

Досліджено кінетичні закономірності процесу епоксидування соєвої олії епоксидуючими системами H_2O_2 /оцтова кислота (ОК)/КУ-2×8 та H_2O_2 /оцтовий ангідрид (ОА)/КУ-2×8. Встановлено, що використання вказаних систем дозволяє досягнути високих значень селективності епоксидування за подвійними зв'язками. Опрацьовано методіку обчислень та перерахунку результатів при епоксидуванні сумішей ненасичених сполук, що дозволяє проводити контроль процесу епоксидування на стадії синтезу та вдосконалювати технологію одержання епоксидованих продуктів. Методами ІЧ- та Раман-спектроскопічних досліджень показано структурні зміни у сировині та підтверджено перебіг реакції епоксидування

Ключові слова: епоксидовані рослинні олії, вміст оксиранового кисню, епоксидне число, кінетичні дослідження, ІЧ-спектроскопія, Раман-спектроскопія

Исследованы кинетические закономерности процесса эпоксидирования соевого масла эпоксидирующими системами H_2O_2 /уксусная кислота (УК)/КУ-2×8 и H_2O_2 /уксусный ангидрид (УА) КУ-2×8. Установлено, что использование указанных систем позволяет достичь высоких значений селективности эпоксидирования ненасыщенных связей. Создана методика вычислений и пересчета результатов при эпоксидировании смесей ненасыщенных соединений, которая позволяет проводить контроль процесса эпоксидирования на стадии синтеза и совершенствовать технологию получения эпоксидированных продуктов. Методами ИК- и Раман-спектроскопических исследований показаны структурные изменения в сырье и подтверждено протекание реакции эпоксидирования

Ключевые слова: эпоксидированные растительные масла, содержание оксиранового кислорода, эпоксидное число, кинетические исследования, ИЧ-спектроскопия, Раман-спектроскопия

EXAMINING THE EPOXIDATION PROCESS OF SOYBEAN OIL BY PERACETIC ACID

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1. Introduction

The main principle of green chemistry is the use of renewable, ecological raw materials, which will contribute to subsequent biodegradation and reduction in toxicity of product in the production of polymers. Vegetable oil (VO) is the cheapest and most common biological raw material, the use of which has such advantages as low toxicity, natural biodegradation [1]. Economic value of vegetable oil can be improved through its epoxidation. Authors of [2] studied VO as an alternative raw material to replace petroleum. In particular, in order to obtain polymeric composite materials with current-conducting properties, a polymer matrix from natural and renewable sources such as soybean, linseed, sunflower oil was used [3]. Epoxidized vegetable oils (EVO), obtained on the base of vegetable oils, are applied in medicine, cosmetics, food industry, agrochemistry. EVO are employed as surface-active substances, lubricating materials, alternative fuel, raw materials for the production of coatings, inks, plasticizers, lubricants [4]. Epoxidized soybean oil (ESO) and epoxidized linseed oil are commercially available as stabilizers and plasticizers for PVC and modifiers for coatings [5, 6].

The high degree of unsaturation (C=C) of bonds of fatty acids (FA) leads to poor thermal and oxidative resistance of materials based on them [7]. Despite the fact that triglycerides contain double bonds, the indicated compounds have low reactivity, which is why the crosslinked polymers based on them can be obtained at limited conditions of reaction [4, 5, 8]. If the structure of triglyceride includes aliphatic chains, the synthesized materials do not possess required rigidity and strength. In order to achieve higher molecular weight and crosslinking density, copolymerization is applied [9], or chemical functional groups are introduced to the structure [10], which are easily polymerized and improve the mechanical properties of polymer grids. Thus, numerous studies were conducted into the reaction of complete or partial epoxidation of unsaturated bonds of triglycerides [8, 11, 12].

The experience of systematic research into epoxidation of olefins and individual compounds of different structure with unsaturated bonds [10, 13, 14] is applied to study the epoxidation of vegetable oils.

Using the triglycerides based on renewable raw materials (natural oils) for the development of new products is extremely important due to fluctuating prices in the petroleum

market. An increase in the application of EVO is related to growth in the production volumes of polyvinyl chloride and polymers based on it. Epoxidized oils are one of the best plasticizers of the indicated compounds. EVOs have a number of advantages over other stabilizers:

- they improve thermal resistance of the material;
- they prevent decomposition of the polymer under the action of ionizing irradiation.

Therefore, it is expedient to investigate kinetic patterns of the epoxidation process of soybean oil by different epoxidizing systems.

2. Literature review and problem statement

Among biological resources, such vegetable oils as soybean, palm, rapeseed and sunflower are an affordable alternative to chemical raw materials. In particular, the polymerization of soybean oil with divinyl benzene, catalyzed by boron trifluoride diethyl etherate, was used to synthesize the crosslinked polymers whose properties depend on the stoichiometry of monomers. The polymerization of soybean oil was used to create polymers applied in the production of printing inks. There are studies into the synthesis of solid polymeric materials, based on soybean oil, with mechanical properties that can be used as construction materials [15]. In this context, one of the most important products is the epoxidized soybean oil. ESO is used as a plasticizer in the production of plastics. The application of ESO instead of phthalates allows improving the flexibility and capacity for processing into products made of PVC. Achieving a higher value of epoxy number contributes to a growth in the stabilizing ability of the composition in terms of heating and UV radiation [5, 11, 14]. ESO is characterized by a lower value of thermal conductivity and oxidative capacity, compared with starting soybean oil, due to the lack of allylic hydrogen atoms, which influence the course of these undesired processes. The coatings are created based on the epoxidized soybean oil, titanium and zirconium, characterised by elasticity and hardness, low content of volatile organic compounds, cost and viscosity. The synthesized non-organic-organic hybrid materials have been used in the field of protection of optical and electronic devices. It is shown that the plasticizers and additives to polymer materials, obtained on the base of vegetable oil, display improved characteristics in terms of high resistance to heat and light [15].

Biodiesel fuel is obtained by the re-esterification of soybean oil [2]. Its use helps reduce the emission of particles; the given fuel is non-toxic, renewable and environmentally friendly. Applying the products based on soybean oil in color pencils make them non-toxic and safe for kids [2, 4]. The properties of lubricants based on renewable raw materials (soybean) are similar to properties of the lubricating materials based on petroleum. The advantages of these materials include resistance to the influence of high temperatures. A new technique was also proposed for the polymerization of ESO using fluoro sulfonic acid [13]. Therefore, the efficiency of utilizing the epoxidized vegetable oil is obvious. Given the high reactivity of oxy-ethylene cycle, epoxides can act as a raw material for the synthesis of various chemical substances [1]:

- alcohols (polyols);
- glycols;
- olefin compounds;

- lubricating materials;
- plasticizers;
- stabilizers for polymers.

Thus, the following methods of epoxidation are investigated:

- by conventional technique [15];
- with the use of acid catalysts or ion-exchange resins [8, 11, 15];
- using the enzymes [9];
- with the use of metal ions as catalysts [12];
- other systems [13].

The following indicators are typically accepted as the characteristics of epoxidized compounds [16]:

- epoxy number that represents the quantity of gram-equivalents of epoxy groups per 100 g of product (g-equiv/100 g) or the content of epoxy groups (in %). In order to calculate the epoxy number, ethylene oxide group with a molecular weight of 43 is used, or propylene oxide group with a molecular weight of 57. Epoxy number can also be expressed by the amount of oxygen contained in the epoxy ring;
- hydroxyl number is the quantity of gram-equivalents of hydroxyl groups per 100 g of product (g-equiv/100 g) or the content of hydroxyl groups (in %);
- etheric number is characterized by a quantity of functional groups per 100 g of product, capable of esterification, and is expressed by the number of moles of monocarboxylic acid that interacts in the esterification with 100 g of product.

A relation between etheric (En), epoxy (Epn) and hydroxyl (Hn) numbers can be expressed by equation [16]:

$$En = 2 Epn + Hn.$$

However, in the epoxidation of vegetable oils (soybean, rapeseed, sunflower), a number of problems occur related to the analytical control over reaction and unambiguous interpretation of the results. Thus, in the case of mixtures of compounds with different structure, the components have different reactivity, and it appears problematic to accurately analyze the consumption of an unsaturated compound. In addition, there is a possibility of such arrangement of unsaturated bonds that renders them low reactive. Steric difficulties may also be possible in the case of epoxidation of unsaturated bonds in vegetable oils. That is why the consumption of unsaturated bonds is determined by chemical analysis to reveal the existence of double bonds – determining the bromine or iodine number. As a consequence, the consumption of unsaturation is described by the curve of change in the bromine (iodine) number of the mixture (g Br₂ (I₂), added to 100 g of the mixture); the peroxide consumption is described by the curve of change in the content of peroxide (in units mol/l). The accumulation of epoxide is described by the curve:

- of change in the epoxy number of the mixture (content of grams of epoxy groups per 100 g of mixture);
- of change in the epoxy number of the mixture, defined as a gram of oxirane oxygen added to 100 g of product.

Another problem is the need to carry out the epoxidation under heterophase conditions (organic phase – water phase) when using the epoxidizing system H₂O₂/organic acid/catalyst. Then in the course of analytical control and computations one should take into account that the reaction participants are in different phases.

Under such circumstances, the graphs typically show three curves:

1 – a curve of the unsaturation consumption (in units of bromine number);

2 – the peroxide consumption (in units of mole/l);

3 – the accumulation of epoxide (in units of epoxy number).

It is difficult to draw unambiguous comparative conclusions about the effectiveness of reagent consumption and the selectivity of reaction by these results as the curves are constructed in different scales and the data cannot be compared directly. Given this, of significant interest is to solve the problems related to the improvement of technology for obtaining the epoxidized compounds. Working out the techniques of recalculation of values of bromine, iodine numbers of the products of epoxidation reaction, unsaturation and epoxy number of the compounds, selectivity of the process will make it possible to unambiguously compare the results of research and to control the course of epoxidation process at the stage of the synthesis.

3. The aim and tasks of research

The aim of present work is to obtain, based on the compounds of complex structure with unsaturated bonds (vegetable oils), the mixtures of epoxides (epoxidized compounds), which can be employed to receive composite materials.

To accomplish the set aim, the following tasks were to be solved:

– to devise a procedure for recalculating the values of indicators of the epoxidized compounds (bromine, iodine, epoxy numbers, unsaturation of the epoxidized compounds, selectivity of the process);

– to establish the basic patterns in the course of epoxidation reaction of soybean oil using different epoxidizing systems;

– to confirm the structure of the received oxidized products (ESO) by the spectral methods of analysis.

4. Materials and methods for examining the process of obtaining the epoxidized compounds based on soybean oil

Vegetable oils typically contain fatty acids with a variable length of chain (14–22 carbon atoms), as well as from one to three unsaturated bonds (C=C). Most often, they contain oleic, linoleic and linolenic unsaturated fatty acids. We examined obtaining the epoxidized compounds (EC) based on soybean oil, which contains:

- 52.5 % linoleic;
- 7.5 % linolenic;
- 25 % oleic;
- 4.5–7 % stearic;
- 3–5 % linolenic;
- 2.5–6 % palmitic;
- 1–2.5 % arachidonic acids.

SO has mean molecular weight of 884, specific weight 0.923 kg/m³, the content of unsaturated bonds is characterized by iodine number (129.4 g I₂/100 g of product), or bromine number (81.52 g Br₂/100 g of product).

In the research, we used the epoxidizing system H₂O₂/organic acid/catalyst. The epoxidation of soybean oil was conducted according to the following technique: 48 ml (44.5 g) of soybean oil is dissolved in 26 ml (22.25 g) of toluene. At intensive stirring, the solution of oil is added with 36 ml (40 g) of the 46 % solution of H₂O₂ (containing 18.1 g of H₂O₂ and

21.9 g of H₂O). Next, the reaction mixture is introduced with 8.7 g of acetic acid (AA) or 7.8 g of acetic anhydride (AAn) and 10–20 g of the catalyst KU-2×8 (Kat). Volume of the organic layer is 74 ml, aqueous layer – 60 ml; weight of organic layer is 66.7 g, of aqueous layer is 63.7 g. In certain intervals of time we analyzed the organic layer on the content of unsaturated compounds and epoxides and analyzed the water layer on the content of peroxide. Epoxidation time for the system H₂O₂/AA/Kat is 6 hours; for the system H₂O₂/AAn/Kat is 3 hours. Upon completion of the process, the reaction mixture was settled, the organic layer was washed with water and a solution of soda. After the separation, volatile components were evaporated out of the organic layer, and the epoxidized soybean oil was received.

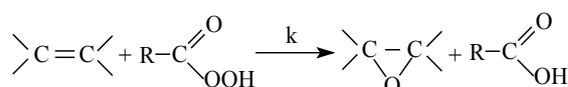
Bromine number of raw materials and the products were determined by the bromide-bromate method, iodine number of SO – by the Gubler's method [17]. Determining the iodine number of the epoxidized soybean oil was carried out by the Kaufman method, determining the epoxy number of ESO was conducted according to procedure [18]. Indicative qualitative composition of the epoxidized products was determined using the method of infrared spectroscopy on the spectrophotometer Thermo Nicolet NEXUS-470 (USA) in the region of 400–4000 cm⁻¹. The samples for analysis were prepared by mixing the epoxidized products with KBr and by pressing tablets from the prepared mixture. These same samples were analyzed by the method of Raman spectroscopy on the device Bruker RFS 100/S (Germany).

5. Results of examining the epoxidation process of soybean oil

5.1. Correlation between characteristics of the epoxidation products of mixtures of unsaturated compounds

It is possible to use as an epoxidizing agent:

1. Peracid solution:



In this case, oxygen from peracid adds to the dual bond with the formation of epoxide.

2. One uses the epoxidizing system H₂O₂/organic acid/catalyst. In this system the epoxidizing agent is also an organic peracid, which is formed *in situ* in the interaction between H₂O₂ and an organic acid or its anhydride in the presence of a catalyst (Fig. 1).

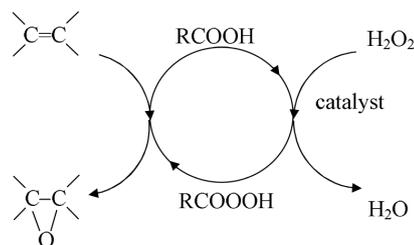
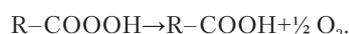


Fig. 1. Scheme of epoxidation by the system H₂O₂/organic acid/catalyst

In the second case, one avoids the stage of obtaining and isolation of peracid, while organic acid is circulating in the

cycle. However, the presence in the mixture of H_2O_2 and H_2O predetermines the need to perform reaction under mild conditions or in a two-phase system. In both cases, a part of the peracid can decompose by reaction:



In addition, a reaction is possible of opening the epoxy cycle with carboxyl groups or water.

The selectivity of epoxidation reaction is estimated:

1. As selectivity of the epoxide formation calculated per consumed quantity of unsaturated bonds:

$$S_{ep}^U = \frac{E_v}{U_{v0} - U_v}, \quad (1)$$

where S_{ep}^U is the selectivity of the epoxide formation calculated per consumed unsaturated bonds; E_v is the epoxy

number (g-equiv. of epoxy groups/l); U_{v0} is the starting unsaturation (g-equiv. of unsaturated bonds/l); U_v is the unsaturation at the given moment t (g-equiv. of unsaturated bonds/l).

2. As selectivity of the epoxide formation of epoxide per consumed peroxide:

$$S_{ep}^P = \frac{E_v}{C_{p0} - C_p}, \quad (2)$$

where S_{ep}^P is the selectivity of the epoxide formation per consumed peroxide; C_{p0} is the starting concentration of peroxide (mol/l); C_p is the concentration of peroxide in the given time t (mol/l).

Based on the aforementioned, we derived formulas for the computation and recalculation of results when epoxidizing the mixtures of unsaturated compounds (Table 1).

Table 1

Formulas for the the computation and recalculation of results when epoxidizing the mixtures of unsaturated compounds

Title	Computational formula	Dimensionality
Correlation of values of iodine and bromine numbers	$I_N = Br_N \cdot k_1$ $Br_N = I_N \cdot k_2$	g (I_2)/100 g of productg (Br_2)/100 g of product
Epoxy number (defined analytically)	E_{Nep}	g of epoxy groups/100 g
	N_{Noxi}	g of oxirane oxygen/100 g of product
Correlation of values of epoxy numbers	$E_{Nep} = E_{Noxi} \cdot k_3$ $N_{Noxi} = E_{Nep} \cdot k_4$	g of epoxy groups/100 g g of oxirane oxygen/100 g of product
Recalculation of bromine number (Br_N) into the quantity of g-equivalents of unsaturated bonds per 100 g of product	$U = \frac{Br_N}{160}$	g-equiv. of unsaturated bonds/100 g of product
Computation of the amount of oxygen that theoretically can be added to all unsaturated bonds of product	$Q = \frac{Br_N}{10}$	g
Computation of oxirane number	$E_{Noxi} = \frac{Q \cdot 100}{100 + Q}$	g of oxirane oxyge /100 g of product
Computation of theoretical oxirane number at the unsaturation of Br_{No}	$E_{Noxi}^T = \frac{100 \cdot Br_{No}}{1000 + Br_{No}}$ $E_{Noxi}^T = \frac{Br_{No}}{10 + 0.01 \cdot Br_{No}}$	g of oxirane oxygen/100 g of product
Computation of theoretical epoxy number at the unsaturation of Br_{No}	$E_{Nep}^T = \frac{2.5 \cdot Br_{No}}{10 + 0.01 \cdot Br_{No}}$	g of epoxy groups/100 g of product
Recalculation of the bromine number of the mixture or product (g of Br_2 /100 g in g-equiv. of unsaturated bonds/l)	$U_v = \frac{Br_N \cdot d}{16}$	g-equiv. of unsaturated bonds/l
Recalculation of the epoxy number of the mixture or product (g of epoxy groups/100 g in g-equiv. of epoxy groups/l)	$E_v = \frac{E_{Nep} \cdot d}{4}$	g-equiv. of epoxy groups/l
Computation of consumption of the unsaturation in epoxidation reaction	$U_{v0} - U_v$	g-equiv. of unsaturated bonds/l
Computation of consumption of peroxide in epoxidation reaction	$C_{p0} - C_p$	mol/l
Computation of selectivity of the epoxide formation to the consumption of unsaturated bonds	$S_{ep}^u = \frac{E_v}{U_{v0} - U_v}$	%
Computation of selectivity of the epoxide formation to the peroxide consumption	$S_{ep}^p = \frac{E_v}{C_{p0} - C_p}$	%

In the computational formulas (Table 1) we used the following characteristics and magnitudes:

- I_N – iodine number, g I_2 , which adds to 100 g of product;
- Br_N – bromine number, g Br_2 , which adds to 100 g pf product (defined analytically in moment t);
- k_1 – recalculation coefficient, $k_1=254/160=1.5875$;
- k_2 – recalculation coefficient, $k_2=160/254=0.63$;
- 254 – molecular weight of I_2 ;
- 160 – molecular weight of Br_2 ;
- Br_{No} – bromine number, g Br_2 , which adds to 100 g of the starting substance (determined analytically at $t=0$);
- E_{Nep} – epoxy number, g of epoxy groups/100 g (defined analytically in moment t);
- E_{Noxi} – oxirane number, g of oxirane oxygen/100 g of product;
- k_3 – recalculation coefficient, $k_3=40/16=2.5$;
- k_4 – recalculation coefficient, $k_4=16/40=0.4$;
- 16 – oxirane oxygen;
- 40 – molecular weight of epoxy group;
- U – number of unsaturated bonds per 100 g of product;
- n – quantity of unsaturated bonds in a substrate molecule;
- M – molecular weight of product;
- Q – amount of oxygen that theoretically can be added to all unsaturated bonds of product, g;
- E_{Noxi}^T – theoretical epoxy number, g of oxirane oxygen/100 g;
- E_{Nep}^T – theoretical epoxy number, g of epoxy groups/100 g (the magnitude required for subsequent construction of graphs and the calculation of selectivity);
- U_V – unsaturation of product, g-equiv. of unsaturated bonds/l;
- U_{Vo} – starting unsaturation, g-equiv. of unsaturated bonds/l;
- E_V – epoxy number, g-equiv. of epoxy groups/l;
- d – specific weight of the starting product or solution;
- S_{ep}^U – selectivity of epoxide formation on the consumption of unsaturated bonds;
- S_{ep}^P – selectivity of the epoxide formation on the consumption of peroxide.

It is obvious that the devised technique for recalculating the values of indicators of the epoxidized compounds eliminates the problems associated with analytical control over the epoxidation reaction. The specified technique allows us to unambiguously interpret the obtained experimental results. Formulas of recalculation the values of indicators of the epoxidized compounds were employed in the construction of kinetic curves of the consumption of reagents and accumulation of products of the epoxidation process of soybean oil.

5. 2. Epoxidation of vegetable oils

The subject of research is the epoxidation of unsaturated bonds of soybean oil. Ion-exchange resins in the H^+ form are the optimal catalysts when obtaining the peracid *in situ*. The main advantage of ion-exchange resins over the catalysts of other types is that these compounds do not catalyze the process of disclosing the epoxy rings. The epoxidation of oils is conducted by the epoxidizing system H_2O_2 /organic acid/catalyst. In particular, the effective systems are: H_2O_2 /acetic acid (AA)/KU-2×8 and H_2O_2 /acetic anhydride (AAn)/KU-2×8. Epoxidation occurs in a two-phase system (Fig. 2, 3).

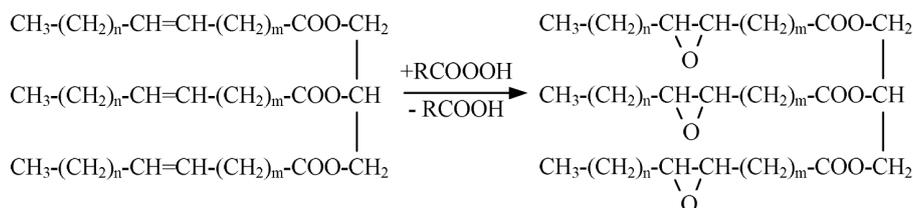


Fig. 3. Schematic representation of the soybean oil epoxidation by peracetic acid created *in situ*

Kinetic curves of the consumption of reagents and accumulation of epoxide in the interaction between the solution of soybean oil in toluene and the epoxidizing system H_2O_2 /AA/KU-2×8 and H_2O_2 /AAn/KU-2×8 are shown in Fig. 4, 5. The values of epoxy and bromine numbers of ESO and the computed selectivities of processes are given in Tables 2, 3. Based on the obtained experimental data, we also computed the rate constants k_{ef} at the epoxidation of SO at temperatures 333, 343, 353 K (Table 4).

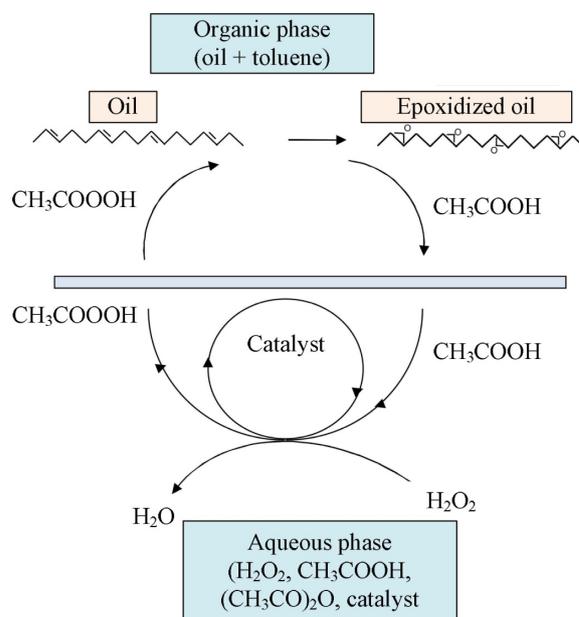


Fig. 2. Scheme of the soybean oil epoxidation under conditions of a two-phase reaction by the epoxidizing system H_2O_2 /CH₃COOH(CH₃CO)₂O/catalyst

Dynamics of the epoxide accumulation and the unsaturation consumption in organic phase (Fig. 4) in the case of employing the system H_2O_2 /AA/KU-2×8 is considerably slower. Thus, when using the specified system, duration of the synthesis stage increases; there occurs the need to elevate the temperature of the process or to use excess reagents. The benefits of using the epoxidizing system H_2O_2 /AA/KU-2×8 also include a reduction of the total volume and weight of the reaction mixture.

Curves 3 and 4 (Fig. 4, 5) that characterize dynamics of the epoxy group accumulation confirm the calculated values of selectivities of the process (Table 2, 3).

In both cases, there is a high selectivity of the epoxidation process by double bonds (S_{ep}^U). Applying in the SO epoxidation process the systems H_2O_2 /AA/KU-2×8 ra H_2O_2 /AAn/KU-2×8 makes it possible to receive the epoxidized soybean oil with a high content of oxirane oxygen and a small bromine number (Table 2, 3).

Table 2

Values of selectivity, epoxy and bromine product numbers at the soybean oil epoxidation by the system $H_2O_2/AA/KU-2 \times 8$ ($T=333$ K)

Oil, g	Toluene, g	H_2O_2 , g	KU-2 \times 8, g	AA, g	S_{ep}^U , %	S_{ep}^P , %	$Br_{N,epoxy\ oil} g Br_2/100 g$
44.5	22.5	18.1	15	8.7	85.4	79.2	1.01

Table 3

Values of selectivity, epoxy and bromine product numbers at the soybean oil epoxidation by the system $H_2O_2/AA_n/KU-2 \times 8$ ($T=333$ K)

Oil, g	Toluene, g	H_2O_2 , g	KU-2 \times 8, g	AA $_n$, g	S_{ep}^U , %	S_{ep}^P , %	$Br_{N,epoxy\ oil} g Br_2/100g$
44.5	22.5	18.1	10.0	7.8	88.3	82.4	1.4
44.5	22.5	18.1	20.0	7.8	84.3	82.1	0.85

Table 4

Value of rate constant k_{ef} at the soybean oil epoxidation by peracetic acid at different temperatures

T, K	333	343	353
$k \pm \Delta k$, l/mol \times min	$5.65 \times 10^{-4} \pm$ $\pm 1.0 \times 10^{-5}$	$8.87 \times 10^{-4} \pm$ $\pm 1.4 \times 10^{-5}$	$16.4 \times 10^{-4} \pm$ $\pm 1.0 \times 10^{-4}$

The resulting values of selectivities of the epoxidation process by double bonds (S_{ep}^U) and by the consumption of peroxide (S_{ep}^P) when studying the epoxidizing system $H_2O_2/AA_n/KU-2 \times 8$ are higher (Table 3).

An increase in the concentration of ion-exchange resin leads to lower selectivity of the epoxidation process by double bonds (Table 3). The use of AA $_n$ makes it possible to receive the epoxidized oils with a high content of oxirane oxygen, in this case, there is a high speed and selectivity of the epoxidation process.

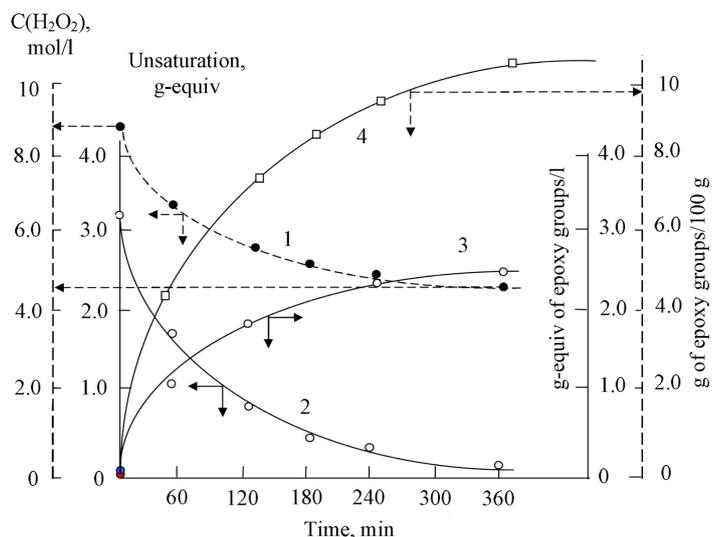


Fig. 4. Kinetic curves of the consumption of reagents and accumulation of epoxide in the interaction between the solution of soybean oil in toluene with the epoxidizing system $H_2O_2/AA/KU-2 \times 8$: 1 – consumption of H_2O_2 in aqueous phase (mol/l); 2 – consumption of unsaturation in organic phase (g-equiv. of unsaturated bonds/l); 3 – accumulation of epoxides (g-equiv. of epoxy groups/l); 4 – accumulation of epoxides (g of epoxy groups/100 g of organic phase). $T=333$ K

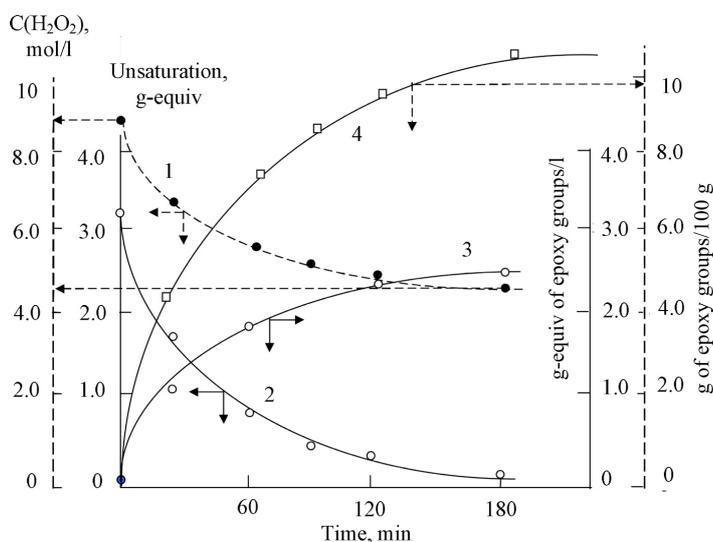


Fig. 5. Kinetic curves of the consumption of reagents and accumulation of epoxide in the interaction between the solution of soybean oil in toluene with the epoxidizing system $H_2O_2/AA_n/KU-2 \times 8$: 1 – consumption of H_2O_2 in aqueous phase (mol/l); 2 – consumption of unsaturation in organic phase (g-equiv. of unsaturated bonds/l); 3 – accumulation of epoxides (g-equiv. of epoxy groups/l); 4 – accumulation of epoxides (g of epoxy groups/100 g of organic phase). $T=333$ K

6. Discussion of results of examining the process of epoxidation of soybean oil

Vegetable oils as renewable natural resources are the raw materials for the synthesis of monomers, linear and crosslinked polymers of different types, in particular polyolefins, polyethers, polyesters, polyamides, epoxy, polyurethane epoxy resins, etc. [1, 2, 4]. The benefits of renewable raw materials given the energy needs at present are obvious.

The epoxidized vegetable oils are the plasticizers-stabilizers of polyvinylchloride and other polymers that are used in the food, medical, construction and other sectors of industries. It is obvious that in the given areas and fields of research there is the potential to use as raw materials various model systems for the purpose of synthesis of new epoxidized compounds (monomers, polymers).

The devised technique of recalculation of values of bromine, iodine numbers of the products of epoxidation reaction, unsaturation and epoxy number, selectivity of the process at the epoxidation of mixtures of unsaturated compounds makes it possible to compare the results of research. The use of the specified technique also allows us to draw unambiguous comparative conclusions about the effectiveness of reagents consumption and the selectivity of reaction. In this case, there is the possibility to improve technology of obtaining the epoxidized compounds. The calculation formulas we derived were applied to analyze the course of the epoxidation process of soybean oil.

The epoxidizing system $H_2O_2/AA(OA)/KU-2\times 8$ (Kat), employed in the epoxidation of soybean oil, provides for obtaining the epoxidized product with high technological indicators. The given system is not involved in disclosing the epoxy rings and makes it possible to obtain high selectivity of the epoxidation process by double bonds. Receiving the ESO with a low resulting value of bromine number provides subsequent good thermal and oxidative resistance of materials based on them.

When considering the mechanism of soybean oil epoxidation by peracids formed *in situ*, it can be conditionally divided into the stage of formation of a peracid and the stage of epoxidation of unsaturated bonds of oil with a peracid. It allows considering the factors that influence the progress of each individual stage and the mechanism as a whole. Using the epoxidizing system $H_2O_2/AA(AAn)/KU-2\times 8$ (Kat) allowed us to avoid a number of problems associated with the use of peracids of varying structure as the epoxidizing agents, in particular the technology of their production and stability of peracids. A necessary condition for the process of epoxidation of oils *in situ* is the existence of interfacial surface between the oil and the epoxidizing system. The specified feature is provided by using as an "acid" component of the system H_2O_2 /organic acid/Kat of acetic acid and its anhydride.

The structure of the obtained epoxidized products was established using the methods of IR- and Raman spectroscopy. Employing the infrared spectroscopy method makes it possible to monitor the progress of the reaction using the qualitative identification of the basic signals that match the epoxy group. For comparison, we analyzed the spectra of raw material (soybean oil) and products of the reaction (a sample of ESO) – Fig. 6, *a, b*, respectively.

In the sample of SO (Fig. 6, *a*), signals of 3020 cm^{-1} , 1650 cm^{-1} , and 719 cm^{-1} correspond to the valency fluctuations of double bonds: $=C-H$, $C=C$, $cis-CH=CH$, respectively. In the IR spectrum of ESO (Fig. 6, *b*), intensity of the specified signals decreased. The vibration of oxirane groups occurs at 1250 cm^{-1} and $830-850\text{ cm}^{-1}$. The identification of this signal and reduction in the intensity of signals of the group of unsaturated bonds (3020 cm^{-1}) is a complementary evidence of progress of the epoxidation reaction. The results received are complemented by the results of spectroscopy of the combination light scattering.

The spectrum of combination scattering of SO is shown in Fig. 7, *a*. Intensive area of absorption, present in the Raman spectrum of the sample of soybean oil in the region of $1300-1900\text{ cm}^{-1}$, matches the fluctuations:

- of $C-H$ groups (at 1450 cm^{-1});
- of unsaturated $C=C$ bonds (at 1660 cm^{-1});
- of $C=O$ groups (at 1707 cm^{-1}).

In the region of $1900-3250\text{ cm}^{-1}$, there are peaks characteristic for flat deformational fluctuations of $C-H$ bonds of methyl and methylene groups. In the absorption range of 2800 to 3000 cm^{-1} we observed intensive peaks characteristic for the fluctuations of groups $=C-H$ (3025 cm^{-1}).

In the Raman spectrum of samples of the product of epoxidation (ESO, Fig. 7, *b*) we observed combination signals, characteristic for the symmetrical valency fluctuations of an epoxy ring (doublet at 1280 and 1260 cm^{-1}). The specified signals are lacking in the spectrum of combination scattering of the starting soybean oil (Fig. 7, *a*). Other peaks that are present in the absorption region of $1500-1490\text{ cm}^{-1}$ and $2800-3000\text{ cm}^{-1}$ are typical for non-flat and flat deformational fluctuations of $C-H$ bonds from the methyl and meth-

ylene groups, respectively. A peak at 1650 cm^{-1} corresponds to the signals of those $C=C$ groups $C=C$ that did not react. Carbonyl group of the fragment of glycerides is observed as a weak peak at 1700 cm^{-1} . A weak signal (shoulder) in the absorption range of $3090-3010\text{ cm}^{-1}$ is a typical fluctuation of the $=C-H$ bonds.

Thus, based on vegetable oils (soybean oil), it is possible to obtain the epoxidized environmentally friendly compounds from renewable natural resources. Under present conditions, in the era of rising oil prices, global warming and ecological problems, accumulation of waste, a transition from traditional raw materials to renewable resources is particularly important. Application of raw materials of plant origin for the synthesis of monomers and polymers is making a significant contribution to the development of innovative technologies.

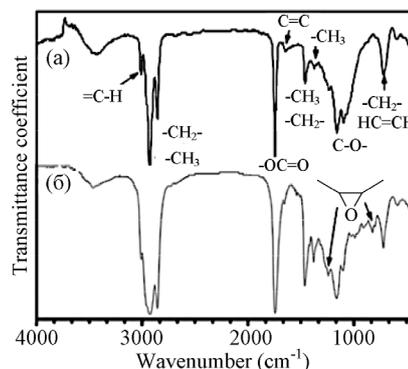


Fig. 6. Infrared spectra of the examined samples: *a* – soybean oil; *b* – epoxidized soybean oil

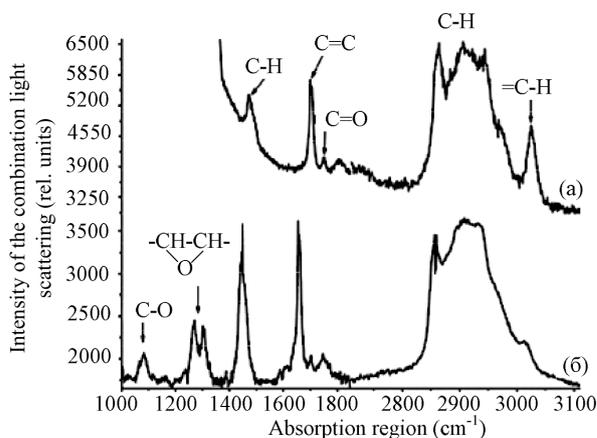


Fig. 7. Raman-spectra of the examined samples: *a* – soybean oil; *b* – epoxidized soybean oil

7. Conclusions

1. In contrast to conventional calculations, the devised technique for recalculating the values of indicators of the epoxidized compounds (bromine, iodine, and epoxy numbers, unsaturation of epoxidized compounds, selectivity of the process) eliminates the problems related to the analytical control over the reaction of epoxidation. The specified technique makes it possible to unambiguously interpret obtained experimental results. The recalculation formulas are applied in the construction of kinetic curves of consumption of reagents and accumulation of products in the epoxidation of soybean oil.

2. Applying in the process of epoxidation of soybean oil the systems $H_2O_2/AA/KU-2 \times 8$ and $H_2O_2/AA/Ku-2 \times 8$ makes it possible to achieve high values of epoxidation selectivity by double bonds (85.4 % and 88.3 %, respectively). It was found that the resulting values of selectivities in the epoxidation process by double bonds and by the consumption of peroxide (S_{ep}^p) in the study of the epoxidizing system $H_2O_2/AA/KU-2 \times 8$ are higher (88.3 % and 82.4 %, respectively). When using the specified system, we received the epoxidized soybean oil with high technological indicators (epoxy number of the product

is 2.5 g-equiv. of epoxy groups/l, the bromine number is 1.4 g $Br_2/100$ g). Obtaining the epoxidized soybean oil with a low resulting value of bromine number provides subsequent good thermal and oxidative stability of materials on its base.

3. Spectral methods of analysis (IR-, Raman spectroscopy) confirmed structural changes in soybean oil in the process of epoxidation, in particular: emergence in the oxidized reaction products of epoxy groups and reduction in the quantity of unsaturated bonds, which is a complementary evidence to the progress of the epoxidation reaction.

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