

Article

Thermolytic Synthesis of Asphaltene-like Nitrogenous Bases and Study of Their Aggregative Stability

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Abstract: The work is devoted to the study of the influence of nitrogenous bases on the composition of oil and the structure of asphaltenes on their colloidal stability in solution. Model petroleum systems with a basic nitrogen content of 1, 2, and 3% wt. were used as objects of study. Asphaltene-like nitrogenous bases were obtained by thermolysis of model petroleum systems with different nitrogen contents. The results were obtained using elemental analysis, non-aqueous potentiometric titration, spectrophotometry, ¹H NMR spectroscopy, and liquid adsorption chromatography. It was established that the content of N_{bas} in asphaltenes increases by 0.3–1.3% wt. with the increase in quinoline content in petroleum components. Quinoline is incorporated into the supramolecular structure of asphaltenes and increases their average molecular weight by 650 amu. and aromaticity by 2%. The aggregative stability of asphaltenes decreases by 1.5–6 times with an increase in their average molecular weight and an increase in N_{bas} in their composition as a component of a dispersion medium. The colloidal stability of synthetic asphaltene-like substances, on the contrary, is due to the appearance of their molecular sequence of fragments containing N_{bas} in aromatic rings.

Keywords: heavy oil; asphaltenes; quinoline; nitrogenous bases; thermolysis; composition; aggregation



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1. Introduction

Reserves of light oils are decreasing, so there is a need to intensify oil production using various methods [1–3]. This is not always effective and economically justified [4], so world hydrocarbon reserves are replenished at the expense of heavy oils, which contain large amounts of asphaltenes [5]. Asphaltenes are the most polar and high-molecular components of oil, with a high content of sulfur, nitrogen, oxygen, and metals. Asphaltenes cause problems during heavy oil production, transportation, and refining processes [6,7]. Asphaltenes are insoluble in n-alkanes, but soluble in aromatic solvents (benzene, toluene). The molecular structure of asphaltenes is very complex and diverse [8–10]. Two models of the molecular structure of asphaltenes have been accepted: “island” and “archipelago”. The “island” is one large polycyclic core framed by short alkyl substituents [11]. The “archipelago” is several polycyclic systems of 2–4 rings connected by long aliphatic chains and heteroatomic bridges [12,13]. Asphaltene molecules form supramolecular structures of various levels (dimers, nanoaggregates, clusters) depending on external thermobaric conditions, the composition of the dispersion medium, etc. [14–16]. Large asphaltene aggregates create problems during the production of heavy oils: (1) an abnormal increase in fluid viscosity; (2) changes in rock wettability; (3) blocking the pores of oil reservoirs; and (4) formation of sediment in technological equipment [17–19]. The formation of asphaltene-containing deposits is the most important unresolved problem in oil production and transportation [20–22]. To prevent complications in oil production, an accurate description of the supramolecular assembly of asphaltenes is necessary. However, the mechanism of asphaltene aggregation and sedimentation is still not well understood [23]. It is believed

that the main force behind asphaltene aggregation is stacking interactions between aromatic cores with the formation of layered stacks [24]. Van der Waals forces are also known to promote asphaltene association through aliphatic side chains [25,26]. In addition, during the supramolecular assembly of asphaltenes, acid–base interactions, hydrogen bonds, metal complexes, clathrates, etc. are possible. [27]. It is known that the formation of asphaltene aggregates in solutions occurs with the participation of aromatic fragments and sulfoxide, ether groups, pyridine, and pyrrole rings [28]. However, it is difficult to establish the role of various heteroatomic fragments in the complex processes of asphaltene aggregation. In this regard, studies of the mechanisms of asphaltene aggregation [29,30] and the stability of petroleum-dispersed systems are very relevant [31,32]. In this aspect, much attention is paid to heteroatoms (N, S, O) [33,34]. It has been shown that functional groups can significantly change the spatial structure of asphaltenes and also affect their aggregation [34–36]. However, this issue causes a lot of controversy [37]. For example, some studies have shown that asphaltene molecules with heteroatoms exhibit a higher tendency to self-associate. In this case, the nature of the heteroelement and its position in the macromolecule influence the mechanism of assembly of aggregates [38–40]. Other studies have shown that the presence of heteroatoms in the molecular structure of asphaltenes is not important in the formation of supramolecular structures [41,42]. The contradictions are partly due to the fact that research results are usually obtained using theoretical calculations by molecular dynamics and density functional theory on various experimental models. In addition, mathematical models of asphaltenes are not able to reflect the entire diversity of the asphaltene fraction and do not take into account the multicomponent composition of the oil dispersion medium. Therefore, to understand the real role of heteroatomic fragments in the processes of asphaltene aggregation, additional field studies are necessary.

One of the factors influencing the aggregation of asphaltenes is nitrogen heterocyclic structures. They are prone to intermolecular interactions due to the presence of conjugated aromatic systems, as well as a lone pair of electrons on nitrogen atoms. Such compounds are represented in oil by homologs of pyridine, quinoline, benzo- and dibenzoquinolines [43,44]. It is known that high molecular weight nitrogenous bases are present in resins and asphaltenes and affect the composition of oil and the structure of asphaltene aggregates. Thus, nitrogenous bases were isolated from petroleum resins, after which they were added to heavy oil in various concentrations. This led to a significant increase in the content of asphaltenes, and their supramolecular structure became looser and more disordered [45,46]. However, the studied nitrogenous bases of resins also contain functional groups with S and O atoms, which are involved in aggregation processes. Therefore, it is difficult to make a reliable conclusion about the effect of “pure” nitrogenous bases on asphaltene aggregation. In addition, the influence of nitrogenous bases in the structure of asphaltenes on the formation of aggregates has not yet been studied.

The purpose of the work is to study the effect of basic nitrogen (quinolone) on the composition of oil and the aggregative stability of asphaltenes.

2. Materials and Methods

2.1. Objects of Study

The objects of study were heavy crude oil from the Republic of Tatarstan (density at 20 °C = 19.03 °API; viscosity at 20 °C 742.9 cSt) and model oil systems obtained by mixing the original oil and quinoline (Merck Life Science LLC, Darmstadt, Germany, 98.0% purity). The ratio of crude oil to quinoline was chosen so that the calculated nitrogen content in the model mixtures was 1, 2, and 3% wt. (Table 1). The resulting mixtures were homogenized using a magnetic stirrer at a temperature of 40 °C for 8 h. Also, the objects of study were asphaltenes isolated from petroleum systems and their thermolysis products.

Table 1. Description of research objects.

Object of Study	Abbreviation	Quinoline Content, % wt.	Nitrogen Content, % wt.
Initial crude oil	P ₀	-	0.4
Model petroleum system 1	P ₁	5.5	1.0
Model petroleum system 2	P ₂	14.6	2.0
Model petroleum system 3	P ₃	23.8	3.0

The characteristics of crude oil are shown in Table 2. The oil is heavy, highly viscous, and characterized by a high content of resins and asphaltenes. The total content of heteroatoms in oil is also high (5.95%), but the nitrogen content is low. Therefore, this oil was chosen as a raw material for the preparation of model oil systems.

Table 2. Composition of the crude oil.

Elemental Composition, % wt.					Group Composition, % wt.		
C	H	N	S	O	Hydrocarbons	Resins	Asphaltenes
81.67	12.38	0.41	4.01	1.53	64.69	24.06	11.25

2.2. Methods

The elemental composition of the original oil and asphaltenes was determined using a Vario EL Cube CHNS analyzer by direct combustion at a temperature of 1200 °C, followed by chromatographic separation of combustion products and identification using a thermal conductivity detector. The detection limit of the element is 0.01% wt.

Determination of the group composition of oil systems was carried out according to the standard method (Figure 1). To determine the content of asphaltenes, oil systems were dissolved in a 40-fold excess of n-hexane and the solution was kept in a dark place for 24 h. The solution was then filtered through a paper filter, which left an asphaltene residue. Asphaltenes in the filter were placed in a Soxhlet apparatus and purified from co-precipitated maltenes with n-hexane for 18 h until the solvent in the apparatus became colorless. Next, the asphaltenes were quantitatively extracted from the filter and dried to a constant weight at a temperature of 50 °C. Maltenes obtained during filtration and purification of asphaltenes were combined and n-hexane was evaporated on a rotary evaporator. The separation of maltenes into hydrocarbons and resins was carried out by liquid adsorption chromatography. Silica gel was used as the stationary phase. The mass ratio of sorbent to maltenes was 40:1. Before applying maltenes, the sorbent in the column was treated with n-hexane to remove the heat of wetting. The hydrocarbons were eluted with n-hexane. Resinous substances were isolated with a mixture of ethanol and benzene in a volume ratio of 1:1.

Determination of the basic nitrogen (N_{bas}) content in asphaltenes was carried out by potentiometric titration using a S80_K SevenMulti (Mettler Toledo, Greifensee, Switzerland). The portion of asphaltenes was 0.05 g. The portion was dissolved in 5 mL of toluene, and 25 mL of acetic acid was added. An acetic acid solution of perchloric acid was used as a titrant. The concentration of the titrant was determined by titration of a solution of quinoline in toluene. We titrated with 0.1 mL of titrant and noted the readings of the device after the addition of each portion of acid, the time between the additions of titrant, 30–60 s, was monitored using a stopwatch. Calculation of the content of N_{bas} in asphaltenes was conducted according to the formula:

$$N_{\text{bas}} = \frac{14 \cdot 100 \cdot K_{\text{HClO}_4} \cdot V_K}{1000 \cdot m}, \quad (1)$$

K_{HClO₄} is the titrant concentration, mol/L; V_K is the amount of titrant used for titration, mL; m is the mass of the oil product, g.

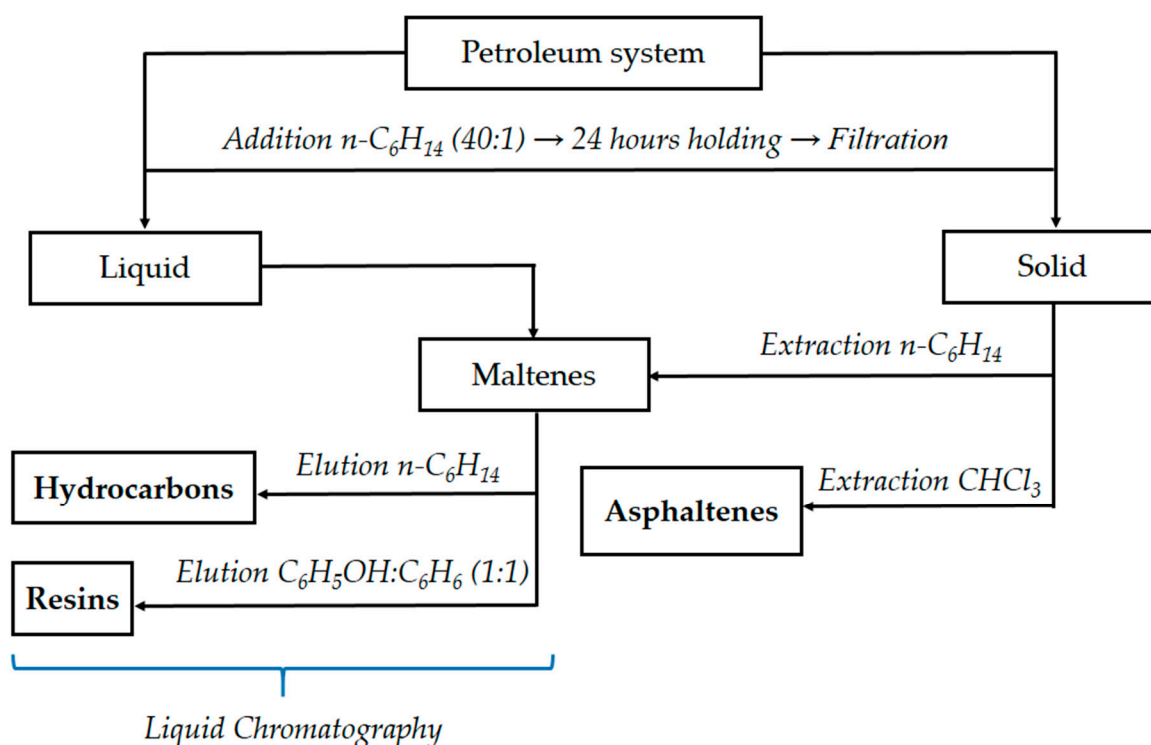


Figure 1. Scheme of separation of the petroleum systems into hydrocarbons, resins, and asphaltenes.

Structural group analysis of asphaltenes was carried out using data on their elemental composition, average molecular weights, and ¹H NMR spectroscopy. The method for calculating the structural group parameters of asphaltenes is given in [47]. Using the method of structural group analysis, the following averaged structural parameters of asphaltenes were calculated:

f_a, f_n, f_p —relative content of carbon atoms in aromatic, naphthenic, and paraffin structural fragments, respectively.

The molecular weights of asphaltenes were measured by cryoscopy in naphthalene. The concentration of the sample in naphthalene was in the range of 0.5–0.7% wt. The relative error in determining molecular masses was no more than 5.0%.

¹H NMR spectra of asphaltenes were obtained using a AVANCE-AV-300 Fourier spectrometer (Bruker, Karlsruhe, Germany) with an operating frequency of 300 MHz. During sample preparation, samples were dissolved in CDCl₃; the concentration of substances in the solution was 1% wt. Hexamethyldisiloxane was used as an internal standard.

The aggregative stability of asphaltenes was studied by spectrophotometry using a Lambda 950 instrument (Perkin Elmer LLC, Norwalk, CT, USA). The analysis was carried out for 7200 s (5 s step). The cuvette thickness was 10 mm and the wavelength was 620 nm. Solutions of asphaltenes in chloroform with a concentration of 1.0% wt. were prepared. These solutions were mixed in a cuvette with n-hexane in a ratio of 1:3. Further, the change in optical density was instantly recorded according to the mode described above. N-hexane was used as a reference solution. The study of asphaltene aggregation was carried out at atmospheric pressure. The temperature of the solutions and the environment was 25–27 degrees Celsius.

The original and model petroleum systems were subjected to thermolysis to obtain asphaltene-like substances with different contents of N_{bas}. It was assumed that in the process of thermolysis, the molecules of quinoline and high-molecular-weight compounds would interact according to the radical chain mechanism, with the formation of asphaltenes enriched with N_{bas}. It is known that non-catalytic oil refining processes (thermal cracking, visbreaking) proceed according to a radical mechanism. In our case, thermolysis is

analogous to visbreaking. Therefore, it is assumed that quinoline is incorporated into the structure of asphaltenes by a radical mechanism. In recent work [48], the formation of new asphaltenes during the visbreaking of petroleum systems was considered. Therefore, it is assumed that quinoline will be a building block in the formation of new asphaltenes during the thermolysis of model petroleum systems.

Thermolysis of model petroleum systems was carried out at 380–400 °C for 4 h. The thermolysis conditions were selected based on preliminary studies. At thermolysis below 380 °C, the yield of asphaltenes is low. At thermolysis above 400 °C, active formation of coke from asphaltenes begins.

Laboratory thermolysis unit with a batch reactor includes a reactor, furnace, thermocouple, programmable logic controller, and pressure gauge. A more detailed description of the thermolysis plant is given in [49].

The installation is a batch reactor with a volume of 12 cm³. The autoclave is equipped with a mechanical stirrer and two thermocouples. The programmable logic controller regulates the agitation speed and temperature and controls the pressure in the system. The sample weight was 6 g. Before testing, the reactor with the sample was purged with an inert gas, then it was closed and heated at a rate of 15 °C/min. When the set temperature was reached, the reactor was maintained for 3.5 h. The yield of gaseous cracking products was calculated from the weight loss of the reactor after the removal of gaseous products. Liquid products of thermolysis were taken and their group composition was determined using the scheme described in Figure 2. Next, the reactor was washed with chloroform and weighed. The resulting difference between the mass of the reactor before and after the experiment was determined as solid products (coke).

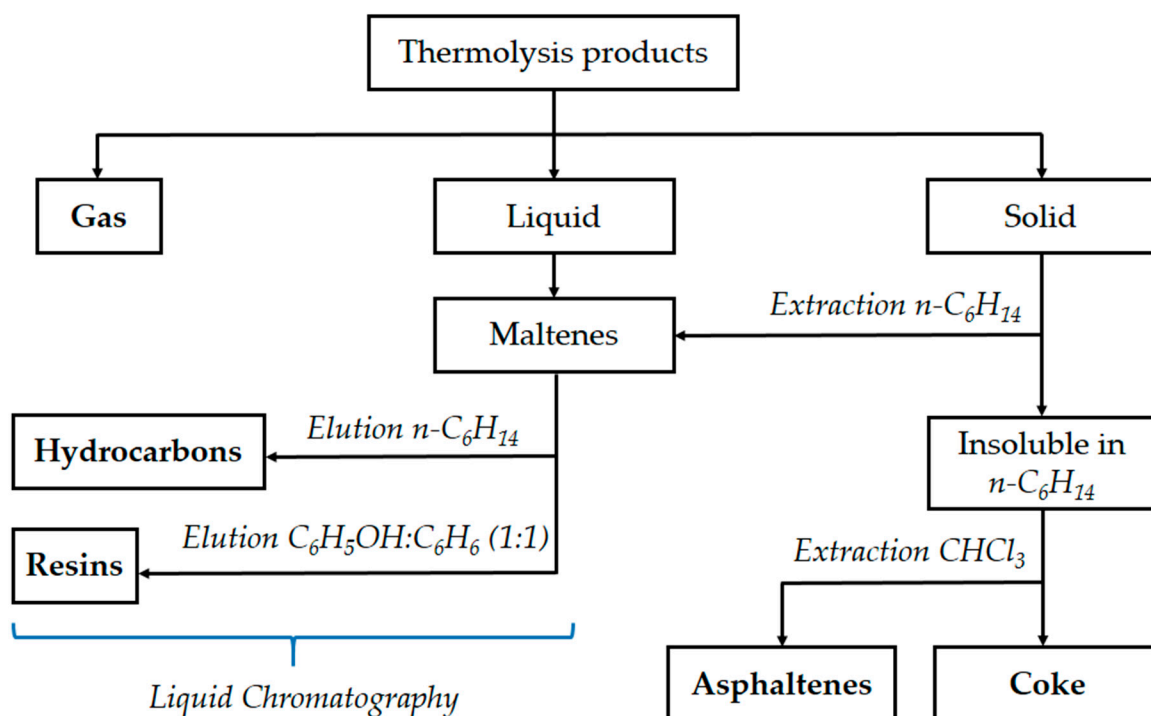


Figure 2. Scheme for separating thermolysis products.

3. Results and Discussion

3.1. Effect of Quinoline as a Component of a Dispersion Medium on the Composition, Structure, and Aggregation Stability of Asphaltenes

Figure 3 shows that the addition of quinoline leads to a change in the group composition of the oil. The asphaltene content decreases by approximately 3% wt. with an increase in the concentration of N_{bas} in the oil system to 3% wt. This is primarily due to the dilution of oil with quinoline. It is also possible to change the parameters of the dispersion medium

with the participation of quinoline, which leads to a change in composition. The resin content, on the contrary, increases by 10–11% wt. due to the accumulation of quinoline in the resinous fraction. The relative hydrocarbon content is reduced by 7% wt.

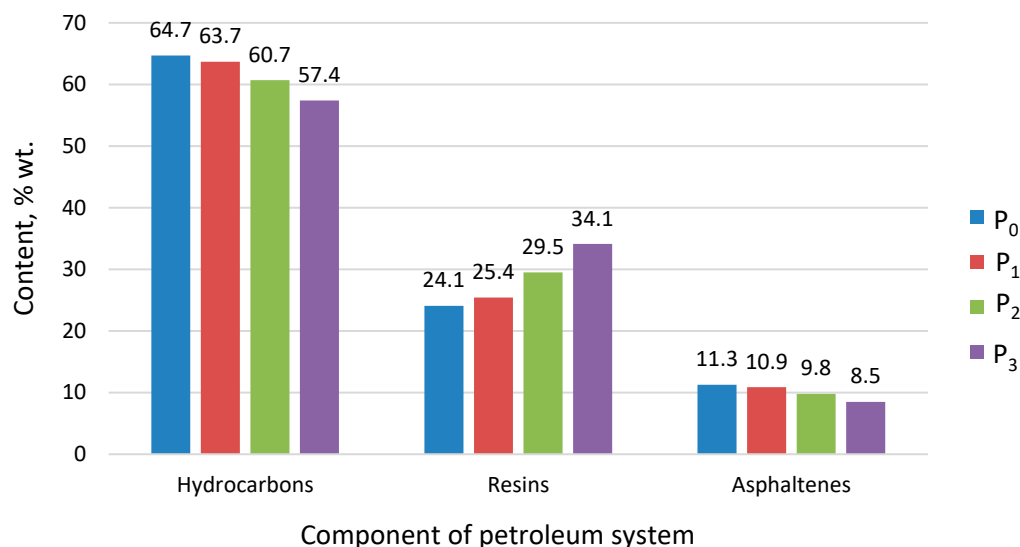


Figure 3. Composition of petroleum systems.

To assess the effect of quinoline on the processes of self-assembly of asphaltenes in petroleum systems, an analysis of their composition and structure was carried out. The results show that quinoline is incorporated into the supramolecular structure of asphaltenes and changes their structure (Table 3). An increase in the content of N_{bas} (quinoline) in the petroleum system leads to a systematic increase in the molecular weight (MW) of asphaltenes from 1368 to 2018 amu.

Table 3. Structural group analysis of asphaltenes from the initial oil and model petroleum systems.

Parameters	Object			
	A ₀	A ₁	A ₂	A ₃
MW, amu	1368	1640	1725	2018
Elemental composition, % wt.				
C	82.17	82.89	82.82	82.91
H	7.96	8.04	7.88	7.91
N _{bas}	1.39	1.72	2.14	2.69
S	4.18	3.98	3.89	3.80
O	4.30	3.37	3.27	2.69
Distribution of carbon among structural fragments of asphaltenes, %				
<i>f_a</i>	47.3	47.6	48.6	49.2
<i>f_n</i>	19.4	20.7	21.6	21.3
<i>f_p</i>	33.3	31.7	29.8	29.5

Note: A₀, A₁, A₂, A₃—asphaltene from initial oil and model oil systems with N_{bas} contents of 1, 2, and 3% wt. respectively.

It is likely that the composition of the macromolecules that form aggregates changes significantly with increasing quinoline concentration in the dispersion medium. Presumably, quinoline stabilizes primary asphaltene aggregates formed by the highest molecular weight compounds with an «island» structure. This quinoline solvate layer prevents the inclusion of compounds with lower molecular weight into aggregates. According to this assumption, the size of primary asphaltene aggregates decreases with increasing concentration of N_{bas} (quinoline). At the same time, the molecular weight of the compounds

that form the aggregate increases. In addition, the elemental composition of asphaltenes changes. The proportion of N_{bas} in asphaltenes systematically increases by 1.3% wt. (for A_3) with an increase in the quinoline content in petroleum systems. This confirms the participation of quinoline in the formation of supramolecular structures and its coprecipitation in the asphaltene fraction. The content of sulfur and oxygen in asphaltenes decreases by 0.4 and 1.6% wt. accordingly, against the background of increasing nitrogen content.

A change in the structure of asphaltenes is also observed. The more N_{bas} in asphaltenes, the higher the aromaticity factor and the proportion of naphthenic carbon, and the lower the content of paraffin carbon atoms. This confirms that quinoline stabilizes small primary aggregates consisting of the most polar and high molecular weight compounds with an «island» structure (large aromatic core and short alkyl chains).

An assessment was made of the influence of the structural group composition of asphaltenes on their aggregation stability. It has been established that the rate of aggregation and sedimentation of asphaltenes correlates with MW and N_{bas} content. Figure 4 shows that the aggregative stability of asphaltenes decreases with an increase in their average MW and an increase in N_{bas} in their composition. So in the series $A_0 \rightarrow A_1 \rightarrow A_2 \rightarrow A_3$, the starting point of sedimentation successively decreases by $300 \rightarrow 500 \rightarrow 250$ s, respectively. Thus, the onset point for asphaltenes with N_{bas} content of 2.69% wt. occurs four times faster compared to asphaltenes with N_{bas} content of 1.39% wt. It should also be noted that with an increase in the composition of asphaltenes' N_{bas} during aggregation, the number of fine particles that can be in a solution in a stable state increases. This is evidenced by the values of the minimum optical densities (plateaus) in the asphaltene sedimentation curves.

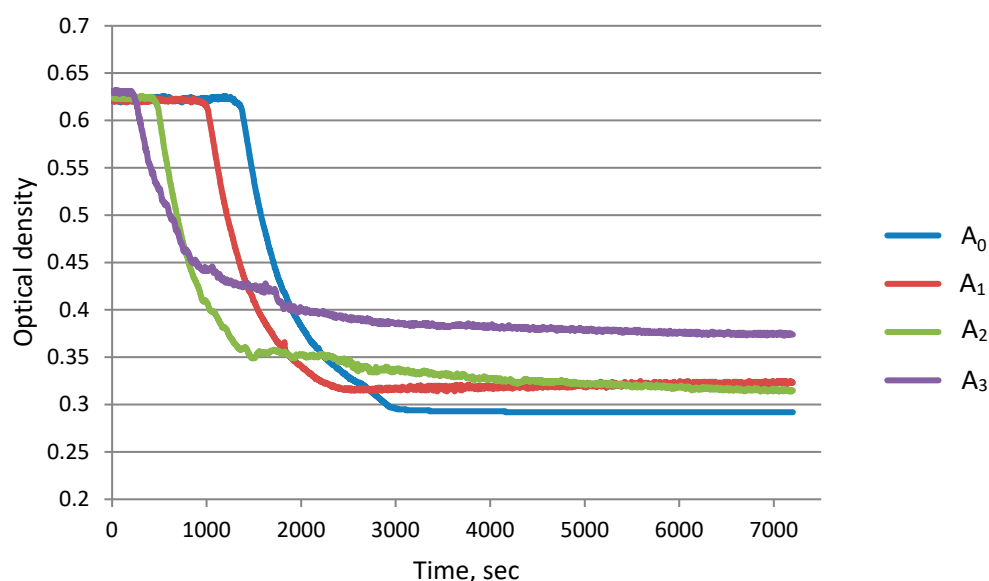


Figure 4. Aggregative stability of asphaltenes from the initial oil and model petroleum systems.

3.2. Thermolytic Synthesis of Asphaltene-like Nitrogenous Bases at Various Temperatures

Thermolysis of the initial oil and model petroleum systems was carried out at temperatures of 380 and 400 °C for 4 h to obtain model nitrogen-containing asphaltenes (asphaltene-like nitrogenous bases). The optimal temperature for the production of model asphaltenes was determined from the composition of thermolysis products. Figure 5 shows the composition of thermolysis products of petroleum systems.

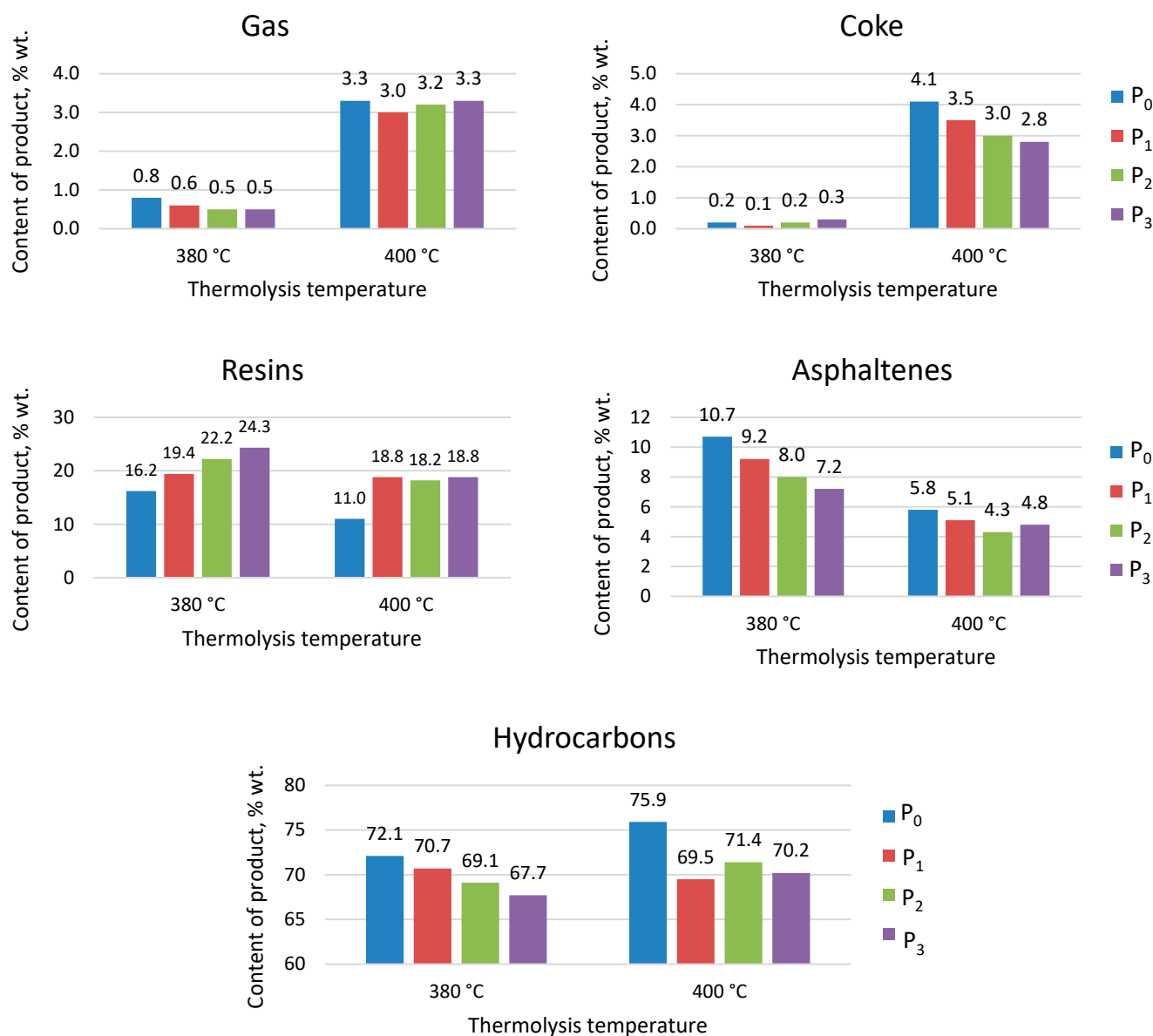


Figure 5. Composition of thermolysis products of petroleum systems at different temperatures.

The formation of gas during the thermolysis of petroleum systems at 400 °C is 3.0–3.3% wt., but at a temperature of 380 °C, 0.5–0.8% wt. of gas is formed. The concentration of quinoline in the oil system has little effect on the content of gaseous thermolysis products. The share of coke in the thermolysis products of all samples at 380 °C does not exceed 0.3% wt., but increasing the temperature to 400 °C leads to a significant formation of solid insoluble products of 4.1–2.8% wt. Coke production decreases with increasing quinoline concentration in the system. This is due to a decrease in the proportion of high-molecular hetero-organic components that are precursors of coke in thermal processes. The content of resinous substances in thermolysis products at 380 °C increases with increasing quinoline content in model oil systems. This indicates incomplete conversion of quinoline under these conditions. During thermolysis at 400 °C, such a tendency is not observed. The resin content in the products of thermolysis of model oils at 400 °C is almost equal to 18–19% wt. This suggests sufficient conversion of quinoline and the establishment of equilibrium in the system at 400 °C for 4 h. The asphaltene content decreases regardless of the thermolysis temperature of petroleum systems. Moreover, the amount of asphaltenes obtained at 400 °C is 1.5–2 times lower than at 380 °C. It is important that in the products of

thermolysis of petroleum systems at 400 °C, the asphaltene content fluctuates in a fairly narrow range (4.3–5.8% wt.). This also confirms that chemical equilibrium has been achieved under these conditions. Increasing the thermolysis temperature seems inappropriate due to the likely formation of significant amounts of coke and a decrease in the content of asphaltene substances, which does not correspond to the purpose of this work. Thus, asphaltenes obtained at 400 °C were selected for further studies based on the data obtained on the composition of the thermolysis products of petroleum systems.

3.3. Composition, Structure, and Aggregation Stability of Asphaltene-like Nitrogenous Bases

Model asphaltene-like bases were obtained during thermolysis of initial oil and model petroleum systems with different contents of N_{bas} (quinoline) at a temperature of 400 °C for 4 h. Structural group composition data show that the average molecular weight of synthetic asphaltenes from thermolysis products is 615–771 amu (Table 4). The change in molecular weight is not directly dependent on the composition of the thermolyzed petroleum system. Asphaltenes obtained by thermolysis of model petroleum systems with a nitrogen content of 1 and 2% wt. have the highest content of N_{bas} . It is likely that an increase in the concentration of quinoline in oil prevents thermal transformations of the petroleum components. This leads to a decrease in the quinoline conversion and reduces the incorporation of quinoline fragments into the structure of asphaltenes.

Table 4. Structural group analysis of model asphaltene-like substances.

Parameters	Object			
	A'0	A'1	A'2	A'3
MW, amu	615	771	715	690
N_{bas} , % wt.	1.95	2.35	2.49	2.04
Distribution of carbon among structural fragments of asphaltenes, %				
f_a	65.2	67.1	67.4	67.8
f_n	21.5	21.2	21.4	21.2
f_p	13.3	11.7	11.2	11.0

Note: A'0, A'1, A'2, A'3—asphaltene-like substances from thermolysis products of initial oil and model oil systems with N_{bas} content of 1, 2, and 3% wt., respectively.

The aromaticity factor of asphaltenes from thermolysis products of model oils is 2–3% higher than that of A'0. This also confirms the incorporation of quinoline into the molecular structure of asphaltenes. The content of carbon atoms in naphthenic cycles of synthetic asphaltenes is 21.2–21.5% and does not depend on the composition of the thermolyzed petroleum system. However, the proportion of paraffinic carbon in synthetic asphaltenes decreases by 1.5–2.3% with increasing concentration of quinoline in the petroleum system. This may be due to the elimination of alkyl fragments and the incorporation of quinoline (aromatic) fragments into the structure of asphaltene substances during thermolysis.

The aggregative stability of synthetic asphaltene-like substances completely correlates with their N_{bas} content. Thus, the colloidal stability of synthetic asphaltenes increases with increasing N_{bas} content (Figure 6).

The starting point of precipitation of A'0 (1.95% wt. of N_{bas}) occurs 20% earlier compared to A'2 (2.49% wt. of N_{bas}). It is important that the average colloidal stability of synthetic asphaltene-like substances is several times higher than asphaltenes from model petroleum systems. This is also confirmed by the fact that the sedimentation process of synthetic asphaltenes lasts more than 7200 s (there is no plateau). In this case, the precipitation of asphaltenes from model oil systems occurs two times faster. Thus, it has been established that asphaltenes from thermally converted hydrocarbon raw materials have significantly higher aggregative stability. It has also been shown that the colloidal stability of asphaltenes increases with an increase in the N_{bas} content in their molecular structure.

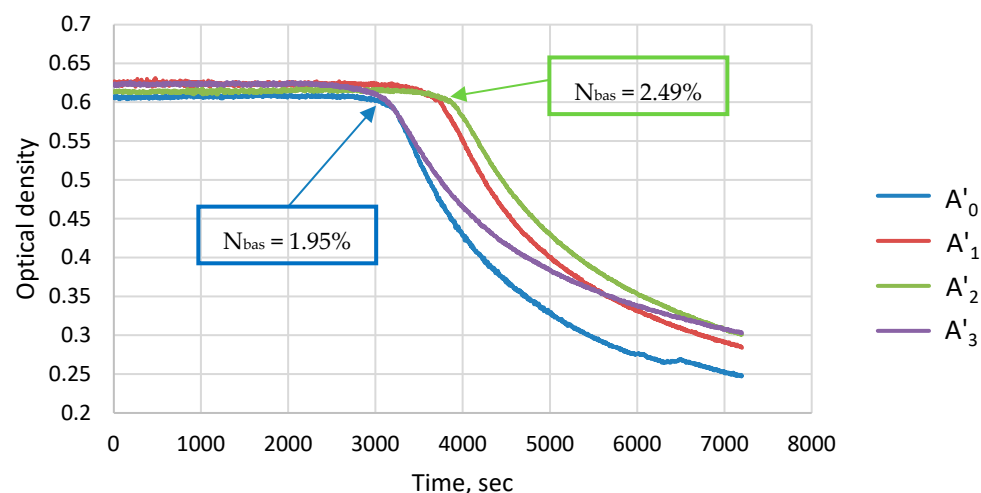


Figure 6. Aggregative stability of model asphaltene-like substances.

4. Conclusions

The influence of quinoline as a component of the dispersion medium on the composition of oil, the structure, and the aggregative stability of asphaltenes was assessed. It has been established that the asphaltene content in oil decreases by 3% wt. with an increase in the concentration of N_{bas} in the oil system to 3% wt. This is due to the dilution of the petroleum system and the participation of quinoline in the formation of supramolecular structures of asphaltenes. It was shown that quinoline accumulates in the resin fraction due to their similar adsorption ability on silica gel.

The content of N_{bas} in asphaltenes increases by 0.3–1.3% wt. with increasing quinoline content in petroleum systems. It has been established that quinoline is incorporated into the supramolecular structure of asphaltenes and changes their structural group composition: it increases the average molecular weight by 650 amu. and aromaticity by 2%. Presumably, quinoline stabilizes small primary asphaltene aggregates, consisting of the most polar and high-molecular compounds with an «island» structure. The aggregative stability of asphaltenes decreases by 1.5–6 times with an increase in their average molecular weight and an increase in N_{bas} in their composition.

As part of the work, synthetic model asphaltene-like substances with different contents of basic nitrogen were obtained using thermolysis of model petroleum systems. The molecular weight of synthetic asphaltenes from thermolysis products is 615–771 amu. and does not depend on the composition of the thermolyzed petroleum system. The aromaticity of synthetic asphaltenes increases, and the proportion of paraffinic carbon decreases with increasing concentration of quinoline in thermolyzed oil.

It has been established that the colloidal stability of synthetic asphaltene-like substances is several times higher than that of asphaltenes from model petroleum systems. Asphaltenes from thermally converted hydrocarbon raw materials have significantly higher aggregation stability. The colloidal stability of asphaltenes increases with the increase in the molecular structure of fragments containing N_{bas} in aromatic rings.

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