*Досліджено технологічні властивості шроту кедрового горіху (ШКГ) та шроту волоського горіху (ШВГ). Встановлено, що горіхові шроти є високодисперсними порошками з більшим ступенем дисперсності ніж борошно пшеничне. Розмір до 40 мкм мають 69 % часток ШКГ, 72 % ШВГ і лише 35 % борошна.*

*У порівнянні з борошном пшеничним за впливу температур 20...60 °С горіхові шроти характеризуються кращою водоутримувальною здатністю. За впливу температури 90 °С шроти та борошно мають близькі значення водоутримувальної здатності. Відмічено, що горіхові шроти краще емульгують рідку олію, ніж тверді жири, що традиційно використовуються в технології здобного печива (маргарин та вершкове масло). Показано, що шротам притаманна висока жироутримувальна здатність (ЖУЗ) по відношенню до рідкої рослинної олії. Відмічено, що значення ЖУЗ для горіхових шротів в інтервалі температур 20...60 °С підвищується в 1,9 рази, в інтервалі 60...80 °С ЖУЗ дослідних зразків майже не змінюється, а за впливу температур 100...140 °С починає зменшуватися.*

*Досліджено якість емульсій для здобного печива у разі заміни 30 % маргарину на рідку рослинну олію з додаванням різної кількості горіхових шротів. Встановлено, що стійкість емульсії з заміною 30 % маргарину рідкою рослинною олією на 37,5 % менше порівняно з контролем на маргариновій основі. Внесення ШКГ та ШВГ сприяє покращенню стабільності такої емульсії. Відмічено, що зразки емульсії з додаванням 40 % та 50 % ШКГ та ШВГ за значенням показнику стабільності максимально наближені до контрольного, жировою основою для якого був маргарин. Це підтверджено результатами дослідження дисперсності, ефективної в'язкості емульсій та результатами мікроскопіювання.*

*Отримані результати мають практичне значення для удосконалення технології здобного печива в напрямку часткової заміни маргарину рідкими оліями. Це дозволить покращити харчову та біологічну цінність здобного печива*

*Ключові слова: шрот, волоський горіх, кедровий горіх, водоутримувальна здатність, жироутримувальна здатність, жироемульгувальна здатність, здобне печиво*

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# ESTIMATION OF TECHNOLOGICAL PROPERTIES OF NUT MEALS AND THEIR EFFECT ON THE QUALITY OF EMULSION FOR BUTTER BISCUITS WITH LIQUID OILS

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## 1. Introduction

A significant segment of the global confectionery market accounts for flour-based products. Specifically, according to statistical data for 2013–2017, the sales of bakery and pastry products in the world grew by 3.9 % [1]. The largest specific weight in the production of the specified products (about 45 %) belongs to cookies [2], including butter biscuits. However, the peculiarity of the chemical composition of butter biscuits is low content of vital nutrients (protein, dietary fiber, vitamins, minerals, etc.). It is predetermined by the fact that mostly refined raw materials are used in its technologies (modified fats, sugar, wheat flour of the highest grade, etc.).

One of the main raw components of butter biscuits (up to 35 %) is fats – butter, solid natural vegetable oils (palm, coconut, etc.), modified hardened vegetable oils (margarine, pastry and culinary fats, spreads, etc.). Fatty raw material should be solid in consistency. Such fats are characterized by plasticity and the capability to crystallize to the finely-crystalline form. It is the fat crystals that are largely responsible for stabilizing the structure of a whipped emulsion [3]. Specifically, fat crystals are kept on air bubbles during emulsifying by capillary forces [4, 5]. This provides for the formation of porous and loose structure of finished products and their respective quality [6].

The use of butter in the technology of butter biscuits is restricted due to its high cost and low microbiological stability. When making the specified products, the advantage is given to hardened vegetable oils that acquired solid consistency as a result of certain modifications – hydrogenation, transesterification, etc. However, these fats are characterized by low biological value, by the high content of saturated fatty acids (FA) and the presence of trans-isomers of FA that can adversely affect the human body [7, 8].

Given this, it is a relevant task to search for possibilities to completely or partially replace the hydrogenated and re-esterified fats in the technologies of butter biscuits with more biologically valuable (due to the presence of significant amounts of polyunsaturated fatty acids, fat soluble vitamins, the absence of trans-isomers of FA) and cheap liquid vegetable oils. However, the use of liquid vegetable oils in the technology of butter biscuits is limited due to the emergence of certain technological problems.

First, fats in the technologies of butter biscuits must be applied in the form of finely-dispersed emulsions. That contributes to better distribution of fat particles in the form of thin films among flour particles, which prevents the swelling of flour colloids. As a result, the bond between components of the solid phase of dough is weakened, the dough acquires plastic properties. The smaller the thickness of the fat films, the looser the structure of ready biscuits [9]. Liquid oils are bad at emulsifying, which is why emulsions on their base, when compared with emulsions on solid fats, are characterized by lower stability. That predetermines the deterioration of quality of the baked biscuits. Second, liquid oils are easily separated from dough during baking and poor at keeping the bubbles of gas, released during the disintegration of looseners. The result is the reduced porosity and worsened organoleptic properties of finished products. Third, they are poorly retained by biscuits during storage. As a result, there is the migration of fat to packing materials with the deterioration of physical appearance and taste characteristics of products [9].

In order to ensure the required structural-mechanical properties of dough and the high quality indicators of finished biscuits when using liquid oils, an additional application of stabilizing additives is required, which should simultaneously possess high fat-emulsifying, fat-retention, and water-retaining properties [9]. Such supplements make use of macromolecular compounds (proteins, starches, gums, dietary fiber, etc.) or natural raw materials, which contain the specified substances. In this regard, it is a relevant task to undertake a research aimed at finding the natural raw ingredients which would exert a stabilizing influence on emulsions for biscuits with liquid oils.

## 2. Literature review and problem statement

In order to stabilize the emulsion systems for biscuits on liquid oils, it is promising to use supplements of plant origin. Their advantage is the presence in their composition of a set of nutrients, useful for human organism (vitamins, minerals, phenolic compounds, etc.), in the most accessible and digestible form.

It was proposed to replace 13.5 % of margarine in the technology of sugar biscuits with pumpkin oil, or 20 % – with sea buckthorn oil [10]. The stabilizing supplement that was used in the technology of biscuits with pumpkin oil was the powder made from dried apples (6.3 % of the mass of finished biscuits), from leaves of raspberry (1.2 %) and from leaves of Calendula officinalis (0.3 %). When making biscuits with sea buckthorn oil, authors propose to additionally introduce powder made from dried apricots (4.9 %) and lungwort (0.3 %). The use of pumpkin and sea buckthorn oils can improve the content of polyunsaturated fatty acids in biscuits (by 2.5 and 3.3 times, respectively), while the introduction of plant powders made from fruit and medicinal raw materials can enrich products with pectin substances, food fibers, mineral substances, and vitamins.

Introducing sea buckthorn meal in the amount of 7 % by weight of flour makes it possible to replace 20 % of fat in the technology of shortcrust biscuits with flax oil [11]. In this case, the authors noted not only the enrichment of biscuits with useful nutrients, but also the improvement of organoleptic and structural-mechanical properties of products – color becomes golden, friability increases, improving the ability of biscuits to soaking, its density reduces.

Paper [12] proposed a complete replacement of margarine in shortcrust biscuits with deodorized refined sunflower oil. However, a given technology implies significant changes to formulation composition – wheat flour is completely replaced with corn flour, which is characterized by high fat-retention properties [13]. In addition, formulation components with high moisture content (condensed milk with sugar, whole eggs, honey) are replaced with dry powdered ingredients (dried fat-free milk, egg powder, glucose). In addition, the formulation is supplemented (1 % by weight of flour) with the citrus food fibers Herbacel AQ Plus – the type N [14]. The technological process becomes more complicated – the dough is made by brewing in hot water (90...100 °C) a mixture of dry formulation components with sunflower oil followed by the introduction of chemical looseners and flavorings. The advantage of the specified technology is obtaining a product for gluten-free diet. However, when compared with the sample based on margarine, in the process of storing there is a slight migration of fat to packing materials.

Paper [15] reported a technology of shortcake butter biscuits with the replacement of 29 % of margarine with a liquid oil with the addition of a 2.1-% mixture (by the weight of oil) of natural plant additives with a stabilizing action (xanthan and guar gum, wheat fiber, and soy protein isolate ). The biscuits, made in line with a given technology, are characterized by the stability of quality indicators in the process of storage – the degree of fat migration to packing materials is almost the same as in the control sample.

The authors of [16] examined a possibility to replace 60 % of a fat component in the technology of shortcake dough with corn oil. Such a high concentration of liquid oil becomes possible owing to two factors. The stabilizer used was the Althea root powder (2.3 % by weight of flour). There is also an additional operation to pretreat corn oil in a specialized unit in a vortex layer of ferromagnetic particles.

Thus, the stabilization of emulsion systems for biscuits with the addition of liquid oils is achieved both by the use of substances-stabilizers and by applying non-traditional technological techniques. However, the latter technique implies changing the hardware implementation of the technology, which is economically impractical. More promising is to use additional natural raw materials, which includes stabilizing substances and biologically active components useful for human body.

Stabilizing effect on the emulsion systems is exerted by protein substances, soluble (specifically, pectin) and insoluble (for instance, cellulose) food fibers, phospholipids, lecithin, and others. That is, it can be assumed that the raw materials containing these compounds would have a positive impact on the properties of emulsions for butter biscuits and, as a consequence, the structural and mechanical properties of the finished product.

It is recommended that the biscuit formulations should be supplemented with components that contain the following substances. Specifically, it is proposed to use cryopowders made from grape pomace (5 % by weight of flour) [17] and a powder from grape seeds (15 % by weight of flour) [18]. There are suggestions to use apple pectin (8 % by weight of flour) [19] or fiber from pumpkin seeds with pineapple (20 % by weight of flour) [20]. A possibility was considered to introduce pumpkin puree (25 % by weight of sugar), Jerusalem artichoke powder (6 % by weight of dry matter in the finished product) [21], microbial polysaccharides [22].

This contributes to improving the structure and consistency of finished products, which could be a prerequisite for the development of biscuit technology with their use by replacing part of the fat component with a liquid oil.

A significant number of substances with high functional and technological properties are included in products from nut processing, namely cedar nut meal (CNM) and walnut meal (WNM). Specifically, these products are characterized by the high content of high-molecular compounds [23, 24], Table 1.

Table 1

Content of biopolymers in CNM and WNM

| Substance | Content, % | |
|---|---|---|
| | CNM | WNM |
| Proteins: | 38.59 | 33.63 |
| Including Albumins | 2.86 | 1.17 |
| Globulins | 10.91 | 2.74 |
| Prolamins | 8.27 | 4.78 |
| Glutenin | 16.55 | 24.94 |
| Starch: | 15.84 | 15.45 |
| Including amylose | 11.76 | 1.03 |
| Amylopectin | 4.08 | 14.42 |
| Food fiber | 18.79 | 10.99 |
| Including hemicellulose | 12.65 | 5.16 |
| Cellulose | 0.90 | 1.85 |
| Lignin | 0.04 | 0.025 |
| Pectin substances | 5.2 | 3.95 |

In addition, nut meals are characterized by the high content of physiologically beneficial nutrients – polyunsaturated fatty acids, minerals (iron, silicon, potassium, manganese, copper, zinc, etc.) and some phenolic compounds [22]. This will promote the improvement of biological value of food products that use them.

Features in the chemical composition of nut processing products predetermine their manifestation of excellent stabilizing properties in emulsion systems – in the technologies of ice cream [25], sauces and mayonnaises [26], cottage cheese products [27], and meat semi-finished foods [28].

An analysis of information sources for the last 10 years reveals that no study into a possibility to stabilize emulsion systems for biscuits with liquid oils using nut meals has been undertaken. There is an unresolved issue related to examining the functional and technological (water-retaining, fat-retention, and fat-emulsifying) properties of walnut and cedar nut meals. There is the lack of systemic realization of the effect of nut meals on the quality of emulsions for butter biscuits with the addition of liquid oils. The above is a prerequisite for conducting the research in this field.

## 3. The aim and objectives of the study

The aim of this study is to estimate the technological properties of nut meals (CNM and WNM) and the prospects of their use in order to stabilize the emulsion for butter biscuits with the addition of liquid oils.

To accomplish the aim, the following tasks have been set:

– to examine the functional and technological properties of CNM and WNM (dispersity, water-retaining, fat-retention, and fat-emulsifying capacities);

– to explore CNM and WNM in terms of properties of the emulsion for biscuits with liquid oils (dispersity, stability, viscosity).

## 4. Materials and methods to study the functional and technological properties of nut meals and the quality of emulsion for butter biscuits with liquid oils

The examined materials used in the study included wheat flour of highest grade; CNM and WNM (made by PP "NVF "Elite phyto") and samples of emulsions for butter biscuits. Controls were the samples of emulsions on margarine (formulation No. 160, "Formulations for biscuits and waffles") (control No. 1) and with the replacement of 30 % of margarine with a liquid oil (control No. 2). The examined ones were the emulsions for butter biscuits with the replacement of 30 % of margarine with a liquid oil and with the addition of CNM or WNM (20, 40, 50 % by weight of emulsion). The liquid oil used was sunflower refined deodorized oil.

The granulometric composition of flour and nut meals was determined by microscopy at magnification ×120 times.

The water-retaining capacity (WRC) of samples was determined by centrifuging the sample suspension with water (1:5) at the ratio of difference between the amount of water used and the weight of the resulting centrifugate to the mass of the batch [29]. The fat-retention capacity (FRC) was estimated by the amount of fat that was retained by the sample following the infusion and centrifugation [29]. The fat-emulsifying capacity (FEC) was determined based on the ratio of the volume of the emulsified layer to the overall volume of the system following the centrifugation for 5 min at a speed of 2,000 rpm [29].

Dispersion of the emulsions was determined at magnification ×400 times at the microscope Bresser Biolux FA 50x-2000x based on the distribution of fatty balls (%) by size. Stability of the emulsions was determined in line with [30], effective (dynamic) viscosity of the emulsions – by applying the rotational viscosimeter Brookfield DV-II+PRO under autonomous mode over the range of spindle rotation speed 0.3...100 rpm.

Statistical processing of results from the experimental study was carried out using the standard software package Microsoft Office for a series of parallel measurements ($n$=4–5, $p$<0.05).

## 5. Results of studying the functionally-technological properties of nut meals and their impact on the quality of emulsion for butter biscuits with liquid oils

### 5. 1. Results of studying the functional and technological properties of nut meals

Functional and technological properties of powder-like raw materials largely depend on the degree of their shredding [31]. Therefore, we considered it proper to estimate the grain composition of CNM and WNM compared with wheat flour of the highest grade (Table 2).

Table 2

Granulometric composition of CNM and WNM compared with wheat flour of the highest grade ($n$=4, $p$=0.04)

| Sample | Granulometric composition of additives (%), μm | | | | | |
|---|---|---|---|---|---|---|
| | 10…20 | 20…40 | 40…60 | 60…80 | 80…100 | 100…160 |
| Flour | 5 | 30 | 43 | 10 | 8 | 4 |
| CNM | 14 | 55 | 14 | 10 | 7 | – |
| WNM | 12 | 60 | 15 | 8 | 5 | – |

Experimental data indicate that the examined supplements represent highly-disperse powders with close granulometric composition. Thus, the size of 69 % of CNM is up to 40 μm, 72 % of WNM, and only 35 % of flour. The maximum size of CNM and WNM particles does not exceed 100 μm, whereas wheat flour contains particles the size of up to 160 μm.

The main functional-technological properties that make it possible to estimate the influence of additives on the structural-mechanical properties of emulsions for butter biscuits are water-retaining, fat-retention, and fat-emulsifying capacities.

The water-retaining capacity (WRC) characterizes the hydrophilic properties of additives and reflects the intensity of intramolecular interaction between water and the surface of their particles. WRC depends on the type of polymers, which are part of the additives, size, density, their particles' surface condition. Given the fact that the main water-retaining component in the formulation of butter biscuits is flour, we estimated the WRC of supplements compared with wheat flour of the highest grade. We investigated WRC of the samples under conditions of exposure to different temperatures (20 to 90 °C), which is predetermined by the presence of a baking stage in the technology of biscuits. Average values for measurement results are shown in Fig. 1, relative error did not exceed 3.2 % (for $n$=4).

It was established in the course of experimental research that the examined supplements, when compared with wheat flour of the highest grade, are characterized by higher water-retaining properties. Specifically, at a temperature of 20 °C, CNM exceeds flour in terms of WRC by 3.2 times, and WNM – by 3.9 times. In the case of increasing the temperature to 90 °C, a better pronounced tendency towards an increase in the value for WRC is observed in wheat flour – by 5.6 times, whereas for CNM this increase is 1.6 times, and for WNM – 1.4 times. It is noted that for WNM the dependence of WRC on temperature is nonlinear in character and slightly decreases in the temperature range 45…60 °C.

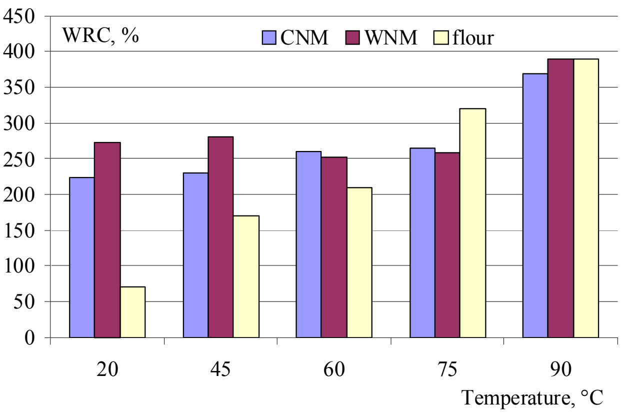



Fig. 1. Water-retaining capacity of nut meals under different temperature

The fat-emulsifying capacity of the examined supplements was estimated based on the ratio to different types of fats: a liquid oil, margarine, and butter. Average data on research results are shown in Fig. 2, relative error of measurements did not exceed 3.5 % (for $n$=5).

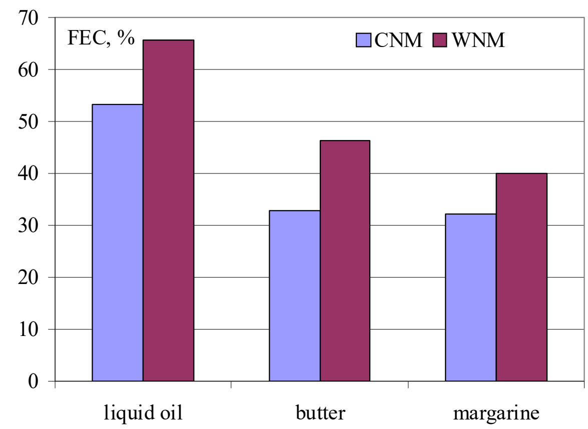



Fig. 2. Fat-emulsifying capacity of CNM and WNM relative to various fats

It was established that CNM demonstrates almost the same fat-emulsifying properties in relation to butter and margarine – FEC is 32.7 and 32.1 %, respectively. For WNM, the capacity to emulsify butter is 16.1 % better than the capacity to emulsify margarine. FEC of the examined samples relative to liquid oil is much higher than that in relation to butter and margarine – for CNM, by 62.7 and 65.7 %, respectively; for WNM – 42.0 and 64.8 %. it is noted that WNM is 23.3 % better at emulsifying liquid oil than CNM.

Fat-retention capacity of the examined samples was assessed in relation to liquid oil in the temperature range from 20 to 140 °C. Average values for data obtained are shown in Fig. 3, relative error of measurements did not exceed 3.2 % (for $n$=4).

It was established that over the entire examined temperature range WNM shows better fat-retention properties than CNM. It was noted that the values of FRC for WNM and CNM in the temperature range from 20 to 60 °C grow by 1.9 times; in the range of 60…80 °C, FRC of the examined samples almost does not change, and under the influence of temperatures 100…140 °C it starts to decrease.

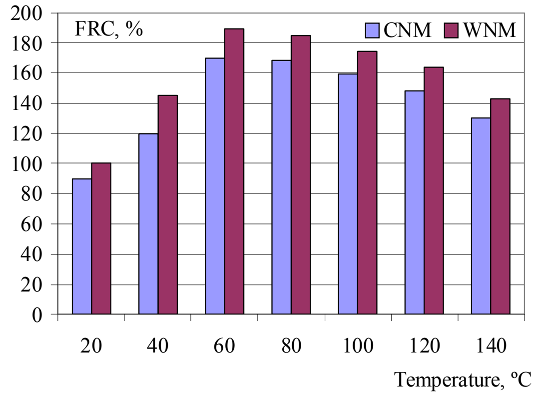



Fig. 3. Fat-retention capacity of nut meals under different temperature

**5. 2. Results of studying the influence of nut meals on the quality of emulsion for butter biscuits with liquid oils**

At the next stage, we investigated the stability of emulsions for butter biscuits in the case 30 % of margarine is replaced with a liquid oil with the addition of varying amounts of nut meals. Average data on results obtained are shown in Fig. 4, relative error of measurement did not exceed 3.0 % (for $n$=4).

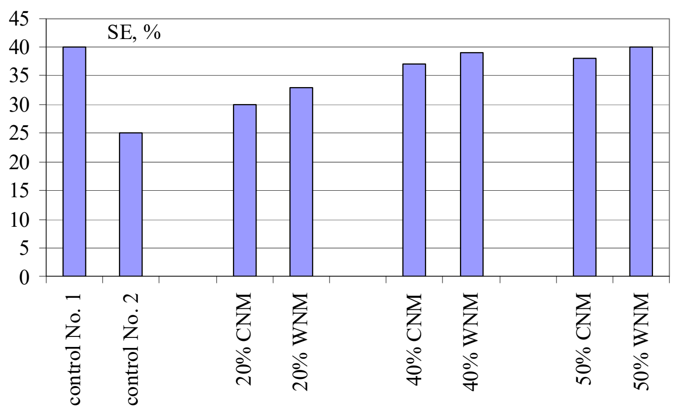



Fig. 4. Stability of the examined samples of emulsions

It was established that the stability of emulsions in which 30 % of margarine was replaced with liquid oil (control No. 2) is 37.5 % less in comparison with the control on a margarine base (control No. 1). Introducing 20 % of CNM and WNM contributes to improving the stability of such an emulsion by 20.0 and 32.0 %; adding 40 % of nut meals – by 48 and 56 %, and 50 % – by 52 and 60 %, respectively. It was noted that the samples of emulsion with the addition of 40 % and 50 % of CNM and WNM in terms of the value for the indicator of stability are maximally close to control sample whose fat base was margarine, which correlates with the results from studying the dispersity of emulsions (Table 3) and results from microscopy (Fig. 5, 6).

It is common knowledge that the stability of emulsion depends on its dispersity and homogeneity – the higher the proportion of fat droplets of smaller size, the higher the stability of emulsion against layering. The research results (Table 3) show that the replacement of 30 % of margarine with a liquid oil leads to an increasing number of large drops of oil in the emulsion. Specifically, in control sample No. 1, 45 % are fat balls the size of 4...6 μm, while 24 % are the size of 6...8 μm. In control sample No. 2, the number of balls the size of 4...6 μm is reduced to 28 %, while that of fat balls the size of 6...8 μm and larger than 8 μm increases to 35 and 24 %, respectively. It was noted that the introduction of 40 and 50 % of nut meals increases the amount of fat balls the size pf 2...4 μm, compared with control samples, by more than 4 times.

Table 3

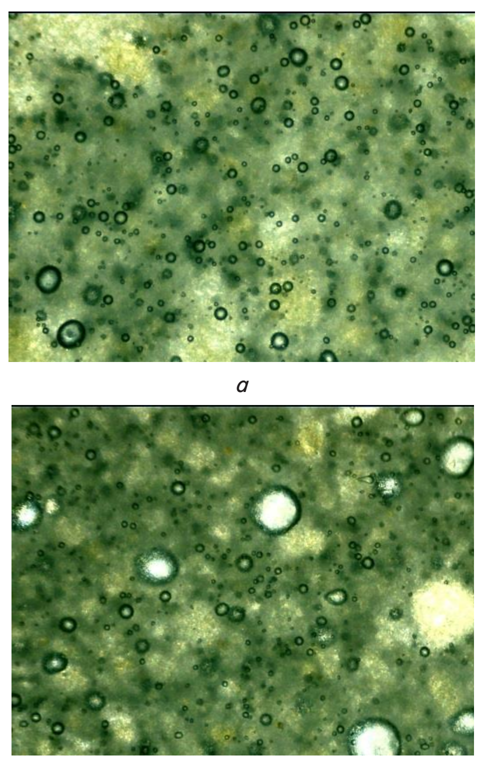
Dispersity of the examined samples of emulsions ($n$=4, $p$=0.03)

| Samples of emulsion | Distribution of fat balls (%) for size, μm | | | | |
|---|---|---|---|---|---|
| | to 2 | 2...4 | 4...6 | 6...8 | exceeding 8 |
| Control No. 1 (Fig. 5, *a*) | 3 | 10 | 45 | 24 | 18 |
| Control No. 2 (Fig. 5, *b*) | 2 | 11 | 28 | 35 | 24 |
| 20 % CNM | 13 | 30 | 26 | 18 | 13 |
| 20 % WNM | 15 | 34 | 24 | 16 | 11 |
| 40 % CNM (Fig. 6, *a*) | 19 | 40 | 23 | 14 | 4 |
| 40 % WNM (Fig. 6, *b*) | 20 | 42 | 20 | 12 | 6 |
| 50 % CNM | 21 | 41 | 23 | 11 | 4 |
| 50 % WNM | 22 | 43 | 21 | 9 | 5 |

The results from microscopy (Fig. 5, 6) reveal that the introduction of CNM and WNM ensures the uniformity of the distribution of small fat balls, which are almost of the same size, throughout the entire structure.

An important rheological characteristic of emulsions, which defines their technological properties, is effective viscosity that characterizes the degree of resistance to flow (Table 4).

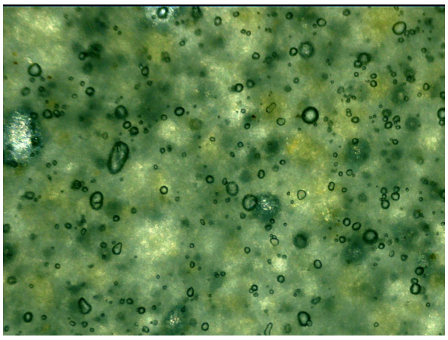
It was noted that for the case of introducing 50 % of nut meals the emulsion acquires high density. Technical possibilities of the instrument do not make it possible to obtain reliable data on the values for effective viscosity of such samples. Therefore, in this series of studies we assessed the samples of emulsions with a maximum dosage of nut meals, 40 %.



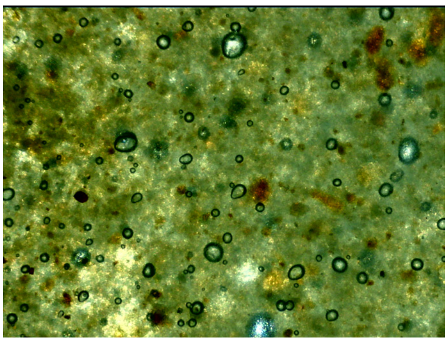
*a*

*b*

Fig. 5. Microstructure of control samples of emulsions (at magnification ×300): *a* – control No. 1; *b* – control No. 2



*a*



*b*

Fig. 6. Microstructure of emulsions with the addition of nut meals in the amount of 40 % (at magnification ×300): *a* — CNM; *b* — WNM

Graphical interpretation of the results obtained is shown in Fig. 7.

The shown curves for effective viscosity of the examined samples of emulsions take a typical form for non-Newtonian fluids [32]. These fluids are characterized by a decrease in the value for effective viscosity of the examined samples of emulsion at an increase in the rotation velocity of the measuring instrument's spindle.

The effective (dynamic) viscosity of examined samples is typically described by equation of the following form:

$$\eta = B\cdot\gamma^{-m}, \qquad (1)$$

where η is the effective viscosity, Pa·s, *B* is the coefficient of consistency, proportional to viscosity, Pa·s, γ is the shear rate, m is the rate of destruction of a structure.

The results from mathematical treatment of experimental data from Table 4 are given in Table 5.

The estimated values for coefficients of determination ($R^2$) indicate high reliability of analytical equations that describe the behavior of each of the examined samples.

It was established that the coefficient of consistency for the emulsion in which 30 % of margarine was replaced with a liquid oil (control No. 2), when compared with the margarine-based control (control No. 1), decreases by 4.6 times while the rate of the structure destruction increases by 2.1 times. When adding 20 % of CNM or WNM, this indicator increases by 1.6 and 2.4 times, respectively. An increase in the concentration of meals to 40 % leads to a growth in the consistency coefficient by 2.6 and 4.2 times, respectively. For the emulsion with a partial replacement of margarine with a liquid oil the rate of structure destruction is 0.97 units. When introducing CNM, regardless of its concentration, the value for this indicator decreases by 10 %. The introduction of WNM leads to a decrease in the rate of structure destruction by 30 %.

Table 4

Evaluation of effective viscosity of the examined samples of emulsions ($\eta\cdot10^{-3}$, Pa·s) ($n$=4, $p$=0.03)

| | Velocity, rev·min$^{-1}$ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0.5 | 1 | 2 | 2,5 | 4 | 5 | 10 | 20 | 50 | 60 | 100 |
| Control No. 1 | 1,090 | 850 | 750 | 610 | 550 | 450 | 380 | 250 | 180 | 140 | 90 |
| Control No. 2 | 355 | 215 | 175 | 100 | 45 | 31 | 15 | 8 | 5 | 4 | 3 |
| 20 % CNM | 394 | 348 | 221 | 183 | 117 | 91 | 35 | 17 | 10 | 9 | 7 |
| 20 % WNM | 630 | 556 | 354 | 293 | 187 | 146 | 55 | 29 | 17 | 15 | 10 |
| 40 % CNM | 400 | 399 | 367 | 322 | 261 | 231 | 139 | 72 | 31 | 26 | 18 |
| 40 % WNM | 720 | 700 | 660 | 580 | 470 | 415 | 250 | 130 | 56 | 46 | 31 |

Table 5

Coefficients for equation (1)

| Sample | *B*, Pa·s | *m* | $R^2$ |
|---|---|---|---|
| Control No. 1 | 0.92 | 0.45 | 0.98 |
| Control No. 2 | 0.20 | 0.97 | 0.97 |
| 20 % CNM | 0.32 | 0.87 | 0.98 |
| 20 % WNM | 0.51 | 0.86 | 0.98 |
| 40 % CNM | 0.49 | 0.67 | 0.93 |
| 40 % WNM | 0.85 | 0.66 | 0.93 |

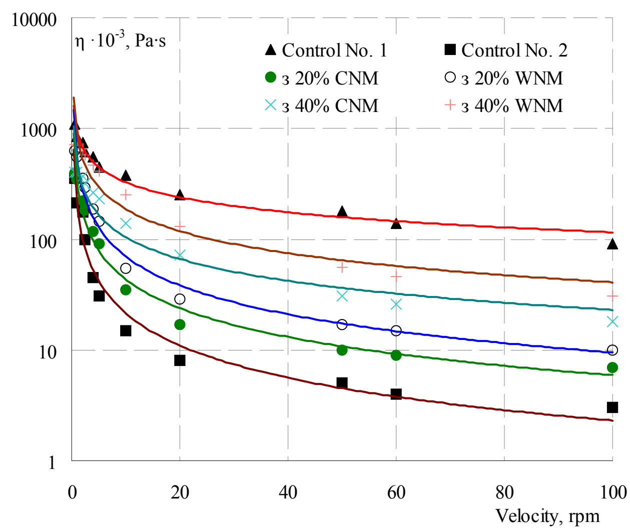



Fig. 7. Dependence of effective viscosity of the examined samples of emulsions on spindle rotation velocity of the measuring instrument

## 6. Discussion of results of studying the functional and technological properties of nut meals and their impact on the quality of emulsion for butter biscuits with liquid oils

Study into the water-retaining properties of the examined supplements (Fig. 1) has established that at 20 °C they are characterized by the higher value for WRC than that of wheat flour. This can be explained by the smaller size of particles in additives (Table 2) and the peculiarities of the protein-polysaccharide composition of the examined samples. Specifically, flour is represented to 70 % by starch, about 78 % of which are amylopectin. Compared with amylose, amylopectin is characterized by better hydrophilic properties due to the high susceptibility to hydrogen bond formation owing to the high molecular mass and branched structure. However, amylopectin is inside a starch grain and can go beyond it only after the destruction of the shell of the grain that occurs when a temperature is above 60 °C (for wheat starch), which explains a substantial increase in WRC of flour in the interval of temperature 60...90 °C. The higher hydrophilic properties of CNM and WNM at a temperature of 20 °C are predetermined by the presence in their composition of a significant amount of food fiber (18.79 and 10.99 %, respectively) and proteins (38.59 and 33.63 %) (Table 1). Even though the content of these biopolymers is higher in CNM, it is slightly inferior in WNM in terms of its capacity to retain water. This can be explained by the qualitative composition of hydrocolloids. Specifically, proteins in CNM contain a significant amount of albumin and globulin factions (their total content is 13.77 g/100 g of meal, and for WNM – 3.91 g/100 g of meal). In addition, even though the examined meals contain the same amount of starch (Table 1), the starch in CNM is represented by amylose (the ratio amylose:amylopectin is 11.76:4,08) while the starch in WNM – by amylopectin (the ratio amylose:amylopectin is 1.03:14,42). In addition, the examined supplements differ in the composition of food fiber – CNM contains a significant amount of water-soluble hemicellulose and pectins (12.65 and 5.2 % against 5.16 and 3.95 % in WNM). As a result, the soluble nutritional substances (albumins, globulins, amylose, hemicellulose, and pectin), when dissolving in a liquid, increase its relative viscosity and inhibit the swelling of insoluble polysaccharides, namely cellulose. It is known that cellulose contains a large number of hydroxyl groups and is characterized by a well-developed system of thin sub-microscopic capillaries, which predetermines its high water-retaining properties [33]. Given the fact that the content of cellulose in WNM is 2 times higher than that in CNM, it shows a higher water-retaining capacity.

At a temperature of 45 °C, there occurs the active swelling of food fiber and starch grains, which causes an increase in the WRC indicator in the examined samples. Since wheat flour contains considerably more starch than the examined additives, it is characterized by an intense increase in the values for a WAC indicator in a given temperature range. When heated to 60 and 75 °C, there occurs the denaturation of proteins the result being that the value of WRC for CNM almost does not change, while decreasing for WNM. This may be associated with a deeper denaturation of proteins in WNM. One can also assume that the starch grains of nut meals are smaller than the grains of wheat starch. As a result, they gelatinize at higher temperatures, consequently an indicator for WRC of meals increases only at a temperature of 90 °C.

Our study into the fat-emulsifying capacity of examined supplements (Fig. 2) has shown that they are better at emulsifying a liquid oil than solid fats that are traditionally used in the technology of butter biscuits (margarine and butter). This can be explained by the fact that margarine and butter are essentially the emulsions in which the emulsifiers are their own protein substances. The stabilizing effect of emulsifiers is predetermined by that their molecules contain the hydrophilic and hydrophobic functional groups that are appropriately oriented at the interphase boundary and reduce the surface tension. In this case, hydrophilic substances bind part of the disperse medium and form a protective solvate sheath around a fat drop. It can be assumed that in the case when the examined nut meals are introduced to the emulsion, the number of emulsifiers in the system significantly increases. As a result, the second layer of stabilizer's molecules forms at the surface of fat droplets, its functional groups are oriented in the opposite way. This fact causes a decrease in the stability of the system [34].

The high fat-retention capacity of nut meals (Fig. 3) is predetermined by their finely-disperse state, which ensures the high availability of hydrophobic groups. In addition, food fiber and protein substances in additives have a porous structure. This makes it possible to physically bind and retain free fat. An improvement in the supplements' FRC in the case of their warming at a temperature of 40 and 60 °C can be explained by the thermal denaturation of proteins. As a result, the conformation of its molecule changes with freeing the hydrophobic sections that were previously grouped within the molecule. A decrease in FRC for nut meals at heating from 100 to 140 °C can be predetermined by the destruction of protein molecules. One can also assume that this is accompanied by interactions between proteins and other components. Consequently, there is the formation of protein-carbohydrate and protein-lipid complexes, accompanied by a general decrease in the functional groups within a protein molecule.

The positive effect of nut meals on the stability (Fig. 4) and dispersity (Table 3, Fig. 5, 6) of emulsion for butter biscuits in which 30 % of margarine is replaced with a liquid oil is explained by their high water-retaining properties and good fat-retention and fat-emulsifying capacities in relation to liquid oils. In addition, it is known that highly-disperse powders can act as solid emulsifiers. In this case, the powder particles are wetted by different places at the surface by the respective phase of the emulsion, they concentrate at the boundary surface and protect fat drops from coalescence by the so-called armored shells [34].

Evaluation of viscous properties of the examined samples (Table 4, Fig. 7) has shown that the replacement of 30 % of margarine in the emulsion with a liquid oil leads to a significant decrease in its effective viscosity. The introduction of nut meals to such an emulsion causes an increase in a coefficient of consistency. A zone of the avalanche destruction of structure in the samples with meals at the same shear rate occurs at larger values for shear rate than in the sample with a liquid oil. The resulting effect can be explained by the presence in the composition of additives of food fiber, which correlates with the results by other researchers [35–37] It was noted that WNM, when compared with CNM, slows down the rate of structure destruction of the emulsion with a liquid oil to a larger degree. This confirms the results of earlier study into the stability of emulsions and it is explained by peculiarities in the composition of biopolymers in additives. Thus, the use of nut meals (CNM, WNM) improves the viscosity of emulsion for butter biscuits with liquid oils and makes it more resistant to destruction.

It is noted that an increase in the concentration of nut meals to 50 % led to that the values for effective viscosity exceeded the permissible measurement range. This indicates that due to the swelling of hydrocolloids in additional raw materials there occurred an excessive compaction of the emulsion. From the technological point of view, such a compaction will make it impossible to obtain the structure characteristic of butter biscuits. That is, one can recommend, in order to improve the properties of the emulsion for butter biscuits with liquid oils, that up to 40 % of the cedar nut or walnut meal should be introduced.

The results obtained suggest the feasibility of using up to 40 % of nut meals for improving the characteristics of emulsion for butter biscuits with liquid oils. However, the quality of butter biscuits depends largely on the quality of dough. That is, it is a promising task to further study the influence of nut meals on the characteristics of dough for butter biscuits with liquid oils and on the quality of baked products.

## 7. Conclusions

1. Our study into the functional and technological properties of nut meals has revealed the following. In terms of the size of particles, the examined meals are the highly-disperse powders with a greater degree of dispersity than wheat flour. The size of 69 % of CNM is up to 40 μm, 72 % of WNM, and only 35 % of flour. It was established that the supplements are characterized by high water-retaining and fat-retention capacity. It was noted that nut meals are better at emulsifying a liquid oil than solid fats that are traditionally used in the technology of butter biscuits (margarine and butter).

2. We have established the positive effect of nut meals on the quality of emulsion for butter biscuits with the replacement of 30 % of margarine with a liquid oil. It was noted that the samples of emulsion with the addition of 40 and 50 % of nut meals in terms of the value for an indicator of stability are maximally close to the margarine-based control sample. This fact correlates with the results from studying the dispersity, effective viscosity of emulsions, and the results from microscopy. It is noted that at an increase in the concentration of nut meals to 50 %, due to the swelling of hydrocolloids in additives, there is an excessive compaction of the emulsion. From the technological point of view, such a compaction will not make it possible to obtain the structure characteristic of butter biscuits.

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