

## Influence of the Composition of Heavy Oil Systems on the Transformation of Their Resins and Asphaltenes During Thermal Cracking

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### **Abstract**

The paper is devoted to studying the influence of petroleum systems composition on the transformation of their resin-asphaltene substances in the process of thermal cracking. The research object included oil, natural bitumen, and their mixture at the ratio of 1:1. As a result of the study, the material balance of thermal cracking, the composition of the initial oil systems and thermolysis products were determined, and the molecular structure of resins and asphaltenes before and after the thermal treatment of oil systems was described. It has been found that bitumen cracking is accompanied by the formation of the largest amounts of gaseous (3.9%) and solid (2.3%) products, while oil cracking leads to the formation of significantly smaller amounts of gas (1.2%) and solid residue (0.1 %). The character of structural changes in resins during thermolysis is predominantly destructive due to dealkylation reactions and the destruction of cyclic systems. Asphaltene molecules are prone to condensation reactions with each other, as well as with resin molecules. Naphthenic cycles are also destroyed in asphaltenes, which leads to an increase in their aromaticity.

**Keywords:** *Heavy oil; Thermolysis; Resins; Asphaltenes; Structural group analysis.*

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### **1. Introduction**

Now in the world of oil refining, there is a tendency to increase the share of heavy oils in the total volume of refined hydrocarbons. Heavy oils and natural bitumens contain large amounts of resins and asphaltenes (high molecular weight heterorganic compounds) and small amounts of distillate fractions. The high proportion of heteroatoms (S, N, and O) and metals (V, Ni, Fe, etc.) in resin-asphaltene substances causes problems in oil refining processes. These problems are associated with premature wear of process equipment, catalyst deterioration, as well as the formation of a significant amount of coke residue. This makes it difficult to process heavy oil raw materials using traditional schemes [1-3].

Today, various non-traditional approaches to the processing of heavy hydrocarbon raw materials based on thermal and catalytic processes are being developed [4-8]. At present, the reaction stability and activity of resin-asphaltene substances in refining processes are widely studied [9-12], and the influence of various factors on the structural changes of resin and asphaltene molecules is investigated [13-14]. The composition of oil disperse systems, and physicochemical conditions of processing determine the development of certain processes, which leads to different patterns in changes in the qualitative composition of molecules of resin-asphaltene compounds of oil [15-20]. In this regard, there are many questions concerning the change in the molecular structure of these components in thermal processes. The creation of effective technologies for the processing of heavy bituminous oils and oil residues is impossible without studying the composition and structure of resins and asphaltenes, as well as the direction of their transformation in the process of thermal destruction [21-24]. Structural group analysis (SGA) occupies an important place in the study of the composition and structure of high-molecular-weight heteroatomic compounds of oil.  $H^1$  NMR spectral data, in combination

with the elemental composition and molecular weight value of the sample under study, are the basis of the structural group analysis. This analysis makes it possible to determine the characteristics of the average molecule and the distribution of carbon atoms between structural groups and to obtain information about the structure and composition of various molecular fragments of resin-asphaltene substances [25].

The aim of this work is to study the direction of structural changes in the molecules of resins and asphaltenes of heavy hydrocarbon crude in thermal processes.

## 2. Experimental

The objects of the study were heavy oil systems: oil of the Barsukovskoye field, natural bitumen of the Ashalchinskoye field, and a model oil system, which is a mixture of equivalent amounts of oil and bitumen. The content of resinous substances and asphaltenes increases naturally in the series oil-mixture-bitumen (Table 1). Thus, we obtained a set of oil objects that differ in the content of resin-asphaltene components and have in their composition both native and supramolecular structures of resins and asphaltenes formed during mixing. We assume that this approach will allow us to estimate the influence of the amount and structure of high-molecular-weight heteroatomic compounds in oil systems on the direction of structural changes of these components in thermal processes.

Table 1. Characteristics of initial oil systems

Sample	Density, kg/m <sup>3</sup>	Content, % wt.		
		Resins	Asphaltenes	Hydrocarbons
Oil	886	11.2	0.9	87.9
Model mixture	921	16.0	4.2	79.8
Bitumen	978	25.9	7.7	66.3

The samples were thermally treated in 12 cm<sup>3</sup> autoclaves at 450 °C for 2 hours in the air. The sample weight was 7 g. According to available data [15], such technological conditions for carrying out the process of thermolysis allow getting the maximum quantity of light fractions from heavy hydrocarbon raw materials. Since resin-asphaltene materials are a source of hydrocarbons, it is advisable to study the structural changes of resins and asphaltenes after cracking.

The content of resins and asphaltenes in the initial objects and liquid products of thermolysis was determined by the following method [26]. The sample weight was dissolved in n-hexane in a volume ratio of 1:40, and the solution was kept for 24 hours. The precipitate (asphaltene) was filtered through a blue ribbon filter (pore size 1-2 nm). The filter with the precipitate was placed in a paper cartridge and washed in a Soxhlet apparatus with n-hexane from oils and resins (maltenes). The asphaltene from the paper cartridge were washed with chloroform, the solvent was evaporated, and the asphaltene were dried to constant weight. The solution of the maltenes in n-hexane was evaporated and applied to ASK silica gel, after which the resulting mixture was loaded into a Soxhlet apparatus. Initially, hydrocarbon components (hydrocarbons) were extracted with n-hexane, and then, with a mixture of benzene and ethanol (1:1), resinous substances were isolated. The obtained solutions of oils and resins in hexane were evaporated to dryness, and the samples were dried to constant weight.

Resins and asphaltene extracted from the initial objects and thermolysis products were studied by structural group analysis (SGA) [27]. The elemental composition of resins and asphaltene was determined on a CHNS Vario EL Cube analyzer. Molecular weights were measured by the cryoscopic method in naphthalene. PMR spectra were recorded using an AVANCE-AV-300 Fourier spectrometer (solvent - deuteriochloroform, internal standard - hexamethyl disiloxane) at 1% concentration of substances.

Distribution of carbon atoms by the main fragments of medium molecules of resins changes in the following order: as the feedstock becomes heavier from oil to blend and bitumen, the relative content of carbon atoms decreases in the aromatic ( $f_a$ ) 34.25 % → 27.95 % and

naphthenic ( $f_n$ ) 32.96 %  $\rightarrow$  20.08 % rings, whereas the proportion of paraffin carbon ( $f_p$ ) increases from 32.79 % ( $C_o$ ) to 51.97 % ( $C_b$ ) (Table 2). Hydrogen saturation increases according to the same pattern: in the series, the oil-mixture-bitumen H/C ratio in the resins increases from 1.36 to 1.47.

Table 2. Distribution of carbon atoms in the original resins and asphaltenes

Resins (source)	Relative content of carbon atoms, %			H/C
	$f_a$	$f_n$	$f_p$	
$C_o$ (oil)	34.25	32.96	32.79	1.36
$C_m$ (mixture)	32.63	29.56	37.81	1.40
$C_b$ (bitumen)	27.95	20.08	51.97	1.47
Asphaltenes (source)	$f_a$	$f_n$	$f_p$	H/C
$A_o$ (oil)	46.12	49.11	4.76	1.00
$A_m$ (mixture)	43.98	45.95	10.07	1.10
$A_b$ (bitumen)	42.58	47.84	9.58	1.11

$f_a, f_n, f_p$  – carbon content in the aromatic, naphthenic, and paraffin structural fragments of the molecule, respectively

Asphaltene molecules of bitumen  $A_b$  are also most saturated with hydrogen, while asphaltenes of oil  $A_o$  H/C are lower by 10 %. In the oil-blend bitumen series,  $f_a$  decreases from 46.1 % for  $A_o$  to 42.6 % for  $A_b$ . The distribution of carbon in the saturated rings and paraffin chains does not obey a strict dependence, but the proportion of carbon of the paraffin chains ( $f_p$ ) in the molecules of asphaltenes of oil  $A_o$  is 2 times lower than in  $A_m$  and  $A_b$ .

### 3. Results and discussion

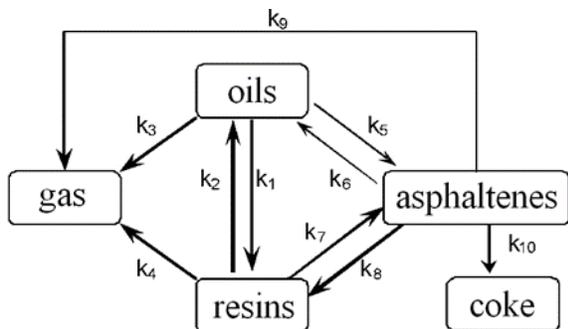


Figure 1. Formalized scheme of thermal transformations of oil components [16]

Previously, the authors of [16] studied the transformation of oil components in the process of thermal treatment of heavy hydrocarbon raw materials. On the basis of the data received in the work, the formalized scheme of transformation of oil components at thermolysis of heavy oils (Fig. 1) is offered. The presented scheme allows us to take into account the transformations of some components into others, which, in turn, gives the possibility to explain the directions and causes of structural changes in resin and asphaltene molecules in thermal processes correctly.

Data of a material balance have shown that thermolysis of initial bitumen is accompanied by the formation of the greatest quantity of gaseous (3,9 %) and solid (2,3 %) products, whereas cracking of initial oil leads to the formation of a much smaller quantity of gas (1,2 %) and solid products (0,1 % wt.) (Table 3).

Table 3. Material balance of the thermolysis process

Sample	Thermolysis product yield, % wt.		
	Gaseous	Solid	Liquid
Oil	1.2	0.1	98.7
Model mixture	1.5	1.1	97.4
Bitumen	3.9	2.3	93.8

Table 4 shows the analysis of the material composition of the initial oil systems and thermolysates, which indicates that the most significant changes are observed in the cracking of oil, where the proportion of asphaltenes in the liquid products of thermolysis increases by 1.5 times, and the content of resins decreases by 1.7 times compared to the initial oil. At the same time, the amount of hydrocarbon components increase by 4.0 %. The thermolysis of the model mixture leads to less significant changes in the content of asphaltenes, resins, and oils. Thus, the share of asphaltenes and oils increased by 0.5 and 1.6 wt. %, respectively, while the decrease in the content of resinous components was 2.1 wt. %. During the thermolysis of bitumen, the content of resins decreased by 10 % with an increase of 10.3 wt. % in oils compared to the original sample, while the amount of asphaltenes changed insignificantly. The thermal cracking process involves the degradation reactions of resinous components, leading to the formation of low-molecular-weight resins and light hydrocarbons and parallel condensation reactions, contributing to the formation of additional amounts of asphaltenes and a solid residue.

Table 4. Changes in the material composition of oil systems during thermolysis

Sample	Asphaltene content, % wt.		Resin content, % wt.		Oils content, % wt.	
	Before thermolysis	After thermolysis	Before thermolysis	After thermolysis	Before thermolysis	After thermolysis
Oil	0.9	1.4	11.2	6.6	87.9	92.0
Mixture	4.2	4.7	16.0	13.9	79.8	81.4
Bitumen	7.7	7.5	25.9	15.9	66.3	76.6

To assess the direction of changes in the structural parameters of resins and asphaltenes, their structural group analysis was carried out. Changes in the average parameters of the molecular structure of the resins. The resins of the initial objects have close molecular weights ranging from 616 to 687 g/mol (Table 5).

Table 5. Main characteristics of resins of initial objects and thermolysis products

Parameters	Resins (source)					
	C <sub>o</sub> (Oil)		C <sub>m</sub> (Mixture)		C <sub>b</sub> (Bitumen)	
	Before thermolysis	After thermolysis	Before thermolysis	After thermolysis	Before thermolysis	After thermolysis
Average molecular weight, g/mol	645	535	687	503	616	532
H/C	1.36	1.40	1.38	1.40	1.47	1.34
Content, % wt						
C	83.54	82.46	79.98	79.49	76.11	79.71
H	9.53	9.68	9.27	9.34	9.40	8.98
N	0.94	1.16	1.01	1.25	0.66	1.10
S	1.96	1.52	4.78	4.11	5.05	4.89
O	4.03	5.18	4.96	5.81	8.78	5.32

The relative content of total carbon in the molecule decreases from resins extracted from oil (C<sub>o</sub>) to bitumen resins (C<sub>b</sub>) from 83.5 % to 76.1 %, while the hydrogen content in each of the samples is ~ 9.5 wt %. Accordingly, in the same series, the H/C ratio increases from 1.36 to 1.47. The nitrogen content in the resin molecules does not exceed 1 %, but the sulfur and oxygen content increases along with the content of resin-asphaltene substances in the oil system and for bitumen resins reaches 5.05 % and 8.78 %, respectively (Table 5). On the whole, the resin molecules represent one polycyclonaphthene-aromatic nucleus, consisting, on average, of 7 rings for C<sub>o</sub> and model blend resins (C<sub>m</sub>) and of 5 rings for C<sub>b</sub>, and the contribution of aromatic (K<sub>a</sub>) and naphthenic (K<sub>nap</sub>) in each molecule is rather close. Since the number of terminal methyl groups (C<sub>γ</sub>) is ~ 3 units, the C<sub>o</sub> molecule has three aliphatic substituents, whereas C<sub>m</sub> and C<sub>b</sub> are substituted mainly by four alicyclic fragments. It should be

noted that more than half of the peripheral carbon atoms of the aromatic rings are substituted, and their degree of substitution ( $\sigma_a$ ) increases from  $C_o$  (0.53) to  $C_b$  (0.65). It should be taken into account that the number of structural blocks of the molecule ( $m_a$ ) varies from 1.14 to 1.30, which means that the molecules of the studied resins contain systems with two or more structural blocks (for example, for  $C_m$ , every third molecule has two structural blocks, the number of three- and polyblock molecules is insignificant).

Thus, the main regularities in the structural characteristics of the average molecules of resins, as the feedstock becomes heavier from oil to bitumen, are: a decrease in the relative content of carbon atoms in aromatic ( $f_a$ ) 34.25 %  $\rightarrow$  27.95 % and naphthenic ( $f_n$ ) 32.96 %  $\rightarrow$  20.08 % rings; an increase in the share of paraffin carbon ( $f_p$ ) from 32.79 %  $C_o$  to 51.97 %  $C_b$ ; an increase in the content of five-member rings ( $q$ ) in the total volume of cyclic systems (0.16  $\rightarrow$  0.31) (Table. 6).

Table 6. Average structural parameters of resins of initial objects and thermolysis products

Parameters	Resins (source)					
	$C_o$ (Oil)		$C_m$ (Mixture)		$C_b$ (Bitumen)	
	Before thermo-lysis	After thermo-lysis	Before thermo-lysis	After thermo-lysis	Before thermo-lysis	After thermo-lysis
Number of atoms in the average molecule. units						
$C_a$	15.37	10.67	14.95	10.69	10.92	12.57
$C_n$	14.79	15.40	13.54	10.20	7.85	11.15
$C_p$	14.71	10.72	17.32	12.43	20.31	11.66
$C_\alpha$	5.77	4.63	6.14	4.82	4.99	5.27
$C_\gamma$	3.16	2.82	3.87	2.60	3.94	2.63
Distribution of carbon atoms. %						
$f_a$	34.25	29.01	32.63	32.08	27.95	35.53
$f_n$	32.96	41.86	29.56	30.61	20.08	31.51
$f_p$	32.79	29.14	37.81	37.31	51.97	32.95
Ring composition. units						
$K_t$	7.28	6.28	7.14	5.18	4.83	5.88
$K_a$	3.65	2.55	3.77	2.65	2.83	3.11
$K_{nap}$	3.63	3.73	3.37	2.52	2.00	2.77
$q$	0.16	0.18	0.22	0.24	0.31	0.22
$m_a$	1.28	1.10	1.30	1.11	1.14	1.19
$\sigma_a$	0.53	0.58	0.60	0.61	0.65	0.59

Thermal treatment of heavy oil systems resulted in both quantitative and structural changes in the average molecules of the resin components of the objects under study. Thus, the molecular weight of thermolysate resins decreased by approximately 100 g/mol for  $C_o$  and  $C_b$  type molecules and by 180 g/mol for  $C_m$ .

Data in Tables 5 and 6 show that after thermolysis, the number of building blocks in a  $C_o$ -type molecule decreased from 1.28 to 1.10. The number of aromatic carbon atoms also decreased by 5 units, which was reflected in the number of aromatic rings (decreased by 1 unit). The same phenomenon is observed for the number of paraffin carbon atoms ( $C_p$ ), which decreased by  $\sim 30\%$ . It should be noted that the number of naphthenic carbon atoms ( $C_n$ ) remained virtually unchanged. Hence, the number of naphthenic rings retained its original value. Probably the decrease in molecular weight and the number of structural blocks of the  $C_o$ -type molecule is caused by the destruction of the side alkyl substituents and aliphatic bridges linking the structural cyclic fragments. The loss of the aromatic ring 1 is probably related to its hydrogenation, provided that the naphthenic cycle is broken in parallel. However,

it is possible that the cracking of the bridging bonds resulted in the detachment of the structural unit of the molecule represented by one benzene ring, which could cause the loss of the aromatic cycle. The practically unchanged number of heteroatoms in the molecule indicates that N, S, and O are predominantly in the thermostable cyclic fragments of the molecule. Nevertheless, the possibility of introducing heteroorganic components from asphaltenes and oils should be taken into account.

As described above, the molecules of the mixture of oil and bitumen ( $C_m$ ) underwent the greatest decrease in molecular weight (by 180 g/mol). First of all, it is associated with a decrease in the number of carbon atoms in the aromatic ( $C_a$ ), naphthenic ( $C_n$ ), and paraffin ( $C_p$ ) fragments  $\sim 3$ -5 units (Table 5), which entailed a decrease in the number of structural blocks, and after thermolysis, there were 1 aromatic and 1 naphthenic cycle less in the resin molecule  $C_m$ . Thus, for a  $C_m$  molecule under thermal stress, the most likely characteristic reactions are the dealkylation of side chains, hydrogenation of aromatic, and opening of naphthenic cycles, followed by the destruction of acyclic fragments. It is important to note that the number of S atoms in the molecule has halved, which may indicate the breaking of weak sulfide bonds.

A slightly different picture is observed in the structural changes of bitumen resin molecules ( $C_b$ ). The number of structural blocks in the average molecule slightly increased with a decrease in the molecular weight by 100 g/mol (Table 6). The  $C_a$  and  $C_n$  values increased by 1.5 and 3.5 atoms.  $K_a$  and  $K_n$  values increased accordingly, while the decrease in  $C_p$  was 9 atoms. From the data of Tables 5, 6 we can assume that molecules of  $C_b$  type are prone to cyclization reactions of aliphatic chains with the formation of naphthenic fragments and their subsequent dehydrogenation, which is indicated by the decrease in H/C ratio by 9 %. However, in this case, such processes seem unlikely or, at least not predominant. The change in the number of heteroatoms after thermolysis attracts attention: the number of S atoms decreases, and the N content changes insignificantly for  $C_o$  and  $C_m$ , whereas for  $C_b$ , it increases by a third. This can be caused by the destruction of asphaltene molecules with the formation of additional amounts of resinous components (route  $k_8$ , Fig. 1) enriched with naphtheno-aromatic nuclei and heteroatomic components.

Thus, with an increase in the proportion of resinous asphaltenes in the oil system, due to the increased frequency of collisions of formed radicals and, accordingly, a greater intensity of the ongoing reactions, as well as the introduction of newly formed resinous components due to asphaltene decomposition, the degree of structural changes in the resin molecules increases. In this regard, the direction of structural changes in the resin molecules of  $C_b$  is mainly destructive in nature due to dealkylation reactions and destruction of cyclic systems (routes  $k_2$ ,  $k_4$ ), but, unlike  $C_o$  and  $C_m$ , in  $C_b$ , an increase in the share of naphtheno-aromatic cycles is observed, which is probably associated with an intensive course of dehydrogenation reactions of cyclic systems (route  $k_4$ ), as well as with the introduction into the system of resinous components formed from asphaltenes (route  $k_8$ ).

Changes in the average parameters of the molecular structure of asphaltenes. Due to the significantly different molecular weights, it seems impractical to compare the absolute values of the average structural parameters of asphaltene molecules of different natures. Therefore, the structure of asphaltene molecules was assessed by analyzing the relative values characterizing the average molecule.

The molecular weights of asphaltenes isolated from the initial oil ( $A_o$ ), the model mixture ( $A_m$ ), and bitumen ( $A_b$ ) are 1175, 1539, and 1094 g/mol, respectively (Table 7). The relative content of carbon atoms in asphaltenes decreases with the increase in their quantity in the raw material from 86 to 78.5 %, while the hydrogen fraction in all samples is 7.2-7.4 %. The H/C ratio increases from asphaltenes of oil  $A_o$  to asphaltenes of bitumen  $A_b$ , which indicates that the molecules of asphaltenes of oil  $A_o$  have the greatest proton deficiency.

Table 7. Main characteristics of asphaltenes of initial objects and thermolysis products

Parameters	Asphaltenes (source)					
	A <sub>o</sub> (Oil)		A <sub>m</sub> (Mixture)		A <sub>b</sub> (Bitumen)	
	Before thermo-lysis	After thermo-lysis	Before thermo-lysis	Before thermo-lysis	After thermo-lysis	Before thermo-lysis
Average molecular weight, g/mol	1175	1707	1539	1571	1094	1106
H/C	1.00	0.94	1.10	0.97	1.11	0.89
Content, % wt						
C	85.94	85.77	80.53	80.50	78.42	78.89
H	7.23	6.76	7.43	6.59	7.30	5.93
N	0.80	0.93	1.09	1.33	1.11	1.46
S	1.86	1.75	6.19	5.88	7.12	6.68
O	4.17	4.79	4.76	5.7	6.05	7.04

In all studied asphaltene molecules, as the feedstock gets heavier, the share of heteroatoms increases from 7 % (A<sub>o</sub>) to 14 % (A<sub>m</sub>), and the individual content of each heteroelement increases. Thus, as the feedstock becomes heavier, the content of nitrogen in asphaltene molecules increases by 0.3 %, oxygen by 1.9 %, and sulfur by 5.3 %. In addition, in the series, oil-blend-bitumen  $f_a$  decreases from 46,1 % for A<sub>o</sub> to 42,6 % for A<sub>b</sub>, and though the dependence is not pronounced, it is still present. An important feature of the samples under study is that the distribution of carbon in the saturated rings and paraffin chains does not obey a strict dependence, but the proportion of carbon atoms of paraffin chains ( $f_n$ ) in the asphaltene molecules of A<sub>o</sub> is two times lower than in A<sub>m</sub> and A<sub>b</sub>. It should also be noted that the degree of substitution ( $\sigma_a$ ) increases from A<sub>o</sub> (0.48) to A<sub>b</sub> (0.61) along with the increase in the proportion of five-membered rings ( $q$ ) in cyclic systems from 0.11 % to 0.21 % (Table 8).

Table 8. Average structural parameters of asphaltenes of initial objects and thermolysis products

Parameters	Asphaltenes (source)					
	A <sub>o</sub> (Oil)		A <sub>m</sub> (Mixture)		A <sub>b</sub> (Bitumen)	
	Before thermo-lysis	Before thermo-lysis	Before thermo-lysis	Before thermo-lysis	Before thermo-lysis	Before thermo-lysis
Number of atoms in the average molecule. units:						
C <sub>a</sub>	38.80	61.46	50.47	51.42	30.45	37.59
C <sub>n</sub>	41.31	56.20	52.73	49.85	34.20	32.86
C <sub>p</sub>	4.01	4.35	11.55	4.11	6.85	2.25
C <sub>α</sub>	11.28	16.37	16.49	15.19	10.86	11.17
C <sub>γ</sub>	4.01	4.35	6.03	4.11	3.86	2.25
Distribution of carbon atoms. %:						
$f_a$	46.12	50.37	43.98	48.79	42.58	51.71
$f_n$	49.11	46.06	45.95	47.30	47.84	45.20
$f_p$	4.76	3.57	10.07	3.90	9.58	3.09
Ring composition. units:						
K <sub>t</sub>	22.74	33.62	26.13	27.83	16.50	21.04
K <sub>a</sub>	9.56	15.36	13.41	13.66	8.18	10.04
K <sub>nap</sub>	13.18	18.26	12.73	14.17	8.32	11.00
q	0.11	0.11	0.18	0.17	0.21	0.18
m <sub>a</sub>	1.80	2.45	2.25	2.26	1.64	1.84
$\sigma_a$	0.48	0.45	0.58	0.52	0.61	0.51

Let's consider the structural characteristics of the asphaltene molecules of each of the samples studied. The average molecule of asphaltenes of oil A<sub>o</sub> has 2 structural blocks (only every

fifth molecule is monoblock), which are almost completely constructed from condensed cyclic fragments since the share of aromatic carbon ( $f_a$ ) in them is 46.1 %, and naphthenic ( $f_n$ ) - 49.1 %. Alkyl fragments of the molecule ( $f_n$ ) make up only 4.8%. The molecular structure of asphaltenes of oil  $A_o$  is mainly represented by two naphthenoaromatic systems consisting, on average, of 9-10 aromatic and  $\sim 13$  naphthenic rings linked by an alkyl bridge and surrounded by four aliphatic substituents  $C_\gamma = 4$ .

The average asphaltene molecule of mixture  $A_m$  is the most polyblock system of those studied in this work ( $m_a = 2.25$ ). At the same time, the proportion of carbon atoms of aromatic and naphthenic fragments is lower than for  $A_o$  and amounts to 44 % ( $f_a$ ) and 46 % ( $f_n$ ), respectively. It should be noted that the content of alicyclic carbon atoms ( $f_n$ ) in  $A_m$  is twice as high as in  $A_o$  and amounts to 10%. Thus, the structure of asphaltenes of mixture  $A_m$  is characterized by the presence in the average molecule of 13 aromatic and cycloalkane rings forming on average two structural blocks in which aromatic rings are replaced by six alkyl chains ( $C_\gamma = 6$ ).

The analysis of the structural characteristics of asphaltene molecules  $A_b$  indicates that among the studied objects, they have the lowest value  $m_a = 1.64$ , i.e., about half of the molecules are double-locked, the rest are mono blocked, if we assume that asphaltenes are represented only by single- and double-blocked systems. The fraction of aromatic carbon is 42.58 %, while naphthenic carbon is 47.84 %. The value of the alkyl carbon content in  $A_b$  is close to this value for  $A_m$  and is 9.58 %. The Asphaltene molecule of bitumen  $A_b$  contains 16 rings, including 8 aromatic and 8 naphthenic cycles, which create a naphthenoaromatic system framed by four aliphatic substituents.

After thermolysis, the range of values of molecular weights of asphaltene molecules was 1106 - 1707 g/mol., and the weight of molecules of mixture  $A_m$  and bitumen  $A_b$  changed slightly, while the average molecular weight of  $A_o$  increased approximately by one-third (Table 7). The elemental composition data indicate that after thermolysis in all samples, there is a slight decrease in the content of hydrogen atoms by about 1 %, and the content of carbon atoms in the molecules is practically not subjected to change. No less important is the fact that the relative content of heteroatoms in the molecules increased by 0.5 - 1%.

Let us consider the structural changes of asphaltene  $A_o$  molecules. Obviously, such a significant increase in the molecular weight is achieved by increasing the number of structural blocks and, accordingly, first of all, the number of carbon atoms in different structural fragments of the average molecule. Thus, after thermolysis, the value of  $m_a$  increased from 1.8 to 2.45; the number of carbon atoms in aromatic and naphthenic fragments increased by 22 and 15 units, respectively, but the number of carbon of paraffin chains did not change and amounted to 4.35 units (Table 8). Thermolysis resulted in the growth of the total number of cyclic fragments in the asphaltene molecule of  $A_o$  ( $K_t$  increased by 11 units), which are represented by 15 aromatic and 18 saturated rings. Taking into account the increase in the number of heteroatoms in the average molecule with the unchanged share of five-membered cycles ( $q = 0.11$ ) and considering the data on the material balance and the material composition, we can conclude that during the thermolysis of oil, asphaltene molecules mainly undergo condensation reactions with one another, as well as with the fragments of resin components, while the process of breaking the aliphatic chains of molecules is suppressed.

A somewhat different picture is observed in the analysis of structural changes in asphaltene molecules of mixture  $A_m$  (Table 8). The average structural parameters of these molecules changed less significantly than in  $A_o$ ; namely, the number of aromatic carbon atoms increased by 1 unit, and naphthenic decreased by 3 units with the same number of structural units in the molecule. It should be noted that the number of carbon atoms in paraffin  $C_p$  chains decreased by 7 units. Consequently, the molecules of mixture  $A_m$  are primarily prone to the reactions of cyclization of aliphatic fragments (possible route  $k_5$ ), as well as to the reactions of aromatization of naphthenic fragments (dehydrogenation, route  $k_5$ ) and degradation of naphthenic cycles to aliphatic chains (routes  $k_6$  and  $k_9$ ).

Bitumen molecules  $A_b$  behave similarly, which is confirmed by the change in the number of atoms of aromatic (increases by 7 units) and naphthenic (decreases by 1.5 units) carbon

atoms (Table 8). The number of paraffin carbon decreased by 4 units, while the number of structural blocks in the molecule increased by 0.2 units ( $m_a = 1.84$ ). Based on this, we can say that during thermolysis,  $A_b$  molecules mainly participate in condensation reactions with other molecules (inevitable formation of a solid residue, route  $k_9$ ), as well as in dehydrogenation reactions of naphthenic systems (route  $k_9$ ) and cyclization of aliphatic fragments.

As for the relative structural parameters of the average molecules, in all samples, there is an increase in the aromaticity factor by 4 - 9 % and a decrease in the aliphatic carbon fraction by 2 - 7 %, and as the feedstock becomes heavier, the decrease in H/C value becomes more significant and for  $A_b$  reaches 20 %. The share of five-membered rings during thermolysis slightly decreases for molecules  $A_m$  and  $A_b$ , while for  $A_o$ , it remains unchanged. After thermolysis, the degree of substitution of asphaltene molecules of all samples decreased on average by 0.1.

#### 4. Conclusions

As a result of the conducted research, the material balance of thermolysis, the material composition of the initial oil systems and thermolysates were determined, and the changes of average structural parameters of resin and asphaltene molecules before and after thermal treatment of the studied oil samples were described. Material balance data showed that the higher the content of resinous asphaltenes in the feedstock, the larger amounts of gas and coke residue are formed during thermolysis. Thus, thermolysis of initial bitumen is accompanied by the formation of the greatest quantity of gaseous (3,9 %) and solid (2,3 %) products, whereas cracking of initial oil results in the formation of much smaller amounts of gas (1,2 %) and solid residue (0,1 %). The analysis of the material composition of initial oil systems and thermolysates testifies that in the process of thermal cracking, there are reactions of the destruction of resinous components leading to the formation of low-molecular-weight resins and light hydrocarbons, and in parallel condensation reactions promoting the formation of additional amounts of asphaltenes and a solid residue. The most significant changes are observed during oil cracking, where the share of asphaltenes in the liquid thermolysis products increases by 1.5 times, and the content of resins decreases by 1.7 times compared to the initial oil. At the same time, the amount of hydrocarbon components increase by 4.0 %.

Structural group analysis showed that with increasing the share of resinous asphaltene substances in the oil system, the degree of structural changes in the resin molecules increases due to a growth in the frequency of collisions of formed radicals. In this regard, the direction of structural changes in the resin molecules is mainly destructive in nature due to dealkylation reactions and destruction of cyclic systems (routes  $k_2$ ,  $k_4$ ), but, unlike  $C_o$  and  $C_m$ , in  $C_b$ , along with significant destruction of the side chains, there is an increase in the proportion of naphtheno-aromatic cycles, due to dehydrogenation reactions of cyclic systems (route  $k_4$ ), as well as with the introduction into the system of resinous components formed from asphaltenes (route  $k_8$ ).

Thermolysis of raw materials with low asphaltene content leads to a significant increase in the molecular weight of asphaltenes. As the feedstock becomes heavier, the decrease in H/C value for asphaltenes becomes more significant due to the intensification of dehydrogenation reactions (route  $k_9$ ). The content of heteroatoms in asphaltene molecules after thermolysis increases equally for each type of molecule regardless of the composition of the feedstock, which indicates condensation reactions of asphaltenes with fragments containing thermally stable functional groups.

During the thermolysis of oil, condensation reactions mainly take place between asphaltene molecules  $A_o$ , as well as with resinous component fragments, while the destruction of aliphatic chains occurs to a small extent. Asphaltene molecules of the  $A_m$  and  $A_b$  types are primarily prone to cyclization reactions of aliphatic fragments, as well as to dehydrogenation reactions of naphtheno-aromatic systems. For asphaltenes of  $A_m$ , the process is accompanied by degradation of naphthenic cycles to aliphatic chains, whereas for  $A_b$ , the reactions of condensation of asphaltene molecules are concomitant.

Thus, during the thermolysis of heavy hydrocarbon feedstock, the amount of resinous asphaltene substances in the feedstock plays a determining role in the direction of structural changes of high-molecular-weight heteroatomic compounds.

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### **References**

- [1] Ancheyta J, Speight JG. Hydroprocessing of heavy oils and residua. CRC Press: Boca Raton, London, New York, 2007; 346 p.
- [2] Mullins OC, Sheu EY, Hammami A, Marshall AG. Asphaltenes, Heavy Oils, and Petroleomics. Springer: N.Y., 2006; 669 p.
- [3] Sviridenko NN, Krivtsov EB, Golovko AK. Effect of ferrospheres as additives on the composition of cracking liquid products of Mordovo-Karmal native bitumen. Chemistry and Technology of Fuels and Oils. 2016; 52(3): 285-292.
- [4] Sviridenko NN, Krivtsov EB, Golovko AK, Krivtsova NI. Cracking of natural bitumen in the presence of nanosized powders Mo and CuO. Petroleum and Coal. 2016; 58: 732-735.
- [5] Ancheyta-Juarez J, Betancourt-Rivera G, Marroquin-Sanchez G, M. Perez-Arellano A, Maity SK, Cortez MaT, Del Rio-Soto R. An Exploratory Study for Obtaining Synthetic Crudes from Heavy Crude Oils via Hydrotreating. Energy and Fuels. 2001; 15(1): 120-127.
- [6] Gulyaeva LA, Khavkin VA, Shmel'kova OI, Vinogradova NY. Technology of synthetic oil production from heavy oil stock and solid fuels. Chemistry and technology of fuels and oils. 2015; 51(4): 422-429.
- [7] Hidalgo-Herrador J, Vrabik A, Jisa P, Cerny R, Hamernikova J. Hydrovisbreaking of vacuum residue from Russian Export Blend: influence of brown coal, light cycle oil, or naphtha addition. Chemical papers. 2015; 69(8): 1075-1083.
- [8] Kapadia PR, Kallos MS, Gates ID. A review of pyrolysis, aquathermolysis, and oxidation of Athabasca bitumen. Fuel Processing Technology. 2015; 131: 270-289.
- [9] Deng W, Luo H, Gao J, Que G. Stability change of asphaltene in the residue during slurry-phase hydrocracking. Energy & Fuels. 2011; 25(11): 5360-5365.
- [10] Stratiev D, Shishkova I, Dinkov R. Reactivity and stability of vacuum residual oils in their thermal conversion. Fuel. 2014; 123: 133-142.
- [11] Hauser A, Bahzad D, Stanislaus A, Behbahani M. Thermogravimetric Analysis Studies on the Thermal Stability of Asphaltenes: Pyrolysis Behavior of Heavy Oil Asphaltenes. Energy and Fuels. 2008; 22(1): 449-454.
- [12] Chiaberge S, Guglielmetti G, Montanari L, Salvalaggio M, Santolini L, Spera S, Cesti P. Investigation of Asphaltene Chemical Structural Modification Induced by Thermal Treatments. Energy and Fuels. 2009; 23(9): 4486-4495.
- [13] Akmaz S, Gurkaynak MA, Yasar M. The effect of temperature on the molecular structure of Raman asphaltenes during pyrolysis. Journal of analytical and applied pyrolysis. 2012; 96: 139-145.
- [14] Akmaz S, Yasar M. The temporal variation of asphaltene structure during Raman crude oil pyrolysis. Journal of analytical and applied pyrolysis. 2015; 113: 672-679.
- [15] Dmitriev DE, Golovko AK. Transformations of resins and asphaltenes during the thermal treatment of heavy oils. Petroleum Chemistry. 2010; 50(2): 106-113.
- [16] Grin'ko AA, Golovko AK. Thermolysis of petroleum asphaltenes and their fractions. Petroleum Chemistry. 2014; 54(1): P. 42-47.
- [17] Savage PE, Klein MT, Kukes SG. Asphaltene Reaction Pathways. 3. Effect of Reaction Environment. Energy and Fuels. 1988; 2(5): 619-628.
- [18] Zhang C, Lee CW, Keogh RA, Demirel B, Davis BH. Thermal and catalytic conversion of asphaltenes. Fuel. 2001; 80(8): 1131-1146.
- [19] Ancheyta J, Centeno G, Trejo F, Marroquin G. Changes in Asphaltene Properties during Hydrotreating of Heavy Crudes. Energy & Fuels. 2003; 17: 1233-1238.
- [20] Zhang S, Liu D, Deng W, Que G. A Review of Slurry-Phase Hydrocracking Heavy Oil Technology. Energy & Fuels. 2007; 21: 3057-3062.
- [21] Dettman H, Inman A, Salmon S, Scott K, Fuhr B. Chemical Characterization of GPC Fractions of Athabasca Bitumen Asphaltenes Isolated before and after Thermal Treatment. Energy and Fuels. 2005; 19(4): 1399-1404.

- [22] Michael G, Al-Siri M, Khan ZH, Ali FA. Differences in Average Chemical Structures of Asphaltene Fractions Separated from Feed and Product Oils of a Mild Thermal Processing Reaction. *Energy and Fuels*. 2005; 19(4): 1598-1605.
- [23] Ancheyta J, Centeno G, Trejo F, Marroquin G. Changes in Asphaltene Properties during Hydrotreating of Heavy Crudes. *Energy and Fuels*. 2003; 17(5): 1233-1238.
- [24] Trejo F, Ancheyta J, Morgan TJ, Herod AA, Kandiyoti R. Characterization of Asphaltenes from Hydrotreated Products by SEC, LDMS, MALDI, NMR, and XRD. *Energy and Fuels*. 2007; 21(4): 2121-2128.
- [25] Golovko AK, Kam'yanov VF, Ogorodnikov VD. High-molecular heteroatomic components of crude oils of the Timan-Pechora petroliferous basin. *Russian Geology and Geophysics*. 2012; 53(12): 1374-1381.
- [26] Pevneva GS Golovko AK, Korneev DS, Levashova AI. Thermal conversion of heavy oil systems and analysis of structural changes their high components of PMR-method. *Procedia Chemistry*. 2014; 10: 15-19.
- [27] Patrakov YF, Kamyayov VF, Fedyaeva ON. A structural model of the organic matter of Barzas liptobiolith coal. *Fuel*. 2005; 84(2-3): 189-199.

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