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Nitrogen Bases of Resins in Bituminous Oil from the Ashalchinskoye Deposit of the Republic of Tatarstan and Their Transformations during Thermal Treatment

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Abstract

The composition and structure of nitrogenous bases of the resins of bituminous oil from the Ashalchinskoye deposit of Tatarstan are investigated using a complex of analytical methods including elemental and functional analyses, determination of molecular masses, ^1H NMR spectroscopy, structural group analysis, gas chromatography, and mass spectrometry. The nitrogen bases of the resins in oil are analysed before and after their thermal treatment at 450 °C for 30 min in the inert medium. It is established that the nitrogenous bases of the initial resins and “secondary” maltenes are represented by high and low molecular weight compounds. High molecular weight bases prevail in both cases, though their proportion in “secondary” maltenes is much lower. Thermally transformed bases are characterised by lower average molecular weights. This is due to the destruction of alkyl and naphthenic moieties proceeding in the course of thermolysis and resulting in the changes in their structure and the formation of lower molecular weight compounds. As revealed by means of structural group analysis, the mean molecules of a significant part of high molecular weight bases of the “secondary” maltenes are more aromatic due to a decrease in the number of naphthenic cycles and in the number of paraffin carbon atoms in their structural blocks. Low molecular weight bases differ from those of the initial resins in a higher number of naphthenic cycles in the structural blocks of their mean molecules. Alkyl-substituted quinolines and benzoquinolines, naphthoquinolines, naphtho[2,1,8-def]quinolines, thiophenoquinolines, and benzothiophenoquinolines have been identified among the major compounds of initial resins and “secondary” maltenes. The maximum in their distribution falls on alkylbenzoquinolines. The bases of “secondary” maltenes are characterized by a higher relative content of alkylquinolines and alkylthiophenoquinolines. A distinctive feature of the bases of secondary maltenes is also an increased proportion of structures with a lower number of carbon atoms in alkyl substituents.

Keywords: resins, organic nitrogen bases, thermal transformations, content, composition

INTRODUCTION

During recent decades, we are witnessing a sharp decrease in the resources of light and medium-weight oil in the oil-producing branch in Russia. Because of this, non-traditional sources of hydrocarbons are actively brought into development, in particular natural bitumen. The major part of bitumen deposits is concentrated in the territory of Tatarstan. The Ashalchinskoye deposit of bituminous oil is characterized by great

total oil reserves (10 248 thousand t) and recoverable resources (3669 thousand t). This deposit is under industrial development at present. One of the specific features of bituminous oil is the high content of resinous asphaltene components, among which the resins account for more than 70 % [1, 2]. The major part of heteroatoms determined in oil are present in the structure of resinous substances, which brings substantial complications in the treatment of extra-heavy oil using the existing technologies [3]. Because of this, one of the condi-

tions for the development of effective technological decisions for the rational use of bituminous oil is the accumulation of the information on the structural transformations of resinous components in high-temperature processes. The data on the thermal transformations of nitrogen bases (NB) of resins deserve special attention because these compounds have a negative effect on the efficiency of catalytic processes involved in oil processing and on the quality of petroleum products [4].

Results of the comparative investigation of the composition of NB in initial and thermally treated resins in bituminous oil from the Ashalchinskoye deposit in Tatarstan are presented in the work.

EXPERIMENTAL

A sample of bituminous oil with resin content 18.4 mass %, and basic nitrogen (N_{bas}) content 0.12 mass % was used in the work.

The resins were extracted from deasphaltenated oil by means of liquid adsorption chromatography on activated silica gel ASK. A mixture of benzene with ethanol (50 : 50 by volume) was used for the desorption of resins after the preliminary extraction of petroleum oil components into a mixture of *n*-hexane and benzene with the volume ratio 70 : 30 [5]. The content of N_{bas} in initial resins of bituminous oil was 0.44 mass %, therefore, the resins accounted for 67.4 rel. % of NB in oil.

The thermal treatment of the resins was carried out at 450 °C in the inert medium for 30 min. Substantiation of the choice of process conditions was presented in [6]. Thermolysis of resinous components leads to the formation of gaseous (1.1 mass %), solid coke-like (0.9 mass %) and benzene-soluble (98.0 mass %) products, which are represented by "secondary" asphaltenes (22.9 mass %) and maltenes (75.1 mass %) [5].

Isolation of NB from the hexane solutions of initial resins and "secondary" maltenes was carried out according to the procedure based on the consequent use of the following procedures: precipitation of high-molecular bases by gaseous HCl (K-1), additional precipitation of hydrochloric salts soluble in hydrocarbon medium through the interaction with diethylamine (K-2) and extraction of low-molecular NB with the acetate solution of sulphuric acid (K-3) [6]. High-molecular bases K-2 differ from high-molecular bases K-1 by better developed aliphatic substitution of aromatic cores. To simplify the composition, K-1 compounds were separated by means of hot ex-

traction with *n*-hexane into the components that were soluble in hexane (K-1^{hs}) and insoluble (K-1^{his}).

For comparative characterization of the NB of initial resins and "secondary" maltenes, we used the data of elemental and functional analysis, measurement of molecular masses (MM), ¹H NMR spectroscopy, gas chromatography – mass spectrometry (GC-MS), and structural group analysis (SGA).

Determination of the mass concentrations of elements (C, H, S, N) was carried out with the help of an automatic analyzer Vario EL Cube (Elementar Analysensysteme GmbH, Germany). Oxygen content was calculated from the difference between the total content (100 %) and the sum of determined elements. The concentration of basic nitrogen (N_{bas}) was determined by means of nonaqueous potentiometric titration [7]. Average MM were measured by means of cryoscopy in benzene [5].

¹H NMR spectra were recorded with an AVANCE AV 300 NMR Fourier spectrometer (Bruker, Germany), deuterated chloroform was used as a solvent, the tetramethylsilane was the internal standard. The spectra were used to calculate the relative content of protons in different structural fragments of molecules: aromatic (H_a), at the carbon atom of an aliphatic substituent in the α -position with respect to aromatic structures (H_α), in methylene groups (H_β) and in the terminal methyl groups (H_γ) [8].

The data on the distribution of the protons, MM values and elemental composition were used to calculate average structural characteristics of the molecules of NB in samples: K-1^{his}, K-1^{hs}, K-2 and K-3 [9]. The parameters that were determined in calculations included m_a – the number of structural blocks in an averaged molecule; K_o^* , K_a^* , K_n^* – total number, number of aromatic and naphthene cycles in the structural block, respectively; C^* – total number of carbon atoms in a structural block; C_p^* – number of carbon atoms in the paraffin fragments of a structural block; C_α^* – number of carbon atoms in the α -position with respect to aromatic cores; C_γ^* – number of carbon atoms in terminal methyl groups that are not bound with aromatic cores.

The individual composition of NB in K-1^{hs}, K-2 and K-3 was studied by means of GC-MS using a DFS mass spectrometer (Thermo Scientific, USA, the energy of ionizing electrons 70 eV, the temperature of ionization chamber 270 °C, interface temperature 270 °C, injector temperature 250 °C). A DB-5MS column 30 m long, 0.25 mm in diameter, with the DB-5MS phase thickness equal to 0.25 μ m was used for chroma-

tographic separation. The carrier gas was helium with a constant flow rate of 0.8 mL/min. Thermostat program: initial temperature 80 °C (3 min), temperature rise to 300 °C (4 °C/min), exposure at the final temperature for 30 min. Mass spectra were scanned every second within the mass range up to 500 a.m.u. The mass-chromatograms of the compounds were reconstructed using the characteristic ions on the basis of chromatograms over the total ion current with the help of Xcalibur software. Individual compounds were identified using a computer-based library of mass spectra NIST 02.

RESULTS AND DISCUSSION

“Secondary” maltenes differ from initial resins by a decreased concentration of N_{bas} (0.31 mass %) and lower total content of the concentrates of high- and low-molecular NB (23.4 against 37.5 mass %) (Table 1). This is connected with the participation of the NB of initial resins in the formation of coke-like products and “secondary” asphaltenes formed during the thermolysis of oil raw material [10–12]. Though the major part of bases extracted from initial resins and “secondary” maltenes consists of high-molecular compounds (K-1 + K-2), their mass concentration in “secondary” maltenes (22.3 mass %) and the fraction of N_{bas} bound with them (62.3 rel. %) are lower than in the initial sample (36.2 mass % and 71.7 rel. %, respectively). It should be stressed that the amount of K-1 compounds decreases during thermolysis (from 35.6 to 15.9 mass %); on the contrary, the amount of K-2 compounds increases almost by a factor of 10. The source of high-molecular bases in K-2 may be the K-1^{his} compounds, which dominate among the basic K-1 compounds in initial resins. Their mass fraction

and the fraction of N_{bas} bound with them decrease substantially during thermolysis. For the concentrates of low-molecular bases in K-3 of initial resins and “secondary” maltenes, the differences in the yields and relative content of N_{bas} in the structure of their bases are insignificant. All NB samples of “secondary” maltenes have lower MM values than the samples of NB of initial resins of the same names. The observed decrease in MM is due to the structural changes of the basic compounds of initial resins during thermolysis.

According to the data of SGA, the average molecules of high-molecular (K-1^{his}, K-1^{hs}, K-2) and low-molecular (K-3) bases of “secondary” maltenes have smaller sizes than the average molecules of the compounds in the products of initial resins of the same names. This is connected with a decrease in the number of structural units (m_a) and their average overall dimensions characterized by the C^* parameter (Table 2). For all NB samples of “secondary” maltenes, a decrease of the total number (C_p^*) of alkyl carbon atoms in the average structural blocks is observed. Among C_p^* , the number of carbon atoms in methyl group that are remote from the aromatic core (C_i^*) decreases, which is the evidence of a decrease in the amount and/or degree of branching of the substituents. Lower values of the C_α^* parameter point to a decrease in aliphatic substitution of the aromatic core. The sizes of polycyclic structures (K_o^*) change ambiguously. Thus, for the structural units of the average molecule of K-2 and K-3 bases, an increase in their size is observed due to the development of naphthene fragments (K_n^*). The general cyclicity of the structural blocks of the average molecules of the compounds of K-1^{hs} remains constant, while the general cyclicity of the structural blocks of average molecules of K-1^{his}

TABLE 1

Characterization of nitrogen bases of initial resins and “secondary” maltenes

Sample	Initial resins				“Secondary” maltenes			
	MM, a.m.u.	Sample yield, mass %	N_{bas} content in sample, mass %	N_{bas} percentage in resins, rel. %	MM, a.m.u.	Sample yield, mass %	N_{bas} content in sample, mass %	N_{bas} percentage in resins, rel. %
K-1, including:	833	35.6	0.87	70.4	626	15.9	0.87	44.6
K-1 ^{hs}	578	6.3	0.76	10.9	458	5.8	1.33	25.0
K-1 ^{his}	1072	29.3	0.89	59.5	920	10.1	0.61	19.6
K-2	636	0.6	0.99	1.3	507	6.4	0.86	17.7
K-3	383	1.3	2.06	6.2	317	1.1	2.10	7.2

TABLE 2

Calculated values of the structural parameters of nitrogen base molecules in initial resins and "secondary" maltenes

Parameters of average structural blocks	Samples							
	Initial resins				"Secondary" maltenes			
	K-1 ^{his}	K-1 ^{hs}	K-2	K-3	K-1 ^{his}	K-1 ^{hs}	K-2	K-3
m_a	2.3	1.6	1.7	1.4	2.1	1.5	1.5	1.1
K_o^*	10.0	4.6	3.1	2.8	9.2	4.6	3.4	4.2
K_a^*	2.8	2.1	2.3	1.7	2.7	2.1	2.1	1.3
K_n^*	7.2	2.5	0.8	1.1	6.5	2.5	1.3	2.9
C^*	32.6	24.5	24.5	18.8	29.7	23.4	21.6	18.0
C_p^*	2.2	5.9	11.9	7.2	1.9	4.9	7.8	1.7
C_α^*	5.2	3.9	3.9	4.4	4.6	4.0	3.5	3.4
C_γ^*	2.2	2.3	2.5	1.8	1.9	1.8	1.8	1.7

Note. m_a is the number of structural blocks in an averaged molecule; K_o^* , K_a^* , K_n^* is the total number, the number of aromatic and naphthene cycles in the structural block, respectively; C^* is the total number of carbon atoms in a structural block; C_p^* is the number of carbon atoms in the paraffin fragments of the structural block; C_α^* is the number of carbon atoms in α -position with respect to aromatic cores; C_γ^* is the number of carbon atoms in terminal methyl groups that are not bound with aromatic cores.

compounds decreases. This is an additional confirmation of the participation of high-molecular bases of K-1^{his} in the formation of K-2 and K-3 compounds.

Analysis of the results of GC-MS studies of K-1^{hs}, K-2, K-3 compounds extracted from initial resins and "secondary" maltenes showed that the qualitative composition of NB determined in them is practically identical. In both types of resins, they are represented by alkyl-substituted quinolines, benzoquinolines, naphthoquinolines, naphtho[2,1,8-def]quinolines, thiophenoquinolines, benzothiophenoquinolines; the maximum of their distribution hits on alkylbenzoquinolines (Table 3). Nitrogen bases of "secondary" maltenes are distinguished by the higher relative content of alkylquinolines and alkylthiophenoquinolines. It may be assumed that an increase in their fraction in the identified NB as a consequence of the destruction of the inseparable complicated mixture of compounds concentrated in so-called naphthenic hump [11, 13]. It is clearly pronounced in the mass-chromatograms of the compounds of initial resins, but it is almost completely absent in the mass-chromatograms of the types of compounds of the same names in the thermally transformed sample. The mass chromatograms of alkylbenzoquinolines (C_x -BQ) of K-1^{hs} of initial resins and "secondary" maltenes for the ions with the ratio $m/z = 207, 221, 235, 249$ and 263 are shown as an example in Fig. 1.

The nitrogen bases of "secondary" maltenes also differ by the increased fraction of low-mo-

TABLE 3

Composition of nitrogen bases of initial resins and "secondary" maltenes

Compounds	Content with respect to identified structures, %	
	Initial resins	"Secondary" maltenes
Alkylquinolines	0.1	18.8
Alkylbenzoquinolines	68.5	45.2
Alkyldibenzoquinolines	1.7	0.6
Alkylazapyrenes	6.0	2.7
Alkylthiophenoquinolines	22.4	32.7
Alkylbenzothiophenoquinolines	1.3	n/d

Note. n/d – not detected.

lecular homologues among all the identified types of compounds.

CONCLUSION

On the basis of the studies of NB composition in initial and thermally transformed resins of bituminous oil from the Ashalchinskoye deposit, it may be concluded that the NB of initial resins and "secondary" maltenes are represented by high- and low-molecular compounds. High-molecular bases dominate in both samples, though their fraction in "secondary" maltenes is substantially lower. Nitrogen bases of transformed resins are characterized by lower average MM than the products of the

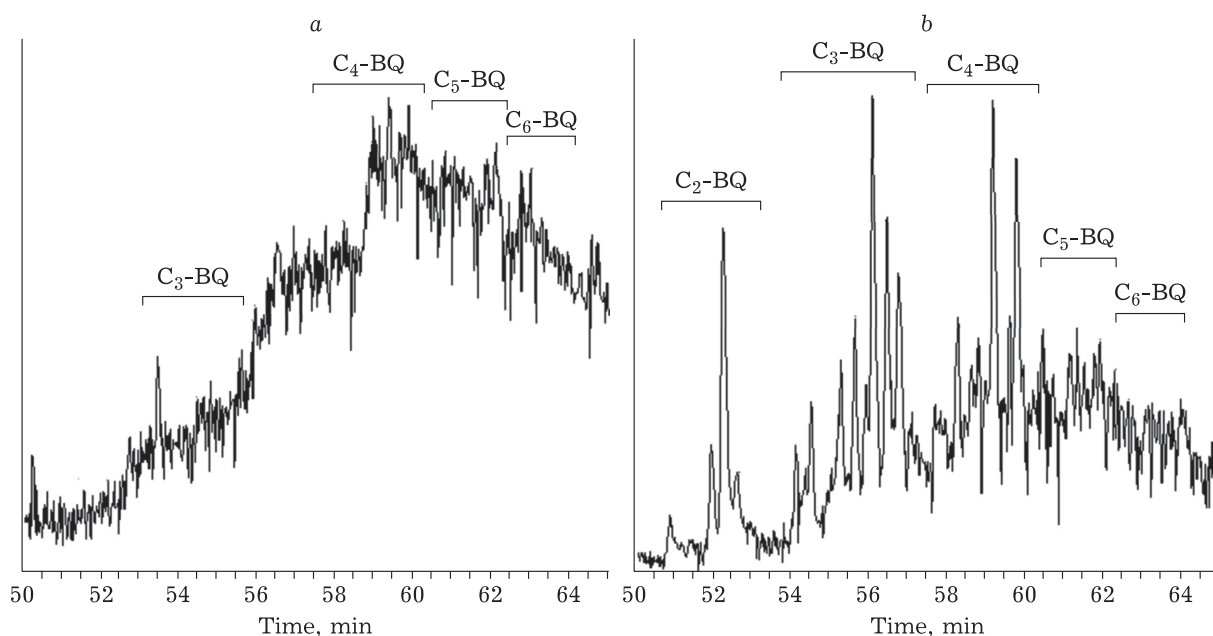


Fig. 1. Mass-chromatograms of C_2 - C_6 -benzoquinolines (BQ) of $K-1^{hs}$ for the ions with the ratio $m/z = 207, 221, 235, 249, 263$ of initial resins (a) and “secondary” maltenes (b).

same names in initial resins, which is connected with the fact that thermolysis involves the destruction of alkyl and naphthene fragments, which leads to the changes in the structure of NB.

A similar set of bases is observed for both samples. This set is represented by the alkyl derivatives of quinoline, benzoquinoline, naphthoquinoline, naphtho[2,1,8-def]quinoline, thiophenoquinoline, benzothiophenoquinoline, and the maximum of distribution falls on alkylbenzoquinolines. A specific feature of the composition of NB of “secondary” maltenes is a higher relative content of alkylquinolines and alkylthiophenoquinolines. This provides evidence that initial resins contain these structures in the bound form, concentrated in so-called naphthenic hump. For thermally transformed NB structures, a higher fraction of low-molecular homologues is typical.

The results obtained in the work are significant for the deepening of our knowledge on the chemical nature of resins in heavy oil systems and for the prediction of the composition of distillate fractions obtained by the thermal treatment of bituminous oil.

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