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Effect of Mechanochemical Treatment on Supramolecular Structure of Brown Coal

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Abstract

Mechanical treatment of brown coal in a centrifugal planetary mill causes partial destruction of cross-linking in the organic mass, mainly oxygen-containing groups. As a result, substantial changes occur in the molecular structure, the amount of graphite-like phase decreases, a sharp increase in the flexibility of macromolecular chains is observed, the rate of penetration of the THF molecules into the organic matter, its swelling ability and the yield of soluble substances. Transport of THF molecules in mechanically treated coal occurs mainly due to relaxation vibrations of the macromolecular chains.

INTRODUCTION

Supramolecular structure is a fundamental feature of coal which in many respects determines its reactivity in thermochemical reactions [1]. Substantial role in the formation of supramolecular structure in brown coal is played by metal-carboxylate, as well as ether and methylene bridging bonds [1, 2]. A linear dependence of swelling factor in tetrahydrofuran (which characterizes supramolecular structure) on the logarithm of Ca content in coal was established [2]. The presence of a substantial amount of ionic carboxylate groups with polyvalent cations (mainly Ca^{2+}) in the organic matter of natural brown coal determines high degree of cross-linking and rigidity of supramolecular network, renders thermal stability to the coal and decreases its reactivity for solvation [3].

Preliminary controlled destruction of the separate oxygen-containing groups is one of the promising routes to the creation of efficient thermochemical processes of obtaining liquid fuel, chemicals, carbon materials and other valuable products from brown coal. For this purpose coal is subjected to preliminary activation treatment with solvents [4, 5], chemical reagents [5–7], physical ionizing radiation [8–10], mechanical treatment in various mills [5, 11–13]. The latter coal treatment procedure is relatively simple and technologically reasonable. The highest efficiency is observed with mechanochemical activation in high-energy mills [5, 13]. Solid-phase mechanochemical activation is comparable with the treatment in HCl solution in the efficiency of action on brown coal [5].

A number of works [14–16] establishing molecular composition, investigating properties of coal after mechanochemical treatment have been published. Under mechanical action, not only particle dispersion and an increase in the specific surface occur, but also the rupture of intermolecular bonds is stimulated, along with various valence bonds, first of all C–O and C–C, and the composition of functional groups changes. As a result, thermal stability of coal decreases [12, 17], the solubility in organic solvents, as well as the extent of conversion under hydrogenation into liquid products [5, 11, 13] and the yield of humic acids under decomposition in alkaline media [18] increase. However the changes in supramolecular structure of coal under mechanochemical action has been explored not adequately.

The goal of the present work is investigation of structural chemical transformations in brown coal with different Ca contents under mechanochemical action in high-energy activator mill, as well as evaluation of changes in the molecular composition and supramolecular arrangement of brown coal using different methods.

EXPERIMENTAL

Brown coals from the Borodino deposit of the Kansk-Achinsk basin and from the Kangalas deposit of the Lena basin were studied. Mechanochemical treatment was carried out in AGO-2 activator mill of centrifugal planetary type with two tightly closed steel drums, 150 ml each, with steel balls 3 mm in diameter. Balls with a total mass of 106 g and 6 g of coal were loaded into a drum; in some runs, solvent was added, which was petroleum fraction with boiling point above 300 °C. Mechanical load was varied by varying the time of treatment from 1 to 60 min. When in operation, the drums were cooled with water to exclude substantial heating of the treated material.

The composition of the organic matter of coal (OMC) was determined by elemental and functional analysis. The content of the main ash-forming macro-components (calcium, silicon, iron) was determined by X-ray spectral fluorescence method. The IR spectra were recorded with Vector 22 IR Fourier-transform spectrometer of Bruker within the range 4000–400 cm^{-1}. The samples were prepared in KBr matrix. The OPUS-3 software, version 2.2 was used to process the spectra.

Changes in the supramolecular structure of coal under mechanical treatment were studied by means of X-ray diffraction, extraction and swelling in organic solvents. Extraction was carried out in Soxhlet apparatus with a mixture of ethanol and benzene at a ratio of 1 : 1. The swelling ability was determined volumetrically in a glass ampoule 8 mm in diameter. Tetrahydrofuran was used as a solvent. The swelling coefficient Q_{THF} was estimated using the ratio of the height of the column of swollen coal to that of dry coal before the solvent was added.

The structural parameters of relatively ordered graphite-like phase of the OMC were determined using the main reflection (002) in the diffraction patterns. The diffraction patterns were recorded with DRON-3 instrument in CuK_α radiation under identical conditions. Subtraction of the background line and isolation of the (002) reflection were carried out according to the procedure described in [19]. The diffraction reflection with (10) index is weakly exhibited for brown coal, so it was not analyzed.

RESULTS AND DISCUSSION

The coal samples under investigation were substantially different from each other in the mineral components content. Calcium content of the samples was 0.75 to 1.65 %, that is, the

TABLE 1

Content of ash and main ash-forming elements in brown coal, %

Coal	Deposit	Ash content	Element		
		A^{d}	Ca	Mg	Fe
Ka_1	Borodino	4.4	0.75	0.10	0.10
Ka_3	Borodino	7.8	1.34	0.20	0.08
Ka_{20}	Kangalas	7.8	1.65	0.30	0.73
Ka_1–I*		1.0	0.02	$<10^{-4}$	0.04

*The Ka_1 coal after treatment with a 0.2 M HCl solution.

TABLE 2

Characteristics of the composition of the organic matter of brown coal, %

Coal	Elemental composition					Functional groups		
	C	H	N	S	O	O_{COOH}	O_{OH}	Other
Ka_1:	69.6	4.7	0.9	0.2	24.6	3.1	6.9	14.6
after MA	70.1	4.7	0.8	0.2	24.2	–	–	–
after treatment with HCl	70.3	4.7	0.9	0.2	23.9	5.8	6.5	11.6
Ka_3	71.3	4.8	0.9	0.2	22.8	2.8	6.3	13.7
Ka_{20}	71.0	5.5	0.8	0.4	22.3	–	–	–

difference was more than two times; for magnesium, it was 3 times, and for iron, 7 times (Table 1). The treatment of coal with 0.2 M HCl solution allowed us to decrease total content of ash-forming components by a factor of 4. This treatment resulted in almost complete removal of the cations of alkaline and alkaline earth metals; mass concentration of Ca reduced to 0.02 %. The organic matter of the initial natural coal has a similar composition (Table 2). After the removal of cations, the content of free carboxylic acids increased almost by a factor of two, while the content of phenol hydroxyl groups changed only slightly. This indicated that polyvalent cations were present in the brown coal mainly in the ion exchange form as the salts of carboxylic acids, which was several times stressed previously [20–22]. The carboxylate groups cause absorption which is observed in the IR spectrum as a shoulder at 1575 cm^{-1} (Fig. 1). One can see in the differential spectrum *3* that the removal of cations with the HCl solution causes an increase in the intensity of absorption bands related to the C=O groups of carboxylic acids (bands at 1720 cm^{-1}), and a decrease in the intensity of the bands with maxima at 1560 and 1410 cm^{-1} belonging to the ionic carboxylate groups COO^-.

Under the action of mechanochemical treatment, the total elemental composition of coal is changed only slightly (see Table 2). The changes in the molecular composition were investigated using the IR spectra. One can see in Fig. 2 that a substantial increase in the intensity of the main absorption bands (including the band at 1600 cm^{-1}) and some increase in band resolution is observed after mechanochemical treatment. The indicated spectral features are likely to be caused mainly by fine state of the mechanically treated coal. At the same time, a

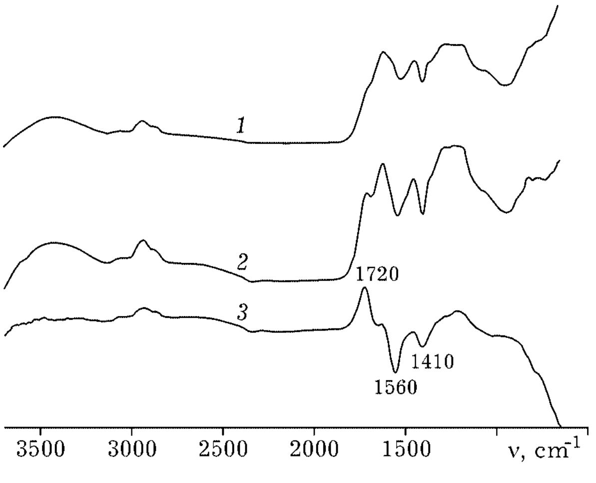

Fig. 1. IR spectra of brown coal from the Borodino deposit: *1* – initial; *2* – after treatment with HCl solution; *3* – differential (the difference between *2* and *1*).

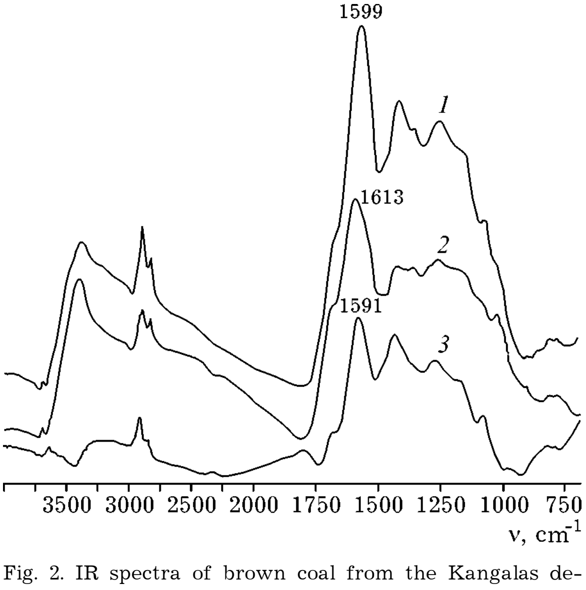

Fig. 2. IR spectra of brown coal from the Kangalas deposit: *1* – after mechanical activation in dry state for 15 min; *2* – initial; *3* – differential (the difference between *1* and *2*).

noticeable decrease in the intensity of absorption bands within 3400–3500 and 1700–1800 cm^{-1} is observed in the differential spectrum shown in Fig. 2. The ratio of intensities of the bands attributed to the stretching vibrations of C–O ester and ether groups at 1170, 1093 and 1036 cm^{-1} to the intensity of the band at 1600 cm^{-1} also decreases. This is an indication of partial destruction of carboxylic acids, esters and ethers, as well as lactones during mechanical treatment.

Mechanical treatment also results in a noticeable shift of the absorption band at 1600 cm^{-1} toward lower frequencies (by 14 cm^{-1}), its narrowing and the disappearance of low-frequency asymmetry related to metal carboxylate groups. It should be noted that the authors of [16] previously also observed an increase in the intensity of absorption band at 1600 cm^{-1} and a shift of the maximum to lower frequencies after mechanical treatment of the gas coal. These authors concluded that the reason was mechanically stimulated aromatization of OMC with the formation of condensed aromatic structures. Because of this, it is necessary to stress that the origin of the band under consideration is of complicated nature. It is usually assigned to the framework vibrations of the aromatic rings [23–26]. However, it is known [24, 25] that the C=O groups conjugated with the aromatic rings and the hydrogen bonded C=O groups including carboxylic acids, esters, lactones 1600–1680 cm^{-1}) and ionic carboxylate COO^{-} groups (1560–1610 cm^{-1}) absorb in the same spectral region. In addition, the position of the absorption band related to skeletal vibrations of aromatic rings depends on the nature and number of substituents [25, 26]. The presence of quinoid C=O, aldehyde and carboxylic groups, as well as phenol hydroxyls as substituents in the aromatic ring causes a substantial increase in absorption intensity and a shift toward lower frequencies (about 1580 cm^{-1}). To the contrary, alkyl substituents cause some shift of the absorption to higher frequencies.

Out-of-plane vibrations of aromatic rings are exhibited within the region 700–900 cm^{-1}. One can see in Fig. 2 that after mechanical treatment the intensity of the band at 870 cm^{-1} decreases in comparison with the band at 750 cm^{-1}. This indicates that mechanical treatment causes detachment of the substituents from aromatic rings. So, the changes in the IR spectra as a whole allow us to assume that mechanical treatment causes disturbance of intermolecular interactions involving carbonyl groups, partial destruction of various oxygen-containing groups: carboxylic acids, esters, metal carboxylate complexes; it also causes detachment of the substituents in the aromatic rings. To somewhat lower extent, the same destruction reactions manifest themselves during mechanical treatment in petroleum paste former.

Mechanically stimulated destruction processes lead to substantial increase in the amount of soluble substances and in the swelling ability of coal. For the coal of the Borodino deposit, as mechanical load increases to 60 min, the yield of the alcohol-benzene extract increases from 1.5–4.5 to 10–15 % (that is, 3–6 times) (Fig. 3). During mechanical treatment of the Kangalas coal in petroleum paste for 5 min, the yield increases from 0.8 to 16 %, that is, by a factor of 20. The obtained results are of substantial practical interest for an increase in the yield of bitumen matter from brown coal processing. After mechanical treatment of decationized coal, the yield of the extract remains almost unchanged.

Swelling of the initial coal (especially those with increased Ca content) in THF occurs rather slowly; the equilibrium is established after 1–2 days. Mechanical treatment causes a

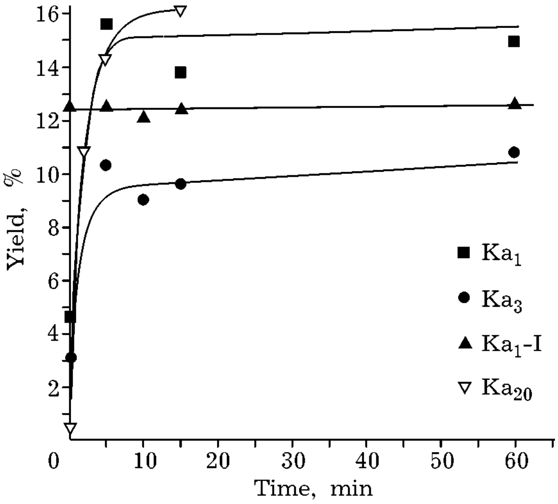

Fig. 3. Effect of mechanical activation of brown coal on the yield of alcohol-benzene extract. The Ka$_{20}$ coal was activated in petroleum paste.

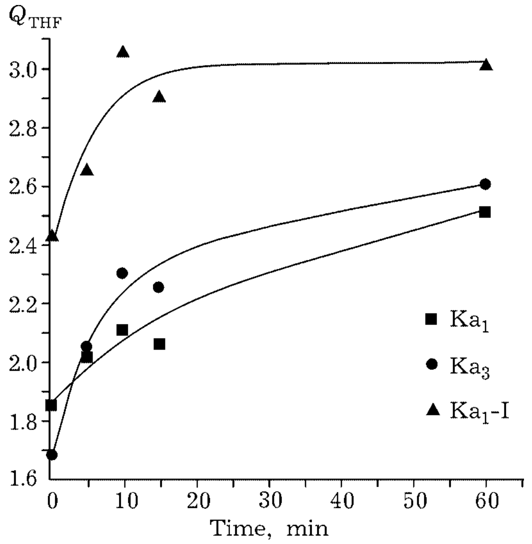

Fig. 4. Effect of mechanical activation on the swelling ability of coal in THF.

substantial increase in swelling ability (Fig. 4). After mechanical treatment of Ka$_3$ coal for 60 min, swelling coefficient Q_{THF} increases from 1.68 to 2.60, which corresponds to an increase in the number of absorbed THF molecules by a factor of 2.5 (from 8 to 20 mmol/cm^3). Decationized coal Ka$_1$–I containing no metal carboxylate groups differs by high Q_{THF} coefficient (2.42). After a short-term mechanical treatment (for 10–15 min), it increases to 2.90–3.05, which corresponds to the absorption of 25 mmol of THF.

The swelling kinetics is shown in Fig. 5; it depicts the properties of the supramolecular network-and the diffusion mechanism for THF in coal. In order to describe the kinetics, equation [27] was used: $(Q_t - 1)/(Q_{eq} - 1) = kt^r$, where Q_t is the equilibrium swelling coefficient, k is the rate constant, r is the experimental factor reflected the properties of supramolecular lattice of coal and the mechanism of solvent molecule diffusion in the coal. According to [28], if solvent transport in coal under swelling is controlled by physical diffusion along pores, then, r = 0.45. For the case of the hole diffusion mechanism connected with the relaxation of coal macromolecule chains, r = 0.85. In Fig. 5, the slope of straight lines gives r, that is, characterizes the mechanism of THF penetration into coal at the limiting stage. One can see that for the Ka$_1$ sample containing decreased amount of Ca (0.75 %), r is close to 0.45. This means that the transport of THF in this coal is governed by physical diffusion along the existing pores, while the supramolecular structure, according to the accepted model [28], can be represented as a rigid framework which is unable to undergo conformation. For coal with high Ca content (1.34–1.65 %), swelling proceeds at a low rate; r is small (0.22), which is not characteristic of the models under consideration. This is likely due to steric hindrance for the diffusion of THF molecule along the pores because of high density of carboxylate cross-links. After removal of cations with HCl solution, that is, after complete destruction of the ion metal carboxylate cross-links, the swelling rate increases sharply [5, 21], while r reaches 0.85, which corresponds to the relaxation mechanism of diffusion process.

After mechanical treatment, similarly to the situation after removal of cations, the rate of swelling in THF increases sharply. The kinetic index r approaches the value typical for diffusion limited by the relaxation of macromolecular chains (for Ka$_3$ coal, r = 0.74). This means that the supramolecular lattice of the mechanically treated coal is distinguished by substantial mobility.

Unlike swelling method, the X-ray diffraction studies give information about the spatial arrangement of the relatively ordered graphite-like phase. The resulting data show (Table 3) that the content of this phase in the initial coal S_{002} decreases with an increase in Ca con-

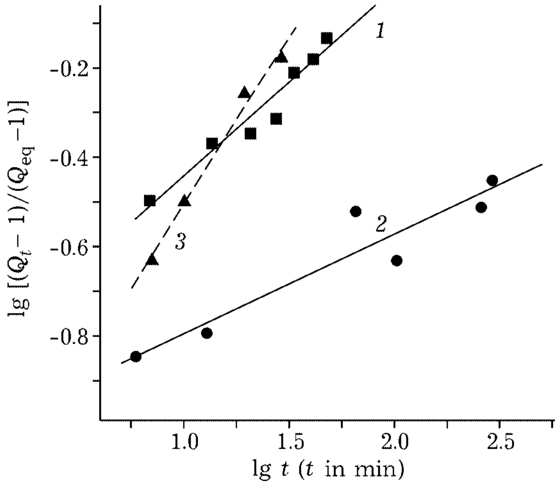

Fig. 5. Swelling kinetics of coal in THF: *1* – Ka$_1$, r = 0.41; *2* – Ka$_3$, r = 0.22; *3* – Ka$_3$ after MA, r = 0.74.

TABLE 3

Effect of mechanochemical treatment on X-ray structural parameters of brown coal

Coal sample	Treatment time, min	S_{002}	d_{002}, Å	n
Ka_1	–	115	3.81	3.4
	5	90	3.85	3.2
	60	94	3.83	3.1
Ka_3	–	84	3.87	3.2
	5	71	3.91	3.1
	60	45	3.87	3.3
Ka_{20}	–	73	3.87	3.2
	15	50	3.90	3.3

tent. Mechanical treatment leads to partial destruction of the graphite-like phase. This process is most intensive in coal with increased Ca content. For example, after mechanical treatment of Ka_3 coal for 60 min, the content of the graphite-like phase decreases nearly by a factor of 2. The composition of packets (n = 3.1−3.3 layers) and the interlayer distance (d = 3.87-3.91) change only slightly, which agrees with the results obtained in [29] for mechanical treatment of low-rank–coal.

CONCLUSION

The data obtained demonstrate that the mechanochemical action is an efficient method to govern the supramolecular arrangement of brown coal. The initial natural brown coal is characterized by tightly cross-linked supramolecular structure in which the diffusion of THF molecules occurs at a low rate. Coal swelling extent and the amount of solvent extractable organic matter are limited by high degree of association through intermolecular bonds and cross-linking with the participation of oxygen-containing groups (firs of all, metal carboxylate groups). Mechanical treatment leads to partial destruction not only of intermolecular interactions but also of the strong cross-links in the organic matter, which results in a sharp increase in the flexibility of macromolecular chains, in the amount and swelling rate, and the yield of extractables. The penetration of THF molecules into mechanically activated coal occurs at a high rate mainly *via* the hole mechanism which is due to the relaxation of flexible macromolecular chains. The most substantial changes occur under mechanical activation of the coal with increased Ca content.

The data obtained are of substantial practical interest for the development of the methods of directed action on coal for the purpose of increasing its reactivity, yield of valuable products. For instance, we demonstrated in [2, 5, 21] that the labilization of the supramolecular structure of coal leads to an increase in the ability to be converted into low-molecular products. An increase in the yield of extract after mechanical treatment can be used to obtain bitumen and wax species from coal.

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