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OPTIMIZATION OF THE COMPOSITION OF FAT SYSTEMS OF NEW GENERATION

Жири є невід'ємною складовою харчування людини. Підвищений вміст транс-ізомерів в їх складі обумовлює низку серцево-судинних захворювань та хвороб порушення метаболізму. Перспективним підходом до вирішення проблеми мінімізації вмісту транс-ізомерів жирних кислот у складі харчових продуктів є створення жирових систем нового покоління – олеогелів, які є об'єктом представленого дослідження. Як дисперсійне середовище олеогелів було використано високоолеїнову соняшникову олію, що на відміну від олії традиційних сортів дає можливість отримувати системи з підвищеною стійкістю до окиснення. Дисперсною фазою вказаних жирових систем було обрано бджолиний віск, трипальмітин та моноацилгліцерини. Вибір комплексу вказаних компонентів ґрунтувався на їх властивостях створювати в олеогелях тривимірну структуру з заданими термомеханічними характеристиками. В теперішній час бракує інформації щодо залежності основних характеристик олеогелів від співвідношення інгредієнтів їх дисперсної фази. Зокрема, одним з найбільш проблемних місць технології олеогелів є їх термостабільність, яка суттєво впливає на параметри виробництва, транспортування, а також на умови і терміни зберігання. Для вирішення вказаного завдання в роботі застосовано методологію поверхні відклику. Визначення невідомих значень вектора параметрів здійснювалось шляхом застосування алгоритмів регресійного аналізу. Мінімізація функціоналу відхилу виконувалась шляхом знаходження відповідних комбінацій експериментальних рядів предикторів. В результаті досліджень розроблено математичну модель, яка дозволяє, виходячи з даних про компонентний склад олеогелів, прогнозувати їх термостабільність. Обґрунтовано раціональні масові частки компонентів дисперсної фази олеогелів: вміст бджолиного воску 3,27 % мас.; вміст трипальмітину 3,07 % мас. та вміст моноацилгліцеринів 4,70 % мас., при яких досягається максимальне значення функції відклику. Отримані результати слугуватимуть науковим підґрунтям для розробки технологічних параметрів промислового виробництва жирових систем нового покоління, умов і термінів їх зберігання та транспортування.

Ключові слова: технологія олеогелів, промислове виробництво жирових систем, термомеханічні характеристики, термостабільність олеогелів.

1. Introduction

Modern requirements for improving the quality and safety of food products lead to the improvement of existing and development of new technologies. In particular, biocatalytic technologies are being developed for the synthesis of lipid systems enriched in omega-3 polyunsaturated fatty acids [1]. Studies are carried out to obtain prebiotic and synbiotic emulsion fat systems and health-wohy vegetable drinks [2, 3].

Another direction to improve the quality of food products is solving the problem of minimizing the content of trans-isomers of fatty acids in their composition. Today, the Ukrainian market is filled with food products based on fats, which are produced by the method of partial hydrogenation and, as a result, contain a high content of trans-fatty acid isomers. At the same time, the results of modern nutritional studies show the presence of a link between the consumption of these fats and a breakdown in the body of enzymes, cell membranes, an increase in blood cholesterol levels and an increased risk of cardiovascular diseases [4, 5]. Trans-isomers not only do not turn into the usual metabolites of cis-acids, but also affect the efficiency of their formation [6]. For example, with trans-trans-linoleic acid, arachidonic acid is not formed – the most important component of biological membranes and the precursor of regu-

latory substances that are very necessary for the body – eicosanoids. Moreover, trans-isomers in large quantities reduce the rate of arachidonic acid formation with cis-cis-linoleic [7]. The use of excessive amounts of trans-isomers leads to a deficiency of essential fatty acids in the body.

Therefore, the development of technology for the production of fat systems with a minimum content of trans-isomers is an important task.

2. The object of research and its technological audit

The object of this research is the prescription composition of oleogel in the form of fat systems of a new generation.

For research, the following fatty ingredients were used as a source of raw materials: high-oleic sunflower oil, served as a supplier of monounsaturated fatty acids, beeswax, tripalmitin and monoacylglycerols. A feature of these prescription components is the almost complete absence of fatty acid trans-isomers in their composition.

One of the most problematic places in the oleogel technology is their thermal stability, which significantly affects the parameters of production, transportation, as well as storage conditions and periods.

To identify the relationship between the coefficient of thermal stability and the oleogel formulation, a technological

audit is conducted, the purpose of which is determination of the relationship between the specified parameters.

The obtained dependences allow to establish the rational content of the oleogel ingredients.

3. The aim and objectives of research

The aim of research is composition optimization of fat systems of the new generation.

To achieve this aim it is necessary to solve the following objectives:

1. To develop a mathematical model that establishes the relationship between the thermal stability coefficient of the oleogel and its composition.

2. To determine the rational content of beeswax, tripalmitin and monoacylglycerol, which provides the maximum values of the thermal stability coefficient of the investigated fat systems.

4. Research of existing solutions of the problem

One of the promising areas for solving the problem of reducing the content of trans-isomers in food products is the creation of a new generation of fat systems, namely, oleogel.

Oleogel is a colloidal system, where the dispersion medium is oil, and the dispersed phase is complex organic compounds of lipid nature, in particular, partial acylglycerols, waxes, fatty acids, sterols, and other.

An analysis of modern scientific works has shown that an important factor in the development of the production technology of the oleogel is the substantiation of the nature of the ingredients of the dispersed phase and their ratio. For example, in [8], a comparative analysis of the use of a number of waxes as a dispersed phase for the oleogel, which are used in ice cream, is performed. Research results have shown that wax-based oleogels based on rice bran provide better structure and improved thermal stability of ice cream compared to carnauba or candelilla waxes. In [9], beeswax was proved in comparison with other waxes to provide oleogels with better adhesion and cohesive properties. These findings are supported by subsequent studies [10], which show the effectiveness of using beeswax-based oleogel as a substitute for animal fat in food systems. According to the authors of the works [11, 12], the introduction of monoacylglycerol in the amount of up to 7 % in oleogel allows to obtain fat systems that will have the textural and thermal properties of soft margarines, however, unlike the others, they will not contain trans fatty acid isomers. The results of the study [13] show the relationship between the crystallization conditions and the formation of the structure of the oleogel on the basis of monoacylglycerol. In [14], it is shown that the interaction of tripalmitin with waxes contributes to the formation of a three-dimensional crystalline structure with improved thermomechanical properties in oleogels. A number of studies are devoted to studying the effect of binary mixtures of gelling agents on the properties of fat systems. In particular, the joint effect of β -sitosterol and stearic acid on the microstructure, texture, and thermophysical properties of oleogel with the sunflower oil as dispersion medium is studied in [15]. The interaction between lecithin, monoacylglycerols and phytosterols in the

oleogel composition are analyzed, respectively, in [16, 17]. In the works of other authors [18], using the methods of cryoscopic electron microscopy and Raman spectroscopy, the synergetic effect of waxes and lecithin is established during the formation of the oleogel structure. The use of ternary mixtures of gelling agents will expand the range of properties of the oleogel and select a lipid system with specified characteristics for each food product [19].

Thus, the results of theoretical and experimental studies of the design of oleogel show the promise of using waxes, monoacylglycerol and tripalmitin as a gelling agent and their complex use as part of fat systems. Along with this, currently there are not enough scientifically based approaches to the development of technologies of these multicomponent fat systems. One of the first steps in this direction is the optimization of their formulation.

5. Methods of research

To optimize the oleogel composition, the response surface methodology is used [20]. This method is a combination of mathematical and statistical techniques aimed at modeling processes and finding combinations of experimental predictor series in order to optimize the response function, which is described in general form by the following polynomial:

$$\hat{y}(x, a) = a_0 + \sum_{i=1}^n a_i x_i + \sum_{k=1}^n a_k x_k^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n a_{ij} x_i x_j, \quad (1)$$

where $x \in R^n$ – the vector of variables; a – the vector of parameters.

The determination of the unknown values of the vector of parameters a is carried out by applying regression analysis algorithms and minimizing the deviation functional:

$$J(x) = \sum_{i=0}^m \|y_i - \hat{y}(x, a)\|^2, \quad (2)$$

where m – the amount of experimental data.

The simulation and processing of experimental data is performed in the environment of the Statistica 10 package (StatSoft, Inc., USA).

The method for determining the thermal stability of the oleogel is based on the exposure of samples of a certain size and shape at a temperature of $(30 \pm 1)^\circ\text{C}$ for 2 hours, followed by the determination of the coefficient of thermal stability, which is determined by the ratio of the diameters of the samples before and after thermostating. The arithmetic average of three parallel determinations is taken as the final result.

6. Research results

The coefficient of thermal stability (TS) is chosen as the criterion for optimizing the oleogel composition. The varied independent factors in the experiment are the wax content (W, wt. %), tripalmitin content (TP, wt. %) and monoacylglycerols content (MAG, wt. %).

Regarding the oleogels that are investigated, a response function is chosen that looked like a second-degree polynomial:

$$\text{TS} = b_0 + b_1 \cdot W + b_{11} \cdot W^2 + b_2 \cdot \text{TP} + b_{22} \cdot \text{TP}^2 + b_3 \cdot \text{MAG} + b_{33} \cdot \text{MAG}^2 + b_{12} \cdot W \cdot \text{TP} + b_{13} \cdot W \cdot \text{MAG} + b_{23} \cdot \text{TP} \cdot \text{MAG}, \quad (3)$$

where TS – the coefficient of thermal stability; b_0 – a constant; $b_1, b_{11}, b_2, b_{22}, b_3, b_{33}, b_{12}, b_{13}, b_{23}$ – coefficients for each element of the polynomial; W – wax content, wt. %; TP – the content of tripalmitin, wt. %; MAG – monoacylglycerols content, wt. %.

Central composite rotatable design is used that is most suitable for the chosen optimization method [20]. The choice of levels and intervals of variation of the factors is carried out according to the results of previous experiments: the content of beeswax and tripalmitin varies in the range of 0.3–5.0 % by weight, and the content of monoacylglycerols is in the range of 0.1–5.00 % by weight.

The design matrix and the experimental values of the response function are presented in Table 1. To reduce the effect of systematic errors caused by external conditions, the sequence of the experiments is randomized.

To test the significance of the regression coefficients (3), a Pareto chart is constructed, presented in Fig. 1 (L – the linear effect, Q – the quadratic effect).

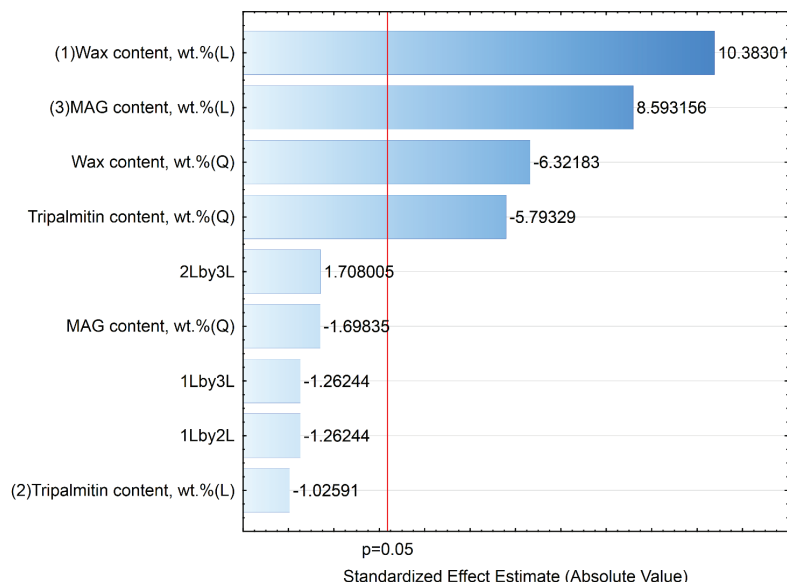


Fig. 1. Pareto chart for testing the significance of regression coefficients: MAG – monoacylglycerols

With this in mind, the indicated regression terms are eliminated from the model. The resulting equation with the calculated coefficients is:

$$TS = 0.080 + 0.282 \cdot W - 0.035 \cdot W^2 - 0.004 \cdot TP + 0.076 \cdot MAG \quad (4)$$

The adequacy of the developed model was checked by the analysis of variance (ANOVA), the results of which are presented in Table 2.

The data given in Table 2, in particular, the lack of loss of consistency (significance level $p < 0.05$) and the values of the coefficients of determination (R^2 and R_{adj}^2), close to one, allow to conclude that the resulting model adequately describes the response.

The cumulative effect of the content of components on the thermal stability of oleogel described by a polynomial is graphically is represented in Fig. 2–4.

The analysis of the obtained dependences leads to the following conclusions. The increase in the formulation of the oleogel content of beeswax from 0.30 to 3.30 wt. % causes the growth of thermal stability. Further increase in the content of the specified component is not rational, since it practically does not affect the response. However, when varying the content tripalmitin from 0.30 to 3.10 wt. % there is an increase in thermal stability, and with a further increase – a decrease in this indicator. In turn, an increase in the content of monoacylglycerol in the investigated fat systems causes a monotonous increase in the response, while the maximum values of the thermal stability coefficient are observed already with the mass fraction of the specified component from 4.0 % and higher.

These conclusions are confirmed by a detailed study of the patterns of influence of these parameters by processing the polynomial (4) in Statistica 10, which allows to establish rational values of the mass fractions of the oleogel components. The maximum value of the thermal stability coefficient is achieved with the following gelatin content: beeswax – 3.27 wt. %; tripalmitin – 3.07 wt. % and monoacylglycerol – 4.70 wt. %.

Design matrix and response function

| No. of experiment | Wax content | | Tripalmitin content | | Monoacylglycerols content | | Thermal stability coefficient |
|-------------------|-------------|-------|---------------------|-------|---------------------------|-------|-------------------------------|
| | Coded level | wt. % | Coded level | wt. % | Coded level | wt. % | |
| 1 | 0 | 2.65 | 0 | 2.65 | 0 | 2.55 | 0.80 |
| 2 | +1 | 4.05 | -1 | 1.25 | -1 | 1.1 | 0.80 |
| 3 | 0 | 2.65 | 0 | 2.65 | +1.682 | 5.0 | 1.00 |
| 4 | 0 | 2.65 | -1.682 | 0.3 | 0 | 2.55 | 0.61 |
| 5 | -1 | 1.25 | -1 | 1.25 | +1 | 4.0 | 0.60 |
| 6 | -1 | 1.25 | -1 | 1.25 | -1 | 1.1 | 0.43 |
| 7 | 0 | 2.65 | +1.682 | 5 | 0 | 2.55 | 0.58 |
| 8 | -1 | 1.25 | +1 | 4.05 | -1 | 1.1 | 0.40 |
| 9 | 0 | 2.65 | 0 | 2.65 | -1.682 | 0.1 | 0.50 |
| 10 | -1 | 1.25 | +1 | 4.05 | +1 | 4.0 | 0.65 |
| 11 | +1 | 4.05 | -1 | 1.25 | +1 | 4.0 | 0.85 |
| 12 | +1 | 4.05 | +1 | 4.05 | +1 | 4.0 | 0.85 |
| 13 | +1 | 4.05 | +1 | 4.05 | -1 | 1.1 | 0.65 |
| 14 | 0 | 2.65 | 0 | 2.65 | 0 | 2.55 | 0.90 |
| 15 | 0 | 2.65 | 0 | 2.65 | 0 | 2.55 | 0.82 |
| 16 | +1.682 | 5 | 0 | 2.65 | 0 | 2.55 | 0.80 |
| 17 | -1.682 | 0.3 | 0 | 2.65 | 0 | 2.55 | 0.35 |
| 18 | 0 | 2.65 | 0 | 2.65 | 0 | 2.55 | 0.80 |

The specified Pareto chart (Fig. 1) shows standardized coefficients, sorted by absolute values. Analysis of the data shows that the quadratic effect of monoacylglycerol content, the linear effect of tripalmitin content, and the interaction effects of the parameters is insignificant, since the evaluation columns of these effects do not cross the vertical line, is a 95 % confidence level.

Table 2

ANOVA for the model

| Factor | Sum of squares, <i>SS</i> | Degree of freedom, <i>df</i> | Mean square, <i>MS</i> | F-value | The level of significance, p-value |
|---|---------------------------|------------------------------|------------------------|----------|------------------------------------|
| (1)Wax content, wt. % (<i>L</i>) | 0.244362 | 1 | 0.244362 | 107.8069 | 0.001906 |
| Wax content, wt. % (<i>K</i>) | 0.084373 | 1 | 0.084373 | 37.2236 | 0.008846 |
| Tripalmitin content, wt. % (<i>K</i>) | 0.070083 | 1 | 0.070083 | 30.9190 | 0.011475 |
| (3)MAG content, wt. % (<i>L</i>) | 0.167376 | 1 | 0.167376 | 73.8423 | 0.003313 |
| Lack of fit | 0.039392 | 10 | 0.003939 | 1.7379 | 0.355891 |
| Pure Error | 0.006800 | 3 | 0.002267 | – | – |
| The total sum of squares | 0.589850 | 17 | – | – | – |

Coefficient of determination $R^2=0.921$
Adjusted coefficient of determination $R^2_{adj}=0.898$

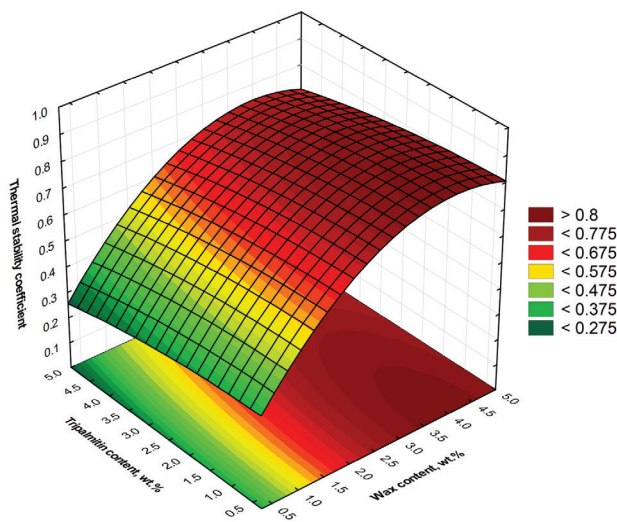


Fig. 2. The dependence of the thermal stability coefficient of the oleogel on the wax and tripalmitin content

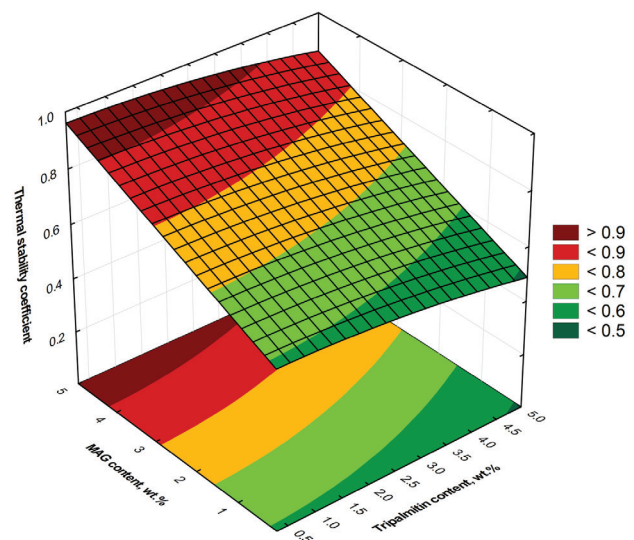


Fig. 4. The dependence of the thermal stability coefficient of the oleogel on the tripalmitin and monoacylglycerols content

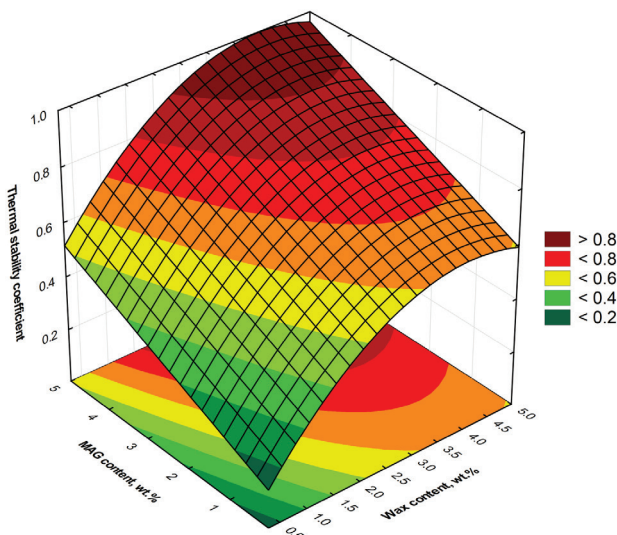


Fig. 3. The dependence of the thermal stability coefficient of the oleogel on the wax and monoacylglycerols content

7. SWOT analysis of research results

Strengths. The strengths of this research should include mathematical modeling and experimental confirmation of the results on the rational content of the components of fat systems of the new generation. The obtained data are the scientific basis for the development of technological parameters of industrial production, conditions and periods of storage, as well as transportation of finished products.

Weaknesses. The weaknesses of the developed product include: higher cost than traditional fat systems and poor consumer awareness of the new product and its benefits.

Opportunities. As for the capabilities of the fat systems of the new generation, this is: competitors in the products-analogues have a high content of trans-isomers of the fatty acids harmful to human health, an insufficient range of fat and oil products for a healthy diet.

Threats. The threats to the entry of a new product on the consumer market include:

- possibility of the emergence of new fat systems with equivalent properties;

- conservatism of the population;
- decrease in consumer purchasing power.

Based on the SWOT analysis, the following strategic solutions are proposed:

- when conducting marketing activities, it is necessary to focus on the absence of trans-isomers from among the proposed fat systems, which increases their safety and nutritional value;
- it is advisable in the formation of prices to focus on the limited purchasing power of the population;
- develop an appropriate packaging design with informative markings.

All of these approaches will contribute to raising consumer awareness of new fat systems and entering new markets.

8. Conclusions

1. A mathematical model is developed that allows, based on the data on the oleogel composition, to predict their thermal stability. In this case, the methodology of the response surface is applied, and the determination of the unknown values of the parameter vector is carried out by applying regression analysis algorithms.

The analysis of the obtained dependences led to the conclusion that an increase in the content of beeswax from 0.30 to 3.30 wt. % in the oleogel formulation causes the growth of thermal stability. Further increase in the content of the specified component is not rational, since it practically does not affect the response. However, when varying the tripalmitin content from 0.30 to 3.10 wt. % there is an increase in thermal stability, and with a further increase – a decrease in this indicator.

2. The optimum values of the mass fractions of the oleogel components are determined: the content of beeswax is 3.27 wt. %; content of tripalmitin is 3.07 wt. % and the content of monoacylglycerol is 4.70 wt. %. The maximum value of the thermal stability coefficient is reached at these values.

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