

## IMPACT OF VEGETABLE OILS ON THE FATTY ACID COMPOSITION OF A MILK-CONTAINING CURD PRODUCT

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### Abstract

For the development of enriching compositions based on vegetable oils, which will expand the range of dairy products with a balanced fatty acid composition, mathematical calculations have been proposed. A study of the fatty acid composition aimed at developing a blend based on natural vegetable oils, followed by partial replacement of milk fat in the technology of milk-containing products was conducted.

Sour milk curd with a mass fraction of fat of 5%, obtained with separation method was used as a sample. To optimize the fatty acid composition of the blend, mathematical calculations were performed using the target matrix. The calculation was based on the fatty acid composition of milk fat. The application of the mathematical method allows to quickly and with a sufficient level of accuracy adjusting the composition of the blend for variable values of the content of individual fatty acids in milk fat. The study of the fatty acid composition of the product of milk-containing curd with 50% replacement of milk fat for a blend of natural vegetable oils was conducted using gas-liquid chromatography.

Selection of vegetable oils for blending - corn, rapeseed and walnut oils was conducted taking into account the possibility of balancing the fatty acid composition of the milk-containing curd product and their compatibility with each other according to organoleptic evaluation. Organoleptic evaluation of fermented milk pastes was performed by the State Standards of Ukraine ISO 6564:2005.

The percentage of replacement of milk fat for a blend of vegetable oils is substantiated by that the group of dairy products include products whose degree of replacement of components does not exceed 50%. Quantitative fatty acid content was determined by the peak area on the chromatogram compared to the peak area of fatty acids with a known concentration. The fatty acids at the peaks of the chromatogram are indicated by the number of carbon atoms in it, followed by a colon indicating the number of double bonds in the molecule. As a control, sour milk curd with a mass fraction of fat 5% was used, which corresponds to the test sample.

The analysis of chromatograms allowed making a conclusion about reduction in comparison with the control sample, almost twice, quantity of saturated fatty acids of a product of milk-containing curd - 30% with the percentage of monounsaturated fatty acids increasing slightly by 4.44%. The total amount of polyunsaturated fatty acids increased by 23.6%, an increase in the amount of  $\omega$  - 6 by 2.2%.

It was determined that the proposed 50% replacement of the mass fraction of milk fat of milk-containing curd product allows to sufficiently increase the content of monounsaturated and polyunsaturated fatty acids, as well as bring the fatty acid composition of milk-containing product to the theoretical "ideal fat" recommended by nutritionists.

**Key words:** Blend, Oil, Chromatography, Milk-containing product.

## 1. Introduction

Blends of vegetable oils are used for purposeful regulation of the content of polyunsaturated fatty acids in the resulting product [1, 2].

The scientists have proposed the use of two or three component blends of sunflower [3], soy [4], corn [5], and olive oils [6] with optimized fatty acid composition. These blends have original organoleptic characteristics and are commercially viable [7, 8].

The disadvantage of their use is restrictions in the products of the oil and fat industry, in particular in the production of mayonnaise and sauces. Also the possibility of combining with a milk base has not been scientifically studied.

The use of rapeseed oil was suggested for creation of dietary products. It contains a sufficient amount of linolenic acid (7 - 15%) and linoleic acid (15 - 25%) [9]. Due to the specific organoleptic properties of rapeseed oil, the quantitative percentage of its use in the blend should be strictly limited to prevent unwanted taste and odor of dairy products.

The possibility of using a blend of three oils was studied: sunflower [10], soy [11] and linseed [12].

Through the production of dairy products it should be taken into account the fact that the composition of blends, which contain linseed oil, should be consumed only in cold form and not subjected to heat treatment as a large amount of polyunsaturated fatty acids is lost. Herewith, the mass fraction of linseed oil in the blend should not exceed 5%, as further it would provoke defects in taste and smell of blends with its use.

Considering the abovementioned, the authors suggest to create a three-component blending system using the following vegetable oils: corn, canola and walnut. It is the presence of  $\gamma$  - tocopherol in the developed blend due to the addition of corn oil [13], that will slow down the oxidative processes of unsaturated bonds, and thus prevent further formation of aldehydes, which will provoke rancidity of the oil mixture with accompanying specific taste and smell [14]. The lack of polyunsaturated fatty acids can be compensated by using rapeseed oil in the blend. The content of which is 27.81% [15, 16].

To give pleasant organoleptic properties to the developed blend and for enrichment with polyunsaturated fatty acids, it was also decided to add walnut oil. In its composition, the oil contains 75% of the total content of polyunsaturated fatty acids, among which  $\omega$ -3 - 13.6% [17].

The purpose of scientific research is to establish the impact of a blend of natural vegetable oils on the fatty acid composition of a curd product, followed by partial replacement of milk fat in the technology of dairy products.

## 2. Materials and Methods

### 2.1 Preparation of etalon (standard)

Sour milk curd with a mass fraction of fat of 5%, obtained with separate method was used as a sample. The sample did not require any preliminary preparation for conducting the scientific research.

### 2.2 Preparation of model samples

Model samples of milk-containing curd product were prepared in the following sequence: a mixture of vegetable oils with emulsifier (a mixture of mono- and diglycerides distilled in the amount of 3 - 4% of the total weight of the prepared mixture) was heated to 80 - 85 °C and cooled to 60 - 70 °C; then received a milk-fat mixture, namely skim milk was heated to a temperature of 60 - 70 °C and with constant stirring was added to the prepared mixture of vegetable oils; the resulting mixture was dispersed for 10 - 15 min. to form a stable emulsion.

The amount of milk-vegetable emulsion administration ranged from 10 to 70% with an interval of 10%.

The milk-fat mixture was subjected to pasteurization under the conditions traditional for the production of sour milk curd: temperature -  $90 \pm 2$  °C with a holding time of 3 - 5 min.; cooled to a temperature of 28 - 30 °C. Bacterial starter culture based on mesophilic lactic acid streptococci was introduced, the number of which is recommended by manufacturers and depends on the temperature of milk for fermentation. After about 1.5 hours, rennet is added to fermented milk with a pH of approximately 6.3, stirred for 10 - 15 min.

Normalization for fat sour milk curd was mixed with cream of 50 - 55% fat. The mass fraction of fat was set depending on the dose of a mixture of vegetable oils and ensures the production of samples of sour milk curd with a mass fraction of fat of 5%.

Based on the organoleptic evaluation of the samples, the possibility of replacing 50% of milk fat with a mixture of vegetable oils was established. Adding more of them caused the appearance of uncharacteristic taste of vegetable fats in dairy products. In addition, the selected percentage is regulated by current regulations, according to which the replacement rate of 50% is indicated as the maximum allowable for dairy products.

### 2.3 Gas-liquid chromatography method

The fatty acid composition was examined by gas-liquid chromatography using a Hewlett Packard HP-6890 gas chromatograph, according to this method a mixture of fatty acid methyl esters 37 Component FAME

Mix, Supelco (Cat. № 47885-U) was used to identify chromatographic peaks and calculate chromatograms. Chromatograms were recorded and processed using a personal computer equipped with HP ChemStation software [18].

### 3. Results and Discussion

#### 3.1 Determination of the rational amount of oils in the blend by mathematical calculations

According to the literature review, the basis of mathematical calculations for the preparation of balance blends using 3 oils, is proposed (recommended by nutritionists) ratio  $\omega - 6:\omega - 3$  from 6 : 1 to 10 : 1, with the ratio of groups saturated fatty acids (SFA), monounsaturated fatty acids (MUFA), polyunsaturated fatty acids (PUFA) should be the closet value to 1 : 1 : 1. The purpose of the calculations: simultaneous optimization of several conflicting functions in the distinctly set determination area (correction of the three main groups of fatty acids - SFA : MUFA : PUFA and essential fatty acids of groups  $\omega - 6:\omega - 3$  in the development blend). One of the possible options for achieving this goal is the implementation of mathematical calculations and their optimization in the environment MatLab15 [19]. Use of MatLab15, the required variable amount of all three selected oils in the blend (rapeseed, corn, and walnut), and the percent of milk fat 50% in the milk-containing curd product is calculated.

Guided by the above goal, we will give a formalized description of the development of a blend with an optimized fatty acid composition based on selected natural vegetable oils.

Let's consider the following matrix of experimental data.

$$Z = \begin{pmatrix} z_{11} & z_{12} & \dots & z_{1n} \\ z_{21} & z_{22} & \dots & z_{2n} \\ \dots & \dots & \dots & \dots \\ z_{m1} & z_{m2} & \dots & z_{mn} \end{pmatrix} = \{z_{ij}\}_{i=1, j=1}^{m, n}, \quad (1)$$

Where:  $i$  - the sequence number of fatty acid (line),  $j$  - sequence number of vegetable oil (column) in the table of experimental data,  $z_{ij}$  - quantity of  $i$  fatty acid in  $j$  vegetable oil,  $n$  - general number of vegetable oils,  $m$  - general number of fatty acids in the table of experimental data.

For the grouping (selection, separation) of essential fatty acids of groups  $\omega - 6:\omega - 3$  and the main groups of fatty acids - SFA, MUFA, PUFA in  $z$  matrix, let's form arrays (vectors) of indices for each group.

$$\alpha_k = (r_1^{(k)}, r_2^{(k)}, \dots, r_{n_k}^{(k)}) \in N^{n_k}, \quad k = 1, 2, \dots, l, \quad (2)$$

Where:  $r_i^{(k)}$  - number of fatty acid (number of line) in matrix  $Z$ , included in  $k$  group of fatty acids,  $N^{n_k}$  - set of  $n_k$  - measuring space, consisted of  $n_k$  - measuring vectors of natural number,  $l$  - general number of fatty acids groups in  $Z$  matrix of experimental data ( $l = 5$ ). We specify:  $a_1, a_2, a_3$  - are the arrays of indices (lines) of fatty acids, correspondingly, SFA, MUFA and PUFA in matrix  $Z$ , and  $a_4$  and  $a_5$  - arrays of indices of essential fatty acids of the groups  $\omega - 6$  and  $\omega - 3$  respectively.

Then the matrix of fatty acids was determined, which elements are calculated by formula:

$$A = \{a_{kj}\}_{k=1, j=1}^{l, n} \quad (3)$$

$$a_{kj} = \sum_{i=1}^m z_{ij}, \quad k = 1, 2, \dots, l, \quad j = 1, 2, \dots, n,$$

Where:  $a_k$  - array of indices of  $k$  group of fatty acids, determined by the ratio (2). We specify, that at the content level  $a_{kj}$  - is a number of fatty acids of  $k$  group in  $j$  vegetable oil.

Given that not all vegetable from the matrix  $Z$  are used to compile balanced blends, but only some subjects of them, we introduce another vector of indices of selected vegetable oils to form a balanced blend. Where  $\beta_i$  - index of selected vegetable oil (column number) in  $Z$  matrix and  $p$  - general number of oils, selected for blend. Note, that  $\beta_p$  (the last element of  $\beta$  vector) - is the number of milk oil in  $Z$  matrix.

Forming the vectors-columns that correspond to the selected set of oils for blend of  $A$  matrix was as follows:

$$c_k = \begin{pmatrix} a_{1\beta_k} \\ a_{2\beta_k} \\ \dots \\ a_{l\beta_k} \end{pmatrix}, \quad k = 1, 2, \dots, p. \quad (4)$$

Let's mark  $x_i$  part  $i$  oil share in general mixture as ( $0 \leq x_i \leq 1$ ). It is obvious, that  $\sum_{i=1}^p x_i = 1$ . Since in the mixture the milk oil should be 50%, that is  $x_p = 0.5$ , so  $\sum_{i=1}^{p-1} x_i = 0.5$ .

Then the vector-function was constructed as:

$$g(x) = c_1 x_1 + c_2 x_2 + \dots + c_{p-1} x_{p-1} + 0.5 c_p = \sum_{i=1}^{p-1} c_i x_i + 0.5 c_p, \quad (5)$$

Where a mixture of oils consists of the share vectors of different vegetable oils:

$$X = (x_1, x_2, \dots, x_{p-1}),$$

And the total amount and ratio of fatty acid groups in the oil mixture consists of the groups of basic fatty acids of each individual oil and is described by the following function:

$$g(x) = \begin{pmatrix} g_1(x) \\ g_2(x) \\ \dots \\ g_l(x) \end{pmatrix}.$$

Let's note that the function  $g_k(x)$  ( $k = 1, 2, \dots, l$ ) describes the general number of fatty acids in the blend, that are related to the  $k$  group of fatty acids ( $k = 1$  - SFA,  $k = 2$  - MUFA,  $k = 3$  - PUFA,  $k = 4$  -  $\omega$  - 6,  $k = 5$  -  $\omega$  - 3) at the set share vector of  $x$  oils in the mixture. The function  $g_k(x)$  can be presented as:

$$g_k(x) = a_{k\beta_1}x_1 + a_{k\beta_2}x_2 + \dots + a_{k\beta_{p-1}}x_{p-1} + 0.5a_{k\beta_p} = \sum_{i=1}^{p-1} a_{k\beta_i}x_i + 0.5a_{k\beta_p}$$

Since  $\sum_{i=1}^{p-1} x_i = 0.5$ , the dimensionality of  $x$  vector can be reduced, so the dimensionality of problem can also reduce by unit, and the one of coordinates of this vector can be determined through the all other. For example, let's determine the coordinate  $x_{p-1}$ ,

$$x_{p-1} = 0.5 - \sum_{i=1}^{p-2} x_i. \quad (6)$$

So, taking into account (6), vector-function (5) can be presented as:

$$g(x) = \sum_{i=1}^{p-2} c_i x_i + c_{p-1} \left( 0.5 - \sum_{i=1}^{p-2} x_i \right) + 0.5c_p = \sum_{i=1}^{p-2} (c_i - c_{p-1}) x_i + 0.5(c_{p-1} + c_p) \quad (7)$$

Where vector  $x$  has now the dimensionality  $p-2$ , and takes into account the dependence:

$$g_k(x) = a_{k\beta_1}x_1 + a_{k\beta_2}x_2 + \dots + a_{k\beta_{p-1}}x_{p-1} + 0.5a_{k\beta_p} = \sum_{i=1}^{p-1} a_{k\beta_i}x_i + 0.5a_{k\beta_p}$$

$$\sum_{i=1}^{p-2} x_i \leq 0.5, \quad 0 \leq x_i \leq 0.5 \quad i = 1, 2, \dots, p-2$$

According to the problem setting, the ratio of the main groups of fatty acids SFA : MUFA : PUFA can be maximally approximated to 1 : 1 : 1, and the ratio of essential fatty acids  $\omega$  - 6 :  $\omega$  - 3 must be from 6 : 1 to 10 : 1. It means that the aim of research can be described by the following criteria functions:

$$\begin{aligned} f_1(x) &= \left( \frac{g_1(x)}{g_2(x)} - 1 \right)^2, & f_2(x) &= \left( \frac{g_1(x)}{g_3(x)} - 1 \right)^2, \\ f_3(x) &= \left( \frac{g_2(x)}{g_3(x)} - 1 \right)^2, & f_4(x) &= \left( \frac{g_4(x)}{g_5(x)} - q \right)^2 \end{aligned} \quad (8)$$

Where:  $q = 6, 7, 8, 9, 10$ .

The synchronous minimization of functions (8) on the set of admissible solutions gives a possibility to receive blend with optimized fatty acid composition.

$$\Omega = \left\{ x : x = (x_1, x_2, \dots, x_{p-2}); \quad 0 \leq x_i \leq 0.5, \quad i = 1, 2, \dots, p-2; \quad \sum_{i=1}^{p-2} x_i \leq 0.5 \right\} \quad (9)$$

Thus, let's come to the following problem of multi-criteria optimization - to determine the optimal vector  $x^* \in R^{p-2}$  ( $R^{p-2}$  Euclid space of dimensionality  $p-2$ ), that provides the accomplishment of the following condition:

$$x^* = \arg \min_{x \in \Omega} f(x) \quad (10)$$

Where the set  $\Omega$  is set by the ratio (9), and  $f(x)$  - vector criterion of optimality of the type as follows:

$$f(x) = \begin{pmatrix} f_1(x) \\ f_2(x) \\ f_3(x) \\ f_4(x) \end{pmatrix}$$

Where components are determined by formula (8).

The method of successive minimization of concessions was used for the solution of optimization problem (10). According to it, the problem of multi-criteria optimization is reduced to the one of nonlinear programming

$$\min_{\gamma \in R^1, x \in \Omega} \gamma$$

With following limitations:

$$f_i(x) \leq w_i \gamma, \quad i = 1, 2, 3, 4$$

Where:  $w_i$  - the set weight multipliers that determine the importance degree of scalar criteria  $f_i(x)$  and  $\gamma$  - artificially introduced additional parameter of optimization (specific concession of criteria).

On the base of this method the program in the environment of mathematical package MatLab15 was elaborated and used at calculating experiments.

Table 1 shows the results of computational experiments, which to obtain a quantitative value of the optimization of a three-component system of natural vegetable oils with such a ratio (SFA : MUFA : PUFA) - 1 : 1 : 1. And for PUFA  $\omega$  - 6 and  $\omega$  - 3 the ratio is: for healthy people - 6 : 1 and 8 : 1; for people with metabolic disorders (lipid metabolism) - 10 : 1.

Data of mathematical calculating are presented in the Table 1.

Analysis of the data shown in Table 1 shows that the optimal ratio of the main three groups of fatty acids, namely SFA : MUFA : PUFA is 1 : 1 : 1, and the ratio of PUFA  $\omega$  - 6 and  $\omega$  - 3, as 6 : 1.

Such a blend of vegetable oils will be biologically complete, will meet the needs of the body in essential substances, will have high quality organoleptic

**Table 1. The results of calculating the optimal fatty acid composition of the created blends**

Mass fraction of fatty acids, %	Correlation SFA : MUFA : PUFA		
	1.2 : 1.1 : 1	1.3 : 1.3 : 1	1.4 : 1.4 : 1
	Correlation $\omega$ -6: $\omega$ -3		
	6 : 1	8 : 1	10 : 1
SFA	36.55	36.77	36.94
MUFA	34.25	36.00	37.28
PUFA	29.02	27.00	25.51

properties and low cost for consumers [20].

The main condition for the inclusion of vegetable oils in the diet is the ratio of essential fatty acids  $\omega$  - 6 and  $\omega$  - 3; for healthy people - from 10 : 1 to 5 : 1; for the elderly, with disorders of lipid metabolism, as well as with cardiovascular disease - from 5 : 1 to 2 : 1 [21].

### 3.2 Control sample fatty acid composition

In accordance with Table 1, developed a blend based on natural vegetable oils (corn, canola and walnut) with a ratio of SFA : MUFA as - 1 : 1 : 1 and PUFA  $\omega$  - 6: $\omega$  - 3 as 6 : 1, which combined with milk-containing curd product. The total mass fraction of fat in the product is 5%. The obtained milk-containing curd product with 50% replacement of the mass fraction of milk fat, experimentally investigated the fatty acid composition. Control sample - sour milk curd with a mass fraction of fat of 5%.

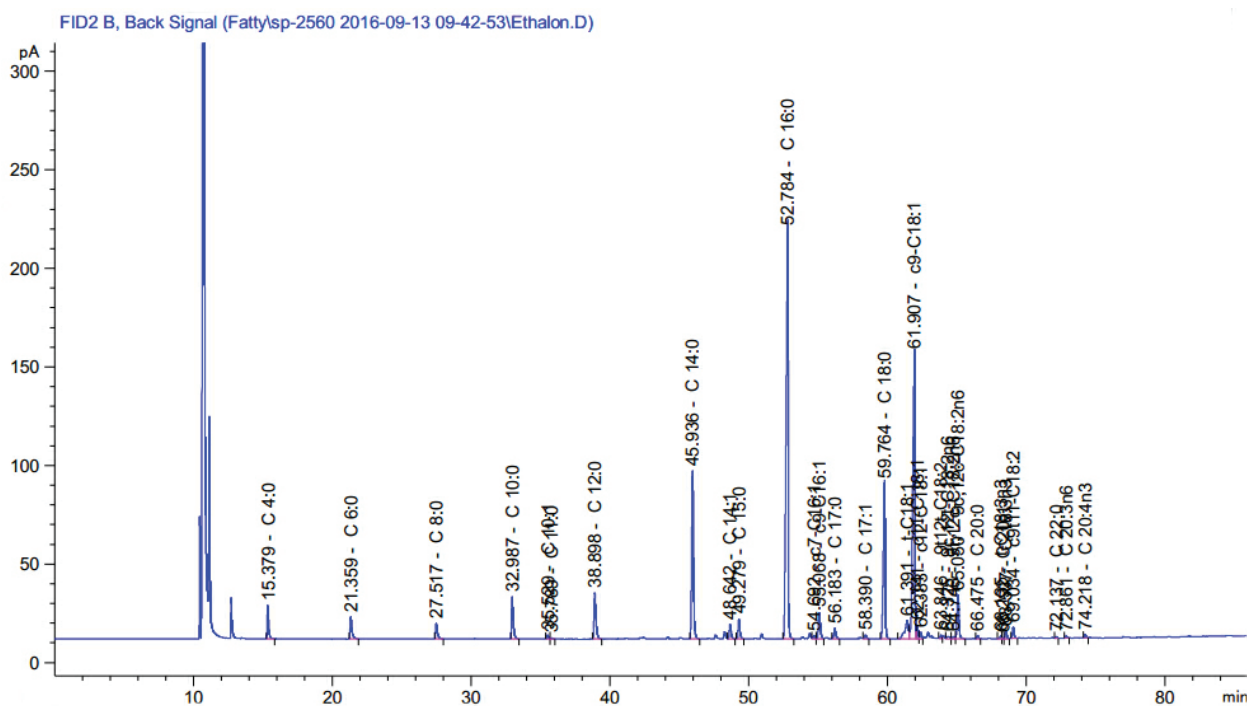
The obtained results of the fatty acid composition by

gas-liquid chromatography of the control sample are shown in Figure 1.

Figure 1 vividly demonstrates the fatty acid composition of milk fat of the sample obtained by chromatography of methylene esters in the form of peak areas (pA) and their composition by the retention time of the peaks on the chromatogram (min), i.e. the dependence of the signal (response) of the detector on the time of analysis.

Each peak is an experimental confirmation of the presence of a fatty acid, the index of which is determined by the content of carbon atoms from C1 to C30 and above (saturated, branched, unsaturated, cis- and trans-isomers, hydroxy fatty acids), and represented by the code of fatty acid (FA) above the peak indicating its quantitative content. Authenticity was established by the presence of FAs with the highest peaks - limiting FAs. In this case, the identification peaks are the highest peaks due to the presence of: palmitic fatty acid (C16:0) in the amount of 30.2%, myristic (C14:0) - 11.19% and stearic (C18:0) - 10.56%. It should be noted that all of these FAs are characteristic representatives of the fatty acid composition of milk fat from the group of unsaturated fatty acids (USFA), with a minimum amount of fatty acids from the groups of MUFA and PUFA. The only limiting indicator - 21.55%, from the group of monounsaturated fatty acids and type  $\omega$  - 9 is (c9-C18:1).

The detailed fatty acid composition and lipid saturation index of milk fat of the sample are presented in the Table 2.


**Figure 1. Chromatogram of the control sample fatty acid composition**



**Table 2. Detailed fatty acid composition and lipid saturation index of milk fat of the sample**

Ret. Time	Type	Area	Amt/Area	Norm	Grp	Name
[min]		[pA*s]		%		
15.379	BB	119.84430	1.51100	2.601367	1	C 4:0
21.359	BB	100.63174	1.28400	1.856179	1	C 6:0
27.517	BB	72.41570	1.17100	1.218174	1	C 8:0
32.987	BB	183.11761	1.10200	2.898889	1	C 10:0
35.529	BV	16.96937	1.08900	0.265469	2	C 10:1
35.789	VB	5.11958	1.07800	0.079282	1	C 11:0
38.898	BB	228.37526	1.057	3.467719	1	C 12:0
45.936	BB	760.10907	1.025	11.192306	1	C 14:0
48.642	VB	65.41635	9.57000e-1	0.899328	2	C 14:1
49.279	BB	86.52435	1.012	1.257878	1	C 15:0
52.784	BB	2102.53491	1	30.203899	1	C 16:0
54.692	VV	16.70796	9.93000e-1	0.238337	2	c7-C16:1
55.068	VV	135.64468	9.93000e-1	1.934959	2	c9-C16:1
56.183	BB	54.67707	9.90000e-1	0.777607	1	C 17:0
58.390	BB	18.33288	9.83000e-1	0.258883	2	C 17:1
59.764	BB	749.87231	9.81000e-1	10.567594	1	C 18:0
61.391	VV	175.28279	9.75000e-1	2.455069	2	t-C18:1
61.907	VV	1539.25403	9.75000e-1	21.559303	2	c9-C18:1
62.141	VV	49.79091	9.75000e-1	0.697388	2	c11-C 18:1
62.383	VV	27.19818	9.75000e-1	0.380947	2	c12-C 18:1
63.846	BV	14.37331	9.68000e-1	0.199872	3	9t12t-C18:2
64.325	VV	15.52675	9.68000e-1	0.215911	3	9c,12t-C18:2n6
64.746	VV	11.92085	9.68000e-1	0.165769	3	9t,12c-C18:2n6
65.050	VB	202.95251	9.68000e-1	2.822212	3	9c,12c-C18:2n6
66.475	VB	11.12626	9.66000e-1	0.154400	1	C 20:0
68.135	BV	9.32302	9.62000e-1	0.128840	3	t-C18:3n3
68.292	VV	3.39328	9.60000e-1	0.046796	2	C 20:1
68.507	VB	32.01176	9.62000e-1	0.442389	3	C 18:3n3
69.034	BV	48.25617	9.68000e-1	0.671039	3	c9t11-C18:2
72.137	VB	4.37722	9.54000e-1	0.059988	1	C 22:0
72.861	BB	7.51360	9.49000e-1	0.102432	3	C 20:3n6
74.218	BV	13.27083	9.43000e-1	0.179775	3	C 20:4n3
Totals :	100					
Group summary						
Group	Use	Area	Norm	Group Name		
ID		[pA*s]	%			
1		4478.72538	66.335281			
2		2047.99044	28.736479			
3		355.14880	4.928239	Polyunsaturated fatty acids		

### 3.3 Fatty acid composition of milk-containing curd products

Fatty acid composition indicators of milk-containing curd product with 50% replacement of milk fat, shown in Figure 2.

Analysis of the chromatogram (Figure 2) of the fatty acid composition of milk-containing curd product - was conducted with the method identical to the chromatogram (Figure 1). It should be noted that

after 50% replacement of the mass fraction of milk fat with the developed blend based on oil of vegetable origin, limiting the FA with the highest peaks are now representatives of the groups MUFA and PUFA. Namely: (c9-C18:1) in the amount of 27.88% and (9c, 12c-C18:2n6) - 23.04%. A significant difference in the FA composition of the milk-containing curd product compared to the standard is observed due to a decrease in the number of unsaturated fatty acid groups: (C18:0) by 5.19%, (C16:0) by 11.02% and

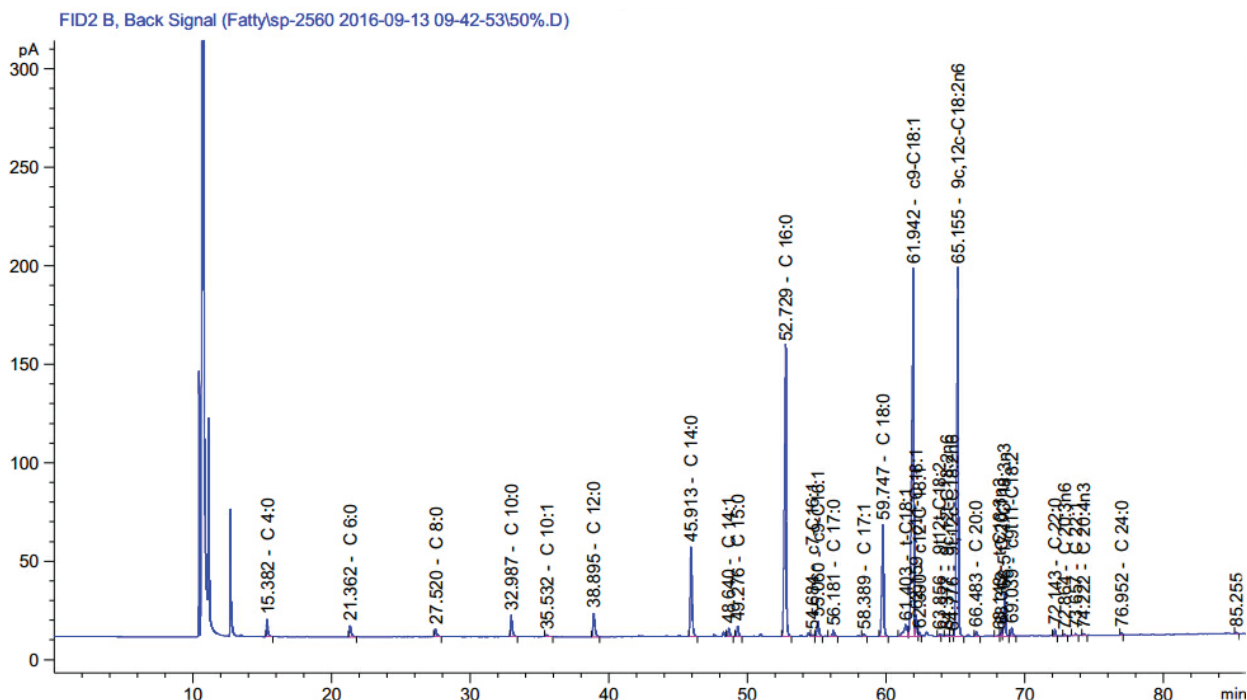


Figure 2. Chromatogram of fatty acid composition of milk-containing curd products

(C14:0) by 5.25%, with a significant increase MUFA and PUFA groups: (c9-C18:1) by 6.33%, (9c, 12c-C18:2n6) by 20.22%, (C18:3n3) by 1.91%, as well as the diversity of their representatives.

The detailed fatty acid composition and lipid saturation index of the milk-containing curd product are presented in Table 3.

Analyzing the results of chromatographic analysis of the fatty acid composition of milk-containing curd product, we see a reduction, almost twice, the amount of saturated fatty acids - 28.1%, compared with the control sample. Percentage of monounsaturated fatty acids increases slightly by - 4.44%.

It should be noted that the total number of PUFAs increased by 23.6%, the increase in the number of  $\omega$  - 6 by 2.2%.

The results showed that as the proportion of corn oil (CO) increased, the levels of short-chain, medium-chain, and saturated fatty acids (SFAs) were decreased ( $p < 0.001$ ), while the oleic and linoleic acid and unsaturated fatty acid (USFA) levels were increased. Blending butter oil (BO) with CO increased the iodine value, refractive index and peroxide value and decreased the saponification value and free fatty acid content. The oxidation rate of BO was reduced as the percentage of dihydroquercetin (DHQ) increased. Thus, it can be concluded that CO and DHQ can be used to increase the shelf life of BO and enhance the health effects of milk fat. The modern trends in healthy eating are such that preference is given to natural products

rather than complex chemical compounds. Blending butter oil with corn oil led to an increase in the level of USFAs and a decrease in the level SFAs as well as an improvement in the proportion of omega-3 fatty acids to omega-6 fatty acids. Moreover, using corn oil to prepare butter blends yields products with desirable properties. Dihydroquercetin helps increase the shelf life of dairy products by 1.5 - 3 times. In addition, dihydroquercetin inhibits the progress of rancidity in dairy products already subjected to oxidation processes [5, 22].

After the comparative characteristics, it is safe to say that 50% replacement of the mass fraction of milk fat by the developed blend of vegetable oils - causes qualitative changes in the fatty acid composition of milk-containing curd product. It is seen that the addition of mixtures of vegetable oils will significantly increase the balance of fatty acid composition of products and the content of polyunsaturated fatty acids deficient for animal fats.

According to scientists, one of the advantages of using vegetable oils is that all SFA in their composition is easily absorbed by the body and is not deposited on the walls of blood vessels [23].

### 3.4 Comparison of predicted and obtained results

The correspondence of the indicators of the fatty acid composition of the developed milk-containing curd product to the results obtained using the mathematical calculations are shown in Table 4.

**Table 3. Fatty acid composition and lipid saturation index of the milk-containing curd product**

RetTime	Type	Area	Amt/Area	Norm	Grp	Name
[min]		[pA*s]		%		
21.362	BB	51.57097	1.28400	0.941173	1	C 6:0
27.520	BB	37.30853	1.17100	0.620961	1	C 8:0
32.987	BB	92.83350	1.10200	1.454071	1	C 10:0
35.532	BB	11.49242	1.08900	0.177885	2	C 10:1
38.895	BB	116.45439	1,057	1.749565	1	C 12:0
45.913	BB	408.27716	1,025	5.948099	1	C14:0
48.64	VB	36.40994	9.57000e-1	0.495258	2	C14:1
49.276	BB	45.86366	1,012	0.659703	1	C15:0
52.729	BB	1349.80103	1	19.185319	1	C16:0
54.684	VV	10.79208	9.93000e-1	0.152319	2	c7-C16:1
55.06	VV	77.77944	9.93000e-1	1.097775	2	c9-C16:1
56.181	VB	30.13986	9.90000e-1	0.424107	1	C17:0
58.389	BB	10.50853	9.83000e-1	0.146823	2	C 17:1
59.747	BB	527.61902	9.81000e-1	5.371099	1	C 18:0
61.403	BV	112.30945	9.75000e-1	1.556396	2	t-C18:1
61.942	VV	2014.19934	9.75000e-1	27.888785	2	c9-C18:1
62.159	VV	76.98659	9.75000e-1	1.066888	2	c11-C 18:1
62.39	VV	16.10002	9.75000e-1	0.223116	2	c12-C 18:1
63.856	BV	8.3375	9.68000e-1	0.114712	3	9t12t-C18:2
64.377	VV	11.78288	9.68000e-1	0.162116	3	9c,12t-C18:2n6
64.776	VV	7.48258	9.68000e-1	0.10295	3	9t,12c-C18:2n6
65.155	VB	1674.62659	9.68000e-1	23.040538	3	9c,12c-C18:2n6
66.483	BB	18.85454	9.66000e-1	0.258876	1	C 20:0
68.143	VV	5.17311	9.62000e-1	1.075684	3	t-C18:3n3
68.312	VV	20.94902	9.60000e-1	0.285847	2	C 20:1
68.517	VB	172.22588	9.62000e-1	2.354901	3	C 18:3n3
69.039	BV	35.17686	9.68000e-1	0.483985	3	c9t11-C18:2
72.143	VB	19.09351	9.54000e-1	0.258901	1	C 22:0
72.864	BB	4.37857	9.49000e-1	1.064011	3	C 20:3n6
73.657	BB	5.87665	9.49000e-1	0.079268	2	C 22:1
74.222	BV	7.97025	9.43000e-1	0.106827	3	C 20:4n3
76.952	BV	8.35953	9.44000e-1	0.112164	1	C 24:0
Totals :	100					
Group summary						
Group	Use	Area	Norm	Group Name		
ID		[pA*s]	%			
1		2768.5637	38.323916	Saturated fatty acid,		
2		2393.40349	33.170360	Monounsaturated fatty acids		
3		1927.15422	28.505724	Polyunsaturated fatty acids		

**Table 4. Comparative characteristics of the fatty acid composition obtained by computational and experimental methods**

Mass fraction of fatty acids, %	Ratio of SFA : MUFA : PUFA, %	
	1.2 : 1.1 : 1	1.5 : 1.2 : 1
	Ratio of $\omega - 6 : \omega - 3$ (6:1)	
	The results of calculating the mathematical model	Experimental results of chromatographic analysis
SFA	36.55	38.33 ± 1.91
MUFA	34.25	33.17 ± 1.65
PUFA	29.02	28.50 ± 1.42



Table 4 shows that the addition of mixtures of vegetable oils will significantly increase the balance of fatty acid composition of products and the content of deficient for animal fats polyunsaturated fatty acids.

Based on the obtained data shown in Table 4, we can see slight deviations of the experimental data of SFA, MUFA, PUFA from the predicted data obtained using the mathematical model, which don't exceed the total allowable readings  $\pm 1.5 - 10\%$ . The difference between these values is related to the reading of chromatograph, which is acceptable and in accordance with generally accepted standards is not more than 5%.

The results obtained experimentally are explained by the use of a rational amount (calculated mathematically) of oils in the blend, which determines the required ratio of fatty acids (1 : 1 : 1). The difference between the obtained results and the predicted ones (for SFA - 1.78; MUFA - 1.08; PUFA - 0.52) associated with:

1. The dependence of the fatty acid composition of oils in the blend on natural factors and the season.
2. Variations in the ratio of fatty acids in cow's milk, which depends on the season, feeding ration, and breed of pet.

Both of the reasons are unpredictable. Therefore the average values of the fatty acid composition of blended oils and whole milk are appropriate. Based on the above arguments, the difference between the ratios of fatty acid groups obtained experimentally and mathematically can be considered acceptable.

Comparing the results of the study of the FA composition of the product of milk-containing curd with the addition of a blend of vegetable oils with similar results of other authors of scientific publications, first, we should say about creating completely different methods of approaching this goal. Secondly, it is a different composition of oils in the developed blends and thirdly, the variety of tasks and results of fatty acid analysis. Therefore, scientists in the food industry have proposed various mathematical methods for calculating the amount of oils in the blend. For example, the authors of the article [24], used the method of linear programming to develop a blend. However, although this method is known in theory, its practical application does not always give a positive result. The disadvantages of this model are resource constraints, which can nullify the decision. The blend of vegetable oils developed with its use (68% - sunflower oil, 25% - olive oil, 7% - linseed oil), has a low level of resistance to oxidation, which in turn will have a detrimental effect on the quality and shelf life of dairy products using such a blend in its composition.

Based on the fact that modern packages of symbolic mathematics do not allow obtaining a sufficiently

compact overview formula for the number of components exceeding the 3-component system, the authors [25], suggest the use of a computer program to create blends. Under such conditions, the optimization of the fatty acid composition of the mixture is based on solving extreme problems with linear non-negative constraints on the variable fractions of the composition of oils in the mixture. In this case, the most effective method of analysis is the use of linear gradient-type optimization. However, the 4-component blend created in this way (46.9% - olive oil, 33.6% - linseed oil, 14.6% - sunflower oil, 15.9% - corn oil), will not only be expensive to use as a component of optimization in the technology of dairy products, but also a further combination of flaxseed and olive oils with a milk base is impossible due to their inherent specific organoleptic properties.

Belynskaia *et al.*, [26], also determined the fatty acid composition (by gas chromatography) of created blends of vegetable oils with the calculation of the percentage of each in the blend (soybean oil - 72%, sesame oil - 13.5 - 15.5%, amaranth oil - 26.4 - 25.88%, for  $\omega - 6:\omega - 3$ , as 9.3 : 1). However, amaranth and sesame oils, which have a low amount of  $\omega - 3$  in their composition (0.34% and 1.3%, respectively), and soybean oil, which has a relatively higher rate of  $\omega - 3$  (7.34%), due to its specific taste and smell - should not be included to the blended mixture, which is further planned to be used in the technology of dairy products, especially in the amount of 72%. According to the study of fatty acid composition (determined by gas chromatography) in [27], it is proposed to create blends based on: sunflower oil - 77.5%, linseed oil - 13% and camelina oil - 9.5%, for  $\omega - 6:\omega - 3$ , as 5.3 : 1. However, the ratio  $\omega - 6:\omega - 3$  chosen for calculations not only does not meet the specified standards (6 : 1), but also the content of linseed and rye oil in the blend will inciting specific pronounced taste and smell. Due to the above, the blend with this FA composition and inherent organoleptic parameters, it is better to use in the technology of meat products.

It should also be noted that various types of chromatography and spectroscopy are now successfully used for the examination of oils, with the help of which it is possible to identify and determine the quality indicators of edible oils. For example, methods: thin thin-layer chromatography, liquid chromatography, gas chromatography and gas-liquid chromatography [28, 29]. Therefore, according to [30, 31], a method of chromatography and determination of adulteration of low-fat products by three criteria is proposed simultaneously: determination of total fatty acid composition, stearin fraction and content of trans-isomers of fatty acids. However, the use of this method in the technology of milk-containing curd product is not rational, because it includes analyzes that do not

meet the purpose of research.

Summarizing feasibility of introducing dairy products with a combined fat component into the daily diet, this is to be promising and relevant for the development of the dairy industry. After all, the partial replacement of the fatty component by the created blend of vegetable oils will optimize the fatty acid composition of dairy products; enrich it with biologically active substances of plant origin.

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### 4. Conclusions

- The proposed method of calculation makes it possible to model the development of blends of vegetable oils taking into account their fatty acid composition. In this case, the blending process means multicriteria optimization of the three-component system by the ratio of the three main groups of fatty acids (SFA, MUFA, PUFA) and the ratio of  $\omega - 6$  and  $\omega - 3$ . According to the results of mathematical calculations, the optimal ratio of selected vegetable oils (corn, rapeseed, walnut) in the composition of the created blend is determined: 1.2 : 1.1 : 1, with the ratio of essential fatty acids  $\omega - 6$  to  $\omega - 3$  as 6 : 1.

- On the basis of experimental data obtained by gas-liquid chromatography, it was investigated that the addition of the developed blend based on natural vegetable oils allows to significantly adjusting the fatty acid composition of milk-containing curd products. Namely, the percentage of SFA is almost halved - 28.1% from the initial SFA - 66.33%. The number of MUFAs is slightly adjusted and increases - by 4.44% (from 28.74 to 33.17%), and the number of PUFAs is significantly increased - by 23.6% from the initial value of PUFAs - 4.92% (Tables 2 and 3). Due to the purposeful change of the fatty acid composition of the developed milk-containing curd product, its introduction into the daily diet can slightly increase the use of essential fatty acids.

- On the basis of the received data insignificant deviations of experimental data of SFA, MUFA, PUFA from the predicted received by means of the mathematical model which do not exceed total admissible indications  $\pm 1.5 - 10\%$  are visible.

- The proposed mathematical calculations can be used to develop enrichment compositions based on

vegetable oils, which will expand the range of dairy products with a balanced fatty acid composition.

### 5. References

- [1] Petryna A., Tymchuk H., Grek O. (2010). New technologies in spreads with fillers. *Food & Ingredients Journal*, 2, pp. 14-16.
- [2] Lotysh N., Arseneva T. (2014). Selection of milk fat substitutes in order to regulate the fatty acid composition of fused cheese product. *Processes and devices of food manufactures Journal*, 3, pp. 135-144.
- [3] de Souza S. M., Lopes F. C. F., Valadares S. D., da Gama M. A. S., Renno L. N., Rodrigues J. P. P. (2019). Milk fatty acid composition of Holstein x Gyr dairy cows fed sugarcane-based diets containing citrus pulp supplemented with sunflower oil. *Semina-Ciencias Agrarias*, 4, pp. 1663-1679.
- [4] Cottica S. M., Amado D. A. V., de Aguiar S. C., Boeing J. S., Franco S. L., Zeoula L. M., Visentainer J. V. (2019). Antioxidant activity and lipid oxidation in milk from cows with soybean oil and propolis extract added to their feed. *Food Science and Technology*, 2, pp. 467-474.
- [5] El-Hadad S. S., Tikhomirova N. A. (2018). Physicochemical properties and oxidative stability of butter oil supplemented with corn oil and dihydroquercetin. *Journal of Food Processing and Preservation*, 10, (42), pp. e13765.
- [6] Aliakbarian B., Casale M., Paini M., Casazza A. B. A., Lanteri S., Perego P. (2015). Production of a novel fermented milk fortified with natural antioxidants and its analysis by NIR spectroscopy. *LWT-Food Science and Technology*, 1, pp. 376-383.
- [7] Prokopenko L., Boiniazheva L., Pavlova E. (2009). Polyunsaturated fatty acids in vegetable oils. *Fat and oil industry Journal*, 2, pp. 11-12.
- [8] Utesheva S., Nechaev A. (2007). Trends in the creation of sauces and mayonnaises functionality. *Fat and oil industry Journal*, 3, pp. 12-16.
- [9] Skoriukyna A., Nechaev A., Kotchetkova A., Barysheva A. (2002). Blended oils with a balanced fatty acid composition for a healthy diet. *Fat and oil industry Journal*, 2, pp. 26-27.
- [10] Tabakaeva O. (2007). New types of vegetable oils as a source of polyunsaturated fatty acids and selenium. *Fat and oil industry Journal*, 6, pp. 26-27.
- [11] Tabakaeva O. (2007). Functional emulsion of new generation products. *Fat and oil industry Journal*, 3, pp. 17-18.
- [12] Paronian V., Voskanina K. (2005). Ways to enrich the fatty acid composition of fat emulsion product. *Storage and processing of agricultural Journal*, 6, pp. 54.
- [13] Yvankyn A. (2007). Fats are composed of modern meat products. *Meat industry Journal*, 6, pp. 8-13.
- [14] Smoliar V. (2006). The concept of the ideal fat diet. *Problems of food Journal*, 4, pp. 14-24.
- [15] Tkachenko N. A., Kurenkova O. A., Kasyanova A. Y. (2015). Spread with symbiotic properties - new products in butter & fat industry. *Scientific Bulletin of LNU of VM*

- and Biotechnology named after S.Z. Gzhytsky, 1 (61), pp. 116-127.
- [16] Pasko O. (2009). Milk-containing products with vegetable raw materials. *Journal Dairy industry*, 7, pp. 40-41.
- [17] Belemets T., Yushchenko N., Lobok O., Radziyevska I., Polonskaya T. (2016). Optimization of composition of blend of natural vegetable oils for the production of milk-containing products. *Eastern-European Journal of Enterprise Technologies*, 5/11 (83), pp. 4-9.
- [18] Belemets T., Yushchenko N., Lobok O., Radziyevska I., Polonskaya T. (2016). Mathematical development program for calculation of fatty acid composition blend of vegetable oils. *Journal EUREKA: Life Sciences*, 5, pp. 57-66.
- [19] Sikoev Z. (2009). Improved oil consumer properties by blending. *Journal*, 1, pp. 1094-1096.
- [20] Simopoulos A. (2008). The importance of the omega - 6 / omega - 3 fatty acid ratio in cardiovascular disease and other chronic diseases. *Exp. Bio. Med. Journal*, 6, pp. 674-688.
- [21] Yatsenko O., Yushchenko N., Kuzmyk U., Pasichnyi V., Kochubei-Lytvynenko O., Frolova N., Korablova O., Mykoliv I., Voitsekhivskyi V. (2020). Research of Milk Fat oxidation processes during storage of butter pastes. *Potravinarstvo Slovak Journal of Food Sciences*, 14, pp. 443-450.
- [22] Belynskaia A., Krychkovskaia L., Zekunova T. (2009). The development of functional food product with a balanced composition of polyunsaturated fatty acids. *Technology and equipment for food production Journal*, 6, pp. 94-98.
- [23] Vasilenko L., Frolova L., Drahan Y., Moshkyna S. (2013). Creating functional blends of vegetable oils with a long shelf life. *Proceedings of the Voronezh State University of Engineering Technologies Journal*, 3, pp. 121-124.
- [24] Nykonovych S., Timofeenko T., Spyllyk Y., Skakalyn E. (2005). New types of vegetable oils "ideal" composition. *Food technology Journal*, 3, pp. 108-109.
- [25] Belynskaia A., Krychkovskaia L., Cherevychna N. (2010). Development of squalene-containing blended oil with a balanced composition of polyunsaturated fatty acids. *Eastern-European Journal of Enterprise Technologies*, 3, (8), pp. 68-70.
- [26] Topchij O., Kotlyar Y. (2015). Principles of blending vegetable oils balanced in fatty acid composition. *Eastern-European Journal of Enterprise Technologies*, 1, (6), pp. 26-33.
- [27] Yashin Y., Yashin A. (2004). Analysis of food products and beverages using high-performance liquid chromatography and ion chromatography with electrochemical detectors. *Analytical Chemistry Journal*, 12, (59), pp. 1121-1127.
- [28] Kryuk T., Trankovskaya T. (2013). Modern methods of food vegetable oil examination. *Chromatography A Journal*, 3, pp. 51-63.
- [29] Sidorova L., Minaeva Y. (2018). New method for setting vegetable fats in milk products. *Strategies for innovative development of natural sciences: Experience, problems and prospects Proceedings, Kropyvnytskyi, Ukraine*, 151, pp. 147-153.
- [30] Kishhenko V., Levchuk I., Golubecz O., Tymchenko V., Kunycya K. (2015). Methodology for detecting chicken fat impurity in sunflower oil. *Technological audit and production Journal*, 6 (4) pp. 4-8.