Changes in the Composition of Residual Fractions and Structure of Asphaltene Molecules during Atmospheric-Vacuum Distillation of Heavy Oil

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Abstract

The changes in the composition of the residual fractions and the structure of asphaltene molecules during the primary processing of heavy oil are investigated. It was established that the atmospheric-vacuum distillation of heavy oil is accompanied by the formation of additional resin-asphaltene substances (more than 20 mass %). The initiation of chemical reactions between oil components occurs at the stage of fuel oil production due to the destruction of mainly sulphur-containing fragments in asphaltene molecules. It was shown that during tar production, the destruction and elimination of asphaltene-saturated fragments occur with a decrease in the content of naphthenic and paraffinic carbon by 5.5 and 1.7 %, respectively. Recombination reactions between the resulting macroradicals of asphaltene molecules contribute to an increase in their aromaticity factor by 7.2 % and the average MM by 190 Da. Collection of the fraction 350–450 °C leads to a decrease in the average MM of asphaltenes by 425 Da with an insignificant redistribution of carbon in various structural fragments.

Keywords: heavy crude oil, primary processing, distillation, fuel oil, tar, oil residues, asphaltenes, composition, structure

INTRODUCTION

Modern world oil production is characterized by an increase in the fraction of heavy oil and natural bitumen in connection with a decrease in the resources of light hydrocarbon raw material [1, 2]. However, heavy and bituminous oil contains substantial amounts of high-molecular polycyclic aromatic compounds: asphaltenes enriched with heteroatoms and microelements, with a disposition to self-association and the formation of coarse supramolecular structures [3, 4]. The high content of asphaltenes and the features of their chemical nature cause the problems in processing heavy hydrocarbon raw material [2]. In this connection, it is necessary to develop new methods and optimize the existing processing methods, relying on the regularities of the behaviour of asphaltenes in thermal, catalytic and hydrogenation processes that are under active investigation at present [5–10]. It is known that even at 100–200 °C asphaltene molecules are prone to get destroyed with the rupture of covalent bonds [11–13]. Substantial amounts of gas, oils and resins are formed in this process, and the molecular structure of asphaltenes changes substantially [12–15]. The data obtained point to the high reactivity of asphaltene molecules in low-temperature processes, which is

confirmed by a noticeable change of their molecular mass and redistribution of carbon atoms between aromatic and saturated structural fragments at the stage of collecting the petrol and diesel fractions during the primary processing of heavy oil [16]. This explains the necessity to carry out a comprehensive investigation of asphaltene transformations in the processes involved in primary oil processing, and their effect on the composition of the formed products. Insufficient knowledge of these aspects hinders the search for methods to optimize the basic processes of heavy oil processing.

The goal of the present work was to study the changes in the composition of residual fractions and the structure of asphaltene molecules during the atmospheric and vacuum distillation of heavy oil.

EXPERIMENTAL

The study was carried out with asphaltenes isolated from the oil of the Usinskoe deposit, the residue from the atmospheric-vacuum distillation of oil from the Usinskoe deposit (mazut), residues from the vacuum distillation of mazut (goudron). Oil residues were obtained under laboratory conditions through fractionation of initial oil according to GOST 11011−85 using an ARN-2 apparatus (Russia). The initial boiling point (i.b.p.) of oil is 156 °C. The fractions boiling out within the temperature range 156−180 °C were collected at atmospheric pressure for 25 min. The maximal temperature of the distilling tank of the ARN-2 apparatus reached 280 °C. The next fraction with the boiling point range 180−320 °C was obtained within 152 min at the residual pressure $1.6 \cdot 10^3$ Pa, which corresponds to the actual temperature 65−180 °C. The temperature of the distilling tank did not exceed 250 °C. Then the residual pressure equal to $2.7 \cdot 10^2$ Pa was set, and the fractions 320−350 °C (32 min) and 350−450 °C (172 min) were collected consecutively. The actual boiling points of the fractions collected at the residual pressure of $2.7 \cdot 10^2$ Pa were 120−150 and 150−250 °C, respectively. At the final stage of fractionation, the maximal temperature of the bottoms was 290 °C. Mazut sample was taken from the tank of the ARN-2 apparatus after the removal of the fraction 320−350 °C, goudron was sampled after the removal of the fraction 350−450 °C.

The density of oil and oil residues was determined at 20 °C using the pycnometric method according to GOST 3900−85. The values for the density of mazut and goudron at 50 °C were obtained, and their density at 20 °C was calculated according to GOST 3900−85.

The component composition of oil and oil residues was determined according to the following procedure. Asphaltenes were isolated by adding *n*-hexane in a 40-fold excess by mass to the weighted portion of the oil disperse system (ODS); then the mixture was kept in the dark for 24 h. The formed asphaltene precipitate was filtered through a paper filter and purified from maltene (resins and oils) in Soxhlet's apparatus for 16−18 h with *n*-hexane until the solvent passing through asphaltene layer became colourless. Thus purified asphaltenes were isolated from the filer with chloroform, and then the solvent was evaporated. After that, asphaltenes were dried to the constant mass. Maltenes obtained during asphaltene filtering and those isolated from their surface in Soxhlet's apparatus were brought together and separated into oils and resins by means of liquid absorption chromatography on silica gel. Oils were eluted with *n*-hexane, oils were eluted with a mixture of ethanol and benzene at the equal volume ratio. Then *n*-hexane and the mixture of ethanol and benzene were removed from the resulting solutions, after which oils and resins were brought to the constant mass.

Determination of the elemental composition of ODS and asphaltenes extracted from it was carried out using a Vario el Cube CHNSO analyzer (Germany) by burning the sample at 1200 °C, followed by the chromatographic analysis of the formed gases.

The average molecular masses (AMM) of asphaltenes were measured by means of cryoscopy in naphthalene using a Krion instrument developed at the Institute of Petroleum Chemistry of the Siberian Branch of the Russian Academy of Sciences (IPC SB RAS). The concentration of asphaltene substances in naphthalene was 0.5 mass %.

The NMR ^{1}H spectra of asphaltenes were recorded with the help of a Fourier transform spectrometer AVANCE-AV-300 (USA), the solvent was $CDCl_3$, hexamethyldisiloxane was used as the internal standard. Asphaltene concentration in $CDCl_3$ was 1 mass %.

On the basis of the results of elemental analysis, NMR ^{1}H spectroscopy, and determination of the AMM of asphaltenes, the structural parameters of their averaged molecules were calculated by means of the structural group analysis (SGA) [17] developed at the IPC SB RAS.

Among the parameters of asphaltene macromolecules calculated by means of SGA, the following ones are presented in the work:

f_a, f_n, f_p − the fractions of carbon atoms in aromatic, naphthene and paraffin structural fragments, respectively;

K_a, K_{sat} − the number of aromatic and saturated cycles in the averaged molecule, respectively;

C_p − the number of carbon atoms in paraffin structural fragments.

RESULTS AND DISCUSSION

The first stage of the studies of asphaltene transformations in the processes of primary oil processing is the investigation of the composition of oil and oil residues. It follows from the data shown in Table 1 that oil content in the sequence of oil → mazut → goudron decreases regularly from 73.9 to 28.0 mass %, and the content of resins and asphaltenes increases from 18.0 to 53.5 mass % and from 8.1 to 18.5 mass %, respectively. In this connection, the density of mazut and goudron is higher than that of oil by 0.017 and 0.028 g/cm³, respectively.

To assess the progress of chemical reactions during the atmospheric and vacuum distillation of oil, a comparative analysis of the calculated content of resins and asphaltenes in mazut and goudron and the actual data (determined experimentally) on the amount of resinous-asphaltene substances in these oil residues is of interest. Taking into account the initial component oil composition and also the density and the volume fractions of oil residues boiling at >350 and >450 °C, one can calculate the contents of resins and asphaltenes in them using the formula:

$$w_c = w_{oil}/(\varphi_f \rho_f)$$

where w_c is the calculated content of the component in the residue, woil is the mass fraction of the component in the initial oil; φ_f is the volume fraction of the residue; ρ_f is the density of the residue at 20 °C, g/cm³.

Resinous-asphaltene substances are high-molecular and therefore nonvolatile, so their calculated and actual content in oil residues should be close to each other if all oil components are thermally stable in the prescribed technological mode, and if there are no chemical reactions between them. A comparative analysis of the experimental and theoretical data on the component composition of oil residues showed that the fraction of asphaltene in mazut and goudron is higher than the calculated values by 1.2 and 2.9 mass %, respectively. The difference between the calculated and actual content of resinous substances in mazut and goudron is 4.3 and 18.9 mass %, respectively (Fig. 1). A disproportionate increase in the amount of asphaltenes in oil residues with respect to initial oil might be linked with the change of the chemical composition of the disperse medium from which the asphaltenes were isolated, and, as a consequence, with the change of their supramolecular structure, in particular with different content of the compounds adsorbed and occluded by them. However, so a substantial

TABLE 1

Composition and physicochemical properties of ODS

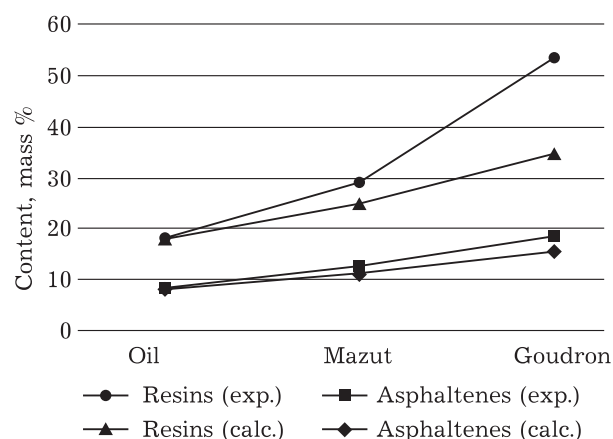| Parameter	Oil disperse system		
	Oil	Mazut	Goudron
Density at 20 °C, g/cm³	0.967	0.984	0.995
Fraction composition, vol. %:			
l.b.−180 °C	3.1	0	0
180−350 °C	23.2	0	0
350−450 °C	21.4	29.0	0
>450 °C	52.3	71.0	100
Component composition, mass %:			
oils	73.9	58.5	28.0
resins	18.0	29.1	53.5
asphaltenes	8.1	12.4	18.5
Elemental composition, mass %:			
H/C$_{at}$	1.68	1.34	1.34
N	0.63	0.78	0.93
S	1.98	1.95	1.96
O	0.47	0.62	0.53

Fig. 1. Experimental and calculated content of resins and asphaltenes in the bottoms of the atmospheric-vacuum distillation of heavy oil.

increase in resin content during primary oil processing is an unambiguous sign of intense chemical reactions between the components of ODS. It is probable that the resinous-asphaltene substances, as the most unstable and reactive compounds in the oil, act as the initiators and most active participants of the thermal transformations of oil components according to the free radical chain mechanism. Additional confirmation of thermodestructive processes during obtaining goudron is the change of the elemental composition of ODS. For instance, the atomic ratio H/C_{at} in mazut is regularly lower by 0.34 than in oil because of the evaporation of the light-weight fractions enriched with hydrogen. The ratios H/C_{at} in mazut and in goudron are the same and equal to 1.34, which is the evidence of hydrogen redistribution between the fraction 350–450 °C and the bottoms during the vacuum evaporation of mazut. The sulphur content in ODS under investigation is almost the same, varying within the range 1.95–1.98 mass %. Provided that sulphur-containing components are thermally stable and nonvolatile, the fraction of sulphur in oil residues should be substantially higher. Of course, a substantial amount of sulphur may be removed with volatile fractions during oil distillation, however, destruction of labile sulphuric fragments occurs in the molecules of resinous-asphaltene substances under these

thermobaric conditions [12, 13, 15], which promotes additional removal of sulphur from oil residues. It is essential to stress that oxygen content in mazut is higher than initial oil and goudron by 0.15 and 0.09 mass %, respectively. This may be evidence of the fact that oxygen compounds get concentrated in the bottoms during the process of obtaining mazut; a substantial part of these oxygenated compounds is later removed within the fraction 350–450 °C. Nonlinear change of oxygen content in ODS under study with an increase in the depth of fraction sampling may also be connected with the relative stability of oxygenated fragments of high-molecular oil components (mainly resins and asphaltenes) during the process of obtaining mazut, and their subsequent destruction and removal during the collection of fraction 350–450 °C. A linear increase in nitrogen content from 0.63 to 0.93 mass % is observed in the row oil → mazut → goudron, which is due to the presence of nitrogen mainly in stable aromatic structures of the molecules of resins and asphaltenes concentrated in the bottoms.

So, more than 20 mass % of resinous-asphaltene substances are additionally formed during the atmospheric-vacuum distillation of heavy oil due to intense chemical reactions between ODS components, which is impermissible from the viewpoint of the rational use of hydrocarbon raw material.

Taking into account the fact that the most reactive resinous-asphaltene substances should be initiators of the thermal destruction of oil components during atmospheric-vacuum distillation, it is interesting to study the direction and the extent of transformation of their molecular structure. Investigation of the changes in the high-molecular hetero-organic compounds of oil was carried out by the example of asphaltenes as the most complicated ODS components. It follows from the data shown in Table 2 that the basic common routes of asphaltene transformations during the primary oil processing are an increase in aromaticity factor and a decrease in the fraction of naphthene and paraffin carbon, which confirms intense destruction of asphaltene molecules. These changes in the structural group composition of asphaltenes in thermal destruction are natural, but it is necessary to stress several specific features of the dynamics of these changes. For instance, carbon atom content in the aromatic fragments of the molecules of asphaltenes in mazut (AM) is higher by 7.2 % than in the

TABLE 2

Structural group composition of the asphaltenes of oil, mazut and goudron

Parameter	Asphaltenes		
	Oil	Mazut	Goudron
AMM, Da	1600	1790	1365
Elemental composition, mass %:			
H/C_{at}	1.12	1.08	1.02
N	1.16	1.58	1.80
S	3.00	2.49	2.23
O	4.41	4.40	3.84
Distribution of carbon atoms			
over structural fragments, rel. %:			
f_a	34.0	41.2	42.2
f_n	59.3	53.8	53.6
f_p	6.7	5.0	4.2
Number of cycles and carbon atoms			
in paraffin fragments, units:			
K_a	9.4	12.8	10.0
K_{sat}	21.1	19.2	17.7
C_p	7.5	6.3	4.1

molecules of asphaltenes in oil (AO). The content of naphthene and paraffin carbon in AM is lower than in AO by 5.5 and 1.7 %, respectively. The AMM of asphaltenes as a result of the process of obtaining mazut increased by 190 Da, which is the evidence that recombination of the formed macroradicals prevails and strongly promotes a substantial increase in the factor of asphaltene aromaticity in spite of intense destruction and detachment of the saturated fragments of asphaltene molecules during collecting the fraction combining the low boiling substances and those boiling up to 350 °C. Subsequent thermal transformations of asphaltene molecules during the process of goudron obtaining lead to insignificant changes in the distribution of carbon atoms over structural fragments. The f_a, f_n and f_p for AM and asphaltenes of goudron (AG) differ from each other by not more than 1 %. However, AMM of AG is lower than AMM of AM by 425 Da, which points to substantial destruction of the hydrocarbon skeleton of asphaltene molecules. So, during the atmospheric-vacuum distillation of heavy oil, the number of aromatic cycles in an average asphaltene molecule increases by 3–4 units during the collection of the fraction i.b.p. −350 °C and then decreases by 3 units during obtaining goudron. The number of saturated cycles in an average asphaltene molecule decreases linearly by 3–4 units, and the alkyl framing of the molecule becomes leaner by 3–4 carbon atoms.

Changes of the content of hetero-elements in the sequence oil − mazut − goudron correspond to the changes in the elemental composition of asphaltenes during the primary processing of heavy oil. For instance, the fraction of nitrogen in asphaltenes increases from 1.16 (AO) to 1.80 mass % (AG), while the content of sulphur and oxygen decreases by 0.77 and 0.57 mass %, respectively. Evidently, as a rule, nitrogen-containing fragments of asphaltene molecules are stable under the given conditions, while sulphur- and oxygen-containing structures are prone to intense destruction. Functional groups containing sulphur are removed from asphaltenes at the stage of obtaining mazut, unlike for oxygen-containing fragments which are removed at the stage of collecting the fraction 350–450 °C.

Taking into account the thermobaric regime in the column of atmospheric-vacuum oil distillation and the changes in the composition of ODS under study and the structure of their high-molecular compounds, we may conclude that the major

factor responsible for so substantial transformations of oil components and for the formation of resinous-asphaltene substances is the process duration. The results of the investigation allow us to assume that active initiation of thermodestruction of oil components occurs at the stage of obtaining mazut, when the temperature of the bottoms reaches the maximal value (280 °C) for the first time. Further on, the process is carried out at the residual pressure and decreased temperature till the final stage at which the fraction 350–450 °C is collected; the temperature of the bottoms again reaches high values (290 °C). Therefore, the key role in the change of the composition of residual oil fractions and the molecular structure of asphaltenes is played by the duration of primary oil processing. It is necessary to take into account the data obtained in this investigation for the development of resource-efficient methods of processing heavy oil and natural bitumen.

CONCLUSION

It was established in the studies that atmospheric-vacuum distillation of heavy oil is accompanied by the formation of additional amount (more than 20 mass %) of resinous-asphaltene substances. The initiation of thermal transformations occurs in the bottoms at the stage of obtaining mazut. The period of intense chemical reactions proceeding according to the radical chain mechanism is observed in the bottoms at the stage of obtaining goudron with the formation of new resins and asphaltenes in substantial amounts. It was demonstrated that the stage of collecting the fraction i.b.p. −350 °C involves destruction and detachment of the saturated fragments of asphaltenes with a decrease in the content of naphthene and paraffin carbon in them by 5.5 and 1.7 %, respectively, and an increase in aromaticity factor of asphaltenes by 7.2 %. The formed macroradicals are active in entering recombination reactions, which results in an increase in AMM of asphaltenes by 190 Da The collection of the fraction 350–450 °C leads to an insignificant change in carbon content in various structural fragments of asphaltene molecules, however, their AMM decreases by 425 Da As a rule, nitrogen-containing fragments of asphaltene molecules are stable during primary oil processing, while labile sulphurous structures are initiators of thermal transformations of oil

components at the stage of obtaining mazut, and oxygen-containing fragments start to take an active part in thermodestructive processes at the stage of obtaining goudron.

So, the application of traditional technologies of primary oil processing to heavy hydrocarbon raw material does not provide its rational use, which causes the necessity to update the technology of atmospheric-vacuum distillation of heavy oil.

REFERENCES

1 Iskritskaya N. I., Makarevich V. N., *Georesources*, 2014, No. 4,(59), P. 35-39. (in Russ.).

2 Ancheyta H., Modeling of Processes and Reactors for Upgrading of Heavy Petroleum.: CRC. Taylor & Francis Group, 2013, XXIII. 524 p.

3 Akbarzadeh K., Hammami A., Kharrat A., Zhang D., Allenson S., Creek J., Kabir S., Jamaluddin A., Marshall A. G., Rodgers R. P., Mullins O. C., Solbakken T., *Oilfield Review*, 2007. Vol. 19, No. 2, P. 22–43.

4 Ganeeva Yu. M., Yusupova T. N., Romanov G. V., *Russ. Chem. Rev.*, 2011, Vol. 80, No. 10, P. 993–1008. (in Russ.).

5 Pevneva G. S., Golovko A. K., Korneev D. S., Levashova A. I., *Proc. Chem.*, 2014, Vol. 10, P. 15–19.

6 Rueda-Velasquez R. I., Freund H., Qian K., Olmstead W. N., Gray M. R., *Energy and Fuels*, 2013, Vol. 27, P. 1817–1829.

7 Kayukova G. P., Kiyamova A. M., Romanov G. V., *Petroleum Chem.*, 2012, Vol. 52, No. 1, P. 5–14.

8 Sviridenko N. N., Krivtsov E. B., Golovko A. K., *Chemistry for Sustainable Development*, 2017, Vol. 25, No. 1, P. 79–84. (in Russ.).

9 Sviridenko N. N., Krivtsov E. B., Golovko A. K., *Chemistry for Sustainable Development*, 2018, Vol. 26, No. 4, P. 427–434. (in Russ.).

10 Nguyen N. T., Park S., Jung J., Cho J., Lee C. W., Park Y. K., *Journal of Industrial and Engineering Chemistry*, 2018, Vol. 61, P. 32–38.

11 Naghizada N., Prado G. H. C., de Klerk A., *Energy and Fuels*, 2017, Vol. 31, No. 7, P. 6800–6811.

12 Grin'ko A. A., Golovko A. K., *Petroleum Chem.*, 2014, Vol. 54, No. 1, P. 42–47.

13 Korneev D. S., Pevneva G. S., Golovko A. K., *Journal of Siberian Federal University-Chemistry*, 2019, Vol. 12, No. 1, P. 101–117.

14 Korneev D. S., Melenevskii V. N., Pevneva G. S., Golovko A. K., *Petroleum Chem.*, 2018, Vol. 58, No. 3, P. 179–185.

15 Korneev D. S., Pevneva G. S., Golovko A. K., *Chemistry for Sustainable Development*, 2018, Vol. 26, No. 2, P. 225–230. (in Russ.).

16 Kopytov M. A., Golovko A. K., *Petroleum Chem.*, 2017, Vol. 57, No. 1, P. 39–47.

17 Golovko A. K., Kamyanov V. F., Ogorodnikov V. D., *Russ. Geology and Geophysics*, 2012, Vol. 53, No. 12, P. 1374–1381.