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OLIGOMERIZATION OF C9 HYDROCARBON FRACTION INITIATED BY AMINO PEROXIDES WITH CYCLIC SUBSTITUTE

Roman Subtelnyy
Corresponding author
PhD, Associate Professor*
E-mail: roman.o.subtelnyi@lpnu.ua
Yevhenii Zhuravskyi
Postgraduate Student*
Dariia Kichura
PhD, Associate Professor*
Bohdan Dzinyak
Doctor of Technical Sciences, Professor*
*Department of
Organic Products Technology
Lviv Polytechnic National University
S. Bandery str., 12, Lviv, Ukraine, 79013

This paper investigates the production of hydrocarbon resins by oligomerization in solution and suspension of the C9 fraction of by-products from oil refining. The disadvantage of existing technologies for oligomers by free radical oligomerization is the use of high reaction temperatures. The application of N-replaced amino peroxides as low-temperature initiators and a suspension oligomerization technology can reduce the temperature and duration of the reaction.

The correlation between oligomerization parameters and yield and characteristics of oligomers has been established. Owing to this, it will be possible to set optimal conditions and predict the properties of the resulting products. The high values of the yield and bromine number correlation in oligomerization in solution (–0.98 and –0.95) and suspension (–0.83 and –0.80) indicate the course of the oligomerization reaction.

The main factor influencing oligomerization in solution is the reaction temperature (correlation 0.80). The softening temperature of oligomers is in the range of 349–353 K and does not depend on the oligomerization conditions in the solution (correlation indicator 0.18).

Suspension oligomerization in the studied intervals does not depend on temperature (correlation –0.08) and initiator concentration (correlation 0.40). It is proved that in the studied intervals of variables, the yield of oligomers depends on the duration of the reaction (correlation 0.88). The color indicator of suspension oligomerization products at the studied intervals varies slightly and is 20–30 mg I_2/100 ml.

The established optimal conditions make it possible to effectively use oil refining by-products by synthesizing light oligomers.

Under the established optimal conditions, the product yield is 22.7 % with oligomerization in solution and 19.4 % with suspension oligomerization

Keywords: petroleum polymer resin, tert-butyl piperidinomethyl peroxide, 2- [4- (tert-butylperoxymethyl) piperazinomethylperoxy]-2-methylpropane, suspension oligomerization, bromine number, oil processing

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1. Introduction

By-products from the production of gaseous olefins account for a significant amount (30–35 %) of liquid pyrolysis products (LPP), which are a complex mixture of various hydrocarbons: olefins, aromatic, cyclic, vinyl aromatic, and others [1]. Fractions with a narrower boiling point interval [1–3] are separated from LPP. In particular, the C_9 fraction (boiling interval, 423–473 K) contains unsaturated aromatic hydrocarbons (about 60 %) and is used to produce aromatic hydrocarbon resins (oligomers) known as petroleum polymer resins (PPR).

Such hydrocarbon resins are used as cheap synthetic substitutes for products of natural origin (vegetable oils, colophony, albumin), phenol-formaldehyde and indene-coumarone resins, in paint and anticorrosive coatings [2] and anticorrosive compositions, for modification of bitumen [4, 5].

The qualified use of LPP, and in particular the C_9 fraction, is a prerequisite for ensuring the profitability and waste-free nature of petrochemical production. Therefore, the synthesis of hydrocarbon resins solves the issue of disposal of by-products from oil refining industries and, at the same time, providing analogs of more expensive synthetic products and scarce natural products.

Oligomers are received by cationic oligomerization in a solution of hydrocarbon fractions using homogeneous and heterogeneous catalysts [6, 7]. Well-known initiators of free-radical oligomerization are acyl peroxides, hydroperoxides, thermostable alkyl peroxides, oligoperoxides, aminoperoxides and silicon-organic peroxides [8]. The main disadvantages of such technologies are significant energy intensity due to the high temperature of the process and a high color indicator of hydrocarbon resins.

An important task of petrochemical industries is to devise new and improve existing technological processes for the production of co-oligomers based on the hydrocarbon fractions of LPP. Reducing the cost of materials and energy resources in order to increase the yield of the product and improve its physicochemical properties, as well as performance. A relevant issue of PPR synthesis is the search for new highly effective initiators, the use of which will reduce the temperature and duration of the process. Nitrogen-containing peroxides and, in particular, N-substituted amino peroxides have been used as low-temperature initiators of polymerization. The introduction of amino group alkyl peroxide into the molecule helps reduce the thermal resistance of the compound. This pattern is explained by the participation of an undivided electron pair of an atom of nitrogen in the redistribution of electron density on the oxygens of the peroxide group, as a result of which the bond becomes less stable [9, 10].

The research results make it possible to establish the main patterns of oligomerization of the hydrocarbon C_9 fraction initiated by amino peroxides with a cyclic substitution, define the optimal conditions, and expand the range of oligomers in accordance with the needs of the industry.

2. Literature review and problem statement

The peculiarity of oligomerization of the C_9 fraction is that it contains (40–50 %) non-resin-forming hydrocarbons (xylene, ethylbenzene, and others). The fraction acts simultaneously as a mixture of monomers and as a solvent of monomers and oligomers. Technological industrial methods of oligomerization of hydrocarbon mixtures are ion (catalytic) and radical (initiated and thermal) oligomerization in the solution of the C_9 fraction [2].

Paper [8] considers methods for obtaining petroleum polymer resins using peroxide initiators. Technological features of the process are the long-term oligomerization reaction (360–480 minutes) at high temperatures (453–473 K). It is also difficult to isolate the product by atmospheric and vacuum distillation.

Study [11] considers the catalytic co-oligomerization of the C_9 fraction using a heterogeneous catalyst – bentonite clay. It is shown that the target product is obtained with a high yield at a low temperature (353 K) and the duration of the reaction (3 hours). However, the resulting product is characterized by a dark color (about 900 mg I_2/100 ml) and the need to launder the catalyst from the reaction mixture. The use as a catalyst of aluminum chloride on cation exchange resin in [7] makes it possible to increase the temperature of softening of hydrocarbon resin without separating the catalytic complex.

Obtaining modified PPR bitumen coatings with epoxy hydroxyl and carboxyl functional groups is considered in work [4]. The use of an additional stage of the technological process and the significant cost of modifying additives make this method unprofitable.

Paper [5] reports the modification of asphalt with a mixture of thermoplastic elastomer and oil polymer resin. With an increase in the concentration of PPR obtained on the basis of the C_9 fraction, the softening temperature of the composition increases, however, permeability and plasticity significantly decrease.

A factor limiting the wider use of such hydrocarbon resins is a high color indicator (up to 100 mg I_2/100 ml on an iodine-metric scale). A high indicator of the color of hydrocarbon resins is associated with the involvement of cyclopentadiene and indene links in the oligomeric chain [2, 3]. These hydrocarbon resins, in addition to some inappropriate physical and chemical characteristics for synthesis, require expensive and sensitive catalytic catalysts and costly technological equipment.

To overcome the problem of significant energy intensity of production and a high indicator of the color of hydrocarbon resins, methods of low-temperature emulsion and suspension oligomerization are proposed [12, 13]. Hydrocarbon resins obtained by emulsion oligomerization of the C_9 fraction are characterized by a narrow range of molecular-mass distribution and a low color indicator (light oligomers), according to their other properties, oligomers are comparable to the products obtained by other methods [12]. Paper [13] considers the emulsion oligomerization of the hydrocarbon fraction in the aquatic environment using emulsifiers of the first and second kinds. This method is characterized by a low temperature of the process (303–353 K) and makes it possible to get oligomers with a low color index. However, it is characterized by the complexity of the separation of the target product, namely the need to destroy the emulsion.

The peculiarity of low-temperature oligomerization is that under the conditions of the process, a valuable component of the fraction dicyclopentadiene (DCPD) does not react to radical polymerization and is inactive in the processes of copolymerization [14]. Reactive in such reactions is its monomer – cyclopentadiene. The reaction of retro diene synthesis by Diels-Alder – the monomerization of DCPD with the formation of two active cyclopentadiene monomers at 5 MPa and 180–240 °C was studied in [15].

The reactivity of vinyl toluene, α methyl styrene, and allylbenzenes is close to the reactivity of styrene. The presence of the cyclopentene bond in the indene determines the proximity of its reactivity to the reactivity of DCPD. For the full use of reactive hydrocarbon fractions (dicyclopentadiene and indene), post-oligomerization (T=453–473 K) in a solution of unproduced residues of suspension oligomerization is proposed. At the same time, cyclopentadiene co-oligomers with a higher color indicator are obtained [13].

To obtain hydrocarbon resins with high yields and proper physicochemical properties, it is important to synthesize at low temperatures for a short reaction time. Low-thermostable amino peroxide initiators can allow this to be achieved. Technological parameters of the process contribute to the synthesis of oligomers with better physical and chemical characteristics than in the case of catalytic and thermal oligomerization, in particular: color, unsaturation, and molecular weight.

3. The aim and objectives of the study

The purpose of this study is to establish the influence of the main factors on the course of oligomerization of the LPP C_9 faction. This will make it possible to define the optimal conditions for obtaining hydrocarbon resins and reduce their cost. That could make it possible to establish optimal conditions for obtaining hydrocarbon resins and reduce their cost by using more affordable initiators and reducing the number of by-products of production.

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

– to determine the influence of temperature and duration of the reaction and concentration of initiators on the course of oligomerization in the solution of the C_9 fraction;

– to determine the influence of temperature and duration of the reaction and concentration of initiators on the course of suspension oligomerization of the C_9 fraction.

4. The study materials and methods

4. 1. Examined materials and equipment used in the experiment

The object of this study is the oligomerization of unsaturated hydrocarbons of the C_9 fraction, as a result of which reaction-positive hydrocarbon resin is synthesized. The raw material for the synthesis of hydrocarbon resins is the C_9 fraction of liquid products of the pyrolysis of diesel fuel obtained at Karpatneftekhim LLC (Kalush, Ukraine): bromine number, 115 g Br_2/100 g; density, 915 kg/m^3. Along with hydrocarbons incapable of polymerization (indan, toluene, trimethylbenzene, etc.), it contains a number of reactive monomers, in particular, styrene – 17.7 %; dicyclopentadiene – 15.88 %; vinyl toluene – 5.23 %; methyl styrene – 0.36 %; allyl benzene – 1.77 %; methyl indene – 1.0 %.

N-substituted amino peroxides of the general formula $C(CH_3)_3$-O O-CH_2-N-R_1R_2 were synthesized by condensation of aromatic amines with *tert*-butyl peroxyl methanol. The structural formulas of amino peroxides used to initiate the oligomerization are shown in Fig. 1.

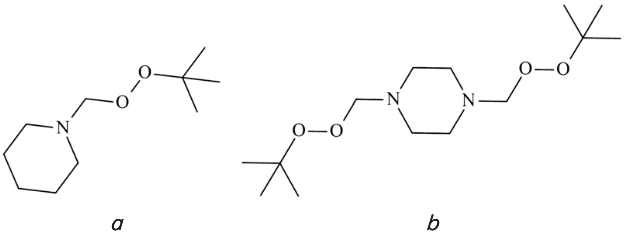


Fig. 1. Amino peroxide initiators with cyclic substituents: *a* — *tert*-butyl piperidinomethyl peroxide; *b* — 2-[4-(*tert*-butylperoxymethyl) piperazinomethylperoxy]-2-methylpropane

Initiator (1) is *tert*-butyl piperidinomethyl peroxide: active oxygen – 7.48 %, refractive index – 1.4522. Thermolysis occurs in 2 stages. Stage 1: 306–383 K, weight loss – 62.04 %, kef=0.8·10^{-2}; stage 2: 384–400 K, weight loss – 3.80 %, kef=9.8·10^{-2}.

Initiator (2) is 2-[4-(*tert*-butylperoxymethyl) piperazinomethylperoxy]-2-methylpropane (2): active oxygen – 9.65 %, refractive index – 1.4590. Thermolysis occurs in 2 stages. Stage 1: 305–355 K, weight loss – 19.02 %, k_{ef}=1.4·10^{-2}; stage 2: 356–386 K, weight loss – 51.04 %, k_{ef}=5.0·10^{-2}.

Oligomerization in the solution of hydrocarbons of the C_9 fraction was carried out in metal thermostat ampoules with a volume of 100 ml. The raw materials (the C_9 fraction of LPP of diesel fuel), in the amount of 50 ml, were mixed with the calculated number of the initiator and loaded in the ampoules previously blown with inert gas (argon). Consequently, the ampoules were hermetically sealed, placed in a thermostat, and oligomerized at the studied temperature. Non-reacted hydrocarbons were removed by atmospheric distillation (pressure, 0.11 MPa; temperature, 423 K), high-boiling hydrocarbons and liquid oligomers were separated using vacuum distillation (pressure, 3 gPa; temperature, 453). At the same time, PPR was obtained in the cube with a softening temperature in the range of 347–354 K.

Suspension oligomerization was carried out in a three-humped flask equipped with a rotary mixer. After loading, the reagents were intensively agitated with a rotary mixer (mixing intensity, *Re*=10120) and simultaneously heated to a given temperature. After the reaction was completed and partially stratified, the reaction mixture was divided into watering cans into the water and organic phases. The organic layer was centrifugated (4000 rpm) and the oligomer was separated. The resulting oligomer was dried in a drying chamber (323 K). The liquid phase, obtained after centrifugation, contained water residues and oligomerisate (oligomer solution in unpolymerized hydrocarbon fractions). The mixture was separated by atmospheric and vacuum distillation of the oligomerisate. Oligomers after centrifugation and distillation were combined to calculate the yield.

4. 2. Methodology for determining sample property indicators

The main characteristics of the properties of hydrocarbon resins, determined in our experiment, were chosen to be the yield, degree of unsaturation, average molecular weight, softening temperature, and a color indicator.

The yield of hydrocarbon resin was determined in terms of the C_9 fraction (deviation range, 2 %).

The unsaturation (bromine number) of hydrocarbon resins was determined by the bromide-bromate method.

The temperature of softening was determined according to the method of "rings and balls".

The color of the hydrocarbon resin was determined visually, comparing the coloration of a 10 % solution in benzene with the reference iodine-metric scale (IMS). The international analog of it is the Gardner scale.

Molecular weight was determined by cryoscopy using benzene solvent.

The oligomerization initiated by amino peroxide initiators in the solution was investigated under the following conditions: reaction temperature, 393–493 K; reaction duration, 360–480 min; concentration of initiators, 0.032–0.096 mol/l.

Suspension oligomerization was carried out under the following conditions: reaction temperature, 318–353 K; reaction duration, 30–240 min; concentration of initiators, 0.032–0.096 mol/l; volume ratio, [fraction C_9]:[water]=[1:3]; mixing intensity, *Re*=10120; stabilizer, – poly vinyl alcohol (0.2 %).

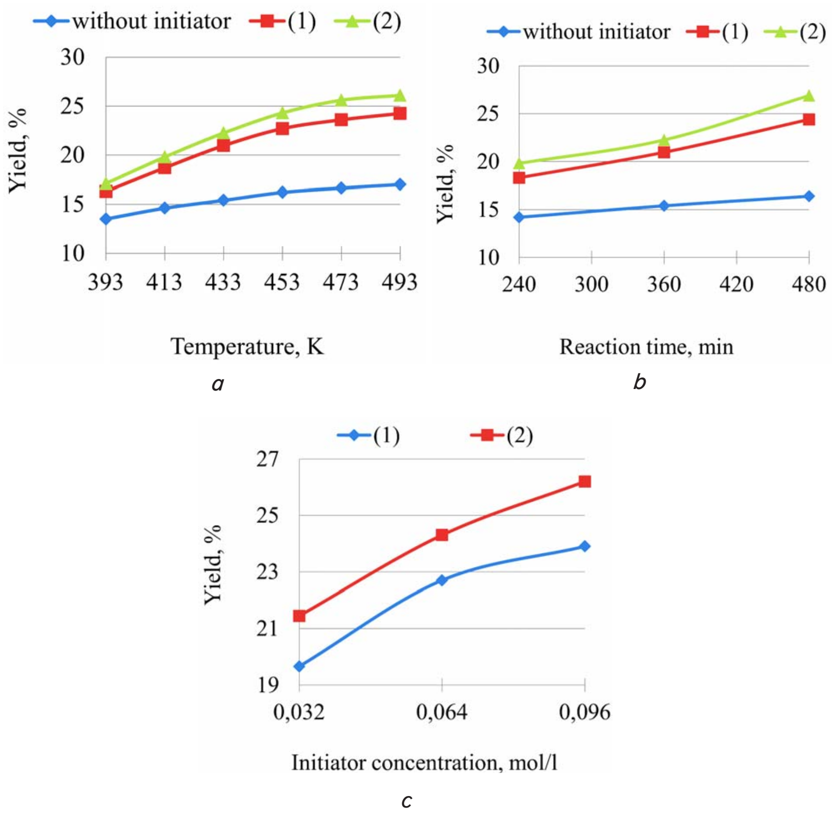
5. Results of studying the oligomerization of the C_9 fraction

5. 1. The influence of temperature and duration of reaction and the concentration of initiators on the course of oligomerization of the C_9 fraction in solution

At the studied temperatures, the reaction will occur during both thermal and initiated oligomerization. Thermal oligomerization (without an initiator) was investigated to assess the influence of initiators on the course of the oligomerization reaction in the solution. Graphical dependences of oligomers' yield on temperature, the duration of oligomerization, and the concentration of initiators, built on experimental points, are shown in Fig. 2 (deviation range, 2 %).

The use of amino peroxide initiators can significantly increase the yield of oligomers within the entire temperature interval (393–493 K) compared to thermal oligomerization. The yield of oligomers with an increase in temperature for thermal oligomerization increases from 13.5 to 17.0 %; when using initiator (1) – from 16.3 to 22.7 %; (2) – from 17.2 to 24.3 %.

The correlation of yield with reaction temperature for thermal oligomerization is 0.84; when using initiator (1) – 0.80, and for initiator (2) – 0.79. The correlation of yield with the duration of the reaction for thermal oligomerization is 0.50; when using initiator (1) – 0.31, and for initiator (2) – 0.33.



a

b

c

Fig. 2. Dependence of oligomers' yield on the oligomerization conditions in solution: *a* – the dependence of oligomeric yield on reaction temperature (reaction duration, 360 min; concentration of initiators, 0.064 mol/l); *b* – the dependence of oligomers' yield on the duration of the reaction (reaction temperature, 433 K; concentration of initiators, 0.064 mol/l); *c* – the dependence of oligomers' yield on the concentration of initiators (reaction temperature, 433 K; reaction duration, 360 min)

The oligomers, obtained by thermal oligomerization, in comparison with products obtained using amino peroxides, are characterized by lower yields and molecular weight (600–630), which nevertheless decreases with an increase in temperature (correlation −0.96). The color of oligomers is 30–60 mg I_2/100 ml and mainly depends on the temperature of oligomerization (correlation 0.77). The softening temperature is in the range of 346–353 K. The bromine number of oligomers naturally decreases with an increase in yield (correlation with reaction temperature –0.97). The characteristics of synthesized oligomers are given in Tables 1, 2.

When using amino peroxides (1) and (2), characteristic is the oligomerisate with a density value (930–945 kg/m^3) at oligomerization reaction temperatures within the 433–493 K. However, the yield curve of co-oligomers (Fig. 1) does not show a sharp increase in the yield gain with a temperature increase above 453 K.

The softening temperature of oligomers is in the range of 349–353 K and does not depend on oligomerization (correlation is in the range of 0.13–0.27).

The optimal conditions for oligomerization in the solution initiated by *tert*-butyl piperidinomethyl peroxide are proposed – eaction temperature, 453 K; reaction duration, 360 min; concentration of initiator, 0.064 mol/l. Under such conditions, an oligomer is obtained with a yield of 22.7 % and a color index of 40 mg I_2/100 ml.

Table 1

Experimental data on the oligomerization in the solution of the C_9 fraction initiated by *tert*-butyl piperidinomethyl peroxide

Reaction temperature, K	Reaction duration, min	Concentration of the initiator, mol/l	Bromine number gBr_2/100 g	Color, mg I_2/100 ml	Molecular weight
393	360	0.064	28.7	40	630
433	360	0.032	27.6	40	625
	240	0.064	27.4	40	610
	360		26.8	40	620
	480		24.3	60	625
	360	0.096	25.7	60	620
453	360	0.032	26.7	40	620
		0.064	25.7	40	615
		0.096	24.7	60	610
473	360	0.032	25.8	60	610
	240	0.064	26.0	60	610
	360		24.7	60	610
	480		25.1	60	610
	360	0.096	23.9	60	605
493	360	0.032	24.9	60	605
		0.064	24.3	80	605
		0.096	23.6	80	600
Correlation with reaction temperature			–0.84	0.78	–0.91
Correlation with the concentration of the initiator			–0.41	0.29	–0.21
Correlation with reaction time			–0.26	0.16	0.15

Table 2

Experimental data on the oligomerization in a solution of the C_9 fraction initiated by 2-[4-(*tert*-butylperoxymethyl) piperazinomethylperoxy]-2-methylpropane

Reaction temperature, K	Reaction duration, min	Concentration of the initiator, mol/l	Bromine number $gBr_2/100$ g	Color, mg $I_2/100$ ml	Molecular weight
393	360	0.032	25.7	40	640
		0.064	24.0	40	630
		0.096	22.8	40	630
433	360	0.032	22.6	40	625
	240	0.064	22.8	60	625
	360		21.2	40	620
	480		14.5	60	620
	360	0.096	19.3	60	620
453	360	0.032	20.1	40	620
		0.064	18.1	40	615
		0.096	16.7	60	610
473	360	0.032	17.4	60	610
	240	0.064	21.0	40	615
	360		15.7	60	610
	480		16.7	60	610
	360	0.096	14.5	60	605
493	360	0.032	15.9	60	605
		0.064	14.0	80	605
		0.096	12.6	80	600
Correlation with reaction temperature			–0.87	0.77	–0.42
Correlation with the concentration of the initiator			–0.31	0.29	–0.08
Correlation with reaction time			–0.35	0.16	–0.10

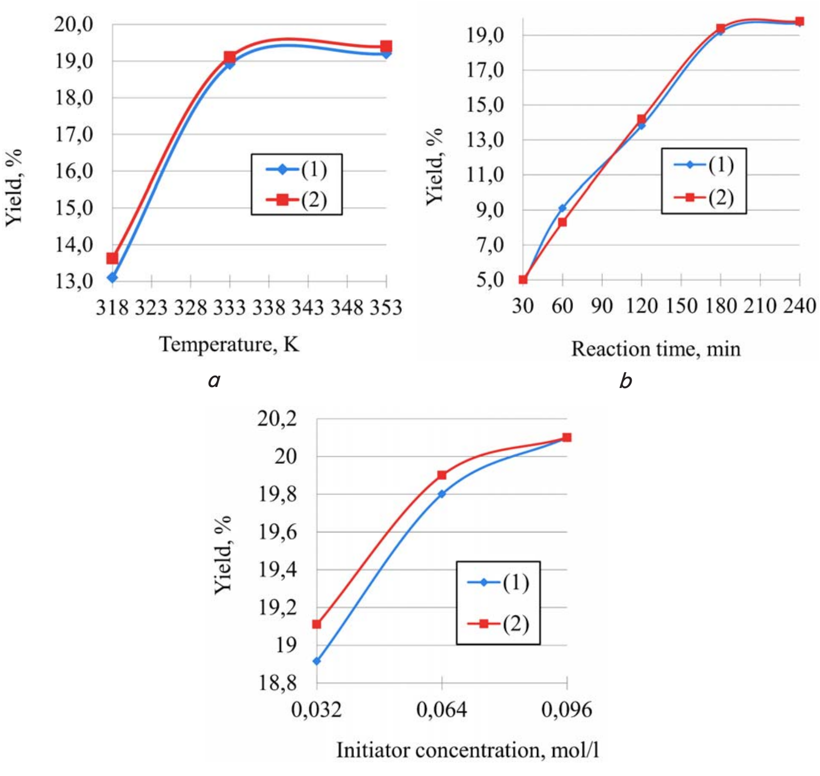
The color of oligomers is 40–80 mg $I_2/100$ ml (10–12 with the Gardner scale). The color value increases with increasing oligomerization temperature.

The optimal conditions for the oligomerization in the solution of the C_9 fraction with the use of 2-[4-(*tert*-butylperoxymethyl) piperazinomethylperoxy]-2-methylpropane were selected – reaction temperature, 473 K; duration of the reaction, 360 minutes; concentration of the initiator, 0.064 mol/l. Under such conditions, the yield of the oligomer is 25.6 % with a color indicator of 60 mg $I_2/100$ ml.

5. 2. The influence of the temperature and duration of reaction and the concentration of initiators on the course of suspension oligomerization of the C_9 fraction

Suspension oligomerization was carried out at pre-established optimal values of mixing intensity and volume ratio dispersion phase – dispersion medium. Graphical dependences of oligomers' yield on the temperature, the duration of suspension oligomerization, and the concentration of initiators are built on experimental points shown in Fig. 3 (deviation range, 2 %). The dependence of the properties of synthesized oligomers on reaction conditions is given in Table 3.

The correlation of product yield during suspension oligomerization with reaction temperature is – 0.08; the correlation with the duration of the reaction – 0.88; the correlation with the concentration of the initiator – 0.40.



a

b

c

Fig. 3. Dependence of oligomers' yield on suspension oligomerization conditions: *a* – the dependence of oligomers' yield on reaction temperature (reaction duration, 180 min; concentration of initiators, 0.032 mol/l); *b* – the dependence of oligomers' yield on the duration of the reaction (reaction temperature, 353 K; concentration of initiators, 0.032 mol/l); *c* – the dependence of oligomers' yield on the concentration of initiators (reaction temperature, 333 K; reaction duration, 180 min

The color indicator of suspension oligomerization products in the studied intervals varies slightly and is 20–30 mg I_2/100 ml (7–8 on the Gardner scale).

The decrease in the bromine number of hydrocarbon resins correlates with an increase in yield (–0.83 and –0.80).

Amino peroxide initiators (1) and (2) demonstrate a similar effect on the course of suspension oligomerization in the studied temperature and concentration intervals. The optimal conditions for suspension oligomerization: reaction temperature, 333 K; reaction duration, 180 min; initiation concentration, 0.032 mol/l. Under such conditions, light oligomers are obtained with a color of 20 mg I_2/100 ml at the oligomer yield of 18.9–19.1 %.

According to the chromatographic analysis of the initial C_9 fraction and the obtained distillates, the conversion of resin-forming hydrocarbons is calculated and the approximate composition of the obtained hydrocarbon resins is established (Table 4).

According to the above results (Table 4), with the oligomerization of the C_9 fraction with amino peroxide initiators (oligomerization in solution), the products obtained are mainly styrene-cyclopentadiene co-oligomers. Suspension oligomerization products are co-oligomers of styrene and its derivatives.

Table 3

Experimental data on the suspension oligomerization of the C_9 fraction initiated by amino peroxides with cyclic substitution

Reaction temperature, K	Reaction duration, min	Concentration of the initiator, mol/l	Bromine number, gBr_2/100 g	Softening temperature, K	Molecular weight
(1) *tert*-butyl piperidinomethyl peroxide					
318	180	0.032	36.3	354	515
		0.064	33.4	348	510
		0.096	32.3	348	510
333	180	0.032	32.2	352	515
		0.064	35.1	347	505
		0.096	34.8	350	510
353	30	0.032	45.6	360	520
	60	0.032	41.3	363	525
	120	0.032	36.0	358	520
	180	0.032	35.4	357	520
	240	0.032	35.4	358	520
	180	0.096	33.8	351	515
(2) 2-[4-(*tert*-butylperoxymethyl) piperazinomethylperoxy]-2-methylpropane					
318	180	0.032	36.3	354	515
		0.064	33.4	348	510
		0.096	32.3	348	510
333	180	0.032	32.2	352	515
		0.064	35.1	347	505
		0.096	34.8	350	510
353	30	0.032	45.6	360	530
	60	0.032	41.3	360	525
	120	0.032	36.0	358	520
	180	0.032	35.6	353	520
	240	0.032	35.7	359	525
	180	0.096	31.2	352	520
Correlation with reaction temperature			0.33	0.68	0.21
Correlation with the concentration of the initiator			–0.36	–0.71	–0.31
Correlation with reaction time			–0.79	–0.60	–0.23

Table 4

Approximate composition of oligomers

Component	(1)	(2)	(1)	(2)
	Oligomerization in solution (453 K)		Suspension oligomerization (333 K)	
Styrene, %	40.73	38.95	72.24	71.92
Cyclopentadiene, %	31.19	33.40	0.53	0.68
Allylbenzene, %	2.78	2.76	4.31	4.02
Vinyl toluene, %	7.36	6.92	9.20	8.68
Methyl styrene, %	0.39	0.54	1.54	1.67
Indene, %	4.74	4.57	1.73	1.20
Neind. hydrocarbons, %	12.81	12.86	10.45	11.83

6. Discussion of results of determining the effect of oligomerization conditions on the properties of hydrocarbon resins

Our data on the influence of temperature, duration, and concentration of the initiator complement and summarize experimental studies into the oligomerization of hydrocarbon fractions, in particular [7, 8, 12, 13]. The initiators of the process of oligomerization of hydrocarbon fractions of C_9 LPP proposed in this work have not been used until now and have ensured the process under milder conditions, in particular, lower values of temperature and reaction time.

However, unlike the results of studies reported in [8, 12], our data on the impact of conditions on the course of oligomerization of the C_9 fraction initiated by amino peroxides suggest the following:

– the determining factor that affects oligomerization in the solution is the reaction temperature; the impact of the duration of the reaction and the concentration of initiators is negligible;

– under the investigated oligomerization conditions in the suspension, an increase in the temperature of the reaction to 353 K does not affect the yield of the oligomer, which allows the process to be carried out at a temperature of 303 K (Fig. 3, *a*);

– increasing the concentration of initiators of suspension oligomerization from 0.032 to 0.096 mol/l has a minimal effect on the yield of the oligomer, which allows the process to be carried out at a concentration of amino peroxides of 0.032 mol/l (Fig. 3, *c*);

– at the optimal values of the intensity of agitation (*Re*=10120) and the volume ratio of the C_9 fraction:water (1:3), the determining factor influencing the yield of the oligomer is the duration of the reaction.

In comparison with work [8], the use of low-thermostable initiators did not contribute to a decrease in the temperature of oligomerization in the solution.

Yields of about 20 % are achieved at oligomerization temperatures in a solution of 413–433 K, with suspension oligomerization of 333 K (Fig. 2, *a*). The reduction in the cost of the product is achieved with suspension oligomerization due to a decrease in temperature (by 120–140 K) and duration (by 180 minutes) compared to industrial technology of free radical oligomerization in solution.

With similar values of the temperature interval reported in [12], a comparable yield of the product is obtained without the use of cost emulsifiers. In suspension oligomerization, there is also no stage of destruction of the emulsion.

The results of studying the effect of the temperature and duration of the process on the initiated oligomerization in the solution of the C_9 fraction confirm that the increase in reaction temperature has a positive effect on the course of the reaction, in particular, the density of oligomerisate and the yield of oligomers increase, but, at the same time, the physical and chemical properties of synthesized resins deteriorate. A decrease in the bromine number of the oligomerisate indicates the loss of $>C=C<$ bonds in the reaction mass. Naturally, the color deteriorates and the bromine number decreases. The decrease in molecular weight is characteristic of the processes of radical oligomerization (Tables 1, 2).

An increase in the oligomerization temperature in a solution above 453 K is impractical. This conclusion is drawn on the basis of the fact that at higher temperatures, the increase in the yield of hydrocarbon resins practically stops but, at the same time, the physical and chemical characteristics of synthesized oligomers (color, molecular weight) deteriorate significantly. The color indicator (due to oxidation processes) increases and the molecular weight decreases (due to the increase in the proportion of the breakaway stage and the transfer of the chain). The temperature has a significant effect on the course of oligomerization in the solution. A clear dependence of the change in the yield of oligomers on temperature is observed only for initiated oligomerization. This can be explained by the fact that the method of thermal oligomerization under the conditions of the reaction does not make it possible to effectively involve all resin-forming components of the fraction in the process.

The continuation of oligomerization in a solution longer than 360 minutes causes in all cases an increase in the yield of co-oligomers (Fig. 2, *b*) and a slight increase in molecular weight but is accompanied by an increase in the color indicator (Tables 1, 2). The duration of oligomerization has a less significant impact on the course of co-oligomerization than the temperature of the process and the concentration of the initiator. Based on our studies, 360 minutes were chosen as the optimal duration of the co-oligomerization reaction.

In the case of oligomerization in solution, amino peroxides make it possible to obtain oligomers with high yields and are characterized by a significant increase in yield throughout the studied temperature range (393–493 K). This can be explained by their low value of the effective decomposition constant at the first stage of thermolysis. The lower value of the initiator decomposition constant (1) indicates the higher thermal resistance of the compound and its ability to generate methyl radicals for a longer time. At the same time, initiator (2) is characterized by a higher value of the effective constant (k_{ef}=1,4·10^{-2} s^{-1}). However, due to two peroxide groups in its structure, it makes it possible to receive oligomers with higher yields than in the case of using initiator (1). Initiator (1) ensures a stable increase in the yield of the oligomer in the entire studied temperature interval at concentrations of 0.032 and 0.064 mol/l; this corresponds to the growth, respectively, of oligomer yields (Fig. 2, *c*). At the concentration of initiator (1) of 0.096 mol/l and a temperature of 413 K and above, there is a sharp increase in the density of oligomerisate, but the corresponding bromine numbers and oligomers' yields change slightly. This can be explained by the formation of a significant number of liquid oligomers, which separated at the oligomerisate distillation stage.

Increasing the concentration of initiators ensures an increase in the yield of hydrocarbon resins but negatively affects their molecular weight. The relatively low molecular weight of the products obtained can be explained by the fact that amino peroxides participate in the stage of chain transmission. This property of amino peroxides is associated with the structure and reactivity of the molecules themselves, as well as the reactivity of polymeric radicals. The transfer of the chain occurs through the cleavage of the hydrogen atom of the methylene bridge [10].

The color of oligomers obtained using initiators (1) and (2) practically does not change with an increase in temperature and oligomerization time. The color and temperature of softening significantly depend on the conditions of oligomerisate distillation. With increasing temperature and duration of distillation, the temperature of softening increases and the resin is darkened.

The use of suspension oligomerization makes it possible at low temperature values (333 K) and reaction duration (180 minutes) to obtain light products with a low color index (20–30 mg I_2/100 ml) and comparable yields and properties. Unlike [8] and oligomerization in a solution using amino peroxides, where products with a color index of 60–80 mg I_2/100 ml are obtained, this result (light color) makes it possible to expand the use of these oligomers as film-forming agents in a variety of paint and varnish composite materials. This becomes possible due to the low temperature of the suspension oligomerization process and the lack of oxidation reactions.

The results of our studies, in particular the optimal conditions for suspension oligomerization that were established, demonstrate the possibility of conducting the process under milder conditions compared to industrial analogs of oligomerization in the solution. The use of the studied amino peroxide initiators in the suspension oligomerization of the C_9 fraction will reduce the cost of hydrocarbon resins by reducing energy costs.

The quantitative and qualitative composition of the C_9 fraction may vary depending on the processing technology and characteristics of petroleum products. Therefore, a limitation of this study is that the absolute numerical values may differ when using, in particular, the pyrolysis products of the gasoline fraction. The properties of hydrocarbon resins also significantly depend on the conditions of separation (distillation) from the reaction mixture.

Dicyclopentadiene does not oligomerize at the temperatures of the suspension process. To involve it in oligomerization, an additional post-co-oligomerization step (453–473 K) is required, the product of which will be a cyclopentadiene oligomer, which is characterized by an increased color index. Further development of this study will be attempts to involve dicyclopentadiene in low-temperature free radical oligomerization initiated by amino peroxides, in particular, with the use of additives of anionic emulsifiers of the second kind.

7. Conclusions

1. It has been established that in the studied intervals of variables, the yield of hydrocarbon resin during oligomerization in the solution depends on the temperature of the reaction. The main factor influencing the yield of hydrocarbon resin during oligomerization in suspension is the duration of oligomerization. The optimal conditions for the oligomerization in the solution of the C_9 fraction were selected: when initiating by *tert*-butyl piperidinomethyl peroxide, the reaction temperature is 453 K, the reaction duration is 360 minutes, the concentration of the initiator is 0.064 mol/l. Under such conditions, the yield of the oligomer is 22.7 %. When using 2-[4-(*tert*-butylperoxymethyl) piperazinomethylperoxy]-2-methylpropane, the reaction temperature is 473 K, the reaction duration is 360 min, the concentration of the initiator is 0.064 mol/l. Under such conditions, the yield of the oligomer is 25.6 %.

2. Our studies confirmed the possibility of obtaining hydrocarbon resins with suspension oligomerization of the C_9 fraction using amino peroxides with a cyclic substitution as initiators. The structure of the amino peroxide initiator does not affect the yield of the product during low-temperature suspension oligomerization. This is due to the low thermal stability of amino peroxides in the studied temperature range. Optimal conditions: reaction temperature, 333 K; reaction duration, 180 min; initiator concentration, 0.032 mol/l. Under such conditions, the yield of the oligomer is 19.1 %.

References

1. Rahmatpour, A., Ghasemi Meymandi, M. (2021). Large-Scale Production of C9 Aromatic Hydrocarbon Resin from the Cracked-Petroleum-Derived C9 Fraction: Chemistry, Scalability, and Techno-economic Analysis. Organic Process Research & Development, 25 (1), 120–135. doi: https://doi.org/10.1021/acs.oprd.0c00474
2. Mildenberg, R., Zander, M., Collin, G. (1997). Hydrocarbon Resins. Wiley Online Library. doi: https://doi.org/10.1002/9783527614653
3. Zohuriaan-Mehr, M. J., Omidian, H. (2000). Petroleum Resins: An Overview. Journal of Macromolecular Science, Part C: Polymer Reviews, 40 (1), 23–49. doi: https://doi.org/10.1081/mc-100100577
4. Pyshyev, S., Gunka, V., Grytsenko, Y., Bratychak, M. (2016). Polymer Modified Bitumen: Review. Chemistry & Chemical Technology, 10 (4s), 631–636. doi: https://doi.org/10.23939/chcht10.04si.631
5. Nie, X., Hou, T., Yao, H., Li, Z., Zhou, X., Li, C. (2019). Effect of C9 petroleum resins on improvement in compatibility and properties of SBS-modified asphalt. Petroleum Science and Technology, 37 (14), 1704–1712. doi: https://doi.org/10.1080/10916466.2019.1602642
6. Salari, D., Jodaei, A. (2006). Petroleum resin preparation by cationic polymerization of pyrolysis gasoline. Iranian Polymer Journal (English Edition), 15 (1), 55–64.
7. Gnativ, Z., Nylukyshyn, I., Pikh, Z., Voronchak, T. et. al. (2014). Catalytic Cooligomerization of Styrene and Dicyclopentadiene: Yield and Properties Dependence on Reaction Mixture Composition. Chemistry & Chemical Technology, 8 (2), 165–170. doi: https://doi.org/10.23939/chcht08.02.165
8. Dzinyak, B. (2014). Cooligomerization of C9 Fraction Unsaturated Hydrocarbons Initiated by Organic Peroxides. Chemistry & Chemical Technology, 8 (2), 183–188. doi: https://doi.org/10.23939/chcht08.02.183
9. Dzumedzei, M. V., Kucher, R. V., Turovskyi, A. A., Koshovskyi, B. I. (1971). Doslidzhennia kinetyky termichnoho rozpadu azotumisnykh perekysnykh spoluk z tret-alkilnym radykalom. Ukrainskiy khimicheskiy zhurnal, 39, 1142–1145.
10. Turovskyi, A. A., Dzumudzei, M. V. (1973). Pro kinetyku peredachi lantsiuha cherez azotvmisni perekysy z tret-butylnym radykalom pry polimeryzatsiyi styrolu v masi. Dopovidi NAN Ukrainy, 5, 1106–1108.

11. Voronchak, T., Nykulyshyn, I., Pikh, Z., Rypka, A. (2012). Synthesis and Properties of Epoxydized Cooligomers Obtained from Petroleum Resins Synthesized by Heterogeneous Catalytic Oligomerization. Chemistry & Chemical Technology, 6 (4), 397–403. doi: https://doi.org/10.23939/chcht06.04.397
12. Fuch, U., Dzinyak, B., Subtelnyy, R. (2015). Study of emulsifier nature effect on the process of hydrocarbon fraction cooligomerization in the emulsion. Eastern-European Journal of Enterprise Technologies, 4 (6 (76), 54–57. doi: https://doi.org/10.15587/1729-4061.2015.47205
13. Subtelnyy, R., Kichura, D., Dzinyak, B. (2021). Correlation between the emulsion oligomerization parameters for C9 fraction and the characteristics of hydrocarbon resins. Eastern-European Journal of Enterprise Technologies, 3 (6 (111)), 6–11. doi: https://doi.org/10.15587/1729-4061.2021.232684
14. Kovačič, S., Slugovc, C. (2020). Ring-opening Metathesis Polymerisation derived poly(dicyclopentadiene) based materials. Materials Chemistry Frontiers, 4 (8), 2235–2255. doi: https://doi.org/10.1039/d0qm00296h
15. Yao, Z., Xu, X., Dong, Y., Liu, X., Yuan, B., Wang, K. et. al. (2020). Kinetics on thermal dissociation and oligomerization of dicyclopentadiene in a high temperature & pressure microreactor. Chemical Engineering Science, 228, 115892. doi: https://doi.org/10.1016/j.ces.2020.115892