

RESINS WITH OXYGEN-CONTAINING FUNCTIONAL GROUPS OBTAINED FROM PRODUCTS OF FOSSIL FUELS PROCESSING: A REVIEW OF ACHIEVEMENTS

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Abstract. To synthesize resins with oxygen-containing functional groups the C₉ fractions of hydrocarbon pyrolysis, heavy gasoline, and light coal tar fraction obtained from coal coking liquid products (CCLP) were used. Various types of initiators and industrial monomers were obtained using the above-mentioned non-target and/or by-products of organic raw materials processing: by the initiated oligomerization method (from C₉ fractions) – petroleum polymer resins with functional groups; by radical cooligomerization (from CCLP) (with RPKV) – coumarone-indene resins with functional groups. The influence of the main factors controlling the synthesis process of resins with functional groups on their quantitative and qualitative characteristics was studied, including the process temperature, duration, and the reaction mixture composition. The structure of the synthesized resins was analyzed by IR spectroscopy, and the presence of epoxy, carboxyl, hydroxyl, and methacrylate functional groups was confirmed.

Keywords: organic raw materials processing products, petroleum polymer resin, coumarone-indene resin, functional group.

1. Introduction

The continuous development of humanity requires an increase in the number and range expansion of organic materials for the production of various consumer and industrial goods. This is particularly true for polymer resins. The source of their synthesis is traditionally processing products of organic raw materials, namely oil and coal. Such products include, for example, the C₉ fraction of pyrolysis petroleum raw materials and coumarone-

indene-containing fractions of coal-coking liquid products. Various petroleum polymer and coumarone-indene resins (PPR and CIR) are obtained on their basis, respectively.¹⁻¹⁰

PPR and CIR, as oligomerization products of unsaturated compounds that are part of the by-products of organic raw materials processing, are characterized by good physicochemical properties and are used as substitutes for various natural origin products, and are also raw material components for the production, for example, plastics, paints, varnishes, textiles, *etc.*¹⁻¹⁰

However, such oligomers do not contain functional groups (epoxy, hydroxyl, carboxyl, *etc.*) in their structure which complicates their use as composite system components. To increase the assortment of PPR and CIR, improve their operational characteristics, and expand the field of practical application, the method and technology for obtaining petroleum polymer and coumarone-indene resins with functional groups, particularly oxygen-containing ones, have been developed. Such resins are a qualitatively new class of oligomeric products. The presence of functional groups in the PPR and CIR structure makes it possible to improve their physical and mechanical properties (impact strength, flexural strength, hardness, gel fraction content, *etc.*), chemical resistance to aggressive mediums of products based on them, and also to significantly expand the scope of their application in various industries.

The methods of obtaining PPR and CIR with functional groups were first developed and studied at the Department of Chemical Technology of Oil and Gas Processing of the Lviv Polytechnic National University.

The purpose of this work was to systematize a sufficiently large amount of scientific research on the study of the main regularities of obtaining petroleum polymer and coumarone-indene resins with oxygen-containing functional groups as well as the structure of these oligomers.

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2. Experimental

2.1. Materials

The raw materials for obtaining PPR with functional groups were C₉ fractions extracted from the pyrolysis pyrocondensate of gasoline and diesel fuel (Table 1).

The content of unsaturated hydrocarbons in them was 50–55 wt. % corresponding to the literature data.⁸

The raw materials for obtaining CIR with functional groups were the fractions separated from the liquid products of coal coking (Table 2). In particular, it is a light coal tar fraction (LCTF) and a heavy gasoline fraction (heavy fraction of “raw benzene”).

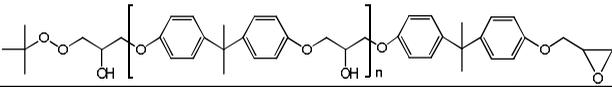
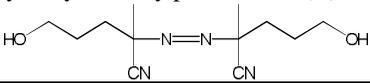
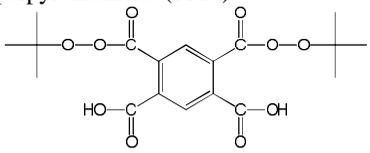
Table 1. Characteristics of raw materials for obtaining petroleum polymer resins with functional groups

Parameter	Value
Density (d_4^{20})	0.908–0.920
Molecular weight (M_n)	110–126
Bromine number, g Br ₂ /100 g	78–120
Refractive index (n_D^{20})	1.5143–1.5313
Boiling point of fractions, K:	
initial	394–420
end	459–471
Content, wt. %:	
Σ C ₅	0.30–5.03
Σ C ₆	0.20–1.00
Benzene	traces
Σ C ₇	0.17–0.30
Toluene	0.40–11.42
Σ C ₈	0.16–0.70
Ethylbenzene	3.20–4.30
Xylenes	15.39–26.30
Styrene	16.93–21.70
α-Methylstyrene	0.60–1.97
Vinyltoluenes	8.70–12.70
Σ C ₉	12.70–17.54
Dicyclopentadiene	7.47–18.50
Indene	3.50–10.21
Σ C ₁₀	4.20–22.95
Σ C ₁₁	1.20–1.40
Cumene	traces–0.41
<i>n</i> -Propylbenzene	traces–0.80
Ethyltoluenes	traces–4.02
Allylbenzene	traces–0.86
Mesitylene	traces–2.18
Pseudocumene	traces–0.73
Hemimellitol	traces–1.84
Indane	traces–0.56

Table 2. Characteristics of raw materials for obtaining coumarone-indene resins with functional groups

Parameter	Value
Boiling point of fractions, K:	
initial	363–396
end	474–478
Content, wt. %:	
Benzene	2.13–35.06
Toluene	1.23–23.78
Ethylbenzene	traces–1.84
Xylenes	10.70–46.87
Styrene	1.26–6.72
<i>o</i> -Ethylbenzene	1.56–4.31
Pseudocumene	1.18–7.69
Hidrindane	2.63–4.37
Coumarone	1.29–5.74
Indene	3.94–44.41
Naphthalene	1.79–6.86
Methylnaphthalenes	traces–3.56
unidentified substance	1.86–4.53

Table 3. Characteristics of reaction initiators for obtaining petroleum polymer resins with functional groups

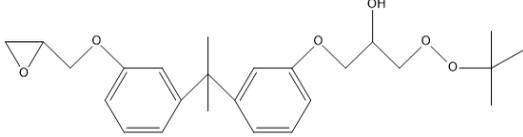
Name, formula	Molecular weight (M_n)	Epoxy number (e.n.), %	Active oxygen [O] _{act.} , %	Hydroxyl group content, %	Carboxyl group content, %
Peroxide derivative of ED-20 epoxy resin (ED-20P resin) n=0-2 	700	5.2	2.3	–	–
2,2'-Azo-bis(5-hydroxy-2-methylpentanenitrile) (AZP)** 	252	–	–	13.5	–
Di-tert-butyl diperpyromellitate (PPM)*** 	398	–	8.0	–	22.6

* It was used for the synthesis of petroleum polymer resin with epoxy groups (PPRE).

** It was used for the synthesis of petroleum polymer resin with hydroxy groups (PPRH).

*** It was used for the synthesis of petroleum polymer resin with carboxy groups (PPRC).

Table 4. Characteristics of reaction initiators for obtaining coumarone-indene resins with functional groups

Name, formula	Density (d_4^{20})	Refractive index (n_D^{20})	Molecular weight (M_n)	Active oxygen [O] _{act.} , %	Epoxy group content, %
2,2'-Azobis(2-methylpropanitrile) (AMP)*	0.858	1.495	–	–	–
Monoperoxide derivative of Bisphenol A diglycidyl ether (PO)** 	–	–	420	2.5	8.4

* It was used as a 0.2 M solution in toluene to synthesize coumarone-indene resins with carboxyl groups (CIRC) and coumarone-indene resins with methacrylate fragments (CIRM).

** It was used as a 50 % solution in toluene to synthesize coumarone-indene resins with epoxy groups (CIRE).

To obtain PPR with oxygen-containing functional groups, organic substances were used as reaction initiators, the type and characteristics of which are given in Table 3.

To obtain CIR with oxygen-containing functional groups, organic substances were used as reaction initiators, the type and characteristics of which are given in Table 4.

The following auxiliary substances were used during the experimental studies:

- petroleum ether – fraction 313-343 K; density $d_4^{20} = 0.650$; aromatic and unsaturated hydrocarbons, water, and mechanical impurities are absent;
- benzene; used a reagent of the highest degree of purity, the content of the main component is 99 %;
- acetone; used a reagent of the highest degree of purity, the content of the main component is 99 %;

- ED-20 epoxy resin; used commercial one without additional purification;
- methacrylic acid (MA) purchased from Aldrich, USA; density $d_4^{20} = 1.015$;
- methyl methacrylate (MMA) purchased from VWR Prolabo Chemicals (CAS: 80-62-6), density $d_4^{20} = 0.935$;
- glycidyl methacrylate (GMA) purchased from Aldrich, USA, density $d_4^{20} = 1.9042$;
- styrene; before use, it was dried with solid alkali and purified by distillation at a temperature of 323 K and a residual pressure of 300-400 Pa; density $d_4^{20} = 0.906$.

2.2. Experimental Procedure

The synthesis of petroleum polymer and coumarone-indene resins with oxygen-containing functional groups was carried out in glass or metal ampoules with a volume of 100 mL. Appropriate mixtures (raw material + initiator) were loaded into ampoules, blown with inert gas, closed, and placed in a thermostat. After the cooligomerization ended at a defined temperature and duration, the ampoules were cooled to room temperature, and their contents were precipitated with petroleum ether. The obtained residue was dried in a vacuum drying cabinet at a temperature of 313 K, after which the yield of the residue was calculated.

2.3. Methods of Analysis

Chromatographic analysis of C_9 fractions was carried out on a Carlo Erba (Model 4130) chromatograph with a flame ionization detector. The capillary column (length 25 m, diameter 0.42 mm) was packed with a sorbent BP-1 or OV. The carrier gas was nitrogen. The temperatures of the column's thermostat were $T_{initial} = 323$ K, and $T_{end} = 398$ K. The programmer was turned on after three minutes. The heating rate was 2 degrees per second. The evaporator temperature was 523 K. The detector temperature was 493 K. The sample volume injected into the chromatograph was 0.02 microliters.

Chromatographic analysis of CCLP was carried out on a Crystal 2000M gas-liquid chromatograph with a flame ionization detector. The column length was 3 m. The general principle of operation was as follows: exposure at 145 degrees – 27 minutes, then heating at a rate of 10 degrees per minute to 210 degrees. The evaporator temperature was 250 degrees, detector 250 degrees. The gas flow rate (helium) was 30 mL/min, hydrogen 30 mL/min, and air 300 mL/min.

Infrared spectra of PPR with oxygen-containing functional groups were recorded on a Specord M-80 spectrophotometer (Germany). Films of PPR, bitumen and polymers were obtained from a solution in benzene (approximate layer thickness 0.03 mm). IR spectra were

recorded in the frequency range of 3800-500 cm^{-1} with an integration time of 1 s.

Infrared spectra of CIR with functional groups were recorded on Nicolet IR 200 (Thermo Electron Co., USA) with a GoldenGate ATR diamond crystal. Each spectrum was recorded with 4 cm^{-1} resolution. The samples were prepared as a powder or dissolved in acetone.

The molecular weight of raw materials and products was determined using a cryoscopy in benzene according to the standard method.¹¹

The refractive index of the raw material was determined according to the standard method.¹¹

The density of raw materials was determined according to the standard method.¹¹

The bromine number of raw materials and products was determined according to the standard method.¹²

The content of active oxygen in raw materials and products was determined according to the standard method.¹³

The acid number of resins was determined according to the standard method.¹⁴

The epoxy number of resins was determined according to the standard method.¹³

The hydroxyl number of resins was determined according to the standard method.¹⁵

The fractional composition of raw materials was determined in the Engler apparatus according to the standard method.¹⁶

The softening point of the resin was determined by the ring and ball test.¹⁷

The content of carboxyl groups was determined using a back titration method.¹⁸

2.4. Calculation Methods

The yield of petroleum polymer and coumarone-indene resins with oxygen-containing functional groups was calculated according to the formula:

$$x_{\text{resin}} = \frac{m_{\text{resin}}}{m_{w.r.m.}} \cdot 100$$

where X_{resin} – resin yield, % by weight of raw materials; m_{resin} – weight of resin, g; $m_{w.r.m.}$ – weight of the reaction mixture, g.

The functionality of resins with epoxy groups was determined by the formula:

$$f = \frac{M_{resin} \cdot E.N_{resin}}{43 \cdot 1000}$$

where f – functionality of resin; M_{resin} – molecular weight of resin; $E.N_{resin}$ – epoxy number of resin; 43 – molecular weight of the epoxy group.

The functionality of resins with carboxyl groups was determined by the formula:

$$f = \frac{M_{resin} \cdot A.N_{resin}}{56 \cdot 1000}$$

where f – functionality of resin; M_{resin} – molecular weight of resin; $A.N_{resin}$ – acid number of resin; 56 – molecular weight of KOH.

3. Results and Discussion

3.1. Petroleum Polymer Resins with Oxygen-Containing Functional Groups

3.1.1. Petroleum polymer resins with epoxy groups.^{19,20}

Petroleum polymer resins with epoxy groups (PPRE) were obtained by initiated oligomerization of unsaturated hydrocarbons contained in the C_9 fraction of hydrocarbon pyrolysis (Table 1), using as an initiator the peroxide derivative of epoxy resin ED-20 (ED-20P resins) (Table 3).

The research results showed (Fig. 1) that an increase in the initiator content in the reaction mixture contributes to a higher yield of PPRE, and the maximum PPRE yield (28.1 wt. % per raw material) is observed at 403 K. A further increase in the oligomerization temperature causes a decrease in the yield due to the rate increase of side reactions, particularly the recombination of the original functional radicals.

When the content of the initiator increases, the molecular weight of PPRE also increases, which is explained by the high molecular weight of functional radicals that initiate the oligomerization process. A characteristic feature of PPRE is a high molecular weight of up to 6000 and even higher.

It was established (Fig. 1) that an increase in the initiator content in the reaction mixture causes an increase in the PPRE epoxy number. This is a consequence of an increase in the concentration of functional radicals in the reaction mixture and an increase in the number of epoxy groups in the PPRE structure. The influence of the process

temperature on the epoxy number is extreme with a minimum at 403 K. An increase in the content of the initiator (ED-20P resin) in the reaction mixture and an increase in the process temperature lead to a decrease in the PPRE bromine number, which is responsible for the unsaturation of the obtained product.

The ED-20P resin initiator content of 5.0 wt. % in the reaction mixture at the oligomerization process temperature of 403 K is optimal in terms of yield, quality, and economic feasibility.

The influence of the oligomerization time of the unsaturated hydrocarbons of C_9 fraction on the yield and main characteristics of PPRE was studied. They were obtained at 403 K for 1-60 hours in the presence of 5.0 wt. % on the raw material of the initiator ED-20P resin. The research results show (Table 5) that increasing the oligomerization duration resulted in a higher yield of PPRE. At the same time, the molecular weight and bromine number of the obtained functional oligomers increase while their epoxy number and functionality (the average number of epoxy groups in the molecule) decrease. The reason is that during initiated oligomerization, the amount of initiator in the reaction mixture decreases over time since it is introduced into the raw material mixture once at the beginning of the process. Therefore, with a long duration of the process at the stage of chain growth, a larger number of reactive unsaturated monomers, which are part of the hydrocarbon C_9 fraction of the pyrocondensate, have time to take part before it is broken.

According to the research results, a method of obtaining PPR with epoxy groups was developed, and its optimal conditions were established: the ED-20P initiator content – 5.0 wt. % of the raw material; temperature – 403 K; oligomerization time – 40 hours.

Fig. 2 shows the results of IR spectroscopic studies that characterize the structure of petroleum polymer resin with epoxy groups.

Table 5. Dependence of PPRE yield and characteristics on the oligomerization time* of C_9 fraction

Process time, hours	PPRE yeald, wt. %	PPRE characteristics			
		M_n	$E.N.$, %	$B.N.$, g Br ₂ /100 g	Functionality
1	14.2	750	1.2	6.4	0.2
5	16.3	1080	1.0	7.7	0.3
10	17.5	2100	0.9	8.5	0.4
20	19.0	3200	0.7	11.1	0.5
30	20.0	4200	0.6	13.0	0.6
40	21.0	5050	0.5	14.0	0.6
50	21.0	5400	0.3	15.8	0.4
60	21.1	5600	0.2	16.5	0.3

*Initiator content (ED-20P) – 5.0 wt. % of raw materials; temperature – 403 K.

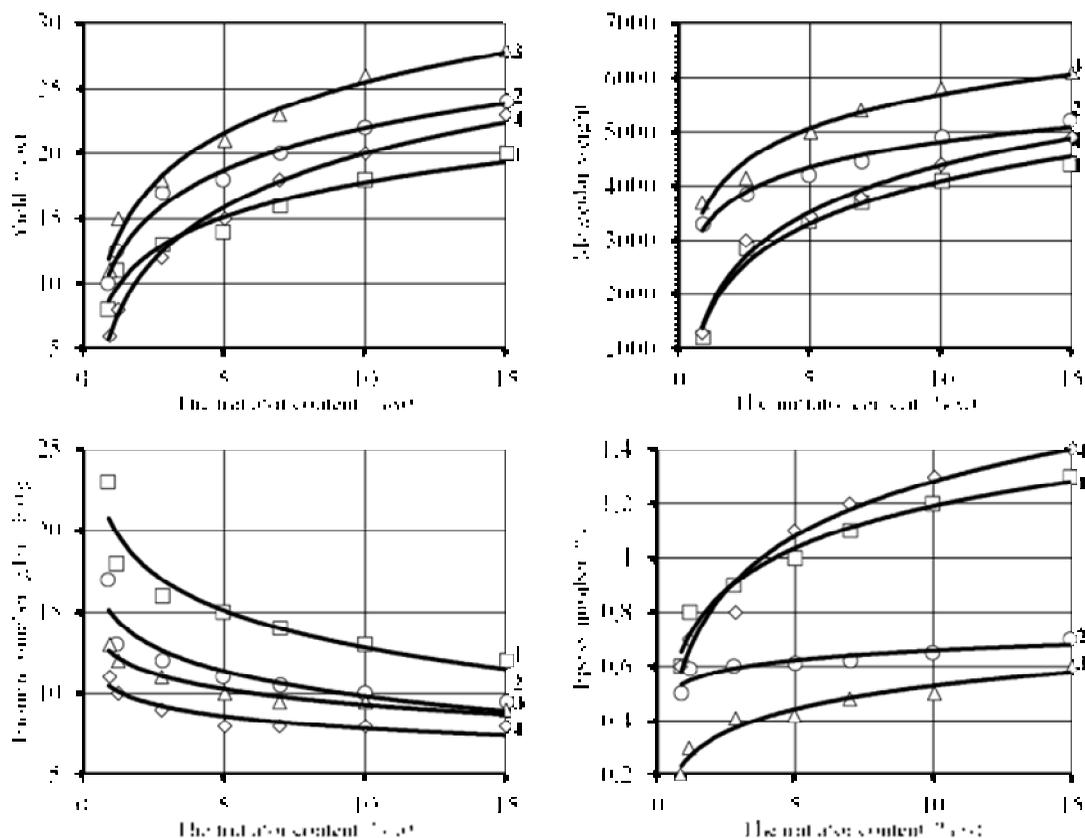


Fig. 1. Dependence of yield and main characteristics of PPRE on the initiator (ED-20P) content according to: 383 K (1), 393 K (2), 403 K (3), and 413K (4). Oligomerization time – 40 hours.

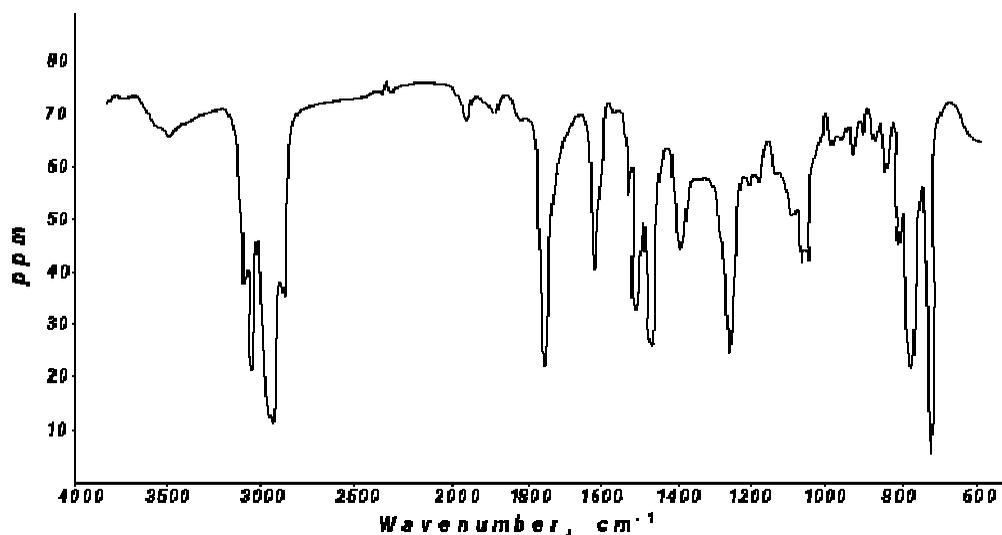


Fig. 2. IR spectrum of PPRE

In the IR spectrum of PPRE (Fig. 2), absorption bands at 910 cm⁻¹ were found, which can be related to the stretching vibrations of the epoxy ring. This absorption band presence indicates that the obtained resin contains epoxy groups in its structure.

ED-20P peroxide resin contains secondary hydroxyl groups. Therefore, when its fragments enter the structure of petroleum polymer resin, an absorption band characteristic of hydroxyl groups appears in the PPRE spectrum: stretching vibrations of ν_{OH} are found at 3456 cm⁻¹.

The presence of OH groups in the obtained resin is also proven by the presence in the spectra (Fig. 2) of absorption bands at $1050\text{--}1040\text{ cm}^{-1}$, which are characteristic of the bending vibrations of the OH group (δ_{OH}).

The inclusion of ED-20P resin fragments in the PPRE structure can also be confirmed by the presence of absorption bands at $1190\text{--}1180\text{ cm}^{-1}$, which are related to stretching vibrations of ether bonds ($\nu_{\text{C-O}}$).

The vibrations at 1600 cm^{-1} can be attributed to both benzene rings and --C=C-- bonds of aliphatic chains. Benzene rings can enter the petroleum polymer resin molecule by an initiator. According to this, it can be concluded that PPRE includes fragments of unsaturated compounds that take part in the oligomerization reaction. The presence of benzene rings in the resin structure is also proved by the absorption bands at $780\text{--}750\text{ cm}^{-1}$, which are characteristic of the bending vibrations of the CH group in the benzene bond.

Thus, the structure of the obtained PPRE was confirmed based on IR spectroscopic studies.

3.1.2. Petroleum polymer resins with hydroxyl groups.^{21,22}

Petroleum polymer resins with hydroxyl groups (PPRH) were obtained by initiated oligomerization of un-

saturated compounds of C_9 fraction of hydrocarbon pyrolysis (Table 1) in the presence of 2,2'-azo-bis(5-hydroxy-2-methylpentanonitrile) (AZP) (Table 3).

It was found that increasing the amount of initiator in the reaction mixture increases the yield of PPRH (Fig. 3), the maximum of which is reached at 343 K. This is because at lower temperatures, the rate of AZP decomposition, and accordingly, the rate of the initiation stage is low. At temperatures above 343 K, the recombination rate of functional radicals increases, so the PPRH yield decreases. This assumption is confirmed by studying results of the influence of the initiator amount on the molecular weight and hydroxyl number of PPRH.

An increase in the AZP content in the reaction mixture led to a higher hydroxyl number and lower molecular weight of the obtained oligomers. This is explained by the acceleration of the recombination of functional radicals with hydroxyl groups at their high concentration in the mixture (Fig. 3). The maximum hydroxyl number of petroleum polymer resins is reached at a temperature of 343 K. At lower temperatures, the rate of initiator decomposition is insufficient. At temperatures above 343 K, a large amount of the radicals formed during the decomposition of the initiator immediately enter the recombination reaction and therefore are not part of the PPRH.

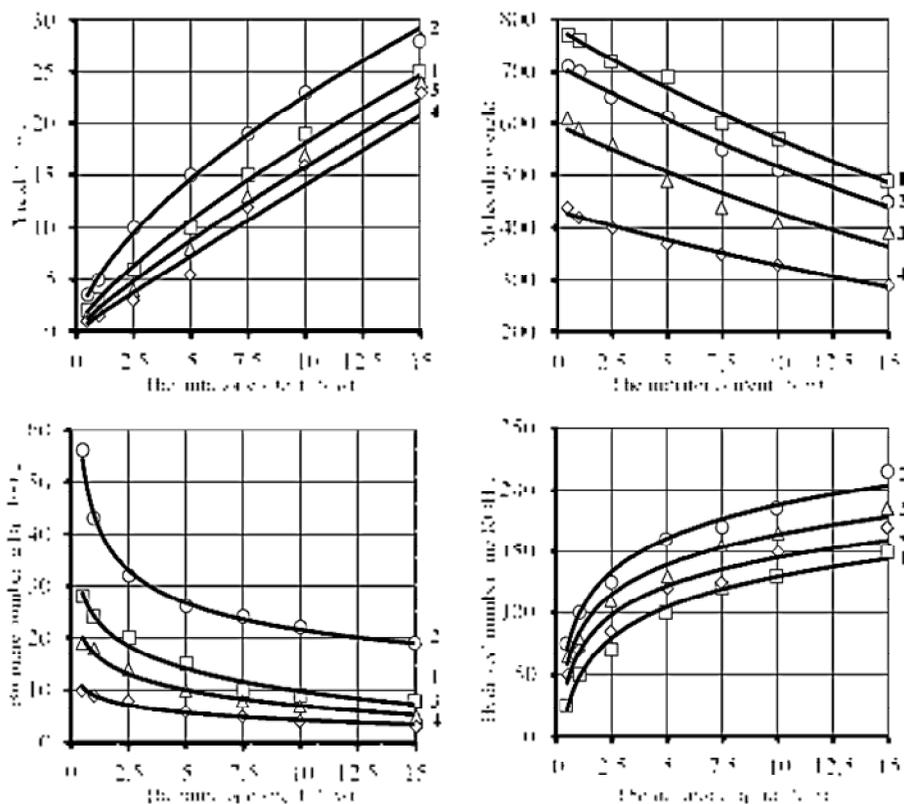


Fig. 3. Dependence of yield and main characteristics of PPRH on the initiator (AZP) content according to: 333 K (1), 343 K (2), 353 K (3), and 363 K (4). Oligomerization time – 50 hours.

The unsaturation of petroleum polymer resins with hydroxyl groups, characterized by the bromine number, decreases with an increase in the initiator content in the reaction mixture. Increasing the AZP content in the reaction mixture increases the probability of recombination of functional radicals and the PPRH formation with low unsaturation. Decreasing the AZP content causes a chain breakage mainly by disproportionation or chain transfer to the solvent, so the unsaturation of functional PPRs increases. Resins obtained at 343 K are characterized by maximum unsaturation. At higher temperatures, the unsaturation decreases due to the increase in the recombination rate.

It was established (Table 6) that an oligomerization time increase resulted in higher yield, higher molecular weight, and a lower hydroxyl number of PPRH. This is due to the decrease in the concentration of the initiator (AZP) in the reaction mixture over time. Therefore, during long-term oligomerization in the chain growth stage, a larger number of reactive unsaturated monomers, which are part of the C₉ fraction, have time to take part before it is broken. A consequence of the decrease in the AZP

amount in the reaction mixture with oligomerization time is also an increase in the bromine number of PPRH.

According to the research results, a method of obtaining PPRH was developed, and its optimal conditions were established: the AZP initiator content – 5.0 wt. % of the raw material; temperature – 343 K; oligomerization time – 50 hours.

Fig. 4 shows the results of IR spectroscopic studies that characterize the structure of petroleum polymer resin with hydroxyl groups.

Analysis of the spectrum (Fig. 4) showed the presence of absorption bands at 3440 cm⁻¹, related to asymmetric stretching vibrations of the hydroxyl group, and OH bending vibrations at 1128 cm⁻¹.

At the same time, in the IR spectrum of PPRH, there are C–H stretching vibration bonds of the benzene ring in the range of 3050-3100 cm⁻¹, as well as vibrations of C–C bonds of benzene rings at 1490-1600 cm⁻¹. The C–H bending vibrations of benzene rings are observed in the range of 704-760 cm⁻¹. All of the above confirms the presence of benzene rings in the structure of petroleum polymer resins with hydroxyl groups.

Table 6. Dependence of PPRH yield and characteristics on the oligomerization time* of C₉ fraction

Process time, hours	PPRH yield, wt. %	PPRH characteristics		
		<i>M_n</i>	<i>H.N.</i> , mg KOH/g	<i>B.N.</i> , g Br ₂ /100 g
10	9.8	340	206.4	11.7
20	11.8	380	195.8	14.8
30	13.9	440	177.9	17.6
40	14.7	510	168.2	23.5
50	15.3	610	155.2	26.2
70	15.9	740	139.6	34.0

*Initiator content (AZP) – 5.0 wt. % of raw materials; temperature – 343 K.

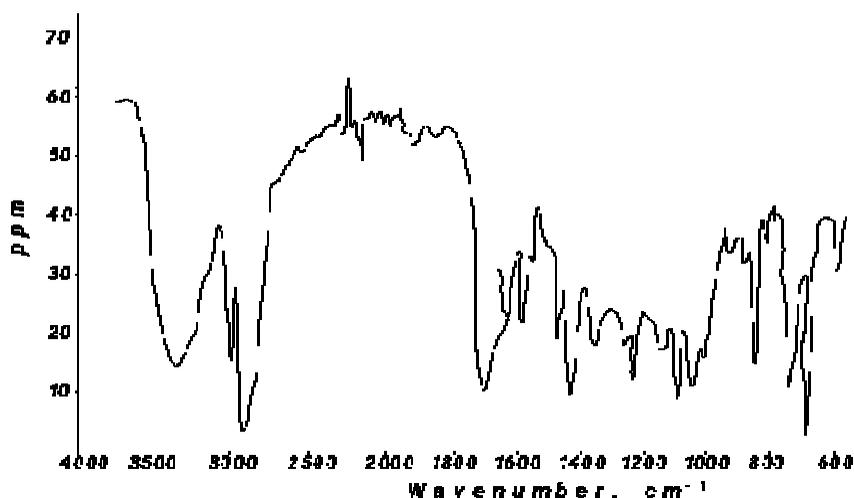


Fig. 4. IR spectrum of PPRH

The structure of PPRH also contains double C=C bonds of aliphatic chains. They are characterized by vibrations in the range of 1600-1650 cm^{-1} . Although they can refer to benzene rings as well. The spectrum of the synthesized resin also contains C=C bending vibration bonds at 888-908 cm^{-1} .

The presence of methyl groups in the PPRH structure is confirmed by vibrations at 2920 cm^{-1} , 2856 cm^{-1} , and 1452 cm^{-1} .

Thus, IR spectroscopic studies of PPRH made it possible to characterize its structure and confirm the presence of functional OH groups.

3.1.3. Petroleum polymer resins with carboxyl groups.²³

Petroleum polymer resins with carboxyl groups were obtained by initiated oligomerization of unsaturated hydrocarbons, which are part of the C₉ fraction of hydrocarbon pyrolysis (Table 1), in the presence of di-tert-butyl diperyromellitate (PPM) peroxide initiator with carboxyl groups (Table 3). It was established with complex thermal analysis that this initiator decomposes in the temperature range of 373-423 K, and therefore PPRC synthesis was carried out in this temperature range.

Fig. 5 shows the study results on the influence of temperature and the initiator content in the reaction mixture on the yield and characteristics of PPRC.

It was established that with an increase in the initiator content in the reaction mixture, the yield and acid number increase, and the molecular weight of PPRC decreases. This is explained by the fact that with the increasing initiator concentration, the number of formed functional radicals increases in the reaction mixture, which accelerates recombination. As a result, an oligomeric product is formed with a lower molecular weight and a higher content of carboxyl groups. The bromine number of PPRC, which characterizes the content of unsaturated bonds, decreases as the initiator amount in the reaction mixture increases. An increase in temperature leads to consequences similar to those of increasing the initiator content in the reaction mixture.

Increasing the oligomerization time of PPRC (Table 7) resulted in its higher molecular weight and a lower acid number. This is due to the decrease in the concentration of functional radicals over time. Increasing the oligomerization time leads to a higher bromine number and yield of PPRC. The PPRC functionality (the content of carboxyl groups in the average oligomer molecule) decreases with increasing oligomerization time.

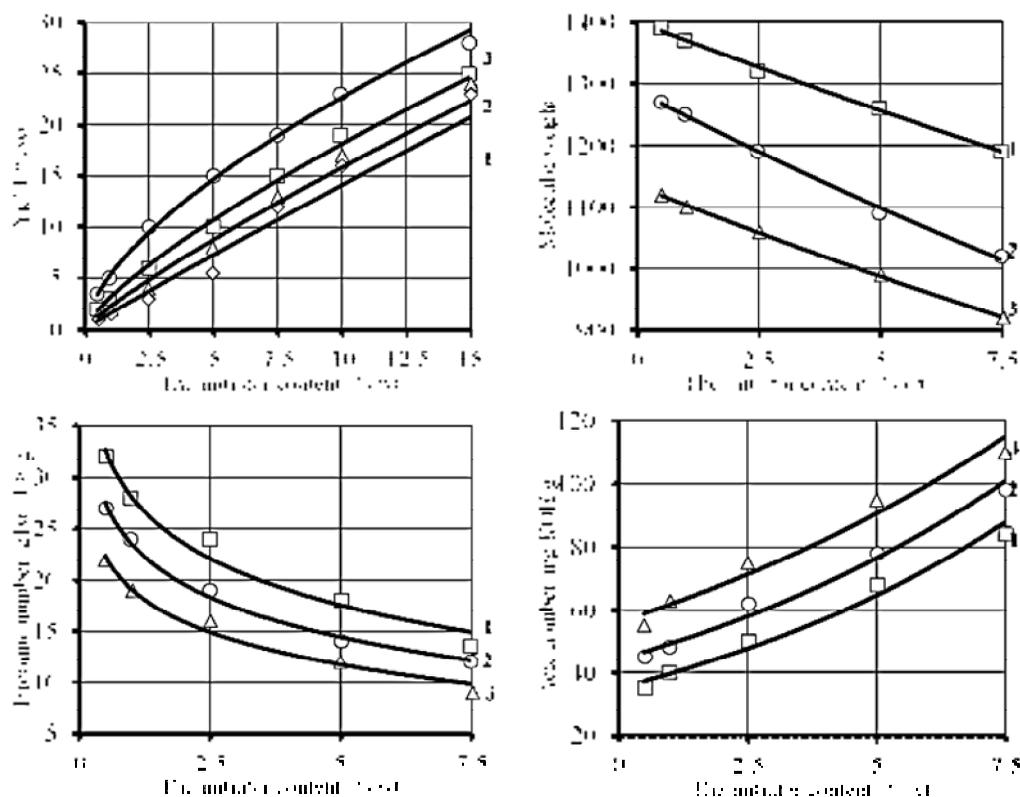
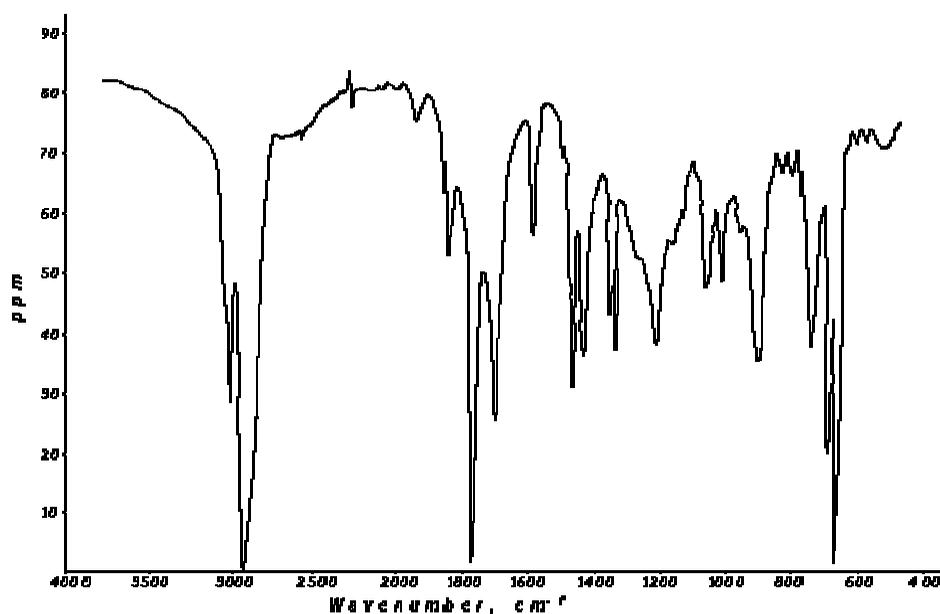


Fig. 5. Dependence of yield and main characteristics of PPRC on the initiator (PPM) content according to: 393 K (1), 403 K (2), 413 K (3). Oligomerization time – 50 hours.

Table 7. Dependence of PPRC yield and characteristics on the oligomerization time* of C₉ fraction

Process time, hours	PPRC yield, wt. %	PPRC characteristics			
		M_n	A.N., mg KOH/g	B.N., g Br ₂ /100 g	Functionality
5	10.9	870	139.2	3.8	2.17
10	13.1	930	130.9	4.9	2.17
20	15.3	990	118.0	7.0	2.09
30	16.5	1060	104.0	8.6	1.97
40	17.4	1070	90.2	12.2	1.72
50	18.1	1080	78.4	14.9	1.51

* Initiator content (PPM) – 5.0 wt. % of raw materials; temperature – 413 K.

**Fig. 6.** IR spectrum of PPRC

According to the research results, a method for obtaining PPRC was developed and optimal conditions were determined: PPM initiator content – 5.0 wt. % of the raw material; temperature – 313 K; oligomerization time – 50 hours.

Fig. 6 shows the results of IR spectroscopic studies that characterize the structure of petroleum polymer resin with carboxyl groups.

The presence of carboxyl groups in the structure of synthesized resin is confirmed by a wide band in the range of 3300-2500 cm⁻¹ (Fig. 6). There is also a band at 1712 cm⁻¹ in the spectrum, which can be attributed to C=O stretching vibration bond. Non-planar bending vibrations of the OH group is consistent with a wide band at 970-888 cm⁻¹. Another confirmation of the carboxyl groups' presence in the PPRC structure is the components of 1224 cm⁻¹ frequency (the band at 1320-1210 cm⁻¹ corresponds to the C=O vibrations in the carboxyl group).

In the spectrum of PPRC, there are C–H stretching vibration bonds of the benzene ring in the region of 3050-3100 cm⁻¹ and C–C vibration bonds of the benzene rings at 1490-1600 cm⁻¹. The C-H bending vibration bonds of benzene rings are observed at 704-760 cm⁻¹. All this confirms the presence of benzene rings in the structure of petroleum polymer resins with carboxyl groups. The structure of the initiator fragment, which according to the previously proposed mechanism is a part of PPRC, can be confirmed by the presence in the spectrum of non-plane bending vibrations of the 1,2,4,5-substituted benzene ring at 900 cm⁻¹.

The presence of ethyl groups in the structure of the synthesized resins is confirmed by vibrations at 2980 cm⁻¹, and 2860 cm⁻¹.

The presence of a *tert*-butoxy group in the PPRC molecule is confirmed with a doublet at 1385 cm⁻¹ and 1365 cm⁻¹, as well as skeletal vibrations at 1224 cm⁻¹ related to C(CH₃)₃ groups.

Thus, the conducted IR spectroscopic studies confirm the structure of the obtained PPRC in the presence of peroxides, particularly carboxyl and *tert*-butoxy groups.

3.2. Coumarone-Indene Resins with Oxygen-Containing Functional Groups

3.2.1. Coumarone-indene resins with carboxyl groups.²⁴

Coumarone-indene resins with carboxyl groups (CIRC) were obtained by radical cooligomerization of unsaturated hydrocarbons that are part of CCLP (Table 2) and styrene in the presence of 2,2'-azobis(2-methylpropionitrile) (AMP) as an initiator (Table 4). To obtain resins with free carboxyl groups, methacrylic acid (MA) was added as a monomer to the mixture. The studied reaction mixture contained: LCTF 45.2 mass parts, styrene 7.3 mass parts, and MA 2 mass parts.

Fig. 7 shows the research results on the influence of the initiator content in the reaction mixture, temperature, and time synthesis on the CIRC yield.

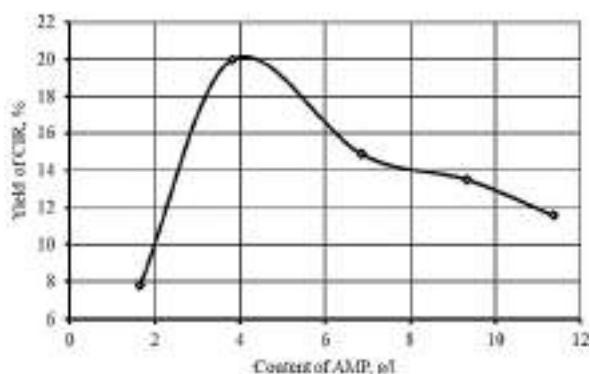


Fig. 7. Influence of the initiator amount on the yield of CIR with carboxyl groups (reaction temperature 353 K, reaction time 6 hours)

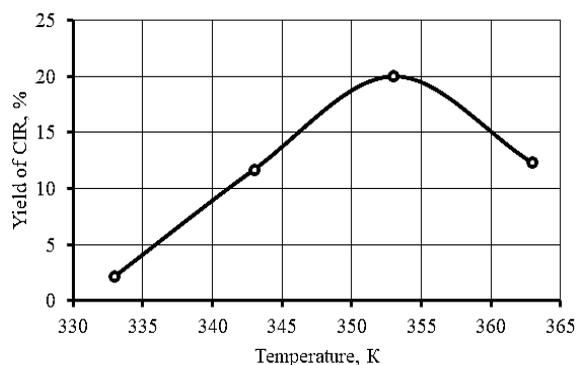


Fig. 9. Influence of temperature on the yield of CIR with carboxyl groups (AMP concentration 3.82 g/L, reaction temperature 353 K)

Analyzing the influence of the initiator amount on the CIRC yield (Fig. 7), it was established that the highest yield is observed in the case of using AMP in the amount of 3.82 g/L per 45.2 g of the initial LCTF. A further increase in the AMP amount in the initial mixture does not increase the CIRC content in the reaction mixture but also leads to a slight decrease relative to the mass of the reaction mixture as a whole. The decrease in the CIRC amount can be explained by the fact that in the case of AMP content higher than 3.82 g/L, based on the initial LCTF2, not only the reaction initiating the cooligomerization of unsaturated compounds contained in the LCTF, styrene, and MA, but also the recombination reaction of radicals formed as a result of the AMP decomposition according to the equation:

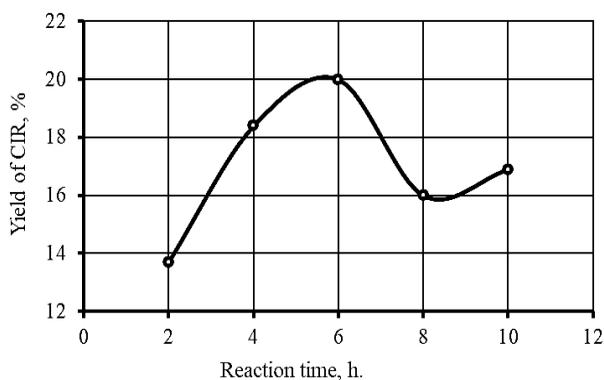
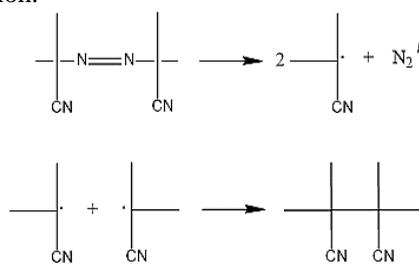


Fig. 8. Influence of reaction time on the yield of CIR with carboxyl groups (AMP concentration 3.82 g/L, reaction temperature 353 K)

Increasing the AMP content in the reaction mixture promotes the reaction according to the above scheme. The removal of free radicals from the reaction mixture leads to a lower CIRC yield, the formation of which occurs only by initiated cooligomerization. The data of Fig. 7 also indicate that the cooligomerization reaction of unsaturated compounds included in the initial reaction mixture does not proceed.

Analysis of the influence of cooligomerization time was shown (Fig. 7) that the highest yield of CIRC is observed after 6 hours. As the reaction time increases, the content of carboxyl groups in CIRC decreases (Table 8). This indicates that during the formation of CIRC, in addition to the cooligomerization reaction, the complex formation between the components of the initial LCTF2 may

occur. The formation of additional complexes at the initial stage contributes to the increase in the yield of CIRC. Further heating probably leads to the complexes' destruction and further cooligomerization and, as a result, decreases in the carboxyl group content due to the entering of styrene, indene, and coumarone molecules into the structure (Table 8).

During the analysis of the temperature effect on CIRC yield (Fig. 7), it was established that CIRC is practically not formed at a temperature of 333 K, and at 363 K its yield is decreased (compared to a temperature of 353 K), which is explained by the rapid decomposition of the initiator molecules and recombination of formed radicals according to the above scheme. In addition, at a temperature of 363 K, the cooligomerization reaction with MA participation is accelerated. The increased content of carboxyl groups in CIRC-11 (Table 8) shows this.

According to the research results, a method for obtaining CIRC was developed, and optimal process parameters were established, namely: temperature 353 K, synthesis time 6 hours, reaction mixture composition – LCTF 45.2 mass parts, styrene 7.3 mass parts, MA 2.0 mass parts and AMP in the amount of 0.25 mass parts.

Fig. 10 shows the results of IR spectroscopic studies characterizing the structure of coumarone-indene resins with carboxyl groups.

Analyzing the spectrum (Fig. 10), the presence of coumarone fragments in the CIRC molecule was noted. This is indicated by the presence of absorption bands at 1200-1100 cm^{-1} associated with the ether bond in alicyclic hydrocarbons. Fragments of aromatic compounds characterizing styrene, indene, coumarone, and hidrindane are confirmed by the presence of three absorption bands at 1620, 1500, and 1480 cm^{-1} .

Table 8. Characteristics of CIR with carboxyl groups

CIRC symbol	Content of carboxyl groups, %	Softening temperature, K	M_n
CIRC-1	16.0	375	–
CIRC-2	14.4	391	950
CIRC-3	12.9	392	900
CIRC-4	13.1	386	–
CIRC-5	12.7	381	–
CIRC-6	14.9	384	–
CIRC-7	14.9	393	–
CIRC-8	14.4	383	–
CIRC-9	12.2	377	–
CIRC-10	16.8	–	–
CIRC-11	13.7	391	–
CIRC-12	14.3	394	–

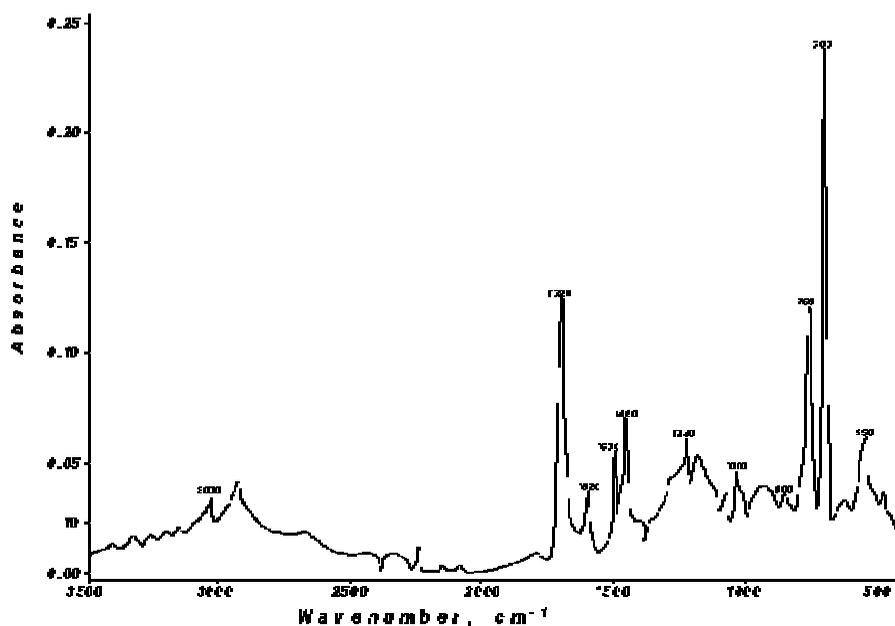


Fig. 10. IR spectrum of CIRC

The presence of free carboxyl groups in the molecule of the synthesized resin is proved by an intense absorption band at 1750 cm^{-1} , which refers to the carbonyl group stretching vibrations in acids. The hydroxyl group in the acid is confirmed by the absorption band at 3000 cm^{-1} and 1010 cm^{-1} .

3.2.2. Coumarone-indene resins with epoxy groups.²⁵

Coumarone-indene resins with epoxy groups (CIRE) were obtained by radical cooligomerization of unsaturated hydrocarbons that are part of CCLP (Table 2) and styrene in the presence of monoperoxide derivative of Bisphenol A diglycidyl ether (PO) as the initiator (Table 4). The epoxy-containing component was glycidyl methacrylate (GMA). The studied reaction mixture contained: LCTF 45.2 mass parts, styrene 5.45 mass parts, and GMA 4.2 mass parts.

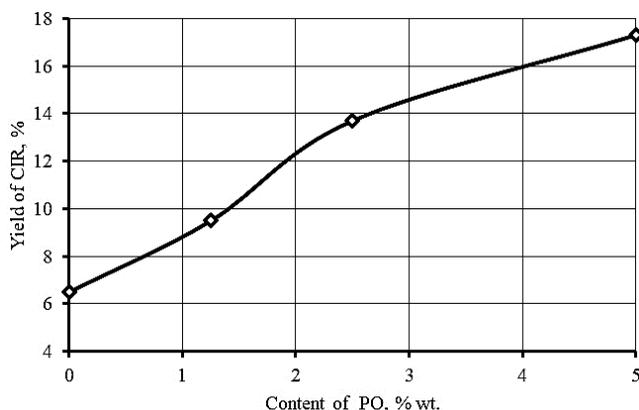


Fig. 11. Influence of the initiator amount on the yield of CIR with epoxy groups (reaction temperature 393 K; reaction time 6 hours; 50 % toluene solution of PO)

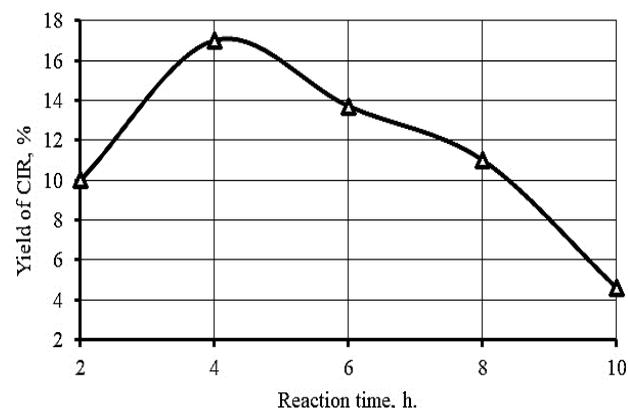


Fig. 12. Influence of reaction time on the yield of CIR with epoxy groups (reaction temperature 393 K; the amount of 50 % toluene solution of PO 2.5 wt. %)

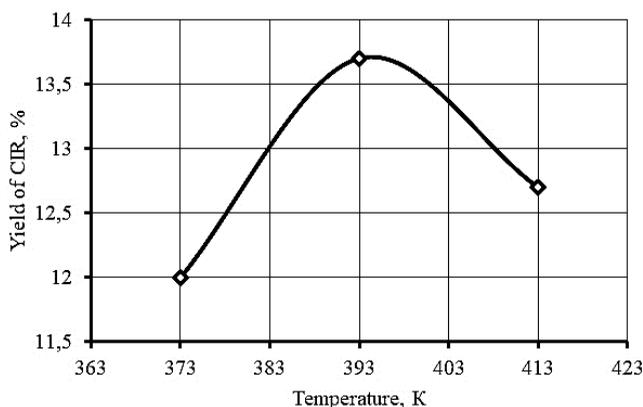


Fig. 13. Influence of temperature on the yield of CIR with epoxy groups (reaction time 6 hours; the amount of 50 % toluene solution of PO 2.5 wt. %)

Figs. 11-13 show the research results of the influence of initiator content in the reaction mixture, temperature, and synthesis time on the CIRE yield.

Analyzing Fig. 11, it was found that unlike previous studies, where AMP was used as an initiator and the process temperature was 353 K, the cooligomerization at 393 K without PO initiator resulted in resin formation. This indicates that the monomers contained in the initial mixture (styrene, GMA) can form resins at such a high temperature due to thermal polymerization. Using an initiator leads to an increase in CIRE yield. This indicates that both thermal polymerization of the reaction mixture monomers and initiated polymerization due to the decomposition of PO molecules with the formation of free radicals can occur here. In addition, PO fragments are included in the structure of the obtained resin.

Considering the PO cost, 2.5 mass parts per 59.85 mass parts of the reaction mixture were chosen as the optimal amount.

The results from the study of the influence of reaction time on the CIRE yield are shown in Fig. 12, from which it is seen that the best yield of the target product is achieved in 4-6 hours. Further reaction mixture keeping at 393 K leads to a significant decrease in the target product yield. This can be explained, in our opinion, by the appearance of destructive processes that lead to the destruction of resin molecules at such a temperature.

The reaction temperature also affects the yield of the synthesized resin (Fig. 13). Moreover, according to the results (Fig. 13), increasing the temperature from 373 K to 393 K increases the CIRE yield in terms of both the reaction mixture as a whole and the content of unsaturated compounds in such a mixture. Further increasing the temperature to 413 K decreases the target product yield.

This can be explained, in our opinion, by an increase in the rate of PO thermal decomposition with the

formation of free radicals. The free radicals formed during this reaction not only initiate the monomers present in the reaction mixture but also recombine with each other, thereby reducing the yield of the formed resin. Therefore, a temperature of 393 K was chosen to study the influence of reaction time on CIRE yield.

The values of the softening temperatures for the synthesized resins are given in Table 9.

The presence of epoxy groups in the synthesized resin is confirmed by absorption bands at 944 cm^{-1} . The presence of hydroxyl group in the structure of the indene-coumarone resin formed due to the initiation of unsaturated compounds contained in the reaction mixture by a monoperoxide derivative of diphenylolpropane diglycidyl ether is confirmed by the absorption band at 3368 cm^{-1} . In

addition, the $\text{H.C}=\text{C}(\text{O}(\text{C}(\text{C}))_2\text{CH}_2)$ initiator fragment included in the resin structure was confirmed by gel-dimethyl vibrations at $1384, 1306\text{ cm}^{-1}$, and the ether bond by the vibration band at 1172 cm^{-1} . The presence of benzene rings is confirmed by absorption bands at 1600 and 1512 cm^{-1} . The inclusion of a glycidyl methacrylate molecule containing an ester bond in the resin structure is confirmed by absorption bands at $1720, 1244,$ and 1046 cm^{-1} .

3.2.3. Coumarone-indene resins with methacrylate fragments.²⁶

Coumarone-indene resins with methacrylate fragments (CIRM) were obtained by radical cooligomerization of unsaturated hydrocarbons that are part of CCLP (Table 2) and styrene in the presence of 2,2'-azobis(2-methylpropionitrile) (AMP) as the initiator (Table 4). To obtain resins with methacrylate fragments, methyl methacrylate (MMA) was added to the mixture.

Table 10 shows the research results on the influence of the initial mixture composition on the CIRM characteristics.

Table 9. Softening temperatures of the synthesized coumarone-indene resins with epoxy groups

CIRE symbol	Softening temperature, K
CIRE-1	349
CIRE-2	337
CIRE-3	336
CIRE-4	376
CIRE-5	308
CIRE-6	325
CIRE-7	315
CIRE-8	—
CIRE-9	352
CIRE-10	335

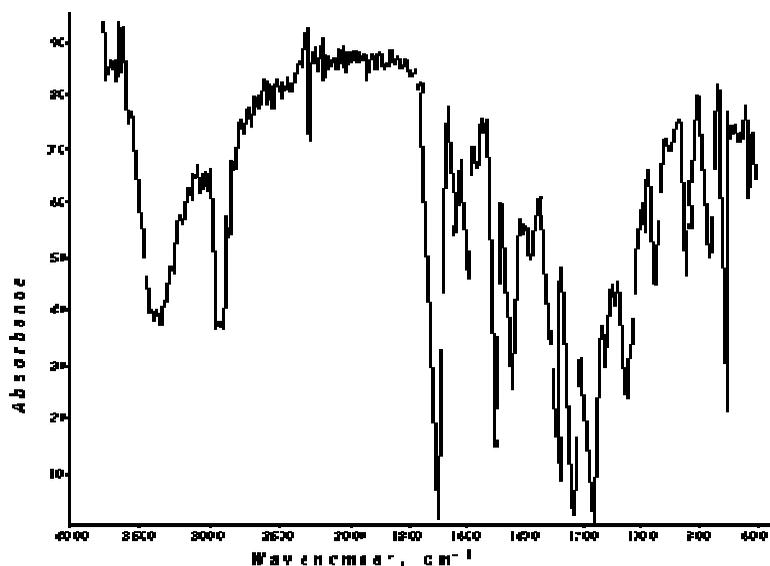


Fig. 14. IR spectrum of CIRE

According to the results presented in Table 10, adding styrene to LCTF in the absence of MMA, the CIRM yield does not exceed 5.1 % (CIRM-1). With a decrease in the amount of styrene and a gradual increase in MMA, an increase in CIRM yield is observed, which in the absence of styrene and MMA amount of 9.35 g per 45.2 g of LCTF is 25.5 % (CIRM-5). At the same time, decreasing the styrene amount and increasing MMA lead to a decrease in the molecular weight and softening temperature of the synthesized resins. As shown in Table 10, it is enough to add MMA to increase the yield of CIRM.

In further studies, the influence of the initiator concentration on the yield and characteristics of the obtained coumarone-indene resins with methacrylate fragments was studied (Table 11).

As seen from Table 11, increasing the AMP concentration to 0.0407 mol/L leads to a higher target product yield and it is 29.7 % (CIRM-7). A further increase in the

amount of AMP to 0.0554 mol/L practically does not affect both the CIRM yield and its characteristics. Since at AMP concentration of 0.0225 mol/L, a sufficiently high yield of the product (CIRM-5) is achieved, and the resulting resin has the highest molecular weight and softening temperature, this amount of initiator was chosen to study the effect of process time (Table 12) and temperature (Table 13) on resin yield and characteristics.

It can be seen from Table 12 that after 4 hours already, the yield of resin increases (CIRM-10). A further increase in the reaction time to 6 h allows obtaining resin (CIRM-5) with a yield of 25.5 %, the molecular weight of 600 g/mol, and softening temperature of 364 K. With a further increase in the reaction time to 8-10 hours, the resin yield and molecular weight practically do not change.

The influence of the reaction temperature on the CIRM characteristic is given in Table 13.

Table 10. Influence of the initial mixture composition on the CIRM* characteristics

Composition of the initial mixture, g			CIRM characteristics			
LCTF	Styrene	MMA	CIRM symbol	Yield on the initial mixture, %	Softening temperature, K	M_n , g/mol
45.2	9.09	0	CIRM-1	5.1	–	–
45.2	7.27	1.87	CIRM-2	7.0	–	840
45.2	3.64	5.61	CIRM-3	13.4	382	700
45.2	1.82	7.48	CIRM-4	17.4	375	670
45.2	0	9.35	CIRM-5	25.5	379	600

*CIRM synthesis conditions: temperature 353 K, time 6 hours, DAC concentration 0.0226 mol/L.

Table 11. Influence of AMP concentration on the CIRM* characteristics

Composition of the initial mixture, g			CIRM characteristics			
AMP, mol/L	LCTF, g	MMA, g	CIRM symbol	Yield on the initial mixture, %	Softening temperature, K	M_n , g/mol
0.0097	45.2	9.35	CIRM-6	9.3	365	540
0.0226	45.2	9.35	CIRM-5	25.5	364	600
0.0407	45.2	9.35	CIRM-7	29.7	337	510
0.0554	45.2	9.35	CIRM-8	29.3	341	490

*CIRM synthesis conditions: temperature 353 K, time 6 hours.

Table 12. Influence of process time on CIRM* characteristics

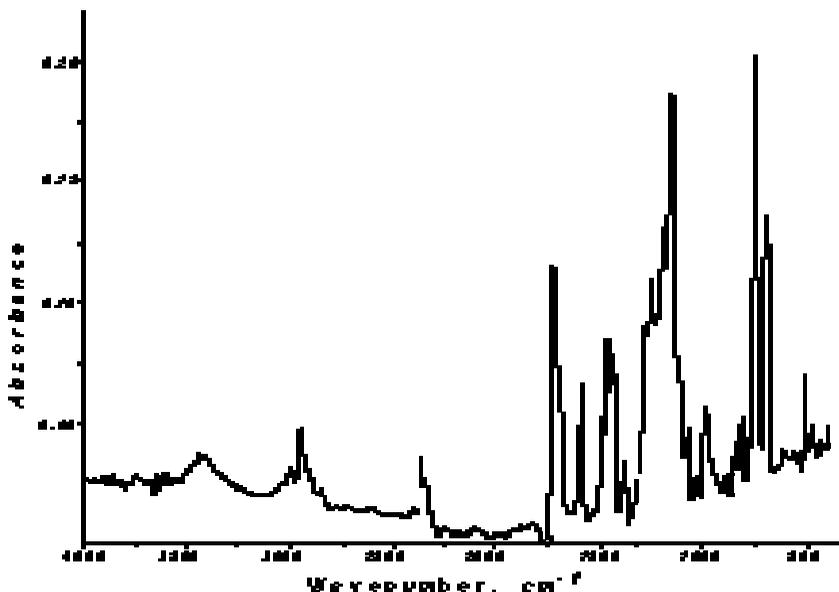
Time, hours	CIRM characteristics			
	CIRM symbol	Yield on the initial mixture, %	Softening temperature, K	M_n , g/mol
2	CIRM-9	18.5	318	470
4	CIRM-10	23.1	328	500
6	CIRM-5	25.5	364	600
8	CIRM-11	25.5	321	590
10	CIRM-12	25.3	325	650

*CIRM synthesis conditions: temperature 353 K, AMP concentration 0.0226 mol/L. The composition of the initial mixture, g: LCTF – 45.2; MMA – 9.35.

Table 13. Influence of process temperature on the CIRM* characteristics

Temperature, K	CIRM characteristics			
	CIRM symbol	Yield on the initial mixture, %	Softening temperature, K	M_n , g/mol
343	KICM-13	15,8	367	510
353	KICM-5	25,5	364	600
363	KICM-14	18,5	359	720

*CIRM synthesis conditions: time 6 hours, AMP concentration 0.0226 mol/L. The composition of the initial mixture, g: LCTF –45.2; MMA – 9.35.

**Fig. 15.** IR spectrum of CIRM

Analyzing the data shown in Table 13, it was found that lowering the reaction temperature to 343 K leads to a decrease in both the resin yield and its molecular weight. Increasing the reaction temperature to 363 K leads, in comparison with the temperature of 343 K, to a slight increase in the resin yield, a decrease in the softening temperature, and also to an increase in the molecular weight. This can be explained by the fact that under these conditions (temperature 363 K), there is a rapid decomposition of the initiator and an increase in the radical recombination reaction. Under these conditions, not all monomers are capable of the oligomerization reaction, resulting in a decrease in the yield of the oligomeric product per initial fraction. The optimum temperature, at which the highest yield is achieved, is 353 K.

Based on the research results, a method for obtaining CIRM was developed, and optimal process parameters were established: temperature 353 K, synthesis time 6 hours, AMP concentration 0.0226 mol/L, MMA amount 9.35 g.

Fig. 15 shows the results of IR spectroscopic studies that characterize the structure of coumarone-indene resins with methacrylate fragments.

The presence of methacrylate fragments in the synthesized resin is confirmed by the stretching vibrations ($\nu_{C=O}$) of the carbonyl group at 1725 cm^{-1} (Fig. 15). The presence of the $-\text{CH}_3$ group in $-\text{C}-\text{O}-\text{CH}_3$ is proved by symmetric bending vibrations at 1386 cm^{-1} . The group $\text{C}-\text{O}-\text{C}$, a part of the methacrylic fragment, is confirmed by asymmetric stretching vibrations at 1145 cm^{-1} . The presence of the indene fragment is confirmed by asymmetric stretching vibrations at 2950 cm^{-1} of CH_2 group, which is directly bounded by the benzene ring in the indene molecule. Fragments of coumarone included in the structure of CIRM are proved by stretching vibrations at 1190 cm^{-1} of the $\text{C}-\text{O}-\text{C}$ group in the coumarone molecule. Benzene rings, which can correspond to styrene, coumarone, and indene molecules, are proved by the presence in the spectrum of stretching vibrations in the region of 1592-1434 cm^{-1} , as well as bending vibrations at 752, 696, 692 cm^{-1} of CH group in the substituted benzene rings. Residues of azo initiator, which are part of the structure of the obtained resins, are confirmed by $-\text{C}\equiv\text{N}$ stretching vibrations bond at 2377, 2358 cm^{-1} .

4. Conclusions

4.1. Petroleum polymer resins with oxygen-containing functional groups

New petroleum polymer resins with functional groups were obtained by initiated oligomerization of unsaturated compounds in fraction C₉ of hydrocarbon pyrolysis (gasoline and diesel fuel).

The influence of the initiator amount, temperature, and reaction time on the yield of functional PPR was determined. The structure of the synthesized resins was confirmed by IR spectroscopy.

The optimal conditions for obtaining petroleum polymer resins with functional groups by initiated oligomerization should be considered:

- with epoxy groups (PPRE): initiator content – ED-20P 5.0 wt. % of the raw materials; temperature – 403 K; oligomerization time – 40 hours;

- with hydroxyl groups (PPRH): the content of the AMP initiator 5.0 wt. % of the raw materials; temperature 343 K; oligomerization time 50 hours;

- with hydroxyl groups (PPRH): content of the AZP initiator 5.0 wt. % of the raw materials; temperature 343 K; oligomerization time 50 hours;

- with carboxyl groups (PPRC): temperature 413 K, time 50 hours, PPM content 5 wt. % of the raw materials.

4.2. Coumarone-indene resins with oxygen-containing functional groups

New functional coumarone-indene resins were obtained by radical cooligomerization of unsaturated compounds contained in coal-coking liquid products with the addition of industrial monomers.

The influence of the initiator amount, temperature, and reaction time on the yield of functional CIR was established. The structure of the synthesized resins was confirmed by IR spectroscopy.

The optimal conditions for obtaining CIR with functional groups by radical cooligomerization should be considered:

- with carboxyl groups (CIRC): temperature 353 K, synthesis time 6 hours, composition of the reaction mixture: LCTF 45.2 mass parts, styrene 7.3 mass parts, MAK 2.0 mass parts and DAK in the amount of 0.25 mass parts;

- with epoxy groups (CIRE): temperature 393 K, time 6 h, PO amount 2.5 mass parts per 59.85 mass parts of the reaction mixture;

- with methacrylate groups (CIRM): temperature 353 K, time 6 h, DAK concentration 0.0226 mol/L, MMA amount 9.35 g.

Acknowledgements

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СМОЛИ З КИСНЕВМІСНИМИ ФУНКЦІЙНИМИ ГРУПАМИ, ЩО ОДЕРЖАНІ З ПРОДУКТІВ ПЕРЕРОБКИ ГОРЮЧИХ КОПАЛИН: ОГЛЯД ДОСЯГНЕНЬ

Анотація. Для синтезу смол з кисневмісними функційними групами використовували фракції C₉ піролізу вуглеводнів, важку бензинову і легку фракцію кам'яновугільної смоли, що отримувалися з рідких продуктів коксування вугілля (РПКВ). Використовуючи вищевказані нецільові та/або побічні продукти переробки органічної сировини, різного роду ініціатори й промислові мономери, отримано: методом ініційованої олігомеризації (з фракцій C₉) – нафтополімерні смоли з функційними групами; методом радикальної коолігомеризації (з РПКВ) – кумарон-інденові смоли з функційними групами. Вивчено вплив основних чинників керування процесом синтезу смол з функційними групами на їхні кількісні і якісні характеристики, зокрема, досліджено вплив температури процесу, його тривалості і складу реакційної суміші. Використовуючи ІЧ-спектроскопію, проаналізовано структуру синтезованих смол і підтверджено присутність у них функційних груп: епоксидних, карбоксильних, гідроксильних і метакрилатних.

Ключові слова: продукти переробки органічної сировини, нафтополімерна смола, кумарон-інденова смола, функційна група.