UDC 662.7:552.57

Studying the Composition and Structure of a High-Boiling Part of Heavy Pyrolysis Resin Resulting from Processing a Broad Fraction of Light Hydrocarbons

M. A. TSEUNOVA[1,2], V. I. MASHUKOV[2] and A. K. GOLOVKO[1]

[1]Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences,
Pr. Akademicheskiy 4, Tomsk 634021 (Russia)

[2]NIOST LLC, SIBUR's Scientific Centre for Chemical Technologies,
Kuzovlevskiy Trakt 2, build. 270, Tomsk 634067 (Russia)

E-mail: lma@niost.ru

(Received August 28, 2012)

Abstract

Analysis was performed concerning heavy pyrolysis resin produced at the Tomskneftekhim Ltd and the products of extraction and chromatographic separation thereof (oil species, resins and asphaltenes) with the use of a pyrolysis gas chromatography-mass spectrometry technique (PGCMS). Main structural fragments were determined for the resins and asphaltenes, as well as an individual composition was obtained for oils in the course of the decomposition thereof within a pyrolytic chamber at 800 °C in an inert atmosphere. It has been found that the oils represent a mixture of low molecular aromatic compounds such as condensed 3–6 ringed aromatic hydrocarbons the molecular mass up to 300 amu, whereas the resins and asphaltenes represent high molecular mass aromatic compounds, whose molecules are consist of 1–2-, 4–5- and 1–2-, 3–4-ringed aromatic fragments, respectively. Using the methods of PGHMS and IR spectroscopy, the composition of the high-boiling part of heavy pyrolysis resin has been identified.

Key words: heavy pyrolysis resins, asphaltenes, resins, oils, pyrolysis, composition of volatile components

INTRODUCTION

Heavy pyrolysis resin (HPR) is formed as a by-product in the pyrolysis plants for producing monomeric ethylene and propylene feedstock. The HPR represents a complex multi-component mixture consisting mainly of the light fraction (aromatic hydrocarbons boiling within the temperature range lower than 200 °C) and the heavy fraction that includes various aromatic condensed high molecular mass compounds [1].

One of the most promising ways for processing the HPR consists in obtaining petroleum resins on this base using a pre-polymerization. This determines the urgency of studying of the heavy part of HPR, whose amount reaches up to 40 % of the total mass. This fraction of HPR determines the nature and properties of the petroleum polymeric resin formed in the course of petroleum processing.

The authors of [1–3], studied in detail the composition of the light part of HPR mainly by means of chromatographic methods, whereas the studies on heavy fractions requires for involving a whole range of physical and chemical methods of research (IR spectroscopy and NMR spectrometry, thermal analysis, mass spectrometry, and others).

In our paper, we propose an algorithm for determining the basic structural fragments inherent in the high-boiling part of the HPR, which algorithm is based on the preliminary extraction separation of heavy components according to the their nature thereof, with subsequent thermal destruction thereof (T = 800 °C) and analyzing the products formed using a chromatography-mass spectrometry technique. According to the composition of the structural fragments and quantitative relationships between them, one could judge about the original structure of the high molecular part of the HPR.

The purpose of this investigation consisted in determining the composition and structure of the HPR by means of the pyrolysis gas chromatography-mass spectrometry technique.

EXPERIMENTAL

As the object of investigation, we used the HPR produced at the Tomskneftekhim Ltd. (Tomsk, Russia).

In order to isolate the components of the heavy part we used the standard extraction separation method for petroleum fractions that allows obtaining oils, resins and asphaltenes [4]. The adsorption extraction was carried out using a Soxhlet extractor; as the extracting solvent we have chosen *n*-hexane (isolation of oils), toluene (isolation of resins), and a mixture of ethanol and toluene (isolation of asphaltenes). The results of the extraction are presented in Table 1.

The HPR fractions obtained were investigated using an Agilent 7890A/MSD5975C gas chromatograph with a mass spectrometric detector and a Pyroprobe CDS 5000 pyrolytic attachment. The pyrolysis oil samples, resins and asphaltenes was performed at 350 to 800 °C during 16 s. The samples were loaded into a quartz boat that was installed inside the spiral made of platinum wire. The operating parameters of the mass spectrometer were the following: ionization energy 70 eV, ion source temperature was 230 °C.

TABLE 1

Yield of HPR adsorption extraction products with the use of the Soxhlet extractor, mass %

Experiment No.	Oils	Resins	Asphaltenes	Total
1	12.1	20.3	10.6	42.9
2	11.8	20.5	10.7	43.0
3	12.5	20.1	10.8	43.4
Average	12.1	20.3	10.7	43.1

The parameters of the gas chromatograph operation were as it follows. A HP-5MS column with the length of 30 m, internal diameter of 0.25 mm and the thickness of the deposited phase equal to 0.25 μm. The temperature program: initial temperature 40 °C (2 min isothermal mode), heating at a rate of 10 °C/min up to 295 °C (25 min isothermal mode), the evaporator temperature being of 280 °C, helium being a carrier gas; flow rate equal to 1 mL/min; injected sample volume being equal to 1 μL; split ratio 100 : 1.

Data acquisition in the SCAN mode was performed using a ChemStation softare package. The composition features of different types of hydrocarbons in the pyrolysis products obtained at 800 °C for different samples were revealed when in the course of a more detailed comparative analysis using the parameters of characteristic fragmentary and molecular ions according to NIST 2008 spectral library.

The ^{13}C NMR spectra were registered by means of a Bruker Avance III 400 MHz NMR spectrometer at a room temperature using stan-

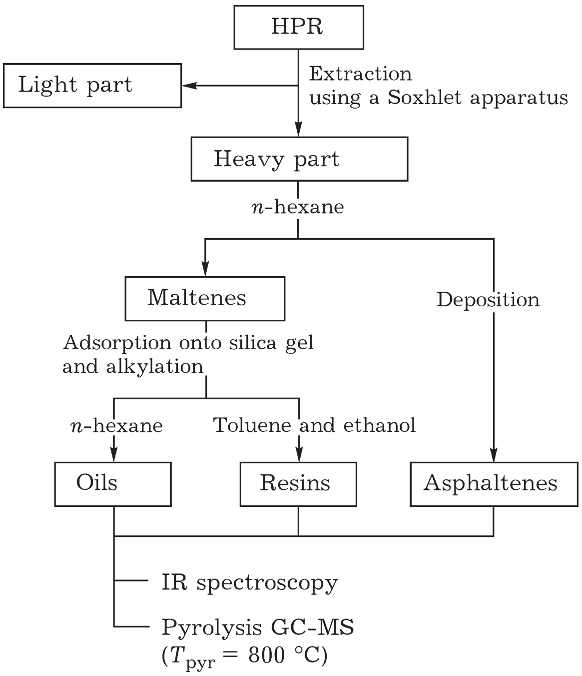


Fig. 1. Algorithm for determining the basic structural fragments of high-boiling HPR part.

dard pulse programs. The samples were dissolved in deuterated chloroform.

IR spectra were registered using a Varian Excalibur HE 3600IR Fourier transform spectrometer with the resolution of 4 cm^{-1} with the help of an ATR attachment within the wavenumber range of 4000–400 cm^{-1}.

The thermal behaviour was studied using a NETZSCH TG 209 F1 thermal analyzer in an argon atmosphere at a heating rate of 10 °C/min up to 800 °C.

The algorithm for determining the basic structural fragments of the high boiling part of HPR is demonstrated in Fig. 1.

RESULTS AND DISCUSSION

The high-boiling part of the HPR represents a fraction complicated in composition and structure that consists mainly of condensed aromatic fragment with an irregular structure. According to [5], the content of this fraction in the HPR, measured by means of thermogravimetry and distillation under vacuum amounts to 40–50 %. At the same time, investigation using these methods involves thermal impact on the HPR, which could lead to compaction and polycondensation reactions and, consequently, to changing the composition and structure thereof. In this regard, we used a method of the extractive separation of HPR as described by the authors of [4], that is used for oil species, oil fractions, naturally occurring bitumen, coal and kerogen pyrolysis products as well as coal species. The method allows one not only to isolate the high boiling part of the HPR, but also to separate it into the fractions different in the nature such as oils, resins and asphaltenes (see Table 1), whose total content amounts up to 40 %. This makes it possible to carry out the most comprehensive chemical analysis of these fractions and to get a more complete concept concerning the object under study.

The ^{13}C NMR spectra of the HPR fractions isolated exhibit no individual signals inherent in the structural fragments due to a high level of the structural irregularity. All the signals are considerably broadened, so one could judge only the fact whether the signals belong to either region (aliphatic, aromatic) of the spectrum. Using the IR spectroscopy, one can distinguish only common structural features for the components of these fractions, so in order to identify the resulting components we used a pyrolytic gas chromatography technique with mass selective detection.

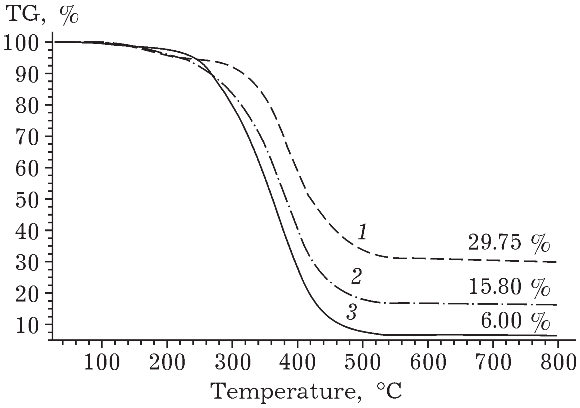


Fig. 2. Thermographic profiles of asphaltenes (*1*), oils (*2*) and resins (*3*).

For choosing the optimal destruction conditions for the fractions of HPR with the use of the pyrolytic attachment to the chromatograph, we performed a preliminary investigation concerning the thermal behaviour of these samples in an inert atmosphere by means of thermogravimetry (Fig. 2). It is seen that within the temperature range of 100–350 °C the mass loss is negligible for the samples under investigation, which, to all appearance, could be mainly caused by the processes of evaporation of low molecular mass components. At higher temperature values, a dramatic mass loss is observed due to a thermal destruction of the samples. The temperature values higher that 500 °C exhibit an almost complete ceasing the intense mass loss, thereby the residual mass for the oil is equal to almost 6 %, being of almost 16 % for resins, and amounting to about 30 % for asphaltenes. The data obtained could be, to all appearance, caused by a high tendency of asphaltenes and oil species to coking, which is necessary to consider in the course of using them as raw materials for the production of carbon black.

Thus, high pyrolysis temperature (800 °C) provides an almost complete destruction of the sample and, therefore, allow performing a more complete analysis of all the structural fragments. At the same time, the analysis of low

TABLE 2

Composition of pyrolysis products of the resins and asphaltenes at 800 °C

Retention time, min	Components	Content, mass %	
		Resins	Asphaltenes
1.85	1,3-Cyclopentadiene	0.32	0.20
2.46	1,3-Hexadiene-5-yne	0.43	0.38
2.50	1,3-Cyclohexadiene	0.16	0.18
2.67	Benzene	0.13	0.11
4.07	1,3,5-Cycloheptatriene	0.75	1.13
5.72	Ethylbenzene	0.37	0.69
5.87	*p*-Xylene	0.99	1.69
6.26	Styrene	1.25	2.19
6.30	*o*-Xylene	0.36	0.48
7.55	1-Ethyl-3-methylbenzene	1.49	2.13
7.91	α-Methylstyrene	1.06	0.98
8.20	1-Ethenyl-4-methylbenzene	1.54	1.54
10.96	1-Methyl-1H-indene	0.57	2.18
11.24	1,3-Dimethyl-1H-indene	0.64	0.83

molecular components contained in the fractions isolated (oils, asphaltenes and resins), preferably require for a lower temperature (350 °C), wherewith the destruction of components is minimal.

With increasing the pyrolysis temperature from 350 to 800 °C, the chromatographic profiles of the resins and asphaltenes exhibit additional peaks to appear (Table 2) corresponding to ethylbenzene, *p*-xylene, styrene, *o*-xylene, 1-ethyl-3-methylbenzene, and other components those were not revealed at 350 °C. The composition of the pyrolysis products formed

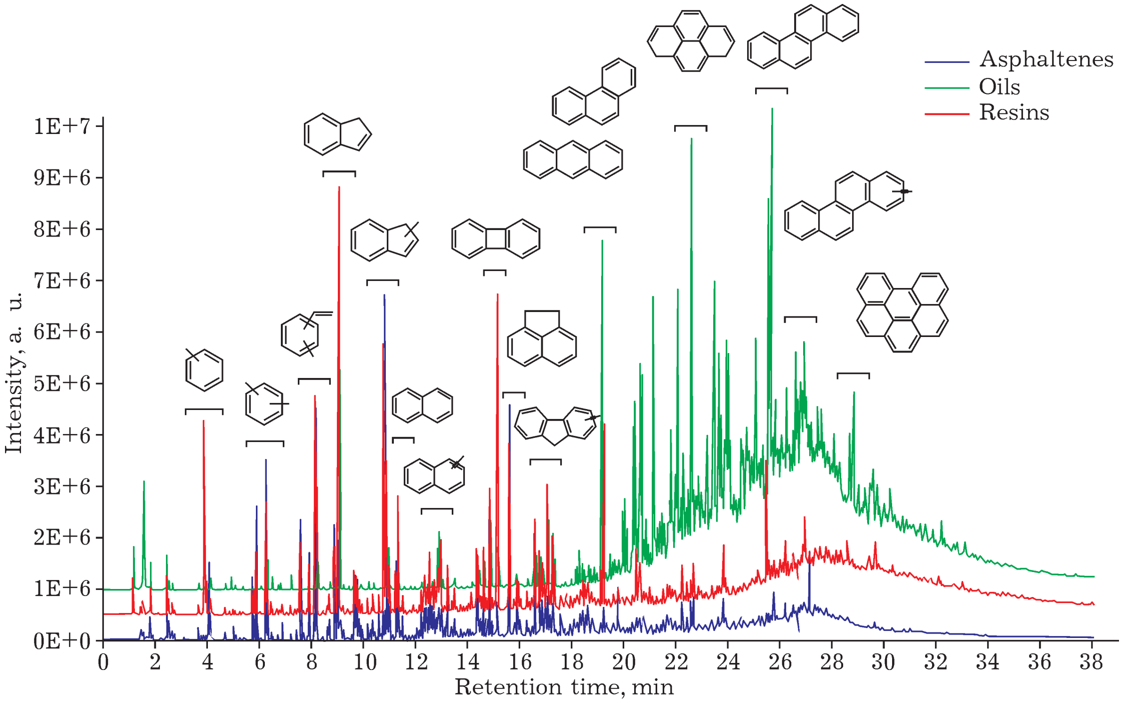


Fig. 3. Chromatographic profiles for the pyrolysis products of oils, resins and asphaltenes (800 °C). The profiles are shifted with respect to each other for suitable presentation.

TABLE 3

Identified composition for the pyrolysis products of oils, resins and asphaltenes in HPR

Fragmentary ion (*m*/*z*)	Formula	Compounds and homologues	Content, mass %		
			Oils	Resins	Asphaltenes
92	C_7H_8	C_1-benzene	0.01	2.73	0.98
106	C_8H_{10}	C_2-benzene	0.02	0.84	1.87
120	C_9H_{12}	C_3-benzene	0.02	0.97	1.87
118	C_9H_{10}	C_3(//)-benzene	0.32	3.87	6.02
132	$C_{10}H_{12}$	C_4(//)-benzene	0.08	1.11	2.14
130	$C_{10}H_{10}$	C_4(2//)-benzene	0.08	0.52	0.91
	Σ Homologues of benzene		**0.53**	**10.04**	**13.79**
116	C_9H_8	Indene	0.64	4.10	4.89
130	$C_{10}H_{10}$	C_1-indene	0.16	2.25	3.73
144	$C_{11}H_{12}$	C_2-indene	0.06	1.63	2.94
158	$C_{12}H_{14}$	C_3-indene	0.01	–	0.04
	Σ Indene and its homologues		**0.87**	**7.98**	**11.60**
128	$C_{10}H_8$	Naphthalene	0.17	1.90	0.51
142	$C_{11}H_{10}$	C_1-naphthalene	0.54	3.42	3.12
156	$C_{12}H_{12}$	C_2-naphthalene	0.20	1.40	2.45
170	$C_{13}H_{14}$	C_3-naphthalene	0.02	0.42	0.47
130	$C_{10}H_{10}$	1,4-Dihydronaphthalene	0.03	0.66	0.91
	Σ Naphthalene and its homologues		**0.96**	**7.80**	**7.46**
154	$C_{12}H_{10}$	Diphenyl	0.02	1.14	1.23
168	$C_{13}H_{12}$	C_1-diphenyl	0.05	0.78	0.73
182	$C_{14}H_{14}$	C_2-diphenyl	0.01	0.17	0.65
196	$C_{15}H_{16}$	C_3-diphenyl	0.03	0.07	0.31
	Σ Diphenyl and its homologues		**0.11**	**2.16**	**2.92**
152	$C_{12}H_8$	Biphenylene	0.53	2.80	3.23
	Σ Biphenylene		**0.53**	**2.80**	**3.23**
154	$C_{12}H_{10}$	Acenaphthylene	0.03	1.32	2.66
	Σ Acenaphthylene		**0.03**	**1.32**	**2.66**
166	$C_{13}H_{10}$	Fluorene	0.54	1.15	3.41
180	$C_{14}H_{12}$	C_1-fluorene	0.23	0.85	3.56
	Σ Fluorene and its homologues		**0.77**	**2.00**	**6.97**
178	$C_{14}H_{10}$	Anthracene/phenanthrene	1.37	1.72	0.78
192	$C_{15}H_{12}$	C_1-anthracene/phenanthrene	3.00	1.60	1.49
206	$C_{16}H_{14}$	C_2-anthracene/phenanthrene	1.42	0.29	0.46
220	$C_{17}H_{16}$	C_3-anthracene/phenanthrene	–	–	0.16
	Σ Anthracene/phenanthrene and their homologues		**5.79**	**3.61**	**2.89**
204	$C_{16}H_{12}$	Phenyl-naphthalene	1.92	1.05	1.83
218	$C_{17}H_{14}$	Phenyl-C_1-naphthalene	1.43	0.71	0.12
232	$C_{18}H_{16}$	Phenyl-C_2-naphthalene	0.24	–	–
	Σ Phenyl naphthalene and its homologues		**3.59**	**1.76**	**1.95**
202	$C_{16}H_{10}$	Pyrene	3.19	0.60	0.68
216	$C_{17}H_{12}$	C_1-pyrene	8.35	1.12	1.39
230	$C_{18}H_{14}$	C_2-pyrene	4.78	0.76	1.16
244	$C_{19}H_{16}$	C_3-pyrene	–	–	0.71
	Σ Pyrene and its homologues		**16.32**	**2.48**	**3.94**
228	$C_{18}H_{12}$	Chrysene	6.75	0.49	0.61
242	$C_{19}H_{14}$	C_1-chrysene	5.39	3.80	2.78
256	$C_{20}H_{16}$	C_2-chrysene	–	0.84	1.15
270	$C_{21}H_{18}$	C_3-chrysene	2.77	1.13	0.90
	Σ Chrysene and its homologues		**14.91**	**6.26**	**5.44**
252	$C_{20}H_{12}$	Perylene/benzopyrene	5.21	0.81	0.70
266	$C_{21}H_{14}$	C_1-perylene/benzopyrene	3.07	5.21	1.03
280	$C_{22}H_{16}$	C_2-perylene/benzopyrene	1.52	0.50	0.06
294	$C_{23}H_{18}$	C_3-perylene/benzopyrene	0.77	–	–
	Σ Perylene/benzopyrene and their homologues		**10.57**	**6.52**	**1.79**
276	$C_{22}H_{12}$	Benzo(ghi)perylene	0.88	0.58	–
290	$C_{23}H_{14}$	C_1-benzo(ghi)perylene	0.04	0.06	–
304	$C_{24}H_{16}$	C_2-benzo(ghi)perylene	0.14	–	–
	Σ Benzo(ghi)perylene and its homologues		**1.06**	**0.64**	**–**
Total			**56.05**	**55.38**	**64.62**

is caused by a more profound level of destruction for the components of the fractions under investigation, and by releasing the fragments, being originally a part of heavier components.

For oils, the main differences in composition with increasing the temperature of pyrolysis from 350 to 800 °C are exhibited only by increasing the intensity of the peaks due to the intensification of evaporation processes within this temperature range.

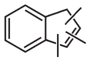
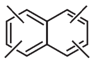
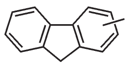
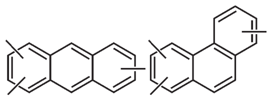
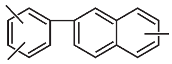
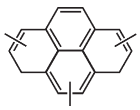
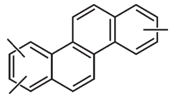
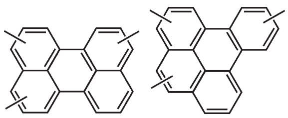
Figure 3 shows chromatographic profiles obtained according to the total ion current for the oils, resins and asphaltenes. It can be seen that the resins and asphaltenes insignificantly differ from each other in composition, whereas oil species exhibit characteristic intense signals at higher retention time values.

Thus, the oils represent a mixture of aromatic hydrocarbons with low molecular mass, m/z 300 amu.

The interpretation of the mass spectra of individual components formed in the course of pyrolysis, according to molecular ions thereof is complicated to a considerable extent by a large number of the fragmentary ions: it is impossible to identify specific structural groups and, therefore, to judge about the nature and structure of the high-boiling fraction. Nevertheless, a detailed analysis of the mass spectra of each component revealed the presence of similar fragmentary ions, which indicates that there are structural groups with identical nature present therein. For performing a complete structural analysis, we used a method of scanning the individual masses for the most informative fragmentary ions inherent in toluene (m/z 92), indene (m/z 116), naphthalene (m/z 128), biphenyl (m/z 154), biphenylene (m/z 152), acenaphthylene (m/z 154), fluorene (m/z 166), anthracene/phenanthrene (m/z 178), phenyl/

TABLE 4

Main structural fragments of oils, resins and asphaltenes (content more than 5 %)

Fragments	Main structural units	Content, mass %		
		Oils	Resins	Asphaltenes
Homologues of benzene		–	10.0	13.8
Indene and its homologues		–	8.0	11.6
Naphthalene and its homologues		–	7.8	7.5
Fluorene and its homologues		–	–	7.0
Anthracene/phenanthrene and their homologues		5.8	–	–
Phenyl/naphthalene and its homologues		3.6	–	–
Pyrene and its homologues		16.3	–	–
Chrysene and its homologues		14.9	6.3	5.4
Perylene/benzopyrene and their homologues		10.6	6.5	–

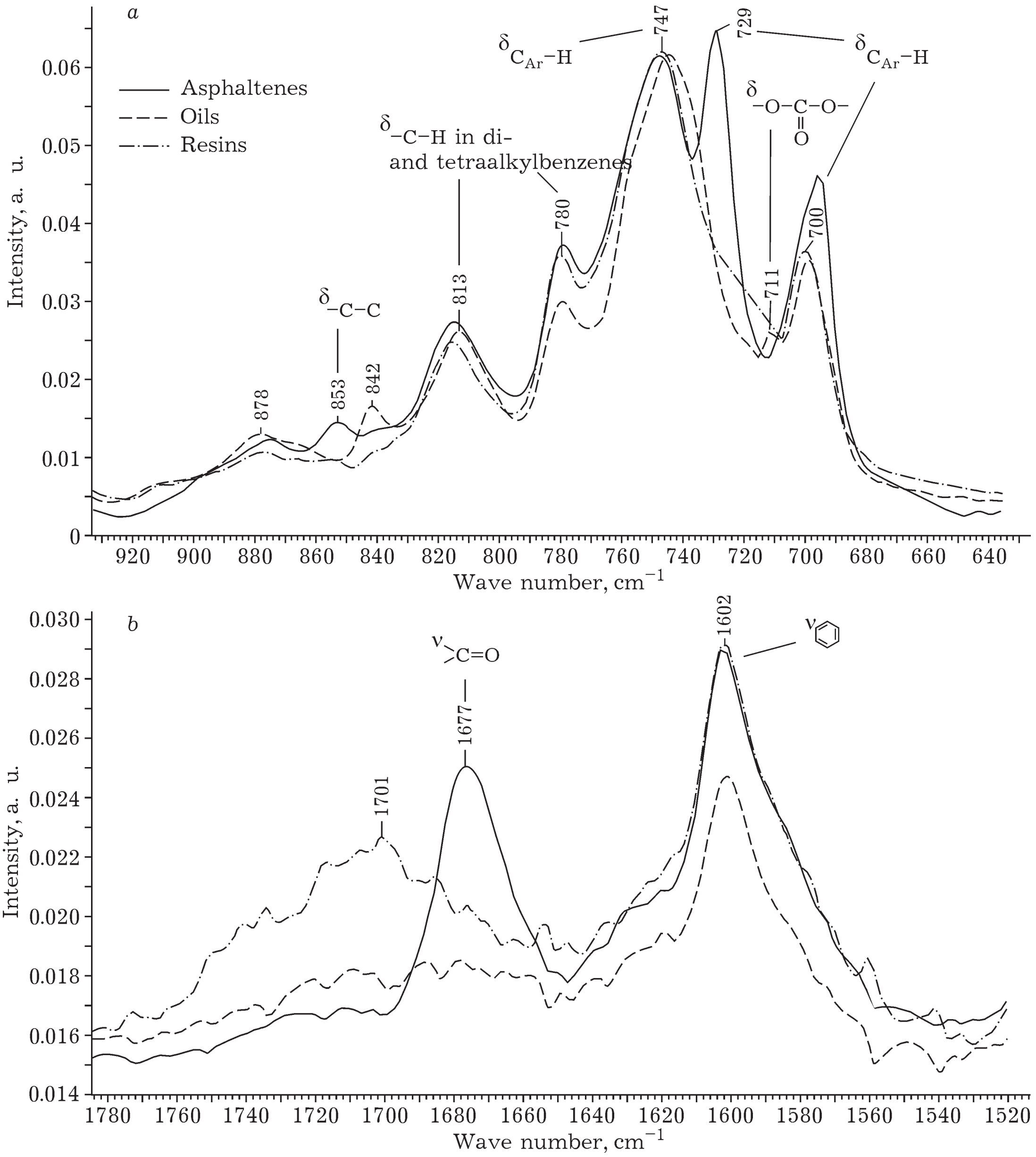


Fig. 4. IR spectra of oil species, resins and asphaltenes within the range of 640–920 (*a*) and 1540–1780 cm^{-1} (*b*).

naphthalene (*m/z* 204), pyrene (*m/z* 202), chrysene (*m/z* 228), perylene/benzopyrene (*m/z* 252), benzo(ghi)perylene (*m/z* 276) as well as for the characteristic ions of the homologues thereof. The results of investigations performed at 800 °C are presented in Table 3.

The resin molecules are constructed of 1–2- and (more rarely) 4–5-ringed aromatic fragments; asphaltene molecules consist mainly of 1–2- and (to a lesser extent) 3–4-ringed aromatic fragments. Asphaltenes and resins are characterized by a high content of the fragments of benzene, indene, naphthalene, chrysene homologues *i. e.*, almost 30 % of the fractions isolated by means of extraction with adsorption (Table 4).

The oils represent a mixture of low molecular condensed aromatic compounds consisting of 3–6-ringed aromatic hydrocarbons. The most part of the oil species (about 40 %) is presented by the homologues of pyrene, chrysene and perylene/benzopyrene (see Table 4).

Additionally, the differences in the composition of resins and asphaltenes were revealed using IR spectroscopy (Fig. 4). So, asphaltenes, unlike oils and resins, contain carbonate ($\nu = 711$ cm^{-1}) and carbonyl group ($\nu = 1677$ cm^{-1}), which indicates a higher polarity of these compounds.

The data obtained could be used in order to simulate the composition of the heavy part of HPR.

CONCLUSIONS

It is demonstrated that the method of adsorption extraction can be used for oil species and petroleum fractions in order to separate HPR into the fractions of oils, resins and asphaltenes; the method of pyrolysis gas chromatography-mass spectrometry has been proved promising for determining the composition of the HPR. The pyrolysis temperature was chosen so that to provide determining a more complete composition of the objects. Individual composition has been established for the oils, species and basic structural fragments have been revealed for resins and asphaltenes. It has been determined that the oils represent a mixture of low molecular mass condensed aromatic compounds, whereas the asphaltenes and resins represent a mixture of high molecular mass condensed aromatics. The oils are composed primarily of a mixture of 3–6-ringed aromatic hydrocarbons. The resin molecules consist of 1–2- and (rarely) 4–5-ringed aromatic fragments. The molecules of asphaltenes mainly consist of 1–2-ringed and (in smaller amounts) 3–4-ringed aromatic fragments.

Using the methods of PGHMS and IR spectroscopy, we have identified more than 70 % of the heavy part of the HPR, which could not be done earlier by means of other methods.

On the basis of earlier obtained data concerning the composition of the light part of the HPR and the results of our studies on the HPR heavy part, we have proposed recommendations concerning the processing of the HPR. An important direction in processing the HPR is presented by naphthalene isolation in pure form provided by its high content (13 %) and low diphenyl content (less than 0.9 %) therein, which diphenyl complicates the process of pure naphthalene isolation. A promising direction of using the HPR consists in obtaining dark petroleum polymeric resins (DPPR). The yield of DPPR is primarily affected by the content of the heavy part of HPR (about 40 %) and the content of unsaturated hydrocarbons (almost 10 %); those could participate in the reactions of polymerization, polycondensation and densification.

REFERENCES

1 Berents A. D., Men'shchikov V. A., *Khim. Prom.*, 5 (1993) 19.

2 Lebedeva I. P., Lazarev D. G., Doshlov O. I., Lubinskiy M. I., Lebedeva N. P., *V Mire Nauchnykh Otkrytiy*, 5 (2009) 25.

3 Mukhina T. N., Lesokhina G. F., Kolesnikova T. A., Tsekhanovich M. S., Sostav i Pererabotka Tyazhelykh Smol (Review), Moscow, 1979.

4 STO 1246–2011 FR.1.31.2011.10353 (IPC, SB RAS). Massovaya Dolya Smolisto-Asfaltenovykh Veshchestv v Neftyakh, Neftyanykh Fraktsiyakh, Prirodnom Bitume, Ugle, Organicheskom Veshchestve Porod, Produktakh Kerogena i Uglya. Gravimetricheskiy Metod Izmereniy.

5 Lebedevz M. A., Kolesnik V. D., Mashukov V. I., Egorov A. V., *Izv. TPU*, 316, 3 (2010) 102.