This study investigates the radical oligomerization of the C9 fraction of liquid by-products from diesel fuel pyrolysis. The task addressed is to establish patterns of influence of the radical oligomerization technique on the properties of C9 hydrocarbon resins.

The effect of radical oligomerization technique on the physicochemical, molecular weight, rheological, and structural characteristics of resins obtained by high-temperature (thermal, initiated) and low-temperature (emulsion, suspension) methods has been studied. It was established that high-temperature methods provide higher yields of resins (15–32%), lower average molecular weight (455–670 g/mol), and a wider molecular weight distribution (1.20–1.25). Low-temperature dispersion processes are characterized by lower yields (4–29.3%), higher molecular weight (550–750 g/mol) and narrower distribution (1.02–1.06). Emulsion and suspension methods provide lighter resins (10–40 mg I2/100 ml) compared to high-temperature analogs (40–80 mg I2/100 ml).

The results and structural differences recorded by IR spectroscopy are attributed to the temperature regime of synthesis. High-temperature resins are characterized by a higher content of condensed cyclic structures. This is explained by the intensification of side chain transfer reactions at high temperatures.

Special features of the results are determining the complex relationship between the oligomerization technique and the characteristics of the resins. This allows for a purposeful selection of synthesis conditions for specific product requirements.

The scope of practical implementation of the results includes the chemical and paint industries; as well as the possibility of directed regulation of the properties of C9 resins for their use in adhesives, sealants, and film formers

Keywords: hydrocarbon resin, C9 fraction, radical oligomerization, styrene, cyclopentadiene, polydispersity, rheology

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ESTABLISHING THE RELATIONSHIPS BETWEEN C9 HYDROCARBON RESIN PROPERTIES AND RADICAL OLIGOMERIZATION TECHNIQUE

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1. Introduction

Petroleum polymer, or hydrocarbon, resins are low-molecular thermoplastic oligomerization products of unsaturated hydrocarbons contained in liquid by-products of pyrolysis of petroleum raw materials [1]. One of the main methods for the production of ethylene and propylene is the pyrolysis of petroleum fractions. About 30–35% of liquid pyrolysis products (LPPs) are formed during pyrolysis. In particular, the C9 fraction is isolated from LPP, which contains vinyl aromatic and condensed unsaturated compounds and is used as a raw material for the synthesis of aromatic hydrocarbon resins [2, 3].

By chemical nature, resins are divided mainly into aliphatic C5, aromatic C9, and hydrogenated C5/C9 resins. ^{13}C PMR and IR spectroscopy methods have shown that aromatic C9 hydrocarbon resins have a complex structure. They contain aromatic, aliphatic, and cyclic fragments. Resins are characterized by styrene, indene, vinyl toluene, and cyclopentadiene structural units [4].

Hydrocarbon resins are widely used as film formers and modifiers of paints and varnishes, as well as components of anticorrosive coatings, adhesives, sealants, rubber mixtures, bitumen, and polymer compositions [2, 3]. Their structure significantly affects the rheological, adhesive, and mechanical properties of such systems [5, 6]. The practical value of resins is determined by their physicochemical properties: molecular weight, bromine number, softening temperature, color, solubility and compatibility with polymer and bitumen systems. The properties of resins significantly depend on the technique of production and oligomerization conditions.

Catalytic and radical oligomerization are used to obtain hydrocarbon resins. High-temperature (453–493 K) radical methods include thermal and initiated oligomerization [2, 3]. Low-temperature (303–353 K) processes in dispersed systems, in particular suspension and emulsion oligomerization, are also being investigated [7, 8].Oligomerization conditions significantly affect the ratio of aromatic and aliphatic fragments in the resin structure, as well as their yield, color, and temperature characteristics. Differential scanning calorimetry, IR, and PMR spectroscopy are used to analyze the structure of hydrocarbon resins [1, 9].

High-temperature processes provide increased resin yields. However, they are accompanied by the formation of more condensed and structurally inhomogeneous products, deterioration of color, and limited control over molecular weight distribution. Increasing the oligomerization temperature intensifies chain transfer reactions and contributes to a decrease in the average molecular weight of resins [3, 9].

Low-temperature emulsion and suspension oligomerization contributes to the formation of resins with a lower color index with a relatively narrow molecular weight distribution, low polydispersity, and a lower content of high-molecular fractions [10, 11]. However, low-temperature oligomerization is characterized by lower product yields, which is associated with the practical non-participation of dicyclopentadiene in radical processes at temperatures of 303–353 K [12].

It is relevant to establish the relationship between the technique of preparation, structure, and properties of C9 hydrocarbon resins. Comparative analysis of resins obtained by different methods of radical oligomerization allows us to assess the influence of synthesis conditions on their physicochemical properties, molecular weight, as well as rheological characteristics.

2. Literature review and problem statement

Fraction C9 is a by-product of the pyrolysis of petroleum raw materials and contains unsaturated aromatic and cyclic hydrocarbons, in particular styrene, vinyl toluene, indene, dicyclopentadiene, and their derivatives. The composition of the fraction determines the reactivity of the system and the properties of the obtained hydrocarbon resins. The complexity of predicting the properties of resins is associated with the complex multicomponent composition of fraction C9 [6]. The cited study lacks a systematic comparison of the physicochemical properties of resins obtained under significantly different temperature conditions.

Styrene and its derivatives form aromatic oligomers with a lower color index and a relatively narrow molecular weight distribution. Cyclopentadiene units contribute to the formation of more condensed structures with increased molecular weight and softening temperature [3]. The regularities of oligomer formation were considered without taking into account temperature factors. That does not make it possible to assess the influence of the process temperature on color change and softening temperature of hydrocarbon resins C9.

In [9] it is shown that the method of oligomerization of the C9 fraction determines the physicochemical characteristics of resins, in particular the molecular weight, color, and softening temperature. It was established that the main structural fragments of resins are styrene and cyclopentadiene co-oligomers. However, the work did not investigate the molecular weight distribution and rheological properties of resins, and low-temperature dispersion synthesis methods were not considered.

In [13], the molecular dynamics method was used to investigate the compatibility of C5- and C9-resins with elastomers. It was shown that compatibility is determined by the chemical nature of the structural fragments of resins and the rubber matrix. The solubility parameters, binding energy, diffusion coefficients, and intermolecular interaction energy were used to assess the interaction. It was established that aromatic styrene fragments provide a stronger interaction of resins with rubbers compared to aliphatic structures. However, the work did not consider the influence of the technique for obtaining resins on the formation of their structure and physicochemical properties.

In [14], the thermal behavior of C9 hydrocarbon resins and their hydrogenated analogs was studied using thermogravimetric analysis, IR spectroscopy, and quantum-chemical modeling. It was found that the thermal decomposition of resins occurs due to the primary destruction of aliphatic fragments with subsequent destruction of aromatic structures. The results confirm the significant influence of the structural organization of resins on their properties. However, the work did not consider the influence of oligomerization technique on the formation of resin structure and the features of their thermal destruction.

The rheological behavior of resins is determined not only by the average molecular weight but also by the width of the molecular weight distribution and the structural heterogeneity of the products [15, 16]. In particular, the influence of C9 resins on the rheological, microstructural, and chemical properties of styrene-butadiene-styrene modified bitumen was studied in [17]. Rheological, spectroscopic, microscopic, and molecular modeling methods were used to study the properties of the compositions. It was found that the introduction of C9 resins improves high-temperature rheological characteristics, increases storage stability, and promotes the formation of a more homogeneous bitumen microstructure due to the compatibility of the aromatic structure of the resin with the bitumen components and the styrene-butadiene-styrene modifier. However, the study was carried out only for commercial resin obtained by catalytic oligomerization of the C9 fraction, without comparing its properties with resins synthesized by radical oligomerization methods.

In earlier papers [11, 15], the molecular weight distribution and rheological properties of C9 hydrocarbon resins obtained by various oligomerization methods were investigated. It was shown that low-temperature processes provide the formation of resins with a narrow molecular weight distribution and low polydispersity (Mw/Mn = 1.01–1.13). The temperature regime and phase composition of the reaction system determine the degree of homogeneity of the resins and the nature of their molecular weight distribution. It was established that resin solutions exhibit pseudoplastic behavior, and their viscosity significantly depends on the temperature and the method of synthesis. Molecular weight and rheological characteristics were considered separately, without a comprehensive analysis of their relationship with the main physicochemical properties of the resins.

The oligomerization technique determines the structure, molecular weight characteristics, and operational properties of C9 hydrocarbon resins. High-temperature and low-temperature processes differ in the mechanism of the reaction, the degree of transformation of the components of the C9 fraction, and the nature of the resulting oligomeric structures. In the literature [3, 6, 9, 13–15], comprehensive comparative studies of the physicochemical, molecular weight, structural and rheological properties of resins obtained by different methods are not detailed. That makes it advisable to conduct a systematic study on the relationship between the synthesis technique and the properties of C9 hydrocarbon resins.

3. The aim and objectives of the study

The aim of our study is to determine the influence of the radical oligomerization technique on the properties of C9 hydrocarbon resins. This will allow for targeted regulation of resin characteristics depending on product requirements.

To achieve this goal, the following tasks were set:

– to determine the physicochemical characteristics of C9 hydrocarbon resins under the influence of different oligomerization techniques;

– to establish the features of the molecular weight distribution and rheological properties of resins obtained by different methods.

4. The study materials and methods

4. 1. The object and hypothesis of the study

The object of our study is the radical oligomerization of the C9 fraction of liquid by-products from diesel fuel pyrolysis. The density of the fraction was 903–936 kg/m^3, the bromine number was 86–102 g Br$_2$/100 g. The fraction contained both hydrocarbons incapable of oligomerization (indane, toluene, trimethylbenzenes, etc.) and reactive unsaturated components, in particular styrene (16.5–17.9%), dicyclopentadiene (13.6–18.0%), vinyl toluene (5.2–7.0%), α-methyl styrene (0.3–2.0%), allylbenzene (0.7–1.8%) and methylidenes (0.6–1.3%). The total content of reactive unsaturated components in the C9 fraction was about 45–50% by weight.

The hypothesis of the study assumed that the technique of radical oligomerization of the C9 fraction significantly affects the physicochemical, molecular weight, structural and rheological properties of the obtained hydrocarbon resins.

It was assumed that the differences in the properties of the resins are determined mainly by the technique of oligomerization as the C9 fraction of the same origin and similar hydrocarbon composition was used for the synthesis.

During the molecular weight and rheological studies, it was assumed that representative samples of resins with average values of physicochemical parameters are characteristic of resins obtained by the corresponding oligomerization technique.

4. 2. Materials and equipment used in the experiment

Oligomerization in solution was carried out in 100 ml metal thermostated ampoules. Fraction C9 (50 ml) was mixed with the calculated amount of initiator, loaded into ampoules, pre-purged with argon, after which the ampoules were sealed and kept at a given temperature. Unreacted hydrocarbons were removed by atmospheric distillation at 423 K, and high-boiling components and liquid oligomers were removed by vacuum distillation at 453 K and a pressure of 3 kPa. A hydrocarbon resin with a softening point of 347–360 K was obtained in the bottom residue.

Suspension oligomerization was carried out in a three-necked flask equipped with a mechanical stirrer. The reaction mixture was intensively stirred and heated to a given temperature. After completion of the process, the system was separated into aqueous and organic phases. The organic layer was centrifuged at 3000 rpm to isolate the product, which was dried at 323 K to constant weight. Unreacted hydrocarbons were removed by atmospheric and vacuum distillation. The obtained resin fractions were combined, and the total product yield was determined.

Emulsion oligomerization of fraction C9 was carried out in a three-necked flask equipped with a stirrer and a reflux condenser. Fraction C9, an aqueous solution of the initiator and emulsifier were charged into the reactor, after which the mixture was intensively stirred and heated to a given temperature. After the reaction was completed, the emulsion system was separated by centrifugation at 3000 rpm for 7 min. The product was dried at 323 K to a constant mass.

The mixing of the reaction mixtures during suspension and emulsion oligomerization was carried out using an overhead mixer "IKA" RW 20 (Germany). The laboratory centrifuge "Elvit" TsNL-6 (Ukraine) was used to isolate the hydrocarbon resin. The basic conditions for obtaining hydrocarbon resins by various techniques of radical oligomerization are given in Table 1.

Table 1

Basic conditions for obtaining C9 hydrocarbon resins

Oligomerization technique	Reaction mixture composition	Temperature, K	Time, min	Re
Thermal	fraction C9	453–493	240–480	–
Initiated	fraction C9, peroxide initiator	433–493	240–480	–
Suspension	fraction C9, water, initiator, stabilizer	313–353	30–240	2290–13450
Emulsion	fraction C9, water, initiator, emulsifier	303–353	30–240	2290–13450
Post-oligomerization	residual fraction C9	453–473	360	–

The following initiators were used for the initiated and suspension oligomerization: benzoyl peroxide, isopropyl benzene hydroperoxide, di-*tert*-butyl peroxide, N-*tert*-butylperoxymethylene-N, N-dimethylamine.

Suspension oligomerization was carried out at the volume ratios [fraction C9]:[water] = [1]:[1] – [1]:[3]. Polyvinyl alcohol, starch, bentonite clay, polyethylene glycols with molecular weights of 1500, 4000, and 6000 were used as suspension stabilizers.

Emulsion oligomerization was carried out at the volume ratios [fraction C9]:[water] = [1]:[1] – [1]:[4]. Sodium stearate, E-30 (a mixture of linear alkanesulfonates of the general formula R–SO$_3$Na with a carbon chain length of C15), and OP-10 (nonionic oxyethylated alkylphenol) were used as type 1 emulsifiers. Hydrogen peroxide and potassium persulfate were used as water-soluble initiators.

4. 3. Methodology for determining the properties of samples

The yield of hydrocarbon resins was determined by the mass of the obtained solid product in terms of the C9 fraction.

The unsaturation of the resins was characterized by the bromine number, which was determined by the bromide-bromate method according to ISO 3839:1996.

The softening point was determined by the "ring and ball" method according to ISO 4625-1:2020.

The color of the resins was determined by the iodometric scale by comparing a 10% resin solution in benzene with reference solutions.

The average molecular weight was determined by the cryoscopic method according to ISO 5764:2009, comparing the freezing point of benzene and a 10% resin solution in benzene.

The structure of the resins was studied by IR spectroscopy. The samples were prepared as thin films from chloroform solutions. The spectra were recorded on the Specord M-80 spectrophotometer in the range of 3800–600 cm^{-1} at 291 K.

The molecular weight distribution was determined by fractional precipitation. Resin solutions in benzene were fractionated by stepwise addition of ethanol as a precipitant at 293–298 K [18]. The precipitated fractions were separated, dried to constant mass; their molecular weight was determined by cryoscopic method. Based on the obtained data, the number average (Mn), weight average (Mw), and z-average (Mz) molecular weights, polydispersity index (Mw/Mn), as well as effective fraction number were calculated [19].

The rheological properties were investigated for 10% resin solutions in benzene by capillary viscometry using an Ostwald viscometer with a capillary diameter of 0.56 mm. Measurements were performed in the temperature range of 293–343 K with a step of 10 K. The leakage time was determined at least three times at each temperature, after which the average value was calculated.

5. Results of investigating the properties of C9 hydrocarbon resins

5. 1. Physicochemical and structural characteristics of resins

According to the results of experimental studies in the ranges of parameters given in Table 1, the yield (Fig. 1), average molecular weight (Fig. 2), and physicochemical characteristics (Table 2) of C9 hydrocarbon resins obtained by various oligomerization techniques were determined.

Table 2 gives the bromine number, softening point, and color index of hydrocarbon resins obtained by various oligomerization methods.

Resins obtained by dispersion methods are characterized by higher bromine number values and lower color indices. The softening point of resins, regardless of the preparation technique, varies in a narrow range of 345–360 K.

Fig. 3 shows typical IR spectra of styrene-cyclopentadiene resin obtained by high-temperature initiated oligomerization and resin of low-temperature emulsion oligomerization with a predominant content of styrene units.

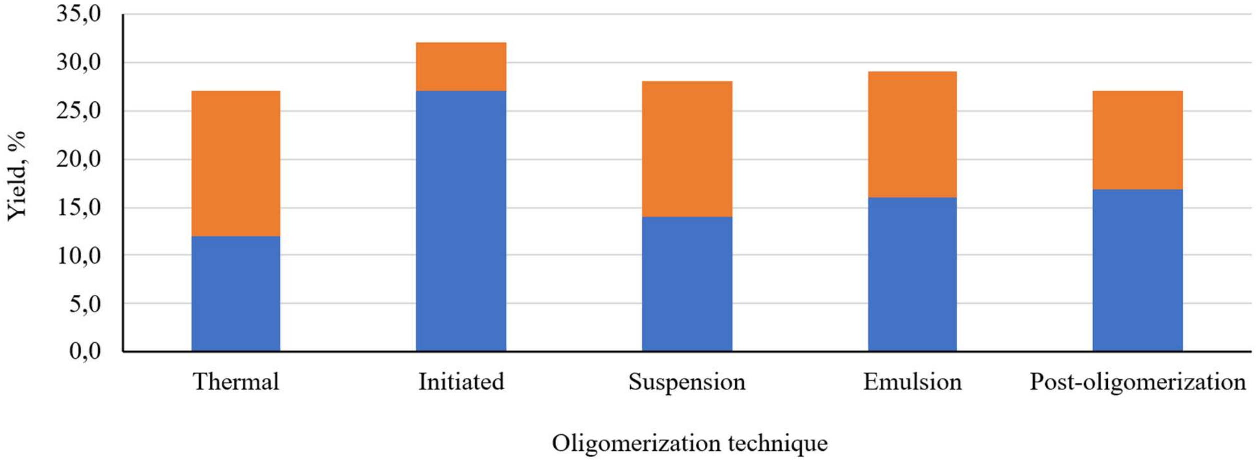

Fig. 1. Yield ranges of C9 hydrocarbon resins obtained by different oligomerization methods

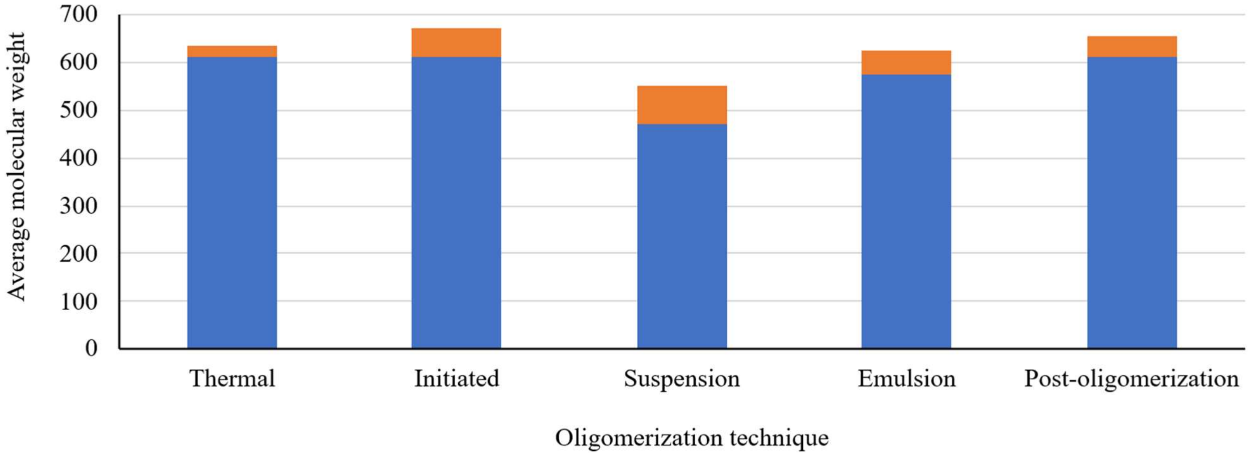

Fig. 2. Average molecular weight ranges of C9 hydrocarbon resins obtained by different oligomerization methods

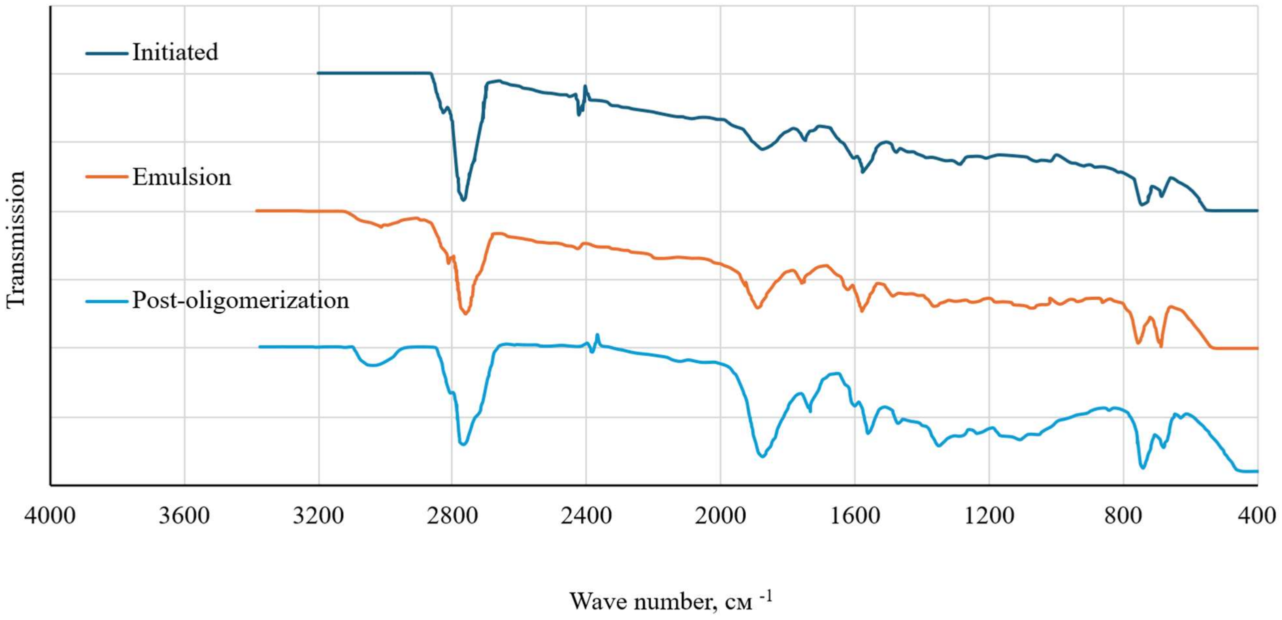

Fig. 3. IR spectra of representative C9 hydrocarbon resins obtained by various methods of radical oligomerization (spectra shifted along the ordinate axis)

Table 2

Physical-chemical characteristics of C9 hydrocarbon resins

Oligomerization technique	Bromine number, g Br_2/100 g	Softening point, K	Color, mg I_2/100 ml
Thermal	10.8–25.0	346–353	40–80
Initiated	17.1–27.3	350–358	40–60
Suspension	29.8–38.4	345–359	20–40
Emulsion	30.3–37.8	348–360	20–30
Post-oligomerization	10.8–22.6	353–354	80–100

The structural differences found affect the molecular weight distribution and, as a consequence, the rheological properties of the resins.

5. 2. Molecular weight and rheological characteristics of resins

To analyze the molecular weight distribution (MWD) of the resins, the fractional precipitation method with the separation of three fractions was used. Cumulative curves of typical samples of C9 resins, representing different techniques of radical oligomerization, are shown in Fig. 4.

Low-temperature dispersion oligomerization resins are characterized by narrower molecular weight distribution, while high-temperature methods are accompanied by the formation of high-molecular-weight fractions. The MWD parameters of the resins are given in Table 3.

The values of *Mw*/*Mn* for the investigated resins vary from 1.02 to 1.25. The lowest polydispersity values are typical for emulsion and suspension resins. Cyclopentadiene resin obtained by oligomerization has the lowest effective number of fractions (1.62).

The rheological properties of C9 resins are shown in Fig. 5, Table 4.

Table 3

Molecular weight distribution parameters of C9 resins obtained by different methods

Oligomerization technique	*Mw*	*Mz*	*Mn*	Polydispersity *Mw*/*Mn*	Effective number of fractions
Thermal	556	675	446	1.25	2.96
Initiated	670	794	567	1.20	2.91
Suspension	601	615	585	1.03	2.24
Emulsion	629	648	638	1.02	2.14
Post-oligomerization	630	638	573	1.06	1.62

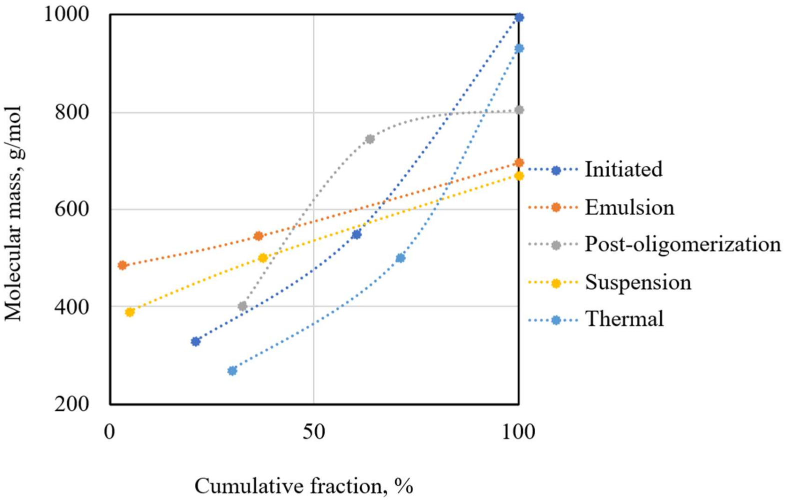

Fig. 4. Cumulative curves of molecular mass distribution of resins obtained by various oligomerization techniques

The temperature dependences of the dynamic viscosity of resin solutions are approximated by second-order polynomials. The values of the coefficients of determination are $R^2 = 0.97–0.99$.

For all the studied systems, a decrease in dynamic viscosity is observed with increasing temperature.

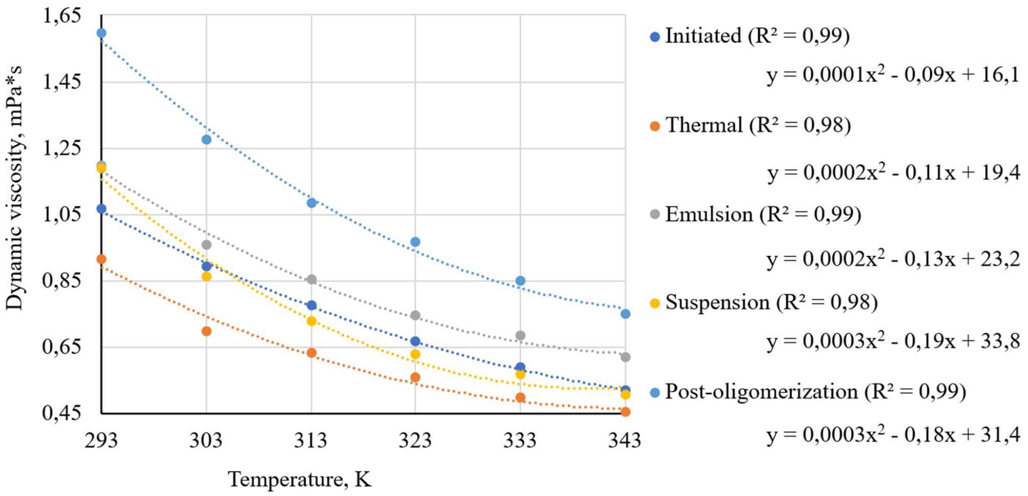

Fig. 5. Temperature dependences of the dynamic viscosity of resin solutions obtained by different oligomerization techniques

Table 4

Rheological characteristics of 10% resin solutions

Oligomerization technique	Temperature coefficient (dη/dT), mPa·s/K	Consistency factor (K), Pa·s^n
Thermal	–0.009	4.0
Initiated	–0.011	3.0
Suspension	–0.014	4.0
Emulsion	–0.017	3.8
Post-oligomerization	–0.017	4.5

The viscosity of 10% resin solutions decreases with increasing temperature, which is typical for oligomeric systems in organic solvents. For the studied solutions, a dependence of viscosity on flow conditions is observed, typical for non-Newtonian systems.

6. Discussion of results based on investigating the influence of oligomerization technique on the properties of C9 hydrocarbon resins

The radical oligomerization technique significantly affects the yield (Fig. 1) and physicochemical characteristics of C9 hydrocarbon resins (Table 2). High-temperature methods provide higher yields of resins (15–32%) compared to low-temperature dispersion methods (4–29%). This is explained by the higher initiation rate. The products of high-temperature methods are characterized by lower values of the average molecular weight (Fig. 2). This is due to the intensification of chain transfer reactions. High-temperature methods provide lower values of the bromine number and increased color indices (40–100 mg $\mathbf{I}_2$/100 ml). Low-temperature dispersion methods are characterized by higher values of the bromine number and the production of lighter resins with a color index of 20–40 mg $\mathbf{I}_2$/100 ml. The softening temperature of resins, regardless of the production technique, varies in a relatively narrow range of 345–360 K (Table 2). These patterns are consistent with the literature data [1, 3, 9], which indicate a similar effect of temperature on the molecular weight and color of resins. However, unlike cationic polymerization [1, 9], the radical processes studied in this work are characterized by a wider molecular weight distribution and higher bromine number values. This is due to the incomplete conversion of unsaturated components of the C9 fraction, in particular dicyclopentadiene [20].

Comparative analysis of IR spectra of hydrocarbon resins C9 obtained by high-temperature, emulsion oligomerization, and post-oligomerization of unreacted fraction residues (Fig. 3) reveals the influence of oligomerization technique on the structure of resins. All samples are characterized by stretching vibration bands of aromatic and aliphatic C–H bonds in the range of 3095–2845 cm^{-1}. This confirms the presence of aromatic-aliphatic fragments in the composition of the resins. The spectral data obtained are consistent with the results of investigating the structure of resins [1, 4, 9].

The resin obtained by initiated oligomerization is characterized by more intense bands in the region of 2916–2845 cm^{-1}. These bands correspond to stretching vibrations of $-CH_2$ and $-CH_3$ groups and indicate an increased contribution of aliphatic fragments. In the spectrum of the resin obtained by emulsion oligomerization, the bands of aromatic structures in the ranges of 1600–1500 and 756–680 cm^{-1} are more pronounced. This indicates the predominance of styrene-vinyl toluene fragments.

The spectrum of the post-oligomerization product is characterized by increased intensity of the bands in the ranges of 1600–1500 and 1175–1000 cm^{-1}. This may be due to the formation of more substituted aromatic and alicyclic structures with the participation of cyclopentadiene components.

High-temperature oligomerization promotes the formation of aromatic-aliphatic structures. Post-oligomerization leads to the formation of products with a higher content of cyclic and cyclosubstituted structural units. Emulsion oligomerization provides the production of resins with a higher proportion of styrene-containing aromatic fragments.

The nature of the molecular weight distribution significantly depends on the method of resin production (Fig. 4, Table 3). This is due to the difference in the mechanisms of initiation and growth of the oligomeric chain. Low-temperature dispersion systems are characterized by relatively narrow molecular weight distributions and the absence of pronounced high-molecular fractions. Emulsion resins are characterized by the most homogeneous distribution (Mw/Mn = 1.02), which is explained by the course of oligomerization in a microheterogeneous environment and the localization of chain growth in dispersed particles. This effect distinguishes the emulsion method from the classical thermal polymerization techniques described in [12, 18]. Suspension resins occupy an intermediate position between emulsion and high-temperature systems.

Thermally and high-temperature initiated resins are characterized by the widest molecular weight distributions and the formation of high-molecular fractions. This is due to the course of parallel oligomerization and condensation reactions, as well as the participation of cyclopentadiene structures formed as a result of the Diels-Alder retro-reaction at 453–473 K [21].

Unlike cationic polymerization resins [1, 9], resins obtained by post-oligomerization are characterized by a shift in the molecular weight distribution to the region of higher molecular weights. This is due to the participation of cyclopentadiene as a reactive component.

Analysis of rheological characteristics (Fig. 5, Table 4) reveals that the viscosity of solutions of hydrocarbon resins C9 is determined not only by the average molecular weight but also by the width of the molecular weight distribution and structural features of the resins. This is explained by the change in the hydrodynamic volume of macromolecules. The presence of condensed structures and a wide MWD changes the resistance of macromolecules to the flow of the solvent and affects dynamic viscosity. The highest values of dynamic viscosity at 293 K are characteristic of emulsion and cyclopentadiene resins and are 1.20 and 1.60 mPa·s, respectively. For emulsion resins, this may be due to the combination of a relatively high molecular weight and a narrow MWD, while for cyclopentadiene resins, it may be due to the increased content of cyclic and condensed structures. These results correspond to theoretical provisions [22] but demonstrate a more pronounced dependence of viscosity on the structure of oligomers.

For the resin obtained by high-temperature initiated oligomerization, the dynamic viscosity at 293 K is 1.07 mPa·s (Fig. 5). The features of rheological behavior are determined by a wide molecular weight distribution and the presence of high-molecular fractions. For the resin obtained by thermal oligomerization, the dynamic viscosity at 293 K is 0.92 mPa·s (Fig. 5). Lower viscosity values may be associated with an increased content of low-molecular fractions in the resin composition. With an increase in temperature to 343 K, the viscosity of all studied solutions decreases to 0.45–0.75 mPa·s. The highest values of the temperature coefficient are characteristic of emulsion and cyclopentadiene resins (–0.017 mPa·s/K), while for thermal resins this indicator is –0.009 mPa·s/K (Table 4). This indicates a higher sensitivity of structurally more homogeneous resins to temperature changes.

The limitations of our study are as follows. The results were obtained only for the C9 fractions of liquid diesel pyrolysis products. The use of gasoline pyrolysis fractions may change the properties of resins due to a different hydrocarbon composition. Low-temperature dispersion processes are effective only in the range of 303–353 K. Rheological regularities were established for 10% resin solutions in benzene in the range of 293–343 K.

The shortcomings of the study are as follows: assessment of the structure of resins according to IR spectroscopy data does not provide comprehensive information about the structure of oligomers. The work did not investigate the thermal-oxidative stability, operational properties of resins, and the influence of process scaling. In further studies, it is planned to use NMR spectroscopy, thermogravimetric analysis, and testing of resins as part of protective coatings.

Further development of this study is associated with establishing the relationship between the composition of hydrocarbon fractions and operational properties of resins, as well as mathematical modeling of the process. The main difficulties in modeling are the nonlinearity of the influence of factors and the complexity of the mathematical description of radical processes for multicomponent hydrocarbon mixtures.

7. Conclusions

1. We have established that regardless of the synthesis technique, the softening temperature of resins is in the range of 345–360 K. High-temperature processes provide increased yields of resins (15–32%) with a color index of 40–80 mg I_2/100 ml. Low-temperature methods make it possible to obtain lighter resins (10–40 mg I_2/100 ml) with a yield of 4–29.3%. A feature of our results is the systematic comparative data for resins synthesized from the same raw material. It is proven that the decrease in yield at low temperatures is explained by the low reactivity of dicyclopentadiene. The improvement of the color of resins is achieved due to the low content of cyclopentadiene structures and the suppression of oxidation reactions at low temperatures.

2. The regularities in the formation of molecular weight distribution and rheological properties of resin solutions have been determined. Low-temperature dispersion methods provide a narrower molecular weight distribution with a polydispersity of 1.02–1.06 and a lower effective number of fractions (2.14–2.24). The molecular weight of the products is higher and is 550–750 g/mol. High-temperature analogs have a lower molecular weight (455–670 g/mol), a wider molecular weight distribution (1.20–1.25), and a higher effective number of fractions (2.91–2.96). The pseudoplastic nature of the flow of solutions has been established, the viscosity of which decreases with increasing temperature in the range of 293–343 K. A feature of our results is the established relationship between the molecular weight distribution and rheology of resins obtained by various techniques of radical oligomerization. The increase in the value of polydispersity and the effective number of fractions in resins obtained by high-temperature methods is explained by the intensification of chain transfer reactions. The increase in the content of cyclic structures is explained by the high reactivity of cyclopentadiene at high temperatures.

Conflicts of interest

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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Data availability

The data will be provided upon reasonable request.

Use of artificial intelligence

The authors confirm the use of OpenAI ChatGPT artificial intelligence technologies (GPT-5.5 model) exclusively for language editing of text and searching for literary sources by keywords. AI tools were not used to obtain, analyze, or interpret experimental data. All scientific results, their analysis, and conclusions were performed by the authors and independently verified by them. The use of AI did not affect the results of the study.

Authors' contributions

Roman Subtelnyy: Conceptualization, Methodology, Investigation, Formal analysis, Writing – review & editing, Visualization, Project administration; **Olha Fedotova:** Investigation, Writing – original draft, Visualization; **Volodymyr Romaniv:** Investigation, Writing – original draft; **Yevhenii Zhuravskyi:** Investigation, Formal analysis; **Bohdan Dzinyak:** Conceptualization, Formal analysis, Writing – review & editing, Project administration.

References

1. Rostami, M.-T., Shahverdi, H., Javanbakht, V., Chermahini, A. N., Fakhar, A. (2026). Experimental petroleum resin production and optimization using response surface modeling. Scientific Reports, 16 (1). https://doi.org/10.1038/s41598-026-36409-1
2. Mildenberg, R., Zander, M., Collin, G. (1997). Hydrocarbon Resins. Wiley. https://doi.org/10.1002/9783527614653
3. 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. https://doi.org/10.1021/acs.oprd.0c00474
4. Liang, T., Lin, X.-H., Zou, Y.-R., Zhan, Z.-W., Peng, P. (2023). Elucidating the chemical structures of petroleum resin using solid-state 13C NMR. Chemical Geology, 630, 121492. https://doi.org/10.1016/j.chemgeo.2023.121492
5. Liang, J., Chang, S., Feng, N. (2013). Effect of C5 petroleum resin content on damping behavior, morphology, and mechanical properties of BIIR/BR vulcanizates. Journal of Applied Polymer Science, 130 (1), 510–515. https://doi.org/10.1002/app.39202
6. Zohuriaan-Mehr, M. J., Omidian, H. (2000). Petroleum Resins: An Overview. Journal of Macromolecular Science, Part C: Polymer Reviews, 40 (1), 23–49. https://doi.org/10.1081/mc-100100577
7. Subtelnyy, R., Zhuravskyi, Y., Dzinyak, B. (2023). Preparation of hydrocarbon resins by suspension oligomerisation of the C9 fraction of gasoline pyrolysis initiated by amino peroxides. Eastern-European Journal of Enterprise Technologies, 6 (6 (126)), 23–30. https://doi.org/10.15587/1729-4061.2023.292527
8. Orobchuk, O., Subtelnyy, R., Dzinyak, B. (2014). Studying the effect of initiator dosing on the process of hydrocarbon fraction suspension co-oligomerization. Eastern-European Journal of Enterprise Technologies, 4 (6 (70)), 14–18. https://doi.org/10.15587/1729-4061.2014.26236
9. Mokryi, Ye., Dziniak, B., Nykulyshyn, I., Budzan, B., Salim Khair Salem (1997). Porivnialna otsinka metodiv oderzhannia naftopolimernykh smol. Dopovidi NAN Ukrainy, 5, 153–156.
10. 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. https://doi.org/10.15587/1729-4061.2021.232684
11. Subtelnyy, R. O., Fedotova, O. B., Dzinyak, B. O. (2026). Molecular-weight distribution of C9 hydrocarbon resins. Voprosy Khimii I Khimicheskoi Tekhnologii, 2, 59–67. https://doi.org/10.32434/0321-4095-2026-165-2-59-67
12. Xiong, Z., Mi, Z., Zhang, X. (2005). Study on the oligomerization of cyclopentadiene and dicyclopentadiene to tricyclopentadiene through diels-alder reaction. Reaction Kinetics and Catalysis Letters, 85 (1), 89–97. https://doi.org/10.1007/s11144-005-0247-9
13. Guo, Y., Liu, J., Lu, Y., Dong, D., Wang, W., Zhang, L. (2018). A combined molecular dynamics simulation and experimental method to study the compatibility between elastomers and resins. RSC Advances, 8 (26), 14401–14413. https://doi.org/10.1039/c8ra00572a
14. Zhou, D., Chen, X., Liang, J., Wei, X., Wu, C., He, Y., Wang, L. (2022). Combustion kinetics and fuel performance of tackifying resins by TG-FTIR and DFT analysis. Fuel, 330, 125656. https://doi.org/10.1016/j.fuel.2022.125656
15. Subtelnyy, R. O., Balitskyi, I. H., Dzinyak, B. O. (2025). Rheological properties of C9 petroleum resin solutions. Voprosy Khimii I Khimicheskoi Tekhnologii, 2, 17–23. https://doi.org/10.32434/0321-4095-2025-159-2-17-23
16. Yan, C., Zhang, T., Hu, K., Gillani, S. T. A., Zhang, W. (2024). Evaluation of the Effect of C9 Petroleum Resin on Rheological Behavior, Microstructure, and Chemical Properties of Styrene–Butadiene–Styrene Modified Asphalt. Buildings, 14 (6), 1599. https://doi.org/10.3390/buildings14061599
17. Chen, Z., Wang, W., Abdukadir, A., Lei, J., Yi, J., Pei, Z. (2025). C9 Petroleum Resin and Polyethylene-Based High-Viscosity Modified Asphalt Binder Proportioning Optimization and Performance Study. Coatings, 15 (3), 343. https://doi.org/10.3390/coatings15030343
18. Lei, G. Y. (1981). Self-consistency of fractional precipitation method for determining molecular weight distribution in a polymer sample. Journal of Polymer Science: Polymer Chemistry Edition, 19 (2), 389–396. https://doi.org/10.1002/pol.1981.170190215
19. Roswell, M., Dushoff, J., Winfree, R. (2021). A conceptual guide to measuring species diversity. Oikos, 130 (3), 321–338. https://doi.org/10.1111/oik.07202
20. Uysal, D. S., Kalıpçılar, H., Karakaş, G. (2025). Kinetic Analysis and Simulation of Dicyclopentadiene/Cyclopentadiene Production by Using Reactive Batch Distillation of Pyrolysis Gasoline. Energy & Fuels, 39 (15), 7592–7604. https://doi.org/10.1021/acs.energyfuels.5c00569
21. 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. https://doi.org/10.1016/j.ces.2020.115892
22. Wutz, C., Kricheldorf, H. R. (2012). Molecular Weight Distribution of Linear Chains in Step-Growth Polymerization Under the Influence of Cyclization Reactions. Macromolecular Theory and Simulations, 21 (4), 266–271. https://doi.org/10.1002/mats.201100084