly depends on the products quality, in the recipe compositions of which it is used [7-9]. By increasing the quality indicators (organoleptic, physicochemical, sanitary and hygienic) of the MP and directionally forming its basic technological properties (heat resistance, cheese suitability, solubility), it is possible to design its food and functional and technological profile, while using various technological techniques and equipment, including baromembrane installations. One of the main stages of MP production is the preliminary milk thickening (concentration) before it is fed to drying plants, which is due to the efficient use of energy resources. In Russia, vacuum evaporators of various types are mainly used for preliminary concentration, which dairy enterprises were massively equipped with in the 60s-70s of the last century. The development of membrane technologies makes it possible to introduce, instead of vacuum evaporation equipment, modern baromembrane reverse osmosis plants, which reduce the mass fraction of moisture evaporated during thickening, save steam and reduce energy consumption. So, for example, the cost of removing 1 ton of moisture from a thickened mixture during vacuum evaporation is 4.5 times higher than when using reverse osmosis. In this case, the water that has passed through the membranes can be used at the enterprise as a diafiltration medium or process water for washing equipment (except for finishing) [1,2,10].

The study of technical literature has shown that there is a demand for the incorporation and structuring of modern scientific information, assessing the impact of various baromembrane technologies on the formation and modification of the MP functional and technological properties and directly on its quality.

Research goal. Analysis and information systematization on the influence of baromembrane methods, integrated into the technological chain of MP obtaining, on its quality and functional and technological properties.

Objects and research methods. The objects of the study were skimmed milk powder (SMP), dried whole milk (DWM) and their milk systems reconstituted in water. The research was based on the scientific postulates of the milk canning and membrane knowledge areas, regulatory, technological and technical support in the MP production. The work uses modern approaches and methods of searching for scientific and technical information using the current abstract and analytical databases of specialized thematic publications and citations.

Results. MP production requires the reservation of a large raw milk amount, which, among other technological manipulations, must be maximally cleared of contaminated microflora. An effective means of arresting negative processes caused by bacterial cells in raw milk is MF, which reduces the total number of microorganisms by an average of two to three orders of magnitude, removing 99.91-99.98% of the initial content of bacteria and their spores. This effective method increases the beneficial effect of

subsequent heat treatment on the remaining microflora. In this case, the temperature regimes can be reduced to an acceptable minimum, which ensures the preservation of the functional properties of whey proteins in the MP and an improvement in its quality [2,3,11].

The successful integration of MF methods into dairy products technology made it possible to separate proteins of different molecular weights without chemical or thermal action, which makes it possible to fractionate (or isolate) high molecular weight casein micelles (in the form of retentate) and low molecular weight whey proteins (in the form of permeate) [12].

Researchers [13] carried out work on the use of MF for skimmed milk, in which the pH is lowered from 6.7 to 6.2. As a result, the retentate contained 28% less calcium. At the same time, the SMP obtained from such raw materials had better thermal stability (alcohol test resistance increased from III-IV to II group) and solubility (by 30-40%). A further decrease in calcium mass fraction (up to 52%) led to the appearance of an organoleptic defect - bitterness.

Other authors [5] made a conclusion about the advisability of a combination of MF and high-temperature processing of raw milk to obtain MP, which, after recovery and coagulation with rennet, forms a clot with increased water-holding capacity (by 20-30%).

Noteworthy are the studies of the MF at temperatures of 50-65 °C. The authors substantiate the effectiveness of using these modes by reducing the microorganism's growth in the retentate, increasing the flow rate, and, as a consequence, reducing the membranes area, reducing energy consumption. Researchers have found that an increase in temperature leads to a decrease in the concentration of casein and whey proteins in the permeate. This may be due to the migration of β -casein back into the micelle, as well as the association of β -lactoglobulin with casein micelles [14].

The work [15] studied the thermal stability of UF, NF and RO concentrates, as well as reduced to 25% mass fraction of dry substances of SMP samples obtained using these membrane technologies. It was found that UF increases the pH in the retentate (from 6.61 to 6.70) through some solubilization of the colloidal calcium phosphate, since calcium is lost in the permeate to restore balance. Conducting NF and RO led to a drop in pH in retentates with respect to the original skimmed milk samples (from 6.60 to 6.54 and from 6.64 to 6.30, respectively). The decrease in pH at RO is due to the precipitation of a certain amount of soluble calcium phosphate on the casein micelle. At the same time, the magnitude of pH change for RO is greater than for NF. The highest increase in the content of ionic calcium in the concentrate (almost 30%) was found at UF, this indicator remained practically unchanged for NF (about 1%), with RO the increase in ionic calcium was only 10%. The values of active acidity and the ionic calcium content of the reduced SMP-RO before heat treatment were the lowest (pH 6.44 and Ca^{2+} 1.28 mM) in relation to the reduced samples of SMP-NF (pH 6.53 and Ca^{2+} 1.36 mM) and SMP-UF (pH 6.68 and Ca^{2+} 1.79 mM). The thermal effect on the reconstituted samples (sterilization at a temperature of 115 °C for 15 minutes) showed the following results, which were assessed visually: SMP-RO gave weak coagulation of the protein, SMP-UF formed a denser clot, SMP-NF had intermediate results - from stable system to weak gelation or the presence of some protein flakes. To increase the thermal stability of SMP-NF, the authors carried out experiments on adding stabilizers of sodium hydrogen phosphate and sodium citrate to retentates, which at concentrations of 0.1% and 0.2% (respectively) led to a positive result. Were obtained thermostable reduced samples, since the addition of stabilizers caused an increase in pH (from 6.52 to 6.59-6.62) and a decrease in ionic calcium (from 1.12 to 0.84-0.94 mM).

The study of the membrane technologies influence on the kinetics of concentrates rennet coagulation is devoted to work [16]. Gelation by rennet occurs in two stages. At the first stage, the rennet cleaves the Phe105-Met106 bond of c-casein, which, as the casein macropeptides are released, leads to a decrease in the negative charge of micelles and a decrease in electrostatic repulsion. As a result, hydrolyzed micelles become more prone to interaction and begin to aggregate, which is the second stage of the coagulation process. As micelles aggregate, salt bridges are formed between them and a gel gradually forms. A shift in equilibrium towards the first or second stage can significantly change the coagulation capacity of the milk system. The authors obtained retentates when processing skimmed milk with RO, NF and UF with a dry matter content of 22.08%; 20.38%; 14.09% and pH 6.31; 6.35; 6.57 respectively. The values of indicators of the original milk were 9.21% and pH 6.64. The increased dry matter content in the samples treated with RO and NF was achieved due to the higher lactose concentration (12.27% and 11.26%, respectively) and ash (1.634% and 1.304%, respectively) in relation to UF (lactose 4.99%; ash 1.045%), which is explained

by the filtration method. The initial lactose content of the skimmed milk was 5.38% and the ash 0.739%. A high mass fraction of dry substances and low active acidity in the case of RO and NF contributes to the improvement of coagulation properties (at their natural pH and the same rennet concentration): the duration of coagulation is reduced, the rate of formation of a denser consistency increases, which is the result of increased viscosity and higher ionic strength in these samples. In this experiment, in order to determine the effect of baromembrane methods on rennet gelation, the active acidity for all retentates was adjusted to pH 6.50. OO and NF concentrates had a longer coagulation duration (45.13 and 48.11 minutes) compared to the UF samples - 24.10 minutes. Examination of all clots after 45 minutes rennet coagulation showed the highest density in the UF samples (modulus of elasticity equal to 470 Pa). For NF and RO concentrates, this indicator had values of 150 and 160 Pa, respectively. These values are the result of increased viscosity and higher ionic strength, leading to disruption of enzymatic activity. Similar data were obtained when developing model samples of cottage cheese and cheese using retentates recovered after drying. There was also no significant difference in their raw material properties between NF and RO. The SMP-UF samples were found to be more suitable for cheese making due to the higher content of colloidal casein and ionic calcium.

Previously, the authors [17] published a study of SMP obtained using preliminary concentration in the form of UF (up to 20% dry matter) and varying the modes of subsequent heat treatment (65-85 °C for 30 minutes to several seconds) and the values of active acidity (pH 6.4-7.0). The developed modified SMP-UF had a higher protein content (by 30-40%) and a lower lactose content (by 10-20%). The use of combinations of technological modes made it possible to obtain various types of dry products with certain technological properties, namely, solubility, whipping, foaming, emulsification, various densities gels creation, which expands the possibility of using SMP-UF in the production of fermented milk products, cheese, ice cream, dairy desserts. So, for example, heat exposure (temperature 65 °C for 30 minutes) and pH 6.4 leads to the strong gel formation; emulsifying ability decreases with increasing temperature at any pH value in the range of 6.4-7.0; all recovered samples remain stable for 2 hours when heated to 100 °C.

Scientists [18] expanded their understanding of the UF effect on the quality and functional and technological properties of dry products by the example of obtaining milk protein concentrates (MPC), produced from skimmed milk and containing all protein fractions (52-55%) and their ratio as in the original milk. The effect of pH on the operation of UF units and on such important properties of MPC as emulsification, solubility and thermal stability was investigated. It was shown that a decrease in the pH of skimmed milk from 6.7 to 5.5 significantly reduced the average size of casein particles (from 200 to 100 nm) and their zeta potential (from -32.8 to -27.6 mV), while increasing the emulsion activity index (from 17 to 23 m²/g) and emulsion stability index (from 61% to 86%) of MPC. However, a decrease in the size of casein micelles due to the calcium removal from them negatively affected membrane fouling. In addition, the solubility of MPC dispersions and their thermal stability decreased with a decrease in active acidity to 5.5 (from 77% to 32% and from 96% to 8%, respectively), but normalization of pH to 6.7 improved the technological properties of dispersions (possibly for by restoring the peculiarities of their structure), increasing their values to 88% and 78%, respectively. The optimal mode for obtaining dry product with improved technological properties without deteriorating the performance of the UF membranes was chosen to have a pH of 5.9 at a temperature of 15 °C.

In work [19], the effect of NF on increasing the solubility of dry milk products is considered, since this method of concentration involves carrying out the process at sufficiently low temperatures and average operating pressure in addition to a high flow rate and selectivity of membranes (only polyvalent anionic salts and organic molecules are transferred to the permeate) with a molecular weight of 0.5-1.0 kDa; losses of calcium and phosphate are also reduced). Milk protein is less exposed to heat as a result, the retentate contains less denatured protein and, therefore, the dried product has increased solubility in comparison with the MP obtained by the classical method. During vacuum evaporation, the interaction of casein micelles increases, leading to compaction of the particles. During NF casein micelles also aggregate, but no significant increase in size is observed. After NF, the microstructure of casein micelles was practically not disturbed. The insolubility index at NF was 65% lower, which indicates an improved solubility of MP-NF.

Whole milk is also subjected to membrane processing to produce DWM with certain technological properties. For example, researchers [20] obtained dry products with a fat mass fraction of 26-59% using

UF, which had specific features: reduced vacuole volume (from 7.0 to less than 0.1 ml/100 g), increased particle size (from less than 50 to 121 microns), high free fat mass fraction of (26.0-95.5 g per 100 g of fat), which made it possible to improve their quality when using such DWM in the production of chocolate and chocolate products.

Thus, modern technologies of baromembrane separation are available for use at present in the dairy industry - microfiltration, ultrafiltration, nanofiltration and reverse osmosis. The use of various membranes and their combination, due to their selectivity, is a highly effective way to improve the sanitary and hygienic indicators of dry dairy products. Also, fractionation of milk constituents using membrane technologies allows the targeted formation of nutritional value and functional potential, improving technological properties such as heat resistance, cheese suitability, solubility, etc. This opens up the possibility of integrating dry products, primarily modernized milk powder, into the types of food products, contributing not only to the optimization and improvement of production due to resource conservation and efficiency, but also to improve the quality of the final product. There is no doubt that the use of membrane technologies is promising for the production of skimmed and whole milk powder.

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БАРОМЕМБРАНАЛЫҚ ТЕХНОЛОГИЯЛАР – ҚҰРҒАҚ СҮТ ӨНДІРІСІНДЕГІ ВАКУУМ-БУЛАНДЫРУДЫҢ ПЕРСПЕКТИВАЛЫҚ БАЛАМАСЫ РЕТІНДЕ

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БАРОМЕМБРАННЫЕ ТЕХНОЛОГИИ КАК ПЕРСПЕКТИВНАЯ АЛЬТЕРНАТИВА ВАКУУМ-ВЫПАРИВАНИЮ В ПРОИЗВОДСТВЕ СУХОГО МОЛОКА

Аннотация. В переработке молока за последние годы находят все большее распространение такие баромембранные технологии, как микрофльтрация, ультрафльтрация, нанофльтрация, обратный осмос, которые играют важную роль в получении безопасного с микробиологической точки зрения молочного сырья, стандартизации массовой доли белка, концентрации и разделения составных частей молока и, безусловно, являются альтернативой традиционным производственным этапам.

Среди сухих молочных продуктов сухое молоко распылительной сушки занимает лидирующую позицию по объемам использования в порошкообразном либо восстановленном виде практически во всех отраслях пищевой промышленности за счет своей высокой пищевой ценности, длительных сроков хранения и пр. В связи с этим от качества и безопасности, а также технологических свойств (термоустойчивости, сыропригодности, растворимости и пр.) сухого молока зависит качество продукции, в рецептурных композициях которых оно применяется.

Улучшая органолептические, физико-химические, санитарно-гигиенические показатели сухого молока и направленно формируя его основные технологические свойства (термостабильность, пригодность сыра, растворимость), можно спроектировать его пищевой и функционально-технологический профиль, используя баромембранные установки в процессе получения сухого молока.

На основе изучения специализированной научно-технической литературы в статье представлен анализ и систематизация информации о влиянии баромембранных методов, интегрированных в технологическую цепочку получения сухого молока, на его качество и функционально-технологические свойства.

Ключевые слова: мембранные технологии, баромембранные методы, сухое молоко, качество, сыропригодность, термоустойчивость, растворимость.

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