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OXIDIZATION RESISTANCE AND SORPTION PROPERTIES OF OLEOGELS AS NEW-GENERATION FATTY SYSTEMS

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Fats as complex mixtures of acylglycerols with lipid and non-lipid substances are an integral part of human nutrition. The presence of acylglycerols of trans-isomers of fatty acids causes many cardiovascular diseases and metabolic disorders. A promising approach to solving the problem of minimizing the content of these undesirable compounds in food recipes is to create a new generation of fat systems, oleogels, which are the subject of this study. High-oleic sunflower oil was used as a dispersion medium of oleogels, which allows obtaining systems with increased resistance to oxidation, as opposed to the oils of traditional kinds. Sunflower seed wax and tocopherols are chosen as a dispersed phase of these fatty systems. The choice of these components was based on their properties to create a three-dimensional structure in oleogels with specified thermomechanical characteristics. Currently, there is a lack of information on the influence of the content of the dispersed phase on the technological parameters of oleogels, namely oxidative resistance and sorption properties. The purpose of the presented work was to study these features of oleogels and establish their dependences on their composition. To solve this problem, the yield surface method is used in the work. The unknown values of the parameter vector were determined by using regression analysis algorithms. Deviation functionality was minimized by finding the appropriate combinations of the experimental series of predictors. A mathematical model was developed which allows predicting oxidative stability and sorption properties of oleogels based on the data on their composition. The suitable mass fractions of the components of the dispersed phase of oleogels have been determined as follows: tocopherol content is 0.10–0.14 wt.% and the sunflower seed wax content is 1.8–4.0 wt.%. The results obtained can serve as a scientific basis for the development of technology for the industrial production of oleogels as new generation fatty systems.

Keywords: oleogel, wax, tocopherol, oxidative resistance, mathematical modeling.

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Introduction

Modern requirements for improving the quality and safety of food products require the improvement of existing and development of new technologies. In particular, biocatalytic processes of the synthesis of lipid systems enriched with omega-3 polyunsaturated fatty acids attract special attention [1]. Another area of improvement of food products in terms of their safety is to solve the problem of minimizing the content of trans-isomers of fatty acids in their composition [2,3]. The results of modern nutritional research show a relationship between the consumption of these fats and an increased risk of metabolic syndrome, diabetes and cardiovascular diseaseы due to increased blood lipoproteins of low and very low density. Moreover, they block the action of high-density lipoproteins, which initiates the deposition of cholesterol plaques on the walls of human blood vessels and provokes the development of atherosclerosis [4,5].

Currently, the volume of production of the so-called fast food is growing rapidly. The amount of frying fats used in the frying of these products is measured worldwide in millions of tons per year. The quality of cooked food depends on the choice of frying fat. The variety of frying fats does not allow choosing a single ideal recipe. Its choice is influenced by the following factors: the nature and safety of fat, the current technology, the nature if fried products, storage conditions and terms, nutritional value and cost. In Ukraine, the vast majority of solid fats in recipes are produced by the method of partial hydrogenation, which causes the presence of a significant number of trans-isomers of fatty acids in their composition. The problem of safety and quality of frying fats is especially important since the main group of consumers of these products is the younger generation, for whom the negative impact of fat oxidation products on health is extremely important.

A promising direction for solving the problem of producing high-quality frying fats and their safety is the synthesis of appropriate fatty systems by designing oleogels with a minimum content of trans-isomers.

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

Some of the main characteristics of oleogels as frying fats are oxidative resistance and sorption properties. The purpose of the presented work was to study these properties of oleogels and determine their dependences on the composition of these fatty systems.

Experimental

The object of the study was oleogels, the dispersion medium of which is a refined high-oleic sunflower oil and the dispersed phase is a sunflower seed wax and tocopherols (vitamin E).

Oleogels were prepared according to the method described elsewhere [6]. The sunflower seed wax content (W, wt.%) and the tocopherol content (E, wt.%) were chosen as independent factors that varied. The choice of levels and predictor variation intervals was made based on the results of previous experiments.

The oxidative resistance of oleogels was evaluated by the accumulation of primary oxidation products, the content of which being determined through the peroxide value measuring [7]. Sorption properties were determined from the oil content of the products, which was established gravimetrically by exhaustive extraction using a Soxhlet extractor [8].

To establish the relationship between the oxidative stability and sorption properties of oleogels and their composition, the response surface method was used. It is a mathematical technique aimed at modeling processes and finding combinations of experimental series of predictors to optimize the yield function. It is generally described by the following equation:

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

where $x \in R^n$ is the vector of variables, and a is the vector of parameters.

The following polynomials of the second degree were chosen for the mathematical description of the studied features of oleogels:

$$PV = a_0 + a_1 W + a_2 W^2 + a_3 E + a_4 E^2 + a_5 WE; \quad (2)$$

$$OA = a_0 + a_1 W + a_2 W^2 + a_3 E + a_4 E^2 + a_5 WE, \quad (3)$$

where PV is the peroxide values of oleogels (mmol $½O_2$ per kg); OA is the oil absorption of products (wt.%); W is the sunflower seed wax content (wt.%); E is the tocopherol content (wt.%); a_0 is a constant; and a_1, a_2, a_3, a_4, a_5 are the coefficients for each polynomial element, correspondingly.

Experimental data were processed by the Statistica 10 (StatSoft, Inc., USA) software package. A central composite rotatable plan was used, which allows varying all process parameters simultaneously, thereby reducing the number of experiments and considering the interaction between all variables.

Results and discussions

The design matrix and experimental values of the response functions are given in Table 1. To reduce the impact of systematic errors caused by external conditions, the sequence of experiments was randomized.

To check the significance of the regression coefficients (2), a Pareto chart was plotted (Fig. 1).

The chart (Fig. 1) shows standardized coefficients, which are sorted by absolute values. Data analysis shows that the quadratic effect of the sunflower seeds wax content is insignificant because the column for estimating this effect does not cross the vertical line, which is a 95% confidence probability. With this in mind, this regression term was removed from the model. Similarly, the significance of the regression coefficients (3) was tested. According to the results obtained, the significance of the linear and quadratic effect of tocopherol content was established.

This work allowed deriving the following equations of the models:

$$PV = 40.2 - 1.5W - 503.5E + 1814.7E^2 + 10.3WE; \quad (4)$$

Table 1

Design matrix and values of response functions

Experiment number	Sunflower seed wax content, W		Tocopherol content, E		Peroxide value, PV, mmol $\frac{1}{2}O_2$/kg	Oil absorption, OA wt.%
	encrypted level	wt.%	encrypted level	wt.%		
1	–√2	0.50	0	0.100	8.3	18.5
2	+√2	5.00	0	0.100	5.7	10.1
3	+1	4.35	–1	0.065	10.6	10.4
4	0	2.75	0	0.100	6.5	15.3
5	–1	1.15	+1	0.135	5.1	16.8
6	0	2.75	0	0.100	6.2	15.2
7	0	2.75	+√2	0.150	5.2	14.0
8	+1	4.35	+1	0.135	4.8	10.6
9	0	2.75	–√2	0.050	17.7	15.9
10	0	2.75	0	0.100	6.4	14.8
11	0	2.75	0	0.100	7.0	15.9
12	–1	1.15	–1	0.065	13.2	17.1

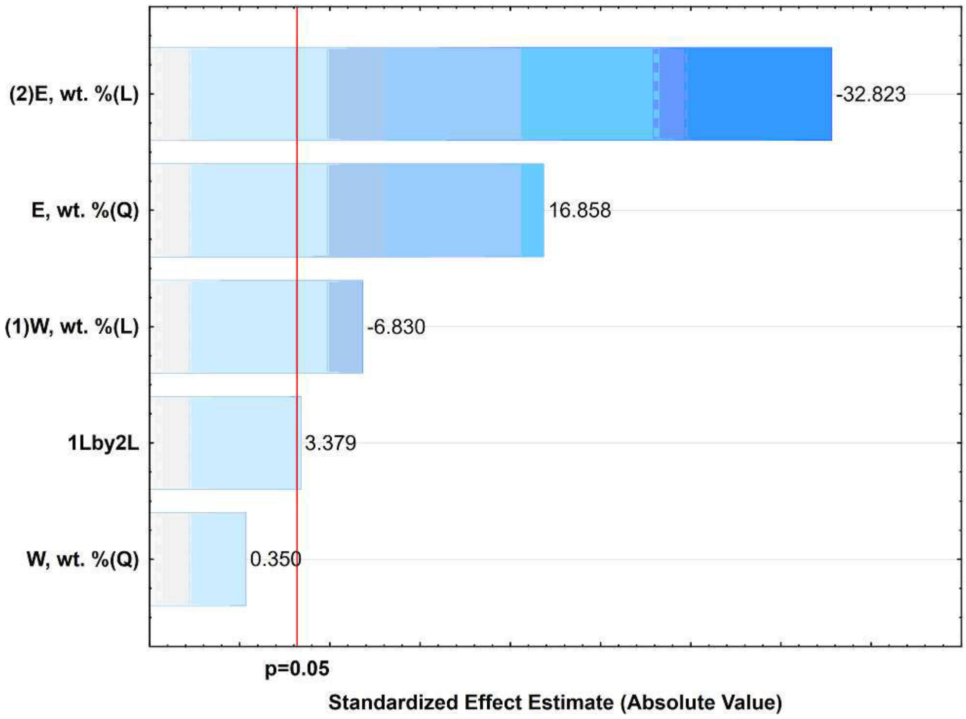

Fig. 1. Pareto chart: L – linear effect and Q – quadratic effect

$$OA = 18.4 - 0.5W - 0.3W^2. \quad (5)$$

The adequacy of the model obtained (Eqs. (4) and (5)) was checked by the analysis of variance, the results of which are presented in Tables 2 and 3.

The data given in Tables 2 and 3, in particular the absence of loss of consistency (significance level $p>0.05$) and the determination coefficient values (R^2 and R^2_{adj}) which are close to one, prove that the obtained models adequately describe the yield function.

Described by polynomials (4) and (5), the total effects of sunflower seed wax and tocopherol contents on the oxidative stability of oleogels and their sorption properties are graphically presented in Figs. 2 and 3.

Analysis of the obtained dependences (Figs. 2 and 3) allows us to draw the following conclusions. The content of tocopherols does not affect the sorption properties of oleogels but is the dominant factor in their resistance to oxidation. The minimum values of the peroxide value, which correspond to the highest oxidative resistance, are observed in the

Table 2

Analysis of variance for the model expressed by Eq. (4)

Factor	Sum of squares, SS	Degrees of freedom, df	Mean square, MS	F-value	The level of significance, p-value
(1) Sunflower seed wax content (L)	5.4034	1	5.4034	46.648	0.006422
(2) Tocopherols content (L)	124.7911	1	124.7911	1077.334	0.000062
Tocopherols content (Q)	34.0348	1	34.0348	293.826	0.000433
1L by 2L	1.3225	1	1.3225	11.417	0.043125
Lack of fit	2.8698	4	0.7175	6.194	0.082992
Pure error	0.3475	3	0.1158		
The total sum of squares	168.7692	11			

Determination coefficient R^2=0.981
Adjusted determination coefficient R^2_{adj}=0.970

Table 3

Analysis of variance for the model expressed by Eq. (5)

Factor	Sum of squares, SS	Degrees of freedom, df	Mean square, MS	F-value	The level of significance, p-value
(1) Sunflower seed wax content (L)	76.76954	1	76.7695	371.4655	0.000305
Sunflower seed wax content (Q)	2.80915	1	2.8092	13.5927	0.034593
Lack of fit	4.59131	6	0.7652	3.7027	0.154991
Pure error	0.62000	3	0.2067		
The total sum of squares	84.79000	11			

Determination coefficient R^2=0.940
Adjusted determination coefficient R^2_{adj}=0.925

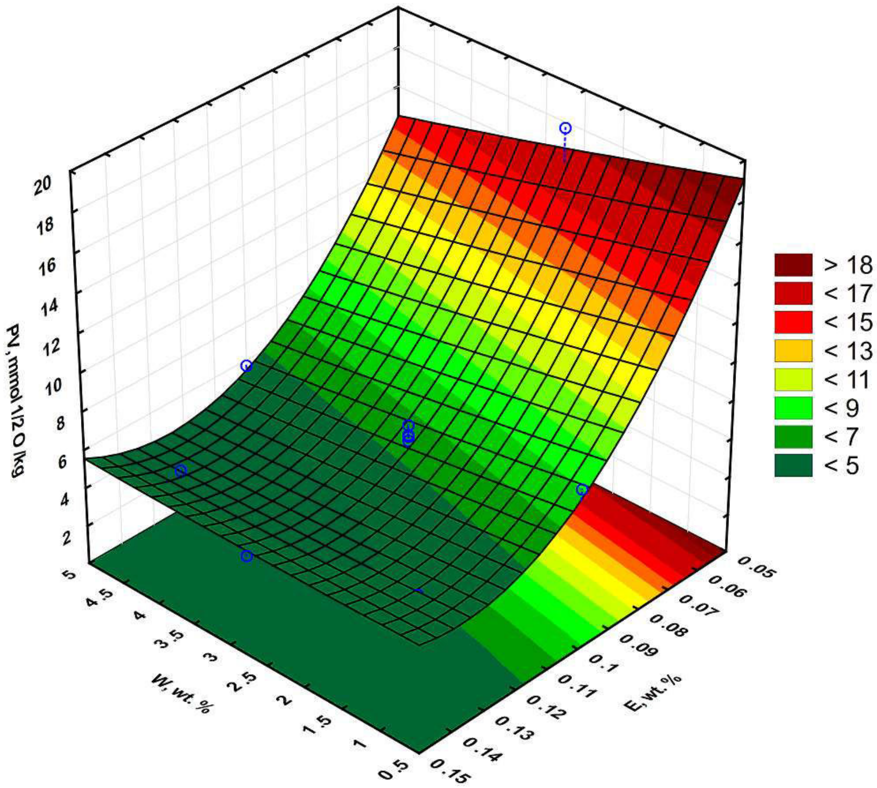

Fig. 2. Dependence of oleogel peroxide value (PV) on sunflower seed wax (W) and tocopherols (E) content

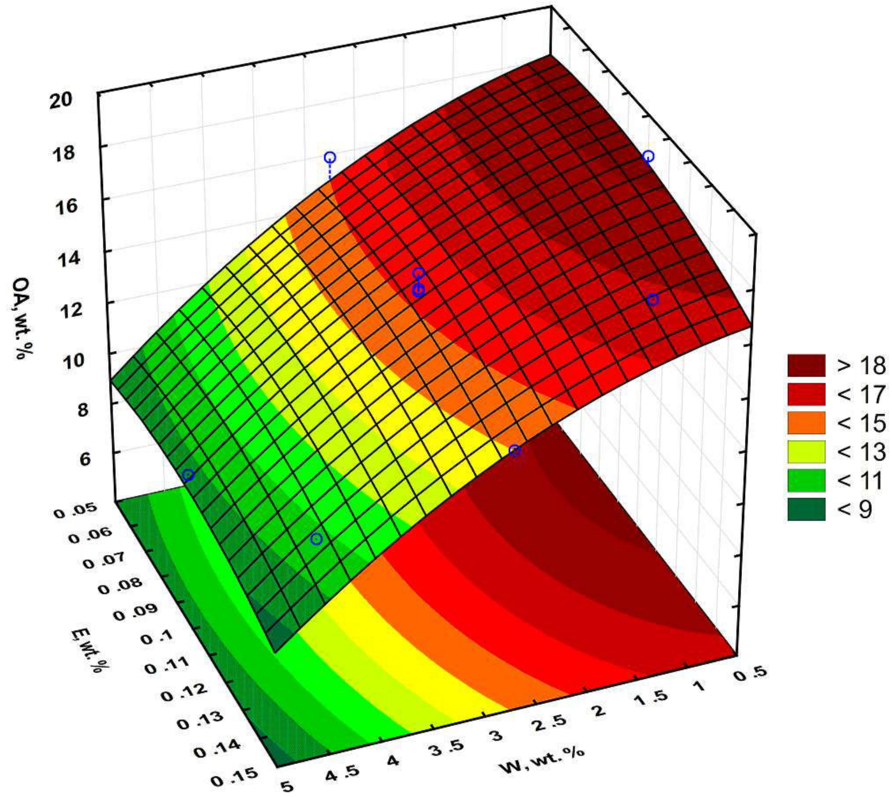

Fig. 3. Dependence of oil absorption (OA) on sunflower seed wax (W) and tocopherols (E) content

range of 0.10 to 0.14 wt.% of tocopherols. The effect of sunflower seed wax content on the studied parameters is less pronounced and is noticeable starting from the mass fraction of 1.8%. In turn, an increase in the content of this component in the studied fatty systems significantly affects their sorption properties. In particular, the oil content of the products decreases monotonically and reaches the minimum values at the sunflower seed wax content of 4 wt.% and above.

Conclusions

We have developed a mathematical model, which allows us to predict oxidative resistance, and sorption properties of oleogels based on their compositions. The intervals of effective values of mass fractions of oleogel components were determined as follows: tocopherol content is 0.10–0.14 wt.% and the sunflower seed wax content is 1.8–4.0 wt.%. At these concentrations, the maximum value of the yield functions is reached. A further increase in the content of these components in the composition of oleogels is inappropriate. In particular, an excessive concentration of tocopherols leads to a prooxidative effect; an increase in the content of sunflower seed wax has little effect on the response, but significantly impairs the rheological properties of oleogels.

The obtained results can serve as a scientific basis for the development of technology for the production of oleogels as novel special-purpose fatty systems.

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ОКИСНЮВАЛЬНА СТІЙКІСТЬ І СОРБЦІЙНІ ВЛАСТИВОСТІ ОЛЕОГЕЛІВ ЯК ЖИРОВИХ СИСТЕМ НОВОГО ПОКОЛІННЯ

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Жири як складна суміш ацилгліцеринів з речовинами ліпідного та неліпідного характеру є невід'ємною частиною харчування людини. Наявність в складі ацилгліцеринів транс-ізомерів жирних кислот обумовлює низку серцево-судинних захворювань та хвороб порушення метаболізму. Перспективним підходом до вирішення проблеми мінімізації вмісту вказаних небажаних сполук у рецептурах харчових продуктів є створення жирових систем нового покоління – олеогелів, які є об'єктом даного дослідження. Як дисперсійне середовище олеогелів було використано високоолеїнову соняшникову олію, що на відміну від олії традиційних сортів дає можливість одержувати системи з підвищеною стійкістю до окиснення. Дисперсною фазою вказаних жирових систем було обрано віск насіння соняшника і токофероли. Вибір вказаних компонентів ґрунтувався на їх властивостях створювати в олеогелях тривимірну структуру із заданими термомеханічними характеристиками. На даний момент бракує інформації щодо впливу вмісту дисперсної фази на технологічні параметри олеогелів, а саме на окиснювальну стійкість і сорбційні властивості. Метою даної роботи було встановлення зазначених характеристик олеогелів та знаходження їх залежностей від рецептурного складу. 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 розроблено математичну модель, яка дозволяє, виходячи з даних про компонентний склад олеогелів, прогнозувати їх окиснювальну стійкість і сорбційні властивості. Обґрунтовано раціональні масові частки компонентів дисперсної фази олеогелів: вміст токоферолів 0,10–0,14 мас.%, вміст воску насіння соняшника 1,8–4,0 мас.%. Отримані результати слугуватимуть науковим підґрунтям для розробки технології промислового виробництва олеогелів як жирових систем нового покоління.

Ключові слова: олеогель, воск, токоферол, окиснювальна стійкість, математичне моделювання.

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