UDC 543.42: 662.67

DOI: 10.15372/CSD2020265

Study of Brown Coals by Method of Infrared Spectroscopy

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Abstract

Results of the IR spectroscopic investigation of brown coal from different deposits of Russia and Mongolia are presented. The obtained IR spectroscopic data indicate the presence of complex structures in brown coals containing aliphatic and aromatic hydrocarbon fragments, fragments of oxygen-containing heteroaromatic compounds, as well as oxygen-containing functional groups (carbonyl, hydroxyl, ether). It was found that the aromaticity index f_a calculated from the results of IR spectroscopy has a linear correlation with the quality indicators of brown coal – the yield of volatiles (V^{daf}), fixed carbon (C_{fix}) and the H/C atomic ratio.

Keywords: brown coal, elemental composition, fixed carbon, IR spectroscopy, aromaticity index

INTRODUCTION

The modern trend in the studies of eth structure of coal and coal products is the application of instrumental physicochemical methods of investigation, one of which is infrared (IR) spectroscopy. This method allows one to establish the nature of atom groups, their content in the substance, the degree and nature of aromatic hydrogen substitution; to obtain the data on the content of functional groups (CH_3, CH_2 (aliphatic), CH (aromatic)) for which the characterization by chemical methods is impossible or very difficult; to reveal the nature of hydrogen bonds, etc. [1–4].

In the present work, we report the results of IR spectroscopic investigation of brown coal, which is lower metamorphized in comparison with black coal. According to GOST 25543–2013, this kind of coal raw material is recommended for use as the energy fuel and as chemical raw material for the production of liquid hydrocarbons and various synthetic compounds, as well as gas and fertilizers. After special treatment, coke suitable for metallurgic works may be obtained from brown coal [5, 6]. It should be stressed that the data on coal composition and characteristics are necessary to predict technological properties [7, 8] and to choose the major directions of the use of coal from specific deposits.

The goal of the work was to study the main structural fragments of the organic matter of brown coal.

EXPERIMENTAL

The objects of the investigation were coal samples from the deposits: Itat (1), Munay (2), Baganuur (Mongolia) (3), Arkhara-Boguchanskoe (4), Kangalas (5). Coal samples were taken from the coal collection formed at the Institute of Coal Chemistry and Chemical Materials Science of the FRC CCC SB RAS.

The Itat brown coal deposit is located in the western part of the Kansk-Achinsk basin at the territory of the Itat and Tisul districts of the Kemerovo Region. The Munay coal deposit is the only coal deposit situated in the Solton district of

the Altay Territory at a distance of 100 km from Biysk. The Archara-Boguchanskoe brown coal deposit (the Nizhne-Zeyskiy basin) is situated in the Arkhara administrative district at a distance of 15 km from the Arkhara station in the Amur Region. The Kangalas brown coal deposit is confined to the south-eastern wing of the Vilyuy syneclise and comprises the southern part of the Yakut-Kangalas coal-bearing region in the Lena basin. The Baganuur brown coal deposit is situated in the central aimak at a distance of 110 km to the east from Ulan-Bator and relates to large significant industrial deposits of Mongolia [9–11].

Technical analysis of coal samples was carried out using standard methods. Fixed carbon was calculated using equation [12, 13]:

$C_{fix} = 100 - W^a - A^d - V^d$

where W^a is analytical humidity; A^d is ash content; V^d is the yield of volatile substances per the dry state. The element composition of the organic mass of brown coal was determined with a Thermo Flash 2000 element analyzer (Thermo Fisher Scientific, Great Britain); determination results were re-calculated per the dry ash-free state of the sample (daf).

The petrographic analysis was carried out using automatic complex for coal mark evaluation, SIAMS-620 system (Russia) in oil immersion according to GOST 9414.1–94, GOST R 55662–2013, GOST R 55663–2013 and GOST R 55659–2013. Calculation of microcomponents was carried out manually with 300 times magnification in the reflected light. Results of the petrographic investigation are shown per pure coal, without taking into account mineral substances.

IR spectra were recorded with an Infralyum FT-08 IR Fourier spectrometer (Russia). A mixture of the sample (10 mg) with KBr (250 mg) was treated in the vibratory mill for 3 min, then tablets were prepared by pressing at a pressure of 20 MPa. The spectra were recorded within the range of 500–4000 cm^{-1}, with 256 scans and 4 cm^{-1} resolution. Baseline correction was carried out using SpektraLyum software.

Analysis of IR spectra included evaluation of the intensity of the following absorption bands (a.b.): stretching vibrations of hydroxyl groups, in particular those in water, – 3400 cm^{-1}, stretching vibrations of C–H bonds in alkyl groups within the range 2930–2860 cm^{-1}, stretching vibrations of C=O bonds at 1710 cm^{-1}, stretching vibrations of C=C in olefins, aromatic and polyaromatic compounds within the range 1630–1600 cm^{-1}, asymmetrical bending vibrations of $-CH_2-$ and $-CH_3$ groups with a signal at 1455 cm^{-1}, bending vibrations of C–H bonds in the aromatic ring at 870, 820 and 750 cm^{-1} [1, 2, 14].

Aromaticity index f_a was determined through the decomposition of IR spectra for the studied samples using equations proposed in [3, 4, 15]:

$$\frac{H_{al}}{H} = \frac{H_{al}}{H_{al} + H_{ar}} = \frac{S_{3000-2800}}{S_{3000-2800} + S_{900-700}}$$

$$\frac{C_{al}}{C} = \left(\frac{H_{al}}{H} \cdot \frac{H}{C}\right) / \frac{H_{al}}{C_{al}}$$

$$f_a = 1 - \frac{C_{al}}{C}$$

where H_{al}/H is the ratio of hydrogen content in aliphatic structures (H_{al}) to hydrogen content (H) in the organic mass of coal, determined from the integral intensity of a.b. for H_{al} at 2800–3000 cm^{-1} ($S_{3000-2800}$) and 900–700 cm^{-1} ($S_{900-700}$) for aromatic hydrogen (H_{ar}); C_{al}/C is the fraction of carbon in aliphatic fragments; H/C is a parameter calculated on the basis of the data of elemental analysis; H_{al}/C_{al} is a coefficient equal to 1.8 (the value accepted for coal) [16].

The ratios of aromatic to aliphatic groups were also calculated using equation

$S_{ar}/S_{al} = S_{900-700}/S_{3000-2815}$

where $S_{900-700}$ is the integral intensity of a.b. of aromatic groups within the range 900–700 cm^{-1}; $S_{3000-2815}$ is the integral intensity of a.b. of aliphatic groups within the range 3000–2815 cm^{-1} [16].

The ratio between the groups CH_2/CH_3 was determined from the ratio of the intensities of a.b. in the IR spectra at 2920 and 2958 cm^{-1}: the higher is this parameter, the longer are aliphatic chains and the lower is their branching degree.

The structural parameter $(R/C)_u$ depicting the extent of condensation of aromatic rings in coal structure was calculated using the Van Krevelen equation [16–18].

RESULTS AND DISCUSSION

The data of technical analysis and the data on elemental composition are presented in Table 1. One can see that the ash content of the studied samples is practically not higher than 10 %. The yield of volatile substances (V^{daf}) in the studied samples varies from 40 to 50 % (see Table 1). The largest V^{daf} value was determined for the coal sample from the Itat deposit (48.5 %), and the lowest one – for Kangalas brown coal (41.4 %). A clearly pronounced linear correlation is ob-

TABLE 1

Characteristics of the studied samples

Deposit	Technical analysis, %					Elemental composition, % per daf			Atomic ratio	
	W^a	A^d	V^{daf}	V^d	C_{fix}	C	H	(O + N + S)	H/C	O/C
Itat	7.0	7.5	48.5	44.9	40.6	68.7	4.6	27.0	0.79	0.29
Munay	8.5	7.2	46.4	43.1	41.2	71.5	4.5	24.0	0.80	0.25
Baganuur	11.3	7.4	45.2	41.9	39.4	70.9	4.9	24.2	0.83	0.26
Arkhara-Boguchanskoe	4.5	10.8	44.1	39.3	42.4	71.0	4.9	24.1	0.83	0.25
Kangalas	2.8	2.8	41.4	40.2	54.2	77.5	5.5	17.0	0.85	0.16

Note. W^a is analytical humidity, A^d is ash content,, V^{daf} is the yield of volatile substances per dry ash-free state, V^d is the yield of volatile substances per dry state, C_{fix} – fixed carbon, fix is fixed carbon content, daf is dry ash-free state of the samples.

TABLE 2

Characterization of the petrographic composition of studied samples

Code of coal sample	Petrographic parameter, %					Vitrinite reflectance	
	V_t	S_v	I	L	∑LC	$R_{o,r}$, %	σ_R
1	54	42	4	1	32	0.39	0.05
2	62	4	31	3	34	0.41	0.05
3	27	8	63	2	68	0.40	0.03
4	41	43	12	4	41	0.40	0.05
5	86	2	6	6	7	0.49	0.03

Note. V_t is vitrinite, S_v is semi-vitrinite, I is inertinite, L is liptinite, ∑LC is the sum of leaning components, $R_{o,r}$ is vitrinite reflectance, σ_R is standard deviation.

served between the yield of volatile substances V^{daf} and H/C atomic ratio (Fig. 1).

Characterization of the petrographic composition of brown coal is presented in Table 2. One can see that vitrinite reflectance ($R_{o,r}$) varies from 0.388 % (sample No. 1, Itat deposit) to 0.490 % (sample 5, Kangalas deposit).

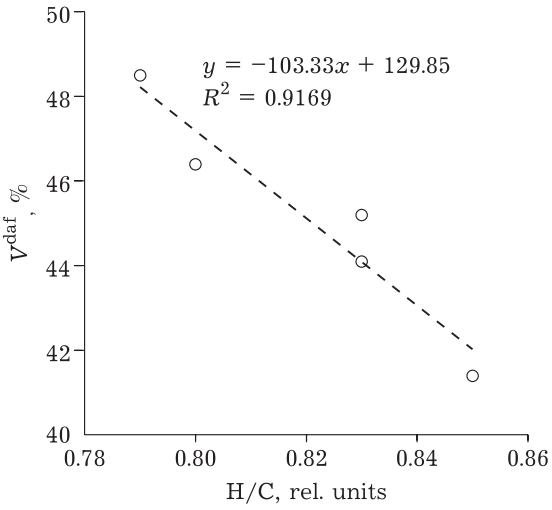

Fig. 1. Interconnection between the yield of volatile substances (V^{daf}) from brown coal and H/C atomic ratio in its organic mass.

The IR spectra of the studied samples (Fig. 2) contain an a.b. in the region of 3420 cm^{-1}, which is related to the stretching vibrations of OH groups connected through hydrogen bonds. A low-intensity a.b. characteristic of the stretching vibrations of aromatic CH groups is observed at 3040 cm^{-1}. The region 2920–2850 cm^{-1} contains intense a.b. of symmetric stretching vibrations of methyl and methylene C–H_x groups, the a.b. at 1445 cm^{-1} is characteristic of the bending vibrations of aliphatic CH_2 and CH_3 groups. A shoulder in the region of 2960 cm^{-1} relates to asymmetrical stretching vibrations of aliphatic CH_3 groups and provides evidence of eth low degree of side chain branching. The band at 1710 cm^{-1} belongs to the stretching vibration of C=O bonds in carboxyl and carbonyl groups. The IR spectra contain an intense a.b. at 1610 cm^{-1}, which may be related to the vibrations of C=C bonds of aromatic structures of C=O bond in carboxyl groups strengthened by oxygenated groups. The absorption band within the region 1166–1280 cm^{-1} is due to the vibrations of oxygen-containing groups, mainly ether C–O bonds. The absorption band at 817 cm^{-1} belongs to the out-of-plane bending vibrations of aromatic CH bonds [19, 20]. The data obtained provide evidence that the organic mass of the studied coal samples contains complicated structures incorporating aliphatic and aromatic hydrocarbon fragments, as well as oxygen-containing functional groups (carbonyl, hydroxyl, ether).

To reveal the features of the molecular structure of the organic mass of studied coal samples, the parameters calculated according to the IR spectra were used (Table 3). Analysis of the obtained data showed that brown coal samples are characterized by different indices of aromaticity of

their organic matter (parameters f_a and S_{ar}/S_{al}). Aromaticity index f_a varies from 0.54 (sample 1) to 0.63 (sample 5).

The largest value of the CH_2/CH_3 parameter is observed for brown coal from the Baganuur and Munay deposits (7.00 and 7.58, respectively), which points to the prevalence of longer aliphatic chains with lower branching degree in their organic mass. The extent of aromatic ring condensation in the structural units of the organic matter of brown coal varies within a rather narrow range (see Table 3, parameter $(R/C)_u$) [16, 21].

TABLE 3

Structural parameters calculated from the data of IR spectra of brown coal samples

Code of coal sample	f_a	S_{ar}/S_{al}	$(R/C)_u$	H_{al}/H	CH_2/CH_3
1	0.54	0.004	0.32	1.00	3.42
2	0.57	0.006	0.32	0.99	7.00
3	0.58	0.104	0.29	0.91	7.58
4	0.59	0.113	0.29	0.90	6.75
5	0.63	0.289	0.26	0.78	5.15

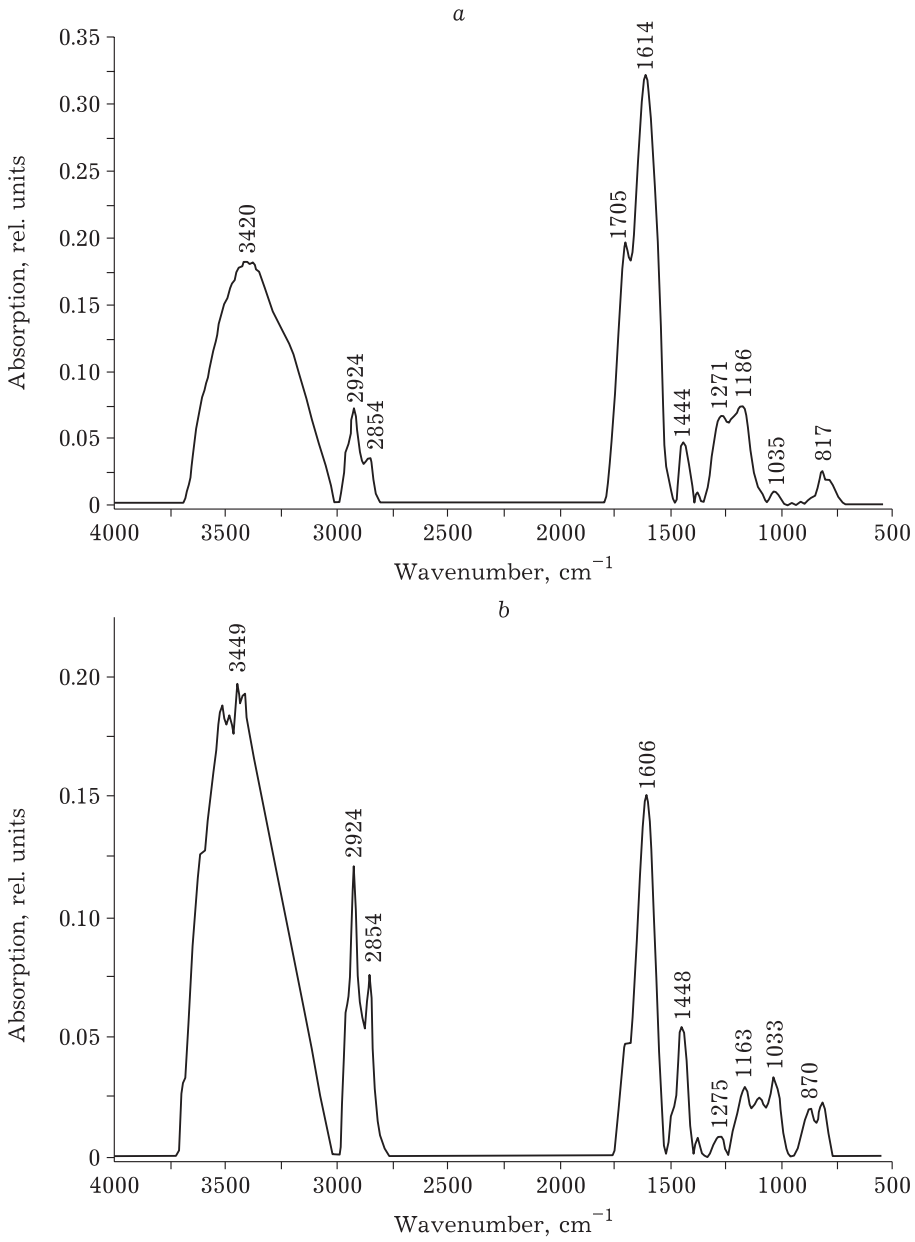

Fig. 2. IR spectra of the studied samples of brown coal from the Itat (*a*) and Kangalas (*b*) deposits.

TABLE 4

Correlation between structural and technological parameters of brown coal

Structural parameter	C_{fix} (R)	V^{daf} (R)	H/C (R)
f_a	$f_a = 0.004x + 0.369$ (0.86)	$f_a = -0.012x + 1.140$ (0.99)	$f_a = 1.277x - 0.466$ (0.95)
H_{al}/H	$H_{al}/H = -0.012x + 1.485$ (0.87)	$H_{al}/H = 0.032x - 0.567$ (0.99)	$H_{al}/H = -3.593x + 3.862$ (0.97)
S_{ar}/S_{al}	$S_{ar}/S_{al} = 0.017x - 0.65$ (0.89)	$S_{ar}/S_{al} = 0.004x^2 - 0.447x + 11.06$ (0.98)	$S_{ar}/S_{al} = 4.477x - 3.569$ (0.94)
$(R/C)_u$	$(R/C)_u = -0.003x + 0.456$ (0.86)	$(R/C)_u = 0.009x - 0.130$ (0.97)	$(R/C)_u = -1.023x + 1.136$ (0.98)

Note. R is correlation coefficient.

Graphical analysis was carried out between the calculated structural parameters and standard quality characteristics of brown coal. Results are presented in Table 4. One can see that a rather narrow correlation is observed for structural parameters f_a, H_{al}/H, S_{ar}/S_{al} and $(R/C)_u$ with the amount of fixed carbon, the yield of volatile substances V^{daf} and H/C atomic ratio. Therefore, the parameters calculated from the data of IR spectra allow revealing the features of the structure of organic matter in coal samples.

CONCLUSION

Five brown coal samples from different deposits were investigated by means of IR spectroscopy. Analysis of the spectra shows that brown coal samples contain aliphatic functional groups (CH_2 and CH_3), aromatic functional groups (C=C), aromatic ring (−CH) and oxygenated functional (−OH, C=O and C−O) groups.

Structural parameters calculated from IR spectra allowed us to reveal the features of the molecular structure of the organic matter in the studied brown coal samples. It was demonstrated that the degree of aromaticity of the organic mass of coal increases with an increase in the genetic maturity of the samples (an increase in vitrinite reflectance).

Correlation relations were established between the studied structural parameters and standard parameters of the quality of brown coal, namely the yield of volatile substances, the content of fixed carbon, and H/C atomic ratio.

Acknowledgements

The work was carried out using the equipment of the Kemerovo Shared Equipment Centre at the FRC CCC SB RAS.

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