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## Preparation of Oxygen-Containing Organic Products from Bed-Oxidized Brown Coal by Ozonation

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**Abstract**—The possibility of modifying the functional composition of humic acids by gas-phase ozonation of bed-oxidized brown coal was examined. About 90% of the organic matter of brown coal was converted to low-molecular-weight soluble oxygen-containing products by stepwise liquid-phase ozonation (in chloroform and acetic acid).

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Hydrocarbons of oil and natural gas are considered today as major sources of raw materials for chemical industry. At the same time, the substance composition of solid fossil fuels of low chemical ripeness (humus brown, liptobiolite, sapropelite coals) suggests the possibility of using them not only in power engineering but also as natural raw materials for production of liquid fuel, fertilizers, sorbents, benzenecarboxylic acids, biologically active substances, lignite wax, and other valuable products [1, 2].

Search for alternative applications of coals (other than their use as fuel and in coal-tar chemical industry) was actively performed in the beginning of the XX century and then in the 1970s, in the period of oil crisis [3]. The shortage of readily accessible oil resources is outlined again, and therefore it becomes topical to examine the possibilities of producing valuable organic products by processing of solid fuels.

Along with a wide series of coals occurring in Kemerovo oblast, in its northern part there are deposits of humus brown coals. The upper stripping strata of the deposits being mined consist, as a rule, of naturally oxidized weathered coals with poor power-engineering characteristics: low calorific value, increased ash and moisture content, large amount of fine fractions, etc. Furthermore, these strata are sources of environmental pollution [1]. In this connection, it is appropriate to develop economically efficient and environmentally safe procedures for processing of such coals oxidized under natural conditions.

The treatment procedures usually used in coal fuel chemistry are based on deep degradation of the organic matter of coal (OMC). In the process, numerous valuable chemical compounds are lost in the course of decomposition of OMC structural fragments. One of mild oxidation methods is ozonation. It allows both introduction of oxygen-containing functional groups into OMC and preparation of new organic products.

In this study we examined the possibility of preparing oxygen-containing organic substances by gas- and liquid-phase ozonolysis of weathered brown coal from the Barandat deposit of Kemerovo oblast.

### EXPERIMENTAL

A sample of weathered brown coal taken from the upper unit of the coal bed (Barandat deposit, Kaichak open pit) had the following characteristics (%): ash  $A^d$  26.0, yield of volatiles  $V^{daf}$  51.0, moisture content  $W^a$  12.0.

The initial coal sample was first demineralized with 10% HCl and 3% HF solution ( $A^d$  of decalcified sample 3%) and then debituminized with chloroform. The characteristics of the coal are given in Table 1.

Ozonation of the coal (1–1.5 vol % ozone, fraction 0–0.063 mm, sample weight 2 g) was performed at 25°C in a temperature-controlled rotating reactor. The amount of ozone at the inlet and outlet of the reactor was determined by volumetric iodometric titration [4] of intermittently taken gas samples. Ozonides formed

**Table 1.** Characteristics of brown weathered coal and ozonation products

Coal, product*	Elemental composition, % of OMC			H/C	O/C	Functional composition, mg-equiv g <sup>-1</sup>			Oxygen in groups, %		Yield, % of OMC
	C	H	O + N + S			COOH	OH	CO	O <sub>act</sub>	O <sub>inact</sub>	
Initial coal	64.4	2.8	32.8	0.52	0.36	4.44	1.52	3.28	20.58	9.42	** n/d 94
HA	52.5	2.4	45.1	0.56	0.64	4.86	0.76	3.76	19.78	25.27	
Gas-phase ozonation											
Ozonized coal	64.6	2.7	32.7	0.50	0.35	4.77	1.64	3.23	21.96	8.23	n/d
HMWA	54.9	2.1	43.0	0.46	0.59	5.57	0.63	4.49	22.42	20.55	91
Ozonation in chloroform											
WIS	60.5	3.2	36.3	0.63	0.45	4.54	1.60	4.79	20.92	15.36	23.7
WS	52.1	2.3	45.6	0.53	0.66	7.32	1.47	5.05	29.83	15.83	65.8
RC	64.4	2.6	32.9	0.48	0.36	2.49	1.67	3.50	20.46	10.54	11.5
Total											100.7
Ozonation in acetic acid											
WIS	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	0
WS	51.6	3.1	45.3	0.72	0.65	9.69	1.31	4.72	36.88	8.42	81.6
RC	60.8	2.5	36.7	0.49	0.44						13.0
Total											94.6

\* (HA) Humic acids, (WIS) water-insoluble substances, (WS) water-soluble substances, (HMWA) high-molecular-weight acids, and (RC) residual coal.

\*\* (N/d) Not determined.

as intermediates in gas-phase reaction of ozone with polyaromatic OMC fragments were decomposed in the treated coal by heating at 100°C for 2 h. The time of one ozonation cycle, determined from the maximal rate of formation of soluble substances, was 3 h in the gas-phase process and 5 h in the liquid-phase process.

After the end of the liquid-phase process, the residue was filtered off. With acetic acid as solvent, the residual coal was washed on the filter with a fresh portion of the acid to remove soluble components. After ozonation in chloroform, coal was additionally extracted with acetone to remove oxygen-containing compounds insoluble in the weakly polar reaction medium. Then the solvent was distilled off in a vacuum from the extract, 100 ml of distilled water was added, and the mixture was heated on a water bath for 2 h, after which the water-soluble and water-insoluble substances were separated. The unchanged residual coal was taken to the second step of the ozonation.

Native humic acids from the initial coal and polyfunctional high-molecular-weight acids from the coal ozonized in the gas phase were isolated by treatment of the samples with 1% NaOH, followed by acidification with an HCl solution.

The products were characterized by elemental analysis, chemical functional analysis, IR spectroscopy, and gas chromatography–mass spectrometry (GC–MS).

The amount of carbonyl groups was determined by the reaction with hydroxylamine hydrochloride; the amount of carboxy groups, by the acetate method; and the sum of carboxy and hydroxy groups, by ion exchange with sodium hydroxide [5]. The content of oxygen in “active” groups was determined by summation of its percentage in the identified carboxy, carbonyl, and phenolic groups, and the content of “inactive” oxygen O<sub>inact</sub>, by the difference between the total oxygen content and O<sub>act</sub>.

The IR diffuse reflection spectra were recorded on a Tensor-27 spectrometer (Bruker). The GC–MS analysis was performed on an Agilent 1909IS-433 device in the range 15–500 amu, using an HP-5MS capillary column (5% diphenyl–95% dimethylsiloxane), 30m × 0.25 mm × 0.25 μm, with helium as carrier gas. Prior to chromatographic analysis, the products were methylated with diazomethane in diethyl ether [6].

Figure 1 shows how the content of unchanged ozone in the gas mixture at the reactor outlet depends on the process duration. The high initial rate of reactions of the

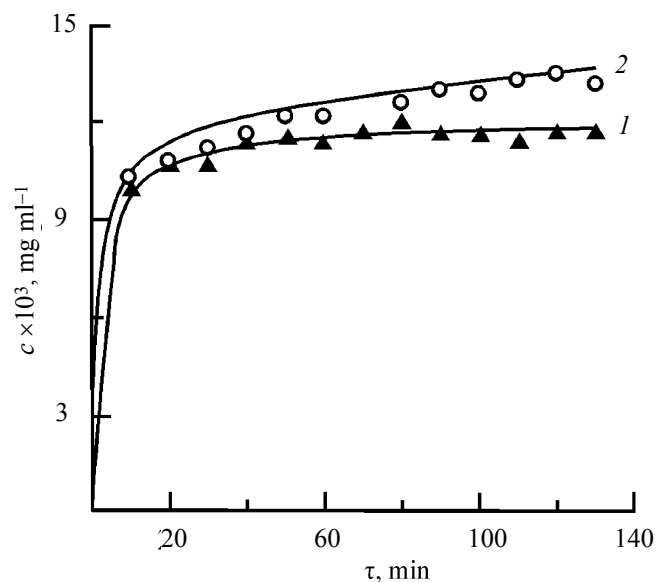


Fig. 1. Ozone breakthrough  $c$  in ozonation of weathered brown coal as a function of time  $\tau$ . Ozonation: (1) in gas phase and (2) in glacial  $\text{CH}_3\text{COOH}$ .

organic matter of the weathered coal with ozone may be due to the presence in its structure of a relatively large amount of highly reactive [7] weakly condensed aromatic fragments [1]. Decrease and stabilization of the rate of the gas-phase process with increasing ozonation time are apparently due to the arising hindrance to diffusion of ozone molecules as a result of blocking of pore issues by OMC ozonolysis products (both low-molecular-weight volatile substances and peripheral O groups) [8], and also to a decrease in the amount of OMC fragments that are sterically accessible and reactive toward ozone. At the same time, intensification of the ozonolysis in the liquid phase is associated with gradual dissolution of the forming reaction products, so that a new reaction surface becomes accessible. Therefore, this procedure can be used for preparing relatively low-molecular-weight oxygen-containing compounds directly in the reaction space.

Ozonolysis does not lead to significant changes in the elemental (Table 1) and functional (Fig. 2) composition of brown coal saturated with oxygen under the hypergenesis (weathering) conditions, because accumulation of new O groups is apparently compensated by oxidative degradation of oxygen-containing fragments already available in OMC. Phenolic groups are an exception. Their content in OMC rapidly decreases already in the initial step of the ozonation because of high reactivity of ozone toward O–H bonds of phenolic hydroxyls ( $k = 1 \times 10^2$ – $1 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ ) [7].

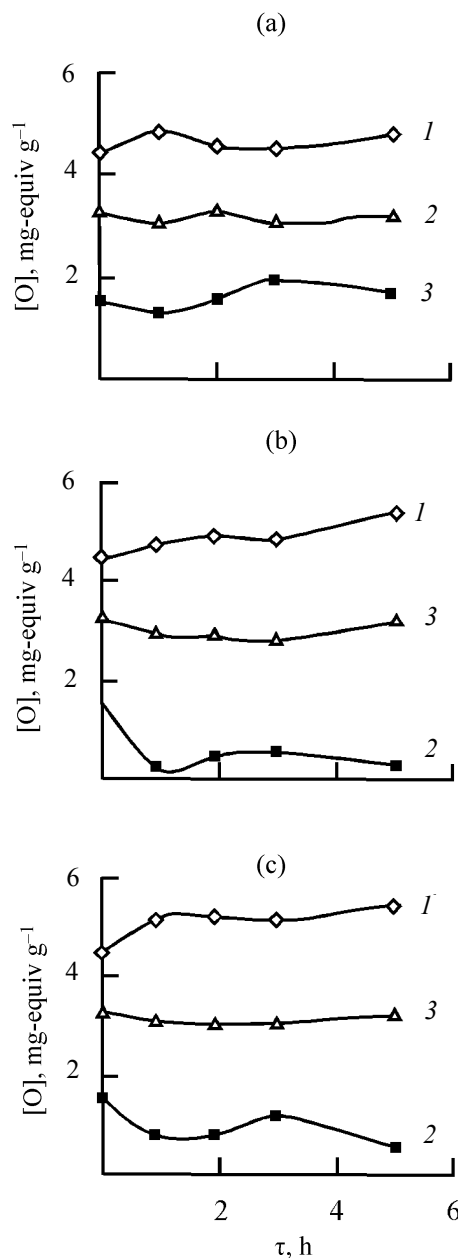
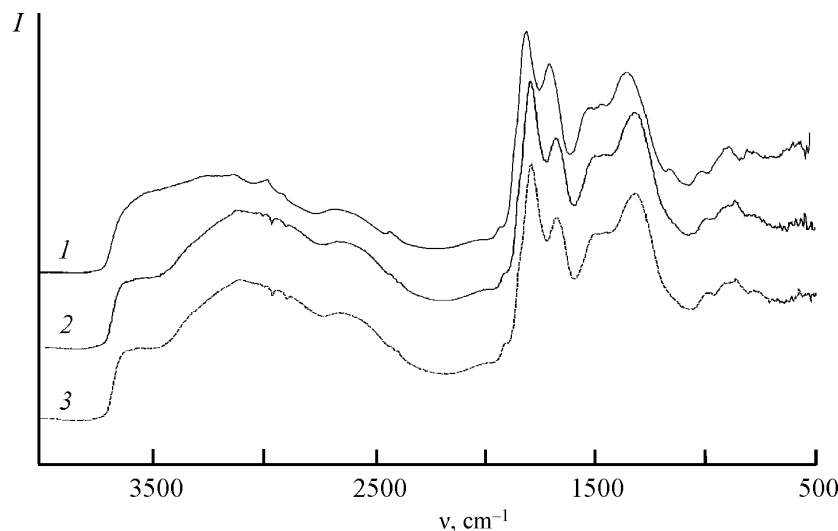
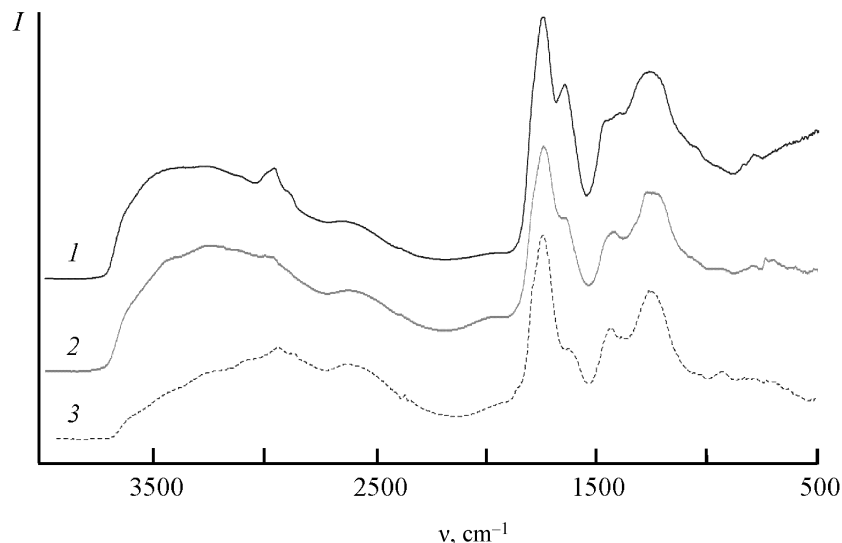


Fig. 2. Yield of oxygen-containing groups [O] in ozonation of weathered brown coal as a function of time  $\tau$ . Ozonation in (a) gas phase, (b) chloroform, and (c) acetic acid. Groups: (1) carboxy, (2) phenolic, and (3) carbonyl.

The yield of HA from the initial sample was 94 wt%, which suggests high extent of oxidation of the examined brown coal sample under natural conditions [1]. Humic acids are low-ash (up to 3%) substances containing about 45% oxygen. Examination of the chemical forms of bound oxygen showed that the largest amount of oxygen was in the form of carboxy and carbonyl groups (Table 1). Unidentifiable oxygen can be in both ether and heterocyclic forms.



**Fig. 3.** IR spectra of (1) brown weathered coal and HMWA from (2) initial and (3) ozonized coal. (I) Absorption intensity and (ν) wavenumber; the same for Fig. 4.



**Fig. 4.** IR spectra of (1) WIS and (2, 3) WS products of ozonation of weathered brown coal in (1, 2) chloroform and (3) acetic acid.

After the coal ozonation, the HMWA yield decreased by 3% (Table 1). This decrease could be due to oxidative degradation of peripheral acidic groups (phenolic and partially carboxy groups) with the formation of intermolecular and interfragment cross-links. High-molecular-weight acids of the ozonized coal, compared to HA of the initial coal, contain more organic carbon owing to a decrease in the oxygen content.

Changes in the functional composition of O groups consist in an increase in the content of carboxy and carbonyl groups with a decrease in the oxygen content in unidentifiable groups. Apparently, the observed changes are associated with the effects of both the

ozonolytic transformations of OMC and the oxidative-hydrolytic processes occurring under the conditions of base hydrolysis. This is not, however, accompanied by significant changes in the macromolecular structure of HMWA, as judged from the identity of the spectral patterns of HA and HMWA (Fig. 3).

The IR spectra of HA and HMWA contain typical absorption bands characteristic of OH groups of phenols and carboxylic acids [3200–3400 (free) and 2500–2700 cm⁻¹ (hydrogen-bonded)]; C=O groups of aromatic and aliphatic acids, ketones, and anhydrides (1650–1800 cm⁻¹); C–O groups of alcohols, phenols, and ethers (1100–1300 cm⁻¹). Among aromatic structures, C=C

**Table 2.** Component composition of WS ozonation products

Class of compounds	Relative content of components, % of sum of chromatographically detected compounds	
	ozonation in chloroform	ozonation in acetic acid
Methyl esters of palmitic (C <sub>16</sub> ) and stearic (C <sub>18</sub> ) acids	74	–
Dimethyl esters of acids:		
oxalic	–	26.6
succinic and adipic	6.9	5.3
phthalic	12.9	19.5
Trimethyl benzene- 1,2,4-tricarboxylate	–	9.5
Tetramethyl benzene- 1,2,3,4- and -1,2,4,5- tetracarboxylates	–	20.6
Methyl hydrophenanthreneca rboxylate	3.7	–
Dibutyl phthalate	9.7	10.4
Ethyl hexyl phthalate	54.4	3.8
Unsaturated hydrocarbons C <sub>23</sub>	5	4.3

bonds exhibit the most pronounced absorption (1600 cm<sup>-1</sup>). At the same time, poor resolution of the C<sub>ar</sub>–H bands at 3040 cm<sup>-1</sup> and relatively strong absorption in the range 670–870 cm<sup>-1</sup> suggest high degree of hydrogen substitution in the aromatic structures.

Insignificant changes in the composition of brown coal humic acids are apparently due to diffusion hindrance to the gas-phase process and its occurrence in the surface layer of coal particles, and also to formation in the course of ozonation of an additional amount of relatively low-molecular-weight products contributing to the acid-soluble fraction (fulvic acids). At the same time, increased content of active O groups (carboxy and carbonyl) in HMWA makes them promising for some new applications, along with traditional ones (e.g., in agriculture). In particular, it was shown [9] that increased content of carboxy groups in HA positively affects the service life of electric plates of lead batteries.

In five cycles of liquid-phase ozonation (25 h) in chloroform and acetic acid, 90 and 82% of OMC, respectively, was converted to the soluble state (Table 1). In chloroform, the product balance was positive, and in

acetic acid, negative. Apparently, a decisive effect on the yield of ozonation products in chloroform is exerted by the subsequent extraction with acetone of oxygen-containing substances insoluble in the reaction medium. Products of natural weathering of coal (yield of acetone extract from the initial coal 8%) are removed from the surface of coal particles together with ozonation products, which results in apparent increase in the yield of extractable substances in each step of the process. Probably, products dissolving in acetic acid in the course of ozonation more readily undergo secondary oxidative transformations leading to the loss of a part of OMC with gaseous substances and thus to a decrease in the yield of target products.

The content of WS substances was 74% of the sum of extractable substances in ozonation in chloroform and 100% in ozonation in acetic acid. High yield of low-molecular-weight products is possible owing to ozonolysis of weakly fused aromatic rings which form the basis of brown coal macromolecules [1]. The possible additional source of these products is the release of hydrocarbons and higher acids (products of degradation of plant material and of subsequent coal weathering) from the coal matrix. The absence of higher-molecular-weight WIS substances in products of ozonation in acetic acid is probably due to competition of selective ozonolytic reactions with more destructive radical-chain oxidation processes.

Water-soluble products isolated from the acetic acid solution are characterized by increased H/C atomic ratio and higher content of carboxy groups (Fig. 2). The IR spectra of these substances suggest increased content of aliphatic dicarboxylic acids (2500–2700 cm<sup>-1</sup>); the absorption bands of aliphatic CH<sub>x</sub> groups (2920, 1460, 1380 cm<sup>-1</sup>) are less intense than those of C=C and aromatic C–H bonds (3040, 1600, 780 cm<sup>-1</sup>) (Fig. 4). High-molecular-weight WIS products are characterized by lower atomic ratio O/C and lower content of oxygen in active groups. They are characterized by higher intensity of bands of alkyl CH<sub>x</sub> (2940, 1460 cm<sup>-1</sup>) and aromatic C=C (1600 cm<sup>-1</sup>) groups, apparently because of the presence of long-chain aliphatic and cyclohydroaromatic compounds.

In WS products of ozonation in chloroform, we identified by GC–MS mono- (C<sub>18</sub>) and dicarboxylic (C<sub>4</sub>, C<sub>6</sub>) aliphatic acids, steroid (hydrophenanthrenecarboxylic) acids, and phthalic acid derivatives (Table 2). Along with oxygen-containing compounds, we detected long-chain alkenes of the carotinoid class (5%), which represent structural fragments of plant origin. The major (~80%)



components of WS products are aromatic dicarboxylic acids, which is consistent with the concepts of more aromatized structure of coals of low chemical maturity, subjected to oxidative weathering [1].

The composition of high-molecular-weight WIS products is very diverse. Along with dicarboxylic aliphatic (3.5%) and aromatic (45%) acids, oxygen-containing substances include oxo, oxy, and hydroxy compounds of aromatic and hydroaromatic series. Long-chain alkanes ( $C_{20}$ – $C_{30}$ ) account for 20% of WIS products.

An essential distinctive feature of WS products from coal ozonized in acetic acid is the presence of large amounts of oxalic acid (26%) and of tri- and tetracarboxylic aromatic acids (30%) (Table 2). This fact indicates that ozonation in a more polar solvent leads to higher degree of degradation of the organic matter of coal with the formation of low-molecular-weight aliphatic dicarboxylic acids and gaseous products.

### CONCLUSIONS

(1) Substance composition of substandard brown coals subjected to natural oxidation allows them to be considered as a promising raw material for preparing polyfunctional humic products.

(2) Preliminary gas-phase ozonation of coal allows transformation of the functional composition of humic acids, with the prevalence of carboxy groups.

(3) By liquid-phase ozonation, more than 90% of the organic matter of weathered brown coal can be converted

to products soluble in polar organic solvents. Uniform composition and high yield of water-soluble compounds in ozonation in chloroform allows oxidized coals from stripping strata to be recommended as raw material for preparing benzenecarboxylic acids.

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