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Investigation of the Stability of Oil Pyrobitumen by Means of Thermal Destruction

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Abstract

Thermolysis of the samples of pyrobitumen of petroleum from the Usinsk deposit was carried out at a temperature of 160, 200, 250, 300, 450 and 650 °C. Pyrobitumen samples after thermolysis were analyzed by means of IR spectrometry, the elemental composition of the samples was determined, as well as the molecular masses and the structural group characteristics, and the hypothetic structures of average molecules were constructed. Liquid and gaseous products formed as a result of pyrobitumen thermolysis were analyzed by means of GLC and GLC/GAC. On the basis of the data on the thermal stability of saturated aliphatic and cyclic sulphureous fragments and change in the total sulphur content in thermolyzed pyrobitumen, we calculated the amounts of alkyl and thiacyclane sulphur incorporated into the molecules of pyrobitumen.

Key words: oil pyrobitumen, thermolysis, composition of products, structure of pyrobitumen

INTRODUCTION

A trend to weighting the processed oil stock at petroleum refining plants is observed during the recent years. One of the most important problems connected with heavy oil processing is the high content of high molecular mass compounds – resins and pyrobitumen (up to 30 and 15 mass %, respectively). To develop the new methods for processing this kind of raw material, it is necessary to possess the information about the composition and structure of pyrobitumen and resin; this information is obtained using various methods of chemical and thermal destruction (thermolysis).

Thermolysis method is widely used to study the composition and structure of pyrobitumen [1–9]. For instance, the authors of [1] carried out a comparative analysis of the stability of various pyrobitumen species during isothermal thermolysis. The authors of [2] studied the thermal stability of the pyrobitumen of various residues from the atmospheric distillation of heavy raw oil from the deposits of Kuwait. The authors of [3] carried out pyrolysis of pyrobitumen

and studied the products using GC/MS; as a result, they succeeded in identifying thiophene, alkyl thiophene, benzothiophene and alkyl benzothiophene structural fragments in pyrobitumen molecules. The authors of [5] performed thermolysis of pyrobitumen and analyzed the phase that is soluble in *n*-pentane; the authors of [6, 7] carried out pyrolysis at 600 °C for 20 s and analyzed the pyrolyzate by means of GC/MS; in [8] pyrobitumen samples were exposed to thermal destruction at 350 °C for 15 h. The authors of [9] performed thermolysis of malthenes and asphaltenes samples at 350 °C and above, and studied reaction products by means of NMR, IR, and mass spectroscopy. Those authors concluded that there is a metal-porphyrinic fragment in the centre of pyrobitumen molecule, while aromatic and heterocyclic compounds connected through alkyl chains comprise a framework. However, almost all the works mentioned above did not include estimation of the quantitative content of heteroatomic fragments of different types that are incorporated into pyrobitumen molecules (in particular, sulphur-containing ones), pyrobitu-

men species that are the products of thermal destruction were not studied, the amount of sulphurous compounds in liquid thermolysis products was not determined. At the same time, on the basis of the information about the kind and amount of heteroatoms incorporated into the high molecular mass components of petroleum, new approaches to the preparation and processing of heavy oil raw material may be proposed.

The goal of the present work is investigation of the thermal stability of pyrobitumen species of heavy oil and the products of their thermal destruction, in particular determination of the content of different types of sulphur in pyrobitumen species.

In order to study the reactivity of oil pyrobitumen and their changes during thermal destruction, we compiled hypothetical structures of average molecules on the basis of the data of structural group analysis.

EXPERIMENTAL

The subject of investigation was pyrobitumen of heavy high-sulphur petroleum from the Usinsk deposit ($\rho = 966.7 \text{ kg/m}^3$). The physico-chemical characteristics of petroleum are: molecular mass 365 a. m. u., density 966.7 kg/m^3 ; elemental composition, mass %: C 84.94, H 11.98, S 1.98, N 0.63, O 0.47; content, mass %: oil 73.9, tar 18, pyrobitumen 8.1; fractional composition: boiling over point 140°C , 5.0 vol. % boils off at a temperature up to 200°C , and 33.0 vol. % at $200\text{--}350^\circ\text{C}$.

Pyrobitumen species were isolated from petroleum through deposition in excess hexane (40 : 1) for 1 day followed by purification from tar and oil (hydrocarbons) in Soxhlet's apparatus for 16–18 h (Fig. 1).

Thermolysis of pyrobitumen was carried out in closed steel reactors with the volume of 12 cm^3 that were pressurizable up to 150 atm, for 1 h at a required temperature in argon. Process temperature was varied within the range $160\text{--}650^\circ\text{C}$, from the start of pyrobitumen thermal destruction to almost complete their decomposition.

Within this temperature range, destruction of tar and pyrobitumen proceeds due to the rupture of the weakest carbon-sulphur bonds, with sulphur atom present in different func-

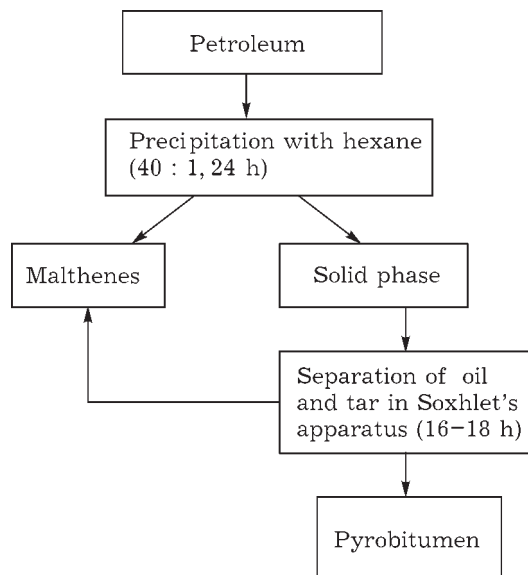


Fig. 1. Scheme of pyrobitumen isolation from petroleum.

tional states. Within the range $160\text{--}250^\circ\text{C}$, mainly the rupture of the bonds between sulphide sulphur and paraffin non-branched rather short chains occurs, within the range $300\text{--}450^\circ\text{C}$ the bonds of sulphide sulphur with long and/or branched alkyl chains takes place, while at $450\text{--}500^\circ\text{C}$ thiacyclane bonds are destroyed.

The most complete destruction of pyrobitumen and tar occurs within temperature range $450\text{--}500^\circ\text{C}$, which corresponds to the destruction of sulphide aliphatic bonds and intense breakage of thiacyclane bonds. Sulphur incorporated into benzo- and dibenzothiophene does not undergo substantial changes with an increase in thermolysis temperature to 800°C at atmospheric pressure and to 700°C at a pressure of 100 atm and above. Sulphur bound with two aromatic nuclei (aryl sulphide) passes into the aromatic state at these temperatures [10, 11].

The composition of the products of thermolysis of initial pyrobitumen species is presented in Table 1.

With an increase in process temperature, the yields of gas, coke and tar increase and reach the maximum at 650°C ; the maximal yield of oil is observed at 160°C (the start of destruction, rupture of bridging bonds C–S, C–O) and 450°C (cracking). Intense coke- and gas formation starts at 450°C , because at lower temperatures the destruction of the main framework of pyrobitumen molecules proceeds

TABLE 1

Composition of the products of pyrobitumen thermolysis

Thermolysis temperature, °C	Concentration, mass %					Pyrobitumen conversion degree, %
	Oil	Tar	Pyrobitumen	Coke	Gas	
160	6.88	0.80	90.83	0.06	1.43	9.17
200	2.96	0.74	92.56	0.04	3.70	7.44
250	0.81	0.60	94.14	0.07	4.38	5.86
300	2.28	1.97	93.42	0.04	2.29	6.58
450	12.82	1.97	28.35	36.70	20.18	71.65
650	0.00	2.20	0.00	39.57	58.23	100

only weakly. The minimal yield of tar, oil and the minimal degree of pyrobitumen destruction are observed at 250 °C.

The analysis of the composition of gaseous thermolysis products (hydrocarbon composition, carbon dioxide) was carried out using a Khromaton chromatograph through a combination of gas-liquid and gas adsorption chromatography with the heat conduction detector. Hydrogen sulphide, methyl- and ethyl mercaptans were determined with a Kristall 2000M gas-liquid chromatograph using a flame photometer detector and a quartz capillary column (30 m × 0.25 mm) with the stationary phase (polydimethylsiloxane SE-54) under the linear temperature rise from 80 to 290 °C (heating rate 15 °C/min). The results of analysis are presented in Table 2.

One can see that the maximal decomposition of pyrobitumen is observed at 450 °C with the formation of approximately equal amounts of methane, ethane and propane. Hydrogen sulphide, ethyl- and methyl mercaptans are formed in small amounts because sulphide sulphur content of initial pyrobitumen samples is not high. Destruction of sulphur bonds in pyrobitumen molecules starts at 200 °C (hydrogen sulphide and mercaptanes are formed), at 300 and 650 °C mercaptans are absent from the gas phase of thermolysis.

The results of elemental analysis of pyrobitumen and coke after thermolysis are listed in Table 3.

For coke samples C_{450}^A and C_{650}^A obtained in the thermolysis of pyrobitumen samples A450 and A650, sulphur content is 7.39 and 1.78

TABLE 2

Composition of the gas phase of pyrobitumen pyrolysis

Components	Yield, vol. %					
	at thermolysis temperature, °C					
	160	200	250	300	450	650
CO ₂	0.10	0.09	0.09	0.35	1.35	0.13
CH ₄	—	—	—	—	10.61	4.8
C ₂ H ₆	—	0.01	—	0.05	11.01	0.18
C ₃ H ₈	—	—	—	—	14.31	—
<i>i</i> -C ₄ H ₁₀	—	—	—	—	2.02	—
C ₄ H ₁₀	—	—	—	—	5.11	—
<i>i</i> -C ₅ H ₁₂	—	—	—	—	0.49	—
C ₅ H ₁₂	—	—	—	—	0.29	—
C ₆₊	—	—	—	—	3.82	—
H ₂ S	—	$1.60 \cdot 10^{-10}$	$4.72 \cdot 10^{-8}$	$6.069 \cdot 10^{-9}$	$1.07 \cdot 10^{-10}$	$1.04 \cdot 10^{-10}$
CH ₃ SH	—	$2.26 \cdot 10^{-10}$	$2.55 \cdot 10^{-10}$	—	$2.01 \cdot 10^{-10}$	—
C ₂ H ₅ SH	—	$2.53 \cdot 10^{-10}$	$1.57 \cdot 10^{-10}$	—	$2.70 \cdot 10^{-10}$	—

Note. In gas samples under analysis the rest is argon.

TABLE 3

Elemental analysis of the samples of initial pyrobitumen and after thermolysis

Samples	Yield, mass %	MM*, a.m.u	Concentration, mass %									
			C	C'	H	H'	N	N'	S	S'	O	O'
A0	—	1633	78.99	100.00	6.33	100.00	1.13	100.00	3.95	100.00	9.60	100.00
A160	90.83	2761	80.61	99.14	7.89	99.00	0.51	44.49	3.69	92.08	7.30	74.95
A200	92.56	3007	79.09	96.42	8.60	99.00	1.81	100.00	3.85	93.86	6.65	66.71
A250	94.14	1887	82.63	93.61	8.40	99.50	1.02	86.31	3.35	81.10	4.60	45.82
A300	93.42	1257	80.89	100.00	8.91	99.56	1.62	100.00	3.12	77.18	5.46	55.57
A450	28.35	512	82.94	86.70	10.35	99.90	2.53	100.00	3.05	63.76	1.13	9.72
A650	Complete destruction of pyrobitumen											

Notes. 1. A0 is initial pyrobitumen, A160–A650 – residual pyrobitumen after thermolysis at temperatures 160–650 °C, respectively. 2. C', H', N', S', O' is content calculated with respect to initial pyrobitumen before thermolysis.

* Molecular mass.

mass %, respectively. The amount of sulphur in coke obtained after thermolysis of pyrobitumen at 450 and 650 °C was 36 and 17.83 rel. %, respectively, of its content in initial pyrobitumen A0. Increased sulphur content in C_{650}^A

with respect to C_{450}^A is connected with the fact that complete destruction of thiacyclane fragments in pyrobitumen molecules does not occur at 450 °C, and a part of them passes into coke. In addition, one can see (see Table 3) that total relative sulphur content (S') decreases with an increase in thermolysis temperature. Relying on the difference between sulphur content in initial pyrobitumen and in the products of thermolysis at 450 and 650 °C – residual pyrobitumen species and coke – we may estimate the content of sulphide and thiacyclane bonds of sulphur in initial pyrobitumen samples A0 [10, 11].

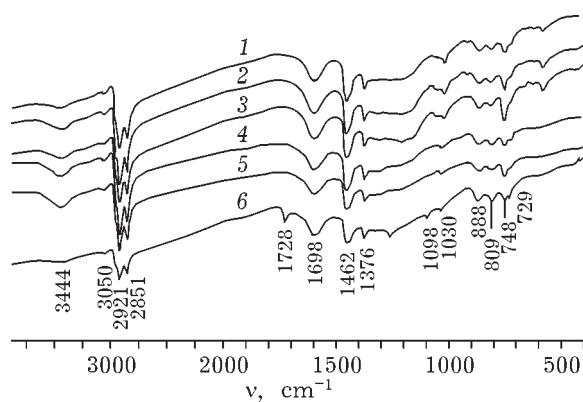


Fig. 2. IR spectra of pyrobitumen: initial and thermolysis products. Samples: A0 (1), A160 (2), A200 (3), A250 (4), A300 (5), A450 (6).

Calculations showed that the amount of alkyl sulphide sulphur accounts for 0.24 rel. % of the total sulphur content in initial pyrobitumen, thiacyclane sulphur – 81.93 rel. %, aryl sulphide, benzo- and dibenzothiophene sulphur – 17.83 rel. %.

TABLE 4

Data on relative optical density of absorption bands (Δ)

ν , cm^{-1}	Samples					
	A0	A160	A200	A250	A300	A450
578	—	0.203	0.219	—	—	—
619	—	0.124	0.129	—	—	—
677	—	0.132	0.151	—	0.147	—
751	0.330	0.420	0.558	0.345	0.450	0.456
810	0.338	0.314	0.326	0.309	0.313	0.439
862	0.475	0.325	0.344	0.296	0.303	0.402
915	—	0.187	0.188	—	—	—
1030	0.964	0.418	0.435	0.303	0.297	0.485
1211	—	0.697	0.390	—	0.588	—
1248	—	0.685	0.751	—	—	0.949
1282	—	—	—	—	—	0.823
1307	0.655	0.680	0.625	0.674	—	—
1375	0.754	0.769	0.781	0.779	0.804	—
1409	—	—	—	—	—	0.700
1600	0.568	0.563	0.565	0.538	0.570	0.717
1726	—	—	—	—	—	0.321
2851	—	1.660	1.639	1.620	1.615	1.219
2921	—	2.248	2.130	2.144	2.068	1.574
2949	—	—	—	—	—	0.928
3052	—	0.124	0.123	—	—	0.318
3430	—	0.297	0.278	0.358	0.502	0.351

The IR spectra of pyrobitumen before and after thermal destruction were recorded within the range 400–4000 cm^{-1} (Fig. 2) with a Nicolet 5700 FT-IR spectrometer in mixture with KBr, at the pyrobitumen/potassium bromide ratio 2/300 (in mg/kg). Processing of IR spec-

tra was carried out using the Omnic 7.2 Thermo Nicolet Corp. software.

Relative optical densities (Table 4) of the most intensive absorption bands of pyrobitumen before and after thermolysis were calculated with respect to the band at 1452 cm^{-1} ,

TABLE 5

Data of structural group analysis of pyrobitumen samples: initial and after thermolysis

Parameters	Samples					
	A0	A160	A200	A250	A300	A450
Molecular mass, a.m.u	1620	2761	3007	1887	1257	512
Number of atoms in the medium molecule:						
C	106.64	185.47	198.19	129.94	84.73	35.39
H	101.73	216.11	256.55	157.25	111.11	52.57
N	1.31	1.01	3.89	1.37	1.45	0.93
S	2.00	3.18	3.62	1.98	1.23	0.49
O	9.72	12.60	12.50	5.43	4.29	0.36
H/C	0.96	1.17	1.29	1.21	1.31	1.49
Ring composition:						
K_t	31.08	31.27	24.66	24.50	9.96	2.37
K_a	11.67	21.30	22.61	12.97	9.53	2.32
K_n	19.41	9.97	2.05	11.53	0.43	0.05
Fraction of five-membered rings (q)	0.18	0.18	0.25	0.16	0.22	0.30
Distribution of C atoms, %:						
f_a	42.71	46.58	43.45	40.56	45.20	44.35
f_n	52.36	21.16	4.49	36.19	2.37	0.00
f_{al}	4.39	32.26	52.06	23.25	52.43	55.65
Number of carbon atoms of different types in the medium molecule:						
C_a	45.55	86.40	86.12	52.70	38.30	15.69
C_n	40.82	39.24	8.89	47.03	2.01	0.05
C_{al}	25.82	59.83	103.18	30.21	44.42	19.69
C_α	16.55	27.27	29.22	19.06	13.07	7.35
C_γ	5.26	9.22	9.68	7.87	4.81	1.65
Number of blocks in molecule (m_a)	3.35	5.30	5.61	3.68	2.87	3.80
Number of carbon atoms of different types in the medium structural unit of the molecule and their ring composition:						
C^*	31.79	34.98	35.30	35.34	29.52	9.32
C_{al}^*	8.77	11.29	18.38	8.22	15.48	5.19
C_α^*	4.94	5.14	5.20	5.18	4.55	1.94
C_γ^*	1.57	1.74	1.72	2.14	1.68	0.43
K_t^*	9.27	5.90	4.39	6.66	3.47	0.62
K_a^*	3.48	4.02	4.03	3.53	3.32	0.61
K_n^*	5.79	1.88	0.36	3.14	0.15	0.01

Note. C_a – aromatic carbon; C_n – carbon in naphthene rings; C_{al} – carbon in aliphatic chains; C_α – carbon in α position to cycles; C_γ – carbon in terminal methyl groups; K_t – total amount of rings; K_a – amount of aromatic rings; K_n – number of naphthene rings; * structural fragments in units.

corresponding to C–H bond absorption in aliphatic chains [12, 13].

All the spectra contain the absorption band of aromatic compounds (1600 cm^{-1}); its relative optical density (Δ) is maximal for the spectrum of A450 sample. Absorption in the region of 1726 cm^{-1} , which corresponds to oxygen-containing groups, is observed only in the spectrum of pyrobitumen sample A450. Relative branching of paraffin chains (Δ for $\nu = 1375\text{ cm}^{-1}$) for all samples obtained after thermolysis within temperature range $160\text{--}300\text{ }^\circ\text{C}$ is higher than that for initial pyrobitumen samples. Relative optical density of the absorption band at 1030 cm^{-1} , corresponding to sulfoxide groups, is maximal for the spectrum of initial pyrobitumen and minimal for the spectrum of A300 sample [14].

The samples of initial pyrobitumen and pyrobitumen after thermolysis were studied by means of structural group analysis (SGA) [15] using the data of elemental analysis, average molecular mass and PMR spectroscopy (Table 5).

The presented data on the amount of fragments of average hypothetic molecules provide evidence that thermolysis of pyrobitumen below $300\text{ }^\circ\text{C}$ involves aggregation reactions (molecular mass and the number of carbon atoms in saturated and aromatic structures increase), above $300\text{ }^\circ\text{C}$ destruction processes start (the amount of aromatic rings decreases, saturated rings disappear almost completely, carbon content of aliphatic chains and molecular mass decrease). The minimal conversion degree is observed at $250\text{ }^\circ\text{C}$ (see Table 1); the amounts

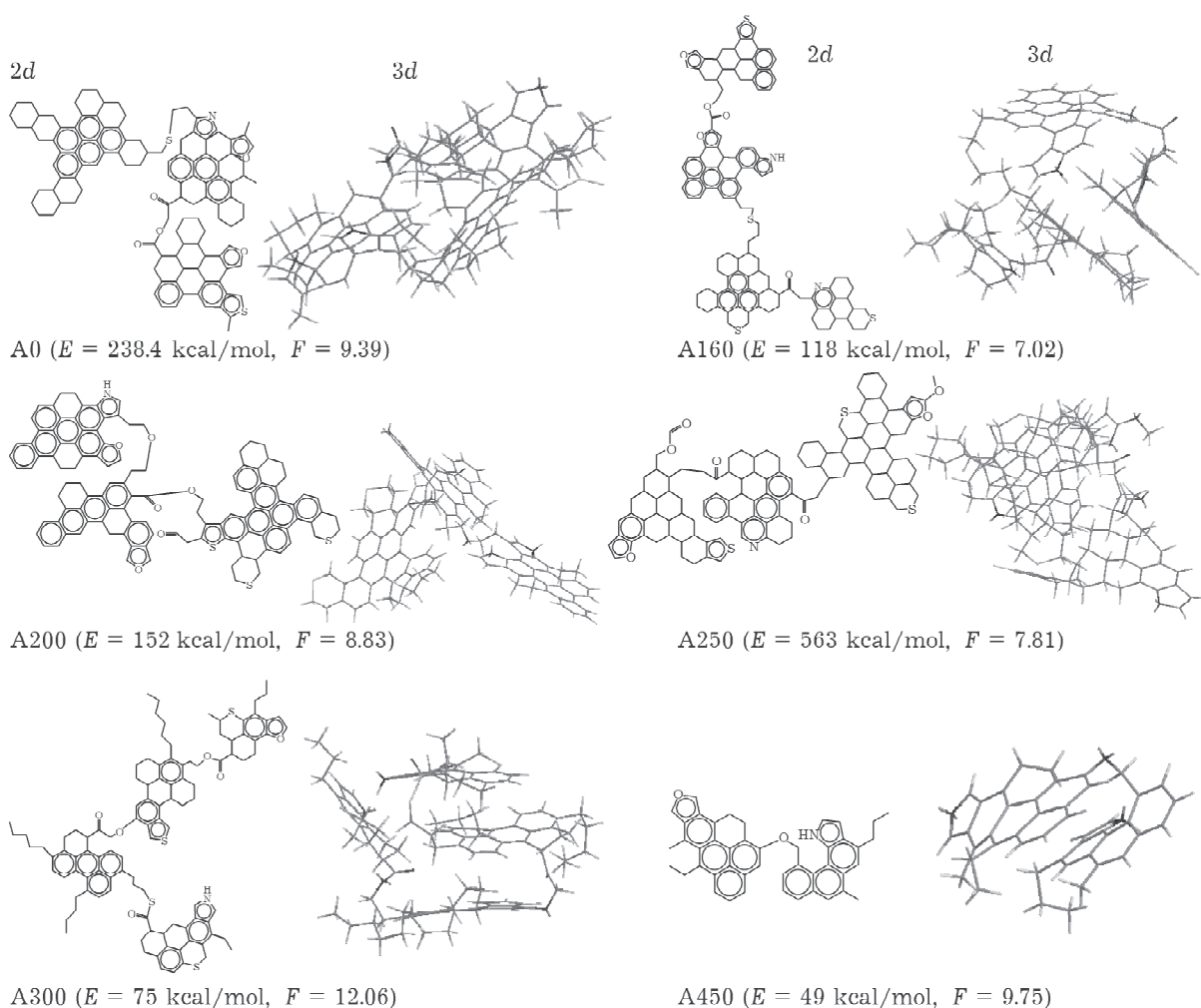


Fig. 3. Hypothetic structures of the medium molecules of pyrobitumen before and after thermolysis (2d and 3d images). E – total (steric) energy of a molecule, F – coefficient of the deviation of characteristics of the constructed structural model of pyrobitumen molecule from experimental data.

of saturated and aromatic rings and carbon atoms in the structure of the molecule are comparable in pyrobitumen samples A250.

Construction of the average structures of pyrobitumen molecules and calculation of their minimal steric energy were carried out with the help of the software developed at the IPC, SB RAS [16], based on the approach described in [17]. About 1000 hypothetical structures of average molecules were constructed, and their full steric energies (E) were calculated by means of molecular dynamics. The structures with the smallest deviation (F value) between calculated and experimental parameters were chosen from a large set of structures constructed.

The constructed structures of pyrobitumen molecules, both initial and formed after thermolysis, with minimal energies and the least deviations (2d and 3d images) are shown in Fig. 3.

One can see that the steric energy of molecules decreases with a decrease in the number of naphthene rings in pyrobitumen molecules; pyrobitumen (A450) molecules with the chain-packed spatial location of structural units have the least steric energy. An average molecule of pyrobitumen sample A250 is the least stable one.

The liquid products of pyrobitumen thermolysis – oils – were analyzed on a GC/MS-QP5050 Shimadzu quadrupole system, using the MIM (multiple ion monitoring) procedure, scanning the mass chromatograms over characteristic ions in the temperature programming mode, with a capillary quartz column DB5-MS (30 m × 0.32 mm). The results were processed using the GCMS Postrun Analysis Program.

The content of benzo-, dibenzothiophene and benzonaphthothiophene was determined with an internal standard in oils formed after thermolysis

(deuteronaphthalene was used as the additive) on the basis of corresponding characteristic ions (m/z 134–175 for benzothiophene species, 184–240 for dibenzothiophene species and 234 for benzonaphthothiophene species) (Table 6).

Bare-ring benzothiophene is absent from all the samples of oil after thermolysis but its alkyl derivatives were discovered in the sample obtained at 450 °C, while dibenzothiophene species are formed in oil even at 250 °C. At a temperature of 450 °C, we observe the maximal yield of oil in which dibenzothiophene content exceeds that of benzothiophene by a factor of 3.4; small amounts of benzonaphthothiophene species are formed. Analysis of thermolysis oil by means of GC with flame photometric detector also showed the absence of benzothiophene structures, except for the samples obtained at 650 °C.

By means of GC-MS, we detected C_4 and higher alkyl naphthalenes, phenanthrene and alkyl phenanthrene, C_{12} and higher alkyl benzenes in thermolysis oil; the content of these species increases with an increase in thermolysis temperature. In oil obtained at 450 °C, we detected pyrene, benzopyrene and perylene structures. Paraffins are present in all the samples of thermolysis oil, starting from C_{12} to C_{30} and higher. Olefins were detected in thermolysis oil within the range 160–300 °C (from C_{12} to C_{30} and higher) in amounts not higher than 2.02 mass %. In oil samples obtained at 450 °C, olefin content is minimal (0.13 mass %). The formed paraffin structures are incorporated into aliphatic alkyl chains connected with the naphthene aromatic framework of pyrobitumen molecules containing three- and four-nuclear condensed aromatic fragments.

TABLE 6

Content of aromatic sulphureous compounds in oils obtained by thermolysis of pyrobitumen

Thermolysis temperature, °C	Total content of aromatic sulphureous structures, mass %		
	Benzothiophene	Dibenzothiophene	Benzonaphthothiophene
160			
200			
250		0.00170	
300		0.0169	
450	0.0303	0.104	0.00340

CONCLUSION

Thus, two temperature ranges corresponding to the maximal conversion of pyrobitumen are observed in the process of pyrobitumen thermolysis: 160–200 and 450–650 °C. Within temperature range up to 300 °C, destruction of C–S and C–O (including bridging) bonds occurs, and radicals are formed; as a result of their recombination, pyrobitumen molecules are likely to get larger (aggregation), and molecular mass increases. At a temperature of 300 °C, intense destruction of stronger carbon-heteroatom bonds and

C–C bonds starts, which leads to a decrease in molecular mass; complete decomposition of pyrobitumen starts at a temperature of 650 °C. Decomposition of sulphide structures incorporated in pyrobitumen molecules starts at 200 °C from the rupture of alkyl sulphide bonds. The major fraction of sulphur (81.93 rel. %) is present in pyrobitumen molecules in thiacyclane fragments, and a smaller part (17.83 rel. %) is present in aromatic fragments. According to the data of the chromatographic analysis of oil species formed during pyrobitumen thermolysis, the content of dibenzothiophene structures in pyrobitumen is higher than that of benzothiophene and benzonaphthothiophene structures.

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