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This paper investigates the production of hydrocarbon resins by emulsion oligomerization of the C₉ fraction hydrocarbons in liquid by-products of oil refining. Such oligomers have a wide range of applications as film-forming agents in paints and anti-color coatings.

Emulsion oligomerization was carried out using emulsifiers of the first and second kind. The study was performed at different values of the reaction temperature of the reaction duration, the intensity of agitation; concentrations of the emulsifier; C₉:water fraction ratio. The resulting products were estimated according to the following indicators: the yield, unsaturation degree, softening temperature, mean molecular weight, color.

Statistical analysis was carried out, the correlation of parameters of emulsion oligomerization and the yield and characteristics of oligomers was established. Given that, it would be possible to establish the optimal conditions for emulsion oligomerization and predict the properties of the products obtained.

Specifically, it was established that the yield of hydrocarbon resins does not correlate with the reaction temperature (0.15 and 0.30) and the concentration of emulsifiers (0.08 and 0.03). It was proven that in the intervals studied the variable yield of oligomers depends on the duration of the reaction (correlation 0.88 and 0.81). In the case of oligomerization in the reverse emulsion, a significant correlation with the yield is also demonstrated by agitation intensity (0.51) and a C₉:water fraction ratio (0.51). That has made it possible to derive an equation of the yield multiple linear regression dependent on the most significant process parameters. The high values of the yield and bromine number correlation (0.94 and 0.93) give grounds to argue about the progress of oligomerization reaction. The relationship among the characteristics of oligomers has been confirmed. This indicates the possibility of directed adjustment of certain characteristics of hydrocarbon resins

Keywords: liquid pyrolysis products, hydrocarbon resin, petroleum polymer resin, emulsion oligomerization, C₉ fraction

CORRELATION BETWEEN THE EMULSION OLIGOMERIZATION PARAMETERS FOR C₉ FRACTION AND THE CHARACTERISTICS OF HYDROCARBON RESINS

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1. Introduction

The production of gaseous olefins (ethylene and propylene) involving the pyrolysis of oil fractions (gasoline, diesel fuel) yields 30–35 % of by-products – liquid pyrolysis products (LPPs) are formed. LPPs are fractionated into pyro condensate (up to 473 K) and heavy pyrolysis resin. The total yield of pyro condensate is about 80 % of LPP amount. The following fractions with a slower boiling point interval [1–3] are separated from pyro condensate:

- C₅ fraction (303–343 K) contains linear and cyclic olefins and is used to obtain aliphatic hydrocarbon resins;
- C₆₈ fraction (343–423 K) contains few unsaturated hydrocarbons, specifically, dienes 3–5 %, mainly of aliphatic composition; it is not used for the production of hydrocarbon resins;
- C₉ fraction (423–473 K) contains unsaturated aromatic hydrocarbons and is used to obtain aromatic hydrocarbon resins (oligomers) termed petroleum polymer resins.

Petroleum polymer resins (PPRs) are used as cheap synthetic substitutes for products of natural origin (vegetable oils, colophony, albumin), phenol-formaldehyde and indene-coumarone resins, in paint-and-varnish anti-corrosion [1–3] and asphalt bitumen formulations [4–6]. A factor limiting the wider use of such hydrocarbon resins is a high color index (up to

100 mg I₂/100 ml on an iodometric scale). The use of low-temperature emulsion oligomerization makes it possible to obtain light styrene oligomers (up to 20–40 mg I₂/100 ml), expand the scope of their application in paints and varnishes. The reported research results enable predicting the yield and characteristics of hydrocarbon resins under different conditions of the emulsion oligomerization reaction.

2. Literature review and problem statement

The oligomerization methods of hydrocarbon mixtures technologically represent the ionic (catalytic) and radical (initiated and thermal) oligomerization [4].

Paper [4] considers methods for obtaining petroleum polymer resins involving peroxide initiators. Technological features of the process are the long-term oligomerization reaction (6–8 hours) at a high temperature (453–473 K). It is also difficult to separate the product with atmospheric and vacuum distillation.

Obtaining bitumen-resin coatings involving PPR with oxygen-containing functional groups is considered in work [5]. This complicates the technology due to the additional stage of modification of petroleum polymer resins.

In study [6], a mixture of thermoplastic elastomer and petroleum polymer resins (up to 8 %) is used for the modification of asphalt. With an increase in the concentration of PPR obtained on the basis of C_9 fraction, the softening temperature of the formulation increases, however, permeability and ductility are significantly reduced.

Paper [7] considers the catalytic co-oligomerization of C_9 fraction involving a heterogeneous catalyst – bentonite clay. It is shown that the target product is obtained at a high yield at a low temperature (353 K) and a short 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. Using aluminum chloride on cation-exchange resin as a catalyst makes it possible for the authors of [8] to increase the softening temperature of hydrocarbon resin without separating the catalytic complex.

One of the options for obtaining products with improved properties, including color, is the synthesis of modified petroleum polymer resins. Thus, paper [9] investigated the introduction of epoxy, carbonyl, and hydroxyl groups to the composition of resin.

A high color index of hydrocarbon resins is associated with the involvement of cyclopentadiene and indene links in the oligomer chain [4]. This limits the use of such resins in paint-and-varnish formulations.

An option proposed to overcome the issue of significant energy intensity of production and the high color indicator of hydrocarbon resins is the emulsion oligomerization of C_9 fraction. The method involves the oligomerization of reaction-capable monomers in the C_9 fraction in the aquatic environment using initiators soluble in a dispersion medium. This method is characterized by a low temperature of the process (303–353 K) and makes it possible to simplify the separation of the target product. That was confirmed, specifically, in work [10], which investigated the influence of the nature of the emulsifier on the co-oligomerization process. The optimal emulsifier (E-30) and initiator (potassium persulfate) were selected, which allow for the highest yields of the product. Emulsion polymerization in the presence of emulsifiers of the first kind (forming a direct emulsion of the “oil in water” type) occurs in the presence of water-soluble initiators (potassium persulfate, peroxide hydrogen, etc.). Using emulsifiers of the second kind produces a reverse emulsion of the “water in oil” type. In this case, the initiators are used that are soluble in a monomer (benzoyl peroxide) [10].

Hydrocarbon resins that are obtained by the emulsion oligomerization of C_9 fraction are characterized by a low color index (light) and a narrow range of molecular mass distribution; according to their other properties, oligomers are comparable with products obtained by other methods [11].

The peculiarity of low-temperature emulsion 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 [12]. Reactive in such reactions is its monomer – cyclopentadiene. Paper [13] investigated the Diels-Alder retrodiene synthesis reaction – DCPD monomerization with the formation of two active cyclopentadiene monomers at 5 MPa and 180–240 °C [13].

Low-temperature emulsion oligomerization makes it possible to obtain light resins due to the synthesis of sty-

rene co-oligomers. However, the issues related to the use of dicyclopentadiene remained unresolved. Therefore, for the complete utilization of reaction-capable hydrocarbons, a two-stage method [14] for the synthesis of hydrocarbon resins based on C_9 fraction has been proposed:

- the first stage is low-temperature (303–333 K) emulsion oligomerization. The resulting product contains monomer links of the most active components of C_9 fraction – styrene and its derivatives. The oligomer is characterized by a low color index (10–20 mg $I_2/100$ ml on an iodometric scale), which makes it possible to expand the scope of its application in paint and varnish formulations;

- the second stage is post-oligomerization ($T=453$ K) in a solution of the non-reacted residues of C_9 fraction of the emulsion oligomerization, enriched with DCPD and indene, followed by obtaining co-oligomers with a higher color indicator.

The reactivity of vinyl toluene, α -methyl styrene, and allylbenzene is close to the reactivity of styrene. The presence of cyclopentene link in indene causes the proximity of its reactivity to the reactivity of DCPD.

3. The aim and objectives of the study

The purpose of this study is to establish a correlation between the parameters of the emulsion oligomerization of LPP C_9 and the characteristics of hydrocarbon resins. That would make it possible to set the optimal conditions for obtaining hydrocarbon resins and reduce their cost.

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

- to statistically evaluate the results of experimental studies;

- to determine the correlations of oligomerization conditions with the characteristics of hydrocarbon resins, and build a multiple linear regression of yield dependent on reaction conditions, and establish a correlation among hydrocarbon resins.

4. The study materials and methods

4.1. The examined materials and equipment used in the experiment

Raw material: the C_9 fraction of diesel fuel LPP (bromine number, 68 g $Br_2/100$ g; density, 936 kg/m³; the content of unsaturated compounds, up to 45 % by weight, including styrene, 17.85 %, dicyclopentadiene, 18.0 %, vinyl toluene, 6.99 %; indene, 1.25 %). Given that DCPD does not react under the conditions of the process, the content of resin-forming components of the fraction is 26.09 %. The C_9 fraction is both a mixture of monomers and a solvent of the oligomer.

The used emulsifiers of the 1st kind (direct emulsion) are as follows:

- anion-active surfactants (SAS): sodium oleate, sodium stearate, E-30 (a mixture of linear alkanesulfonates with the length of the carbon chain of C15; the general formula is $R-SO_3Na$);

- non-ionic SAS: Neonol (oxyethylated nonylphenol (α -isononyl phenol)- Ω -hydroxy-polyoxy-1,2-ethanediol), Savenol (a mixture of hydrated non-ionic SAS).

The applied emulsifiers of the 2nd kind (reverse emulsion) are as follows:

–polyglycerol polyricinoleate (PGPR), the number of hydrophilic-lipophilic balance is 6;

– “Esther A” (a mixture of mono- and di-glycerides of oleic acid) is a complex ether of polyglycerol and high-molecular fatty acids of vegetable origin, the number of hydrophilic-lipophilic balance is 3.

Water-soluble potassium persulfate ($K_2S_2O_8$) was used as the initiator of oligomerization in a direct emulsion. In the reverse emulsion, benzoyl peroxide was used for initiation. The pH of the reaction mixture in the absence of buffer additives is 2.8.

The reaction mixture was loaded into a three-hole flask equipped with a rotary stirrer, intensively mixed ($Re=6,870-10,120$), and heated to 303–333 K. The oligomerization was carried out for 20, 40, 60, 120, 180 minutes. After the experiment ended and the mechanical agitation was stopped, the reaction mixture was partially delaminated. The reaction mixture (emulsion) after the reaction was separated by centrifugation ($4,000 \text{ min}^{-1}$); the separated oligomer was dried.

The non-reacted hydrocarbons were used as raw materials for the synthesis of cyclopentadiene resin by thermal oligomerization [14]. To this end, the raw materials were loaded into thermostat ampoules pre-blown by argon with a volume of 100 ml, hermetically sealed. The ampoules then were placed in the thermostat; the oligomerization was carried out at a temperature of 453 K for 6 hours. The non-reacted hydrocarbons were separated by atm vacuum distillation (pressure, 3 gPa, temperature, 453 K). At the same time, the resin was obtained in the cube with a softening temperature in the range of 339...350 K.

The composition of the products obtained was determined on the basis of data from the IR spectroscopic analysis of oligomer samples and chromatographic analysis of the C_9 fraction and distillates. It was established that the composition of such hydrocarbon resins obtained by emulsion oligomerization includes styrene and its derivatives (vinyl toluene, methyl styrene, and others).

4. 2. Procedure for determining the indicators of sample properties

The main characteristic properties of hydrocarbon resins, determined in the experiment, were the yield, unsaturation degree, mean molecular mass, softening temperature, color indicator.

The yield of the hydrocarbon resin was determined by recalculating for the C_9 fraction.

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

Molecular weight was determined by the cryoscopy method involving a gasoline solvent.

The coloration of hydrocarbon resin was determined visually, by comparing the coloration of 10 % of the solution in benzene to the reference iodometric scale (IMS).

The softening temperature was determined according to the ring and ball method. The procedure involves determining the temperature at which the sample located in the ring of the specified dimensions is softened and, under the action of a steel ball, touches the control disc of the machine.

The main examined parameters of emulsion oligomerization:

- reaction duration, 20, 40, 60, 120, 180 min.;
- reaction temperature, 303, 313, 333 K;
- emulsifier concentration, – 0.6–1.0 %;
- agitation intensity ($Re=6,870-10,120$);
- the volumetric fraction C_9 :water ratio:

a) for oligomerization in a direct emulsion – [1:1], [1:2], [1:3], [1:4]. The percentage of C_9 fraction is 50 %, 33 %, 25 %, 20 %;

b) for oligomerization in a reverse emulsion – [1:1], [2:1], [3:1], [4:1]. The percentage of C_9 fraction is 50 %, 66 %, 75 %, 80 %.

5. Results of studying the emulsion oligomerization of C_9 fraction

5. 1. Statistical evaluation of experimental research results

The relevant Microsoft Excel functions were used to establish statistical indicators. Statistical analysis treated the results from 104 experiments: 47 – oligomerization in a direct emulsion, 57 – oligomerization in a reverse emulsion, which were considered in works [10, 11, 14]. The results are given in Table 1.

Table 1

Statistical analysis of the yield and physical-chemical characteristics of hydrocarbon resins

Title	Yield, %	Bromine number, g $Br_2/100 \text{ g}$	IMS-based coloration, mg $I_2/100 \text{ ml}$	Softening temperature	Molecular weight
Oligomerization in direct emulsion/Oligomerization in reverse emulsion					
Mean value	10.84/8.81	44.80/47.61	24.00/23.86	352.42/357.44	666.59/564.04
Maximum	21.00/18.00	64.97/62.57	50.00/40.00	358.00/365.00	795.00/600.00
Minimum	2.00/1.00	32.00/31.30	10.00/20.00	340.00/340.00	400.00/495.00
Variance spread	19.00/17.00	32.97/31.27	40.00/20.00	18.00/25.00	395.00/105.00
Mean linear deviation	4.51/4.44	7.31/7.48	10.06/5.42	4.26/3.87	42.49/19.22
RMS deviation	5.25/5.22	9.07/8.90	10.20/6.42	5.02/4.81	67.25/24.73
Oscillation factor	1.75/1.93	0.74/0.66	1.67/0.84	0.05/0.07	0.59/0.19
Variance coefficient	0.49/0.60	0.20/0.19	0.43/0.27	0.01/0.01	0.10/0.04

The value of a variation coefficient is in the range of 0.01–0.60, which indicates a low variability of indicators [15].

5. 2. Establishing a correlation of hydrocarbon resin characteristics with reaction conditions

Based on our experiments, the correlations of emulsion oligomerization conditions regarding the yield of hydrocarbon resins and their characteristics were calculated (CORREL function in Microsoft Excel). The results are given in Table 2.

Table 2

Correlation of the yield and characteristics of hydrocarbon resins to oligomerization conditions

Indicator	Yield	Bromine number	Molecular weight	Softening temperature	Coloration
	Oligomerization in direct emulsion/Oligomerization in reverse emulsion				
Oligomerization duration	0.88/0.81	-0.83/-0.83	0.35/-0.28	-0.36/0.11	0.58/0.54
Oligomerization temperature	0.15/0.30	-0.02/-0.27	-0.50/0.02	-0.54/0.15	0.28/0.45
Emulsifier concentration	0.08/0.03	0.02/0.08	0.05/0.59	-0.36/0.31	0.18/-0.52
C ₉ :water fraction ratio	-0.05/0.51	-0.16/-0.57	-0.05/0.24	0.02/0.23	-0.05/0.05
Agitation intensity	0.01/0.51	0.01/-0.06	0.10/0.05	0.13/-0.05	0.01/-0.26

Based on the algorithms described in work [15], we calculated the multiple linear regression of the oligomer (*B*) yield depending on the most significant parameters of oligomerization – equations (1) and (2).

For oligomerization in the reverse emulsion, the process parameters characterized by the highest values of correlation bonds were selected: the duration of oligomerization (0.81), the volumetric ratio of fraction C₉:water (0.51), and the intensity of agitation (0.51). Calculations were carried out using a least-square method (LINEST function in Microsoft Excel). Free regression terms (*b*₀) and angular regression coefficients (*b*₁, *b*₂, *b*₃) were derived. The resulting factors of the multiple linear regression are given in Table 3.

Table 3

Established factors of multiple linear regression of the yield of hydrocarbon resin

Oligomerization in direct emulsion		
regression free term	<i>b</i> ₀	1.9116
oligomerization duration (<i>T</i>)	<i>b</i> ₁	0.0662
Oligomerization in reverse emulsion		
regression free term	<i>b</i> ₀	-8.9825
oligomerization duration (<i>T</i>)	<i>b</i> ₁	0.0603
<i>phase ratio</i> (<i>C</i>)	<i>b</i> ₂	0.0924
mixing intensity (<i>I</i>)	<i>b</i> ₃	0.0046

Oligomerization in direct emulsion:

$$B = 1.9116 + T \cdot 0.0662. \quad (1)$$

Fisher's criterion for equation (1) is 179.463.

Oligomerization in reverse emulsion:

$$B = -8.9825 + T \cdot 0.0603 + C \cdot 0.0924 + I \cdot 0.0046. \quad (2)$$

Fisher's criterion for equation (2) is 95.593.

To assess the relationship of the yield and physical-chemical characteristics of hydrocarbon resins, we calculated the intercorrelations of the yield, bromine number, color indicator, softening temperature, and mean molecular weight. The resulting correlation values are given in Table 4.

Table 4

Correlation of the physical-chemical characteristics of hydrocarbon resins

Correlation pair	Correlation rate (Oligomerization in direct emulsion/oligomerization in the reverse emulsion)
Yield – Bromine number	-0.94/-0.93
Yield – Color	0.40/0.28
Yield – Molecular Weight	-0.03/0.10
Yield – Softening temperature	-0.19/0.32
Bromine number – Color	-0.44/-0.43
Bromine number – Softening temperature	0.20/-0.27
Bromine number – Molecular weight	0.06/0.01
Color – Softening temperature	-0.46/-0.09
Color – Molecular weight	-0.30/-0.55
Softening temperature – Molecular weight	0.54/0.73

At the oligomerization in reverse emulsion, the highest correlation values to the yield are demonstrated by reaction duration (0.81), volumetric phase ratio, and agitation intensity (0.51).

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

The data reported in this paper complement and generalize experimental studies into the dispersion oligomerization of hydrocarbon fractions, specifically, from works [10, 11, 14].

The results from the statistical treatment of our findings from the experimental study into the oligomerization in direct and reverse emulsion indicate the similarity of the basic properties of products (Table 1). Values of the root mean square deviations that indicate the similarity extent are close in both considered oligomerization options. However, on average, individual molecular weight values (67.25) are slightly more significantly deviated from their mean value compared to the reverse emulsion (24.73) for oligomerization in a direct emulsion. The oscillation factor indicates similar relative fluctuations in yield limits, bromine number, and softening temperature to the mean value. In the case of oligomerization in a direct emulsion, a higher deviation value for the coloration of the molecular weight is observed. This is also evidenced by the spread of variation.

The correlation of the yield and characteristics of oligomers, obtained in direct and reverse emulsions do not differ significantly (Table 4). The highest correlation value is for the yield and bromine number -0.94 and -0.93, respectively. This confirms the reaction of the oligomerization of monomers by unsaturated bonds and does not depend on the type of emulsion [16].

When determining the effectiveness of the effect of the duration of oligomerization in direct and reverse emulsions, as it follows from the obtained results (Tables 2, 3), it is nat-

ural to observe an increase in the yield of hydrocarbon resin depending on the prolongation of reaction time, that is, the yield has a clearly defined correlation only with the duration of the reaction (0.88). This is due to the steady rate of emulsion polymerization reaction throughout the process until the initiator is completely exhausted [20]. However, at the same time, prolonging the reaction duration negatively affects the color of hydrocarbon resins, causing them to darken.

There is no effect of other reaction conditions on the yield of the product. The absence of a correlation of the concentration of the emulsifier with the yield of the oligomer is explained by the fact that our study was carried out using emulsifiers in quantities exceeding the critical concentration of micelles (CCM) [10, 16].

Fisher's calculated criteria for the proposed multiple linear regressions (1), (2) are 179.463 and 95.593, respectively. The values of the criterion are approximate; those greater than 100 indicate the high adequacy of the proposed model [15].

The coloration of hydrocarbon resins under the considered reaction conditions most depends on the duration of oligomerization (0.58 and 0.54) and increases with the extension of reaction time. The softening temperature in the case of oligomerization in a direct emulsion has a slightly pronounced relationship with the oligomerization temperature (0.54); for the reverse emulsion, such a relationship is absent.

Table 4 demonstrates that the coloration, softening temperature, and molecular weight have low correlation bonds with the yield of the oligomer (0.19–0.40 modulo). This is true for oligomerization in direct and reverse emulsions. In the case of oligomerization in reverse emulsion, the correlation of the mean molecular weight of oligomers with the temperature of their softening (0.73) and coloration (0.55) is higher.

However, unlike the results of studies reported in [10, 11, 14], our data on the statistical analysis of the effect of conditions of emulsion oligomerization of C₉ fraction on the yield and physicochemical properties of hydrocarbon resins allow us to assert the following:

– when using emulsifiers in quantities exceeding CCM, their concentration does not affect the course of the process and the yield of hydrocarbon resin;

– in the studied temperature range (303–353 K), the yield of hydrocarbon resins does not depend on the temperature, which allows the process to be carried out at a temperature of 303 K;

– increasing the intensity of agitation from $Re=6,870$ to $Re=10,120$ does not affect the course of oligomerization in a direct emulsion;

– the volumetric ratio fraction C₉:water does not affect the yield and physicochemical properties of hydrocarbon resin during oligomerization in a direct emulsion. This means the possibility of selecting the amount of C₉ fraction in the reaction mixture depending on the technological characteristics of the reactor (ensuring a stationary thermal regime).

The comparison of the physical-chemical characteristics of hydrocarbon resins indicates their certain relationship (Table 4). This is consistent with the data given in works [4, 10, 11]. The results obtained make it easier to select the optimal conditions for emulsion oligomerization, taking into consideration the high yield and predicted physicochemical characteristics.

According to their characteristics, the manufactured oligomers meet the requirements set by TU U 6-05743160.020-99 for synthetic petroleum polymer paint and varnish resin.

The above results take into consideration the correlation of oligomerization conditions, the yield and characteristics of oligomers but do not directly indicate the nature of the impact. In the future, the results of our study could be used in predicting the properties of resins based on petrochemical raw materials of various hydrocarbon compositions.

7. Conclusions

1. Our study has confirmed the possibility of obtaining hydrocarbon resins by low-temperature emulsion oligomerization of C₉ fraction using emulsifiers of the first and second kind.

2. It was established that in the examined intervals of variables, the yield of hydrocarbon resin during oligomerization in a direct emulsion depends on the duration of the reaction. The main factors influencing the yield of hydrocarbon resin during oligomerization in the reverse emulsion are the duration of oligomerization, the intensity of agitation, and the ratio of fraction C₉:water. The derived equations of multiple linear regression make it possible to predict the yield depending on the determinative parameters of the reaction. The absence of correlation relations between the coloration, softening temperature, and mean molecular weight and the yield of hydrocarbon resins was established. The high correlation values for the yield and bromine number of hydrocarbon resins confirm the progress of the oligomerization reaction. The correlation between the color and bromine number and the molecular weight and the softening temperature has been confirmed. This indicates the possibility of directed adjustment of certain characteristics of hydrocarbon resins.

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