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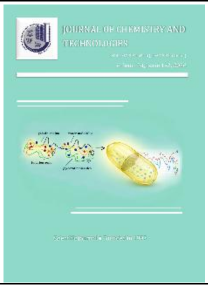

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STUDY OF THERMODYNAMIC INDICATORS OF THE MOISTURE STATE IN EXPERIMENTAL CUPCAKE FORMULATIONS WITH THE ADDITION OF NON-TRADITIONAL RAW MATERIALS USING THE THERMOGRAVIMETRIC ANALYSIS

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Abstract

The object of research was the technology of cupcake production using non-traditional raw materials. The study focused on investigating the forms of moisture binding in experimental cupcake samples in comparison with the control sample, the "Stolichny" cupcake. The experimental cupcake samples included buckwheat, oat, rye, and corn flours, powders of non-traditional plant raw materials, whey and skimmed milk powder, and beekeeping products, which replaced part of the wheat flour. The inclusion of these ingredients contributed to an increase in the content of vitamins, minerals, and essential amino acids in the experimental cupcake samples. Margarine was also partially replaced with vegetable oils (sesame, pumpkin seed, and walnut oil) to reduce the content of trans-isomers of fatty acids and increase the content of polyunsaturated fatty acids of the ω-3 and ω-6 families. At each stage of the production of experimental cupcake samples, an analysis of biological, chemical, and physical hazardous factors was carried out. A derivatographic study of experimental cupcake samples was carried out using the Q-1000 derivatograph device in the range from 25 to 220 °C. Based on the results of thermogravimetric analysis, it was established that the amount of free moisture in the control sample of the "Stolichnyi" cupcake accounted for 63.0 % of the total amount of moisture. In the experimental cupcake samples, a decrease in the proportion of free moisture was found: "Kunzhutnyi" cupcake – by 1.0, "Moryachok" – by 2.8, "Osinniy Aromat" – by 3.1, "Chornychnyi" – by 3.3, "Mitsnyi Horishok" – by 9.3, "Elitnyi" – by 15.9 and "Medok" – by 17.4 % compared to the control sample.
Keywords: confectionery; cupcakes; non-traditional raw materials; bound moisture; free moisture; thermogravimetric analysis; derivatograms; freshness.

ДОСЛІДЖЕННЯ ТЕРМОДИНАМІЧНИХ ПОКАЗНИКІВ СТАНУ ВОЛОГИ В ЕКПЕРИМЕНТАЛЬНИХ РЕЦЕПТУРАХ КЕКСІВ З ДОДАВАННЯМ НЕТРАДИЦІЙНОЇ СИРОВИНИ МЕТОДОМ ТЕРМОГРАВІМЕТРИЧНОГО АНАЛІЗУ

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Анотація

Об'єктом дослідження є технологія виробництва кексів із використанням нетрадиційної сировини. Дослідження базується на вивченні форм зв'язування вологи в експериментальних зразках кексів у порівнянні із контрольним зразком – кексом «Столичний». До складу експериментальних зразків кексів вносили гречане, вівсяне, житнє та кукурудзяне борошно, порошки нетрадиційної рослинної сировини, молочну сироватку та сухе знежирене молоко, продукти бджільництва, якими заміняли частину пшеничного борошна. Включення зазначених інгредієнтів сприяло підвищенню вмісту вітамінів, мінеральних речовин та незамінних амінокислот у складі експериментальних зразків кексів. Також частково замінювали маргарин на рослинні олії (кунжутну, гарбузового насіння, ядер волоського горіха), для зменшення вмісту транс-ізомерів

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жирних кислот та підвищення вмісту поліненасичених жирних кислот ω-3 та ω-6. На кожному етапі виробництва експериментальних зразків кексів проводився аналіз біологічних, хімічних та фізичних небезпечних факторів. Дериватографічне дослідження експериментальних зразків кексів проводили з використанням дериватографа Q-1000. Для отримання дериватограм з високою роздільною здатністю сигналу встановлені оптимальні параметри проведення аналізу: середня маса наважки – близько 240 мг, температурний інтервал від 25 до 220 °C, швидкість нагрівання зразків – 10 °C/ хв, чутливість дериватографа для кривої ТГ – 94.25 мг, ДТГ – 500 мкВ, ДТА – 250 мкВ, швидкість руху паперу – 2.5 мм/хв. Прилад одночасно записував декілька кривих: Т – зміну температури, ТГ – зміну маси, ДТГ – диференційну криву зміни маси, ДТА – диференційно-термічна крива. На підставі аналізу отриманих дериватограм було встановлено, що кількість вільної вологи в контрольному зразку кекса «Столичний» становить 63.0 % від загальної кількості вологи. В експериментальних зразках кексів встановлене зниження частки вільної вологи: кекс «Кунжутний» – 1.0, «Морячок» – 2.8, «Осінній аромат» – 3.1, «Чорничний» – 3.3, «Міцний горішок» – 9.3, «Елітний» – 15.9 та «Медок» – 17.4 % порівняно з контрольним зразком.

Ключові слова: кондитерські вироби; кекси; нетрадиційна сировина; зв'язана волога; вільна волога; термогравіметричний аналіз; дериватограми; свіжість.

Introduction

On the market, confectionery products are presented in a wide range of shapes, weights, and designs. They are characterized by a pleasant sweet taste and aroma, and by an elastic, finely porous crumb structure. The surface of many confectionery products is smooth and shiny. Some confectionery products are sprinkled with powdered sugar, crumbs, poppy seeds, seeds of various crops, crushed nuts, etc. to improve their appearance and increase competitiveness. Some representatives are characterized by a clear pattern on the surface in the form of squares, diamonds, or a pattern applied using a special stamp.

The recipe for confectionery products contains at least 14 % sugar and fat, which can also be used for decoration; therefore, these products are high-calorie.

The main disadvantages of flour confectionery products are their short shelf life and the rapid staling process, which is a consequence of complex biochemical processes that occur in the high-polymer substances of the crumb and lead to a deterioration in the structural and mechanical properties of the products. Given this, a pressing problem in the confectionery industry is extending the freshness and shelf life of flour confectionery products, in particular, cupcakes [1–3].

The development of food products with predetermined physicochemical and organoleptic properties is carried out on the basis of food combinatorics. The creation of food products with improved nutritional and biological value is currently an important direction in the development of food technologies. The design of specialized products is based on three fundamental principles:

1. Elimination - removal of undesirable or harmful nutrients from the formulation (for example, delactosation for people with hypolactasia).
2. Fortification (enrichment) – targeted introduction of missing or deficient micro- and macronutrients into the formulation of products to increase their biological value.
3. Substitution (replacement) – replacement of traditional components with functional analogues with higher biological value or specific properties [4–5].

The production of flour confectionery products (FCP) with an extended shelf life is one of the current tasks of the food industry and trade. An effective way to preserve the consumer properties of finished products is to use food additives of directed action [6]. The storage capacity of a product depends on the magnitude of the internal interaction forces between the components of the system. The presence of various forms of moisture binding with the dispersed phase of the product determines its total content in confectionery masses and the rate of biochemical, colloidal, and chemical processes. According to the form of binding with the surface of the solid phase, the following types of moisture can be distinguished: chemically bound, adsorption bound, osmotically bound, and mechanically bound [7].

To reduce the calorie content and prolong the freshness of flour confectionery products, it is recommended to include non-traditional plant raw materials, food additives, complex baking improvers, multicomponent mixtures, rice bran, sweet potato flour, rice, amaranth, millet, eggshell waste, etc. [8].

Currently, the production of products containing cereals is quite common. To avoid crumb stickiness when using sprouted cereal grains in the product formulation, rice bran is widely introduced into flour confectionery products [9].

Thanks to the use of carob powder and "Health" flour in the formulation of new products, which are produced from grains germinated in a sea salt solution containing a wide range of macro- and micronutrients, in particular organic iodine, they are characterized by an increased content of biologically active substances and improved structural properties, and extended shelf life [10–11].

Scientists have studied the consistency, structure, and moisture-holding capacity of rice, amaranth, millet, and spelt flours with a combination of tapioca or potato starch. The finished products were characterized by satisfactory organoleptic indicators, soft texture, uniform porosity, stable shape after baking, and extended shelf life [12–16].

Scientists have also analyzed the effect of spelt, hemp, and chickpea flour on the organoleptic and physicochemical parameters, as well as the shelf-life extension, of the developed biscuit semi-finished products [17–18].

Separate studies [19] also indicate positive results from the use of complex baking improvers, multicomponent mixtures, and food additives.

To prolong the freshness of bakery and flour confectionery products, the Dutch company "Zeelandia" offers a complex improver, "Gamma Soft", which includes soy flour, enzymes, emulsifiers, and ascorbic acid [20].

When using sprouted grains in the technology of confectionery products, the crumb darkens, so it is necessary to lighten it. The use of an improver containing soy flour will, unfortunately, contribute to an even greater darkening of the finished product [21].

When adding cinnamon at a level of 4 % of the flour mass, high consumer characteristics of the finished product are ensured; however, due to the pronounced aroma and taste of cinnamon, the number of consumers of this product may decrease. When adding 6% cinnamon to the recipe, a deterioration in the volume of the product and an increase in flavor intensity are observed. However, the effect of cinnamon on the structural and mechanical properties of the dough and the processes of staling has not been studied [22]. It has been established that the aroma compound of cinnamon, namely cinnamaldehyde, negatively affects the microflora of the dough [23].

As a result of the research, it was found that when pectin is added to the recipe of flour products, the macromolecular aggregation of gluten is enhanced and the rheological properties of the dough are improved, which leads to the formation of a dense gluten network. The presence of pectin in the recipe leads to a decrease in the content of α-helices but an increase in the β-sheet and β-turn structures of gluten. It has been established that pectin, having a moisture-retaining ability due to its high degree of methoxy groups, is an effective food additive for improving the consumer properties of bakery and flour confectionery products [24].

The introduction of pumpkin paste into the recipe of cupcake contributes to an increase in their organoleptic properties, improves the structural and mechanical properties of the dough, and extends the shelf life. Its optimal dosage is 25–30 % [25].

Flour confectionery products enriched with sweet potatoes have high nutritional value, a high content of dietary fiber, protein, and minerals, improved rheological properties, and extended shelf life [13; 26].

The range of multicomponent mixtures is very diverse, depending on the direction of their action. All components of multicomponent mixtures are carefully selected for their activity and synergistic effect on each other. Complex baking improvers and multicomponent mixtures act throughout the entire technological process; therefore, they are designed to improve organoleptic and physicochemical indicators, biological value, rheological properties, and to extend shelf life [27–32].

The aim of the work is to study the content of free and bound moisture in the crumb of experimental cupcake samples and to study the influence of recipe components on slowing down the processes of staling of finished products.

The objectives of the study were:

1. the development of recipes for experimental cupcakes using the method of mathematical modeling;
2. the conducting of an organoleptic evaluation of experimental cupcake samples;
3. the conducting of a comprehensive evaluation of experimental flour confectionery samples;
4. the conducting of a study of thermodynamic indicators of the moisture state in experimental cupcake recipes with the addition of non-traditional raw materials using thermogravimetric analysis.

Experimental

The object of the study is the technology of cupcake production using non-traditional raw materials. The subject of the study is cupcakes with non-traditional raw materials according to the author's recipes “Kunzhutnyi”, “Moryachok”, “Mitsnyi Horishok”, “Osinniy Aromat”, “Chornychnyi”, “Medok”, and “Elitnyy”, with the control sample for comparison being the cupcake "Stolichnyi".

The study of the organoleptic quality indicators of experimental cupcakes was carried out in accordance with the requirements of the regulatory documentation DSTU 4505:2005 [33] and using the five-point quality assessment scale developed by the authors.

The scoring system provides for the assessment of the quality of cupcakes according to all organoleptic indicators as "excellent", "good", "satisfactory" and "unsatisfactory". A maximum of 5 points is provided for each indicator. In addition, a weighting coefficient was determined for the indicators regarding their influence on the formation of product quality [34].

The overall quality score was calculated using the following formula:

$$X = a_1B_1 + a_2B_2 + ... + a_nB_n \quad (1)$$

where a – weighting factor of a single indicator;

B – score in points for an individual indicator.

The quality assessment of experimental samples was carried out by the organoleptic method, taking into account the following indicators: shape, surface, color, appearance in the fracture, smell, and taste. In addition to the standard indicators, the consistency indicator, the sensory indicator of flavor and the severity of the additive were also selected for a more complete characterization of the impact of the proposed non-traditional raw materials on the experimental samples of cupcakes [35]. To eliminate errors and subjectivity the during studies of organoleptic indicators of cupcake quality, data for each indicator were averaged using the following formula:

$$\overline{Q_i} = \frac{1}{n}\sum_{k=1}^{n} Q_i k \, , \quad (2)$$

where Q_i – average value of the quality indicator;

Q_{ik} – value of the indicator in each of the experiments;

n – number of experiments conducted.

All studies were conducted with three- and five-fold replication in order to eliminate errors. The probability of a possible error was calculated using the t tables proposed by Student's t-test tables.

A comprehensive commodity assessment was established using the methods of theoretical qualimetry. Data processing was carried out using the formula:

$$K_0 = f(K_1, K_2, K_3 ... K_n). \quad (3)$$

Taking into account the importance of individual indicators, the mathematical model of the complex quality indicator takes the following form:

$$K_0 = f(M_i \cdot K_i) \quad (4)$$

where M_i - weighting coefficient of individual indicators;

Ki – evaluation of these indicators.

The determination of relative indicators P_1 was carried out according to the formulas:

$$q_i = \frac{P_i}{P_{ib}} \, , \quad (5)$$

$$q_i = \frac{P_{ib}}{P_i} \, , \quad (6)$$

where P_i – value of the i-th indicator (i=1, 2, 3 … n) of the quality of the product being evaluated,

P_{ib} – base value of the i-th indicator;

n – number of evaluated indicators.

To assess the quality by the complex indicator K_0, it is necessary to know the weight coefficients that were determined by the expert method, provided that:

$$\sum_{i=1}^{n} M_i = 1,0 \quad (7)$$

where M_i – weight coefficient of the i-th indicator ($Mi>0$);

n – number of product quality indicators.

$$M_i = \frac{1}{N}\sum_{j=1}^{N} M_{ij} \, , i = 1,2,3 ... n, \quad (8)$$

where M_i – arithmetic mean value of the weight coefficient of the i-th quality indicator,

N – number of experts,

M_{ij} – weight coefficient of the i-th indicator provided by the j-th expert.

To summarize the estimates of individual properties, the following formula was derived:

$$K_0 = \sum_{i=1}^{n} M_i \cdot K_i, \quad (9)$$

The calculation of a complex quality indicator, taking into account the influence of each property of experimental cupcake samples on the overall quality indicator with weight coefficients, was carried out using the formula:

$$K_0 = M_1\frac{(P_1)}{(P_1^b)} + M_2\frac{(P_2)}{P_2^b} + M_3\frac{(P_3)}{P_3^b} + M_4\frac{(P_4)}{P_4^b)} + M_5\frac{(P_5)}{P_5^b)} + M_6\frac{(P_6)}{P_6^b} + M_8\frac{(P_8)}{(P_8^b)} + M_9\frac{(P_9)}{P_9^b} \, , \quad (10)$$

where M_i – weight coefficient of indicators;

P_i – corresponding indicator (property) under investigation;

P_1^b – quality indicator of the base sample [36–37].

Water in the crumb of flour confectionery products is present in different qualitative states. The process of staling is determined by the transition of bound moisture, and the speed of this process is proportional to the humidity gradient.

The method of derivatographic analysis is a physicochemical method that allows researchers to study the behavior of both individual substances and mixtures under controlled heating conditions. The most traditional approach

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involves heating the sample at a constant speed with continuous measurements of sample temperature and weight. In addition, methods can be used in which the temperature is maintained constant or changes depending on the rate of sample decay [38].

Fig. 1. Derivatograph Q-1000

A derivatographic study of the form of moisture binding in experimental cupcakes was carried out using the Q-1000 derivatograph device (Fig. 1).

Derivatography is based on a combination of differential thermal analysis (DTA) with physical or physicochemical methods, for example, thermogravimetry, dilatometry, and mass spectrometry [39]. To obtain high-resolution derivatograms, the optimal analysis parameters were established: the average weight of the sample was about 240 mg, the temperature range was from 25 to 220 °C, the sample heating rate was 10 °C/min, the sensitivity of the derivatograph for the TG curve was 94.25 mg, DTA was 250 μV, and the paper speed was 2.5 mm/min. The device simultaneously recorded the following curves: T – temperature change; TG – sample mass change; DTA – differential thermal curve [40].

This method is used to determine the heat and temperatures of phase transitions and to study the processes of recrystallization, desolvation, thermal decomposition, and chemical compatibility.

Results and Discussion

The content of non-traditional recipe components in experimental cupcake samples is presented in Table 1 [41].

Table 1

Features of the recipe composition of experimental cupcakes

Alternative raw materials and natural supplements	Amount of raw materials in the formulation of cupcakes, kg/t						
	"Kunzhutnyi"	**"Moryachok"**	**"Mitsnyi Horishok"**	**"Osinniy Aromat"**	**"Chornychnyi"**	**"Medok"**	**"Elitnyi"**
Wheat	rye (57.2)	oatmeal (38.1)	buckwheat (19.06)	corn (57.2)	buckwheat (15.25)	corn (53.06)	oatmeal (35.52)
Powders and their mixtures	(1.9) blueberry leaves (1.9), black currant leaves (3.8), chamomile flowers (1.9)	leaves of thick-leaved bergenia (0.95). raspberry leaves (1.9), coltsfoot (19.1), deep-sea tangles (0.95)	peppermint leaves (1.91), wal-nuts (1.91)	perforate St John's-wort (1.91), heart linden flowers (1.91), purple echinacea (0.95)	chicory roots (0.95), tricolor violet flowers (5.7)	heart linden flowers (1.77), flower pollen (4.42)	peppermi nt leaves (1.77), haricot (13.69), propolis (3.69)
Whey	38.1	–	38.12	–	–	53.05	53.29
Dry skimmed milk	–	–	–	38.12	57.2	–	–
Vegetable oils	sesame (21.0)	pumpkin seeds (16.3)	walnuts (21.0)	–	–	pumpkin seeds (15.12)	–

In the "Osinniy Aromat" cupcake, raisins were completely replaced with candied apple and cherry, while raisins in the "Mitsnyi Horishok" cupcake were partially replaced with walnut kernels (22.9 kg/t), and blueberries were used in the "Chornychnyi" cupcake (22.9 kg/t). Cupcakes with fillings contain 150.6 kg/t of natural honey with pollen in the "Medok" cupcake and 150.6 kg/t of natural honey with propolis in the "Elitnyi" cupcake.

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Below are the technological schemes for the production of the control sample of the cupcake (Fig. 2) and the experimental cupcakes using non-traditional raw materials (Fig. 3).

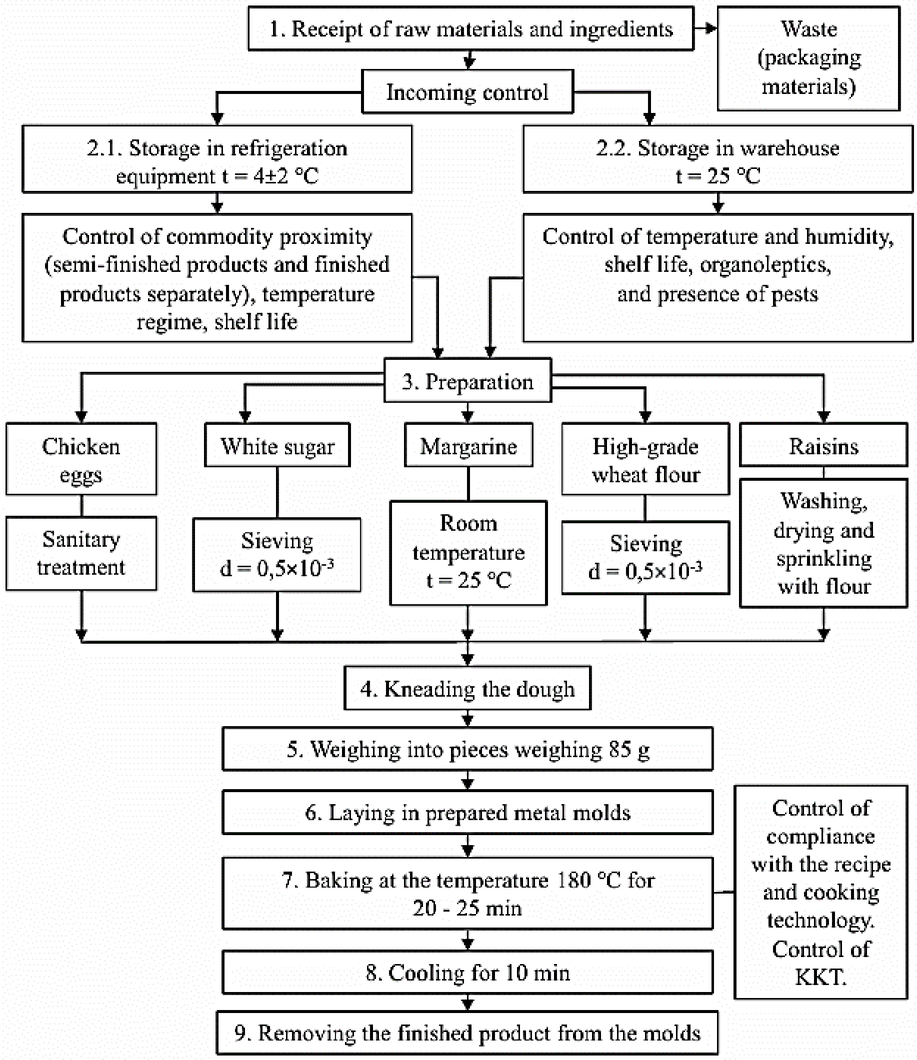

Fig. 2. Technological scheme for manufacturing a control sample of a cupcake

This technological scheme includes not only ready-to-sell cupcakes, but also products that can be stored for a certain time for sale in the retail chain as a separate food product [33].

The experimental cupcake recipes included various types of flour (buckwheat, oat, corn, rye), dairy products (whey, skimmed milk powder), beekeeping products (flower pollen, propolis, natural honey), and non-traditional plant raw materials.

Organoleptic properties are one of the most important indicators of the quality of food products, in particular, cupcakes. Experimental samples of cupcakes without filling and with filling significantly exceed the control sample in terms of organoleptic indicators, which is shown in the profilograms (Fig. 4.1, 4.2).

Experimental cupcake samples received a higher total score compared to the control sample (41.84). The total score of the experimental samples ranged from 48.69 for "Kunzhutnyi" and 48.98 for "Osinniy Aromat" – and "Chornychnyi" to 49.00 for "Mitsnyi Horishok", 49.16 for "Moryachok", and 49.52 for "Medok". According to the results of the tasting assessment, the highest total score was received by the cupcake "Elitnyi" – 49.57.

During the tasting evaluation, the "Moryachok" and "Elitnyi" cupcakes received 4.96 points each for the "color" indicator, while the control received only 4.53 points. According to the "appearance in the fracture" indicator, the highest points were received by the "Medok" cupcakes – 4.93, "Mitsnyi Horishok" – 4.92, and "Elitnyi" – 4.91 (control – 4.55).

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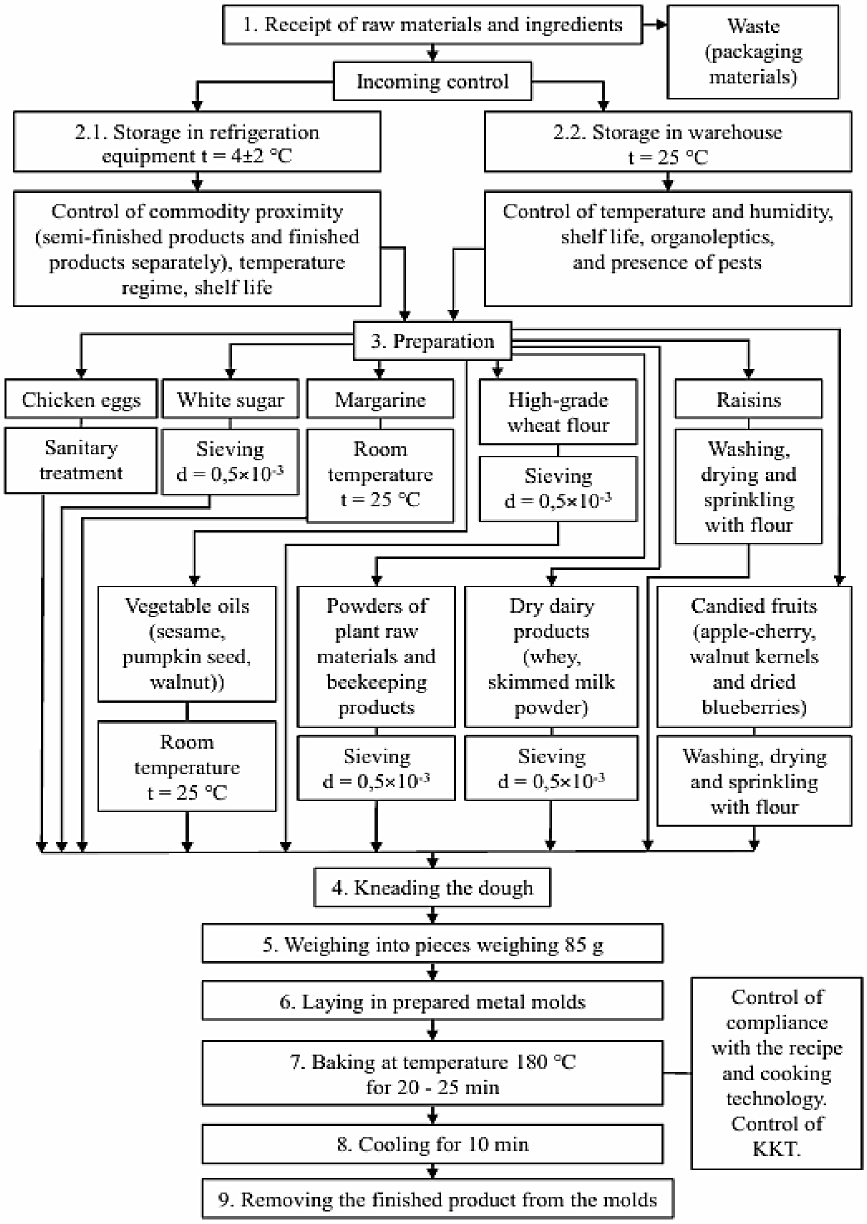


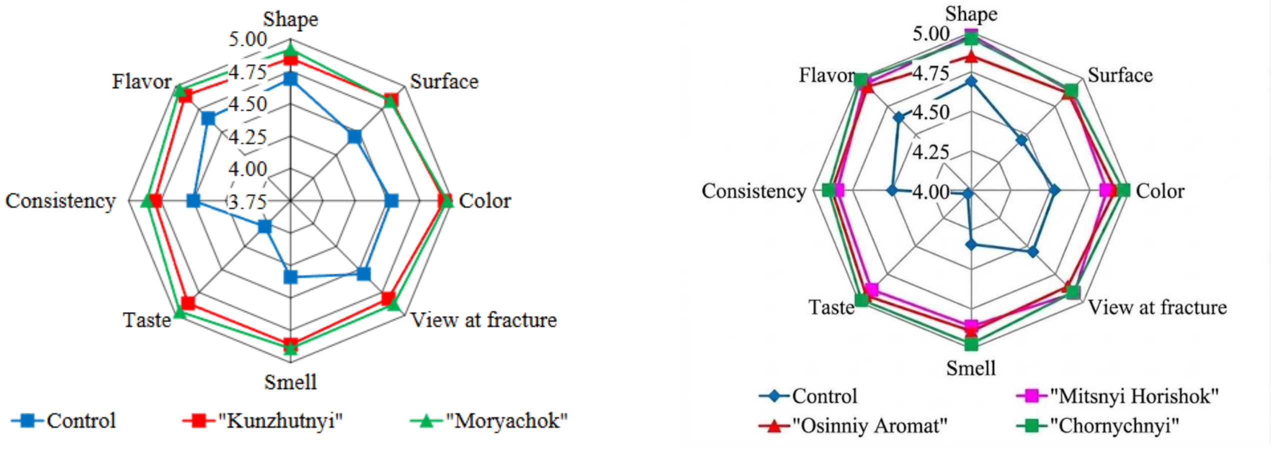
Fig. 3. Technological scheme for the production of experimental cupcakes

The most important indicators of flour confectionery products are taste and smell. According to the "taste" indicator, the weighting factor of which is 2.5, the highest points were received by the "Medok" and "Elitnyi" cupcakes – 12.45 points each, and the "Moryachok" cupcake – 12.4 points. It is worth noting that the experimental cupcake samples had significant advantages compared to the control sample, which scored only 10.08 points for this indicator.

According to the “smell” indicator, the weighting factor of which is 1.5, the highest number of points was received by cupcakes with filling, namely, “Elitnyi” – 7.46 and “Medok” – 7.44, as well as cupcakes without filling, namely, “Moryachok” and “Osinniy Aromat” – 7.34 points each. The control sample of the cupcake received only 6.51 points for this indicator.

High results of the tasting evaluation according to the “flavor” indicator were received by cupcakes “Elitnyi” – 4.99 points, “Medok” – 4.98, and “Moryachok” – 4.96, which significantly exceeded the assessment of the control sample (4.78 points). The “consistency” indicator during the tasting of the experimental samples was estimated at 2.4 to 2.45 points (the control sample scored 2.25 points).

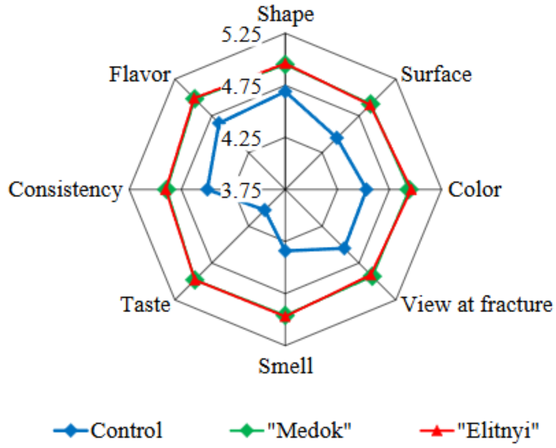
The results of the tasting evaluation of the experimental cupcakes give reason to claim a higher level of quality of all developed products. The cupcakes "Medok" and "Elitnyi" have a quality level equal to 0.99 units, the cupcake "Kunzhutnyi" – 0.97, the remaining samples – 0.98, and the control – only 0.84 units [42].



a b

*Note: Scores are given without taking into account the weighting factor and the indicator "severity of the additive"

Fig. 4.1. Profiles of the control sample and experimental cupcakes without filling "Kunzhutnyi", "Moryachok" (a), "Osinniy Aromat", "Mitsnyi Horishok", and "Chornychnyi" (b)



*Note: Scores are given without taking into account the weighting factor and the indicator " severity of the additive"

Fig. 4.2. Profiles of the control sample and experimental cupcakes (without filling) "Medok" and "Elitnyi"

The determination of the complex product evaluation was carried out taking into account the following indicators: organoleptic and physicochemical properties of the experimental cupcakes, nutritional and biological value, and safety indicators. The calculation was carried out taking into account the influence of each property of the experimental cupcakes on the overall quality indicator with weighting factors. The obtained data are shown in Fig. 5.

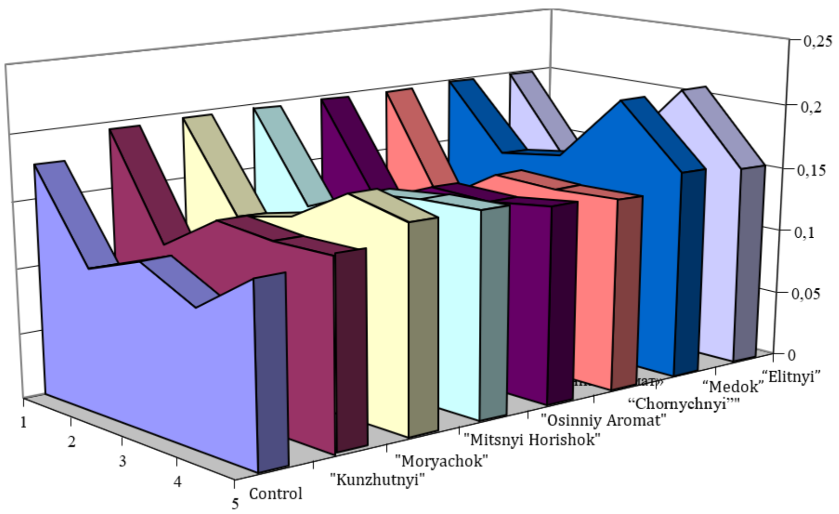


Fig. 5. Quality models of experimental cupcakes, taking into account: 1 – organoleptic indicators, 2 – physicochemical indicators, 3 – nutritional value indicators, 4 – biological value indicators, and 5 – safety indicators

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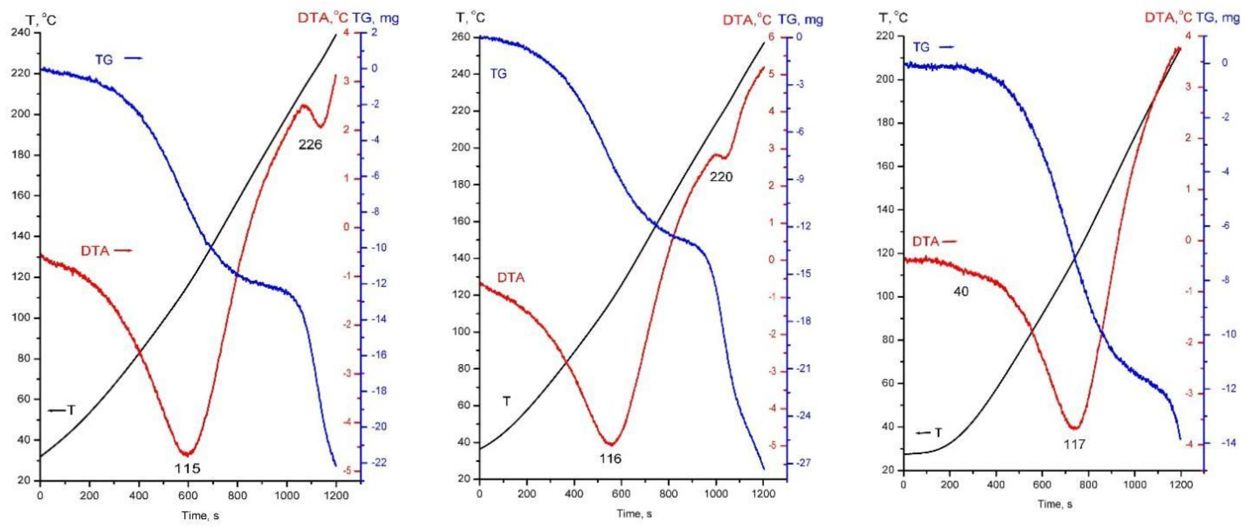
The comprehensive quality assessment conducted showed that the experimental cupcakes enriched with natural additives of plant and animal origin have better organoleptic and physicochemical indicators, indicators of nutritional and biological value, as well as safety indicators, compared to the control. The overall comprehensive assessment of the experimental flour confectionery products enriched with the proposed additives, compared to the control sample, increased by 15.7 % ("Kunzhutnyi"), 16.3 % for "Chornychnyi", 17.5 % for “Osinniy Aromat”, 21.0 % for "Moryachok", 24.6 % for "Mitsnyi Horishok", 27.4 % for "Elitnyi", and 30.7 % for "Medok".

Literary sources indicate that the ability of flour confectionery products to maintain freshness is associated with the content of bound water. Therefore, it was necessary to determine the content of bound and free water in the crumb of experimental cupcakes and compare the obtained data with the control sample. In the control sample of the “Stolichnyi” cupcake (Fig. 6a) during heating from 26 °C to 115 °C (temperature peak) 63.0 % of the total amount of moisture was removed – this is free moisture from macro- and microcapillaries. In the temperature range from 115 °C to 226 °C (II range), the removal of adsorptive and osmotically bound moisture accounted for 37.0 %.

The shape of the DTA curve of the derivatogram in the “Kunzhutnyi” cupcake indicates the differentiated removal of moisture in different binding forms (Fig. 6b). After analyzing the derivatogram, it was found that in the first temperature range (26 – 116 °C), there is only a slight change compared to the control sample, and the removal of free moisture from the cupcake sample accounts for 62.0 %. The temperature range from 116 °C – 230 °C (II range) indicates a loss of 38.0 % of bound moisture.



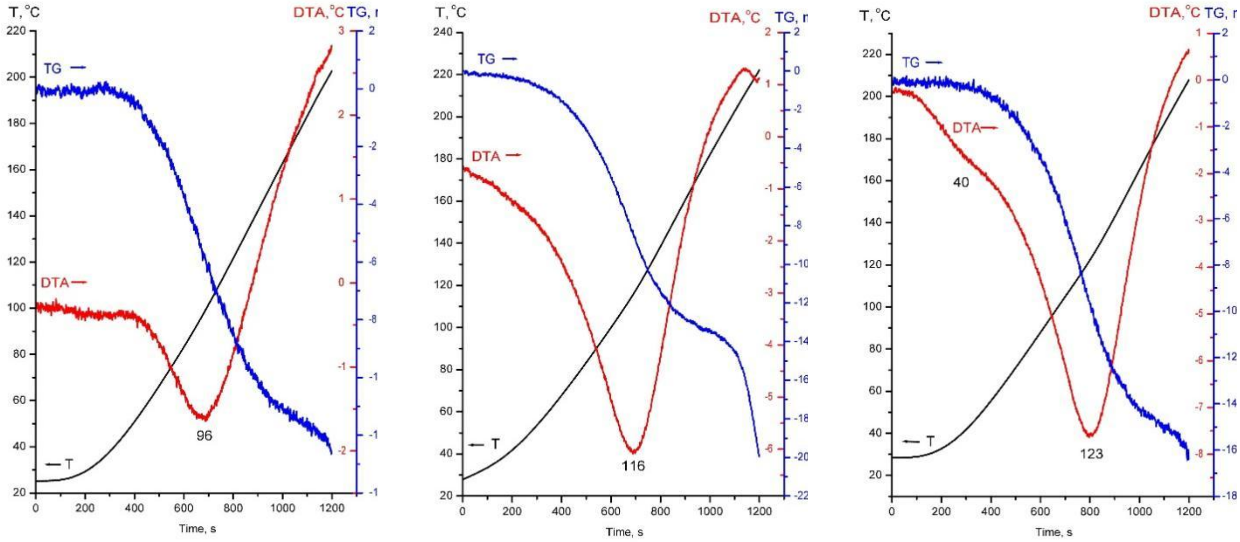
a b c

Fig. 6. Derivatograms of the “Stolichnyi” (control sample) (a), “Kunzhutnyi” (b), and “Moryachok” (c) cupcakes

As a result of heating the “Moryachok” cupcake, the analysis of the curves of temperature and body weight changes shows a loss of 60.2 % of free moisture in the temperature range from 24 °C to 117 °C. Further heating of the sample to 200 °C (II range) characterizes the removal of swelling moisture (osmotically bound) and adsorption-bound moisture – 39.8 %. (Fig. 6c). In this sample of cupcake, the proportion of bound moisture increases by 2.8 % compared to the control, which is explained by the inclusion of oat flour and kelp flakes in the recipe, which are able to bind moisture.

During the study of the moisture state in the "Mitsnyi Horishok" cupcake using the thermogravimetry method, a derivatogram (Fig. 7a) was obtained, which characterizes the forms of moisture and the strength of its bond with the product. At the first stage of heating in range I (from 25.9 °C to 96 °C), 53.7 % of free moisture is removed, which is in the capillaries and cells of the dough and microcapillaries with low binding energy. Further heating of the dough to 185 °C (temperature range II) leads to a loss of 46.3 % of mass, which is due to the removal of adsorption and osmotically bound moisture. Compared to the control sample, the amount of bound moisture is 9.3 % higher, which is due to the presence of whey, buckwheat flour, and walnut leaf powder in the product formulation.

Fig. 7b shows the derivatogram of the experimental sample of the “Osinniy Aromat” cupcake with the inclusion of non-traditional raw materials and natural additives. From the analysis of the obtained data, it can be seen that the removal of weakly bound moisture occurs in the temperature range of 25–116 °C and is 59.9%. Upon further heating, the removal of strongly bound moisture in the cupcake occurs at a temperature of 220 °C and is 40.1 %. This is explained by the inclusion of corn flour in the formulation, which binds and retains moisture less effectively.

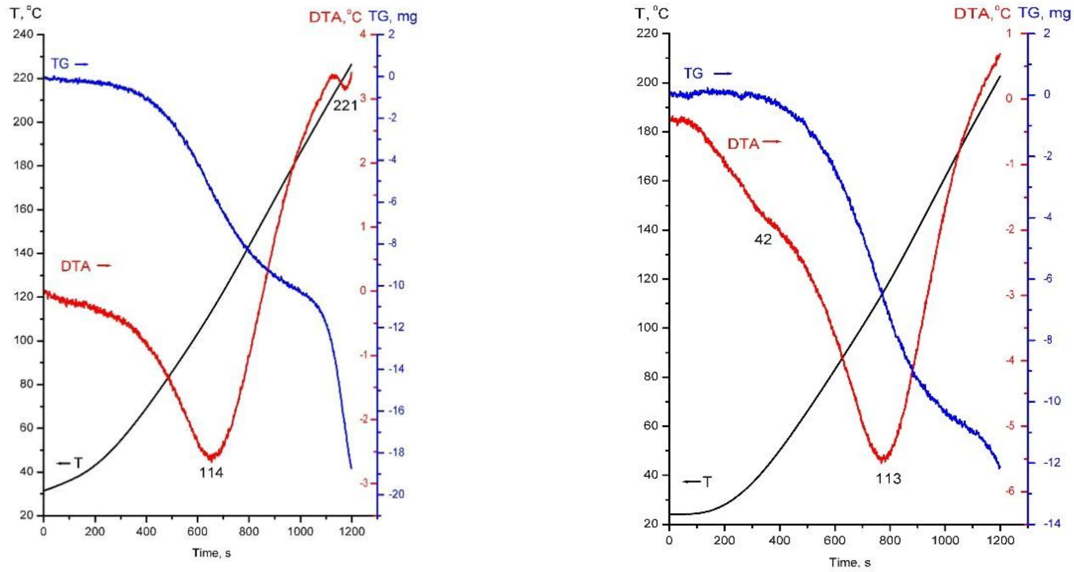


a b c

Fig. 7. Derivatograms of the “Mitsnyi Horishok” (a), “Osinniy Aromat” (b), and “Chornychnyi” (c) cupcakes

Analysis of the derivatorgam of the “Chornychnyi” cupcake (Fig. 7c) indicates a noticeable removal of moisture with a weak binding energy in the range of 26–123 °C – 59.7 %. In the temperature range of 123–205 °C (II range), 40.3 % of osmotically and adsorptively bound moisture is removed.

Studies were conducted to determine the moisture state using the thermogravimetry for experimental samples of cupcakes with the “Medok” filling (Fig. 8, a) and “Elitnyi” (Fig. 8, b). At the first stage of heating the “Medok” cupcake in the first temperature range from 25–114 °C, there is observed a slight loss of free moisture from capillaries and cells in the amount of 45.6 % of all moisture. In the second temperature range, heating to 230 °C occurs with the removal of 54.4 % of bound moisture.



a b

Fig. 8. Derivatograms of the “Medok” (a) and “Elitnyi” (b) cupcakes

The total content of tightly bound moisture in this cupcake was 17.4 % higher than in the control sample (the "Stolichnyi" cupcake). This indicates a high energy of bonds between the product components and its aqueous phase, which can be explained by the introduction of whey and beekeeping products into the recipe, which act as moisture-retaining substances. The process of heating the "Elitnyi" cupcake from 24 °C to 113 °C (range I) takes place with the removal of free moisture in the amount of 47.1 % of the total. Upon further heating to a temperature of 190 °C (range II), the loss of mass of the sample continues due to the evaporation of bound moisture in the amount of 52.9 %. Analysis of the derivatogram of the "Elitnyi" cupcake indicates the influence of the included non-traditional raw materials and additives on the increase in the amount of tightly bound moisture by 15.9 %.

Table 2

Results of analysis of derivatograms of samples of experimental cupcakes with non-traditional raw materials and natural additives and of the control sample

$p \le 0,05$; n = 3

Cupcake samples	Range I					Range II				
	Temperature, °C	Weight loss, mg	Mass fraction of removed moisture W, %: in % to weight	Mass fraction of removed moisture W, %: in % to total amount of water	**Free water content, %**	Temperature, °C	Weight loss, mg	Mass fraction of removed moisture W, %: in % to weight	Mass fraction of removed moisture W, %: in % to total amount of water	**Bound water content, %**
Control	26 - 115	100	11.1± 0.22	12.5	**63.0**± 1.28	115 – 226	64	6.8± 0.13	7.3	**37.0**± 0.76
"Kunzhutnyi"	26 - 116	96	10.6± 0.21	11.9	**62.0**± 1.25	116 – 230	64	6.8± 0.13	7.3	**38.0**± 0.77
"Moryachok"	24 - 117	92	10.1± 0.20	11.3	**60.2**± 1.21	117 - 200	65	6.9± 0.14	7.5	**39.8**± 0.79
"Mitsnyi Horishok"	25.9 - 96	85	9.3± 0.2	10.2	**53.7**± 1.07	96 - 185	75	8.1± 0.16	8.8	**46.3**± 0.93
"Osinniy aromat"	25 - 116	92	10.1± 0.19	11.2	**59.9**± 1.20	116 – 220	65	7.1± 0.14	7.5	**40.1**± 0.80
"Chornychnyi"	26 - 123	91	10.0± 0.2	11.1	**59.7**± 1.19	123 - 205	65	7.0± 0.14	7.5	**40.3**± 0.81
"Medok"	25 - 114	72	7.7± 0.15	8.4	**45.6**± 1.07	114 – 230	84	9.2± 0.18	10.0	**54.4**± 1.09
"Elitnyi"	24 - 113	74	8.0± 0.16	8.7	**47.1**± 0.98	113 - 190	82	8.9± 0.18	9.8	**52.9**± 1.06

The established redistribution of moisture forms in the experimental cupcake formulations is explained by a change in the chemical composition of the system due to the inclusion of non-traditional raw materials. The increase in the proportion of adsorption- and osmotically bound moisture is due to the high concentration of hydrophilic functional groups (–OH, –COOH) in the composition of biopolymers of phytopowders (fiber, pectin substances) and whey proteins, which act as active hydration centers and form strong hydrogen bonds with water molecules. This contributes to the formation of a developed capillary-porous structure, where moisture is retained due to capillary condensation mechanisms, which requires a higher activation energy for its removal and is confirmed by an increase in mass loss in the second temperature interval (Table 2). Such redistribution creates a thermodynamic barrier that limits the mobility of moisture and its migration to the surface of the product, slowing down the processes of starch retrogradation and protein aggregation. Thus, at the molecular level, the feasibility of using the selected raw materials to slow down rancidity and preserve the elasticity of the crumb during the storage period was substantiated.

Based on the analysis of the derivatograms, it was established that the amount of free moisture in the control sample of the "Stolichnyi" cupcake is 63.0 % of the total amount of moisture. In the experimental cupcake samples, a decrease in the proportion of free moisture was established as follows: "Kunzhutnyi" cupcake – 1.0, "Moryachok" – 2.8, "Osinniy Aromat" – 3.1, "Chornychnyi" – 3.3, "Mitsnyi Horishok" – 9.3, "Elitnyi" – 15.9 and "Medok" – 17.4 % compared to the control sample (Fig. 9).

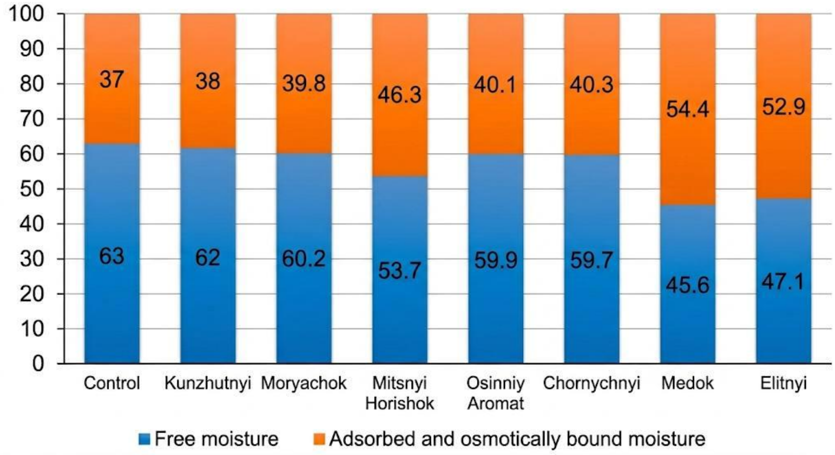


Fig. 9. Moisture ratio of different forms in the experimental cupcake samples

At the first stage of moisture removal from the cupcakes samples, a significant loss of moisture occurs. In this temperature range, free moisture, moisture contained in macro- and microcapillaries, and immobilized water are removed. The total amount of this moisture in the product samples is 63.0 % of the total mass of water for the control sample and 45.6–62.0 % of the total mass of water in products with the inclusion of non-traditional raw materials. The second temperature interval corresponds to the removal of chemically bound water. Its amount in the control sample was equal to 37.0 %, and in the experimental cupcake samples – from 38.0 to 54.4 %.

Thus, the results of the analysis of moisture binding in samples of flour confectionery products with the introduction of non-traditional raw materials indicate that the slowdown in the staling of these samples is associated with a lower content of free moisture in macro- and microcapillaries and with an increase in the amount of osmotically bound moisture. This correlates with the data obtained to determine the total deformation of the product.

Conclusions

1. Seven new cupcake recipes were developed ("Kunzhutnyi", "Moryachok", "Mitsnyi Horishok", "Osinniy Aromat", "Chornychnyi", "Medok", and "Elitnyy"), in which wheat flour was substituted with buckwheat, oat, rye, and corn flour. It was found that the use of phytopowders, beekeeping products, and vegetable oils allows researchers not only to increase the biological value of the products, but also to purposefully influence their structural and mechanical properties.

2. According to the results of the tasting assessment on the developed five-point scale, it was found that the experimental cupcake samples have a higher quality level (0.97–0.99) compared to the control sample of the "Stolichnyi" cupcake (0.84). The highest scores for the indicators of “taste”, “smell” and “flavor” were received by cupcakes with “Elitnyi” and “Medok” fillings (49.57 and 49.52 points, respectively).

3. Using theoretical qualimetry methods, it was established that the overall comprehensive assessment of experimental cupcake samples increased by 15.7–30.7% compared to the control. This is due to the improvement of the nutrient composition (vitamins, minerals, fatty acids of the ω-3 and ω -6 families) and the preservation of high physicochemical characteristics throughout the entire technological process.

4. Using the method of thermogravimetric analysis on a Q-1000 derivatograph, regularities of the redistribution of moisture bond forms were revealed. It was established that the introduction of non-traditional raw materials contributes to a significant transition of free moisture into a bound state. While the control contains 63.0 % free moisture, in the experimental samples of cupcakes this indicator is significantly lower (from 1.0 % in the "Kunzhutnyi" cupcake to 17.4 % in the "Medok" cupcake).

5. It was established that the dominance of adsorption and osmotically bound moisture in the experimental samples is due to the high concentration of hydrophilic functional groups (–OH, –COOH) in the composition of phytopowders and non-traditional types of flour. This enhances the interaction between biopolymers and water molecules through hydrogen bonds, which physicochemically prevents starch retrogradation. As a result, a decrease in the proportion of free moisture (by 1.0–17.4 % compared to the control) directly correlates with a slowdown in the staling process and the preservation of crumb elasticity during storage.

Further research will be aimed at finding plant-based additives that would affect the starch retrogradation process, ensure crumb elasticity, and extend the shelf life of finished products, which is important for the confectionery industry.

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