Розроблено теоретичну модель стеричної стабілізації структури повітряно-горіхового напівфабрикату, шляхом додаткового введення дистильованих моногліцеридів та натрій-карбоксиметилцелюлози. Експериментально доведено, що введення низькомолекулярних поверхнево-активних речовин в олію забезпечує гідрофілізацію жирової фази та зменшує десорбцію білка з бульбашок повітря. Введення натрій- карбоксиметилцелюлози забезпечує підвищення в'язкості, зменшує флотацію твердих частинок горіхів, забезпечує стійкість системи до перемішування

Ключові слова: напівфабрикат повітряно-горіховий, стерична стабілізація, флотація, піноутворююча здатність, стійкість піни, міжфазні шари

Разработана теоретическая модель стерической стабилизации структуры воздушно-орехового полуфабриката путем дополнительного введения дистиллированных моноглицеридов и натрий-карбоксиметилцеллюлозы. Экспериментально доказано, что введение низкомолекулярных поверхностно-активных веществ в масло обеспечивает гидрофилизацию жировой фазы и уменьшает десорбцию белка из пузырьков воздуха. Введение натрий-карбоксиметилцеллюлозы обеспечивает повышение вязкости, уменьшает флотацию твердых частиц орехов, обеспечивает устойчивость системы к перемешиванию

Ключевые слова: полуфабрикат воздушно-ореховый, стерическая стабилизация, флотация, пенообразующая способность, устойчивость пены, межфазные слои

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DEVELOPMENT OF A MODEL OF STERIC STABILIZATION OF THE AIR-NUT SEMI-FINISHED PRODUCT STRUCTURE

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1. Introduction

Baked aerated air-nut semi-finished products (ANSFPs) and sponge cakes are confectionery items that belong to complex colloidal systems with a mixture of food ingredients. Such systems simultaneously contain several phases in gaseous, liquid and solid states: air bubbles, fat droplets, and solid particles of crushed nuts (CN). During the manufacturing process, ANSFPs have signs of foam in the stage of churning an egg white and sugar mixture. Adding CN to the aerated egg white and sugar mixture creates some slurry and emulsion. The final stage in the process of making an ANSFP is either drying or baking. After baking and cooling, the semi-finished product is in the air phase of a solid medium. Baking entails that it is necessary to ensure stability of the disperse system in the technological process. It requires creating such conditions in which there is no adhesion of fatty or solid particles in the air bubbles. This structure of the ANSFP makes it possible for baking to provide the products with a high specific volume.

The development of scientific principles of stabilizing foam structures is an important result of research. The practical value of the issue is to reduce the cost of making the ANSFP and to create conditions for expanding the range of culinary and confectionery products on its basis. As the ANSFP is produced manually or with minimal mechanization due to the low stability of the foam, industrialization of manufacturing ANSFPs is constrained by the lack of the scientific groundwork for stabilizing egg white-based disperse systems containing CN. The CN is a factor that leads to the foam destruction by the appearance of fat from the crushed nuts and by the adhesion of solid particles to the air bubbles.

The present study is a continuation of research to develop the theoretical aspects of providing stability of colloidal food systems with a complex phase microstructure [1, 2].

2. Literature review and problem statement

The problem of maintaining the foamy egg white system stability after the adding of fat is solved by using low molecular weight surfactants (LMS). For example, in [3] the quantitative characteristics of the foam have shown that adding LMS of different nature to oil can increase the stability of the foam of a food system. The mechanism of action of low molecular weight surfactants was linked in [4] to the process of competitive adsorption by the surface activity values of the formed complexes. A significant factor in this arrangement is the chemical nature of the egg white and LMS and the type of the oil-water and water-to-air interfaces [5]. Competitive adsorption in multicomponent food systems is complicated by the presence of several phases, including fat crystals [6].

When considering foamy food systems that are based of egg whites, the decision to use LMS as a foam stabilizer remains rational. Thus, in [7] the use of natural gums and polymers allowed regulation of the structural and mechanical properties of the foam with the end result of its stabilization to a state that allowed its drying.

A significant role in the stabilizer is played by the organoleptic properties of the final product [8] or the structural and mechanical properties of the foam. [9] The understanding of the dependence of the final food quality on the physical properties of the foam is not a resolved issue, so it requires further research [10]. This dependence is characterized by taking into account the following physical properties as quantitative measures:

– the height of the foam;
– the amount and spatial arrangement of the components;
– the texture and surface characteristics of the products.

Thus, the height of the foam in a food system (for example, in ice cream) may be increased by introducing the water-soluble surfactants Tweens and reduced by adding the fat-soluble surfactants Spans. The conventional model explains these tendencies by the rheological properties of an interfacial layer (IL) and the medium size of the air bubbles [11]. This model, however, is unable to predict the spatial distribution of fat particles in the system. In [12], the complex texture of a food colloidal structure is found to be formed by three main factors: the IL formation as well as flocculation and adsorption of dispersed particles across the interfacial surface. Thus, the churned emulsion of a uniform composition has different mechanical properties depending on the conditions of foaming and the interfacial processes [13].

The previously proposed models of Pickering stabilization [1] or steric Pickering stabilization [2] of the structure cannot be used in this case. The reason consists in fat and solid particles of CN getting into the water-air interface. The heating process leads to the destruction of the foam. The mechanism of steric stabilization by the use of egg whites [14], egg white complexes with LMS [15], and protein complexes with polysaccharides [16] is effectively implemented to stabilize foams and emulsions. These colloidal systems are stabilized due to the formation of interfacial layers with high structural and mechanical properties.

The analysis of the literature has shown that the use of low molecular weight surfactants and stabilizers in the technology of making foamy protein systems with the introduction of fat makes it possible to stabilize the foam. However, the problem is not solved as to the spatial distribution of different phases in such systems, including ANSFPs. This factor is crucial to the quality of the finished product in the technologies of baking churned preparations. From this perspective, the development of a model of steric stabilization is a prerequisite for improving the existing technology of making ANSFPs.

3. The aim and objectives of the study

The aim was to perform a theoretical and experimental study of improving the technology of making an ANSFP by steric stabilization.

To achieve this aim, it was necessary to solve the following problems:

– to implement the mechanisms of steric stabilization by achieving the required rheological parameters of the interfacial layers and the whole system, which would ensure the stability of the multiphase structure of the food system;
– by the example of the real food product (ANSFP), to confirm the practical implementation of the stabilization mechanisms that constitute the essence of the model of steric stabilization;
– to justify the parameters of obtaining ANSFPs;
– to assess the quality parameters of the baked ANSFP.

4. Materials and methods of studying air-nut semi-finished products (ANSFPs)

4. 1. The study materials and equipment

The study was based on using the following food grade reagents:

1) food ingredients: dry egg white (ovalbumin fraction) with a protein content of 88±2 % (BELOVO S. A., Belgium), sunflower oil (refined, deodorized, and frozen), white sugar, and peeled almonds;

2) food supplements:

– distilled monoglycerides (GMS – Glyceryl MonoStearate, E471) with an iodine value of 3.0±0.1 g I_2/100 g;
– sodium carboxymethyl cellulose (NaCMC – Natrium CarboxyMethyl Cellulose, E466), Blanose 7H4XF (Aqualon France B. V., France);
– diacetyl tartaric acid ester of mono- and diglycerides of fatty acids (DATEM – DiAcetyl Tartaric acid Esters of Monoglyceride, E472a);
– sodium stearoyl lactylate (SSL – Sodium Stearoyl Lactylate, E481).

The average size of the crushed nuts particles was determined by using the microscope Biolam P15 (Lomo, Russia) with the digital camera eyepiece ScopeTek DCM-130 E of 1.3 Mp (Hangzhou Scopetek Opto-Electric Co., Ltd., China). The photographing and processing of the images were performed using the software Scope Photo 3.0 (Hangzhou Scopetek Opto-Electric Co., Ltd., China).

The yield shear stress (YSS) of the interfacial layers was performed on the surface viscometer, the design of which is given in [1]. It was found by using two crystallizers connected with a tube to simulate the presence of two interface boundaries in the studied systems. An aqueous protein system was poured into the crystallizers, and the system was kept for 2.5 hours at t=20±1 °C, after which sunflower oil was poured onto the solution surface of one of the crystallizers. The system was kept for 2.5 hours at t=20±1 °C and then the YSS of the interfacial layers was determined at the water-air and water-oil interfaces.

The effective viscosity was measured by the viscometer VPN-0.2 M (Russian National Research Institute of the Bakery Industry, VNIIHP, Russia).

4. 2. Preparation of the research samples and methods

Fat surfactant solutions were obtained by dissolving in sunflower oil at a temperature of 65–70 °C.

The foaming ability (FA, %) was determined by the formula:

$$FA = \frac{V_f}{V_s} \cdot 100\,\%, \tag{1}$$

where V_f is the volume of the foam, cm^3; V_s is the volume of the solution before churning, cm^3.

The foam stability (FS, %) was calculated using the formula:

$$FS = \frac{V_e}{V_i} \cdot 100\,\%, \tag{2}$$

where V_e is the volume of the foam after 1 h, cm^3; V_i is the initial volume of the foam, cm^3.

The specific volume (M, m^3/kg) of the baked ANSFP was determined by the ratio of the sample volume to its mass according to [17].

4. 3. Statistical analysis of the experimental data

The statistical processing was based on the single-factor analysis of variance (ANOVA) for a series of parallel measurements (n=3–4). The difference in the values was analyzed by Student's t-test with a statistical significance of ($p<0.05$). All experimental values were given in the form of X±ΔX, where X was the average of the experimental values and ΔX was its confidence interval. The statistical data processing was performed using the Excel program package of Microsoft Office 2010 v. 10 (Microsoft Corp., USA) and IBM SPSS Statistic v. 20 (IBM Corp., USA).

5. Development of a model of steric stabilization of the air-nut semi-finished product structure

The process of making an ANSFP by the traditional technology entails churning of egg whites with 10 % of white sugar. The next step is to add CN, mixed with 40–45 % of sugar powder, to the obtained foam, with further mixing, dosing, and baking. The main disadvantage of this technology is the low stability of the foam. The reason for this is the raw nut solids and oil droplets that are adsorbed on the surface of the water-air interface (Fig. 1, *a*). Baking reduces the volume of the foam. It is possible to prevent adsorption by adding the required amount of egg whites to the system. As a result, an IL is formed on each interface: water-air, water-oil-water, and water-solid substance. Addition of egg white increases the viscosity of the medium. Both factors counteract adsorption. However, such a decision is not appropriate economically.

A more rational approach is to add certain surfactants for each interface in the system. This means using egg whites to make the foam, low surfactant to emulsify the oil, and surfactant polysaccharides to increase the viscosity of the medium. From the technological point of view, this approach should provide a high interfacial shear stress in the IL on air bubbles and fat particles. It can also eliminate flotation of hydrophobic fatty and solid particles of the CN. Both factors reduce desorption of protein from the interfacial surface of water-air by hydrophilizing other dispersed particles.

To implement this approach, a model is suggested for steric stabilization of the ANSFP structure (Fig. 1, *b*). It includes two mechanisms of stabilization. The first one is related to emulsification and hydrophilization of fat particles while adding surfactants to the oil. The second mechanism reduces the flotation of suspended particles of CN while increasing the viscosity of the dispersion medium by using a stabilizer with surface-active properties.

An important step in the development of these models is the choice of the stabilizer. To ensure a high volume resistivity, it was considered to use xanthan gum, acacia gum, and sodium carboxymethylcellulose. The first two ingredients did not help obtain products with the necessary textural properties. The baked items were soft, rather than crispy. The use of NaCMC, however, provided the necessary textural properties. This stabilizer has the necessary surface-active properties, and it can be adsorbed at the water-solid particle interface [18]. This will prevent flotation of dispersed solid particles of the nut material.

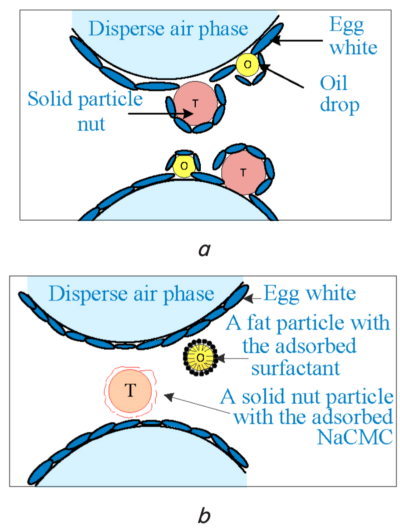


Fig. 1. Spatial distribution of phases in the ANSFP: *a* – by the traditional technology; *b* – by the model of steric stabilization

If there is a significant prevalence of the egg white content over the content of NaCMC, the system is not thermodynamically stable. [19] This factor prevents the process of desorption of the egg white from the water-air interface in the volume of the solution when adding NaCMC to the solution of churned egg whites.

6. Discussion of research results about the structure of the air-nut semi-finished product

6. 1. The rheological properties of interfacial adsorption layers

Previous rheological studies of the YSS of the interfacial layers on separate water-air and water-oil interfaces failed to reveal a correlation between oil-containing egg whites and the foam stability [3, 20]. Based on these patterns, research was conducted on ILs in systems that in addition to the water-air interface had the water-oil interface. The emergence of the new surface interface initiates a process of competitive adsorption.

The YSS of the interfacial layers at the water-oil interface after adding oil to the egg white solution (7.5 %) decreases 4.3 times in 2.5 hours (Table 1). Further keeping of the system has no virtual effect on the YSS of the interfacial layers. These results correlate with the ability of foaming and the stability of the foam that is based on the egg white after adding oil to the system [3].

Table 1

The dynamics of the yield shear stress of the interfacial layers at the water-air interface after adding oil to the system

Time, τ, h	0	1.0	1.5	2.0	2.5
YSS, $P_s \times 10^3$, N/m	0.4725	0.2625	0.21	0.1575	0.105

Adding surfactants to oil provides an extreme dependence character of the YSS of the interfacial layers at the water-air interface (Fig. 2). Thus, the maximum YSS of interfacial layers in systems containing GMS is achieved if the content is 0.8 % (Fig. 2, *a*). Almost the same YSS is achieved in systems with the DATEM content of 0.075 %. Based on the data, it is possible to conclude that if the DATEM content is 0.6 %, the YSS of the interfacial layers corresponds to the YSS of interfacial layers with egg whites without using surfactants. When using SSL, the maximum YSS is achieved if the surfactant content is 0.6 %. Based on the principles of food safety, foaming ability, foam stability and the YSS of the interfacial layers, the chosen surfactant among the ones studied was GMS.

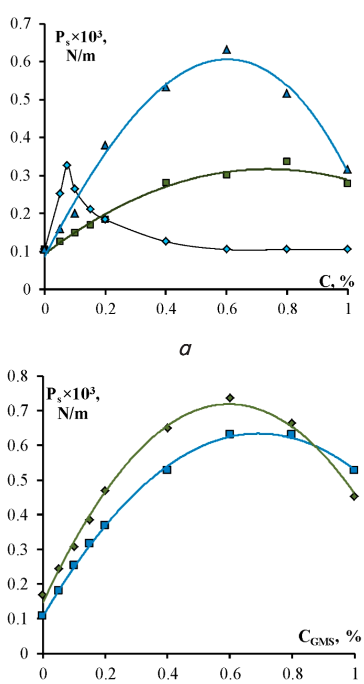


Fig. 2. The yield shear stress of the interfacial layers: *a* — "egg white-surfactant", depending on the content of the surfactant at the water-air interface and the surfactant content: □ — GMS; ◊ — DATEM; Δ — SSL; *b* — "egg white-surfactant-sugar", depending on the content of GMS at the water-air interface and the content of sugar, %: □ — 10.0; ◊ — 50.0

The resulting patterns of the YSS of the interfacial layers depending on the type and content of the surfactants make it possible to assert that adding the surfactants to oil can increase the YSS of the interfacial layers bordering on air. The explanation for this fact is that adding a surfactant reduces the interfacial tension between water and oil, providing for the hydrophilization of the fat phase, thereby reducing the driving force of desorption of the egg white from the water-air interface.

As part of the ANSFP recipe, the sugar content is 50–55 %, which can change the ratio of egg white and surfactants and increase the YSS of the interfacial layers. Thus, adding 10.0 % of sugar to 7.5 % of the egg white solution increases the YSS of the interfacial layers bordering on air in systems with two interfaces – water-air and water-oil. The maximum YSS of the interfacial layers corresponds to the content of GMS being 0.6–0.8 % (Fig. 2, *b*). If the content of sugar is increased to 50.0 %, it increases the absolute values of the YSS of the interfacial layers when the content of GMS is 0.6 %. A similar tendency as to the impact of sugar was noted in [21] while studying the modulus of elasticity in the interfacial layer of ovalbumin. As shown in Fig. 2, *b*, adding 0.6 % of GMS to the "egg white-GMS-sugar" system can increase the YSS of the interfacial layers at the water-air interface 4.4–6 times compared with systems containing only egg white.

6. 2. Rational parameters for obtaining the air-nut semi-finished product

The rational parameters of churning egg white are determined by finding the dependence of the churning duration on the value of the foaming ability (FA) of the 7.5 % solution of egg whites. It was found that the churning duration of 8–10 minutes and the machine rotation speed of n=18 s^{-1} maximize the FA up to 629 %, with 100 % of the foam stability (FS). Adding crushed nuts (almond) in the amount of 20–40 % reduces the amount of the foam from 320 to 110 % (Table 2).

Table 2

The impact of the crushed nut (CN) content ω_{CN} on the foam parameters

ω_{CN}, %	20	25	30	35	40
FA, %	320	260	210	160	110
FS, %	100	100	100	100	100

In the experiment, the model system was used as a recipe mixture. The model system was prepared as follows: the churned solution contained 7.5 % of egg white and 10 % of sugar. Then 30 % of crushed almonds were added with 0.6 % of GMS and the sugar that would totally amount to 50 % in the solution. The FA reduction can be explained as destruction of the foam during mixing the churned egg white with the CN. After stopping the mixing process and after further proofing, the foam remains stable.

It was determined that the recipe mixture with CN below 150 % is characterized by a low specific volume after baking and does not comply with the set quality parameters. Given this, the rational CN content is 30–35 %. This content is also typical of the traditional technology of making ANSFPs. Baked semi-finished products containing CN below 30 % are characterized by a low intensity of the nutty flavor. Therefore, reduction of the raw nut content to enhance the stability of the foam is not rational in terms of quality indicators.

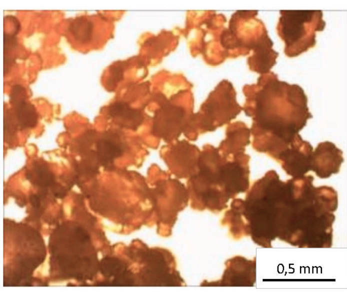
As the degree of grinding in the CN determines the FA and the FS, it was found what the average size of particles of the main fraction of CN could ensure the maximum FA (Table 3). The analysis of the data from Table 3 showed that the maximum FA is typical of systems that contain CN with an average particle size of 0.4 mm (a fraction content of 60 %). With a further increase of dispersion, the FA decreases, probably due to particle clumping in the nut material. A decreased dispersion reduces both the FA and the FS. It happens because significant dimensional characteristics of raw nuts lead to the destruction of the foam by sedimentation.

Table 3

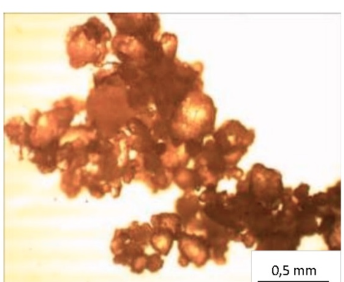
Foam characteristics of the recipe mixture, depending on the average size of particles of the main fraction of raw nut particles

Average size, 10^{-3}, m	FA, %	FS, %
0.2±0.1	142±7	99±1
0.4±0.1	210±11	99±1
0.6±0.1	155±8	99±1
0.8±0.1	112±6	94±1

It was additionally proved that adding GMS under the same conditions during the crushing of raw nuts increases the degree of crushing and reduces the clumping of the particles (Fig. 3).



a



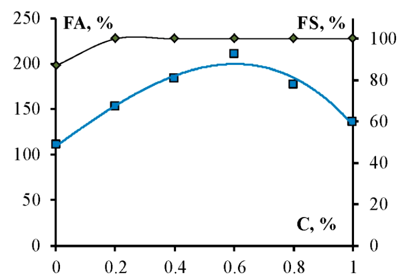
b

Fig. 3. Photos of crushed nut material:
a — after adding GMS; *b* — without GMS

The increased dispersion of raw nut particles after adding GMS can be explained by a decrease in the strength of the CN in the presence of the surfactant (the Rebinder effect). The fact of the reduced clumping of particles is explained by the action of the fat crystallization process due to the high melting temperature of GMS. Thus, GMS should be efficiently added during the crushing of raw nuts to improve dispersion and to reduce adhesion.

The adequacy of the rationally selected content of GMS is proved by the research results on the FA and the FS for the recipe mixture that contained 30 % of the CN (Fig. 4, *a*). Adding 0.6 % of GMS ensures 100 % of the FS and 210 % of the FA, which is a good result. Thus, adding 0.6 % of GMS produces a positive impact on the degree of crushing the raw nuts, the FA, and the FS.

The improvement of the technology of making ANSFPs is based on ensuring stability of the foam to implement industrial production, which involves mechanical stirring of the recipe mixture with the introduction of a crushed nut material. Mechanical mixing provides even distribution of the CN in the system if the mixing lasts for 1–2 minutes at a speed of the machine rotation of n=3–4 s^{-1}. However, under these conditions, the foam volume is reduced to the size of 106–112 %. If the recipe mixture was left for 1–2 hours, no further destruction of the foam was revealed: the stability was 100 %. The use of GMS does not ensure foam resistance to mechanical action in the presence of particulate nut material. Thus, the study has proved the necessity to add NaCMC as a stabilizer.



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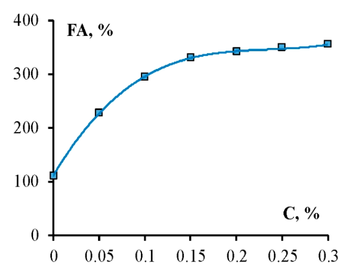

b

Fig. 4. The foaming ability (□) and the foam stability (◊) of the recipe mixture: *a* — depending on the content of GMS; *b* — depending on the content of NaCMC (if the content of GMS is 0.6 %)

Adding NaCMC to the recipe mixture under mechanical stirring for 1–2 minutes at a speed of the machine rotation of n=3–4 s^{-1} helps preserve the foam volume. Thus, if the content of NaCMC is 0.15–0.25 %, the FA is 340 %, which is 3.1 times higher than without NaCMC (Fig. 4, *b*). Presumably, this can be explained by an increase in the system viscosity, which prevents flotation. The analysis of the data has revealed that the rational content of NaCMC in terms of the foaming ability is 0.15–0.25 %.

The conducted rheological study has determined that the effective viscosity (at a shear rate of 100 s^{-1}) with 7.5 % of the egg white solution and 50 % of sugar after adding 30 % of CN is reduced 7.5 times (Table 4). Putting 30 % of nut flour into the system containing 0.2 % of NaCMC results in a slight decrease in the effective viscosity of 1.48 times

(Table 4). Thus, the rate of decrease in the effective viscosity is 5.0–5.1 times less.

Table 4

The effect of mixing on the effective viscosity η of the recipe mixture

The state of the system	effective viscosity, Pa·s	
	without NaCMC	with NaCMC (0.2 %)
Before mixing	0.15	0.68
After mixing	0.02	0.46

Effective viscosity is reduced probably because adding CN leads to adsorption of the egg white on the surface of the solid particles. This causes a decrease of viscosity. NaCMC is adsorbed on the solid particles and reduces the polarity difference between the solid and aqueous phases. This reduces desorption of the egg white from the water-air interface, diminishes the foam destruction, and facilitates a high viscosity of the system, which prevents flotation of dispersed particles.

6. 3. Evaluation of the quality features of the air-nut semi-finished product

According to the conventional technology, the temperature for baking ANSFPs is 140–150 °C. In the improved technology, the baking temperature was the same. The full-factor experiment helped determine the rational duration of heat treatment depending on the different masses of dough. While varying the mass of dough from 5 to 200 g, the heat treatment duration was 12–45 minutes.

Fig. 5 shows samples of ANSFPs obtained by the traditional and advanced technologies. The specific volume of the air-nut semi-finished product obtained by using the traditional technology is M=3.1 m^3/kg.

a *b*

Fig. 5. The views of the air-nut semi-finished product samples: *a* – the traditional technology; *b* – the improved technology

The organoleptic evaluation was used to determine the specific volume of the air-nut semi-finished product that is characterized by the maximum quality and is M=3.7 m^3/kg. The comparison of these values is in favor of the sample obtained by the improved technology.

7. Conclusion

1. The model of steric stabilization has been developed to ensure sustainability of food systems with several phases in various states of aggregation. The model facilitates the process of making a food product by implementing two important mechanisms. The first relates to the provision of high values of rheological parameters of interfacial layers. High values of the yield shear stress of the interfacial layers prevent the getting of fat or solid particles onto the surface of the water-air interface. The second mechanism helps achieve a desired viscosity of the system, which prevents flotation of dispersed particles.

2. The practical use of the developed model of steric stabilization is described in the study by an example of making an air-nut semi-finished product. The undertaken experiments have confirmed the effective mechanism of the steric stabilization model. Adding sufficient amounts of surfactants made it possible to obtain interfacial layers with a high interfacial shear stress. Additional introduction of low molecular surfactants to oil boosted the yield shear stress of the interfacial layers at the water-air interface in a system with two phases. The use of sodium carboxymethyl cellulose as a stabilizer facilitated a high viscosity of the dispersion medium to counteract flotation of dispersed particles under a mechanical effect on the system. The model can be used in other technologies of food production. This applies, in particular, to the technologies of making chocolate sponge cakes, nut biscuits, and other baked foam-based products.

3. The study has substantiated rational parameters of churning egg whites. The mixing duration should be 8–10 min at a speed of the machine rotation of 18 s^{-1}. The substance is churned with 10 % of white sugar. Then the added content of crushed nuts is 30–35 %. It has been shown that the grinding of nut raw materials with GMS to the average size of particles of the main fraction of 0.4 mm provides a high degree of foaming. It has been determined that adding 0.6 % of GMS and 0.2 % of NaCMC can ensure stabilization of the air-nut semi-finished product before mechanical mixing. The above factors can help obtain air-nut semi-finished products with the desired organoleptic characteristics.

4. It has been found that the advanced technology can help obtain an air-nut semi-finished product by industrial methods for a specific volume of 3.7 m^3/kg instead of 3.1 m^3/kg obtained by the traditional technology.

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