ТЕХНОЛОГИЯ ПРОДОВОЛЬСТВЕННЫХ ПРОДУКТОВ | TECHNOLOGY OF FOOD PRODUCTS

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СВОЙСТВА МИЦЕЛЛЯРНОГО КАЗЕИНА И ПРИМЕНЕНИЕ В ПИЩЕВОЙ ПРОМЫШЛЕННОСТИ

PROPERTIES OF MICELLAR CASEIN AND APPLICATION IN FOOD INDUSTRY

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Аннотация

Казеин молока обладает важными свойствами, которые обуславливают широкое применение данного белка в промышленности и повышенный интерес к его изучению со стороны исследователей. Исследования структуры казеина в нативном состоянии обнаружили его мицеллярную структуру. Присутствие крупных ионов приводит к увеличению объема мицелл, а подкисление среды – уменьшению. При хранении способность КМК к регидратации и растворению понижается, наблюдаются агрегация и деградация структуры, с повышением температуры хранения эти показатели также заметно снижаются. Термостабильность максимальна вблизи нейтрального уровня pH. КМК обладает геле- и пенообразующими свойствами. В присутствии трансглутаминазы повышается устойчивость мицелл. Таким же образом действует и повышенное давление – время коагуляции мицелл увеличивается. Поверхностная активность и гидрофильность мицеллярного казеина напрямую зависят от степени агрегации мицелл, чем она меньше, тем выше значения этих показателей. Органолептические показатели данного препарата благоприятны.

Благодаря высокому содержанию белка и особенностям его усвояемости КМК активно применяется при производстве специализированного питания, например, диетического, спортивного, детского и т.д. Процесс получения йогурта, десертов, сыров (плавленых и твердых) представляет собой агрегацию казеина молока в различной степени, использование коммерчески доступных препаратов мицеллярного казеина позволяет делать процесс производства более контролируемым и повышает качество готовых продуктов. В мясоперерабатывающей промышленности активно применяются функциональные добавки, содержащие молочные белки и казеин, в частности, однако отсутствуют данные о внесении в функциональные смеси мицеллярного казеина в качестве индивидуального компонента.

Приведен подробный анализ данных касательно физико-химических и технологических свойств концентрата мицеллярного казеина, таких как термостабильность, растворимость, влагоудерживающая и гелеобразующая способности, поверхностно-активные свойства, пенообразование и влияние на органолептические свойства продуктов. Рассмотрены имеющиеся примеры его применения в различных отраслях пищевой промышленности: в производстве высокобелковых и низкоуглеводных напитков, спортивного питания, йогуртов и десертов, твердых и плавленых сыров, а также в мясопереработке.

Ключевые слова: концентрат мицеллярного казеина, молочные белки, молочные продукты, функциональные добавки, физико-химические свойства, технологические свойства.

Abstract

Milk casein has important properties that ensure the widespread use of this protein in industry and increased interest in its study by researchers. Studies of the structure of casein in its native state have revealed its micellar structure. The presence of large ions leads to an increase in the volume of micelles, while acidification results in a decrease. During storage, the ability of MCC to rehydrate and dissolve reduces, aggregation and degradation of the structure are observed, with an increase in storage temperature, these indicators noticeably decrease. Thermal stability is greatest near neutral pH. MCC has gel and foaming properties. In the presence of transglutaminase, the stability of micelles rises. In the same way, under the increased pressure – the coagulation time of micelles increases. The surface activity and hydrophilicity of micellar casein directly depend on the degree of aggregation of micelles, the lower it is, the higher the values of these indicators. The organoleptic characteristics of this additive are favorable.

Due to the high content of protein and the peculiarities of its digestibility, MCC is actively used in the production of specialized nutrition, for example, dietary, sports, children's, etc. The process of producing yogurt, desserts, cheeses (processed and hard) is an aggregation of milk casein to varying degrees, the use of commercially available micellar casein makes it possible to make the production process more controlled and improves the quality of final products. In the meat processing industry, functional additives containing milk proteins and casein are actively used, however, there are no data on the introduction of micellar casein into functional mixtures as an individual component.

A detailed analysis of the data regarding the physicochemical and technological properties of micellar casein concentrate, such as thermal stability, solubility, water-retaining and gelling abilities, surface-active properties, foaming and influence on the organoleptic properties of products, is given. The existing examples of its application in various fields of the food industry are considered: in the production of high-protein and low-carbohydrate drinks, sports nutrition, yoghurts and desserts, hard and processed cheeses, as well as in meat processing.

Key words: *micellar casein concentrate, milk proteins, dairy products, functional additives, physicochemical properties, technological properties.*

There are two main groups of milk proteins – caseins and whey proteins. Due to the ease of isolation, milk proteins became the object of research at the very beginning of the emergence of protein chemistry, and the term "protein" was proposed as early as 1838 by Melder [9]. However, it was only in the second half of the 20th century that the properties of these proteins began to be studied in detail, on the basis of which, in 1979, Morr described possible ways of using them [15]. There is a high nutritional value of milk proteins, emulsifying, stabilizing, water-retaining, gelling and foaming abilities, etc. This opens up great opportunities for the use of milk proteins in food production. At the same time, whey proteins have more unambiguous properties and therefore have been studied to a greater extent. In the case of casein, the situation is complicated by the fact that its properties vary greatly depending on the method of isolation. This article discusses the use of casein in the native "micellar" state.

If, when studying the properties of whey proteins, their molecules in the vast majority of cases are in a state close to native, then in the case of casein, most attention is paid to studying the properties of casein processing products. These include various caseinates, acid, rennet caseins, etc. This is due to the fact that initially casein was a homogeneous structure, and only at the beginning of the 20th century was its heterogeneity discovered. Over time, scientists came to the conclusion that casein contains αS_1 - and αS_2, β -, and κ - caseins [25]. At the same time, the micellar nature of casein was discovered, this discovery led to the development of a number of studies devoted to the study of the structure of micelles. Discussions on this topic do not stop until now, but it is generally recognized that micelles are formed due to electrostatic interactions of charged amino acid residues of casein proteins with a calcium phosphate complex (it contains most of the calcium and phosphorus of milk), as well as non-valent interactions of various nature between these proteins. For a long time, the isolation of casein in its native state was a rather difficult task, and only with the introduction of membrane milk fractionation processes into production, it was possible to obtain preparations such as micellar casein isolate and micellar casein concentrate (MCC) [7]. If the properties of various casein derivatives, for example, sodium and calcium caseinates, are sufficiently well studied and widely used [11], then such studies for micellar casein preparations began to be carried out only in recent decades. Currently, research in this area is actively developing.

The great interest in micellar casein concentrates and the possibility of its use in many industries are associated with the unique properties of this product. The functional properties of MCC are similar to those of milk protein concentrate, and the existing differences, for example, greater thermal stability, are due to the reduced content of whey proteins in MCC. The properties of casein micelles have been studied in various studies [6, 10]. The works showed that the addition of sodium chloride led to an increase in the volume of casein micelles, while a decrease in pH from 6.5 to 5.5 had the opposite effect. Another study of micelle structure recovery was carried out by Schokker, who found that the rehydration capacity of MCC decreases over time at 30°C due to changes in the intermolecular bonds of micelles. By varying the type of membranes used to isolate MCC, as well as using the diafiltration method, MCC preparations of various compositions are obtained. Increasing the whey protein content of MCC and increasing the temperature will decrease the viscosity, while increasing the casein content will have the opposite effect. When studying the thermal stability of MCC, it was found that in the temperature range from 110 °C to 150 °C and at pH less than 6.7, MCC aggregation occurs. However, MCC becomes more stable and does not aggregate at pH values greater than 6.9 [20]. The solubility of concentrated MCC increases as the temperature rises to 50°C. At low temperatures (≤20 °C) more time is needed for a sufficient level of solubility. During storage of MCC, its solubility decreases, while a change in color and darkening occurs [16]. It forms a gel at room temperature and the addition of sodium chloride improves this functional property [14]. Such properties of MCC, as the yield and stability of the resulting foam, turned out to be higher than for other dairy products. Volume, surface area, foam stability and yield strength decrease as it dries, this especially affects foam stability, which may be due to the denaturation of whey protein, which is still present in MCC preparations. However, the heat stability of neither liquid nor dried protein is affected.

Recently, new approaches have been used to study the properties of MCC. The effect of transglutaminase on various functional properties of casein micelles was studied. The enzyme transglutaminase increased resistance to the action of alcohols and elevated temperatures. Despite this, the solubility of MCC decreased upon hydration in water at room and elevated temperatures [19]. MCC was also subjected to high-pressure and ultrasonic treatment. It has been found that the application of elevated pressure leads to the formation of liquid gels and an increase in coagulation time under the action of rennet. On the other hand, the use of ultrasound increased the electrical conductivity, solubility, emulsibility, gelling, and hydrophobicity of the surface as the time of ultrasonic treatment increased [4].

Micellar casein exhibits hydrophilic and surface-active properties to varying degrees, depending on the degree of micelle aggregation. Therefore, the values of these properties for sodium caseinate, for example, differ significantly from those for casein in the native state [18]. There are not many works devoted to the emulsifying and foaming properties of casein micelles. For example, in a study [12], these properties were studied for micellar casein depending on the degree of aggregation. It has been shown that aggregated micelles practically do not show surface activity, and with an increase in the degree of their dissociation, the activity increases. Micellar dissociation can be achieved using various chelating agents such as citrates, phosphates or EDTA, also called emulsifying salts. Under the action of these compounds, calcium ions are bound, including those in the composition of calcium-phosphate complexes. This leads to the disaggregation of micelles, an increase in thermal stability, and a number of other consequences that are important from a technological point of view. This technique is actively used in the production of processed cheeses.

According to organoleptic characteristics, MCC is characterized by a mild or almost imperceptible taste. Rennet and acid caseins tend to have more intense aroma, cardboard flavor, feed flavor and other organoleptic defects. This further expands the scope of application of MCC [5].

MCC is used in the production of many dairy and non-dairy products due to its high nutritional value, mild taste, physicochemical and functional properties.

The possibility of using MCC in the production of high-protein and low-carbohydrate drinks is being actively explored, since it contains a large amount of protein, and the lactose content is minimized [23]. Moreover, due to the unique micellar structure of caseins in MCC, it acts as a stable delivery system for calcium and phosphorus, which retains its stability at high temperatures. As a result, it can be used in the production of protein-fortified beverages that require sterilization to increase the shelf life of these products. MCC also has a subtle flavor and can provide the same flavor as 1.5-2% fat milk, making it suitable for low-fat versions of these drinks. A number of works show the effectiveness of the use of MCC in the nutrition of athletes as a source of so-called "slow" proteins [3, 22].

MCC has found application in the production of yogurt and desserts. Yogurts are made by "coagulation" of casein in milk, using starter culture to reach a pH of 4.6 (isoelectric point). MCC is a good source of protein for enriching the milk base of yogurt due to its nutritional value and functional properties. Fortification of yogurt with this protein has been found to improve its rheological and physical properties. American scientists have used MCC to make Greek yogurt [2]. They noticed that adding MCC increased the rate of acidification when making Greek yogurt compared to using regular milk. The reason for this phenomenon is the higher content of non-protein nitrogen in milk enriched with MCC. In the works of Russian scientists [27, 28], micellar casein was used in the production of a frozen dessert for sports nutrition and high-protein ice cream.

Another area of application for MCC is the production of cheese. They are produced by precipitation of milk casein by the action of rennet (cheddar and mozzarella) or acid (cottage cheese or sour curd cheese). MCC is used for milk enrichment or as a substitute for milk in cheese production. Micellar casein obtained by microfiltration [17] makes it possible to obtain cheeses with high yields and modify their properties. In many cases, it is also important to investigate the influence of various factors on side processes. Thus, in [14], we studied how a change in the concentration of protein, calcium, and pH affects the process of spontaneous cold coagulation of micellar casein. The introduction of casein in the preparation of cheeses increases the total amount of nitrogen-containing compounds, calcium and phosphates, as well as buffering capacity. In a study [21], to achieve pH 4.6, 1.2–1.4 times more lactic acid was required compared to the control sample. A number of works are devoted to the development of technology for the production of various types of cheese using MCC [1, 7, 26]. For example, cheddar cheese was obtained with partial and complete replacement of milk with micellar casein concentrates, the organoleptic characteristics of which were close to the control sample. Similar conclusions were reached in [13], the authors of which believe that the use of MCC is very promising in the production of hard cheeses with controlled properties. In the production of feta cheese, MCC preparations of various concentrations were used, which made it possible to get rid of the stage of whey removal, organoleptic indicators deteriorated, but slightly, the product yield was increased.

Micellar casein preparations are also widely used in the production of processed cheeses and processed cheese products. Processed cheese production has been actively developing in recent years, and therefore a lot of research is aimed at finding new approaches to process optimization. As already mentioned, the technological properties of this product are largely due to the interaction of emulsifying salts on casein micelles. If initially ready-made cheeses were used in production, in which the depth of rennet fermentation and, accordingly, the state of casein micelles varied greatly, then recently there has been a tendency to manufacture processed cheeses using MCC, in which this parameter is controlled [24]. The use of native casein preparations makes it possible to achieve the desired characteristics of the composition, texture, structure, meltability and stability of the products obtained. MCC was also used to obtain processed cheese products without emulsifying salts when combined with whey proteins in a given ratio [8].

As shown in [29], milk proteins are also widely used in the meat industry. The most commonly used concentrates and isolates of whey proteins, various caseinates, coprecipitates, milk powder and some others. At the same time, casein in its native state is found only in the composition of milk powder. To study the effect of micellar casein, which is one of several components of milk powder, on the properties of the emulsion is a rather difficult task, because such studies are practically not found. The deterioration in the quality of milk powder in Russia, which is noted by manufacturers and scientists, further complicates this task [30]. Obviously, the use of MCC, which, in fact, is a monocomponent preparation, will allow us to study the effect of casein micelles on the properties of meat emulsions. In our opinion, the study of this issue will allow us to develop effective approaches to the use of MCC in the meat industry, both individually and as part of functional modules. The relevance of such studies is also confirmed by the fact that in the domestic literature there are works devoted to obtaining MCC and studying his properties [31].

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