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Changes in the Molecular Structure of Resins and Asphaltenes of Natural Bitumen during Thermal Cracking

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Abstract

The results of exploring cracking of high-sulphur bitumen (sulphur content of 3.7 %) from the Mordovo-Karmalskoye field with a mass content of fractions boiling out to 200 °C of 6.7 % are presented. The yields of gaseous, liquid, and solid products were determined at 450 °C and process time of 60–120 min. The hydrocarbon composition of liquid products from cracking was analysed. The effect of bitumen thermal treatment length on changes in molecular structures of high molecular mass heteroatomic compounds (resins and asphaltenes) was investigated. It was found that at cracking time of 100 min, molecules of asphaltenes of bitumen from the Mordovo-Karmalskoye field became larger due to an increase in the number of naphthenic rings. Whereas at 120 min, asphaltenes decomposed and got more aromatized.

Keywords: natural bitumen, cracking, hydrocarbons, resins, asphaltenes, molecular structure

INTRODUCTION

Heavy oils and natural bitumens play an increasingly significant part to meet the global demand for hydrocarbon energy resources. Currently, as a rule, they are initially transformed into synthetic oils, from which then light oil products and industrial chemicals are produced [1, 2]. One of the main problems of processing heavy hydrocarbon materials is related to significant contents therein of high molecular mass heteroatomic compounds, i.e. asphaltenes and resins prone to coke generating and catalysts poisoning [3, 4].

Search for efficient procedures of processing and further using conversion products of heavy oil or natural bitumen is based on the ideas, in which way temperature and catalyst nature have an effect on various functional groups in the structure of species of resins and asphaltenes and their decomposition [5–8]. This information is required to more deeply understand changes that occur in resins and asphaltenes in thermal and catalytic cracking processes, to select optimum schemes for modernization of setups and determine modes of heavy hydrocarbon raw materials processing at oil processing enterprises [8–11].

The present work goal is the examination of the effect of the cracking duration on the composition of liquid products and changes in the molecular structure of resins and asphaltenes of natural bitumen.

EXPERIMENTAL

Research object

Bitumen from the Mordovo-Karmalskoye field (Tatarstan Republic) is charactrised by high contents of resinous-asphaltenic com-

TABLE 1

Characteristics of bitumen from Mordovo-Karmalskoye field (initial boiling point, IBP = 111 °C)

Composition	Content, mass %
Elemental:	
C	81.5
H	11.6
S	3.7
N	1.2
O	2.0
H/C	1.71
Componential:	
Oils	70.3
Resins	24.5
Asphaltenes	5.2
Fractional:	
IBP of 200 °C	6.70
IBP of 200–360 °C	34.6
Residue (IBP >360 °C)	58.7

pounds (29.7 mass %) and total sulphur (3.7 mass %), and also by a low concentration of fractions boiling out to 200 and 360 °C (41.3 mass %). Table 1 gives raw materials synopsis.

Experimental conditions

Bitumen cracking was carried out in an autoclave with a capacity of 12 cm^3. The mass of bitumen loaded into the reactor was 7 g. the Experiments were performed in air at 450 °C and a duration of 60, 80, 100, and 120 min.

The mass of the reactor prepared to cracking without a sample and with it was recorded during the experiments. After thermal treatment of natural bitumen, the yield of gaseous products was determined according to the mass loss of the reactor with the sample after the removal of gaseous products from the solution. Afterwards, the liquid products of cracking were collected and the reactor was rinsed with chloroform and weighed. The resulting difference between the mass of the reactor prior to the experiment and after was determined as the solid products “coke”.

Determination of material composition of liquid products

The content of asphaltenes was determined as follows. A sample of natural bitumen was diluted with *n*-hexane in a volume ratio of 1 : 40, the solution was aged for 1 day, the fallen precipitate was filtered off, placed to a paper cartridge and rinsed with hexane from oils and resins in a Soxhlet apparatus. Afterwards, asphaltenes therefrom were washed out with chloroform and dried until constant mass.

The hexane solution was attached to natural bitumen, solvent excess was evaporated, the remaining part of maltenes were applied onto a layer of activated silica gel (ASG) (1 : 15 ratio), the resulting mixture of silica gel with the adsorbed material was loaded into the Soxhlet extractor and petroleum oils were washed out with n-hexane, resins – by a mixture of ethanol and benzene (1 : 1) at boiling temperatures of these solvents. After the removal of the alcohol-benzene solvent, there was determined the content of silica gel resins (STO 1246-2011).

Determination of group composition of oils

The group composition of oils in the initial raw materials and products of its cracking was determined using liquid-adsorption chromatography over activated Al_2O_3 with 3 mass % of water (II degree of activity by Brockmann). The chromatographic column (75 × 1.8 cm) was filled with a sorbent by the wet method in a mass ratio of sample/sorbent of 1 : 80. The sample was mixed with hexane and evenly distributed over the entire surface of the sorbent. Aftewards, fractions of saturated, mono- and biaromatic hydrocarbons (HC) were isolated using n-hexane, triaromatic HC were eluted with a mixture of hexane/benzene (3 : 1 by volume), polyaromatic - with a mixture of alcohol/benzene (1 : 1). Monitoring over the separation of HC of different classes was carried out on the electronic absorption spectra of eluates, taken on Specord UV-vis spectrometer. Losses during distillation of solvents from eluates did not exceed 2.5 mass %.

Sulphur determination

The total sulphur content in the samples under study was determined by the X-ray fluorescence energy dispersive method using SPECTROSCAN S device (GOST R 51947-2002) that provided a measuring range of 0.002–5 %.

Structural-group analysis of resin and asphaltene molecules

Resins and asphaltenes isolated from natural bitumen and cracking products were examined by means of structural-group analysis (SGA) according to a procedure based on the joint use of the results of determining the elemental composition, molecular mass (MM), and PMR spectroscopy data (proton magnetic resonance) [12].

Elemental analysis of resins and asphaltenes of the initial bitumen and cracking products was performed using Vario EL Cube CHNS analyzer. Molecular masses were measured by cryoscopy in naphthalene using the “Krion” instrument (Institute of Inorganic Chemistry SB RAS, Novosibirsk). The PMR spectra were taken on Avance-AV-300 Fourier spectrometer using deuterochloroform as a solvent, the internal standard is hexamethyldisiloxane with concentrations of resins and asphaltenes of 1 %.

RESULTS AND DISCUSSION

Bitumen cracking

Table 2 presents material balance and physical composition data of liquid products of bitumen cracking. It can be seen that cracking for 60 min leads to condensation hydrocarbon and heteroorganic compounds of oils in resin, oil contents decrease by 4.1 mass %, resin concentrations increase by 2.9 mass %. With increasing the duration of cracking to 80 min, resin decomposition increases and additional amounts of gas and coke are generated (the total yield of 2.3 mass %). Herewith, the oil content is 1.7 mass % lower than that in the initial bitumen. When the cracking duration is 100 min, resin decomposition increases by 6.6 % and additional amounts (2.6 mass %) of oily components are generated.

There is the deep decomposition of resins and asphaltenes during bitumen cracking for 120 min and their contents are reduced by 12.9 and 2.6 mass %, respectively, compared to the initial bitumen. However, the yield of oily components decreases by на 4.9 mass %, which is due to higher yields of side products, *i.e.* gas and coke (totally over 20 mass %). Apparently, with increasing coke amounts, deep decomposition reactions of bitumen components proceed on its surface and gaseous compounds are produced.

To deeper explore the process, group analysis of oils was carried out (Table 3). It can be seen that upon the cracking duration of 60 min, the content of oils decreases by 4.1 mass %, probably because of condensation reactions of their components. There is the formation of bi- and triaromatic HC, the content of which increases by 5.1 and 3.1 mass %, respectively; the content of saturated compounds decreases by 3.5 mass %.

With an increase in the cracking duration to 80 min, the content of oily components decreases by 1.7 mass %. Herewith, the trend of changing the composition of oily components remains. The fraction of monoaromatic hydrocarbons decreases and the content of bi - and triaromatic HC increases. With the cracking duration of 100 min, the yield of oils increases by 2.6 mass % at the expense of bi- and triaromatic HC, the fraction of which increases by 6.7 and 3.3 mass %, respectively, compared to the initial bitumen. The quantity of polyaromatic HC decreases by 4.2 mass % in relation to the initial bitumen.

TABLE 2

Componential composition of bitumen thermal cracking products

Bitumen sample	Composition, mass %				
	Oils	Resins	Asphaltenes	Gas	Coke
Initial	70.3	24.5	5.2	0	0
After cracking with duration, min:					
60	66.2	27.4	4.8	0.6	1.0
80	68.6	23.7	5.4	0.9	1.4
100	72.9	17.9	5.4	1.8	2.0
120	65.4	11.6	2.6	14.2	6.2

TABLE 3

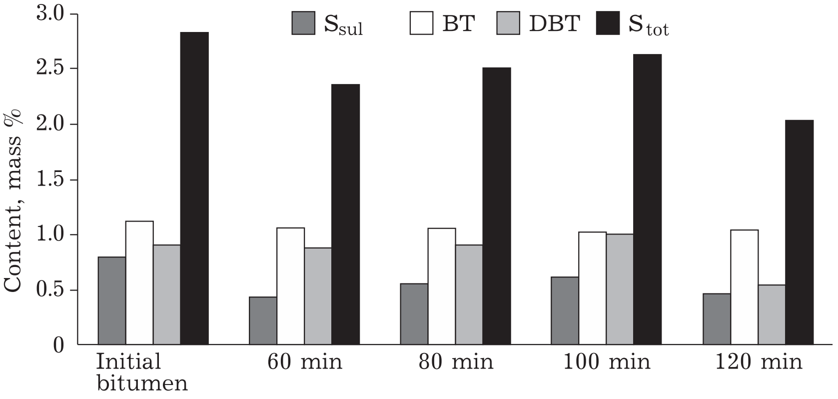
Hydrocarbon (HC) composition of oils of natural bitumen cracking products (450 °C)

Bitumen sample	Yield of oils, mass %	Content of HC, mass %				
		Saturated	Aromatic			
			Mono-	Bi-	Tri-	Poly-
Initial	70.3	24.9	9.3	5.8	18.2	12.1
After cracking with duration, min:						
60	66.2	21.4	8.0	10.9	21.3	4.6
80	68.6	21.8	7.9	11.7	21.6	5.6
100	72.9	23.2	7.8	12.5	21.5	7.9
120	65.2	21.0	7.2	7.4	19.6	10.0

With the cracking duration of 120 min, the yield of oils decreases by 5.1 mass % compared to the initial bitumen. There is the deep decomposition of resins and oily components. At the same time, with increasing the time from 100 to 120 min, the content of saturated components decreases by 3.9 mass %, mono- and polyarenes – by 2.1 mass %. Due to the deeper decomposition of resinous components, there is an increase in the contents of bi- and triaromatic compounds by 1.6 and 1.4 mass %, respectively.

As can be seen from the data in Table 2, cracking with a duration of 60 min is accompanied by an increase in the content of resinous components. As it follows from analysis of the data regarding the hydrocarbon composition of oils, an increase in the amount of resins in cracking products is due to condensation of polyaromatic components. It can be assumed that the main products of decomposition of resins are biaromatic HC, the content of which increases with rising the cracking duration from 60 to 100 min (see Table 3).

Benzothiophenes (BT) and dibenzothiophenes (DBT) prevail in oils of the initial bitumen (Fig. 1). With bitumen cracking for 60 min, the total sulphur content in oils is reduced by 0.46 mass % due to sulphide sulphur (0.37 mass %) and insignificant degradation of BT and DBT (0.06 and 0.03 mass %, respectively.) In case of 80 min of cracking, the total sulfur content increases by 0.14 mass %, and the distribution of sulphur compounds in com-



	Initial bitumen	60 min	80 min	100 min	120 min
▩ S_{sul}	0.80	0.43	0.55	0.61	0.46
☐ BT	1.12	1.06	1.06	1.02	1.04
▨ DBT	0.91	0.88	0.90	1.00	0.54
■ S_{tot}	2.83	2.37	2.51	2.63	2.04

Fig. 1. Contents of series of sulphur compounds in oils of the initial bitumen and cracking products: S_{sul} – sulphide sulphur, BT – benzothiophenes, DBT – dibenzothiophenes, S_{tot} – total sulphur.

parison with 60 min of cracking is as follows: the content of DBT increases (by 0.02 mass %). That of BT remains unchanged, while of sulphide sulfur increases by 0.12 mass % due to the decomposition of resinous components.

When the cracking duration is 100 min, this trend remains and the total sulphur (sulphide and DBT) content increases in the composition of oils. With increasing the duration of cracking to 120 min, the sulphur content in oils is reduced by 0.79 mass % compared to the initial bitumen. The content of BT in all experiments decreases slightly.

Structural group analysis of resins and asphaltenes

To determine the main trends of decomposition of high-molecular-mass components, SGA of resins and asphaltenes isolated from the initial bitumen and cracking products was performed. Tables 4 and 5 give the main calcu-

TABLE 4

Structural-group characteristics of molecules of asphaltenes of bitumen from Mordovo-Karmalskoye field and products of its cracking

Characteristics	Initial bitumen	Liquid products of cracking with duration of, min			
		60	80	100	120
Average molecular mass, amu	1921	1293	1545	1668	820
Elemental composition, mass %					
C	81.2	79.9	81.1	80.4	79.1
H	8.3	8.0	8.1	8.7	6.4
N	2.2	2.0	1.6	2.1	1.5
S	6.5	6.0	6.0	4.7	6.3
O	1.8	4.1	3.1	4.1	6.7
H/C atomic ratio	1.22	1.20	1.20	1.29	0.95
Number of atoms in average molecule:					
C	130.1	86.1	104.5	111.7	54.1
H	157.4	102.2	124.8	143.6	51.8
N	3.1	1.9	1.8	2.5	1.6
S	3.9	2.4	2.9	2.5	1.6
O	2.2	3.4	3.0	4.2	3.4
Number of rings:					
K_{tot}	24.3	15.7	18.3	21.2	10.7
K_a	14.7	10.1	12.2	10.8	8.7
K_{sat}	9.6	5.6	6.1	10.4	2.0
Fraction of five-membered rings, q	0.21	0.22	0.20	0.26	0.2
Number of units in molecule, m_a	4.0	3.0	3.4	6.6	2.4
Degree of substitution of aromatic rings, σ_a	0.54	0.50	0.53	0.36	0.36
C atom distribution, %:					
f_a	43.1	45.5	46.4	54.0	65.0
f_{napht}	29.9	26.1	23.0	25.5	14.0
f_{par}	27.0	28.4	30.6	20.5	21.0
Number of different type atoms in average molecule:					
C_a	56.1	39.1	48.4	60.3	35.2
C_{napht}	39.0	22.5	24.1	28.4	7.5
C_{aliph}	35.0	24.4	32.0	23.0	11.4
C_α	19.4	12.7	16.8	16.8	8.2
C_γ	7.8	4.4	4.3	5.3	1.7

TABLE 5

Structural-group characteristics of molecules of asphaltenes of bitumen from Mordovo-Karmalskoye field and products of its cracking

Parameter	Initial bitumen	Liquid products of cracking with duration of, min			
		60	80	100	120
Average molecular mass, amu	743	773	696	768	454
Elemental composition, mass %:					
C	80.2	80.5	79.9	80.8	81.3
H	8.6	9.0	8.9	8.0	8.2
N	1.2	0.7	1.2	1.6	1.1
S	5.2	5.8	5.0	4.7	5.5
O	4.8	4.0	5.0	4.9	3.9
H/C atomic ratio	1.28	1.34	1.33	1.19	1.21
Number of atoms in average molecule:					
C	49.7	51.9	46.4	51.7	30.8
H	63.1	68.7	61.7	60.8	36.8
N	0.6	0.4	0.6	0.9	0.4
S	1.2	1.4	1.1	1.1	0.8
O	2.2	1.9	2.1	2.4	1.1
Number of rings:					
K_{tot}	10.8	8.7	8.4	11.6	5.4
K_a	3.8	4.4	3.7	5.0	3.5
K_{sat}	7.0	4.3	4.7	6.6	1.9
Fraction of five-membered rings, q	0.20	0.21	0.22	0.19	0.19
Number of units in molecule, m_a	1.7	1.8	1.7	1.9	1.6
Degree of substitution of aromatic rings, σ_a	0.63	0.60	0.61	0.57	0.47
C atom distribution, %:					
f_a	31.1	35.6	32.5	39.3	49.9
f_{napht}	58.1	33.4	41.6	51.9	24.1
f_{par}	10.8	31.0	25.9	8.8	26.0
Number of different type atoms in average molecule:					
C_a	15.4	18.5	15.1	20.3	15.4
C_{napht}	28.9	17.3	19.3	26.8	7.4
C_{aliph}	5.4	16.1	12.0	4.6	8.0
C_α	7.3	8.1	6.9	8.3	5.5
C_γ	3.8	4.0	3.7	3.3	1.8

lated parameters of mean molecules of resins and asphaltenes. The number of carbon atoms: C_{arom} and C_{napht} are in aromatic and naphthenic rings, respectively; C_{alif} is in aliphatic fragments, C_α is in the α-position to the aromatic ring, C_γ is in the γ-positions and further from the aromatic ring. The number of rings: K_{tot} is total, K_a is aromatic, K_{sat} is saturated. The fraction of carbon atoms: f_a is in aromatic; f_{napth} and f_{par} are in naphthenic and paraffinic fragments, respectively.

According to SGA data, the average molecule of asphaltenes of the initial bitumen has a molecular mass of 1921 amu and consists of four units (see Table 4); it contains 24 rings, in other words, 15 aromatic and 9 naphthenic ones. The H/C atomic ratio is 1.22. A significant number of heteroatoms in the composition of the average molecule should be noted. There are two oxygen atoms, four sulfur atoms, and three nitrogen atoms.

The average structure of asphaltene molecules changes during bitumen cracking for 60 min. The MM of asphaltene molecules decreases from 1921 to 1293 amu; the number of structural units – from four to three; the total number of rings – from 24 to 16 (due to aromatic and naphthenic ones). The number of carbon atoms in aliphatic fragments (C_{alif}) decreases from 35 to 24.4, and their length (C_γ) – from 7.8 to 4.4. For example, at 60 min of bitumen cracking, asphaltene molecules decrease due to reducing the number of units, the molecule itself becomes more condensed, the number of aliphatic fragments is reduced.

With increasing bitumen cracking duration to 80 min, the average molecular composition of asphaltenes undergoes the following changes: MM increases to 1545 amu. the number of units – from 3 to 3.4, the total number of rings – from 15.7 to 18.3, the number of carbon atoms in aliphatic fragments – from 24.4 to 32.0, carbon atoms distribution in aromatic rings of the average asphaltene molecule, $f_a = 46.4$ %. These changes are due to the fact that decomposition, which prevails over the condensation process with 80 min of cracking, promotes the addition of radicals formed during the decomposition of resins and oily components to asphaltene structures and the formation of larger molecules.

During cracking for 100 min, the enlargement process of the average molecule of asphaltenes continues. The molecular mass increases until 1668 amu, which by 123 amu higher than with 80 min of cracking, due to an increase in the number of C and N atoms in the composition of the average molecules of asphaltenes by 7.2 and 18.8, respectively. The number of units increases from 3.4 to 6.6, and their size decreases compared to the results of cracking for 80 min, which is probably due to condensation of oils and resins with the formation of asphaltenes. The total number of rings in the average molecule of asphaltenes increases by 2.9 due to increasing naphthenic rings (by four) and partly because of cyclization reactions of aliphatic fragments (C_{aliph}), the number of which decreases (by nine).

With the duration of cracking of 120 min, there is the decomposition of all components of bitumen (see Table 2). There is a decrease in MM of the average molecule of asphaltenes from 1668 to 820 amu, in the number of units therein – from 6.6 to 2.4. The fraction of carbon atoms in aromatic rings continues increasing: $f_a = 65$ %, the total number of cycles in the molecule reaches 11 (nine aromatic and two naphthenic). The minimum number of carbon atoms in aliphatic fragments (11) attests to deep decomposition of asphaltene molecules. Thus, at 120 min of cracking, the average structures of asphaltene molecules are subjected to deep degradation due to dealkylation and aromatization reactions.

The average molecule of resins of the initial bitumen with MM of 743 amu mainly consists of naphthenic and aromatic rings. The content of aromatic carbon atoms (C_a) is only 1/3 of the total number of carbon atoms and the fraction of carbon atoms in aromatic rings is low (31.1 %). The average resin molecule is predominantly two-unit, the total number of rings is 10.8 (3.8 – aromatic, 7.0 – naphthenic). The low H/C ratio (1.28) is due to high contents of rings and their significant substitution (σ_a). It is also worth noting that there are two oxygen, one sulphur, and nitrogen atoms.

The content of resins during bitumen cracking for 60 min increases (see Table. 2) due to condensation reactions of oily components, and also sulphur compounds, *i.e.* sulphides and DBT. The MM of resins increases (up to 773 amu) and the total number of rings is reduced to nine (due a reduction in naphthenic C 7.0 to 4.3 and a slight increase in aromatic C from 3.8 to 4.4). The number of carbon atoms in aliphatic fragments (C_{aliph}) increases by 11 due to condensation of oil components, which also indicates an increase in the H/C ratio to 1.34 (0.06). Increasing the sulphur content in the composition of average molecules of resins from 1.2 to 1.4 % is due to the transition of sulphide sulphur and DBT (see Fig. 1), as evidenced by an increase in the fraction of five-membered rings. Herewith, it can be seen (see Table. 3) that oils are enriched with bi- and three aromatic components due to partial decomposition of resins and asphaltenes.

During the cracking duration of 80 minutes, the structure of the average resin molecule changes slightly. The MM decreases (from 773 to 696 amu) and the number of rings (up to 8.4) and units remains unchanged (1.7). The number of carbon atoms in the aliphatic fragments (C_{aliph}) decreases from 16.1 to 12, which also points to the slight decomposition of resin fragments compared to bitumen cracking for 60 min. In the composition of liquid products, the fraction of oils increases due to bi- and polyaromatic hydrocarbons. Apparently, radicals generated during the decomposition of resins and asphaltenes form components of oils.

With increasing the cracking duration to 100 min, the average MM of resins of liquid products increases from 696 to 768 amu and the content of C atoms – by 5.5, and H species decreases by 0.9. The number of rings rises by 3.2 (to 11.6) due to one aromatic and two naphthenic rings, whereupon the fraction of carbon atoms in aromatic rings (f_a) increases by 6.8 %. The number of carbon atoms in aliphatic fragments (C_{aliph}) decreases (from 12 to 4.6), as a consequence, there is a decrease in H/C (from 1.33 to 1.19). The quantity of oxygen and nitrogen in the composition of the average molecule increases slightly.

Upon the cracking duration of 120 min, the MM of the average molecule of resins is reduced from 768 to 454 amu and the number of rings – from 11.6 to 5.4 (from 5.0 to 3.5 K_a and from 6.6 to 1.9 K_{sat}), units – from 1.9 to 1.6. Almost 50 % of carbon atoms (f_a) is located in aromatic rings. The amount of carbon in aliphatic fragments increases from 4.6 to 8 probably due to the cleavage of naphthenic cycles. In liquid products, there is a decrease in the content of oils (5.1 mass %), resin (12.9 mass %), and asphaltenes (on 2.6 mass %) (see Table 2). In liquid products, there is a decrease in the number of aromatic structures (by 3.2 mass %), and in asphaltenes and resins, the fraction of C atoms increases in aromatic cycles (f_a) in the composition of the average molecule (by 21.9 and 18.8 %, respectively) increases, and the number of naphthenic structures decreases more than twice. This points to the progression of aromatization reaction of resin and asphaltene molecules and the formation of coke from asphaltenes.

CONCLUSION

Thus, with increasing the duration of cracking of bitumen from the Mordovo-Karmalskoye field (450 °C, 60–120 min), gas and coke yields increase. During thermal treatment for 60 and 80 min, condensation reactions prevail and the content of oils decreases by 4.1 and 1.7 %, respectively, due to polyaromatic components. Herewith, cracking with a length of 80 minutes is accompanied by the minor decomposition of resins (0.8 %), while at 60 min, their content increases by 2.9 mass %. A rise in the duration of thermal treatment of bitumen to 100 min contributes to more substantial decomposition of resins (by 6.6 %) and an increase in the content of oils by 2.6 %, while further cracking leads to deep decomposition of all components of bitumen: oils (4.9 mass %), resins (12.9 mass %), and asphaltenes (2.6 mass %). The main products of decomposition of resinous components are biaromatic components, while polyaromatic ones are prone to condensation.

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