Hydrocarbons in Products of Thermo-Hydrolytic Decomposition of Sapropelites

V. YU. ROKOSOVA, P. V. GORYUNOVA, YU. V. ROKOSOV, N. N. ROKOSOVA, S. A. SOZINOV

Institute of Coal Chemistry and Material Science, Federal Research Center of Coal and Coal Chemistry, Siberian Branch, Russian Academy of Sciences, Kemerovo, Russia

E-mail: chemgeo@rambler.ru

Abstract

Using gas chromatography-mass spectrometry the qualitative and quantitative composition of hydrocarbons generated during thermo-hydrolytic decomposition of sapropelites from the Kushmurun and Maoming deposits in Kazakhstan and China, respectively, was identified. Thermo-hydrolytic decomposition of sapropelite organic mass in an aqueous alkaline medium at 400 °C by approximately 40−60 % was related to the generation of neutral and acid heteroatomic compounds and only by 5−10 % − to paraffin-naphthene-aromatic, mainly, normal C_{12}−C_{27} and C_{12}−C_{31} alkanes, C_{13}−C_{23} and C_{14}−C_{27} alkenes, and also aromatic and naphthene-aromatic components, as discovered. It was noted that unlike anhydrous pyrolysis results, thermal hydrolysis products contained more monounsaturated olefins with different double bond positions. Proceeding from the composition of biomarker hydrocarbons, it was concluded that they were associated with the lithogenetic maturity of sapropelite organic mass. In addition, the sea origin of the initial biomass of lipid structural elements was suggested..

Keywords: sapropelite, thermo-hydrolytic decomposition, hydrocarbons, gas chromatography-mass spectrometry, biomarkers

INTRODUCTION

Conditions of thermo-hydrolytic treatment of sapropelite organic matter in supercritical aqueous and aqueous-organic media at temperatures of 400−415 °C can be considered as the optimum conditions for its extraction [1, 2]. Recent advances in the structural-molecular structure of sapropelite [3, 4] may be used for the methods of assessment of its chemical and technological properties according to the molecular composition of thermo-hydrolytic treatment products in aqueous media [5]. Sapropelites from the Kushmurun deposit of the Turgay basin in Kazakhstan (ash content of 29.2 %;

combustible mass composition (%): C 72.1, H 9.5, N 3.4, S 0.7, O 14.3) and the Maoming deposit in China (ash content of 73.7 %; the composition of the combustible mass (%): C 79.4, H 9.6, N 1.0, S 1.7, O 8.3) were objects of research in this work. Similar studies of oil shale in Kuzbass and Mongolia demonstrated that thermo-hydrolytic transformations of sapropelite organic mass in an aqueous alkaline medium at 400 °C by approximately 30−40 % were related to the generation of paraffin-naphthene-aromatic hydrocarbons, mainly, normal C_{10}−C_{31} alkanes and C_{14}−C_{28} alkenes [6].

A work goal was to reveal distribution regularities and composition peculiarities for the

TABLE 1

Comparative results of separation of products of thermal hydrolysis of sapropelite

Sapropelits	Fraction yields (in terms of organic mass), %		
	Paraffin-naphthene-aromatic compounds	Neutral heteroatomic compounds	Acid heteroatomic compounds
Kushmurun	9.7	20.8	29.3
Maoming	5.9	22.8	15.2

main hydrocarbon products generated during thermo-hydrolytic processing of sapropelite in Kazakhstan and China, under conditions close to optimum (400 °C, 1 h), according to organic matter extractability.

EXPERIMENTAL

Products of thermo-hydrolytic decomposition of sapropelite were produced in a rotating autoclave made of IX18H10T steel with 0.5 L capacity equipped with a thermocouple, high-pressure valve and manometer. The autoclave was loaded with 10 g of the sample under study, 300 mL of a 5 % KOH solution, and nitrogen gas (5 MPa) and heated during rotation (200 rpm) in an electrical furnace for 50−60 min until a temperature of 400 °C. Autoclave temperature was maintained within ±2 °C of the specified for 1 h. Afterwards, the autoclave was cooled to 40 °C with stirring the contents and unloaded. Liquid and solid products were extracted from the autoclave and filtered through a glass filter, while the filter cake was rinsed with ether (150 mL). Neutral decomposition products of the sample under study were separated from the total reaction mass by ether extraction from an alkaline solution.

Aqueous alkali-soluble products (acid heteroatomic compounds) were extracted with ether after neutralization with a 2 % HCl solution.

Column chromatography of neutral products was performed using untreated silica gel (100−160 μ); a column height of 50 cm, 2.5 cm in diameter. The first fraction to separate paraffin-naphthene-aromatic was eluted with hexane (300 mL), the second one − with ether (300 mL to separate neutral heteroatomic compounds).

Table 1 gives the yields of compound mixtures of sapropelite thermo-hydrolytic processing products.

Fractions of paraffin-naphthene-aromatic components were analysed using Agilent 6890N gas chromatograph with 5973 mass-selective detector. Separation conditions were as follows: helium carrier gas; HP-5MS column (30 m × 25 mm), evaporator temperature of 250 °C, column temperature increase from 50 °C (3 min) to 250 °C at a rate of 2 °C/min and then the column kept for 2 h at 250 °C. The energy of ionizing electrons is 70 eV. Identification of individual compounds of different classes and their homologues was carried out according to the most informative of the fragmented ions typical of n-alkanes and isoprenoids (m/z 57 and 99), alkylcyclohexanes (m/z 83), alkylbenzenes (m/z 91), n-alkenes (m/z 97), hopanes (m/z 191 and 369), steranes (m/z 217), and diasteranes (m/z 232 and 259). Individual compounds and their homologs were determined according to mass spectra using AMDIS and ChemStation databases.

RESULTS AND DISCUSSION

Gas chromato-mass-spectrometry of fractions of paraffin-naphthene-aromatic components produced from Kushmurun and Maoming sapropelites revealed a mixture of hydrocarbon components that appeared as approximately 120 and 100 main peaks, respectively. The identification of many unsaturated aliphatic

TABLE 2

Content (in %) and distribution range (C_n−C_m) of direct-chain hydrocarbons in the fraction of paraffin-naphthene aromatic components obtained from sapropelites

Hydrocarbons	Sapropelites	
	Kushmurun	Maoming
n-Alkane	25 (C_{12}−C_{27})	57 (C_{12}−C_{31})
n-Alkene	20 (C_{13}−C_{23})	18 (C_{14}−C_{27})

TABLE 3

Alkylaromatic and naphthene-aromatic hydrocarbons in products of thermo-hydrolytic decomposition of Kushmurun sapropelite

No.	Components	Formula	Yield time, min	Relative content, %
1	1-Methylnaphthalene $C_{11}H_{10}$ (M 142)		32.06	0.24
2	2-Methylnaphthalene $C_{11}H_{10}$ (M 142)		33.11	0.20
3	1,2,3,4-Tetrahydro-6-trimethylnaphthalene $C_{13}H_{18}$ (M 174)		35.89	0.07
4	1,2,3,4-Tetrahydro-1,1,6-trimethyl-naphthalene $C_{13}H_{18}$ (M 174)		36.82	0.22
5	n-Heptylbenzene $C_{13}H_{20}$ (M 176)			
6	1-Methyl-2-n-Hexylbenzene $C_{13}H_{20}$ (M 176)		37.15	0.11
7	2-Ethenylnaphthalene $C_{12}H_{10}$ (M 154)		37.60	0.20
8	2-Ethylnaphthalene $C_{12}H_{12}$ (M 156)		38.40	0.46
9	2-Ethylnaphthalene $C_{12}H_{12}$ (M 156)		39.10	0.64
10	1,6-Dimethylnaphthalene $C_{12}H_{12}$ (M 156)		39.94	0.47
11	1,7-Dimethylnaphthalene $C_{12}H_{12}$ (M 156)		40.12	0.12
12	1,5-Dimethylnaphthalene $C_{12}H_{12}$ (M 156)		41.10	0.32
13	2,6-Dimethylnaphthalene $C_{12}H_{12}$ (M 156)		41.28	0.21
14	1,3-Dimethylnaphthalene $C_{12}H_{12}$ (M 156)		42.00	0.49
15	1,2-Dihydro-1,1,6-trimethylnaphthalene $C_{13}H_{16}$ (M 172)		42.98	0.48
16	n-Octylbenzene $C_{14}H_{22}$ (M 190)		43.21	0.75
17	2-Phenyloctane $C_{14}H_{22}$ (M 190)		43.50	0.34
18	Acenaphthene $C_{12}H_{10}$ (M 154)		43.76	0.69
19	4-Methyl-1,1'-biphenyl $C_{13}H_{12}$ (M 168)		44.59	0.47
20	1,6,7-Trimethylnaphthalene $C_{13}H_{14}$ (M 170)		46.61	0.76
21	1,4-Dihydro-2,5,8-trimethylnaphthalene $C_{13}H_{16}$ (M 172)		47.00	0.47
22	1,4,6-Trimethylnaphthalene $C_{13}H_{14}$ (M 170)		47.54	0.20

TABLE 3 (ENDING)

No.	Component	Formula	Yield time, min	Relative content, %
23	Fluorene $C_{13}H_{10}$ (M 166)		49.44	1.61
24	2,3,6-Trimethylnaphthalene $C_{13}H_{14}$ (M 170)		49.80	0.25
25	1-Allylnaphthalene $C_{13}H_{12}$ (M 168)		50.09	0.72
26	1-Isopropenylnaphthalene $C_{13}H_{12}$ (M 168)		50.26	0.23
27	2-Methyl-1,1'-biphenyl $C_{13}H_{12}$ (M 168)		50.48	1.09
28	2,2'-Dimethylbiphenyl $C_{14}H_{14}$ (M 182)		51.73	0.43
29	2-Ethyl-1,1'-biphenyl $C_{14}H_{14}$ (M 182)		53.62	0.43
30	9-Methyl-9H-fluorene $C_{14}H_{12}$ (M 180)		56.20	1.17
31	4,4'-Dimethylbiphenyl $C_{14}H_{14}$ (M 182)		58.76	0.75
32	Phenanthrene $C_{14}H_{10}$ (M 178)		59.88	0.45
33	Anthracene $C_{14}H_{10}$ (M 178)		60.40	0.72
34	2,2',5,5'-Tetramethyl-1,1'-biphenyl $C_{16}H_{18}$ (M 210)		63.91	0.22
35	1-Methylanthracene $C_{15}H_{12}$ (M 192)		66.36	0.66

compounds in sapropelite thermo-hydrolytic processing products appears to be the most substantial fact. The exact location of double bonds in the alkyl chain is hard to identify according to mass-spectrometry data, but their presence itself and various locations become obvious. A method for the detection of the ions with m/z 97 allowed recording numerous peaks of monounsaturated compounds with retention times that are different from the retention time of an isomeric saturated alkane towards both greater and lower values.

Table 2 gives information concerning the content of straight chain hydrocarbons in the fractions.

These fractions also contain in substantial amounts alkylaromatic, naphtheno-aromatic, alicyclic, and branched (isoprenoid) hydrocarbons (to 20 and ~15 % in a fraction produced from Kushmurun and Maoming sapropelite, respectively).The fraction of unidentifiable paraffin-naphthene-aromatic components for Kushmurun sapropelite is 35 %, for Maoming one − 10 %.

Products of thermo-hydrolytic processing of Kushmurun sapropelite are n-heptylcyclohexane, 2,6,10-trimethyldodecane, 1-octylcyclopentene-1, n-nonylcyclohexane, 1-(1,5-dimethylhexyl)-4-(methylpentyl)cyclohexane, (1-ethyldecyl) cyclohexane, 2,6,10,14-tetramethylhexadecane. At the same time, 2,6,10-trimethyldodecane, n-nonylcyclohexane, and 7,9-dimethylhexadecane have been detected among products of thermo-hydrolytic processing of Maoming sapropelite.

Tables 3 and 4 give identification results for alkylaromatic and naphtheno-aromatic hydrocarbons.

TABLE 4

Alkylaromatic and naphthene-aromatic hydrocarbons in products of thermo-hydrolytic decomposition of Maoming oil shale

No.	Components	Formula	Yield time, min	Relative content, %
1	1,2,3,4-Tetrahydro-1,1,6-naphthalene $C_{13}H_{18}$ (M 174)		36.26	0.02
2	2-Ethylnaphthalene $C_{12}H_{12}$ (M 156)		38.38	0.09
3	1,6-Dimethylnaphthalene $C_{12}H_{12}$ (M 156)		39.04	0.08
4	1,4-Dimethylnaphthalene $C_{12}H_{12}$ (M 156)		39.94	0.14
5	1,7-Dimethylnaphthalene $C_{12}H_{12}$ (M 156)		40.12	0.06
6	2,6-Dimethylnaphthalene $C_{12}H_{12}$ (M 156)		41.27	0.04
7	1,3-Dimethylnaphthalene $C_{12}H_{12}$ (M 156)		41.98	0.09
8	Acenaphthene $C_{12}H_{10}$ (M 154)		43.70	0.20
9	Tetrahydro-5,6,7-tetramethyl-naphthalene $C_{14}H_{20}$ (M 188)		46.13	0.33
10	1,6,7-Trimethylnaphthalene $C_{13}H_{14}$ (M 170)		46.58	0.41
11	1,4-Dihydro-2,5,8-trimethylnaphthalene $C_{13}H_{16}$ (M 172)		46.96	0.30
12	1,4,6-Trimethylnaphthalene $C_{13}H_{14}$ (M 170)		47.49	0.26
13	Fluorene $C_{13}H_{10}$ (M 166)		49.40	0.58
14	1,6,7-Trimethylnaphthalene $C_{13}H_{14}$ (M 170)		49.77	0.27
15	1-Allylnaphthalene $C_{13}H_{12}$ (M 168)		50.06	0.80
16	1-Isopropenylnaphthalene $C_{13}H_{12}$ (M 168)		50.22	0.37
17	2-Methylbiphenyl $C_{13}H_{12}$ (M 168)		50.43	0.88
18	2,2'-Dimethylbiphenyl $C_{14}H_{14}$ (M 182)		51.70	0.42
19	1,2,3,4-Tetramethylnaphthalene $C_{14}H_{16}$ (M 184)		55.31	0.43
20	4,4'-Dimethylbiphenyl $C_{14}H_{14}$ (M 182)		56.16	2.35
21	2,4-Dimethylbiphenyl $C_{14}H_{14}$ (M 182)		57.54	1.74
22	1-Methyl-3-(3-methylbenzyl)benzene $C_{15}H_{16}$ (M 196)		58.29	1.02

TABLE 4 (ENDING)

No.	Components	Formula	Yield time, min	Relative content, %
23	2,2'-Dimethylbiphenyl $C_{14}H_{14}$ (M 182)		58.73	0.55
24	Phenanthrene $C_{14}H_{10}$ (M 178)		59.86	0.20
25	Anthracene $C_{14}H_{10}$ (M 178)		60.36	0.40
26	3,5-Dimethyl-1-(phenylmethyl) benzene $C_{15}H_{16}$ (M 196)		61.68	0.27
27	1-Methylanthracene $C_{15}H_{12}$ (M 192)		66.33	0.65
28	1,1,7,8,12-Pentamethyl-1,2,3,4,9,10,11,12-octahydrophenanthrene $C_{19}H_{28}$ (M 256)		75.06	0.90
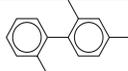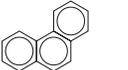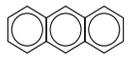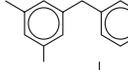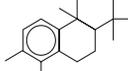
Proceeding from the total content of alkylaromatic and naphtheno-aromatic hydrocarbons that in the event of Kushmurun sapropelite is approximately 17 % and in case of Maoming one − about 14 %, one could suggest that by the lithogenetic maturity of the organic mass, these sapropelites are insignificantly different from each other. However, the data about the content of aromatic neutral heteroatomic components isolated from hydrolysis products of this sapropelite contradict this assumption. Thus, based on the data given in Table 5, the total content of arylalkylketones, alkylphenols, and indanoles in case of Maoming oil shale is substantially higher than the composition of the same aromatic components in the event of Kushmurun coal (39 % against 20 %). The much higher total content of aromatic components attests to the higher lithogenetic maturity of organic matter in Maoming oil shale.

Figures 1 and 2 give the results of determination for the composition of normal alkanes and alkenes in hydrocarbon fractions of Kushmurun and Maoming sapropelites.

The distribution pattern in n-alkenes in case of Kushmurun sapropelite is much poorer, in other words, it contains a less diverse set of straight chain compounds with double bonds than in case of Maoming sapropelite.

Hydrocarbon generation is related to transformations of organic matter of the lipid origin including those with decarboxylation of fatty-acid structural elements. The distribution character of alkanes is the reflection of the nature and origin of the initial substance. The transformation of the initial biomass of continental genesis that is higher plant lipids leads to relatively high contents of $C_{25}-C_{33}$ n-alkanes in aqueous hydrolysis products [7]. However, a relatively high concentration of

TABLE 5

Content of neutral heteroatomic components in fractions produced from coal/shale

Heteroatomic components	Content, %	
	Kushmurun coal	Maoming oil shale
n-Alkyl ketones	60.34	43.71
Aryl alkyl ketones	4.09	9.78
Alkylphenoles	11.33	22.11
Indanoles	4.50	7.04
Nitrogen compounds	5.27	7.10
Rest	14.47	10.26
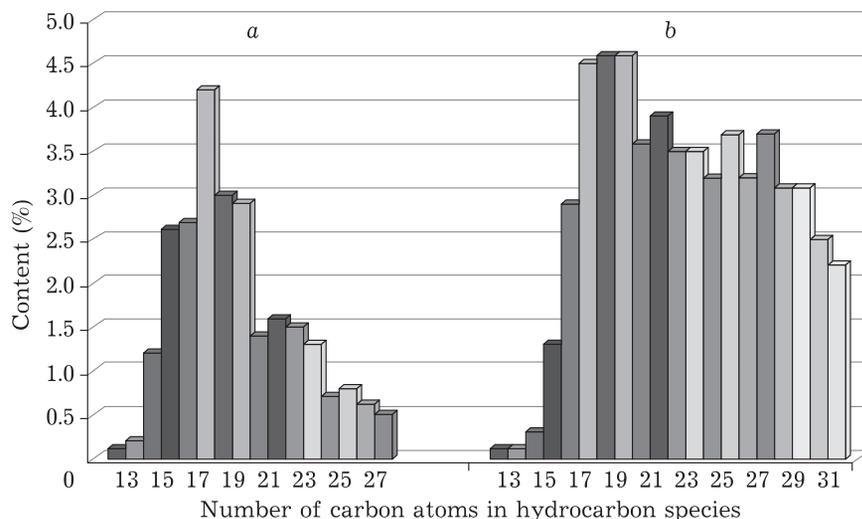
Fig. 1. Content of C_{12}–C_{31} *n*-alkanes versus the number of carbon atoms in species of factions of paraffin-naphthene-aromatic components isolated from Kushmurun (*a*) and Maoming (*b*) sapropelites.

C_{10}–C_{24} and low contents of C_{25}–C_{33} *n*-alkanes are typical for products of thermo-hydrolytic transformation of Kushmurun and Maoming sapropelites. The ratio of the total content of C_{25}–C_{33} *n*-alkanes to that of all normal alkanes is 0.07 and 0.37, respectively. These values attest to the fact that initial sapropelite biomass was of the sea origin.

In the plant world, lipidic biomembranes are partially constructed from unsaturated structural elements. These structural elements have unbranched or weakly-branched chains and are sometimes isoprenoid links of aliphatic and acyclic types. The origin of alkanes identified in thermo-hydrolytic transformation products may

be explained by the presence of unbranched lipidic components in biomembrane composition. Gas chromatography-mass spectrometric detection of m/z 97 ions allowed recording numerous alkene peaks with retention times that are different from the retention time of the corresponding alkane towards both higher and lower values. Table 6 gives the data about the content of all normal unsaturated hydrocarbons in fractions of paraffin-naphthene-aromatic compounds isolated from products of thermo-hydrolytic decomposition of Kushmurun and Maoming sapropelites.

Products of thermo-hydrolytic decomposition of sapropelites always contain compounds
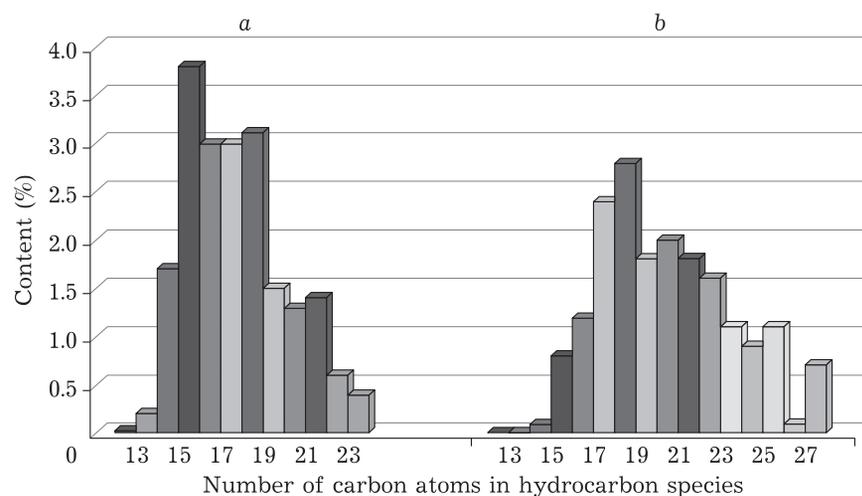
Fig. 2. Content of C_{13}–C_{27} *n*-alkanes versus the number of carbon atoms in species of factions of paraffin-naphthene-aromatic components isolated from Kushmurun (*a*) and Maoming (*b*) sapropelites.

TABLE 6

Results of the study of alkenes with normal structuture

n-Alkene	Molecular mass	Content in the fraction of paraffin-naphthene-aromatic compounds, %
Kushmurun coal		
$C_{13:2} + C_{13:3}$	182	0.2
$C_{14:2} + C_{14:3} + C_{14:5}$	196	1.7
$C_{15:1} + C_{15:2} + C_{15:3} + C_{15:7}$	210	3.8
$C_{16:1} + C_{16:3} + C_{16:7}$	224	3.0
$C_{17:2} + C_{17:3} + C_{17:8}$	238	3.0
$C_{18:1} + C_{18:3} + C_{18:5}$	252	3.1
$C_{19:1} + C_{19:3} + C_{19:5}$	266	1.5
$C_{20:3} + C_{20:5}$	280	1.3
$C_{21:10}$	294	1.4
$C_{22:3}$	308	0.6
$C_{23:1} + C_{23:9}$	322	0.4
Maoming oil shale		
$C_{14:2} + C_{14:3}$	196	0.1
$C_{15:1} + C_{15:2} + C_{15:3}$	210	0.8
$C_{16:3} + C_{16:7}$	224	1.2
$C_{17:3}$	238	2.4
$C_{18:1} + C_{18:3} + C_{18:5}$	252	2.8
$C_{19:3} + C_{19:5}$	266	1.8
$C_{20:3} + C_{20:5}$	280	2.0
$C_{21:8} + C_{21:10}$	294	1.8
$C_{22:1} + C_{22:3}$	308	1.6
$C_{23:1} + C_{23:9}$	322	1.1
$C_{24:1} + C_{24:10}$	336	0.9
$C_{25:1} + C_{25:12}$	350	1.1
$C_{26:9}$	364	0.1
$C_{27:1}$	380	0.7

that have molecular structural components of hopane [6]. In fractions of paraffin-naphthene-aromatic hydrocarbons isolated from both sapropelites, there are the following hopanes: 17α(H),21β(H)-30-nor-hopane ($C_{29}H_{50}$), nor-hop-17(21)-ene ($C_{29}H_{48}$), 17β(H),21α(H)-30-nor-moretane ($C_{29}H_{50}$), 17α(H),21β(H)-30-hopane ($C_{30}H_{52}$), hop-17(21)-ene ($C_{30}H_{50}$), 17β(H),21α(H)-30-moretane ($C_{30}H_{52}$).

CONCLUSION

Summarizing the results obtained, it can be stated that Kushmurun coal and Maoming oil shale generate 4–6 times lower amounts of paraffin-naphthene-aromatic hydrocarbons than earlier studied oil shales from Demetrius and Houtbosch deposits [6]. However, similarity of all the studied sapropelites lies in the fact that the main hydrocarbon straight chain components generated by their organic mass under thermo-hydrolytic treatment conditions are normal alkanes and alkenes. The total content of these hydrocarbons in paraffin-naphthene-aromatic fractions of thermo-hydrolytic processing of Kushmurun coal and Maoming sapropelites is 45 and 75 %, respectively. Distribution ranges of n-alkanes are C_{12}–C_{27} and C_{12}–C_{31} with the maxima at C_{17}, C_{18} and C_{19}. Monosubstituted n-alkenes have more narrow distribution ranges (C_{12}–C_{27}

and $C_{12}-C_{31}$) compared to *n*-alkanes. Products of thermo-hydrolytic decomposition contain more monounsaturated olefins with different double bond positions compared to paraffin-naphthene-aromatic fractions that are produced by the common method of anhydrous pyrolysis of sapropelites [8]. In addition to alkanes and alkenes, they contain substantial amounts of (no less than 20 and 15 % in case of Kushmurun and Maoming sapropelites, respectively) aromatic, naphthene-aromatic, alicyclic, branched, and isoprenoid hydrocarbons. Elevated total contents of aromatic components in thermal hydrolysis products attest to more lithogenetically mature organic matter in Maoming oil shale compared to Kushmurun coal.

Acknowledgement

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