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*R.O. Subtelnyy, Y.V. Zhuravskiy, B.O. Dzinyak***SUSPENSION OLIGOMERIZATION OF C9 HYDROCARBON FRACTION INITIATED BY ALIPHATIC N-SUBSTITUTED AMINOPEROXIDES****Lviv Polytechnic National University, Lviv, Ukraine**

We investigated the production of petroleum resins by suspension oligomerization of C9 hydrocarbon fraction initiated by aliphatic aminoperoxides. The reaction mixture consisted of a dispersion medium (water), a dispersed phase (C9 fraction), an initiator, which is soluble in the dispersed phase, and a suspension stabilizer. In the range of variables studied, reaction temperature (313–353 K) and initiator concentration (0.032–0.096 mol/l) do not have a significant effect on the oligomers yield. The process conditions most influencing the course of suspension oligomerization of the C9 fraction are as follows: stirring intensity ($Re=2290-13450$) with the correlation index of 0.88, reaction time (30–240 min) with the correlation index of 0.87 and the ratio of dispersed phase to dispersed medium (1:1–1:4) with the correlation index of –0.91. The correlation between the yield and bromine number (correlation index of –0.82) confirmed the passage of oligomerization reaction via the unsaturated bonds of the monomer. The hydrocarbon resins obtained by low-temperature suspension oligomerization were mainly cooligomers of styrene and its derivatives. As a result of suspension oligomerization at low temperatures, products were obtained which were characterized by a light color (color index of 10–20 mg I₂/100 ml), a molecular weight of 505–530 and a softening point of 347–354 K.

Keywords: C9 fraction, petroleum resin, suspension, initiator, styrene, aminoperoxide, oligomerization.

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Introduction

Production of gaseous olefins (ethylene and propylene) is carried out by pyrolysis of gasoline and diesel fuel. Ethylene production by-products are liquid pyrolysis products (LPPs), which is a complex mixture of various aliphatic, cyclic, aromatic, vinylaromatic and other hydrocarbons. Fractionation of LPPs yields, in particular, C9 fraction (422–473 K) [1,2].

C9 fraction contains a significant amount of vinylaromatic hydrocarbons (about 60 wt.%) and can be used for the synthesis of oligomers known as petroleum resins (PRs). PRs are used as cheap synthetic substitutes for products of natural origin (vegetable oils, rosin, and albumin), phenol-formaldehyde and indene-coumarone resins, in a variety of applications, such as adhesion, coatings, and printing inks [3,4]. Qualified use of LPPs, and in particular the C9 fraction, is a necessary condition

for ensuring profitability and waste-free petrochemical production. It solves the issue of disposal of by-products and provides analogues of expensive synthetic natural products.

As initiators of free-radical oligomerization, acyl peroxides, hydroperoxides, heat-stable alkyl peroxides, oligoperoxides, aminoperoxides and silicon-organic peroxides can be applied [5,6]. Oligomers are also produced by cationic oligomerization in a solution of hydrocarbon fractions using homogeneous and heterogeneous catalysts [7].

The current technologies for the synthesis of oligomers based on the C9 hydrocarbon fraction have a number of significant drawbacks, such as high temperatures (453–493 K) and long processing times (6–12 hours) for initiated and thermal methods, the requirement for an additional stage of catalyst washing, and a high color index of the oligomers for the catalytic method. The desired product must be

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Suspension oligomerization of C9 hydrocarbon fraction initiated by aliphatic N-substituted aminoperoxides

separated from the hydrocarbon solution in an energy-intensive process.

The macroradical's initiation stage and the polymer chain's termination are both significantly influenced by the temperature of the polymerization process. The oligomer's color deteriorates and its molecular weight reduces when the polymerization temperature rises. At the same time, the polymerization rate rises [2,5].

To overcome the problem of significant energy consumption and high color index of hydrocarbon resins, a method of low-temperature (313–353 K) suspension and emulsion oligomerization has been proposed [8,9]. Hydrocarbon resins prepared by suspension oligomerization of the C9 fraction show a narrow range of molecular mass distribution and a low color index (light oligomers). In terms of their other properties, oligomers are comparable to products obtained by other methods [9]. Low-temperature suspension oligomerization of a mixture of hydrocarbons dispersed in an aqueous medium makes it possible to reduce energy costs, the temperature and duration of the process in comparison with industrial methods.

In suspension oligomerization, it is appropriate to use low temperature nitrogen-containing peroxides, particularly N-substituted amino peroxides. These are less thermally stable due to the addition of an amino group to the alkyl peroxide molecule. The involvement of the lone pair of electrons on the nitrogen atom in shifting the electron density on the oxygen atoms of the peroxide group is responsible for the decrease in peroxide stability of the bond [9,10]. The use of aminoperoxides should allow producing petroleum resins with higher molecular weight and lower color index, as they allow the process to start at low temperatures due to their low decomposition temperature [5,6].

The disadvantage 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. The reactive component in such reactions is its monomer, cyclopentadiene. It is formed from DCDP by the Diels-Alder reaction at elevated pressures and temperatures of 453–513 K [8,9].

To fully utilize the reactive hydrocarbon fractions (with a high content of DCPD), post-oligomerization (453–473 K) in a solution of unproduced suspension oligomerization residues is proposed. At the same time, cyclopentadiene co-oligomers with a higher color indicator can be

obtained. It was established that the metered supply of the initiator during the suspension oligomerization of the hydrocarbon fraction did not have a significant impact on increasing the yield of the product [10,11].

The composition of the feedstock has a considerable impact on how peroxides dissolve into free radicals and the subsequent free radical processes in which they participate. According to the studies [3,12] on the effect of the medium on the kinetics of nitrogen-containing peroxides decomposing with a tert-alkyl radical, the rate constants of peroxide decomposition rise as the medium's polarity increases. It was found that the preexponential factor value, which varies greatly, is considerably influenced by the solvent's type.

The oligomerization feedstock studied (C9 fraction) consists mainly of non-polar solvents (benzene, allylbenzene, trimethylbenzenes, etc.). The results on the kinetics of decomposition of aminoperoxide initiators can be used for future research.

Experimental

C9 hydrocarbon fraction of diesel fuel and gasoline pyrolysis liquid by-products was used as a raw material for the petroleum resins production. It is transparent liquid of light-yellow color without impurities; the main characteristics are summarized in Table 1.

The reaction mixture for the suspension oligomerization contained C9 fraction as a dispersed phase, water as a dispersion medium, initiator, and polyvinyl alcohol as a stabilizer. The initiator was soluble in the dispersed phase. A stabilizer was added to the suspension to prevent the droplets of C9

Table 1
C9 fraction properties and composition

Properties	Values
density, kg/m ³	934
molecular weight	106
bromine number, g Br ₂ /100 g	68.02
color index, mg I ₂ /100 ml	10
refractive index, n _D ²⁰	1.516
mass fraction of water, %	0.3
Fractional composition (422–467 K), %	
resin-forming components, including:	53.19
styrene & α-methylstyrene	18.06
dicyclopentadiene	15.88
indene & methylindene	2.81
allylbenzene	1.77
vinyl toluene	5.23
unidentified	9.44
non-resin-forming components	47.71

fraction from coalescing.

Suspension oligomerization was carried out in a three-necked flask equipped with a rotary stirrer. After loading, the reagents were intensively mixed using a rotary mixer and simultaneously heated to the specified temperature. After completion of the reaction and partial stratification, the reaction mixture was divided into aqueous and organic phases in a separatory funnel. The organic layer was centrifuged (4000 rpm) and the oligomer was separated. The resulting oligomer was dried in an oven (323 K). The liquid phase obtained after centrifugation contained water residues and oligomerizate (oligomer solution in unpolymerized hydrocarbon fraction). The mixture was separated by atmospheric and vacuum distillation of the oligomerizate. Oligomers after centrifugation and distillation were combined and the yield was calculated.

The yield, unsaturation (bromine number), softening point, average molecular weight and color index of the resulting oligomers were characterized. The recalculation for the C9 fraction allowed determining the hydrocarbon resin yield. The unsaturation (bromine number) of the hydrocarbon resins was analyzed using the bromide-bromate method. Molecular weight was determined using a benzene solvent and the cryoscopic method. The color of the hydrocarbon resin was evaluated visually by comparing the color of 10% of the benzene solution with the iodometric reference scale. The ring and ball technique was used to determine the softening temperature.

N-substituted aminoperoxide initiators were prepared by condensation of the corresponding aliphatic amines with tert-butylperoxymethanol and cooling to 268–263 K.

The chemical structures of N-substituted aliphatic aminoperoxides used are shown in Fig. 1.

Thermogravimetric data were used to determine the kinetic characteristics of thermolysis:

(I): active oxygen of 10.88%. Thermolysis occurs in two stages. Stage 1: temperature of 309–366 K, weight loss of 64.45%, $k_{ef}=1.6 \cdot 10^{-2}$, activation energy of 50 kJ/mol, and preexponential factor of $8.9 \cdot 10^5$; stage 2: temperature of 367–405 K, weight loss of 29.55%, $k_{ef}=2.2 \cdot 10^{-2}$, activation energy of 29 kJ/mol, and preexponential factor of $1.9 \cdot 10^2$.

(II): active oxygen of 9.81%. Thermolysis occurs in two stages. Stage 1: temperature of 315–371 K, weight loss of 33.15%, $k_{ef}=0.9 \cdot 10^{-2}$, activation energy of 60 kJ/mol, and preexponential factor of $1.2 \cdot 10^7$; stage 2: temperature of 372–402 K, weight loss of 48.75%, $k_{ef}=3.4 \cdot 10^{-2}$, activation energy of 74 kJ/mol,

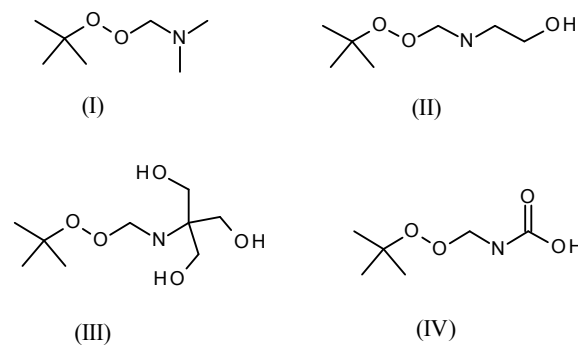


Fig. 1. The structures of N-substituted aliphatic aminoperoxides:

- (I) – N-tert-butylperoxymethylene-N,N-dimethylamine;
 (II) – N-tert-butylperoxymethylene-1-amino-2-hydroxyethane;
 (III) – 2-(tert-butylperoxymethylamino)-2-hydroxymethyl-1,3-propanediol; and (IV) – tert-butylperoxymethylcarbamic acid

and preexponential factor of $1.9 \cdot 10^8$.

(III): active oxygen of 7.17%. Thermolysis occurs in one stage. Temperature of 316–378 K, weight loss of 15.0%, $k_{ef}=0.9 \cdot 10^{-2}$, activation energy of 39 kJ/mol, and preexponential factor of $6.6 \cdot 10^3$.

(IV): active oxygen of 9.03%. Thermolysis occurs in two stages. Stage 1: temperature of 322–371 K, weight loss of 40.75%, $k_{ef}=1.0 \cdot 10^{-2}$, activation energy of 64 kJ/mol, and preexponential factor of $4.3 \cdot 10^3$; stage 2: temperature of 372–428 K, weight loss of 30.75%, $k_{ef}=2.6 \cdot 10^{-2}$, activation energy of 62 kJ/mol, and preexponential factor of $3.3 \cdot 10^6$.

The following conditions were used to perform suspension oligomerization: reaction temperature of 313–353 K; reaction time of 30–240 min; initiator concentration of 0.032–0.096 mol/l; volume ratio [fraction C9]:[water]=[1:1]–[1:4]; and mixing intensity $Re=2290$ –13450. Polyvinyl alcohol (0.2%) was used as a stabilizer.

Results and discussion

The study was carried out at different ratios of dispersed phase to dispersed medium. The ratios were as follows: 1:1, 1:2, 1:3, and 1:4, where the content of the C9 fraction in the mixture was 50%, 33%, 25%, and 20%, respectively. The results are shown in Fig. 2. The correlation between the yield of oligomers and the content of the C9 fraction in the reaction mixture was -0.91 .

A significant increase in oligomer yield is observed at the turbulent region (Fig. 3). However, when the Reynolds criterion is above 10120, the product yield does not increase. The correlation between mixing intensity and oligomer yield is 0.88.

The main increase in the yield of oligomers is observed during the first 60 minutes of the reaction

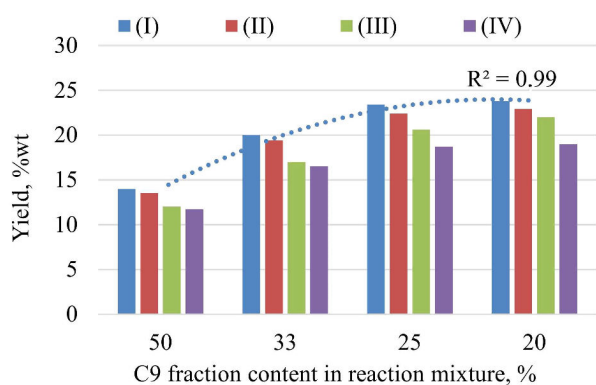


Fig. 2. Oligomer yield as a function of diesel fuel pyrolysis C9 fraction in the mixture and stirring intensity (temperature 333 K, time 180 min, and initiator concentration 0.064 mol/l)

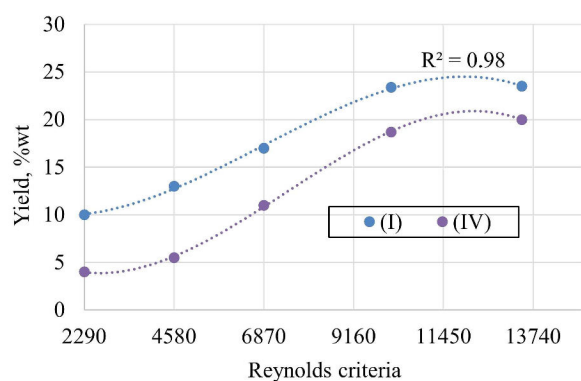


Fig. 3. Oligomer yield as a function of mixing intensity (diesel fuel pyrolysis C9 fraction, temperature 333 K, time 180 min, and initiator concentration 0.064 mol/l)

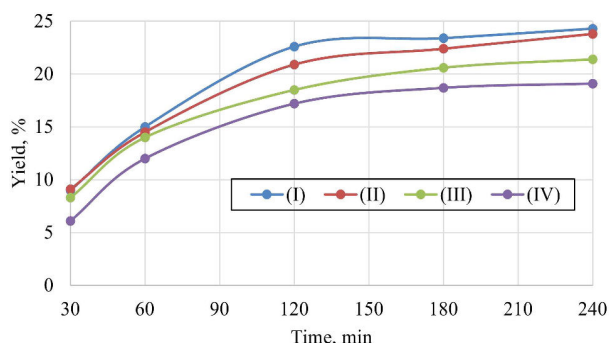


Fig. 4. The effect of reaction time on the yield of hydrocarbon resins (reaction temperature 333 K, initiator concentration 0.064 mol/l, and $Re=10120$)

(12.0–15.1%) (Fig. 4). Increasing the reaction time beyond 180 min is not recommended, as the product yield will be slightly bleached (less than 1%). The correlation between reaction time and oligomer yield is 0.87.

The main results concerning the effect of the reaction time on the properties of hydrocarbon resins

are given in Table 2.

A decrease in the oligomer bromine number indicates the consumption of unsaturated bonds in the reaction mass and correlates with an increase in their yield, the correlation index is -0.82 .

The softening temperature of the petroleum resins is in the range of 347–353 K. These values are similar to those obtained for oligomerization in solution of the C9 fraction. This indicates that the softening point of the oligomers does not depend on the oligomerization method (correlation index is 0.28).

The color index of the suspension oligomerization products varies slightly over the intervals studied and is 10–20 $mg I_2/100 ml$. Increasing the reaction time leads to an increase in the color index (correlation index is 0.78).

Table 2
Experimental data on the dependence of the properties of hydrocarbon resins on the reaction time (reaction temperature 333 K and initiator concentration 0.064 mol/l)

The reaction time, min	Bromine number, g $Br_2/100 g$	Color index, $mg I_2/100 ml$	Molecular weight	Softening point, K
(I)				
30	45.9	10	505	348
60	35.0	10	510	349
120	31.2	20	515	351
180	30.8	20	525	350
240	30.8	20	520	353
(II)				
30	46.0	10	505	350
60	35.4	10	510	352
120	32.3	10	515	350
180	32.1	20	525	349
240	29.0	20	515	351
(III)				
30	47.2	10	505	351
60	36.0	10	510	350
120	34.1	10	515	352
180	30.3	20	510	353
240	31.2	20	515	350
(IV)				
30	49.0	10	500	348
60	37.9	20	510	353
120	36.0	10	505	353
180	31.3	20	505	353
240	31.0	20	515	350
correlation index with the reaction time	-0.82	0.78	0.65	0.28

The molecular weight of the suspension oligomers (505–525) is lower than in the case of oligomerization in C9 fraction solution (615–660) [10].

All aminoperoxides studied show similar effects on suspension oligomerization progress in the temperature and concentration ranges investigated (Table 3).

In the temperature and initiator concentration ranges studied, the yield of oligomers varies from 8.3% to 23.8%. The variation is 15.5%.

For the suspension oligomerization of the C9 fraction, the product yield is slightly dependent on the reaction temperature (correlation coefficient of 0.26) and the initiator concentration (correlation coefficient of 0.39). Thus, for aminoperoxide (II) at the concentration of 0.064 mol/l, an increase in temperature from 313 to 353 K causes an increase in the oligomer yield from 19.1 to 23.3%. An increase in initiator concentration from 0.032 to 0.096 mol/l at 353 K results in an increase in yield from 21.9 to 23.8%.

The bromine number of the oligomers decreases with increasing yield. This indicates that the oligomerization reaction proceeds via unsaturated hydrocarbon bonds.

The color index of the resins obtained is in the range of 10–30 mg I₂/100 ml. This value increases with increasing temperature (correlation index is 0.74) and does not depend on the concentration of amino peroxides (correlation index is 0.45).

The average molecular weight values are in the range of 505–530 and are not sensitive to changes

in reaction temperature and initiator concentration over the range studied. The correlation indices are 0.53 and –0.39, respectively.

Based on the algorithms described elsewhere [14], we have calculated the multiple linear regression of the oligomer yield (Y) as a function of the main parameters of the suspension oligomerization (Eq. (1)).

$$Y = -0.166 + 0.57 \cdot t + (-0.267) \cdot C + 0.003 \cdot Re. \quad (1)$$

Based on the results of the experimental studies, the parameters with the most significant influence on the process were identified. These are as follows: stirring intensity (Reynolds criteria) (correlation index is 0.88); reaction time (correlation index is 0.87); and the content of the C9 fraction in the reaction mixture (correlation index is –0.91). Calculations were performed using the least squares method. Free regression terms (b₀) and angle regression coefficients (b₁, b₂, b₃) were derived as follows:

regression free term b₀ = –0.166,
oligomerization time (T) b₁ = –0.057,
C9 fraction content in reaction mixture (C) b₂ = –0.267,
Reynolds criteria (Re) b₃ = 0.002.

Multiple linear regression of oligomer yields during suspension oligomerization (313–353 K) of the diesel fuel pyrolysis C9 fraction initiated by aminoperoxides (Fisher's criterion is 86.33) is given by Eq. (1).

Additional (post) oligomerization was carried out to include the less reactive DCPD and indene, the total content of which is 18.69% (Table 1). After

Table 3

Experimental data on the dependence of the properties of hydrocarbon resins on the reaction temperature and initiator concentration (reaction time 180 min)

Reaction temperature, K	Concentration of initiator, mol/l	Yield, %	Bromine number, g Br ₂ /100 g	Yield, %	Bromine number, g Br ₂ /100 g	Yield, %	Bromine number, g Br ₂ /100 g
		(I)		(II)		(III)	
313	0.032	18.7	32.3	18.7	33.6	16.3	35.4
	0.064	19.0	29.4	19.1	30.7	16.8	32.5
	0.096	20.9	28.3	20.7	29.6	18.3	31.4
333	0.032	22.4	28.2	21.1	29.5	18.7	31.3
	0.064	23.5	30.8	22.4	32.1	20.6	30.3
	0.096	24.1	30.3	23.1	31.6	20.7	33.4
353	0.032	22.3	31.4	21.9	32.7	19.5	34.5
	0.064	23.9	30.1	23.3	31.3	21.1	33.1
	0.096	24.3	29.8	23.8	31.1	21.4	32.9

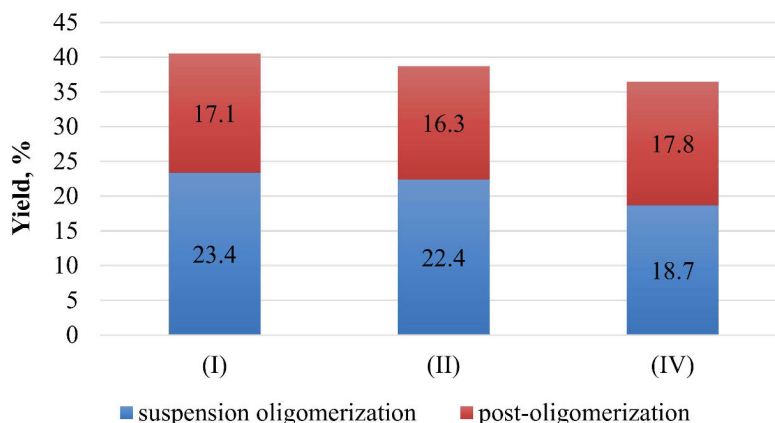


Fig. 5. Yields of hydrocarbon resins at the suspension (reaction temperature 333 K, initiator concentration 0.064 mol/l, $Re=10120$) and post-oligomerization stages (453 K, 360 min)

separation of the oligomer by suspension oligomerization, the unpolymerized hydrocarbons were oligomerized (453 K, 360 min) in the presence of 1% isopropylbenzene hydroperoxide. The results are shown in Fig. 5.

The hydrocarbon resins obtained at this stage are mainly cyclopentadiene-indene cooligomers. Regarding their physicochemical properties, the oligomers obtained at the post-oligomerization stage are characterized by a lower unsaturation index (16.0–18.4 g $Br_2/100$ g), a high softening point (354–358 K) and a much higher color index (60–80 mg $I_2/100$ ml).

The total yield of the product in the two stages is 36.5–40.5%. For comparison, a hydrocarbon resin with a yield of 31.5% was obtained by oligomerization in a solution of the diesel fuel pyrolysis C9 fraction initiated by aminoperoxide (I) under optimal conditions (initiator concentration is 0.064 mol/l, and temperature is 433 K for 360 min) [6].

Conclusions

Our study has confirmed the possibility of preparing hydrocarbon resins by the C9 fraction suspension oligomerization initiated by N-substituted aliphatic aminoperoxides. The hydrocarbon resins obtained in this way are mainly cooligomers of styrene and its derivatives. As a result of suspension oligomerization at low temperatures, products are obtained which are characterized by a light color (color index is 10–20 mg $I_2/100$ ml), a molecular weight (505–530) and a softening point of 347–354 K. According to their characteristics, the prepared oligomers meet the requirements for synthetic paints and varnishes. The process conditions that have the greatest influence on the course of suspension oligomerization of the C9 fraction are as follows: stirring intensity (Reynolds criteria)

(correlation index is 0.88), reaction time (correlation index is 0.87), and the content of the C9 fraction in the reaction mixture (correlation index is –0.91). Compound (I) is the most efficient initiator. Under optimal conditions (reaction temperature of 333 K, C9:water ratio of 1:3, initiator concentration 0.064 mol/l, and stirring intensity $Re=10120$) during the reaction time of 120 min, the oligomer was obtained with a 22.6% yield. In order to maximize the participation of all resin-forming components of the fraction (dicyclopentadiene and indene), a high-temperature (453 K) post-oligomerization was carried out. As a result, a hydrocarbon resin was obtained which is a cyclopentadiene-indene cooligomer and characterized by a darker color.

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СУСПЕНЗИЙНА ОЛІГОМЕРИЗАЦІЯ ВУГЛЕВОДНЕВОЇ ФРАКЦІЇ C9, ІНІЦІЙОВАНА АЛІФАТИЧНИМИ N-ЗАМІЩЕНИМИ АМІНОПЕРОКСИДАМИ

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Досліджено одержання нафтових смол шляхом суспензійної олігомеризації вуглеводневої фракції C9, ініційованої аліфатичними амінопероксидами. Реакційна суміш складається з дисперсійного середовища – води, дисперсної фази – фракції C9 і ініціатора, розчинного в дисперсійній фазі та стабілізатора суспензії. У досліджуваному діапазоні змінних температура реакції (313–353 K) і концентрація ініціатора (0,032–0,096 моль/л) не мають суттєвого впливу на вихід олігомерів. Умови процесу, що найбільше впливають на перебіг суспензійної олігомеризації фракції C9, є наступними: інтенсивність перемішування ($Re=2290-13450$) – коефіцієнт кореляції 0,88; час реакції (30–240 хв) – коефіцієнт кореляції 0,87 та співвідношення дисперсної фази до дисперсійного середовища (1:1–1:4) – коефіцієнт кореляції –0,91. Кореляція для виходу і бромного числа (коефіцієнт кореляції –0,82) підтверджує перебіг реакції олігомеризації за ненасиченими зв'язками мономера. Вуглеводневі смоли, одержані методом низькотемпературної суспензійної олігомеризації, є, переважно, коолігомерами стирену та його похідних. В результаті суспензійної олігомеризації при низьких температурах одержують продукти, які характеризуються світлим кольором (показник кольору 10–20 мг I₂/100 мл), молекулярною масою 505–530 і температурою розм'якшення 347–354 K.

Ключові слова: фракція C9, нафтополімерна смола, суспензія, ініціатор, стирен, амінопероксид, олігомеризація.

SUSPENSION OLIGOMERIZATION OF C9 HYDROCARBON FRACTION INITIATED BY ALIPHATIC N-SUBSTITUTED AMINOPEROXIDES

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We investigated the production of petroleum resins by suspension oligomerization of C9 hydrocarbon fraction initiated by aliphatic aminoperoxides. The reaction mixture consisted of a dispersion medium (water), a dispersed phase (C9 fraction), an initiator, which is soluble in the dispersed phase, and a suspension stabilizer. In the range of variables studied, reaction temperature (313–353 K) and initiator concentration (0.032–0.096 mol/l) do not have a significant effect on the oligomers yield. The process conditions most influencing the course of suspension oligomerization of the C9 fraction are as follows: stirring intensity ($Re=2290-13450$) with the correlation index of 0.88, reaction time (30–240 min) with the correlation index of 0.87 and the ratio of dispersed phase to dispersed medium (1:1–1:4) with the correlation index of –0.91. The correlation between the yield and bromine number (correlation index of –0.82) confirmed the passage of oligomerization reaction via the unsaturated bonds of the monomer. The hydrocarbon resins obtained by low-temperature suspension oligomerization were mainly cooligomers of styrene and its derivatives. As a result of suspension oligomerization at low temperatures, products were obtained which were characterized by a light color (color index of 10–20 mg I₂/100 ml), a molecular weight of 505–530 and a softening point of 347–354 K.

Keywords: C9 fraction; petroleum resin; suspension; initiator; styrene; aminoperoxide; oligomerization.

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