

Low Temperature Pyrolysis of Sapropelite Coals for Obtaining Initial Products for Industrial Organic Synthesis

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Abstract

Results of experiments on low-temperature pyrolysis of sapropelite coals that can be used to develop scientific foundations of technology for processing of sapropelite fossil fuels in order to transform them into synthetic fuel and raw materials for chemical industry are described and discussed. Pyrolysis products have been obtained from sapropelite coals of various deposits with different degree of catagenetic maturity of the organic matter. The yield of liquid products for some coal samples was as high as 60 % (by mass). Liquid pyrolysis products have been studied ¹H and ¹³C NMR spectroscopy and separated into fractions column chromatography and distillation. According to chromatato-mass spectrometry the obtained fractions are complex mixture of hundreds of compounds. The bulk of pyrogenetic products of the samples consists of alkanes and alkenes of normal structure. The high yield of liquid pyrolysis products obtained from sapropelite coals permits considering them as a promising raw material for obtaining artificial liquid fuels. Similarly to the traditional use of petroleum, processing of these products with a wide use of fractionation and hydrogenization is necessary.

INTRODUCTION

The problem of development of technologies for obtaining products from coals which could compete with petroleum processing products has arisen long ago and has not lost its importance until the present time [1–3]. The excess of coal reserves over the reserves of other organic raw materials permits considering coals as the most promising source of obtaining liquid fuels [4]. A special place among solid fossil fuels is occupied by sapropelite coals; they differ from other coals by a high hydrogen content, and this is their advantage over the majority of alternative raw materials. Besides, sapropelite coals are related to petroleum in their origin and similar to it with respect to the initial organic matter [5]. The yield

of volatile compounds from sapropelite coals is as high as 60 % and more. These coals seem to be the most attractive from the viewpoint of their use for obtaining chemical products.

The oldest and simplest method of extracting liquid products from coal is pyrolysis. In order to evaluate the potential yield of products in pyrolysis and to compare the data from various types of raw materials, the method of low-temperature pyrolysis is usually used. The method is carried out according to technical specifications (GOST 3168–66). The heating leads to degradation of the organic matter of the coal and is accompanied by redistribution of hydrogen between the formed volatile products and the solid carbonaceous residue. The formed low-temperature pyrolysis products represent a complex mixture of hundreds of

compounds. Group composition of pyrolysis product of sapropelite coals and oil shales related to them has mainly been investigated [6–15]. However, in order to choose the optimal conditions of the technological process and intensify it, and for an efficient storage and use of liquid products, a detailed study of their molecular composition is necessary. Besides, it is important to know the presence and concentration of chemical compounds in the liquid products of coal processing which may have a carcinogenic and mutagenic effects.

EXPERIMENTAL

Data of proximate, ultimate and petrographic analysis of the coals used are presented in Table 1.

NMR spectra were recorded on a WP-200 (Bruker Physik AG). As the internal standard in ^1H NMR spectra recording, hexamethyldisiloxane (0.04 δ); in recording ^{13}C NMR spectra, chloroform (76 of TMC) was used. Chromatomass spectrometry analysis was carried out on a Hewlett-Packard HP-5971A (a glass capillary column 25 m length, inner diameter of 0.33 mm, the immobile phase SE-30; the column heating regime: 2 min 40 °C, 40–100 °C (5 °C/min), 6 min 100 °C, 100–200 °C (10 °C/min), 6 min 200 °C, 200–300 °C (15 °C/min), 15 min 300 °C; the evaporator temperature 320 °C, separator temperature 300 °C (helium as the carrier gas). The energy of ionizing electrons was 70 eV.

RESULTS AND DISCUSSION

The liquid and gaseous products of the low-temperature pyrolysis were obtained from sapropelite coals of different degree of catagenetic maturity of the organic substance. The yield of pyrolysis products of the coals is presented in Table 2.

It was established that gaseous products formed in low-temperature pyrolysis consisted mainly of CO , CO_2 , H_2O , alkanes $\text{C}_1\text{--C}_4$, and alkenes $\text{C}_2\text{--C}_4$. Pyrogenetic water has phenols and carbon acids in a small amounts. The yield

TABLE 1
Characteristics of samples of sapropelite coals

Sample No.	Coal basin, deposit Rank or mine	Стадия карбонизации	Proximate analysis, % mass		Ultimate analysis, % mass			Petrographic composition, %					
			W^a	A^d	V^{daf}	C^{daf}	H^{daf}	S^{daf}	N^{daf}	Vitrinite	Inertinite	Leiptinite	Alginite
1	Balkhashite	Peat	2.9	7.8	95.1	72.9	10.7	0.8	0.6	0	0	0	100
2	Kansk-Achinsk, Sobolevskiy	Brown	10.1	25.4	73.9	70.3	10.2	0.8	0.9	27	0	0	73
3	Podmoskovny, Sereideiskiy mine	»	3.1	19.3	73.8	74.6	8.6	3.2	–	8	1	3	88
4	Irkutsk, Budagovo	Subbituminous	1.1	11.7	86.3	80.5	10.4	0.2	1.2	10	0	0	90
5	Lensk, Taimylyr	»	1.1	3.5	84.3	82.6	9.5	0.3	0.7	13	0	0	87
6	Donetz Basin, Torez mine	Bituminous	0.7	12.7	40.4	86.1	4.9	1.1	–	56	8	7	29

Note. W^a – analytical water, A^d and V^{daf} – ash content and yield of volatile compounds in terms of dry and dry ash-free mass, respectively.

TABLE 2

Yield of pyrolysis products of sapropelite coals (% of coal mass) and fractions obtained from pyrolysates of these coals by column chromatography and distillation (% of pyrolysate mass)

Sample No.*	Pyrolysis		Колоночная хроматография						Перегонка				
	Pyro-lysate	Solid residue	Pyroge-netic water	Gas and losses		Fraction		Residue		Fraction			
				hexane	benzene	ether	Residue	I	II	III	Residue	Gas and losses	
1	65	17	9	9	37	24	11	28	13.5	13.6	39.7	24.6	8.6
2	26	48	15	11	15	9	10	66	14.4	34.6	19.3	26.9	4.8
3	39	40	8	13	15	11	7	67	15.0	43.0	18.5	13.1	10.4
4	47	37	4	12	18	13	13	56	28.9	15.2	37.5	7.9	10.5
5	55	28	7	10	20	15	12	53	7.5	24.8	48.4	15.6	3.7
6	10	72	3	15	12	30	8	50	-	-	-	-	-

*See Table 1.

of liquid products (pyrolysate) is essentially different for various coals. It mainly depends on the degree of maturity of the organic matter and the composition and amounts of the mineral matter. The highest yield of the pyrolysate was obtained for the most young coal (Balhashite) with a small ash content (see Tables 1, 2). A high yield of the liquid products was obtained for Taimylyr coal (ash content of 3.5 %). Among the studied sapropelite sedimentary rocks the Torez coal was characterized by the highest maturity degree of the organic matter, by the greatest contribution of vitrinite and a low hydrogen content. The lowest yield of liquid pyrolysis products was obtained with this coal.

Initially, pyrogenetic products were characterized by means of NMR spectroscopy. Comparing of the spectra of the liquid products showed that they differed only slightly from each other and consisted mainly of aliphatic hydrocarbons; they contained small amounts of olephine and aromatic compounds. The presence of straight alkane chains was witnessed by intense CH_2 group signals at 22.7, 29.4, 29.6, 29.7 (the most intense signal), 21.9 and CH_3 group signals at 14.0 ppm of TMS. In the spectra of all samples there was a signal at 33.8 ppm attributed to the methylene group which neighbored on the terminal double bond. In the interval of 32.0 to 45.0 ppm of TMS, there appeared signals of carbon atoms which either were centres of ramification within the chain or neighbored on the ramification centres. Peaks of low intensity in this region were found in pyrolysates obtained from samples of Budagovo and Sobolevskiy coals and Balkhashite. In the spectra of liquid products of the same samples, weak signals in the region of 23.4–23.8 ppm of TMS were also observed. Probably, they belonged to methylene groups localized at the distance of one or two bonds from the ramification centers. The signals observed at 114 and 139 ppm correspond to terminal alkenes. The group of the lowest peaks between 114 and 139 ppm of TMS characterizes aromatic components. Group belonging in NMR spectra was determined on the basis of literature data [16–19]. As it follows from [17], using NMR spectra and in particular the data on the intensity of signals of carbon atoms of me-

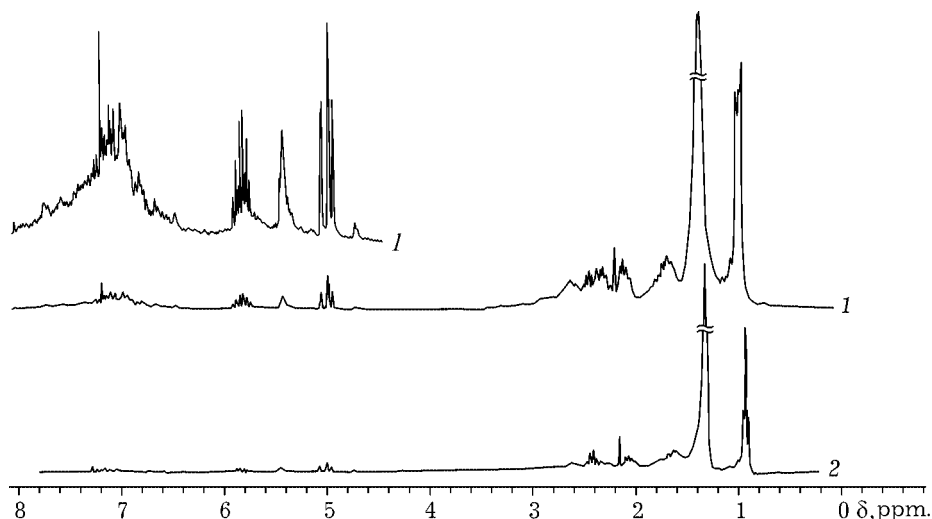


Fig. 1. ^1H NMR spectra (5 % solutions in CDCl_3) of pyrolysates of Budagovo (1) and Taimylyr (2) coals.

thylene groups (taken into account the most intense peaks at 29.7 and 29.6 ppm of TMS) and those of carbon atoms of methyl groups (14.0 p.p.m. of TMS), it is possible to estimate approximately the length of alkane chains. When calculating this parameter for the liquid products, it turned out that the mean length of alkane chains for the Sobolevskiy, Taimylyr and Torez coals was about 18 (17–19) carbon atoms, and for other samples it was shorter; the smallest length (15 carbon atoms) was calculated for Balkhashite.

In ^1H NMR spectra (Fig. 1) signals at 1.3 and 0.9 δ corresponding to methylene and methyl groups were dominant. Besides, peaks of low intensity were observed in the region of 1.7–3.1 δ characteristic of hydrogen of methylene groups situated at the aromatic ring or neighbouring on the olephine bond. The wide signal at 2.3 δ in the same region corresponds to the proton of a group of CH_2CO type. Signals in the region of 4.9–6.2 δ were deciphered as signals of olephine groups. Within the range of 6.3–8.0 δ , protons of aromatic structures are manifested. Using the data on the integral intensity the relative number of aromatic structures was calculated. It was found that their contribution increased as so did the degree of maturation of the organic matter of the coal. The relative number of aromatic structures in pyrolysis products of Torez coal turned out to be by 7 times greater than the same parameter of Balkhashite.

With the help of NMR spectroscopy, only the main classes of compounds present in pyrolysates of the studied sapropelite coals were determined. For more detailed analysis of the composition of pyrogenetic products, their preliminary separation into fractions was carried out by two methods - column chromatography and distillation. A pyrolysate of 0.3–0.4 g was placed into the column filled with aluminium oxide and eluted successively with hexane, benzene and diethyl ether (see Table 2). The obtained fractions were studied by chromatomass spectrometry. As an example, mass chromatograms of the hexane and benzene fractions of pyrolysate of Sereideisky coal are presented in Fig. 2. The content and contribution of separate compounds were calculated by peak intensities on full ion current mass chromatograms. The bulk (>60 %) of the hexane fraction in the products was made up by *n*-alkanes (Table 3). The range of distribution of *n*-alkanes varied within the limits of C_{12} to C_{30} with the maximum at C_{15} – C_{17} . Only for the Sobolevskiy sample the maximum was observed in the region of C_{20} – C_{21} . As one can see in Fig. 3, distributions of alkanes for various pyrolysates do not coincide. In the case of Balkhashite, the distribution of alkane hydrocarbons was bimodal with maxima at C_{17} and C_{24} (see Fig. 3, a). For pyrolysate of Sobolevsky coal the distribution is shifted in the direction of more high-molecular compounds, the maximum being observed at C_{20} – C_{21}

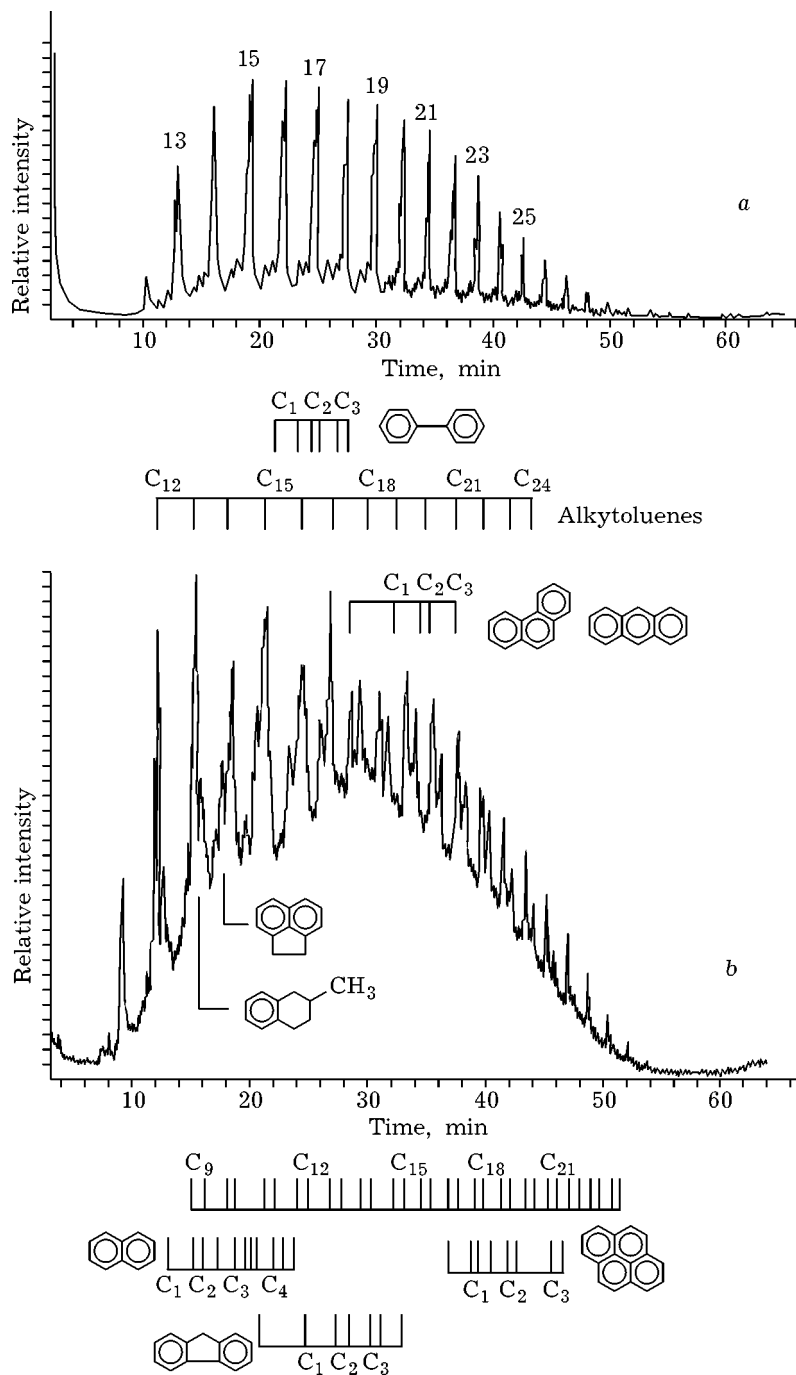


Fig. 2. Mass chromatograms of hexane (a) and benzene (b) fractions of pyrolysate of Seredeisky coal (numbers indicate the carbon numbers of the molecule).

(see Fig. 3, b). The distribution ranges of *n*-alkanes for the hexane fraction of Seredeiskiy and Budagovo coals coincide and are shifted towards more low-molecular homologs whose distribution maximum is at C₁₆-C₁₇. In the case of Taimylyr coal, a uniform distribution of pyrogenetic alkanes with the maximum at C₁₇ is observed.

A considerable part of the hexane fraction (17-32 %) of all pyrolysates is made up by *n*-alkenes. The distribution of these compounds, judging by mass-fragmentograms recorded by the ion with *m/z* 97, varies from C₁₂ to C₂₇; the distribution maximum corresponds to hydrocarbons C₁₅-C₁₇, more low-molecular compounds being prevalent (see Table 3).

TABLE 3

Results of chromatomass spectrometry studies of hexane fractions

	Номер образца*					
	1	2	3	4	5	6
<i>n</i> -Alkanes	C ₁₂ -C ₂₉	C ₁₂ -C ₃₀	C ₁₂ -C ₃₀	C ₁₃ -C ₂₇	C ₁₂ -C ₂₇	C ₁₂ -C ₂₇
Content, %	68	64	60	61	68	65
Distribution maximum	C ₁₇	C ₉ , C ₂₁	C ₁₆	C ₁₇	C ₁₇	C ₁₅ -C ₁₈
Contribution, %:						
C _H -C ₁₈ **	49	36	54	60	75	52
C ₁₈ -C _I **	51	64	46	40	25	48
<i>n</i> -Alkenes	C ₁₆ -C ₂₇	C ₁₃ -C ₂₇	C ₁₂ -C ₂₉	C ₁₃ -C ₂₇	C ₁₃ -C ₂₅	C ₁₃ -C ₂₆
Content, %	18	25	32	19	17	25
Distribution maximum	C ₁₆	C ₂₀	C ₁₅	C ₁₅	C ₁₅	C ₁₆ -C ₁₇
Contribution, %:						
C _H -C ₁₈ **	66	63	62	70	91	68
C ₁₈ -C _I **	34	37	48	30	9	32
Cycloalkanes	C ₁₃ -C ₂₆	C ₁₄ -C ₂₆	C ₁₂ -C ₂₆	C ₁₄ -C ₂₃	C ₁₂ -C ₂₃	C ₁₂ -C ₂₄
Content, %	14	11	8	20	15	10
Distribution maximum	C ₅ -C ₁₆	C ₁₇	C ₁₅	C ₁₄	C ₁₄ , C ₁₅	C ₁₇

*Results of chromatomass spectrometry studies of hexane fractions See Table 1.

**C_i, C_f - initial and final hydrocarbon, respectively.

Cycloalkanes are another class of compounds found in hexane fractions. The fraction of the total mass of these hydrocarbons in different samples varied from 8 to 20 %. The range of their distribution is found in the region of C₁₂-C₂₆, the maximum being at C₁₅-C₁₇ (see Table 3).

In benzene fractions of the pyrolysates the alkyl-substituted aromatic compounds are prevalent. Among them alkylbenzenes (C₆-C₁₉) and alkyltoluenes (C₁₂-C₂₄) are dominant. Apart from naphthalene, fluorene, phenanthrene and pyrene, homologs of these compounds with C₁-C₄ alkyl substituents have been detected. The other aromatic compounds such as tetraline, indan, acenaphthene with C₁-C₄ substituents have been identified. A considerable part of benzene fractions is made up by straight-chain ketones with a distribution range of C₁₁-C₂₅. Small amounts of *n*-alkanes and *n*-alkenes have been found in these fractions.

Another method of separation of low-temperature pyrolysis products is distillation at atmospheric pressure. It has made it possible to study a large number of pyrogenetic products (see Table 2), because in column chromatogra-

phy, after elution of a pyrolysate samples with solvents, there remains still a considerable part of fraction of unidentified high-molecular compounds. In distillation, pyrolysate (2.0-2.5 g) was placed into a quartz bowl, heated at the atmospheric pressure, and fractions were taken depending on the heating temperature. The first fraction was taken at the temperature of 20-220 °C, the second one at 220-350 °C, and the third one at 350-500 °C (see Table 2). Then all these fractions were studied by chromatomass spectrometry. The most interesting are the results of study of Balkhashite and Taimylyr coal pyrolysates in whose distillation the greatest amount of liquid products was formed. In Fig. 4, chromatograms of the three fractions of liquid products of pyrolysis of Taimylyr coal are presented. The data on the first fraction are summarized in Table 4. The most complicated turned out to be the mixture of compounds in the second fraction where more than 600 individual components were identified. The basic homologous series in this fraction are C₈-C₂₅ *n*-alkanes; C₈-C₂₃ *n*-alkenes and their numerous isomers with various localization of double bonds; C₈-C₁₉ alkyldienes

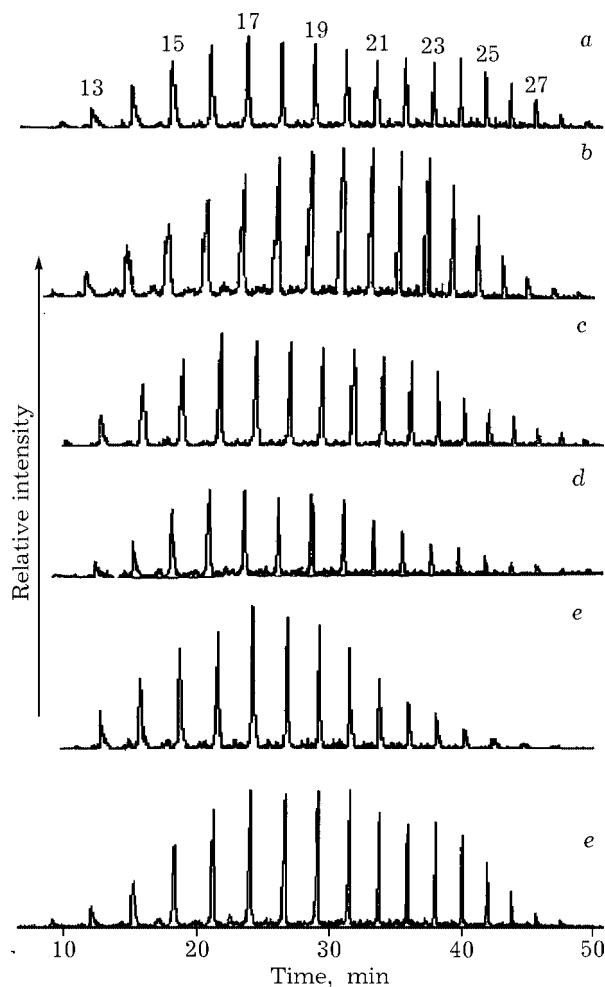


Fig. 3. Mass chromatograms of *n*-alkanes (m/z 99) of hexane fractions of pyrolysates of Balkhashite (a) and Sobolevskiy (b), Seredeiskiy (c), Budagovo (c), Taimylyr (d) and Torez (e) coals.

(numerous isomers); benzene derivatives, first of all alkylbenzenes with C_2 – C_{20} alkyl substituents of normal structure; numerous derivatives of alkylbenzene with substituents having a ramified chain within the limits of C_3 – C_7 ; alkylindane derivatives; alkylindenes with C_1 – C_3 substituents; alkylnaphthalenes with C_1 – C_{16} substituents; alkylnaphthalenes with C_1 – C_8 substituents containing non-saturated bonds; C_9 – C_{23} alkylcyclohexanes and C_8 – C_{10} alkylcyclopentanes; phenanthrenes with methyl substituents in various positions; alkylacenaphthanes with C_1 – C_3 substituents; alkylfluorenes with C_1 – C_3 substituents.

Among oxygen-containing compounds, carboxylic acids of C_4 – C_{12} series, ketones of C_8 – C_{13} series (mainly alkylmethylketones), alkylphenols with C_1 – C_4 substituents of both

linear and ramified type, and carbonyl-containing compounds of $CH_3COC_6H_5R$ type were found.

In the third distillate fraction of Taimylyr coal pyrolysate, mainly the same compound classes as in the second one have been detected. And since this is a more high-boiling fraction, it also includes more high-molecular homologs of the components mentioned above. Thus, the distribution of *n*-alkanes varied from C_9 to C_{29} , and carboxylic acids C_4 – C_{16} homologs were present. An increase of the length of alkyl substituents in cyclic compounds and a decrease of the fraction of alkadienes, alkylcyclohexenes and alkyl cyclopentenes were observed, and alkatrienes were completely absent.

Data for the first obtained fraction in distillation of balkhashite pyrolysate are presented in Fig. 5. In Fig. 5 the most of identified individual compounds are shown. Mass chromatography of the second and the third fractions are presented in Fig. 6, and data on the composition of main products are summarized and grouped in Table 5.

Comparing the chemical composition of liquid pyrogenetic products obtained from Balkhashite and Taimylyr coal, one can make an unequivocal conclusion about their similarity. It is noteworthy that the range of distribution of alkanes, alkenes, alkyldienes and alkyl substituents in cyclic compounds is wider in the case of pyrolysate of Taimylyr coal. Probably, it is caused by the considerably greater degree of maturity of the organic matter of sapropelite coal from the Taimylyr deposit. Distribution of hydrocarbonic components for respective fractions obtained in distillation of Balkhashite and Taimylyr coal pyrolysates practically coincided, especially for the second and the third fractions (see Figs. 4 and 6). The most intense peaks in chromatograms belong to alkanes and alkenes, whose total mass fraction makes up about 90 % of the mass of all the identified compounds.

CONCLUSIONS

In this way, the products of low-temperature pyrolysis (carbonization) of sapropelite coals

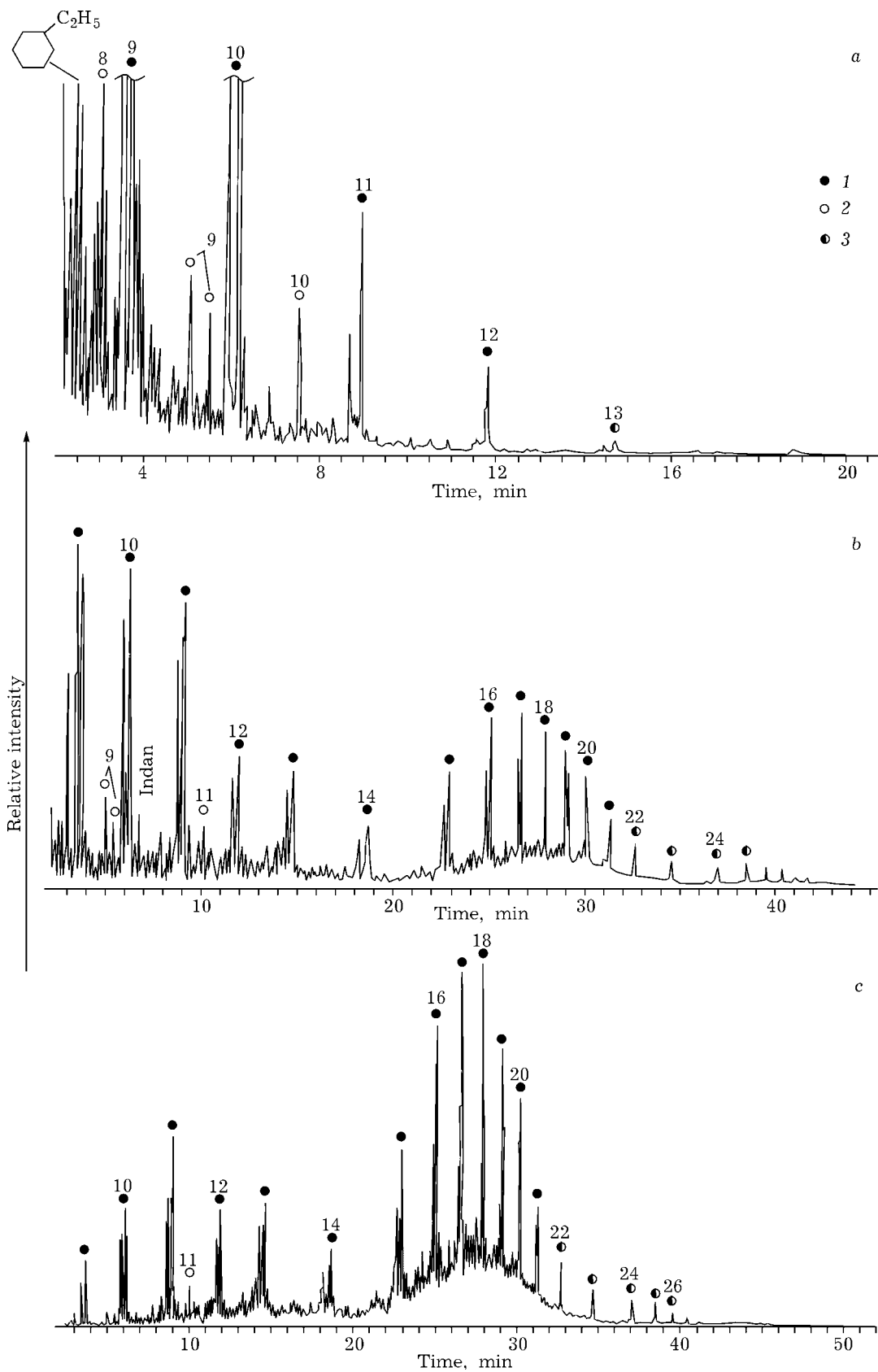


Fig. 4. Chromatograms of fractions obtained by distillation of pyrolysate of Taimylyr coal: a - fraction I, b - fraction II, c - fraction III (numbers over the peaks stand for the number of carbon atoms in the molecule); 1 - alkene-alkane pairs, 2 - alkylbenzenes, 3 - alkanes.

TABLE 4

Product composition of Fraction I obtained with distillation of pyrolysate of Taimylyr coal

Peak number	Retain- ing time, min	Molecu- lar mass	Compound	Peak ника	Retain- ing time, min	Molecu- lar mass	Compound
1	2.135	110	Alkyldiene C ₈	49	5.809	120	Alkylbenzene (C ₃)
2	2.213	112	Alkene C ₈	50	5.893	140	Alkene C ₁₀
3	2.245	110	Alkyldiene C ₈	51	5.955	94	Phenol
4	2.284	110	Alkylcyclopentene (C ₃)*	52	6.142	142	Alkane C ₁₀
5	2.319	110	Alkyldiene C ₈	53	6.261	140	Alkene C ₁₀
6	2.367	112	Alkene C ₈	54	6.400	122	Alkylmethoxybenzene (C ₁)
7	2.438	112	Alkylcyclohexane (C ₂)	55	6.400	138	Alkyldiene C ₁₀
8	2.484	126	Alkylcyclohexane (C ₃)	56	6.470	140	Alkene C ₁₀
9	2.532	110	Alkyldiene C ₈	57	6.528	120	Alkylbenzene (C ₃)
10	2.612	110	The same	58	6.598	134	Alkylbenzene (C ₄)
11	2.659	110	Alkylcyclopentene (C ₃)	59	6.598	138	Alkyldiene C ₁₀
12	2.695	110	Alkyldiene C ₈	60	6.724	138	The same
13	2.730	124	Alkyldiene C ₉	61	6.794	140	Alkylcyclohexane (C ₄)
14	2.776	124	The same	62	6.841	118	Indan
15	2.823	124	»	63	6.947	140	Alkene C ₁₀
16	2.893	106	Alkylbenzene (C ₂)	64	7.096	116	Inden
17	2.965	124	Alkylcyclopentene (C ₄)	65	7.305	138	Alkylcyclopentene (C ₃)
18	3.036	106	Alkylbenzene (C ₂)	66	7.387	134	Alkylbenzene (C ₄)
19	3.107	124	Alkyldiene C ₉	67	7.502	134	The same
20	3.179	124	The same	68	7.643	134	»
21	3.249	124	»	69	7.805	134	»
22	3.320	126	Alkene C ₉	70	7.944	108	Alkylphenol (C ₁)
23	3.390	124	Alkyldiene C ₉	71	8.036	108	The same
24	3.461	106	Alkylbenzene (C ₂)	72	8.141	134	Alkylbenzene (C ₄)
25	3.526	126	Alkene C ₉	73	8.292	132	Alkylindane (C ₁)
26	3.604	126	The same	74	8.487	154	Alkene C ₁₁
27	3.734	128	n-Alkane C ₉	75	8.661	154	The same
28	3.830	126	Alkene C ₉	76	8.743	108	Alkylphenol (C ₁)
29	3.966	124	Alkyldiene C ₉	77	8.764	142	Alkylketone C ₉
30	4.026	124	Alkylcyclopentene (C ₄)	78	8.825	154	Alkene C ₁₁
31	4.146	124	Alkyldiene C ₉	79	8.919	156	Alkane C ₁₁
32	4.217	126	Alkylcyclohexane (C ₃)	80	9.069	154	Alkene C ₁₁
33	4.335	126	Alkylcyclopentane (C ₄)	81	9.300	152	Alkyldiene C ₁₁
34	4.417	122	Alkyltriene C ₉	82	9.765	132	Alkylindane (C ₁)
35	4.464	124	Alkyldiene C ₉	83	10.065	132	The same
36	4.558	124	The same	84	10.500	122	Alkylphenol (C ₂)
37	4.627	122	Alkatriene C ₉	85	10.910	122	The same
38	4.685	124	Alkylcyclopentene (C ₄)	86	11.543	168	Alkene C ₁₂
39	4.733	124	Alkadiene C ₉	87	11.579	122	Alkylphenol (C ₂)
40	4.802	120	Alkylbenzene (C ₃)	88	11.786	170	Alkane C ₁₂
41	4.918	124	Bicyclo[3,3,1]nonane	89	12.220		Not identified
42	5.011	120	Alkylbenzene (C ₃)	90	12.700		The same
43	5.168	120	The same	91	12.850		»
44	5.261	126	Alkylketone C ₈	92	13.695	136	Алкилфенол (C ₃)
45	5.308		Not identified	93	14.421	136	The same
46	5.436	120	Alkylphenol (C ₃)	94	14.421	182	Alkene C ₁₃
47	5.576	140	Alkene C ₁₃₀	95	14.679	184	Alkane C ₁₃
48	5.645	138	Alkyldiene C ₁₀	96	18.758	198	Alkene C ₁₄

Note. In parentheses, the number of aliphatic carbon atoms in the molecule is indicated.

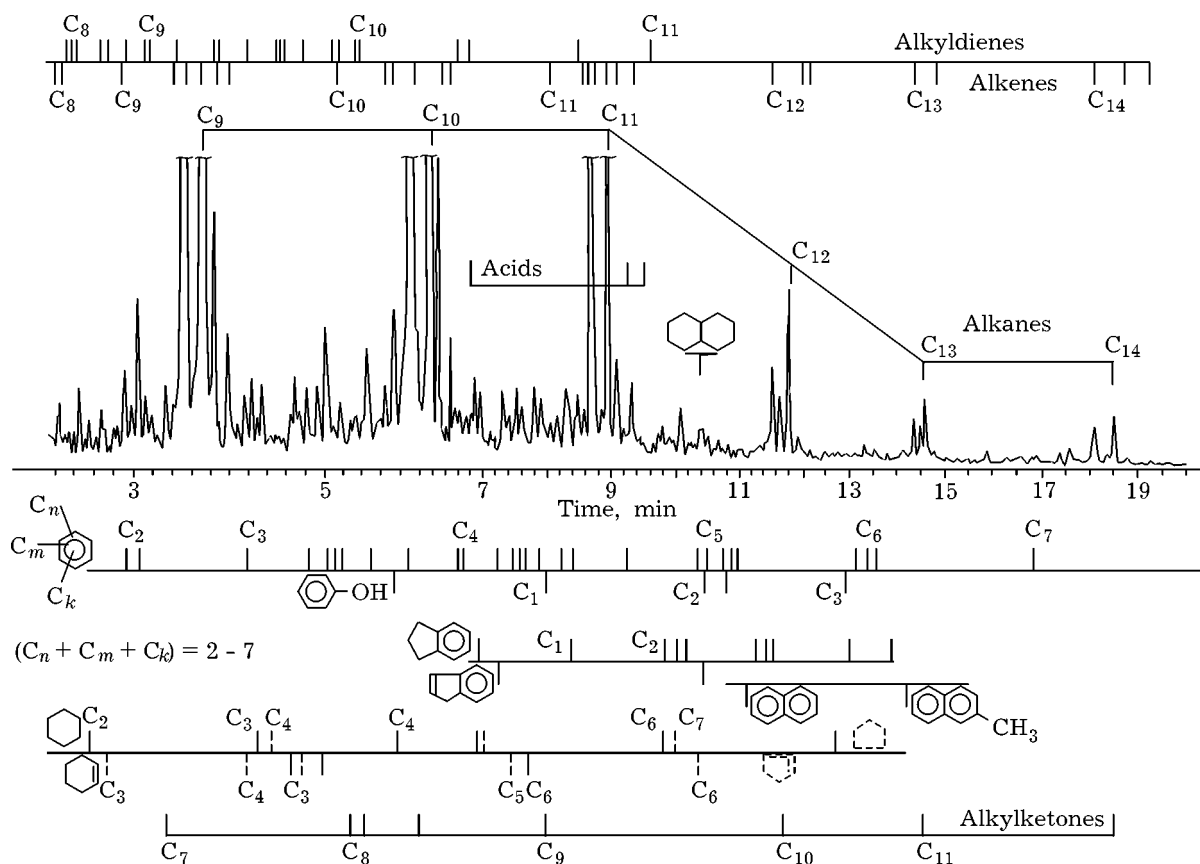


Fig. 5. Mass chromatogram of fraction I obtained by distillation of Balkhashite pyrolysate.

TABLE 5

Composition of main products obtained with Balkhashite pyrolysate distillation

Group of compounds	Molecular formula	Fraction	
		II	III
<i>n</i> -Alkanes	C _n H _{2n+2}	C ₉ -C ₂₂	C ₉ -C ₂₅
<i>n</i> -Alkenes	C _n H _{2n}	C ₈ -C ₂₃	C ₈ -C ₂₃
Alkyldienes	C _n H _{2n-2}	C ₈ -C ₁₅ , C ₁₇	C ₈ -C ₁₉ , C ₂₁
Alkyltrienes	C _n H _{2n-4}	C ₈ , C ₉	C ₉
Alkylketones	C _n H _{2n} O	C ₇ , C ₁₀ -C ₁₃	C ₇ , C ₉ -C ₁₃ , C ₁₈ , C ₁₉
Alkyl derivatives of:			
cyclohexane	C ₆ H ₁₂	C ₈ -C ₁₀ , C ₁₂ -C ₁₉	C ₉ , C ₁₃ -C ₂₀
cyclopentane	C ₅ H ₁₀	C ₉ , C ₁₀ , C ₁₃ -C ₁₅	C ₉ , C ₁₁ -C ₁₅
cyclohexene	C ₆ H ₁₀	C ₈ -C ₁₀	C ₈ -C ₁₀
cyclopentene	C ₅ H ₈	C ₈ , C ₁₀ , C ₁₂ , C ₁₃	C ₈ -C ₁₀ , C ₁₃
benzene	C ₆ H ₆	C ₈ -C ₁₆	C ₈ -C ₂₁
indan	C ₉ H ₁₀	C ₁₀ -C ₁₂	C ₁₀ -C ₁₄
inden	C ₉ H ₈	C ₁₀ , C ₁₁	C ₁₀ -C ₁₃
naphthalene	C ₁₀ H ₈	C ₁₁ -C ₁₂ , C ₁₆ , C ₁₇	C ₁₁ -C ₁₇ , C ₁₉
tetraline	C ₁₀ H ₁₂	C ₁₁	C ₁₁
fluorene	C ₁₃ H ₁₀	C ₁₄	C ₁₄ , C ₁₅
acenaphthene	C ₁₂ H ₁₀	C ₁₄	C ₁₄
phenanthrene	C ₁₄ H ₁₀	Not exposed	C ₁₅
phenol	C ₆ H ₅ O	C ₇ -C ₁₁	C ₇ -C ₁₃

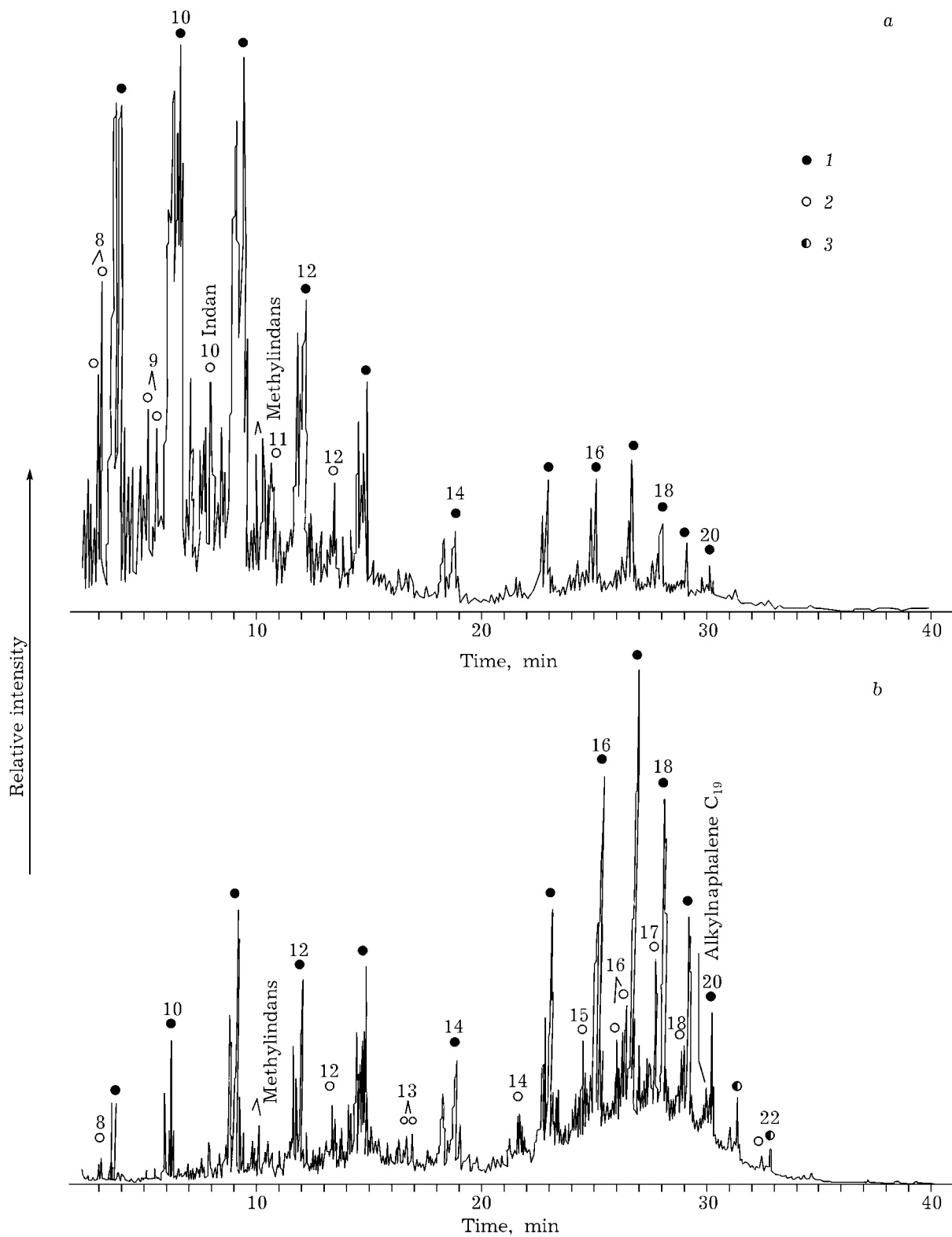


Fig. 6. Chromatograms of fractions obtained by distillation of Balkhashite pyrolysate: *a* - fraction II, *b* - fraction III (numbers above the peak stand for the number of carbon atoms in the molecule); 1 - alkene-alkane pairs, 2 - alkylbenzenes, 3 - alkanes.

are characterized by prevalent content of normal aliphatic hydrocarbons and a low yield of phenols. The compounds with long-chain substituents are dominant in the aromatic part of these products. The considerable yield of pyrogenetic products permits regarding the sapropelite coals as a promising raw material for obtaining chemical products, including artificial liquid fuels. The obtained liquid products cannot be directly used for preparation of standard hydrocarbon fuels. The service properties of fuels depend first of all on their chemical composition. So, *e.g.*, the main indicators of quality of motor fuels [20] are their knock stability (the octane number), fraction composition, chemical and physical stability, sulphur content. Since the bulk of the obtained products is made up by relatively high-molecular (>C₅) alkanes and alkenes of normal structure having a low octane number, subsequent processing of the products is necessary in order to increase the knock stability. This procedure includes such stages as degradation of hydrocarbons to low-molecular ones, isomerization, dehydrocyclization of alkanes to arenes, and in order to increase the chemical stability of fuels during storage it is necessary to remove alkenes. Probably, in this case the most convenient is the industrial process of catalytic reforming intended for heightening of quality of gasolines and carried out at temperatures of about 500 °C under the hydrogen pressure of 1.5 MPa in the presence of a bifunctional catalyst combining an acidifying and a hydration-dehydration functions. By its initial composition, the obtained pyrogenetic products are closer for obtaining diesel fuels. Considered as their service property is the inflammability whose estimation is carried out by the cetane rating. The highest cetane rating are characteristic of alkanes of normal structure, and the lowest inflammability is characteristic of bicyclic hydrocarbons – naphthalene homologs. From this it follows that the best is a diesel fuel containing much alkanes and little arenes. As for jet fuels [20], the density and the combustion heat value are basic properties. The heat value of a hydrocarbon depends on its hydrogen content and on the carbon/hydrogen ratio. The more hydrogen atoms the mole-

cule contains, the higher the heat value is. The highest heat value (in terms of unit mass) is characteristic of alkanes, the lowest one of arenes. The efficiency and the completeness of combustion of a fuel also depend on its chemical composition. Besides, combustion of arenes results in formation of soot and carbon deposit on the walls which have carcinogenic properties.

Although sapropelite coals are undoubtedly interesting as an organic raw material from the point of view of the yield and of the molecular group composition of low-temperature pyrolysis products, on the whole their processing is possible only on small-scale installations. It will probably have only a local significance, since in the majority of coal basins sapropelite coals are found only in the form of lenses and interlayers (sometimes rather powerful ones) in seams of humic coal.

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