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RESEARCH INTO EPOXIDATION PROCESS OF THE C_9 FRACTION HYDROCARBONS AND UNSATURATED CO-OLIGOMERS BY PEROXYETHANOIC ACID

Досліджено закономірності процесу епоксидування фракції C_9 рідких побічних продуктів піролізу вуглеводнів та коолігомерів на основі фракції C_9 пероксіетановою кислотою. Встановлено, що використання вказаного епоксидуючого агенту дозволяє досягнути високих значень конверсії подвійних зв'язків та селективності процесу епоксидування. Використання фракції C_9 (побічного продукту виробництва етилену) як сировини для одержання епоксидів є раціональним методом утилізації фракції. Методами ^{1}H-ЯМР, Раман- та ІЧ-спектроскопії підтверджено вміст епоксидних груп у складі епоксидвмісних коолігомерів та перебіг реакції епоксидування

Ключові слова: фракція C_9, епоксидвмісні коолігомери, селективність епоксидування, епоксидне число, ІЧ-спектроскопія, Раман-спектроскопія, ^{1}H-ЯМР спектроскопія

Исследованы закономерности процесса эпоксидирования фракции C_9 жидких побочных продуктов пиролиза углеводородов и коолигомеров на основе фракции C_9 пероксиэтановой кислотой. Установлено, что использование указанного эпоксидирующего агента позволяет достичь высоких значений конверсии ненасыщенных связей и селективности процесса эпоксидирования. Использование фракции C_9 (побочного продукта производства этилена) в качестве сырья для получения эпоксидов является оптимальным способом ее утилизации. Методами ^{1}H-ЯМР, Раман- и ИК-спектроскопии подтверждено содержание эпоксидных групп в составе эпоксидсодержащих коолигомеров и протекание реакции эпоксидирования

Ключевые слова: фракция C_9, эпоксидсодержащие коолигомеры, селективность эпоксидирования, эпоксидное число, ИК-спектроскопия, Раман-спектроскопия, ^{1}H-ЯМР спектроскопия

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1. Introduction

The processes of oxidation of organic compounds dominate in the industry of organic synthesis as the methods for obtaining oxygen-containing products. Industrial implementation is promoted by the relative simplicity of technological design and the possibility to receive a wide range of monomers. Of special attention in the industry of organic synthesis are the co-oligomers with epoxy groups. The raw material for obtaining epoxides is the individual olefins of different structure and mixture [1–3].

The process of ethylene production, along with targeted gaseous products, produces liquid pyrolysis by-products (LPB). The yield, depending on the conditions of the process, is 2–13 % (when using a raw gaseous material) and 22–40 % (during pyrolysis of gasoline or diesel fuel). Thus, by increasing the capacity of pyrolysis plants, it is annually produced in the world about 45–50 million tons of LPB. It is obvious that the proper utilization is an important issue [2, 4].

Liquid pyrolysis products are a mixture of unsaturated and saturated hydrocarbons C_5–C_{14}. LPB are separated into pyrocondensate and a heavy pyrolysis resin. Pyrocondensate is separated into individual fractions that have a narrower boiling temperature interval: fraction C_5 (303–343 K), fraction C_6–C_7 (343–403 K), fraction C_8 (403–423 K), fraction C_8–C_9 (403–473 K), and fraction C_9 (423–473 K). Obtaining synthetic co-oligomers, known as petroleum polymer resins (PPR), is the rational method for using pyrolysis fractions [2, 4].

Epoxy, polyether, and other resins, obtained based on petrochemical raw materials, are used due to the universality of characteristics. In addition, resins are well compatible with various polymeric materials, improving the properties of the latter. Given the high reactivity of oxyethylene cycle of epoxides, the latter may act as a raw material for the subsequent synthesis of such compounds as alcohols (polyols), glycols, lubricants, plasticizers, stabilizers for polymers, and others. Of special attention is the compositions based on industrial epoxy resins and unsaturated oligomers with functional groups [5, 6]. Epoxides of olefins are used in the manufacture of dyes, emulsifiers, surfactants, composite materials, etc. [7].

Thus, it is a relevant task to study the process of obtaining a mixture of epoxides based on the C_9 fraction of pyrolysis by-products and receiving, based on the unsaturated co-oligomers, epoxy-containing co-oligomers, taking into consideration:

– environmental problems related to the disposal of waste from petrochemical industries;

– needs of the chemical industry for the synthetic substitutes for products of natural origin;

– a wide scope of application of epoxides and composite materials.

2. Literature review and problem statement

The main methods for obtaining both separate and mixed epoxy oligomers imply treatment of the compounds that contain unsaturated bonds with different epoxidizing agents [1, 3, 8, 9]. Specifically, authors of [1] studied the oxidation of raw material by a hydrogen peroxide of acetate acid. In the specified process, sulfuric acid is a catalyst for the *in situ* formation of peroxyethanoic acid. The shortcomings of this process include the problems of corrosion. Epoxides are also synthesized using the ions of metals as catalysts. However, the output of epoxides is low and is accompanied by the formation of by-products [9].

The methods of poly-condensation of compounds [5–7] and methods of initiated oligomerization of monomers [8] are also used. Specifically, authors in [5] obtained epoxy-oligoether mixtures that are composed of the industrial epoxy resin ED-20, oligoesteracrylate and a carboxyl-containing derivative of the epoxy resin ED-24. Due to the high reaction ability of the epoxy group, epoxides are easily modified by introducing functional groups. In paper [6], authors studied kinetic patterns in the chemical modification of epoxy resins by aliphatic and aromatic two-base acids. Effective constants of reaction rates were calculated.

In paper [7], authors epoxidized oligomers containing epoxy and carboxylic functional groups, and used as a modifier for low-molecular epoxy resin based on bisphenol A. They examined the possibility of the liquid-phase oxidation of aromatic petroleum polymer resins. The process of modification and the properties of the oxidized samples were investigated [8].

A raw material for the synthesis of epoxides includes both individual compounds and the mixtures of monomers, products of oil processing [1, 5, 6, 8], and renewable biological raw materials [7, 9, 10].

High reactivity of epoxy-containing compounds defines the application of epoxides in different areas of organic synthesis. Epoxy resins are used for the production of coatings, adhesives, binders. Epoxides demonstrate biologically-active properties, and cytostatic activity [9]. Compounds containing a functional epoxy group as a structural fragment are used as biologically active supplements [3].

At the same time, obtaining synthetic co-oligomers (petroleum polymer resins), based on the fractions of pyrolysis by-products, is a rational method for the utilization of pyrolysis fractions. First, this enables solving environmental problems related to the disposal waste from petrochemical production. Second, the need of chemical industry for synthetic substitutes for the products of natural origin is met at the same time [1, 2]. Third, the products of co-oligomerization of unsaturated hydrocarbons from the fractions of LPB (petroleum polymer resins) are the co-oligomers that contain the excessive unsaturated bonds [2, 4]. This makes it possible to further modify PPR and obtain products with functional groups. As previously noted, the epoxidation of compounds with unsaturated bonds is one of the techniques for obtaining epoxides.

Therefore, it is expedient to investigate patterns in the process of epoxidation by peroxyethanoic acid the C_9 fraction as a byproduct of the pyrolysis process of diesel fuel. It is also necessary to examine regularities in the epoxidation of co-oligomers (petroleum polymer resins), synthesized based on the C_9 fraction. The proposed method for obtaining epoxy-containing co-oligomers is an alternative technique for processing the C_9 fraction.

3. The aim and objectives of the study

The aim of present study is to obtain a mixture of epoxides based on the C_9 fraction of liquid hydrocarbon pyrolysis by-products, as well as to obtain, based on unsaturated co-oligomers, epoxy-containing co-oligomers (EC). EC to be synthesized EC could be used for obtaining composite materials.

To accomplish the aim, the following tasks have been set:

– to establish basic patterns in the course of epoxidation reaction of the C_9 fraction of liquid by-products of diesel fuel pyrolysis by peroxyethanoic acid;

– to explore the process of obtaining, based on co-oligomers (petroleum polymer resins) with a high residual unsaturation, epoxy-containing co-oligomers, using a method of oxidation of samples by peroxyethanoic acid;

– to confirm the content of epoxy groups in the obtained products by applying spectral methods of analysis.

4. Materials and methods to study the process of obtaining epoxidized compounds based on the C_9 fraction and unsaturated co-oligomers

The raw material is the C_9 fraction of diesel fuel LPB. The content of unsaturated components in this fraction is ≈55 %. Mostly, these include: styrene (≈19 %), dicyclopentadiene (≈18 %), vinyl toluene (≈8 %), α-methyl styrene (≈2 %), allylbenzene (≈1 %). The magnitude of bromine number of the C_9 fraction is 112 g Br_2/100 g. The total content of aromatic hydrocarbons in the C_9 fraction is 27.8 %.

Properties of co-oligomers, obtained by homogeneous-, heterogeneous catalytic, initiated, and thermal co-oligomerization of hydrocarbons of the C_9 fraction [2], are given in Table 1.

The following designations are used in Table 1:

K_{hom} – unsaturated co-oligomer, obtained by homogeneous catalytic co-oligomerization of hydrocarbons in the C_9 fraction [2];

K_{het} – unsaturated co-oligomer, obtained by heterogeneous catalytic co-oligomerization of hydrocarbons in the C_9 fraction [2];

I_{lab} – unsaturated co-oligomer, obtained by the initiated co-oligomerization of hydrocarbons in the C_9 fraction (laboratory sample) [2];

I_{ind} – unsaturated co-oligomer, obtained by the initiated co-oligomerization of hydrocarbons in the C_9 fraction (industrial sample) [2];

T – unsaturated co-oligomer, obtained by the thermal co-oligomerization of hydrocarbons in the C_9 fraction [2].

Table 1

Physicochemical properties of unsaturated co-oligomers

No. of entry	Physicochemical properties of unsaturated co-oligomers	Sample of co-oligomer (petroleum polymer resin				
		K_{hom}	K_{het}	I_{lab}	I_{ind}	T
1	Physical appearance	Matte brown, or dark yellow crystals, without mechanical impurities				
2	Molecular weight	1,210	680	900	520	455
3	Bromine number, g Br_2/100 g of co-oligomer	52	83	59	62	72

To study the process of obtaining epoxy-containing co-oligomers, we also selected samples whose synthesis conditions by the heterogeneous catalytic co-oligomerization of the C_9 fraction, as well as properties, are given in Table 2.

Table 2

Properties of petroleum polymer resins (a substrate for oxidation in order to produce epoxy-containing co-oligomers)

No. of sample	PPR synthesis conditions			PPR yield, %	PPR properties	
	Catalyst	T, K	τ, hours		BN, g Br_2/100 g	Color, mg I_2/100 cm^3
1	ABC	373	3	29.9	68.5	150
2	ABC	393	3	35.1	78.0	280
3	ABC	413	3	45.3	75.1	500
4	ABC	373	1	23.5	79.6	130
5	ABC	393	1	27.9	83.8	160
6	AP	373	3	24.4	71.8	150
7	AP	393	3	29.6	69.8	220
8	AP	413	3	38.9	73.8	260

4. 1. Procedure for the epoxidation of the C_9 fraction

We load into a thermostatic reactor, equipped with a stirring device, a reverse-refrigerator, and a thermometer, 100 g of the C_9 fraction (bromine number 112 g Br_2/100 g of the fraction). The specified amount corresponds to 0.475 g-equiv. of unsaturated bonds/l. While stirring at a temperature of 303 K, we add a calculated amount of the oxidizer (198.5 g of 20 %-solution of peroxyethane acid in benzene). A higher temperature can lead to the decay of peracetic acid. A solution of the peracid contains 39.7 g of peroxyethane acid. This equals the amount of 0.525 mole, which enables a 10 %-mole excess of peroxyethane acid relative to the number of unsaturated bonds in the C_9 fraction. The solution also contains 158.8 g of benzene.

Upon completion of the reaction (the degree of conversion of the peracid is 90 %), the reaction mixture is washed with water and a solution of Na_2CO_3. Following the separation of the water layer that contains acetate acid, excessive peracid and salts, we evaporate from the organic layer benzene and volatile unreacted components of the C_9 fraction and obtain 88.2 g of the mixture of epoxides.

4. 2. Procedure for obtaining co-oligomers with epoxy groups

A batch of co-oligomer (4 g) was dissolved in 17 ml of toluene. Prepared solution was placed into reactor and thermostated to a temperature of 303 K. Upon reaching the temperature of the process, we introduced into reactor, by droplets, the required amount of the oxidizer. The oxidizing agent used is a mixture of the following composition: peroxyethane acid – 16.6 % by weight, hydrogen peroxide – 21.0 % by weight, acetate acid – the rest (preparation «Divozan-Forte»). Thus, the main epoxidizing agent is peroxyethane acid in. In this system, the epoxidizing agent is also peroxyethane acid in that forms *in situ* during interaction between H_2O_2 and acetate acid. The choice of a given oxidizer is motivated by that it is produced industrially at NVPP «Dezo» (according to TU U 24.4-30906521-001-2000, with a change No. 1, in Boryslav, Ukraine) and is quite cheap. The chosen oxidizing agent is produced with a normed concentration of peroxyethane acid. Its concentration is impractical as it would compromise fire safety of the process.

The oxidizing agent was added in the calculated amount to ensure a 15 %-mole excess of peroxyethane acid relative to the number of unsaturated bonds in the co-oligomer. After adding the oxidizing agent, the reaction mixture was held, at a temperature of 303 K and at intensive agitation, for 90 minutes. Upon completion of the reaction, the reaction mixture was taken to a separating funnel where a water layer was separated. The organic layer was subsequently washed four times with distilled water (five-fold excess). The first washing was carried out with the introduction of sodium carbonate in order to neutralize the acids. After each washing, the mixture was separated in the separating funnel into an aqueous (bottom) and an organic (upper) layers.

The resulting epoxy-containing co-oligomer (EC) was deposited from the solution by petroleum ether (chemically pure, GOST 11992-66). The deposited product was dried at a desiccator at room temperature and residual pressure of 10–30 mm Hg until reaching a constant mass. The resulting product is a matte crystal substance of light-yellow color.

The principle of calculation of the degree of conversion of unsaturated bonds in PPR (X), calculation of values for the epoxy number of products (EN), and values for the epoxy number under condition of epoxidation of all unsaturated bonds (EN_{BN}), the selectivity of the epoxidation process (S), is given in [2, 4, 11].

A previously developed procedure for the recalculation of values for unsaturation and epoxy numbers of the epoxidation reaction products, the selectivity of the process at epoxidation of mixtures of unsaturated compounds, makes it possible to compare research results [11]. Application of the indicated procedure also makes it possible to draw unambiguous comparative conclusions on the effectiveness of reagents consumption and the selectivity of the reaction.

Bromine number of raw materials, of products, and a residual bromine number of co-oligomers (BN_R), were determined by the bromide-bromate method [12]. Determining an epoxy number of EC was conducted according to procedure from [13]. Indicative qualitative composition of epoxy-containing products was determined using the method of infrared spectroscopy at the spectrophotometer Thermo

Nicolet NEXUS-470 (USA) in the region of 400–4,000 cm^{-1}. Samples for the analysis was prepared by mixing epoxidized products with powder-like KBr and by pressing tablets from the prepared mixture. The same samples were analyzed by the method of Raman-Spectroscopy at the device Bruker RFS 100/S (Germany).

^{1}H NMR spectra of EC were picked at the device Bruker AV600 (Germany) with an operating frequency of 400 MHz. The samples for this analysis were dissolved in deuterated trichloromethane ($CDCl_3$) with a volume of 0.7 ml. Mass of the samples is 10 mg. The quantitative comparative analysis of NMR spectra of epoxy-containing co-oligomers was carried out based on the values for peak areas, which were calculated by integrating the respective sections of the spectra using the software MestReC.

5. Results of research into epoxidation process of the C_9 fraction and unsaturated co-oligomers (petroleum polymer resins)

5. 1. Epoxidation of the unsaturated hydrocarbons of the C_9 fraction with peroxyethanoic acid

The main direction of using the C_9 fraction (a by-product of the pyrolysis process of diesel fuel when obtaining ethylene and propylene) is the co-oligomerization (obtaining petroleum polymer resins) or hydrogenation with the return of the products to the stage of pyrolysis. An alternative technique to utilize the C_9 fraction is the epoxidation of components with obtaining a mixture of epoxides (potential additives to composite materials).

Kinetic curves for the peracid consumption, unsaturated C=C bonds and accumulation of epoxides in process of epoxidation of unsaturated hydrocarbons of the C_9 fraction with peroxyethanoic acid are shown in Fig. 1.

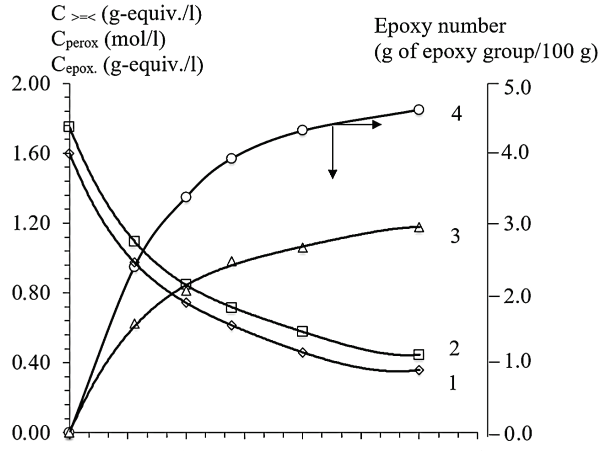

Fig. 1. Kinetic curves of the C_9 fraction epoxidation with a solution of peroxyethanoic acid in benzene: 1 – unsaturation consumption (g-equiv. of unsaturated bonds/l); 2 – change in the concentration of peracid (mol/l); 3 – accumulation of epoxides (g-equiv. of epoxy groups/l); 4 – change in the epoxy number of reaction mixture (g of epoxy groups/100 g). $T=303$ K

The selectivity of the formation of epoxides is: 95 % (selectivity of forming an epoxide on the consumption of unsaturated bonds, calculated in accordance with [11]), and 92 % (selectivity of epoxide formation on the consumption of peroxyethanoic acid, calculated in accordance with [11]). The course of epoxidation of hydrocarbons in the C_9 fraction is contributed to by a high content of aromatic hydrocarbons in it, first of all, *m*-, *n*-xylene and toluene (23.8 %).

The main factor that affects the kinetics of epoxidation reaction is the intra-molecular interaction between peracid and a solvent. In the solvents capable of forming the intra-molecular hydrogen bonds, the concentration of the oxidizing agent in the active form decreases. The reaction rate also decreases. Epoxidation reaction proceeds at the highest rate in inertial non-polar solvents (benzene) in which peracid reacts in a cyclic form with an inner molecular hydrogen bond.

It is obvious (Fig. 1) that the amount of consumed peracid does not match the number of formed epoxides. This is due to the flow of side reactions. At epoxidation, there is a selection of gaseous products whose amount depends on the conditions of the reaction and is 0.02–0.30 moles of gases per 1 mole of reacted peroxyethanoic acid. The reaction of epoxidation of the C_9 fraction hydrocarbons was studied in the temperature range of 293–323 K. The higher epoxidation process temperatures cause a significant thermal decay of peracid. The products of the reaction of an epoxy cycle under the specified conditions of the reaction do not form. Maximum yield of epoxides (52.3 %) was reached at $T=303$ K and a reaction duration of 7,200 s.

5. 2. Obtaining epoxy-containing co-oligomers based on petroleum polymer resins

The subject of research is the epoxidation of unsaturated bonds of co-oligomers (petroleum polymer resins) by the method of oxidation of PPR samples with peracetic acid. For epoxidation, we selected the samples of co-oligomers that have residual unsaturation and were obtained under conditions that make it possible to achieve high yields of PPR. The examined samples of co-oligomers were synthesized by the homogeneous-, heterogeneous catalytic, initiated, and thermal co-oligomerization of the C_9 fraction hydrocarbons [2]. The properties of co-oligomers, obtained by different methods, are given in Table 1. Kinetic curves for the peracid consumption, unsaturation, and epoxide accumulation in the process of epoxidation of co-oligomers with unsaturated residuals are shown in Fig. 2.

It is obvious that a significant reduction in the concentration of peracetic acid and the consumption of unsaturated bonds are observed during 2,000 s of the epoxidation reaction (Fig. 2). An increase in the duration of epoxidation over 4,500 s is impractical, as the selectivity of the reaction is sufficiently high (Table 3). We determined, for the obtained co-oligomers with epoxy groups, the color, residual bromium number (BN_R), and epoxy number (EN) (Table 4). The principle of calculation of the degree of conversion of unsaturated bonds in PPR (X), calculation of values for EN under condition of epoxidation of all unsaturated bonds (EN_{BN}), and the selectivity of the epoxidation process (S), is given in [11].

It is obvious that the absolute values of selectivities for the process of epoxidation of co-oligomers (petroleum polymer resins), obtained by the initiated co-oligomerization of the C_9 fraction hydrocarbons under laboratory and industrial conditions are close in values. The lower values of selectivity for the process of epoxidation, with peroxyethanoic acid, of the co-oligomer obtained by the homogeneous catalytic co-oligomerization of the C_9 fraction can be explained by the traces of catalyst in the structure of PPR, which contribute to the non-selective processes in the epoxidation of a co-oligomer. The residual of the catalyst increases the rate of decomposition of the peroxide group, which is why the peracid is spent non-selectively. In this case, the rate of the epoxidation of unsaturated bonds in PPR is lower. The unsaturated co-oligomers derived by the method of catalytic co-oligomerization are structurally different from the co-oligomers obtained by the initiated or thermal techniques [2]. The most strenuous epoxy groups form at epoxidation of cyclopentane and norbornene double bonds of cyclopentane links of co-oligomers, obtained by the catalytic co-oligomerization of the C_9 fraction [2]. Thus, a high content of such relationships in the structure of PPR leads to the lower selectivity of epoxidation. Part of the remaining unsaturated bonds in such samples is difficult to be reached by epoxidizing agents, which collectively affects the reduction of selectivity in the reaction of epoxidation.

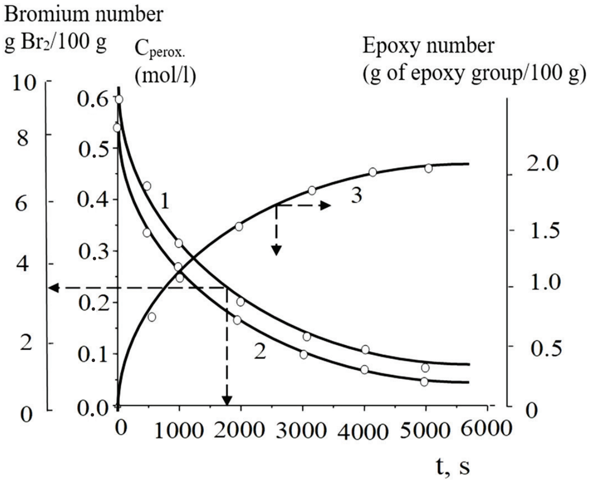

Fig. 2. Kinetic curves of reagent consumption and accumulation of epoxides in the reaction of epoxidation of co-oligomer with unsaturated bonds by peroxyethanoic acid: 1 – consumption of unsaturated bonds (bromium number, g of Br_2/100 g); 2 – consumption of peroxyethanoic acid (mol/l); 3 – accumulation of epoxides (g of epoxy groups/100 g of the mixture). T=303 K

We have investigated, as heterogeneous catalysts of the process of synthesis of unsaturated co-oligomers (PPR), the aluminosilicate materials activated by sulfate acid: clay (bentonitic clay (ABC), palygorskite (AP)). The activated bentonitic clay and activated palygorskite belong to the heterogeneous catalysts of the acidic type of oxide nature. The advantages of such catalysts include low cost, weather resistance (absorption of atmospheric moisture does not lead to the deactivation of the catalyst), and a long life cycle [4]. Petroleum polymer resins, synthesized by the heterogeneous catalytic co-oligomerization of the C_9 fraction hydrocarbons [4], are characterized by high unsaturation (73.8–83.8 g of Br_2/100 g, Table 2), which promotes the implementation of subsequent modification of resins. To study the process of obtaining epoxy-containing co-oligomers, we selected samples whose conditions of synthesis and properties were given in Table 2.

It was established a significant reduction in the indicator of color for the obtained co-oligomers with epoxy groups (15–60 mg I_2/100 cm^3, Table 4), compared with the color of samples of PPR, out of which epoxy-containing co-oligomers had been obtained (Table 3). Such a change in the coloration of epoxy-containing co-oligomers, compared to the starting petroleum polymer resins, also testifies to the course of epoxidation reaction. Bromium number of EC is high (24.3–39.0 g of Br_2/100 g), the magnitudes of the calculated values for the degree of conversion of double bonds (X) are 53.4–65.2 % (Table 4). Thus, part of the unsaturated bonds in petroleum polymer resins remains unreacted.

Table 3

Values of epoxy number and selectivity during epoxidation of co-oligomers with peracetic acid (T=303 K, τ=4,000 s)

No. of entry	Co-oligomer sample	$EN_{(theory)}$, g of epoxy groups/100 g of co-oligomer	$EN_{(actual)}$, g of epoxy groups/100 g of co-oligomer	S, %
1	K_{hom}	10.0	8.9	88.9
2	K_{het}	10.1	10.6	96.1
3	I_{lab}	12.5	11.4	93.5
4	I_{ind}	12.5	11.5	94.7
5	T	16.8	10.9	64.6

Note: S – selectivity of epoxide formation for the consumption of unsaturated bonds [11]

Table 4

Properties of epoxy-containing co-oligomers (T=303 K, 15 % mole excess of CH_3COOOH to the unsaturation of PPR), the degree of conversion of unsaturated bonds in PPR (X), and selectivity of the process of epoxidation (S)

Sample number	Properties of co-oligomers with epoxy groups				X, %	S, %
	Color, mg I_2/100 cm^3	BN_R, g Br_2/100 g	EN, %	EN_{BN}, %		
1	20	26.3	10.1	10.6	61.6	96.1
2	25	28.8	7.9	12.3	63.1	64.6
3	60	32.6	7.8	10.6	56.6	73.8
4	15	28.4	8.7	12.8	64.4	68.1
5	20	39.0	6.7	11.2	53.4	60.2
6	15	27.3	9.5	11.1	62.0	85.8
7	20	24.3	10.5	11.4	65.2	92.0
8	25	33.9	6.8	10.0	54.1	68.4

6. Discussion of results of studying the process of epoxidation of unsaturated co-oligomers

It was established that the epoxidation of co-oligomers, synthesized by the heterogeneous catalytic technique, which are characterized by high residual unsaturation (68.5–83.8 g of Br_2/100 g), makes it possible to obtain an epoxy-containing product with a sufficiently high epoxy number (10.6–11.4 %). Synthesized epoxy-containing co-oligomers retain residual unsaturation (24.3–39.0 g of Br_2/100 g).

It is obvious that the unsaturated bonds of styrene, vinyl toluene, α- methyl styrene, allylbenzene links at the ends of macromolecules of a co-oligomer are easily epoxidized. At the epoxidation of cyclopentadiene, which contains in its structure a strenuous cyclopentane cycle, there are difficulties. The specified bonds have difficulties entering the reaction of epoxidation. At the epoxidation of unsaturated bonds, concentrated inside the macro-chain of a co-oligomer, there are steric obstacles.

The selectivity of co-oligomer epoxidation, obtained by different methods of co-oligomerization of the C_9 fraction hydrocarbons (homogeneous catalytic, heterogeneous catalytic, initiated, and thermal) is different (60.2–96.1 %) and depends on the nature of the starting co-oligomer. Thus, in the case of epoxidation of petroleum polymer resins, synthesized by the initiated co-oligomerization of the C_9 fraction hydrocarbons, the degree of conversion of unsaturated bonds is 81.4 %. The composition of the indicated products actually lacks cyclopentadiene links.

The epoxidation selectivity of co-oligomers, obtained by the co-oligomerization of the C_9 fraction hydrocarbons using, as a heterogeneous catalyst, activated palygorskite, is somewhat lower than in the case of homogeneous catalytic co-oligomerization of monomers or application of activated bentonite clay. It was established that the co-oligomers, synthesized at a higher temperature of the reaction (413 K), are epoxidized with lower selectivity (73.8–68.4 %). It is obvious that the side reactions of the specified process include reactions of hydrolysis of epoxy groups and acidolysis of epoxy groups with acetate acid, which is present in the composition of the epoxidizing system. The hydrolysis reactions of epoxy groups is contributed to by the stage of washing a solution of epoxy-containing co-oligomers with residual water. Accordingly, in the composition of EC, in addition to epoxy groups and unreacted double bonds, there is a small amount of hydroxyl and ester groups. The flow of these reactions reduces the selectivity of the process of epoxidation. The most strenuous epoxy groups enter the reactions of hydrolysis and acidolysis most easily. The indicated groups can be formed at the epoxidation of cyclopentane and norbornene double bonds of cyclopentadiene links.

We used the methods of ^{1}H-NMR-, Raman-, and infrared spectroscopy to study peculiarities of the structure of the obtained co-oligomers with epoxy groups (Fig. 3–5).

The IR spectra of EC samples revealed intense absorption bands of 1,261 and 1,238 cm^{-1}, showing the content of epoxy groups in the structure of a co-oligomer (Fig. 3), absent in the IR spectra of the raw material (samples of petroleum polymer resins) [2, 4]. The spectra of EC demonstrate a peak of absorption at 837 cm^{-1}, which characterizes the epoxy groups of *cis*-compounds, and the absorption region at 950–860 cm^{-1}, characteristic of epoxy groups of *trans*-compounds.

The Raman spectrum of the samples of epoxy-containing co-oligomers (Fig. 4) shows a clear peak at 786 cm^{-1}, which is a characteristic peak for the fluctuation of an epoxy cycle. Peak at 1,600 cm^{-1} matches the signals from groups C=C, which did not react. A C=O group is observed as a weak peak at 1,701 cm^{-1}. The signal in the absorption interval of 3,000–3,100 cm^{-1} is a typical fluctuation of =C–H bonds. In the EC sample (Fig. 5), signals at 3,020 cm^{-1}, 1,650 cm^{-1}, and 719 cm^{-1} correspond to the valent fluctuations of double bonds: =C–H, C=C, cis-CH=CH, respectively. Vibration of the oxirane groups occurs at 1,250 cm^{-1} and 830–850 cm^{-1}.

The presence of epoxy groups, formed based on the end vinyl double bonds, is indicated by the values of integrated intensities of protons 2.5 and 2.7 ppm in the ^{1}H NMR spectrum of EC (Fig. 5). Epoxy groups, formed based on cyclopentane, norbornene, and aliphatic C=C bonds inside the chain, are matched by the values of integrated intensities of protons in the range of 2.9–3.2 ppm. The ^{1}H NMR spectrum of the sample of epoxy-containing co-oligomer has an intense peak at 2.1 ppm, which corresponds to the atoms of hydrogen in the methyl group of acetate acid.

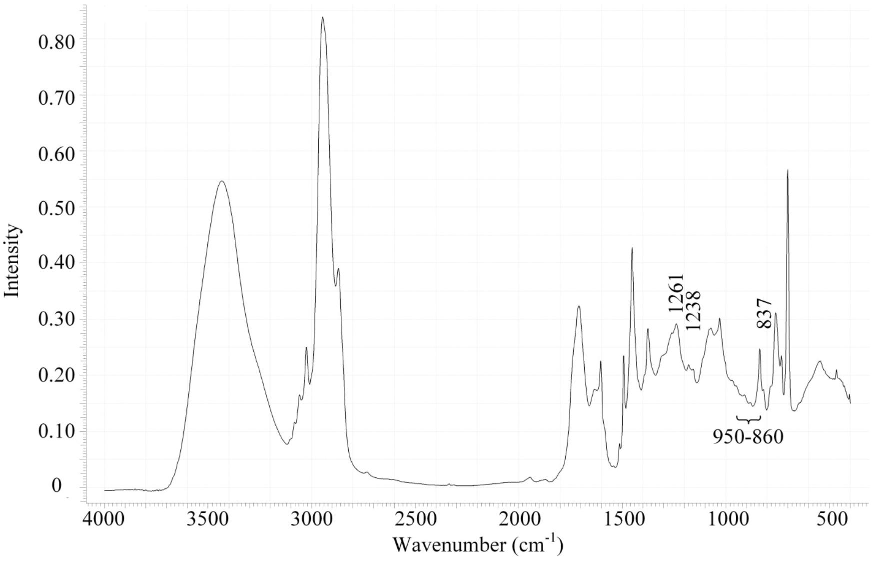

Fig. 3. IR spectrum of the sample of epoxy-containing co-oligomer

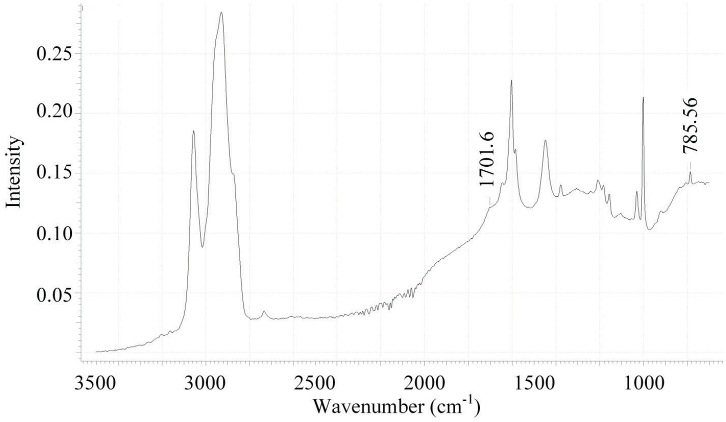

Fig. 4. Raman spectrum of the sample of epoxy-containing co-oligomer

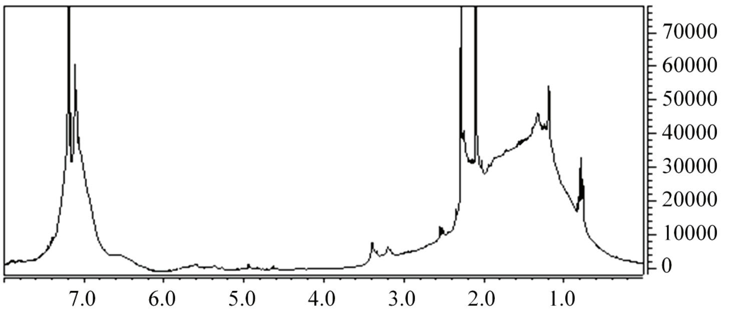

Fig. 5. ^{1}H-NMR spectrum of the sample of epoxy-containing co-oligomer

This confirms the presence of residual acetate acid in the composition of EC as a result of the course of acidolysis reaction of epoxy groups.

Therefore, the main source of unsaturated bonds of the co-oligomer, obtained from the C_9 fraction, is dicyclopentadiene. It contains in its molecule a strenuous cycle and, at the same time, two double bonds: norbornene and cyclopentane. In the case of co-oligomerization for the norbornene bond, cyclopentane remains. In the case of oligomerization for the cyclopentane bond, norbornene remains [2, 4]. In addition to the above mentioned possible mechanisms for the co-oligomerization of dicyclopentadiene, which imply polyaddition for the cyclopentane and norbornene double bond, there is another possible mechanism of its oligomerization – metathesis mechanism with the disclosure of the norbornene cycle [4]. In this case, there remains a cyclopentane double bond, but instead of the norbornene one, there appears the vinyl double bond. With such a mechanism of co-oligomerization of dicyclopentadiene, the number of double bonds is not reduced and we obtain the most unsaturated product. Therefore, the co-oligomers, obtained by the heterogeneous catalytic co-oligomerization of the C_9 fraction hydrocarbons, are characterized by the largest number of unsaturated bonds and are the most promising raw material in the process of epoxidation.

Difficulties in the course of epoxidation are possible when interacting with unsaturated bonds of dicyclopentadiene, which contains strenuous cycles in its structure. Therefore, such unsaturated bonds have difficulties entering the reaction of epoxidation. In addition, at the epoxidation of unsaturated bonds, there may occur possible steric obstacles inside of the chain that are created by neighboring groups, whereas at the epoxidation of vinyl, allyl groups, such obstacles are absent at the end of a chain. Thus, the process of epoxidation of co-oligomers, synthesized by the homogeneous catalytic co-oligomerization of the C_9 fraction, proceeds without the specified steric obstacles. However, given the lower value of unsaturation of such resins (52 g of Br_2/100 g of co-oligomer), selectivity of the specified process is lower (88.9 %).

Combination of epoxy resins with different oligomers makes it possible to improve the properties of compositions based on such mixtures, compared with an individual epoxy resin [5–7]. Of special attention is the compositions based on industrial epoxy resins and unsaturated oligomers containing functional groups [5, 6]. To obtain composite materials with good physical-chemical and mechanical properties and high resistance to aggressive environments, it is necessary that all components of the composition are linked in one three-dimensional polymer. This purpose can be accomplished by the obtained mixtures of epoxides based on the C_9 fraction of liquid by-products of the pyrolysis of hydrocarbons and epoxy-containing co-oligomers, synthesized on the basis of unsaturated co-oligomers, which are characterized by high residual unsaturation (26.3–33.9 g Br_2/100 g of co-oligomer).

7. Conclusions

1. We established the possibility to use the C_9 fraction of liquid hydrocarbon pyrolysis by-products (a by-product of ethylene production) as a raw material for obtaining epoxides, which is the rational method to utilize the fraction. Reaction of epoxidation of the C_9 fraction hydrocarbons is promoted by a high content of aromatic hydrocarbons in it, first of all, *m*-, *n*-xylene and ethyl toluene (23.8 %).

The selectivity of epoxides formation is: 95 % (selectivity of epoxy formation for the consumption of unsaturated bonds) and 92 % (selectivity of epoxy formation for the consumption of peroxyethanoic acid). Epoxidation reaction occurs with the highest rate in inert non-polar solvents (benzene, toluene), in which peracid reacts in a cyclic form with inner-molecular hydrogen bond. The maximum yield of a mixture of epoxides (52.3 %) was reached at the reaction temperature of 303 K and a duration of 7,200 s.

2. It was established that unsaturated bonds of styrene, vinyl toluene, α-methyl styrene, allylbenzene links of co-oligomer macromolecules with residual unsaturated bonds are readily epoxidized. At the epoxidation of cyclopentadiene, which contains in its structure a strenuous cyclopentane cycle, there are difficulties. The selectivity of epoxidation of co-oligomers, obtained by different methods of co-oligomerization of the C_9 fraction hydrocarbons (homogeneous catalytic, heterogeneous catalytic, initiated, and thermal) is different (60.2–96.1 %) and depends on the nature of the starting co-oligomer. The highest selectivity (96.1 %) was achieved in the process of epoxidation of the co-oligomer obtained by the heterogeneous catalytic co-oligomerization of the C_9 fraction hydrocarbons.

3. Using the methods of ^{1}H NMR-, Raman- and infrared spectroscopy, we confirmed the content of epoxy groups in the composition of epoxy-containing co-oligomers and the progress of the epoxidation reaction. The side reactions of the specified process include reactions of the hydrolysis of epoxy groups and the acidolysis of epoxy groups with acetate acid, which is present in the composition of the epoxidizing system. Applying the method of ^{1}H NMR spectroscopy of EC sample, we confirmed the presence of residual acetate acid in its composition as a result of the course of acidolysis reaction of epoxy groups.

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