Розроблено теоретичну модель Пікерінг-стеричної стабілізації структури піноемульсій з низьким вмістом жиру, одержаної із сухої суміші. Експериментально доведено, що граничне напруження зсуву піноемульсії визначається ступенем дестабілізації жирових частинок, які забезпечують Пікерінг стабілізацію піноемульсії. Реалізація комплексоутворення казеїнату натрію та капа-карагінану забезпечує стеричну стабілізацію піноемульсії за рахунок збільшення граничного напруження зсуву міжфазних адсорбційних шарів

Ключові слова: піноемульсія, Пікерінг-стерична стабілізація, сухі суміші, піноутворююча здатність, комплексоутворення, дестабілізація жиру

Разработана теоретическая модель Пикеринг-стерической стабилизации структуры пеноэмульсии с низким содержанием жира, полученной из сухой смеси. Экспериментально доказано, что предельное напряжение сдвига пеноэмульсии определяется степенью дестабилизации жировых частиц, которые обеспечивают Пикеринг стабилизацию пеноэмульсии. Реализация комплексообразования казеината натрия и каппа-карагинана обеспечивает стерическую стабилизацию пеноэмульсии за счет увеличения предельного напряжения сдвига межфазных адсорбционных слоев

Ключевые слова: пеноэмульсия, Пикеринг-стеричесая стабилизация, сухие смеси, пенообразующая способность, комплексообразование, дестабилизация жира

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DEVELOPMENT OF A THEORETICAL MODEL FOR OBTAINING THE WHIPPED EMULSIONS FROM A DRY FAT-CONTAINING MIXTURE AND ITS EXPERIMENTAL VERIFICATION

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1. Introduction

The use of dry mixtures for obtaining food products with a foam-emulsion structure is a promising direction to improve efficiency of functioning of food enterprises. The benefits of using dry mixtures for obtaining the products of a whipped-emulsion structure:

– ease of use;

– predicted indicators of finished products quality;

– potential to create a wide range of products;

– possibility of timely response to changes in demand of restaurant business;

– no need to use refrigeration equipment to store dry mixtures.

In the Ukrainian market, dry fat-containing mixtures are widely represented by mostly foreign manufacturers such as Dr. Oetker (Germany), Cykoria S. A. and Mokate Ingredients (Poland) and others. This product is available in different segments of the market – these include a whitening for coffee and for making cappuccino, mixtures for obtaining creams, ice cream, as a base for sponge cakes, cupcakes, muffins, etc. That is why we may argue about the high demand and wide distribution of dry fat-containing mixtures for obtaining the products with a whipped-emulsion structure.

Dry mixtures for whipping are typically made with the use of hydrogenated vegetable oils, which has a number of shortcomings, including the presence of trans isomers of fatty acids. Dry fat-containing mixtures are received by creating the emulsion of its condensation with subsequent spraying drying. However, it is a rather energy-intensive process, which is implemented at large enterprises, usually with a continuous process of production. That is why using the non-hydrogenated oils, such as sunflower oil, and the introduction of surfactants with high melting point is a relevant task in the creation of safe food products. Reducing energy consumption when obtaining the dry fat-containing mixtures is possible by developing a fundamentally new technology without drying the emulsion. Depending on the scope of application of dry mixtures for obtaining whipped emulsions, the mechanisms for their stabilization are different. This requires theoretical and experimental substantiation.

2. Literature review and problem statement

There is a considerable scientific and practical interest to ensure stability of the food dispersed systems (foam whippeds and emulsions) using the varieties of structural-mechanical stabilization factor (steric stabilization). It is shown [1] that the forces of steric stabilization play an important role in the stabilization of dispersed systems. Steric stabilization is achieved through polymeric surface-active substances [2], which provide resistance to the effect of temperature and electrolytes. The ratio between high molecular and low-molecular surface-active substances, in particular sodium caseinate and monoglycerides, allows control over stability of an emulsion [3]. Aggregation of proteins with substances that do not possess surface-active properties (sugars) makes it possible to increase the steric strength and stability of foam [5]. Another structural-mechanical variety is Pickering stabilization by using the solid particles. The stability of foams using the solid particle can persist for several months [5]. It depends on the speed of adhesion of solid particles [6], contact angle [7]. In food systems they use cellulose [5], micro gels particles [8]. Fat crystals and crystals of surface-active substances are applied in emulsions [9, 10]. For the stabilization of whipped emulsions – crystals of fat with surfactants [11]. Article [12] argues about the prospects of applying the synergetic effect of Pickering stabilization and the use of proteins or surfactant, to stabilize the foams and emulsions simultaneously. Ensuring technological stability (product shell life) of the whipped emulsion systems through a structural-mechanical stabilization factor makes it possible to significantly increase the storage period of these products.

Paper [11] developed a theoretical model for ensuring the technological stability of whipped emulsions by the Pickering stabilization through providing for the conditions of adhesion and agglomeration of solid fat particles on air bubbles. Low content of fat phase in a product, which is typical for products with reduced calories, does not allow employing the given model to stabilize a whipped emulsion. In addition, in order to obtain whipped emulsions, dry fat-containing mixtures are widely used, which also requires consideration of the processes of recovery and whipping.

The type of oil defines the need to substantiate the type of surfactants in whipped emulsions [13]. The given work is a continuation of studies [14–16] and aims to generalize data on the technology of obtaining a dry fat-containing mixture and to develop a theoretical model for the provision of technological stability of whipped emulsions. Preliminary research into a foamed-forming capacity, foam stability, the boundary shear stress of whipped emulsions substantiated the content of sunflower oil, sodium caseinate, surfactants (E471, E322), kappa-carrageenan. However, a significant number of processes require defining the mechanisms for the provision of technological stability of whipped emulsions.

3. The aim and tasks of the study

The aim of present work is the theoretical and experimental substantiation of obtaining technologically stable whipped emulsions from a dry fat mixture by the Pickering steric stabilization.

To achieve the set goal, the following tasks are to be solved:

– to develop a theoretical model for the provision of technological stability of whipped emulsions by the Pickering steric stabilization;

– to confirm experimentally the regularities of the processes underlying a theoretical model of obtaining a whipped emulsion;

– to receive parameters of a dry fat-containing mixture;

– to substantiate parameters for obtaining a dry fat-containing mixture;

– to assess quality indicators of the obtained whipped emulsions based on a recovered fat-containing mixture.

4. Materials and methods for examining the whipped emulsions and dry fat-containing mixtures

4. 1. Examined materials and equipment

In the experiment we used the following reagents:

– sodium caseinate with protein content of 85.6±2 %;

– sunflower oil, refined, deodorized, frozen out;

– E471 distilled monoglycerides with iodine value 3.0±±0.1 g I_2/100 g);

– E322 (soy lecithin) with the content of substances not dissolved in acetone 73.7±0.1 %;

– E407 (kappa-carrageenan, purified) (Marsel Food ingradient, the Philippines);

– white sugar.

All the indicated reagents have the food grade qualification.

The FT-IR spectra of the samples of aqueous solutions were recorded on an spectrophotometer Spectrum One with the DTGS detector (deuterated triglycine sulfate detector) (PerkinElmer, Inc., USA). All spectra in the range of 400–4000 cm^{-1} are the average of two counts, with 36 scans each and a resolution of 1 cm^{-1}.

Determination of the mean diameter of fatty particles and air bubbles was carried out by microscopy on an microscope Biolam R15 (Lomo, Russia) with the digital camera-eyepiece ScopeTek DCM-130 E 1.3 Mp (Hangzhou Scopetek Opto-Electric Co., Ltd., China); the images were received using the Scope Photo 3.0 software (Hangzhou Scopetek Opto-Electric Co., Ltd., China). Microphotograph data were processed automatically using the ImageJ 1.47 software (National Institutes of Health, USA).

Scanning electron microscopy (SEM) of the samples was examined at the raster electron microscope Jeol JSM-480 (JEOL Ltd, Japan) with a cryo-SEM.

4. 2. Preparation of the samples and research techniques

Fat solutions of surfactants were received by dissolving in sunflower refined oil when heated to temperature 50...80 °C.

Techniques utilized for determining:

– foam-forming capacity;

– foam stability;

– yield shear stress of whipped emulsions;

– degree of destabilized fat;

– yield shear stress of the the adsorbed interfacial layers (AIL) of emulsions;

– mean diameter of fat particles and air bubbles;

– morphology of a whipped emulsion is given in [11].

Wetting angle was determined by [17].

4. 3. Statistical processing of results

For the statistical processing we used a one-factor analysis (ANOVA) for a series of parallel measurements (n=3–4). Difference in the values was analyzed by the Student t-test with a statistical significance ($p<0.05$). All experimental magnitudes are given in the form of $X \pm \Delta X$, where X is the mean value of experimental magnitude and ΔX is its confidence interval.

Statistical data processing was performed using the Excel software of Microsoft Office 2010 package (Microsoft Corp., USA) and IBM SPSS Statistic ver. 20 (IBM Corp., USA).

5. Theoretical and experimental verification of the model for obtaining a whipped emulsion based on a dry fat-containing mixture

5. 1. Development of a theoretical model of the formation of a whipped emulsion from a dry fat-containing mixture

Based on analysis of the scientific literature and in line with the purpose of present work, we formulated a working hypothesis of research, which implies the dispergation of a fatty phase in the powdered hydrophilic filler with the formation of polymolecular layers. This will allow us to develop an energy-efficient technology for obtaining a dry fat-containing mixture. Recovery of the dry mixture will provide simultaneous progress of processes of emulsifying and foaming through the use in the composition formulation of proteins and low-molecular surfactants. This will make it possible to obtain food products with a whipped-emulsion structure.

Within the framework of the formulated working hypotheses, we proposed a theoretical model for obtaining a technologically stable whipped emulsion based on a dry fat-containing mixture (Fig. 1). At a low amount of the fat phase in a whipped emulsion, stabilization can be achieved by a joint action of two factors – Pickering and steric stabilization.

Underlying the formation and provision of technological stability of whipped emulsions based on a dry mixture are the following controlled processes:

– formation of the adsorbed interfacial layers on fat particles while dispersing in the powdered hydrophilic filler through the introduction of surfactants into a fat phase and provision of its contact with a hydrophilic condensed surface;

– provision during foaming of low shear stress limit values of the adsorbed interfacial layers on fat particles and air bubbles;

– provision of low viscosity of the dispersed medium for the destabilization of fat particles;

– provision of flotation, adhesion and agglomeration of fat particles on air bubbles (Pickering stabilization);

– at the final stage of whipping – an increase in the values of yield shear stress of the adsorbed interfacial layers on air bubbles (steric stabilization).

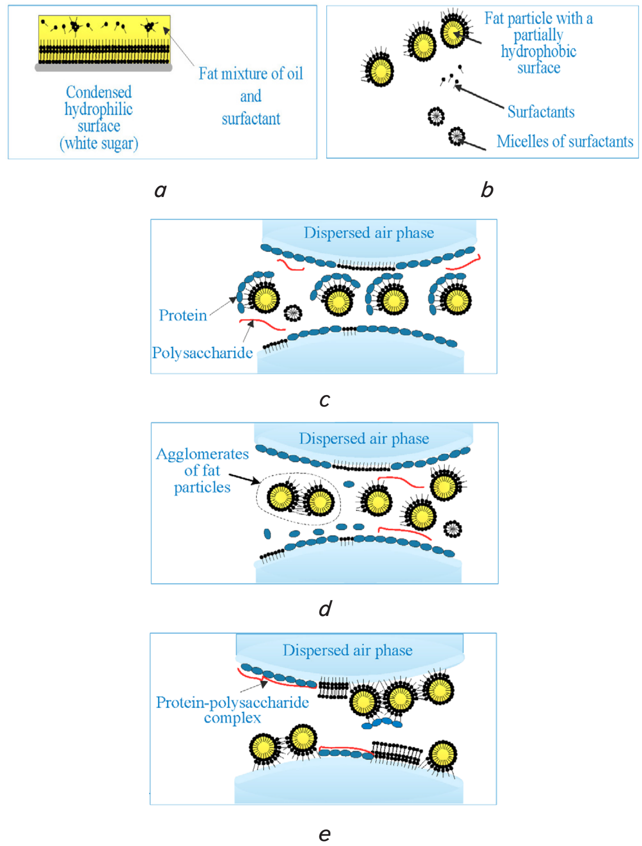

Fig. 1. Theoretical model of obtaining technologically stable whipped emulsions by the Pickering- steric stabilization: *a* – quasi-emulsifying; *b* – recovery of a dry fat-containing mixture; *c* – whipping stage I (foaming and emulsifying); *d* – whipping stage II (destabilization and agglomeration of fat particles); *e* – whipping stage III (stabilization of the whipped emulsion)

Obtaining a dry fat-containing mixture without a spraying drying should be based on the provision of formation of the adsorbed interfacial layers on dispergated fat particles. That is, similar to the traditional method of obtaining – by forming the emulsion and its drying. This approach can be implemented by the dispergation of oil that contains surfactants, with a direct contact between fat particles and a hydrophilic surface. A hydrophilic surface in this case is sugar with the subsequent provision of conditions for the crystallization of oil with obtaining a loose powder mixture (Fig. 1, *a*).

Since the process of dispersing the fatty phase with a surfactant dissolved in it at contact with a hydrophilic condensed phase is similar in principle to the emulsification, then this process can be called a quasi-emulsification. The implementation of this process will make it possible to develop and reduce energy consumption for obtaining a dry whipped fat-containing mixture. However, in terms of the model for the provision of technological stability of whipped emulsions, the first stage can take the form both of quasi-emulsification and of emulsification. Since in terms of equilibrium thermodynamics a simultaneous dispersing in the system of air and fatty phase is not rational and requires a sequential process of dispersing the phases (fatty and air).

Recovery of the dry fat-containing mixture is accompanied by the emulsification of dispergated fat particles in the system (Fig. 1, *b*) and foam-formation of the system (Fig. 1, *c*). At mechanical impact on the system, there will occur the destabilization, floatation and agglomeration of fatty particles (Fig. 1, *d*). In order to ensure the adhesion of fatty particles on air bubbles, it is required to control the yield shear stress of the adsorbed interfacial layers. Reduction in the yield shear stress of the adsorbed interfacial layers at the water-oil interface is necessary for the destabilization of fatty particles, agglomeration and flotation. Reduction in the yield shear stress of the adsorbed interfacial layers at the water-air interface is necessary to ensure the adhesion of fatty particles. This can be achieved at a low content of proteins in the system and the introduction of low molecular surfactant.

At the final stage of whipping, there will occur the stabilization of a whipped emulsion through the agglomeration of fatty particles on air bubbles (Pickering stabilization). After the adhesion of fatty particles, there happens an increase in the yield shear stress of the adsorbed interfacial layers at the water-air interface. The latter can be implemented through the complex-formation of protein-polysaccharide or the formation of polymolecular crystalline adsorbed interfacial layers due to surfactants (steric stabilization) (Fig. 1, *e*). It could be implemented technologically by adjusting the temperature during foaming. In particular, it is necessary to recover and whip the mixture at a temperature above the temperature of complex-formation and crystallization. This will ensure foaming, destabilization and agglomeration of fatty particles. At the final stage of whipping, it is necessary to lower the temperature for increasing the yield shear stress of the adsorbed interfacial layers and adhesion of fatty particles on air bubbles. This will provide for the stabilization of a whipped emulsion.

In order to solve the set tasks, we should explore the systems in stages. At the first stage, it is necessary to determine the patterns of sequential formation of whipped emulsions, which implies the emulsification of oil in the aqueous medium of surfactants with subsequent whipping. The second stage is the application of the obtained regularities for the transformation of system into a dry fat-containing mixture, the recovery and whipping of which will make it possible to receive whipped emulsions with similar physico-chemical parameters. This model can be successfully employed to receive food products with a foam-emulsion structure with a low content of fat phase, which should not be exposed to heating since the basis of stabilization of the systems is the principle of Pickering stabilization through the adhesion of fatty particles, while heating will cause the melting of fatty particles and lead to the destruction of the foam.

Increasing the temperature will cause the destruction of a whipped emulsion. The given whipped emulsions are characterized by low viscosity due to the use of liquid oil and the absence of thickeners, which opens up broad opportunities to extend the range of food products with the possibility of introducing a significant quantity of fillers.

5. 2. Experimental verification of the progress of processes of formation a whipped emulsion and its stabilization

Based on previous studies [16], it was found that the introduction of E471 provides for an increase in a foaming capacity and stability of foam of a whipped emulsion based on sodium caseinate and sunflower oil. However, introducing only E471 does not ensure the required indicators of foam stability of a whipped emulsion. It was assumed that this was due to the insufficient degree of destabilization of fatty particles at whipping and, as a result, low ability of adhesion on air bubbles. Thus, the degree of destabilization of fat is 68.9±3.4 % in the whipped emulsion "sodium caseinate (0.5 %)-E471 (3.0 %)-sunflower oil (5.0...7.0 %)" (Fig. 2, *a*). Increasing the content of E471 from 3.0 % to 6.0 % does not increase the degree of destabilization of fat. Therefore, to increase the degree of destabilization of fat, it is necessary to introduce the surfactant with a high surface activity – E322. An introduction of E322 in the amount of 0.08...0.14 % into the system "sodium caseinate (0.5 %)-E471 (3.0 %)-E322-sunflower oil (5.0...7.0%)" provides for a full degree of the destabilization of fat (Fig. 2, *b*).

An introduction of E322 in the amount of 0.08...0.1 % does not affect the foaming capacity of whipped emulsions (at the content of oil 5.0...7.0 %). However, it provides the stability of foam 99±1 % for 24×60^2 s of the system "sodium caseinate (0.5 %)-E471 (3.0 %)-E322-sunflower oil" [16].

Increasing the share of crystallized oil and the degree of its destabilization enhances the yield shear stress of a whipped emulsion at increasing the content of E471 [14]. It happens, probably, due to the agglomeration of fatty particles and adhesion on air bubbles. Reducing the degree of destabilization of fat with the introduction of E322 higher that 0.2 % leads to lowering the yield shear stress of a whipped emulsion [14]. Therefore, we can state that the degree of destabilization of fat determines the yield shear stress of a whipped emulsion. In the case of insufficient amount of fat particles, in order to ensure the Pickering stabilization of air bubbles, it is necessary to increase the yield shear stress of the adsorbed interfacial layers of water-air (steric stabilization). The latter is achieved through the complex-formation of proteins with polysaccharides.

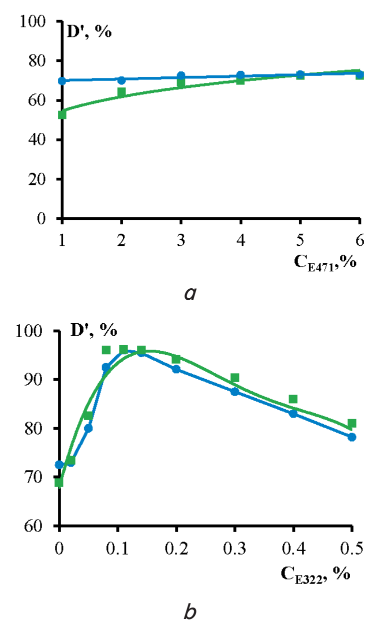

Fig. 2. Degree of destabilization (D′) of fat in the whipped emulsions: *a* – "sodium caseinate (0.5 %)-E471-sunflower oil"; *b* – "sodium caseinate (0.5 %)-E471 (3.0 %)-E322-sunflower oil" on the content of E322 at the content of sunflower oil: ■ – 5.0 %; ● – 7.0 %

It is promising to use kappa-carrageenan, which is capable of complex-formation with the proteins of milk. The influence of kappa-carrageenan on the foaming capacity and yield shear stress of whipped emulsions was examined for "sodium caseinate (0.5 %)-E471 (3.0 %)-E322 (0.08 %)-sunflower oil (5.0 %)-kappa-carrageenan". Maximum foaming capacity matches the content of kappa-carrageenan in the system at 0.5...1.0 %. The yield shear stress of a whipped emulsion grows with increasing content of kappa-carrageenan [14]. An extreme increase in the foaming capacity is due to the complex-formation of kappa-carrageenan and sodium caseinate, which provides an increase in the foaming capacity of whipped emulsions through the growth in yield shear stress of the adsorbed interfacial layers.

We established influence of kappa-carrageenan on the yield shear stress of the adsorbed interfacial layers of the systems "sodium caseinate-kappa-carrageenan" at the water-air and water-oil interfaces (Fig. 3). In order to ensure the liquid phases, the content of formulation components was reduced 10 times to maintain the interrelations (for the absence of oil crystallization at the introduction of surfactants or gel formation at the introduction of kappa-carrageenan). A dependence of yield shear stress of the adsorbed interfacial layers on the content of kappa-carrageenan in the system "sodium caseinate-kappa-carrageenan" is of extreme character with a local maximum. Such dependence is characteristic of the water-air and water-oil interface. This is probably due to the formation of complexes sodium caseinate-kappa-carrageenan. The obtained patterns correlate with a foaming capacity.

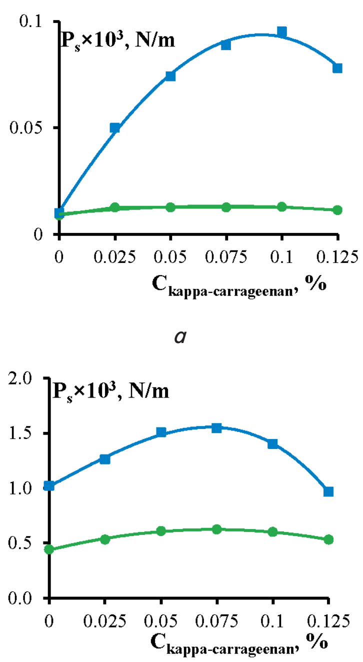

Fig. 3. Yield shear stress of the adsorbed interfacial layers of the systems "sodium caseinate (0.05 %)-kappa-carrageenan" on the content of kappa-carrageenan at the interface: *a* – water-air; *b* – water-oil; at temperature: ■ – 20±1 °C; ● – 70±1 °C

To confirm the complex formation of sodium caseinate kappa-carrageenan, we conducted infrared spectroscopy of aqueous solutions (Fig. 4). As a result of adding the sodium caseinate, the intensity of absorption grows at wavelengths 1450 cm^{-1} and 1260 cm^{-1}. The appearance of absorption bands is registered at wavelengths 1140 cm^{-1}, 1063 cm^{-1}. There is a shift in absorption band 1260 cm^{-1} to 1278 cm^{-1}.

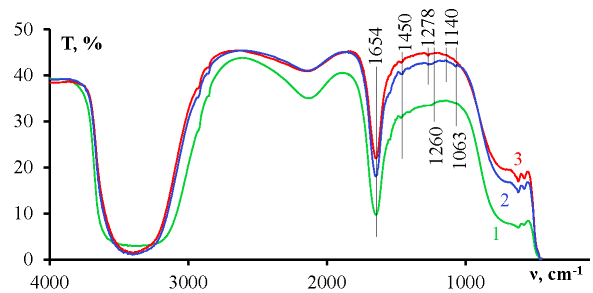

Fig. 4. FT-IR spectra of solutions: 1 – sodium caseinate (2.5 %); 2 – kappa-carrageenan (0.4 %); 3 – a solution of kappa-carrageenan and sodium caseinate

This evidences the participation of groups ($-SO_3^-$) in the formation of complexes. Comparison of the intensity of absorption band for Amide I and shift in the absorption band 1650 cm^{-1} to 1654 cm^{-1} of sodium caseinate with kappa-carrageenan confirms the formation of electrostatic complexes. The complexes are formed with the participation of amino group of sodium caseinate and a ($-SO_3^-$) group of kappa-carrageenan. Similar data were obtained by authors for the systems gelatin-kappa-carrageenan [18].

5. 3. Experimental substantiation of parameters for obtaining a dry fat-containing mixture by the quasi-emulsification

In order to confirm the need for a contact between a fatty phase and a hydrophilic condensed phase, we examined a foaming capacity, foam stability, yield shear stress of whipped emulsions and the angle of wetting of fatty particles. In line with the first technique, a dry fat-containing mixture was received by spraying the fat phase in the chamber, which models the process of spraying drying, but, in this case, only a fatty phase is sprayed, rather than the emulsion. In order to implement the given concept, we designed a laboratory test bench to spray the fat in a chamber with powder-like filler, which is in the suspended state (Fig. 5).

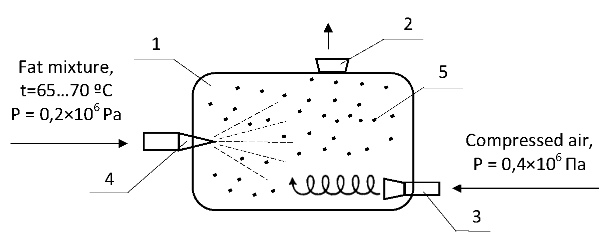

Fig. 5. Laboratory test bench for obtaining a dry fat-containing half-finished product: 1 – spraying chamber; 2 – excess pressure valve; 3 – fan nozzle; 4 – spraying nozzle; 5 – powder-like filler

The chamber contained in the suspended state a part of powder-like filler (sodium caseinate, sugar powder, and kappa-carrageenan) to reduce fat particles agglomeration during spraying. Received fat mixture with a crystallized fatty phase was mixed with powder-like filler that remained. Thus, we obtained a dry fat-containing mixture without a contact with a hydrophilic condensed phase during fat crystallization.

At pressure of fat mixture feed 0.2×10^6 Pa and diameter of the nozzles 1.5×10^{-3} m, we received fatty particles of average diameter $(5...10)\times10^{-6}$ m. Recovery of a dry fat-containing mixture and whipping allows obtaining whipped emulsions with foaming capacity of 400±16 %, foam stability of 99±1 % and the yield shear stress of 550±28 Pa. The magnitude of foaming capacity and yield shear stress is significantly lower than the values of indicators of whipped emulsions, received in the sequential process of formation. At this method of obtaining, an edge angle of wetting the fat particles with water is 1.5±0.5°. A low magnitude of foaming capacity is probably associated with the low content of surfactants in the dispersion medium. High hydrophilicity of fatty particles leads to the lack of agglomeration, flotation and, as a consequence, does not provide for the high values of yield shear stress of whipped emulsions. Considering the obtained results, it is necessary to provide conditions under which surface of the fatty particles will be partially hydrophilized (partial wetting $0°<\theta<90°$). Partial hydrophilization of fatty particles can be achieved by applying the fatty mixture on the crystals of sugar. A contact between a hydrophilic condensed phase and a fatty phase during its crystallization contributes to the formation of adsorbed interfacial layers.

It was experimentally proven that by applying a fatty phase on the crystals of sugar, the surface of fatty particles is partially wetted during the emulsification. The edge angle of wetting with water is 25±2° thus confirming the formation at the surface of the particles of fat of polymolecular layers of surfactants. Probably, during the dissolution of sugar crystals, the adhesion bonds sugar-oil are destroyed with the transition of the outer layer of surfactants into a water dispersion medium. That is, fatty particles keep a layer of surfactants with the orientation of hydrophobic radicals to the water dispersion medium. This predetermines the required flotation conditions and increases the agglomeration and adhesion of fatty particles on air bubbles.

By employing the technique, which implies a contact between a fatty phase during its crystallization and a hydrophilic condensed surface (sugar crystals), we received a dry fat-containing mixture, recovery and whipping of which provides for the foaming capacity of 795±30 % and the yield shear stress of 1150±57 Pa. That is, at magnitudes, similar to the magnitudes of whipped emulsions received at sequential emulsification and foam-formation. Characteristics of physical-chemical indicators of dry fat-containing mixtures depending on the technique of dispersing the fat phase are given in Table 1.

Table 1

Physical-chemical indicators of whipped emulsions obtained based on a dry fat-containing mixture

Technique for dispersing the fat phase	Indicator title			
	Foaming capacity, %	Foam stability, %	Yield shear stress of whipped emulsions, Pa	Contact angle of wetting the fatty phase with water θ, °
Without applying on the condensed surface	400±16	99±1	550±28	1.5±0.1
Applying on the condensed surface	795±30	99±1	1150±57	25.0±2.0

We defined rational temperature of a powder-like filler, which is 15...20 °C, at which the mean diameter of the predominant fraction of fatty particles in the emulsion is $(20...30)\times10^{-6}$ m. It was established that at higher temperature, there occurs the agglomeration of fatty particles in a dry mixture and it leads to an increase in the average diameter in an emulsion. By using the raster electron microscopy, it was confirmed that the formation of agglomerates takes place at the temperature of a filler of 35±1 °C [19].

We defined a rational rotation rate of the mixer body at 17...19 s^{-1} and the duration of mixing, which is $(5...7)\times60$ s, which ensures minimum mean diameter of fatty particles in the emulsion of $(23\pm2)\times10^{-6}$ m.

During an analysis of physical appearance and consistency, we considered product flow ability, the presence of agglomerates and destruction. It was established that the rational content of a fat-containing mixture is 30...35 %. In such mixture, the content of E471 is 30...37.5 % of the total amount of fat that ensures its crystallization and opens up the possibility of using liquid oils for obtaining the dry fat-containing mixtures. Thus, it is necessary to recover a dry fat-containing mixture at hydrological module 1:3, which will provide for the rational content of formulation components, which was substantiated when examining the model systems at sequential emulsification and foam-formation.

Therefore, it is proved that a dry fat-containing mixture for obtaining the whipped emulsions can be received through the quasi-emulsification. By providing conditions of contact between a fatty phase with the surfactant dissolved in it and a condensed hydrophilic phase, which is actually white sugar. The recovery of a dry fat-containing mixture and whipping provides the formation of a whipped emulsion. The magnitudes of foaming ability, foam stability and the yield yield shear stress are similar to the magnitudes of the whipped emulsions obtained by the emulsification of oil with subsequent whipping.

6. Discussion of results: assessment of quality indicators of the received whipped emulsion using a dry mixture

The task of receiving high quality indicators of a whipped emulsion implies determining the rational parameters in the recovery of a dry fat-containing mixture, at which maximum foam ability would be ensured. In order to reach maximum foam ability, the rational water temperature for the recovery of a dry fat-containing mixture is 65...70 °C. Further increase in temperature does not affect foam ability. Enhancing the foam ability by increasing the temperature of water to recover a dry whipped fat-containing mixture is associated with the melting point of E471 (65...67 °C), in particular with the increase in the amount of surfactants in the dispersion medium.

Increasing the number of revolutions of the working body of the agitation mechanism from 5 s^{-1} to 25 s^{-1} provides for an increase in the foam capacity from 201±8 % to 825±33 %. Based on the received data, it may be stated that the rational rotation frequency of the working body during whipping is 17...19 s^{-1}. An increase in the rotation frequency above the specified one does not provide for a marked increase in foam. The obtained data are within the error of measurement. With the increasing rotation frequency, foaming capacity increases, due to the destabilization of a fatty phase. The magnitude of rotation frequency of the agitation mechanism defines such processes as the destabilization of fatty particles, an increase in the surface area of the water-air interface for adhesion.

We determined the rational duration of whipping a recovered fat-containing mixture, which is (3...5)·60 s (Fig. 6).

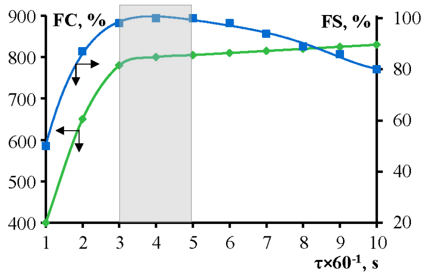

Fig. 6. Dependence of foaming capacity (FC) (♦) and foaming stability (FS) (■) on the duration of whipping a recovered fat-containing mixture (dark color designates the rational zone)

It was found that the temperature of whipped emulsions in 5×60 s of whipping reduced from 65...70 °C to 20...25 °C. This is predetermined by the intensive process of cooling during whipping through both stirring and dispersing a large volume of air in the system.

Increasing the duration above 5×60 s is ineffective, since the foaming capacity does not actually change at the simultaneous decrease in the stability of foam. This is probably due to the mechanical destruction of the gel of kappa-carrageenan. At the decrease in temperature, there is the formation of solid fatty particles, which is confirmed by the electron microscopy of whipped emulsions. It has a positive effect on the stability of foam due to the adhesion and agglomeration of fatty particles on air bubbles.

Electron microscopy data confirm the adhesion of fatty particles on air bubbles. There is a reduction in the mean diameter of the predominant fraction of fatty particles from (23±2)×10^{-6} m to (4.5±0.2)×10^{-6} m during whipping of the systems (Fig. 7).

Based on the initial data on foaming ability, we calculated mean diameters of air bubbles (50±1.5)×10^{-6} m, fatty particles (4.5±0.2)×10^{-6} m. The average number of fatty particles is 1.68×10^{18}, air bubbles (6.40×10^{15} pcs./kg. In the calculations, the mean diameter of channels between the air bubbles was 12.0 µm. Based on the given data, we calculated the mean total areas of fatty particles and air bubbles – 2.67×10^{7} and 5.04×107 m^2. An analysis of the obtained data demonstrates that the average total area of air bubbles is 1.9 times larger than the total area that can be covered with the fatty particles. Based on the obtained data, it can be argued that at partial coverage of air bubbles with fatty particles and the formation of adsorbed interfacial layers with a high boundary shear stress, it is possible to achieve a technological stability of whipped emulsions. Conducted theoretical and experimental studies confirm functionality of the model for obtaining technologically stable whipped emulsions through the Pickering-steric stabilization.

It was established that the foaming capacity of the developed dry fat-containing mixture exceeds that of products-analogues, available in the Ukrainian market. The developed product is characterized by higher indicators of foaming capacity – 1.7...2.0 times higher at identical indicators of foam stability and yield shear stress of a whipped emulsion (Table 2).

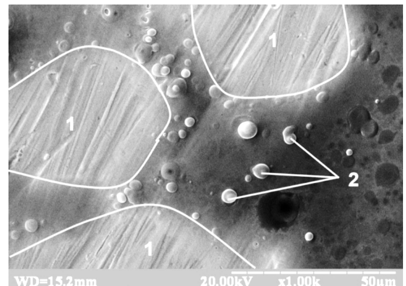

Fig. 7. SEM image of the structure of a whipped emulsion received based on the recovered fat-containing mixture (magnification ×1000): 1 — air bubbles; 2 — fatty particles

Table 2

Physical-chemical indicators of the recovered and whipped fat-containing mixture and products-analogues available in the Ukrainian market

Name of a dry mixture, manufacturer, country	Indicator title		
	Foaming capacity, %	Foam stability, %	Yield shear stress, Pa
The developed product "Dry whip mixture "Air mix" TU U 10.7- 01566330-297:2014	795±30	99±1	1190±30
Dry mixture "Whipped cream", Dr. Oetker, Germany	450±5	99±1	1200±30
Dry mixture for cooking whipped cream-like mass, Cykoria S. A., Poland	400±4	99±1	1100±30
Whipping semi-finished product "Dry Whip Mokaero 10", Mokate ingredients, Poland	400±4	99±1	1000±30

Therefore, the technology we developed for obtaining a dry fat-containing mixture by mixing the fatty phase with powder-like filler is energy-efficient, which does not imply the creation of an emulsion with its subsequent drying. Comparison of the quality of the new product to the products-analogues represented in the Ukrainian market allows us to assert that the new product is characterized by higher foaming ability.

7. Conclusions

1. We developed a theoretical model for providing a technologically stable whipped emulsions with a low content of fat phase through the Pickering-steric stabilization. Underlying the provision of technological stability are the processes of foaming, destabilization of a fatty phase, adhesion of fatty particles on air bubbles. As well as the formation of adsorbed interfacial layers with a high yield shear stress due to the complex formation of sodium caseinate and kappa-carrageenan.

2. We defined the patterns of the provision of technological stability of whipped emulsions. In particular, the introduction of surface-active substances E471 3.0 % and E322 0.08...0.1 % into whipped emulsions based on sodium caseinate 0.5 % and sunflower oil 5.0...7.0 % makes it possible to achieve the full degree of destabilization of

fatty particles. Destabilized fatty particles are capable of adhesion on the surface of air bubbles. This provides the Pickering stabilization. Additional introduction in the whipped emulsions of kappa-carrageenan in the amount of 0.5...1.0 % ensures increasing the yield shear stress of the adsorbed interfacial layers due to the complex formation. This provides the steric stabilization.

3. Parameters of receiving a dry fat-containing mixture are substantiated. It is necessary to mix sunflower oil with E471, E322 with a powder-like filler that contains white sugar, sodium caseinate and kappa-carrageenan, instead of spraying a fat mixture. The need for mixing is caused by the formation of contact between fatty particles with hydrophilic condensed surface, which is white sugar, by the principle of quasi-emulsification.

4. It is proven that the dry fat-containing mixture we obtained is characterized by a higher foaming ability, which is 1.7...2.0 times higher than that of the products-analogs. A technology of obtaining the dry fat-containing mixture by the principle of quasi-emulsification relates to the energy efficient one because of the absence of such operations as the formation of an emulsion and its drying.

References

1. Liang, Y. Interaction forces between colloidal particles in liquid: Theory and experiment [Text] / Y. Liang, N. Hilal, P. Langston, V. Starov // Advances in Colloid and Interface Science. – 2007. – Vol. 134-135. – P. 151–166. doi: 10.1016/j.cis.2007.04.003
2. Tadros, T. Viscoelastic properties of sterically stabilised emulsions and their stability [Text] / T. Tadros // Advances in Colloid and Interface Science. – 2015. – Vol. 222. – P. 692–708. doi: 10.1016/j.cis.2015.03.001
3. Day, L. Tailoring the digestion of structured emulsions using mixed monoglyceride-caseinate interfaces [Text] / L. Day, M. Golding, M. Xu, J. Keogh, P. Clifton, T. J. Wooster // Food Hydrocolloids. – 2014. – Vol. 36. – P. 151–161. doi: 10.1016/j.foodhyd.2013.09.019
4. Wierenga, P. A. Reconsidering the importance of interfacial properties in foam stability [Text] / P. A. Wierenga, L. van Norel, E. S. Basheva // Colloids and Surfaces A: Physicochemical and Engineering Aspects. – 2009. – Vol. 344, Issue 1-3. – P. 72–78. doi: 10.1016/j.colsurfa.2009.02.012
5. Jin, H. Super stable foams stabilized by colloidal ethyl cellulose particles [Text] / H. Jin, W. Zhou, J. Cao, S. D. Stoyanov, T. B. J. Blijdenstein, P. W. N. de Groot et. al. // Soft Matter. – 2012. – Vol. 8, Issue 7. – P. 2194–2205. doi: 10.1039/c1sm06518a
6. Ettelaie, R. Effect of particle adsorption rates on the disproportionation process in pickering stabilised bubbles [Text] / R. Ettelaie, B. Murray // The Journal of Chemical Physics. – 2014. – Vol. 140, Issue 20. – P. 204713. doi: 10.1063/1.4878501
7. Miller, R. Composite interfacial layers containing micro-size and nano-size particles [Text] / R. Miller, V. B. Fainerman, V. I. Kovalchuk, D. O. Grigoriev, M. E. Leser, M. Michel // Advances in Colloid and Interface Science. – 2006. – Vol. 128-130. – P. 17–26. doi: 10.1016/j.cis.2006.11.004
8. Deshmukh, O. S. Hard and soft colloids at fluid interfaces: Adsorption, interactions, assembly & rheology [Text] / O. S. Deshmukh, D. van den Ende, M. C. Stuart, F. Mugele, M. H. G. Duits // Advances in Colloid and Interface Science. – 2015. – Vol. 222. – P. 215–227. doi: 10.1016/j.cis.2014.09.003
9. Ergun, R. Kinetic effects on interfacial partitioning of fat crystals [Text] / R. Ergun, R. W. Hartel, P. T. Spicer // Food Structure. – 2015. – Vol. 5. – P. 1–9. doi: 10.1016/j.foostr.2015.02.001
10. Rousseau, D. Trends in structuring edible emulsions with Pickering fat crystals [Text] / D. Rousseau // Current Opinion in Colloid & Interface Science. – 2013. – Vol. 18, Issue 4. – P. 283–291. doi: 10.1016/j.cocis.2013.04.009
11. Goralchuk, A. Developing a model of the foam emulsion system and on firming the role of the yield stress shear of interfacial adsorption layers to provide its formation and stability [Text] / A. Goralchuk, S. Omel’chenko, O. Kotlyar, O. Grinchenko, V. Mikhaylov // Eastern-European Journal of Enterprise Technologies. – 2016. – Vol. 3, Issue 11 (81). – P. 11–19. doi: 10.15587/1729-4061.2016.69384
12. Murray, B. S. Stabilization of foams and emulsions by mixtures of surface active food-grade particles and proteins [Text] / B. S. Murray, K. Durga, A. Yusoff, S. D. Stoyanov // Food Hydrocolloids. – 2011. – Vol. 25, Issue 4. – P. 627–638. doi: 10.1016/j.foodhyd.2010.07.025
13. Munk, M. B. Stability of whippable oil-in-water emulsions: Effect of monoglycerides on crystallization of palm kernel oil [Text] / M. B. Munk, A. G. Marangoni, H. K. Ludvigsen, V. Norn, J. C. Knudsen, J. Risbo et. al. // Food Research International. – 2013. – Vol. 54, Issue 2. – P. 1738–1745. doi: 10.1016/j.foodres.2013.09.001
14. Kotlyar, O. Influence of formulation ingredients of dry fat semi-finished products for whipping on mechanical strength of foam masses [Text] / O. Kotlyar, A. Goralchuk, O. Grinchenko // Eastern-European Journal of Enterprise Technologies. – 2014. – Vol. 3, Issue 10 (69). – P. 45–49. doi: 10.15587/1729-4061.2014.24662
15. Kotlyar, O. The Study of Surface-Active Agents’ Impact on the Strength of Interfacial Adsorption Layers [Text] / O. Kotlyar, A. Goralchuk, O. Grinchenko // The Advanced Science Journal. – 2014. – Vol. 2014, Issue 10. – P. 37–42. doi: 10.15550/asj.2014.10.037
16. Kotlyar, O. Discourse of the form and concentration of surfactants to ensure the sustainability foam-emulsive products [Text] / O. Kotlyar, A. Goralchuk, O. Grinchenko // Ukrainian Food Journal. – 2014. – Vol. 3, Issue 3. – P. 361–371.
17. Bonn, D. Wetting and spreading [Text] / D. Bonn, J. Eggers, J. Indekeu, J. Meunier, E. Rolley // Reviews of Modern Physics. – 2009. – Vol. 81, Issue 2. – P. 739–805. doi: 10.1103/revmodphys.81.739
18. Maklakova, A. A. Vzaymodeystvye zhelatyni s -karrahynanom po dannim YK-spektroskopyy [Text] / A. A. Maklakova, N. H. Voron’ko, S. R. Derkach, H. Y. Kadirova, K. V. Zotova // Vestnyk MHTU. – 2014. – Vol. 17, Issue 1. – P. 53–60.
19. Kotlyar, O. Obgruntuvannya tekhnolohichnykh parametriv vyrobnytstva sukhoho zhyrovoho napivfabrykatu dlya pinopodibnoyi desertnoyi produktsiyi [Text] / O. Kotlyar, A. Goralchuk, O. Grinchenko // Prodovol’cha industriya APK. – 2014. – Issue 5. – P. 22–24.