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Composition of Aromatic Hydrocarbons, the Pyrolytic Products of Resins and Asphaltenes from Heavy Crude Hydrocarbon Feedstock

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Abstract

A composition was studied for polycyclic aromatic hydrocarbons formed in the course of the pyrolysis (160–650 °C) of the resin-asphaltene components of heavy crude oil from the Permian–Carboniferous age deposits of the Usinskoye field (Komi Republic). It was demonstrated that the molecules of resins and asphaltenes inherent in the oil contain the same set of aromatic fragments. Among them there were identified bi- and tricyclic fused aromatic hydrocarbons and (C₁–C₃ alkyl derivatives, tetra -, penta -, hexacyclic substances and phenyl-substituted compounds (diphenyl-, phenylnaphthalenes, terphenyls, phenylphenanthrenes). Tri- and tetracyclic aromatic hydrocarbons are prevailing, which hydrocarbons should form the basis for the composition of oil fractions produced by means of thermal processing the heavy hydrocarbon feedstock.

Key words: resins, asphaltenes, pyrolysis, aromatic hydrocarbons, composition, structure

INTRODUCTION

For the last years, there is steadily increasing the proportion of heavy crude oil species in the total amount of hydrocarbon feedstock under extraction and processing [1] those are characterized by a high content of resinous and asphaltene components [2].

The difficulties encountered in the course of the processing of such oil species could be overcome due to novel technological solutions those should be based to a considerable extent on the knowledge concerning the specific features of heavy crude hydrocarbon feedstock. In this regard, of particular importance is the work aimed at detailed studying the molecular structure of resins and asphaltenes, their thermal stability and reactivity. The latter depends to some extent on the composition and content

of polycyclic aromatic naphthene structures as well as structures containing a heteroatom in the molecules of resinous and asphaltene compounds. Aromatic hydrocarbons (AH) and heteroatomic compounds formed in the course of the degradation of resins and asphaltenes are converted into the oily components of oil species to further affect the production processes and the quality of fuels.

In this study we first studied the composition of polycyclic AH in oils obtained in the course of pyrolyzing the resins and asphaltenes inherent in heavy crude oil.

EXPERIMENTAL

The objects of study were resinous and asphaltene components of heavy crude oil deposits

TABLE 1

Characteristics of resins and asphaltenes from the Usinskoye oil deposit

Samples	Yield, mass %	Elemental composition, mass %					MM*, amu
		C	H	N	S	O	
Resins	18.0	83.06	9.32	1.07	2.91	3.64	845
Asphaltenes	8.1	78.99	6.33	1.13	3.95	9.60	1633

*MM – molecular mass.

from the Permian-Carboniferous deposit of the Usinskoye field (Komi Republic).

In order to isolate asphaltenes and resins from the original oil we used a technique described in [3]. The characteristics of the components obtained are presented in Table 1.

The pyrolysis of the samples was performed for 1 h using a steel reactor with the volume capacity equal to 12 cm³ in an inert atmosphere (Ar) at preset temperature values such as 160, 200, 250, 300, 450, 650 °C. The pyrolysis temperature values ranged from starting the decomposition temperature of resins and asphaltenes (160 °C) to the temperature of almost complete destruction (650 °C) [2, 4].

The pyrolysis products were extracted with chloroform to obtain soluble and insoluble substances (coke). From the soluble products we extracted petrolenes by hexane, which petrolenes were separated into the fractions of oils and resins using a technique of liquid adsorption chromatography on silica gel ASK (adsorbent/adsorbate ratio = 20 : 1), using as eluents benzene-hexane (4 : 1) and alcohol-benzene (1 : 1) mixtures in series.

The analysis of oils was performed by means of gas chromatography-mass spectrometry (XMQ, employing a Shimadzu GSMS-QP5050 spectrometer with the use of a MIM (multiple ion monitoring) technique that consists in scanning the mass chromatograms for the characteristic ions in a programming temperature mode. The chromatograph was equipped with a DB5-MS quartz capillary column 30 m long and 0.32 mm in diameter. Helium was used as a carrier gas. The identification of compounds was performed from the retention time by means of comparing the mass fragmentation profiles obtained with mass spectra available from the NIST and WILEY library systems, and with

data published [5–8]. The quantitative evaluation of component content in oils was carried out according to the area of corresponding peaks. The relative abundance of each type of compounds was calculated as a ratio between its total intensity and the sum of the areas of all the compounds under investigation.

RESULTS AND DISCUSSION

The results of CMS analysis concerning the oils from resins (OR) and asphaltenes (OA) demonstrate that among the OR formed at the pyrolysis temperature equal to 160, 200, 250 and 300 °C, the AH are presented only by the holocyclic structures of naphthalene (C_nH_{2n-12}) and phenanthrene (C_nH_{2n-14}), whereas among the OA they are presented only by the holocyclic structures of phenanthrene.

Starting from the pyrolysis temperature equal to 450 °C, the set holocyclic AH structures exhibits a considerable extension (Table 2). The OR obtained at this temperature (OR₄₅₀) in addition to naphthalene and phenanthrene demonstrated the presence of anthracene (C_nH_{2n-18}), pyrene (C_nH_{2n-22}), triphenylene and chrysene (C_nH_{2n-24}) perylene (C_nH_{2n-28}). The OA₄₅₀ samples in addition to phenanthrenes exhibited the presence of all the mentioned compounds and fluoranthene (C_nH_{2n-22}). Among the holocyclic OR₄₅₀ and OA₄₅₀ structures identified is tricyclic compounds predominate (8.2 and 14.6 rel. %, respectively).

The analysis of oils obtained at 650 °C, gives more complete information concerning the fragments of molecules presented by holocyclic AH. At this temperature, the resins and asphaltenes additionally generate significant amounts of compounds containing five and six benzene rings in the structure (see Table 2). Their com-

TABLE 2

Content of aromatic hydrocarbons in the oils of resins and asphaltenes, rel. %

Compound number	General formula	Compound, m/z	Code of compound*			
			OR ₄₅₀	OR ₆₅₀	OA ₄₅₀	OA ₆₅₀
		<i>Condensed AH</i>				
1	C_nH_{2n-12}	Bicyclic AH	60.2	0.8	41.1	1.5
		Naphthalene (N)				
		C_0H , $C_{10}H_8$, 128	3.4	0.1	4.1	1.1
		C_1H , $C_{11}H_{10}$, 142	10.0	0.3	6.3	0.4
		C_2H , $C_{12}H_{12}$, 156	25.4	0.2	15.4	Abs.
2	C_nH_{2n-18}	C_3H , $C_{13}H_{14}$, 170	21.5	0.2	15.3	Abs.
		Tricyclic AH	34.7	23.8	38.2	24.6
		Phenanthrene (P)				
		$C_0\Phi$, $C_{14}H_{10}$, 178	5.5	19.9	13.1	21.2
		$C_1\Phi$, $C_{15}H_{12}$, 192	12.8	0.8	9.9	1.1
3	C_nH_{2n-22}	$C_2\Phi$, $C_{16}H_{14}$, 206	6.9	3.0	8.7	2.4
		$C_3\Phi$, $C_{17}H_{16}$, 220	3.5	0.1	3.3	Abs.
		Anthracene (A)				
		C_0A , $C_{14}H_{10}$, 178	2.7	0.8	1.5	1.1
		C_1A , $C_{15}H_{12}$, 192	3.4	Abs.	1.7	Abs.
4	C_nH_{2n-24}	Tetracyclic AH	4.3	31.8	15.1	34.2
		$C_{16}H_{10}$, 202	0.8	25.2	12.5	26.3
5	C_nH_{2n-28}	$C_{18}H_{12}$, 228	0.8	7.1	2.6	7.9
		Pentacyclic AH	0.7	21.2	3.1	21.8
6	C_nH_{2n-30}	$C_{20}H_{12}$, 252	0.7	18.7	3.1	19.6
		$C_{22}H_{14}$, 278	Abs.	2.5	Abs.	2.2
		Hexacyclic AH	Abs.	10.9	Abs.	9.3
7	C_nH_{2n-32}	$C_{22}H_{12}$, 276	Abs.	7.8	Abs.	6.3
		$C_{24}H_{14}$, 302	Abs.	3.1	Abs.	3.0
		<i>Phenylsubstituted AH</i>				
8	C_nH_{2n-14}	Biphenyl	Abs.	1.4	0.9	1.1
		$C_{12}H_{10}$, 154				
9	C_nH_{2n-20}	Phenylnaphthalene (PN), $C_{16}H_{12}$, 204	Abs.	5.7	1.7	4.2
		<i>para</i> -PN	Abs.	0.9	Abs.	0.8
		<i>ortho</i> -PN	Abs.	4.8	1.7	3.4
10	C_nH_{2n-22}	Terphenyls (TP), $C_{18}H_{14}$, 230	Abs.	0.9	Abs.	0.5
		<i>ortho</i> -TP	Abs.	0.1	Abs.	0
		<i>meta</i> -TP	Abs.	0.6	Abs.	0.3
		<i>para</i> -TP	Abs.	0.3	Abs.	0.2
11	C_nH_{2n-26}	Binaphthyls (BN), $C_{20}H_{14}$, 254	Abs.	0.8	Abs.	0.6
		1,2'-BN	Abs.	0.2	Abs.	0.1
		2,2'-BN	Abs.	0.6	Abs.	0.5
		Phenylphenanthrenes (PP), $C_{20}H_{14}$, 254	Abs.	2.9	Abs.	2.4
12	C_nH_{2n-26}	9-PP	Abs.	0.2	Abs.	0.2
		1-PP	Abs.	0.1	Abs.	0.1
		2-PP	Abs.	1.3	Abs.	1.0
		3-PP	Abs.	1.3	Abs.	1.1

Note. Abs. – absent.

*OR₄₅₀, OR₆₅₀, OA₄₅₀, OA₆₅₀ – oils derived from original resins and asphaltenes at appropriate temperature values, °C.

position could contain benzofluoranthenes (C_nH_{2n-28}), benzopyrenes (C_nH_{2n-28}), dibenzanthracenes (C_nH_{2n-30}), benzochrysenes (C_nH_{2n-30}), dibenzophenanthrenes (C_nH_{2n-30}), benzoperylene (C_nH_{2n-32}), dibenzo-substituted chrysenes (C_nH_{2n-32}), and pyrenes (C_nH_{2n-34}).

The distribution character of AH holocyclic structures identified in OR_{650} and OA_{650} indicates that the molecules of resins and asphaltene inherent in heavy crude oil from the Usinskoye deposit do not differ between each other in the composition fragments, whose structure involves condensed aromatic rings. The main elements of the resinous asphaltene components of the oil under study are presented by tricyclic compounds (21.2 and 23.6 rel. % for OR_{650} и OA_{650} , respectively) and tetracyclic compounds (35.2 and 36.3 rel. %, respectively), with the maximum concentration of phenanthrenes (20.2 and 22.5 rel. %, respectively) and pyrene (19.0 and 19.7 rel. %, respectively). It should be noted that there is a quite high content of penta- and hexacyclic compounds inherent in OR_{650} and OA_{650} , wherein the maximum concentration is exhibited by AH presented by the compounds having general formulae such as C_nH_{2n-28} (m/z 252, 18.7 and 19.6 rel. %) and C_nH_{2n-32} (m/z 276, 7.8 and 6.3 rel. %, respectively) (see Table 2).

Alongside with the condensed structures inherent in OR_{650} and OA_{650} , phenyl-substituted AH are contained in significant amounts therein (11.7 and 8.8 rel. %, respectively). Their appearance was registered in OA at 450 °C, but at this temperature, they are presented only by biphenyl and *o*-phenylnaphthalene. Among the phenyl-substituted compounds OR_{650} and OA_{650}

(Table 2 and Fig. 1) there is a representative set of AH observed containing phenyl substituent in the structure (in parentheses are presented the numbers of compounds, see Table 2) biphenyl (**6**), 1- and 2-phenylnaphthalenes (**7a, b**), *o*-, *m*- and *p*-terphenyls (8a-c), 1,2'- and 2,2'-binaphthyls (**9a, b**), and 9-, 1-, 2- and 3-phenylphenanthrenes (**10a-d**).

Both products exhibit prevailing phenyl substituted naphthalenes (5.7 and 4.2 rel. %, respectively) and phenanthrenes (2.9 and 2.4 rel. %, respectively). The content of biphenyls, terphenyls and binaphthyl is lower: for OR_{650} the fraction is equal to 1.4, 0.9, and 0.8 rel. %, respectively, whereas for OA_{650} the value amounts to 1.1, 0.5, and 0.6 rel. %, respectively. The maximum in the distribution phenylnaphthalenes, terphenyls, binaphthyls and phenylphenanthrenes falls on *o*-, *m*-, 2,2'-, 2- and 3-isomers, respectively. The phenyl-substituted AH identified are noteworthy, since it could be not excluded that they are not only a part of the structure of the molecules resinous and asphaltene substances but they are secondary products. So, the phenyl substituted AH were revealed both in geological samples [5], and in coal tar [6, 7], as well as in the decomposition products of organic substances [8].

Starting from the pyrolysis temperature of 450 °C, among the AH there appear alkyl-substituted structures. Chromatograms MS_{450} and MA_{450} demonstrate the peaks of (C_1 - C_3) naphthalenes, (C_1 - C_3) phenanthrenes, C_1 anthracene (see Table 2). Alkyl naphthalenes are prevailing (56.8 and 38.0 rel. % for the samples of OR_{450} and OA_{450} , respectively), whereas the content

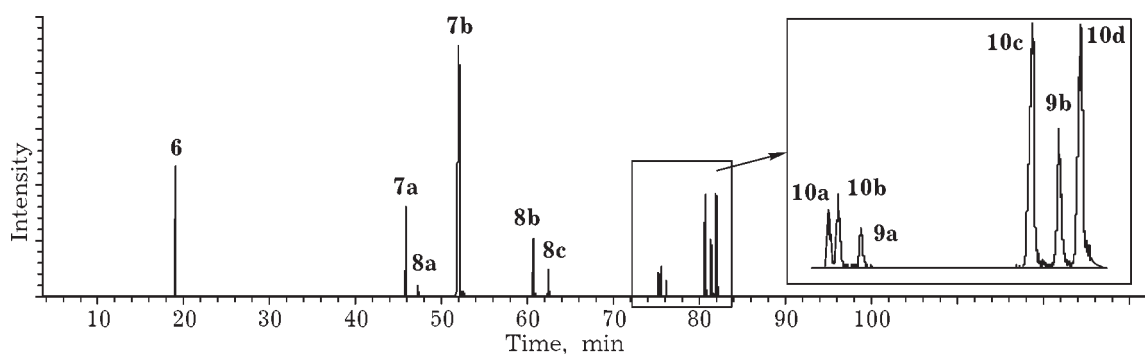


Fig. 1. Distribution of aromatic hydrocarbons in OR_{650} : **6** – biphenyl, m/z 154; **7a,b** – phenylnaphthalenes m/z 204; **8a-c** – terphenyls, m/z 230; **9a,b** – binaphthyls, m/z 254; **10a-d** – phenylphenanthrenes, m/z 254.

of C₂-C₃ homologues is increased (46.9 and 31.5 rel. %, respectively). The relative content of alkylphenanthrenes in OR₄₅₀ and OA₄₅₀ samples is equal to 23.2 and 22.4 %, respectively, that of alkylanthracenes amounts to 3.4 and 1.7 %, respectively. The maximum concentration for both products is inherent in C₁ phenanthrenes (12.8 and 10.2 rel. %, respectively). As the pyrolysis temperature increases the character of distribution for the hydrocarbons identified is violated. So, sample OR₆₅₀ demonstrates an abrupt increase of the concentration of (C₁-C₃) naphthalenes (down to 0.7 rel. %) and that of (C₁-C₂) phenanthrenes (down to 3.1 rel. %), with disappearing C₃ phenanthrene and C₁ anthracene. The OA₆₅₀ sample contains only C₁ isomers of naphthalene (0.4 rel. %) and phenanthrene (2.4 rel. %).

A detailed analysis of alkyl substituted AH allowed us to reveal that the composition contains 2- and 1-methyl-, dimethyl-, ethylmethyl-, trimethylnaphthalenes, 2-, 3-, 9-, 1-methyl-, dimethyl- and trimethylphenanthrenes, 2-methylanthracenes. In the oils of asphaltenes and resins obtained at temperature values equal to 450 and 650 °C there are thermodynamically stable compounds prevailing such as 2-methylnaphthalene, and 2-, 3- methylphenanthrenes [9].

CONCLUSION

Thus, basing on the analysis of oil species resulting from the pyrolysis of resins and asphaltenes, data were obtained concerning polycyclic aromatic hydrocarbons those could form high

molecular components inherent in heavy crude oil. The molecules of resins and asphaltenes from the heavy crude oil of the Usinskoye field contain the same set of fragments those are presented by condensed aromatic rings with a maximum content of tri- and tetracyclic compounds such as phenanthrenes and pyrenes in the two cases. Thus, these compounds should predominantly compose the aromatic hydrocarbons inherent in oil fractions obtained by means thermal processing heavy crude hydrocarbon feedstock.

The data obtained concerning the composition of polycyclic aromatic hydrocarbons from the resinous-asphaltene components and the features of their transformations in the course of thermal destruction should be considered in tackling the questions connected with the processing of heavy crude oil species to obtain high-quality products basing on them.

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