Research of technology for tranesterification of oils and fats on efficient catalysts

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Abstract. The state and prospects for the development of technology for transesterification catalysts are analyzed. The technological processes of transesterification of vegetable oils and solid fats using new modifications of effective catalysts have been studied. The main changes in triglycerides in intra- and intermolecular transesterification technology have been established. The optimal technology modes have been determined to ensure the production of edible fats with the desired properties. Intra- and intermolecular transesterification of oils and fats was carried out using a standard installation. Transesterification of the fat mixture was carried out at a temperature of 55-60°C in the presence of 0.15-0.25% sodium ethoxide for 20-30 minutes. Deactivation of the catalyst, after achieving the desired degree of transesterification, was carried out with softened water introduced in an amount of 2-3% by weight of fat. The transesterification was washed with water at a temperature of 60-90°C until a negative reaction to soap. It has been established that mixtures of triglycerides, similar in molecular composition to partially transesterified fats, can be obtained by mixing the original and transesterified fat mixtures in certain proportions. This option is also feasible from an economic point of view, since it reduces waste and fat loss during the transesterification process.

1 Introduction

The production of oil and fat products on a global scale has recently increased several times compared to previous decades [1-3]. Technologies for producing products based on cottonseed oil are being improved. More and more research is being carried out around the world to expand the raw material base and improve the quality of fats obtained by transesterification of vegetable oils, modernizing production technology using new and highly effective methods [4-6]. Research work to improve the properties of margarine products, optimize technological processes for creating a composition and production technology with a reduction in the amount of trans fatty acids in interesterified fats is increasingly being developed. The republic pays special attention to the cultivation of sunflower, soybeans and other types of non-traditional oilseeds, which has led to certain achievements in the field of delivery and installation of modern equipment in oil and fat enterprises in the food industry, reducing losses in the processes of production and processing of vegetable oils, as well as in the production of imported products as part of the localization

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program. The production of high-quality fat and oil products using local raw materials for transesterification is of particular importance. Research continues to expand the range of raw materials in the production of transesterified fats, reduce the mass fraction of trans isomers of fatty acids in finished products, enrich the composition with polyunsaturated fatty acids, and increase the efficiency of using transesterified fats in the production of physiologically harmless margarine products**.** In connection with the above, the development of technology for producing interesterified fats with a balanced fatty acid composition and optimal physicochemical characteristics is of both scientific and practical interest. Transesterification is the redistribution of acyl groups in fat triglycerides. The process is carried out using catalytic systems [7]. A distinction is made between intra- and intermolecular transesterification. During intramolecular transesterification, the relative position of acyl groups in the triglyceride changes. During intermolecular transesterification, acyl groups are exchanged between triglycerides. As a result of intra- and intermolecular transesterification of molten (liquid) fat or a mixture of fats, a statistical distribution of fatty acids in a mixture of triglycerides is achieved.

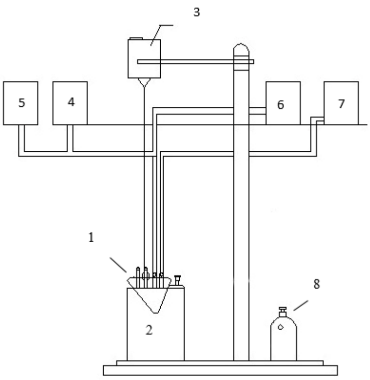
2 Methods

The main experimental and scientific studies on the catalytic modification of vegetable oils and fats were carried out in laboratory settings.

Intra- and intermolecular transesterification of oils and fats was carried out using the installation shown in Fig. 1.

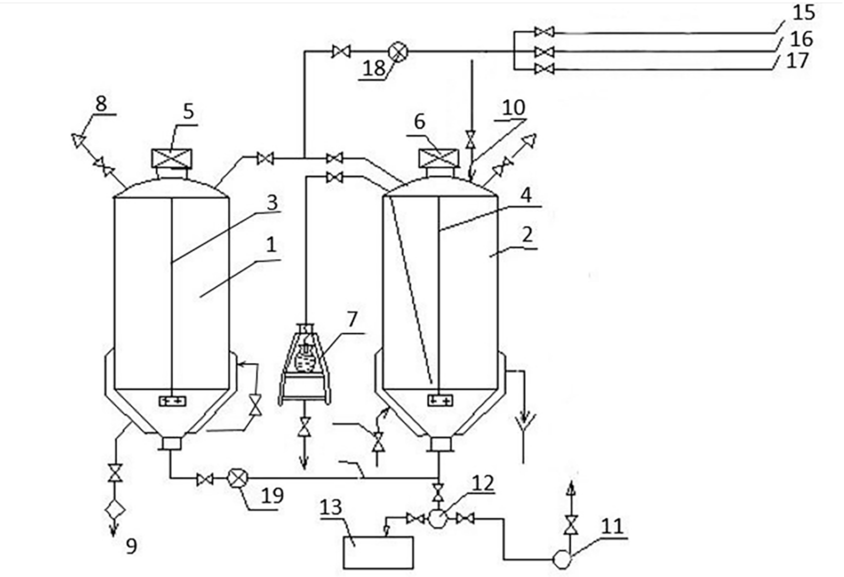
The studies were carried out as follows.

The necessary ingredients of the transesterified composition (mass) were supplied to the transesterifier reactor (1) from containers (4-6). In the thermostat (1), the reaction system was heated and the temperature was maintained within the established limits. The reaction mass was mixed with a paddle stirrer connected to an electric motor (3); the speed of the stirrer was controlled by a rheostat (8). After completion of the transesterification process, a certain amount of water was added to container (7) to deactivate the catalyst and stirred for 5 minutes. Then the transesterified mixture from the transesterifier reactor (1) entered a long-term funnel, where it was washed with water until a neutral reaction. Quality indicators and physicochemical quality indicators were determined in the dried and deodorized transesterified product.



1-transesterifier reactor; 2-thermostat-heater; 3- electric motor; 4- oil container; 5-tank for hydrogenation product; 6- container for fats; 7- container for distilled water; 8-rheostat

Fig. 1. Laboratory experimental installation for catalytic transesterification of oils and fats.



1,2-transesterifier reactors; 3,4-stirrers; 5.6 engines; 7-protective box for catalyst; 8.9 lines to the vacuum pump; 10-process water supply line for catalyst deactivation; 11-pump; 12-view window; 13-tank for fat waste; 14-line for supplying dried (to a moisture content of 0.015%) initial working mixture for transesterification; 15,16,17 lines for supplying initial fats, oils and lard; 18,19-flow sensor; 20-pressure saturated steam supply line; 21-circuit cooling water supply line.

Fig. 2. Technological diagram of the pilot production plant.

The research at the pilot production plant is as follows: cottonseed oil and other types of fatty raw materials were sent to reactor 1 to prepare them for transesterification; the dried mixture was pumped through line 14 using a vacuum into the transesterification reactor-2, where in the presence of a transesterification catalyst the working mixtures are redistributed to their melting point (31-36°C), the remaining catalyst was deactivated with 2-3% process, softened water; the finished transesterification was pumped through pump 11 for further processing; the released fatty waste was monitored through viewing window 2 and fed into the fatty waste tank 13.

The research was carried out as follows: starting oil and fatty products with a temperature of 55-60°C using flow sensors were dosed into a reactor for drying the starting material at a temperature of 110-120 0C and a residual pressure of 4 kPa (30 ml Hg) until the residual moisture more than 0.015%. Transesterification of the fat mixture was carried out at a temperature of 55-60°C in the presence of 0.15-0.25% sodium ethoxide for 20-30 minutes.

Deactivation of the catalyst, after achieving the desired degree of transesterification, was carried out with softened water introduced in an amount of 2-3% by weight of fat. The transesterification was washed with water at a temperature of 60-90°C until a negative reaction to soap. The interesterified fat was dried at a temperature of 90°C and a residual pressure of no more than 6.6 kPa (50 mmHg) to a moisture content of no more than 0.2%.

3 Results and discussion

Catalysts used in modification production are divided into dispersed (powdery) and stationary (stationary) based on their macrostructure and technique of use.

In this regard, it is important to assess the importance of the catalyst in heterogeneous thermodynamic processes. This allows for the correct selection of the catalyst and its most effective use in certain catalytic modification processes of oils and fats.

To speed up the reaction, chemical catalysts of an acid-base nature, as well as biocatalysts (lipase enzymes), are used.

For transesterification of fats, powdered sodium methylate and ethoxide were used.

The high reactivity of sodium alcoholates leads to their irreversible interaction with impurities of water, free fatty acids, hydroperoxides, phosphatidic acids, etc. found in fats. The reactions that occur in this case lead to the termination of the transesterification chain and the formation of by-products in fat, of which the main are soaps, as well as esters of fatty acids, which must be removed during deodorization. Complete removal of the resulting esters is important when using sodium methoxide. For this reason, sodium ethoxide was also preferably used as a catalyst in the studies.

Table 1 shows the technological characteristics of the transesterification catalysts used in the work. Technochemical characteristics of sodium methylate and ethoxide are given in Table 2.

Table 1. Technological characteristics of types of fat transesterification catalysts.

Catalyst	**Range of working concentrations, %**	**Operating temperature range, °C**	**Reaction time, min**
Alkali metals Na. K. Na-K alloy	0.1-0.15	25-270	1-120
Alkoxides CH_3ONa. C_2H_5ONa	0.1-0.15	50-120	5-120
Alkali metal peroxides NaOH, KOH	0.5-2	150-250	90
Alkali metal peroxides	0.05-0.1 NaOH); 0.1-0.2 glycerol	60-160	30-45
Soap (sodium stearate)	0.5-1	250	60
Metal hydrides, metal amides NaH, NaNH.	0.2-2	170	3-120

Transesterification of triglycerides on chemical catalysts occurs only in the liquid fat phase and affects all three ester bonds in the triglyceride molecules.

The dynamics of the redistribution of fatty acids within and between triglyceride molecules was studied using model mixtures of liquid vegetable oils, hydrogenated high-hard edible lard with a melting point of 31–42°C and cotton palmitine, which differed in different contents of saturated fatty acids, isomerized monounsaturated acids and linoleic acid.

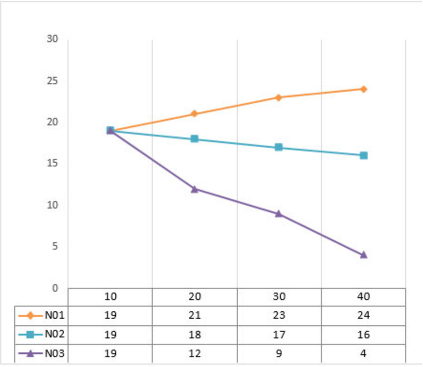
Using the lipase hydrolysis method, it was established that the distribution of fatty acids between the extreme and middle positions of glycerides changes gradually during the process of transesterification and ends with the achievement of the same fatty acid composition for all positions, equal to the fatty acid composition of the original fat mixture. The fatty acid composition of mono-, di-, and triglycerides, mono-esters of fatty acids and free fatty acids present in transesterified fat also corresponds to the composition of the original fat, which indicates the equivalence of fatty acids in the process of transesterification, regardless of their structure and initial location in the molecules triglycerides.

Table 2. Technochemical characteristics of sodium alcoholates.

The name of indicators	**Characteristics and standards**	
	Sodium methylate	**Sodium ethoxide**
Appearance	Fine, dusty, caustic, hygroscopic powder	
Color	White	White to light yellow
Particle size, mm	0.01- 0.30	0.01- 0.30
Bulk density, т/ m^3	Near 0.2	Near 0.2
Chemical composition:		
Mass fraction of sodium alcoholate, %, not less	92.0	90.0
total mass fraction of caustic soda, carbonates and sodium formate, in terms of caustic soda, %	1-6	4-8
Self-ignition temperature in humid air, °C	50	55
Lower concentration limit of flammability (explosiveness) of air suspension, %	45	50

The ratio of symmetrical and asymmetrical mono- and disaturated triglycerides in the mixture during the transesterification process continuously changes and in transesterified fat reaches 1:2. As a result, when transesterifying mixtures of the same fatty acid composition, the same molecular composition of statistically transesterified fat is achieved, and the change in triglyceride composition occurs gradually as the transesterification process progresses and ends with the formation of a glyceride structure corresponding to the statistical distribution of fatty acids (Fig. 3).

Designations:



1, 2, 3 - mixtures of salad oil with edible lard (60:40), palmitine (58:42) and deeply hydrogenated fat (78:22), respectively; N$_{01}$, N$_{02}$, N$_{03}$- triglyceride composition of the original fat mixtures 1, 2, 3, respectively.

Fig. 3. Statistical transesterification of mixtures of oils and fats with the same fatty acid and different triglyceride composition (molar fraction of saturated acids in the original fat mixtures N01 = N02 = N03 = 30%).

As can be seen from the data in Fig.3, by selecting mixtures of a certain fatty acid composition and transesterifying them to a certain extent, it is possible to obtain any triglyceride composition between the composition of the original fat mixture and the statistical distribution.

The dots indicate the compositions of fats obtained by transesterification; solid line - compositions obtained by mixing the original and interesterified fat.

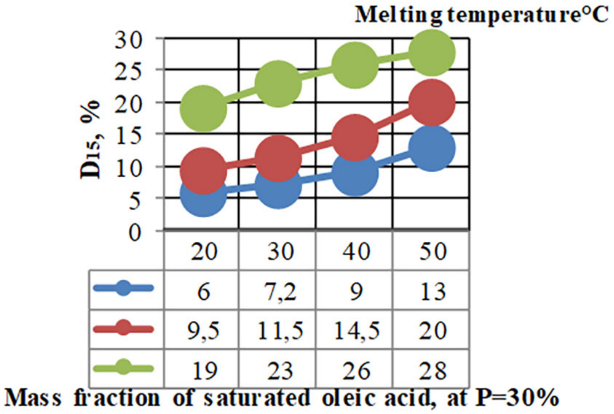
However, in practice, the reproducibility of partial transesterification is insufficient due to fluctuations in catalyst concentration, the quality of preparation of fatty raw materials, the relatively high speed of the process and the lack of express methods for direct control of triglyceride composition.

It has been established that mixtures of triglycerides, similar in molecular composition to partially transesterified fats, can be obtained by mixing the original and transesterified fat mixtures in certain proportions. This option is also feasible from an economic point of view, since it reduces waste and fat loss during the transesterification process.

It has been shown that the most important advantage of statistical transesterification of fats is the possibility of obtaining transesterified fats that are similar in physicochemical parameters from various fat mixtures having the same group fatty acid composition. The basic physicochemical parameters of these fats coincide within the accuracy of the analytical methods, which is explained by the similar properties of the acid triglycerides palmitic and stearic, as well as oleic and linoleic acids.

Experimental data characterizing the dependence of the physicochemical parameters of interesterified fats on their group fatty acid and triglyceride composition are systematized.

The effect of the fatty acid composition of interesterified fat on the melting point, hardness and solid phase content at 15°C is shown in Fig. 4.



	20	30	40	50
🔵	6	7,2	9	13
🔴	9,5	11,5	14,5	20
🟢	19	23	26	28

Fig. 4. Dependence of physicochemical parameters of interesterified fats on the concentration of saturated fatty acids and trans-isomerized acids.

With an increase in the content of high-molecular saturated fatty acids (palmitic and, especially, stearic) from 25 to 45%, the melting point of interesterified fat increases from 28 to 41°C. At the same time, the hardness of the interesterified fat increases from 20 to 220 g/cm and the mass fraction of the solid phase at 15°C increases from 8 to 28%.

When the content of trans-isomers of oleic acid increases from 0 to 35% against the background of a constant content of saturated fatty acids (P = 30%), the melting point of interesterified fat increases slightly, but the hardness (from 40 to 120 g/cm) and the mass fraction of solids increase significantly phase at 15°C.

The properties of interesterified fat are especially strongly influenced by the replacement of part of the unsaturated fatty acids with medium molecular weight saturated acids. In fats containing 30% saturated fatty acids, with an increase in the content of medium molecular acids from 0 to 60%, the melting point increases from 32 to 36 ° C, hardness - from 40 to 650 g/cm, the mass fraction of the solid phase at 15 ° C - from 11 to 71% (Fig. 5).

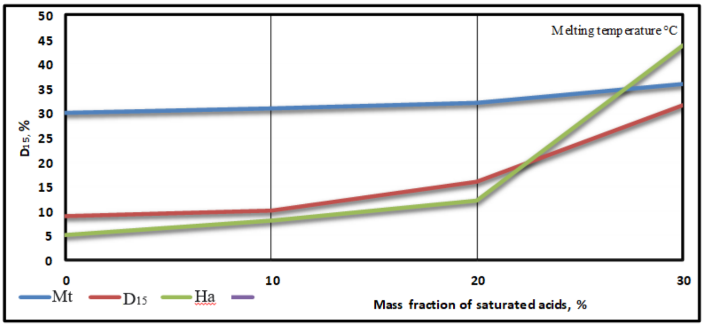


Fig. 5. Dependence of physicochemical parameters of interesterified fats on the concentration of saturated fatty acids (at P = 30%).

Fat, to a first approximation, is a heterogeneous two-phase system, the liquid phase of which is formed by molten triglycerides. The solid phase of this system consists of triglycerides, which at a given temperature are insoluble or partially soluble in the liquid phase (structuring glycerides).

When the temperature changes, the composition of the structuring triglycerides also changes, depending on their melting point and solubility in the liquid phase of the system.

At a temperature of 35°C, the most highly melting trisaturated acid glycerides are the structuring ones. At a temperature of 15°C, the structuring composition also includes tri- and disaturated glycerides containing trans isomers of oleic acid and medium molecular weight saturated acids:

$$C_{35} = P_3 \tag{1}$$

$$C_{15} = P_3 + P_2T + P_2H + PT_2 + T_3 + P_2M + PM_2 + M_3 \tag{2}$$

where: CT is the mole fraction of structuring triglycerides at temperature “T”, %; P - saturated (saturated) acids; M-medium molecular weight saturated acids; T-trans isomers of oleic acid; N-unsaturated acids.

Considering the group of structuring fat glycerides as a dissolved substance, and lower melting triglycerides as a solvent, we can consider phase equilibria in narrow temperature ranges as equilibria in a two-component system and apply to them relations that are valid for ideal solutions.

The equation for the ideal solubility of a solid has the general form:

$$\ln\cdot x = - A/T + B, \tag{3}$$

where x is the solubility of the solid, % mol.;

T – absolute temperature, K.

When applied to plastic fats, this equation takes the form:

$$\ln\cdot a\cdot CT/100 = - A/T + B, \tag{4}$$

where CT is the mole fraction of triglycerides structuring at a given temperature in transesterified fat, %;

a – solubility of structuring triglycerides, %;

At the temperature of complete melting of the solid phase, ST = P3, a = 100%, from which we obtain the solubility equation for the most refractory component:

$$\ln\cdot P_3 = - A/M_t + B, \tag{5}$$

Since determining the temperature of complete melting of fat by the dilatometric method is associated with large errors, the same equation was used to estimate the melting temperature determined by the capillary method, at which the fat still contains about 3% of the solid phase in the form of microcrystals.

Approximately.

$$\ln P_3 = К_{Mt} \cdot M_t + V M_t$$
$$M_t = К_{Mt} \cdot \ln \cdot P_3 + V M_t \qquad (6)$$

The equation for the ideal solubility of the solid phase for plastic fat can be written in another form:

$$\ln(CT\text{-}DT/KT) = -A/T + B \qquad (7)$$

where DT is the mass fraction of the solid phase in plastic fat at temperature "t", %; CT – coefficient for converting mass fractions into moles.

$$\text{At } T = \text{const} \qquad DT = CTST + VT$$

Thus, for each specific temperature there should be a linear relationship between the mole fraction of triglycerides structuring at this temperature and the mass fraction of the solid phase in the fat.

Processing of experimental data showed that the dilatometric characteristics and glyceride composition of interesterified fats are indeed related by approximate linear dependencies of the indicated type (Table 3).

Table 3. Linear relationship between molecular composition and physico-chemical indicators of interesterified fats.

Dependent Variable	Independent variable, %	K	V
D_{35}. %	P_3	1.0 ± 0.1	– (0.5 ± 0.3)
D_{15}. %	C_{15}	1.0 ± 0.1	– (11.0 ± 2.0)
Hardness. g/sm	C_{15} (< 40)	5.2 ± 0.8	– (71.0 ± 9.0)
M_t	$\ln \cdot P_3$	24.9 ± 0.9	– (7.4 ± 0.6)

In fats containing saturated and trans-isomerized acids, in the concentration range of structuring glycerides less than 40%, a similar relationship relates the total content of structuring glycerides and fat hardness at 15°C:

$$H = KHS_{15} + VTV \qquad (8)$$

The parameters of the approximate linear dependencies obtained after processing the experimental data are given in Table. 3.

As follows from the data presented, the solid phase at 15°C appears when the fat contains more than 11% structuring glycerides. When the content of such glycerides in fat is more than 14% (that is, when the solid phase content at 15°C is more than 3%), the fat acquires a certain hardness, depending on the concentration of structuring glycerides.

The obtained dependences are, of course, purely approximate due to the different melting temperatures of individual structuring triglycerides and their unequal contribution to the general physicochemical parameters of transesterified fats. Nevertheless, they are very useful for practical purposes, since they allow one to calculate the approximate technological characteristics of transesterified fat of a known acid composition and, conversely, to calculate the required acid composition of the fat mixture subjected to transesterification using the required dilatometric characteristics of fat.

Interesterified fats are characterized by an optimal content of linoleic acid, a 2-3 times lower content of trans-isomerized acids, and a significantly lower T/P ratio = 0-1.0, while in selectively hydrogenated fats this ratio is 1.7-3.0. Interesterified fats contain significantly less triglycerides of the T_3 and PT_2 types, and their main structuring triglycerides, as in natural fats, are triglycerides of the P_2H type.

Due to the predominance of unsymmetrical disaturated triglycerides and, in general, the maximum diversity of triglyceride composition, interesterified fats have a stable finecrystalline structure in the solid state, mainly of the β-primopolymorphic form, and retain it during long-term storage.

Thus, transesterification of fat mixtures makes it possible to obtain plastic and hard edible fats with a melting point of 25-36°C and a hardness of 20 to 650 g/cm. At the same time, the physicochemical parameters of interesterified fat can be adjusted within wide limits by changing the fatty acid composition of the original fat mixture.

By selecting mixtures of the required fatty acid and triglyceride composition and transesterifying a certain part of the mixture, it is possible to obtain fat of any triglyceride composition between the composition of the original fat mixture and statistically transesterified fat.

4 Conclusion

A high nutritional value has been achieved for interesterified edible fats prepared on the basis of new types of raw materials (cotton-soybean salad oil and cotton-soybean palmitine using effective catalysts); the location of linoleic acid in the sn-2 position in the triglycerides of solid modified fats is ensured with its constant quantitative content in them.

The process of fractionating a blend of cottonseed oil with soybean oil made it possible to determine the optimal conditions for conducting this process. Products with high quality and food safety indicators have been produced based on modified and interesterified fats due to the content of saturated and unsaturated (mono- and di-) fatty acids and their location in triglycerides of cottonseed oil, as well as the content of vitamins and biologically active substances.

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