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Investigation of Sapropelite Coals by Means of NMR Spectroscopy

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Abstract

Seven samples of sapropelite coals from the deposits differing from each other in the catagenetic maturity of the organic matter were studied by means of solid-state ^{13}C NMR spectroscopy. Analysis of the obtained analytical data showed that carbon in the organic mass of the samples is largely concentrated in aliphatic structures since the most intense signals in the ^{13}C NMR spectrum fall on the region of 0–50 ppm, corresponding to the absorption of carbon of methyl and methylene groups, as well as tertiary and quaternary carbon atoms. The largest amount of aliphatic carbon was found in the sample, which is characterized by the highest values of the yield of volatiles and the H/C atomic ratio. It was found that with a decrease in the H/C atomic ratio in the samples, their degree of aromaticity increases against the background of a decrease in the proportion of aliphatic structures and carbon bonded to oxygen by a single bond.

Keywords: sapropelite coals, kerogen, elemental composition, NMR spectroscopy, degree of aromaticity

INTRODUCTION

In view of the limited fuel and energy resources, a search for various sources of raw hydrocarbons is carried out in many countries. Among these raw hydrocarbons, a special position is allocated to sapropelite coal, which is characterized by high concentrations of hydrogen (up to 12 %), volatile substances (75–90 %), and a substantial yield of primary tar (up to 50 %) [1–3]. Poorly suited for energy purposes, sapropelite coal, due to its chemical composition, may serve as a raw material for obtaining various hydrocarbon products [1–8].

The choice of the technologies for processing solid fossil fuel, in particular sapropelite coal, into the products for various purposes requires a detailed physicochemical investigation of its properties. An essential issue from the fundamental and practical points of view is the determination of the structure of organic matter in solid fuels, its major structural fragments and the methods of their bonding. To solve the problems of this kind, it is necessary to use an integrated approach involving a set of physicochemical methods of investigation in the high-resolution instrumental arrangement, one of which is ^{13}C NMR spectroscopy. Unlike destructive methods of investigation, ^{13}C NMR spectroscopy allows direct determination of the content of carbon atoms in different chemical surroundings. The degree of aromaticity (f_a) of the structure of the organic mass, expressed in the fraction of carbon in aromatic fragments, is one of the basic structural characteristics defining the reactivity of coal in different technological processes and determining the yield and composition of processing products [2, 9, 10].

In the present work, we describe the results of the studies of sapropelite coal from different deposits by means of ^{13}C NMR spectroscopy.

EXPERIMENTAL

Materials

The objects of the investigation were seven samples of sapropelite coal taken from the collection of Coal Bank formed at the Institute of Coal Chemistry and Chemical Materials Science, FRC CCC SB RAS. The studied samples included (sample codes): sapropelite from the Ala-Kul Bay of Lake Balkhash (1), the Charchik (2) and Taymylyr (7) bogheads of the Lena basin; sapropelite of the Kushmurun deposit of the Turgay basin (3); sapropelite from the Podmoskovniy coal basin, sampled at the Seredeyskaya mine (4); sapropelite from the Sobolevskoye deposit of the Kansk-Achinsk basin (5); sapropelite from the Budagovo deposit of the Irkutsk basin (6).

The preparation of sapropelite samples for analysis (to obtain kerogen) included their crushing to particle size less than 0.2 mm and extraction with an ethanol-benzene mixture (1 : 1) according to Graefe procedure for 6 h. Extraction was carried out to remove soluble organic substances from the samples. After extraction, the samples were dried at a temperature of 105 °C in a drying box to a constant mass. The samples from the Sobolevskoye and Budagovo deposits, with ash content in the native state 25.3 and 44.5 %, respectively, were additionally subjected to sequential demineralization with concentrated hydrochloric and hydrofluoric acids.

Methods of investigation

Proximate analysis was carried out using standard methods. Fixed carbon (C_{fixed}) was calculated using the equation: $C_{fixed} = 100 - W^a - A^d - V^d$, where W^a is analytical moisture, A^d is ash content, V^d is the yield of volatiles per the dry state of the sample [11–13]. The elemental composition was determined using a Thermo Flash 2000 element analyzer (Thermo Fisher Scientific, United Kingdom). Oxygen content was estimated as a difference between 100 % and the sum of C, H, N, S elements. Results of determinations were recalculated for the dry ash-free (daf) state of the fuel.

High resolution ^{13}C NMR spectra in solids were recorded with the help of an Avance III 300 WB spectrometer (Bruker, Germany) using the standard procedure of cross-polarization with magic angle spinning (CPMAS) with proton uncoupling at a frequency of 75 MHz. Contact time was 1000 μs, with the accumulation of 4096 scans, the delay between scans was 2 s, the frequency of sample rotation was 7 kHz. To obtain quantitative data, the spectra were simulated with the help of Dmfit software [14].

Deconvolution of the spectra allows distinguishing the ranges corresponding to the resonant absorption by the following groups of carbon atoms, ppm: 235–180 – carbon atoms of carbonyl groups (C=O); 180–170 – carbon atoms of carboxylic groups and their derivatives (COO–); 170–150 – carbon atoms of aromatic systems bound with an oxygen atom ($C_{ar}O$); 150–90 – carbon atoms of aromatic systems with a substituted and non-substituted hydrogen atom ($C_{ar} + CH_{ar}$); 90–60 – carbon atoms of ether groups (C–O); 51–0 – carbon atoms of alkyl fragments (C_{alk}). Aromaticity degree was calculated from the results of simulation using equation $f_a = (C_{ar} + C_{ar}O + CH_{ar})/100$. To compare the contribution from aliphatic carbon ($\sum C_{al}$) into kerogen structure with respect to the aromatic carbon ($\sum C_{ar}$), we compared the integral intensities of the signals in the regions of 0–50 and 90–150 ppm related to $\sum C_{al}$ and $\sum C_{ar}$, respectively [15].

RESULTS AND DISCUSSION

The results of proximate analysis and the elemental composition of sapropelites are listed in Tables 1 and 2, respectively. One can see that all the samples are characterized by increased yields of volatile substances per the dry ash-free state (V^{daf}), which vary from 56.4 (sample 7) to 91.8 % (sample 1). The ash content A^d of the samples is less than 6.9 %. The majority of the samples are low-sulphur, because sulphur content in their organic mass is less than 2 %. However, sample 4 (Seredeyskaya mine) may be related to sulphur-containing ones because sulphur content in its organic mass is 3.2 %.

The elemental composition of kerogen, first of all, hydrogen content with respect to carbon, is the most important criterion to evaluate the type of organic matter and the stage of its catagenic maturity [16, 17]. The elemental composition of the studied samples provides evidence that their organic mass is enriched with hydrogen (see Table 2). The atomic ratio H/C in samples 1–6 varies from 1.70 (sample 1) to 1.51 (sample 6). The lowest H/C value equal to 1.19 was detected in sample 7, which may point to a higher degree of the maturity of its organic mass. It should be stressed that V^{daf} values of the studied samples correlate with the atomic ratio H/C (Fig. 1).

TABLE 1

Data of the proximate analysis of the studied sapropelite coal samples

Sample code	Proximate analysis, %				
	W^a	A^d	V^d	V^{daf}	C_{fixed}
1	1.8	6.9	85.5	91.8	5.8
2	1.7	3.1	81.2	83.8	14.0
3	1.6	3.5	79.1	82.0	15.8
4	5.3	3.9	73.5	76.5	17.3
5	1.5	1.5	72.8	73.9	24.2
6	5.1	4.1	69.5	72.5	21.3
7	6.7	6.4	52.8	56.4	34.1

Note. 1. W^a is analytical moisture, A^d is ash content, V^d is the yield of volatile substances per the dry state of the sample, V^{daf} is the yield of volatile substances per the dry ash-free state of the sample, C_{fixed} is fixed carbon. 2. Samples: 1 – balkhashite, 2 – Charchik, 3 – Kushmurun, 4 – Seredeyskaya mine, 5 – Sobolevskoye deposit, 6 – Budagovo, 7 – Taymylyr.

The ^{13}C NMR spectra of sapropelite coal samples are shown in Fig. 2, where they are arranged according to a decrease in the atomic ratio H/C in the studied samples. The appearance of the spectra corresponds to numerous ^{13}C NMR spectra of various fossil fuels and contains two characteristic regions corresponding to the resonance absorption by carbon in aromatic systems and in aliphatic fragments, as well as in functional groups (carboxylic, phenol, alcohol, and methoxy) [15, 18–20]. The major differences are observed in the integral intensities of the signals in these separate spectra regions.

The most intensive signal in the ^{13}C NMR spectra of all the studied samples appears in the region 10–50 ppm. This signal is due to the presence of aliphatic carbon atoms of different configurations. Among the signals in the aliphatic region, the most intensive signal is that observed at 30 ppm, which corresponds to the absorption by carbon in methylene links (see Fig. 2). Rather clearly identified signals are those at 14 ppm – carbon in the terminal methyl groups of alkyl structures, at 24 ppm – carbon of methyl groups connected with the ternary carbon atom of aliphatic chains and with aromatic cores. In the region 35–50 ppm, there are signals related mainly to the presence of aliphatic cycles, in particular those bound with aromatic structures [15, 19, 21].

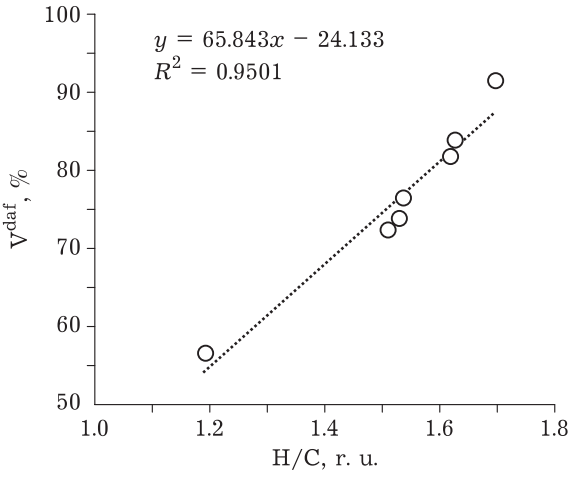

Fig. 1. Correlation between the yield of volatile substances (V^{daf}) and the atomic ratio H/C in the studied sapropelite coal samples.

TABLE 2

Elemental composition of the studied sapropelite coal samples

Sample code	Elemental composition, % per daf					Atomic ratio	
	C	H	S	N	O	H/C	O/C
1	75.5	10.7	0.6	0.7	12.5	1.70	0.12
2	74.3	10.1	0.7	0.7	14.2	1.63	0.14
3	74.0	9.9	0.8	1.1	14.3	1.62	0.14
4	74.9	9.6	3.2	0.8	11.5	1.54	0.12
5	77.8	9.9	0.3	0.9	11.1	1.53	0.11
6	77.2	9.7	0.7	1.5	10.9	1.51	0.11
7	88.7	8.8	0.4	0.4	1.7	1.19	0.01

Note. For sample designations, see Table 1.

The data on the relative distribution of carbon atoms over structural fragments in the aliphatic regions of spectra are shown in Table 3. Analysis of the presented data shows that the amount of aliphatic carbon ($\sum C_{al}$) in all the studied samples is rather high and varies from 77.41 % (sample 1) to 46.85 % (sample 7). The presence of intense signals in the regions 25–35 ppm (polymethylene fragments $(-CH_2-)_n$) and 0–18 ppm (terminal CH_3 groups) is the evidence that long-chain aliphatic fragments are present in the structure of the organic matter of the studied samples. In sapropelite samples 1–3, the fraction of carbon in long aliphatic chains ($C_{25-35}/\sum C_{al}$) is more than 0.50. It should be stressed that with an increase in the genetic maturity of samples (with a decrease in the atomic ratio H/C) the amount of these fragments decreases against the background of a slight increase in the fraction of carbon in aliphatic cycles ($C_{35-50}/\sum C_{al}$). The largest amount of carbon of aliphatic cycles was detected in sample 4 (Seredeyskaya mine) and in sample 5 (the Sobolevskoye deposit) – 0.48 and 0.50, respectively (see Table 3).

In NMR ^{13}C spectra, a broad carbon signal related to the aromatic fragments is essentially less

intense than the signal of carbon atoms from aliphatic groups (see Fig. 2). The aromatic region of the spectrum contains a set of merging signals within the range of 90–150 ppm, which correspond to different aromatic fragments. The ^{13}C NMR spectrum of sample 7 contains the most intense peak at 126 ppm and a small shoulder at 137 ppm (Fig. 3, spectrum 7). The authors of [10, 15, 19, 20] attribute the signals at 126 ppm to protonated aromatic carbon, and the signals at 137 ppm to quaternary (non-protonated) carbon atoms (carbon in aromatic ring substituted with an alkyl radical).

Results of deconvolution of NMR ^{13}C spectra of the studied samples in the aromatic region are presented in Table 4. One can see that sapropelite samples 1–6 are characterized by the lowest aromaticity f_a, varying from 0.10 to 0.26. The largest value (f_a = 0.42) was determined for sample 7 (the Taymylyr deposit), but the ratio $\sum C_{al}/\sum C_{ar}$ in this sample remains larger than unity (see Table 4).

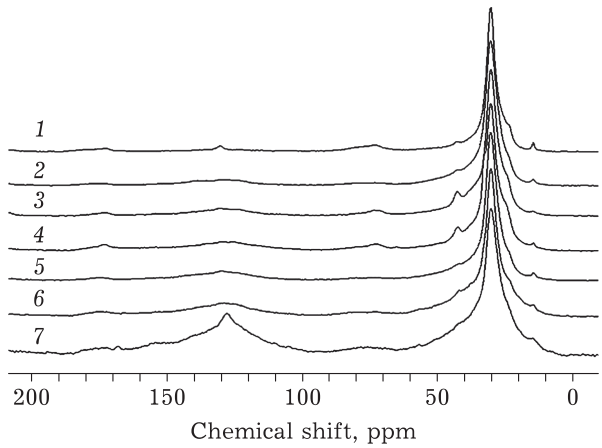

Fig. 2. The ^{13}C NMR spectra of the samples of sapropelite coal: balkhashite (*1*), Charchik (*2*), Kushmurun (*3*), Seredeyskaya mine (*4*), Sobolevskoye deposit (*5*), Budagovo (*6*), Taymylyr (*7*).

According to the data presented in Fig. 3, an increase in aromaticity index f_a is proportional to a decrease in the amount of aliphatic carbon in

TABLE 3

Parameters of the fragment composition of sapropelite coal samples according to the data of ^{13}C NMR spectra in the aliphatic region (0–90 ppm)

Sample code	Distribution of carbon atoms over structural groups, rel. %						$C_{25-35}/\sum C_{al}$	$C_{35-50}/\sum C_{al}$
	The range of resonance absorption, ppm							
	0–18	18–25	25–35	35–50	$\sum C_{al}$	50–90		
1	0.64	3.70	52.55	20.53	77.41	9.30	0.68	0.27
2	0.30	2.80	44.86	26.43	74.44	5.42	0.60	0.36
3	0.13	4.51	39.25	28.02	71.91	4.52	0.55	0.39
4	0.10	3.79	32.85	34.58	71.31	2.97	0.46	0.48
5	0.22	4.12	30.97	35.64	70.95	1.80	0.44	0.50
6	0.44	5.74	27.21	29.96	63.35	5.02	0.43	0.47
7	0.41	8.33	19.36	18.75	46.85	6.19	0.41	0.40

Note. 1. $\sum C_{al} = C_{0-18} + C_{18-25} + C_{25-35} + C_{35-50}$. 2. For sample designations, see Table 1.

TABLE 4

Parameters of the fragment composition of sapropelite coal samples according to the data of ^{13}C NMR spectra in the aromatic region (90–235 ppm)

Sample code	Distribution of carbon atoms over structural groups, rel. %						f_a	$\sum C_{al}/\sum C_{ar}$	$C_{90-130}/C_{130-150}$
	The range of resonance absorption, ppm								
	90–130	130–150	$\sum C_{ar}$	150–170	170–180	180–235			
1	1.82	6.76	8.58	1.38	2.15	1.18	0.10	7.77	0.27
2	9.41	5.61	15.02	1.08	2.38	1.66	0.16	4.62	1.68
3	10.88	8.32	19.20	0.89	2.22	1.26	0.20	3.58	1.31
4	12.42	5.96	18.38	1.33	4.07	0.94	0.21	3.44	2.08
5	13.92	7.79	21.71	1.88	2.73	0.93	0.24	3.01	1.79
6	16.62	6.94	23.56	2.31	3.97	0.79	0.26	2.45	2.39
7	26.52	9.10	35.63	6.32	3.47	1.54	0.42	1.12	2.92

Note. 1. $\sum C_{ar} = C_{90-130} + C_{130-150}$. 2. $f_a = (C_{90-130} + C_{130-150} + C_{150-170})/100$. 3. $\sum C_{al}$ see Table 3. 4. For sample designations, see Table 1.

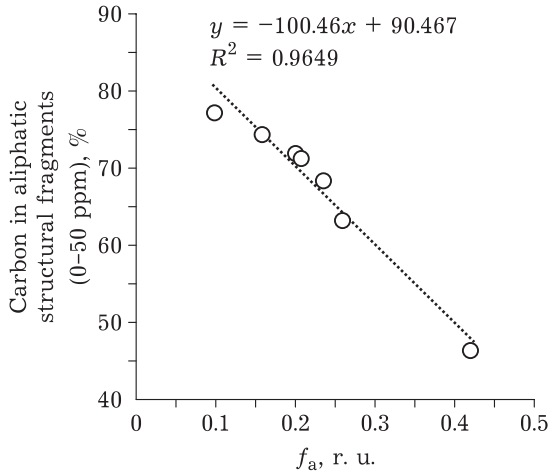

Fig. 3. Dependence of carbon content in aliphatic structural fragments on the degree of aromaticity (f_a) of the studied sapropelite coal samples.

structural fragments within the range of 0–50 ppm. An increase in this parameter occurs due to an increase in the amount of inter-cycle and protonated carbon (the region 90–130 ppm) with the relative stability of the concentration of substituted aromatic carbon (the region 130–150 ppm.) (see Table 4). It may be stated that the growth of the genetic maturity of the studied sapropelite samples (a decrease in the atomic ratio H/C) is accompanied by the transformation of the chemical structure of kerogen due to an increase in the concentration of aromatic cores in the organic matter of the samples and due to the loss of methyl groups.

Aromaticity index f_a calculated according to the data of NMR spectroscopy is inversely proportional to the yield of volatile substances V^d, atomic ratio H/C, and is directly proportional to the amount of bound carbon C_{fixed} in the organic mass (Fig. 4).

It is known that oxygen plays an essential part in the chemical structure of kerogen. In some cases, it acts as a bridge linking local carbonaceous structures; in addition, it may participate in the formation of kerogen by entering the peripheral groups [16, 17]. The NMR ^{13}C spectra of all the studied sapropelite samples are characterized by the presence of a peak in the region 50–90 ppm, which corresponds to carbon bound with oxygen through a single bond (typical for ethers, esters and alcohols). The highest intensity of this signal (9.3 %) was detected in sample 1, and the lowest one in sample 5 (1.8 %) (see Table 3).

Using the data obtained from the spectra of the studied sample, we also determined the value

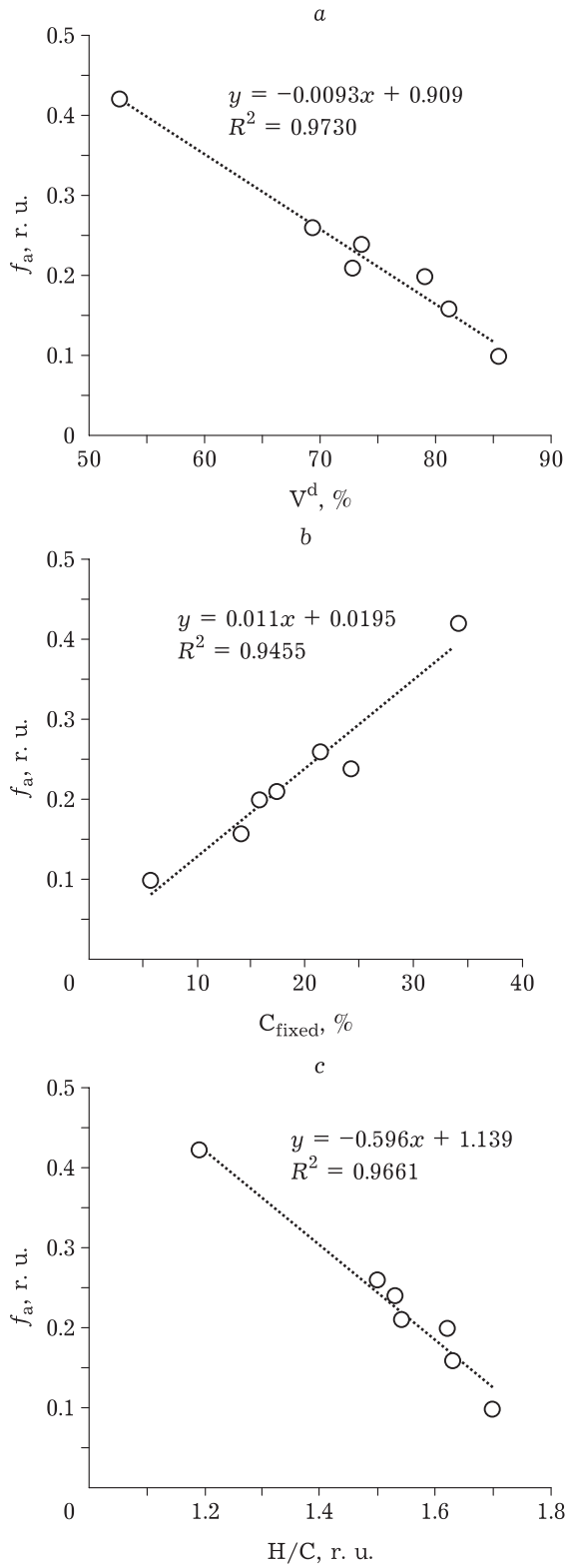

Fig. 4. Correlation between the degree of aromaticity (f_a) and the yield of volatile substances (V^d) (*a*), fixed carbon (C_{fixed}) (*b*) and the atomic ratio H/C (*c*) in the studied sapropelite coal samples.

of the signal from carbon in the aromatic core (see Table 4), bound directly with oxygen –

phenol carbon (the region 150–170 ppm). The fraction of phenol carbon in samples 1–6 does not exceed 2.33 %. The highest value of this parameter (6.32 %) was detected in the spectrum of sample 7 (the Taymylyr deposit).

The NMR ^{13}C spectra contain the signals related to carboxylic and carbonyl oxygen-containing groups. Carboxyl carbon gives a peak at 175 ppm, the content of carboxylic fragments in the samples does not exceed 4.6 % (see Table 4). The content of the carbonyl group (the region 180–235 ppm) is comparable in all the samples and varies between 0.79 % (sample 6) and 1.66 % (sample 2).

To compare the contribution from different forms of oxygen into the kerogen structure in the studied samples, we used the ratio of integral intensities of the signals from oxygenated groups in the regions 50–90 and 150–235 ppm; the values of $C_{50-90}/C_{150-235}$ ratio are presented in Table 5. One can see that in sample 1, the amount of aliphatic carbon atoms connected through a single bond with oxygen is two times higher than in other oxygenated structures different from ethers or esters. In samples 2 and 3, the ratio $C_{50-90}/C_{150-235} = 1$, while in samples 4–7 it is approximately equal to 0.5. Therefore, it may be stated that the oxygen of kerogen in sample 1 is mainly concentrated in ether and ester bonds, in samples 4–7 – mainly in phenol, oxo and carboxy groups, while in kerogen of samples 2 and 3 – also in ether bonds.

So, the obtained data do not contradict the existing notions that the kerogen of sedimentary rocks is a high-molecular substance containing both cyclic elements and the elements with an open chain. Aliphatic and cyclic fragments of kerogen are bound to each other through oxygen, ether and thioether bridges, and also partially through carbon-carbon bonds [16, 17].

TABLE 5

Relations between oxygen-containing structural groups according to the data of ^{13}C NMR spectra

Sample code	Distribution of carbon atoms over structural groups, rel. %		$C_{50-90}/C_{150-235}$
	C–O–C	$C_{ar}O$ + COOH + C=O	
	The range of resonance absorption, ppm		
	50–90	150–235	
1	9.30	4.71	2.0
2	5.42	5.12	1.1
3	4.52	4.37	1.0
4	2.97	7.31	0.4
5	1.80	5.54	0.3
6	5.02	8.07	0.6
7	6.19	11.33	0.5

Note. For sample designations, see Table 1.

CONCLUSION

Solid-state ^{13}C NMR spectroscopic investigation was carried out over seven samples of sapropelite coal from different deposits, differing from each other in the catagenic maturity of their organic matter, which is confirmed by the changes of the yield of volatile substances V^{daf} (from 91.8 to 56.4 %) and the atomic ratio H/C (from 1.70 to 1.19).

The method of ^{13}C NMR spectroscopy allowed us to reveal the features of carbon atom distribution in the studied samples. It was determined that carbon of the organic mass is greatly concentrated in aliphatic structures because the most intense signals in ^{13}C NMR spectra appear in the region 10–50 ppm, corresponding to the absorption by carbon atoms of methyl and methylene groups, as well as ternary and quaternary carbon atoms. The largest amount of aliphatic carbon ($\sum C_{al}$) was revealed in the sample which is characterized by the highest yield of volatile substances and the atomic ratio H/C. With a decrease in the atomic ratio H/C, an increase in the degree of aromaticity of the organic matter is observed in all the studied samples, against the background of a decrease in the fraction of aliphatic structures and carbon bound with oxygen through a single bond.

Results of the studies of sapropelite coal samples by means of solid-state ^{13}C NMR spectroscopy may be used to model the fragments of their chemical structure for the purpose of vivid representation of the contributions from separate groups of organic compounds into the composition of coal matrix.

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REFERENCES

1 Problems of non-traditional power engineering, Proceedings of the scientific session of the Presidium of SB RAS, Publishing House of SB RAS, Novosibirsk, 2006. (In Russ.).
2 Bodoev N. V., Sapropelite coal, Nauka, Siberian Branch, Novosibirsk, 1991. (In Russ.).
3 Gudzenko V. T., Varenichev A. A., Oil shales (informational-analytical review), *Geologiya, Geofizika i Razrabotka Neftyanykh i Gazovykh Mestorozhdeniy*, 2014, No. 9, P. 45–55. (In Russ.).
4 Liu G., Sun P., Ji Y., Wang Y., Wang H., You X., Current status and energy analysis of oil shale's retorting process in the worls, *Petrol. Chem.*, 2021, Vol. 61, No. 2, P. 123–138.
5 Korol I. S., Savelyev V. V., Golovko A. K., Composition of the soluble organic matter of oil shale of boghead from the Taimylyrskoe deposit, *Vestn. Tomsk. Gos. Un-ta. Khimiya*, 2017, No. 9, P. 6–14. (In Russ.).
6 Zykov I. Yu., Dudnikova Yu. N., Kozlov A. P., Fedorova N. I., Ismagilov Z. R., Adsorption characteristics of carbon sorbents from naturally oxidized Barzas coal, *Chemistry for Sustainable Development*, 2017, Vol. 25, No. 6, P. 564–568.
7 Oumam M., Abourriche A., Mansouri S., Mouiya M., Benhammou A., Abouliatim Y., Hafiane Y., Hannache H., Birot M., Pailler R., Naslain R., Comparison of chemical and physical activation processes at obtaining adsorbents from Moroccan oil shale, *Oil Shale*, 2020, Vol. 37, No. 2, P. 139–157.
8 Patrakov Yu. F., Pavlusha E. S., Fedorova N. I., Thermal dissolution of mechanically activated Barzas sapromyxite coal with benzene under supercritical conditions, *Solid Fuel Chem.*, 2011, Vol. 45, No. 4, P. 244–249.
9 Gyulmaliev A. M., Golovin G. S., Gladun T. G., Theoretical Foundations of Coal Chemistry, MGU, Moscow, 2003. (In Russ.).
10 Bushnev D. A., Burdel'naya N. S., Mokeev M. V., Gribanov A. V., Chemical structure and ^{13}C NMR spectra of the kerogen of carbonaceous rock masses, *Doklady Earth Sciences*, 2010, Vol. 430, No. 2, P. 210–213.
11 Zolotukhin Y. A., Coal classification in terms of the vitrinite reflection coefficient, *Coke and Chemistry*, 2018, Vol. 61, No. 4, P. 117–130.
12 Jiang J., Yang W., Cheng Y., Liu Z., Zhang Q., Zhao K., Molecular structure characterization of middle-high rank coal *via* XRD, Raman and FTIR spectroscopy: Implications for coalification, *Fuel*, 2019, Vol. 239, P. 559–572.
13 Fedorova N. I., Ismagilov Z. R., Determining the vitrinite reflectance of coal from its fuel ratio, *Coke and Chemistry*, 2020, Vol. 63, No. 5, P. 219–222.
14 Massiot D., Fayon F., Capron M., King I., Le Calv S., Alonso B., Durand J. O., Bujoli B., Gan Z., Hoatson G., Modelling one and two-dimensional solid-state NMR spectra, *Magn. Reson. Chemistry*, 2002, Vol. 40, P. 70–76.
15 Ding D., Liu G., Fu B., Influence of carbon type on carbon isotopic composition of coal from the perspective of solid-state ^{13}C NMR, *Fuel*, 2019, Vol. 245, P. 174–180.
16 Bogorodskaya L. I., Kontorovich A. E., Larichev A. I., Kerogen: Methods of Investigation, Geochemical Interpretation, Publishing House of SB RAS, Geo, Novosibirsk, 2005. (In Russ.).
17 Tissot B. P., Welte D. H., Petroleum Formation and Occurrence, Springer-Ferlag, Berlin, 1984.
18 Fedorova N. I., Lyrshchikov S. Yu., Ismagilov Z. R., NMR spectroscopy of black coal from the Kuznetsk Basin, *Chemistry for Sustainable Development*, 2016, Vol. 24, No. 3, P. 393–397.
19 Bushnev D. A., Burdel'naya N. S., Mokeev M. V., Results of ^{13}C NMR and FTIR spectroscopy of kerogen from the Upper Devonian domanik of the Timan-Pechora basin, *Geochem. Int*, 2019, Vol. 57, No. 11, P. 1173–1184.
20 Erdenetsogt B.-O., Lee I., Lee S. K., Ko Y.-J., Bat-Erdene D., Solid-state C-13 CP/MAS NMR study of Baganuur coal, Mongolia: Oxygen-loss during coalification from lignite to subbituminous rank, *Int. J. Coal Geol.,* 2010, Vol. 82, No. 1, P. 37–44.
21 Tarakanova A. V., Kardasheva Yu. S., Isichenko I. V., Anisimov A. V., Maksimov A. L., Karakhanov E. A., Physicochemical analysis of shaile oil, *Vestn. Mosk. Un-ta. Ser. 2. Khimiya*, 2016, Vol. 57, No. 5, P. 356–363. (In Russ.).