

The object of research is the production of C9 hydrocarbon resins by oligomerization of oil refining by-products.

In the technology of hydrocarbon resins by free radical oligomerization, there is a disadvantage in the use of high temperatures and a long reaction time. The resulting products have a dark color, which limits their use in paints and varnishes.

The technology of hydrocarbon resins, which consists in the suspension oligomerization of hydrocarbons of the C9 fraction in an aqueous medium, at low temperatures and stirring, was studied.

N-substituted amino peroxides, which are characterized by a low temperature of use, were used as initiators. The raw materials used were C9 fractions of liquid gasoline pyrolysis products with an unsaturated compound content of 54.7 %.

The optimal conditions were established: temperature – 364 K, time – 180 min,  $Re=10120$ , initiator concentration – 0.064 mol/l, the share of C9 fraction in the reaction mixture – 25 %. Under these conditions, a light hydrocarbon resin with a color index of 20 mg I<sub>2</sub>/100 ml and a softening point of 352 K was obtained.

The use of amino peroxide initiators allows for the suspension oligomerization of the hydrocarbon fraction C9 at low temperatures (303–353 K) and within a short reaction time (180 min). This oligomerization technology makes it easy to remove excess heat and maintain isothermal conditions in the reaction zone. This prevents the development of side oxidation reactions that cause darkening of the product.

The research results make it possible to improve the process of oligomerization of the hydrocarbon fraction using new initiators and obtain light-colored hydrocarbon resins. This will reduce energy costs for production and improve the characteristics of hydrocarbon resins.

**Keywords:** C9 hydrocarbon resin, suspension oligomerization, N-substituted amino peroxide, light color

# PREPARATION OF HYDROCARBON RESINS BY SUSPENSION OLIGOMERISATION OF THE C9 FRACTION OF GASOLINE PYROLYSIS INITIATED BY AMINO PEROXIDES

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Received date 19.09.2023

Accepted date 29.11.2023

Published date 22.12.2023

**How to Cite:** Subtelnyy, R., Zhuravskiy, Y., Dzinyak, B. (2023). Preparation of hydrocarbon resins by suspension oligomerisation of the C9 fraction of gasoline pyrolysis initiated by aminoperoxides. *Eastern-European Journal of Enterprise Technologies*, 6 (6 (126)), 23–30. doi: <https://doi.org/10.15587/1729-4061.2023.292527>

## 1. Introduction

One of the main methods for producing gaseous olefins (ethylene and propylene) is the pyrolysis of petroleum raw materials (gasoline and diesel fuel). In the pyrolysis process, a significant amount (30–35 %) of by-products, the so-called liquid pyrolysis products (LPP), is obtained. LPP is a complex mixture of various hydrocarbons: dienes, olefins, aromatic, cyclic, vinyl aromatic, and others [1, 2].

In the process of further processing, a light pyrolysis resin, containing components with a boiling point of up to 473 K, and a heavy pyrolysis resin are isolated from LPP. The total yield of light pyrolysis resin, known as pyro condensate, is about 80 % of the volume of liquid pyrolysis products. From the pyro condensate, fractions with a narrower boiling temperature range are separated, in particular, the C9 fraction with a boiling range of 423–473 K. The C9 fraction contains unsaturated aromatic hydrocarbons and is used to produce aromatic hydrocarbon resins (oligomers) known as naphthopolymer resins (NPR) [2, 3].

Hydrocarbon resins are used in paint and anti-corrosion coatings as synthetic substitutes for products of natural origin (vegetable oils, rosin), phenol-formaldehyde and indene-coumarone resins [2, 4].

A factor limiting the wider use of hydrocarbon resins in paint materials is a high color index (up to 100 mg I<sub>2</sub>/100 ml on the iodometric scale). The dark color of NPR is associated with high temperatures and the duration of the process, as well as with the involvement of cyclopentadiene and indene units in the composition of the oligomeric chain [2]. It is proposed to use low-temperature suspension oligomerization initiated by N-substituted amino peroxide initiators [5].

Nitrogen-containing peroxides and, in particular, N-substituted amino peroxides have been used as polymerization initiators at low temperatures. The introduction of an amino group into the alkyl peroxide molecule contributes to a decrease in the thermal stability of the compound. This is explained by the participation of the unshared electron pair of the nitrogen atom in the redistribution of the electron density on the oxygen atoms of the peroxide group. And as a result, it causes a decrease in the stability of the bond [6, 7].

Hydrocarbon resins obtained by suspension oligomerization are characterized by a low color index – up to 20–40 mg I<sub>2</sub>/100 ml on the yodometric scale (YMS). This expands the scope of their application in paint compositions.

The results of the research will make it possible to establish the basic regularities of the suspension oligomerization of hydrocarbons of the C9 fraction of liquid by-products of

gasoline pyrolysis initiated by amino peroxides. This will provide an opportunity to build a regression model of the process and determine optimal conditions.

Therefore, it is a relevant task to investigate the development of technology of low-temperature suspension oligomerization of by-products of oil refining for the production of light hydrocarbon resins.

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## 2. Literature review and problem statement

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A feature of the oligomerization process of the C9 fraction is the presence in its composition of a large amount of non-tar-forming hydrocarbons (40–50 %), such as indane, xylenes, ethylbenzene, and others. The fraction is both a mixture of monomers and a solvent of monomers and oligomers. Technological methods of oligomerization of hydrocarbon mixtures include catalytic and radical oligomerization in a solution of fraction C9.

In [8] it is proposed to use  $Al^{3+}$  cation exchange resin based on styrene. Products with a softening temperature lower than the softening temperature of resins obtained by catalysis with anhydrous aluminum chloride were received. The disadvantage is the difficulty of preparing the catalyst and obtaining dark-colored resins.

Catalytic co-oligomerization of C5/C9 using a heterogeneous catalyst – divinylbenzene-crosslinked polystyrene/titanium tetrachloride (DVB-PS/ $TiCl_4$ ) is considered in [9]. The catalyst used is characterized by hardness and a developed inner surface. The main side reactions of chain transfer into the polymer with the formation of cross-linked and cyclic structures are suppressed. Thanks to this, the amount of hazardous waste is reduced. The disadvantage is obtaining a dark-colored product and the need to separate the heterogeneous catalyst from the reaction mixture.

C5 hydrocarbon resin with a light color (3 on the Gardner scale) and a high softening temperature (378 K) was obtained by catalytic oligomerization in [10]. The disadvantage is the need to use significant amounts of solvent, which is undesirable on an industrial scale.

In industry, hydrocarbon resins are also obtained; free-radical oligomerization of hydrocarbon fractions, in which initiators are soluble in hydrocarbon raw materials. The following can be used as process initiators: acyl peroxides, hydroperoxides, heat-stable alkyl peroxides, amino peroxides, and organic silicon peroxides. The technological features of the process are the long-term conduct of the oligomerization reaction (6–8 h) at a high temperature (453–473 K). It is also difficult to isolate the product by atmospheric and vacuum distillation [5, 11].

The improvement of the color of the hydrocarbon resin based on the C9 fraction was studied in [12]. Elucidation of the product was achieved by hydrogenation of the aromatic rings of the oligomers. For the starting resin, which contained only aromatic monomer units, with a color on the Gardner scale of 17.1, the color decreased to 5.7 after hydrogenation. The disadvantage of this technique of obtaining light hydrocarbon resins is the need for an additional stage of technologically complex hydrogenation.

As a result of hydrogenation of C9 hydrocarbon resin using the Ni-PEG1000/FC3R catalyst, the bromine number is significantly reduced, and the color changes from the initial yellow to water-white. This is due to the fact that unsaturated bonds (aromatic rings and ethylene bonds) of

C9 hydrocarbon resins can be oxidized during operation. This leads to darkening of the product and deterioration of thermal stability [13]. The process is complicated by an additional stage of hydrogenation and the difficulty of preparing the catalyst under ultrasonic conditions.

In works [5, 14], low-temperature dispersion methods of oligomerization of hydrocarbon fractions are considered – oligomerization in emulsion and suspension. The resulting products are characterized by a narrow range of molecular mass distribution and a light color.

In work [14], the emulsion oligomerization of the hydrocarbon fraction in an aqueous medium using emulsifiers of the first and second kind is considered. The method is characterized by low temperature conditions (303–353 K), short reaction time (180 min), and the possibility of obtaining light hydrocarbon resins. The disadvantage is the complex process of isolating the target product, which involves the destruction of the emulsion.

Low-temperature (333–353 K) suspension oligomerization of the C9 LPP fraction of diesel fuel using amino peroxides with cyclic substituents was studied in [5]. As a result, light hydrocarbon resins with a color index of 20–30 mg  $I_2/100$  ml and a yield of up to 27 % are obtained.

The disadvantage of a number of studies [5, 11, 14] is the use of the C9 fraction of the LPP of diesel fuel as a raw material. These fractions contain significant amounts of dicyclopentadiene (DCPD) – up to 18 %. Under conditions of low temperatures, DCPD does not enter into a radical polymerization reaction and is not very active in copolymerization processes [15, 16]. Therefore, for a more complete use of raw materials, it is proposed in the cited works to use an additional high-temperature stage - pre-oligomerization (453–473 K) of unreacted hydrocarbons. As a result of pre-oligomerization, dark hydrocarbon resins are obtained – cyclopentadiene co-oligomers. This is due to the fact that the reactive monomer, cyclopentadiene, is formed by the Diels-Alder retro diene synthesis reaction at 5 MPa and 453–513 K [16].

In order to obtain hydrocarbon resins with high yields and appropriate physicochemical properties, it is important to implement the synthesis process at low temperatures and a short reaction time. The use of amino peroxide initiators of low thermal stability simplifies the achievement of this goal. Technological parameters of the process contribute to the formation of oligomers with improved color. Fraction C9 of the LPP of gasoline contains a lower amount of non-reactive DCPD, compared to the LPP of diesel fuel. This creates an opportunity to increase yields of hydrocarbon resins in low-temperature oligomerization processes. This allows us to argue that it is appropriate to conduct a study aimed at the suspension oligomerization of the C9 fraction of gasoline pyrolysis byproducts using low-temperature stable amino peroxide initiators.

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## 3. The aim and objectives of the study

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The aim of our study is to optimize the synthesis of hydrocarbon resins by means of suspension oligomerization of the C9 fraction of gasoline LPP. This will make it possible to increase the quality and efficiency of production, reduce costs, and improve the productivity of the production process.

To achieve the goal, the following tasks were solved:

– to establish the influence of parameters of suspension oligomerization of C9 fraction on yield and physicochemical characteristics of hydrocarbon resins;

– build a regression model of suspension oligomerization of the C9 fraction and establish optimal process conditions.

#### 4. Research materials and methods

##### 4.1. Researched materials and equipment used in the experiment

The object of our research is the oligomerization of the C9 hydrocarbon fraction of liquid products of gasoline pyrolysis obtained at Karpatnaftohim LLC (Kalush, Ukraine). The main characteristics of fraction C9 of liquid products of gasoline pyrolysis are given in Table 1.

N-substituted amino peroxides of the general formula  $C(CH_3)_3-O-O-CH_2-NR_1R_2$  were synthesized at the Department of Organic Products Technology of the Lviv Polytechnic National University by condensation of aromatic amines with *tert*-butylperoxymethanol. The structural formulas of the amino peroxides used to initiate oligomerization are shown in Fig. 1.

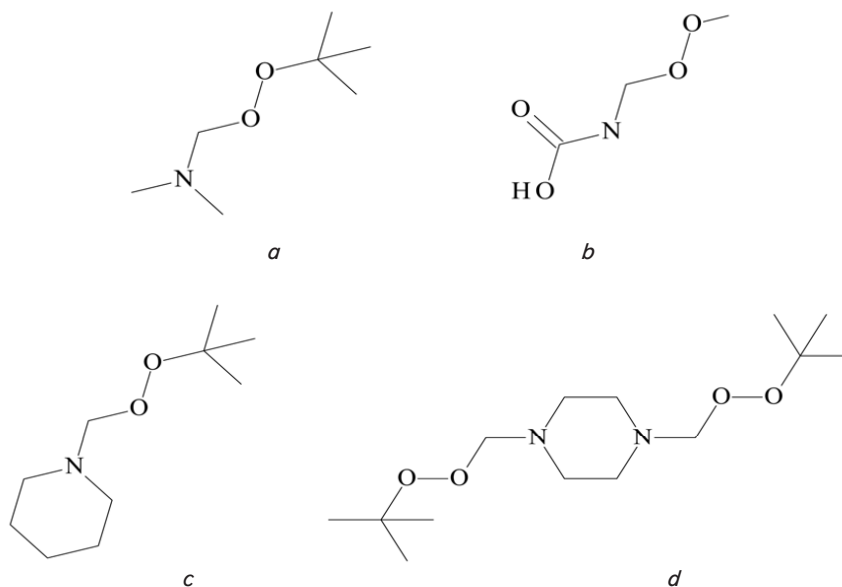


Fig. 1. Amino peroxide initiators: *a* – *N-tert*-butylperoxymethylene-*N,N*-dimethylamine; *b* – 2 (*tert*-butylperoxymethylamino)acetic acid; *c* – *tert*-butyl piperidinomethyl peroxide; *d* – 2-[4-(*tert*-butylperoxymethyl) piperazinomethylperoxy]-2-methylpropane

Table 1

Properties and composition of fraction C9 of liquid products of gasoline pyrolysis

Density, kg/m <sup>3</sup>	915
Bromine number, g Br <sub>2</sub> /100 g	84.1
Molecular mass	102
Color index, mg I <sub>2</sub> /100 ml	10
Fractional composition (422–467 K), %	
Resin-forming components:	54.7
Vinyl toluene	20.9
Styrene	15.1
Dicyclopentadiene	3.4
α-methyl styrene	1.4
Indene	1.2
Methyl indene	0.9
Allylbenzene	0.9
Others (unidentified)	10.9
Non-resin-forming components	45.3

The thermal stability of amino peroxides was determined on the Derivatograph – 1500 D of the Paulik-Paulik-Erday system:

(1) – *N-tert*-butylperoxymethylene-*N,N*-dimethylamine: active oxygen – 10.88 %, Thermolysis occurs in 2 stages: 309–366 K, 367–405 K;

(2) – 2 (*tert*-butylperoxymethylamino)acetic acid: active oxygen – 9.03 %, Thermolysis occurs in 2 stages: 322–371 K, 372–428 K;

(3) – *tert*-butyl piperidinomethyl peroxide: active oxygen – 7.48 %, Thermolysis occurs in 2 stages: 306–383 K, 384–400 K;

(4) – 2-[4-(*tert*-butylperoxymethyl) piperazinomethylperoxy]-2-methylpropane (2): active oxygen – 9.65 %, Thermolysis occurs in 2 stages: 305–355 K, 356–386 K.

Reaction mixture of suspension oligomerization:

- dispersion medium – water;
- dispersed phase – C9 hydrocarbon fraction of liquid by-products of gasoline pyrolysis;
- suspension stabilizer (soluble in dispersion medium – polyvinyl alcohol 0.1 %);
- amino peroxide initiator (soluble in the dispersed phase).

A methodology for the suspension oligomerization experiment of the C9 hydrocarbon fraction was devised. The C9 fraction with the dissolved initiator and water with the dissolved suspension stabilizer were sequentially loaded into a three-necked flask equipped with a rotary stirrer. The reaction mixture was intensively dispersed/stirred and simultaneously heated to a given temperature. After completion of the reaction, the resulting suspension was divided into organic and aqueous phases. Hydrocarbon resin was isolated from the obtained organic phase by centrifugation (4000 rpm). The obtained hydrocarbon resin was dried to a constant mass in a drying cabinet (323–343 K). The liquid phase obtained after centrifugation contained water residues and oligomerizate, which is a solution of hydrocarbon resin in unreacted hydrocarbons of fraction C9. Unreacted hydrocarbons were removed by vacuum distillation of the oligomerizate (pressure – 3 hPa, temperature – 453 K). At the same time, a hydrocarbon resin was obtained in the cube, which was combined with the resin after centrifugation, and the yield and characteristics were determined.

A top-drive mixer “IKA” RW 20 was used for mixing. Hydrocarbon resin was extracted in a laboratory centrifuge “Elvit” TsNL-6.

##### 4.2. Methodology for determining the parameters of sample properties

As part of this study, the main parameters characterizing hydrocarbon resins were selected: product yield, color, unsaturation, color, softening temperature, molecular weight.

These are the basic parameters regulated for synthetic paint resins.

The yield of hydrocarbon resin was calculated by the mass of the obtained solid product. The calculation was performed for the entire C9 fraction.

The unsaturation of hydrocarbon resins was characterized by the bromine number and determined by the bromide-bromate method (ISO 3839:1996).

The color was determined according to the iodometric scale (YMS), by comparing a 10 % solution of hydrocarbon resin in benzene with standards. The international analog is the Gardner scale (ISO 4630:2015).

Determination of the softening temperature of hydrocarbon resin was carried out by the “ring and ball” method (ISO 4625-1:2020).

Determination of the average molecular weight of the hydrocarbon resin was carried out by the cryoscopic method (ISO 5764:2009), comparing the freezing temperature of benzene with the freezing temperature of a 10 % solution of the hydrocarbon resin in benzene.

### 5. Results of investigating the suspension oligomerization of C9 fraction

#### 5.1. Influence of parameters of suspension oligomerization of C9 fraction on yield and properties of hydrocarbon resins

The [disperse phase]:[dispersion medium] ratio and the intensity of their mixing are important parameters of suspension polymerization. Carrying out the reaction at optimal values of these parameters contributes to the uniform distribution of monomer particles in the volume of the reaction system and simplifies the control of the temperature regime. Intensive mixing also prevents agglomeration of monomer particles. The influence of the mixing intensity in the range of values of the Reynolds criterion 2290–13450 is shown in Fig. 2.

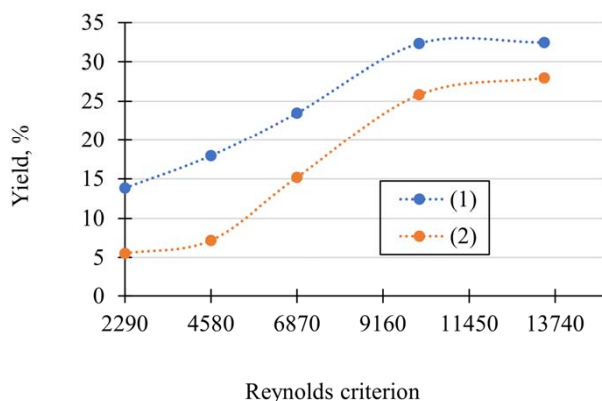


Fig. 2. Influence of mixing intensity on the yield of hydrocarbon resins (temperature – 333 K, reaction duration – 180 min, initiator concentration – 0.064 mol/l, ratio [fraction C9]:[water]=[1:3])

A significant increase in oligomer yield is observed in the turbulent region. However, when the mixing intensity is increased from Re=10120 to Re=13450, the resin yield does not increase. With this in mind, further research is carried out at a mixing intensity of Re=10120.

The study of the content of the C9 fraction in the reaction mixture on the course of oligomerization was carried out at different ratios of the dispersed phase and dispersion medium. The ratio [1:1] corresponds to the content of the C9 fraction in the mixture and is 50 %, [1:2] – 33 %, [1:3] – 25 %, [1:4] – 20 %. The results are shown in Fig. 3.

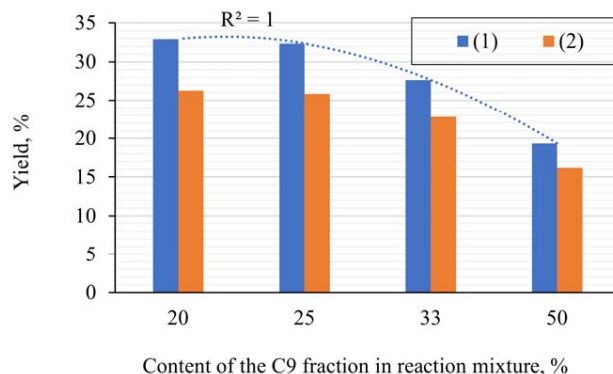


Fig. 3. Dependence of the yield of oligomers on the content of the C9 fraction in the reaction mixture (temperature – 333 K, reaction duration – 180 min, initiator concentration – 0.064 mol/l, Re=10120)

The influence of the temperature and duration of suspension oligomerization and the concentration of initiators on the yield of oligomers is shown in Fig. 4–6.

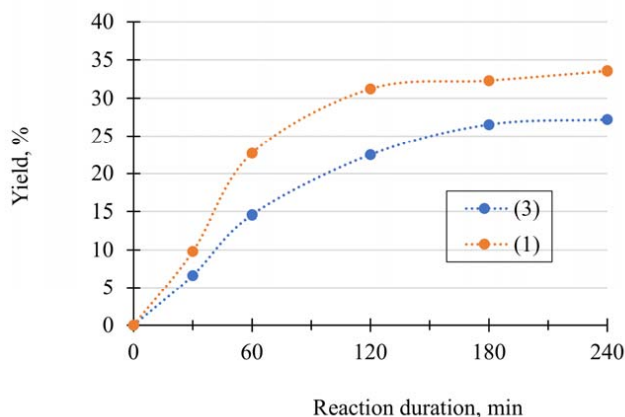


Fig. 4. Dependence of the yield of oligomers on reaction duration (Re=10120; content of the dispersed phase – 25 %; reaction temperature – 333 K; amino peroxide (1) – 0.064 mol/l; amino peroxide (3) – 0.0032 mol/l)

In the studied range of variables, the correlation of the yield of oligomers with the duration of the reaction is 0.83. A significant increase in the yield of hydrocarbon resin is observed at a temperature of 333 K. The correlation of the yield of the product with reaction temperature is 0.86.

Synthesis conditions and characteristics of hydrocarbon resins corresponding to the maximum obtained values of product yield are given in Table 2. In all cases, the ratio [fraction C9]:[water]=[1:3].

In all cases, the molecular weight of NPR is in the range of 500–535; the softening temperature is 347–353 K.



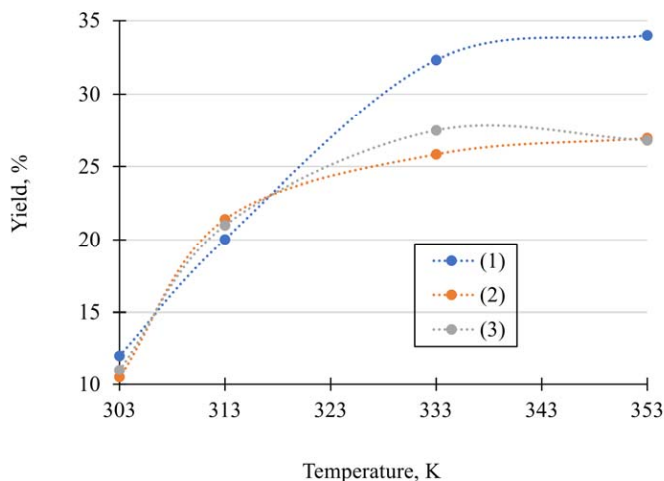


Fig. 5. Dependence of the yield of oligomers on reaction temperature (reaction duration – 180 min,  $Re=10120$ , dispersed phase content – 25 %, initiator concentration – 0.064 mol/l)

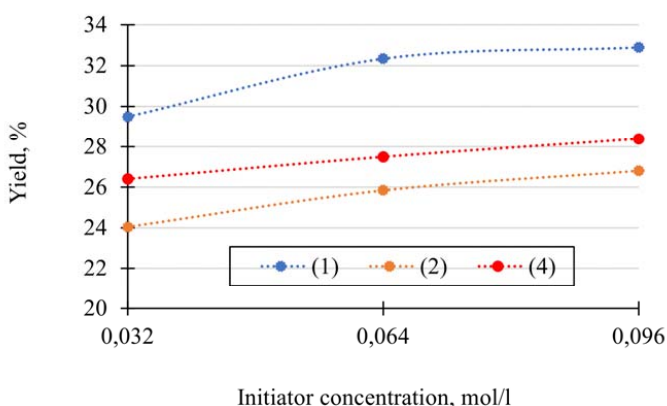


Fig. 6. Dependence of the yield of oligomers on the concentration of initiators (temperature – 333 K, duration of the reaction – 180 min,  $Re=10120$ , content of the dispersed phase – 25 %)

Experimental data on suspension oligomerization of C9 fraction of liquid products of gasoline pyrolysis initiated by amino peroxides

Initiator	Reaction conditions	Yield, %	Bromine number, g $Br_2/100$ g	Color, mg $I_2/100$ ml
(1)	temperature – 353 K; time – 180 min; $Re=10120$ ; initiator concentration – 0.064 mol/l	34.0	26.1	20
(2)	temperature – 333 K; time – 180 min; $Re=13450$ ; initiator concentration – 0.064 mol/l	27.9	31.2	30
(3)	temperature – 353 K; time – 180 min; $Re=13450$ ; initiator concentration – 0.096 mol/l mol/l	28.1	30.4	30
(4)	temperature – 353 K; time – 180 min; $Re=10120$ ; initiator concentration – 0.096 mol/l mol/l	29.4	30.1	40

### 5. 2. Construction of a regression model and optimization of suspension oligomerization of fraction C9 of liquid products of gasoline pyrolysis

Based on the algorithms described in [17], a multiple linear regression of the yield of hydrocarbon resins was calculated depending on the main parameters of suspension oligomerization. The concentration of initiators was not used in the calculations since this factor is not decisive. Calculations

were performed using the method of least squares (LINEST function in Microsoft Excel). Free regression terms ( $b_0$ ) and angular regression coefficients ( $b_1–b_4$ ) were obtained: the results are given in Table 3.

To assess the adequacy of the constructed regression model, a comparative plot was built (Fig. 7), on which the experimental and calculated values of the yield of oligomers are presented. The correlation between experimental and calculated values is 0.91. For a 95 % confidence level, the confidence interval is  $\pm 3.83$  %.

Optimization was carried out according to the regression model (SOLVER function in Microsoft Excel), choosing the product yield as the criterion for maximization. The results are given in Table 4.

Table 3

Factors of multiple linear regression of hydrocarbon resin yield

Name	Designation	Value
The free term of the regression	$b_0$	-111.91
Time of oligomerization	$b_1$	0.09
Oligomerization temperature	$b_2$	0.35
The share of fraction C9 in the reaction mixture	$b_3$	-0.40
Reynolds criterion	$b_4$	0.002

Table 4

Optimized parameters of the process of suspension oligomerization of fraction C9 of liquid by-products of gasoline pyrolysis

No.	Yield, %	Reaction conditions			
		Time, min	Proportion of C9 fraction in the reaction mixture, %	Temperature, K	$Re$
1	42.4	310	18.6	337	17,930
2	40.6	378	13.4	340	10,120
3	40.2	406	25	341	10,120
4	38.6	420	25	333	10,120
5	36.7	180	25	364	10,120

Table 2

To verify the obtained data, experiments were conducted according to optimized conditions No. 3 and No. 5 at the concentration of amino peroxide (1) – 0.064 mol/l. The results are given in Table 5.

On the basis of our experiments and the solution to the optimization problem, the optimal conditions of the process of suspension oligomerization of the C9 fraction of LPP gasoline were determined.

Table 5

Experimental data on the characteristics of hydrocarbon resins under optimal conditions

No.	Yield, %	Relative error, %	Bromine number, g $Br_2/100$ g	Color, mg $I_2/100$ ml	Softening Point, K	Molecular mass
3	38.1	5.2	21.6	60	525	353
5	36.0	2.0	23.2	20	520	352

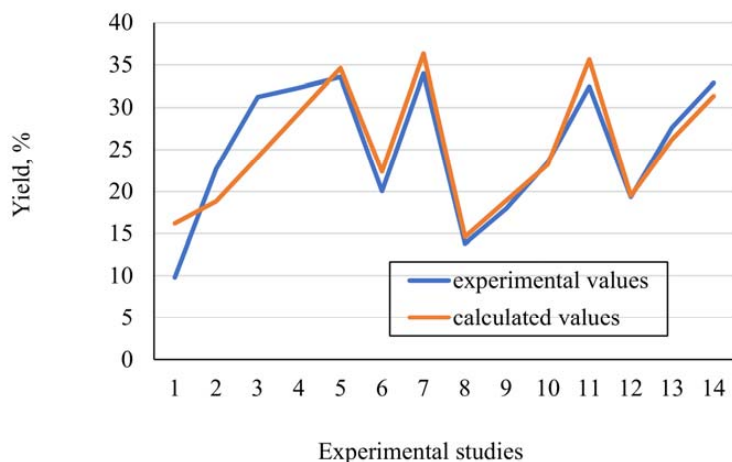


Fig. 7. Plot of experimental model validation

## 6. Discussion of results of determining the influence of oligomerization conditions on the yield of hydrocarbon resins

The data reported in the current work complement and generalize experimental studies on the oligomerization of hydrocarbon fractions, in particular [8, 10, 13–15].

But, in contrast to the results of research published in [13–15], the obtained data on the influence of conditions on the course of oligomerization of the C9 fraction of LPP gasoline allow us to state the following:

- under the studied conditions, the maximum yield of hydrocarbon resin is achieved when the reaction is carried out in the turbulent region at the value of the Reynolds criterion – 10120;

- the concentration of amino peroxide initiators does not have a determining effect on the course of suspension oligomerization;

- reducing the proportion of the dispersed phase in the reaction mixture to 25 % contributes to the growth of the oligomer yield.

The product yield increases with increasing intensity of mixing (Fig. 2). The resin yield is maximum at  $Re=10120$ . A further increase in the intensity of mixing does not affect the yield of the product. This may be due to a decrease in the concentration of reaction components in the reaction region and an excessive increase in particle distribution. The correlation between the intensity of mixing and the yield of hydrocarbon resins when using amino peroxide (1) is 0.96.

A decrease in the share of the C9 fraction, and accordingly, an increase in the share of the dispersion medium (water) contributes to the course of suspension oligomerization (Fig. 3). From a technological point of view, it is important to use less dispersing medium in view of reducing the volume of wastewater.

As the duration of the reaction increases, the increase in product yield decreases (Fig. 4). Thus, for amino peroxide (3) in the first 60 min of the reaction, the yield increase is 14.6 %. In the next 60 minutes – 7.9 %, in the next 120 minutes – 4.7 %. This dependence is characteristic of radical (block and suspension) polymerization processes. The correlation of the yield of oligomers with the duration of the reaction is 0.83.

An increase in the reaction temperature contributes to an increase in the yield of hydrocarbon resin. In all cases, increasing the temperature to 333 K provided the maximum

product yield. For amino peroxide (1) – 32.3 %, (2) – 25.8 %, (3) – 27.5 % (Fig. 5). A further increase in temperature is accompanied by a slight increase in output (within the margin of error). The correlation of the product yield with the reaction temperature is 0.86.

In the studied interval, the concentration of the initiator does not have a determining effect on the course of suspension oligomerization (Fig. 6). In all cases, increasing the concentration of amino peroxides from 0.032 to 0.096 mol/l provides an increase in yield by 1.3–3.4 %.

Hydrocarbon resin with the highest yield is obtained when using amino peroxide (1) – 34.0 %, amino peroxides (2) to (4) – about 29 % (Table 2). The decrease in the bromine number correlates with the yield of hydrocarbon resins (correlation – 0.81), indicating the consumption of unsaturated, capable of polymerization.

The relatively low average molecular weight (500–535) of the obtained products can be explained by the fact that amino peroxides are involved in chain transfer. The transfer of the kinetic chain occurs due to the detachment of a hydrogen atom from the methylene bridge [7].

The color index of suspension oligomerization products in the investigated intervals varies in the range of 20–40 mg  $I_2/100$  ml. The production of particularly light hydrocarbon resins is explained by the use of suspension oligomerization at low temperatures and during a short reaction time. This prevents the development of undesirable side reactions of oxidation, which lead to darkening of the product. In addition, under the reaction conditions, a monomer is obtained that practically does not contain monomer units of cyclopentadiene and indene, which are responsible for the darkening of the oligomer. At reaction temperatures, DCPD does not monomerize with the formation of cyclopentadiene. Indene is characterized by a much higher solubility in water than other resin-forming components of the fraction – 2.425 g/l (styrene – 0.161, vinyl toluene – not soluble in water). The color and softening temperature of hydrocarbon resins significantly depend on the oligomerization distillation conditions.

The initiator concentration factor was not used to construct the regression model due to its low influence on the course of suspension oligomerization. On the basis of the model, the optimal parameters of the process were determined, according to the criterion of maximum yield (Table 4). The calculated yield of the product is in the range of 36.7–42.4 %. Conditions No. 1 involve a high intensity of mixing ( $Re=17930$ ), which is an objective difficulty for technological implementation. Conditions No. 2 require a long reaction (378 min) and a significant proportion of water in the reaction mixture (86.6 %). This is undesirable for ensuring waste-free and ecological production.

Experimental verification of optimal conditions No. 3 and 5 confirmed the adequacy of the regression model. The relative errors of the experimentally determined and calculated value of oligomer yield are 2.0 and 5.2 % (Table 5). With similar values of molecular weight and softening temperature, under conditions No. 3, a resin with a high color index is obtained – 60 mg  $I_2/100$  ml. This is explained by the considerable duration of the reaction (406 min). With this in mind, optimal conditions No. 5 are proposed for use.

The result (light color) makes it possible to expand the use of these hydrocarbon resins as film formers in paint and varnish materials. The low temperature and duration of the reaction will reduce the cost of the product.

Limitations of this study are in that one specific hydrocarbon fraction with a unique quantitative composition was used as raw material. Oligomerization was carried out under atmospheric pressure at temperatures not exceeding the boiling point of the dispersion medium. The effect of stabilizer concentration and pH regulators is not taken into account.

Disadvantages of this study are that the properties of hydrocarbon resins significantly depend on the conditions of isolation from the reaction mixture. In particular, the significant duration of the vacuum distillation of the oligomerizate contributes to a significant darkening of the product.

The further development of this research will be the study of the influence of the pH of the medium and the surface tension of the reaction mixture on the course of the suspension oligomerization of the C9 fraction.

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## 7. Conclusions

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1. Our studies have confirmed the possibility of obtaining hydrocarbon resins based on fraction C9 of liquid products of gasoline pyrolysis by suspension oligomerization. Low-temperature N-substituted amino peroxides were used as initiators, which allow the process to be initiated in the temperature range of 303–353 K. It was established that the production of hydrocarbon resins with a high yield is facilitated by carrying out suspension oligomerization in the turbulent region and reducing the proportion of the dispersed phase in the reaction mixture.

2. A regression model was built that describes the yield of hydrocarbon resins depending on the main parameters of the process (intensity of mixing, composition of the reaction mixture, duration, and temperature of the reaction). Optimal process conditions were established and experimentally verified. Optimal conditions: reaction temperature – 364 K, reaction duration – 180 min,  $Re=10120$ , the concentration of the initiator is 0.064 mol/l, the share of fraction C9 in the reaction mixture is 25 %. Under these conditions, a light hydrocarbon resin (20 mg  $I_2/100$  ml) is obtained with a yield of 36.0 %.

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## Conflicts of interest

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The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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## Funding

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The study was conducted without financial support.

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## Data availability

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The data will be provided upon reasonable request.

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## Use of artificial intelligence

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The authors confirm that they did not use artificial intelligence technologies when creating the presented work.

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