

Product Composition for the Ozonization of Various Genetic Type Low-Metamorphized Coals in Chloroform Medium

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Abstract

An effect of the ozonization in chloroform medium on the change in chemical composition of solid fossil fuels of various genetic type with the petrographic composition corresponding to lignite maturity stage has been studied. It is established, that the character of the ozonolytic transformations of organic matter, the yield and componental composition of the products of coal ozonization are determined by the features of their structural organization. It is demonstrated that using the technique of liquid-phase ozonization in chloroform the organic substance of solid fossil fuels could be transformed into soluble products with the yield higher than 90 %. A maximal reactivity with respect to ozone is exhibited by the organic matter of sapromixite coal. With the H/C atomic ratio decrease in coals one can observe an increase in the fraction of dicarbinic aromatic acids in the composition of water-soluble ozonization products.

Key words: liquid-phase ozonization, coals of various genetic type

INTRODUCTION

For the last decades a great deal of data has been gathered concerning the obtaining of benzene-carbonic acids (BCA) from coals and the products of their processing (carbonized residues, coal pitch fractions, humic acids) [1–5]. The analysis of the literature data shows that three methods of oxidation can be, as a matter of principle, used for the industrial production: the oxidation via sodium hypochlorite at atmospheric pressure, the treatment by 33 % nitric acid at the temperature of 170 °C at its own vapour pressure, as well as the oxidation by molecular oxygen in an alkaline aqueous solution under pressure.

Other methods (the oxidation by hydrogen peroxide, potassium permanganate, manganese acetate, sulphuric acid, electrochemical oxidation in aqueous solutions of acids, salts and alkalis in the presence of catalysts [4, 5]) have found no practical application and were used, mainly, for studying the molecular structure

and the oxidation mechanism for coals under laboratory conditions.

An optimum choice of raw material is of important value for the obtaining of benzene-carbonic acids. For example, it was reported [6] that the oxidation of liptobiolite coal by air in alkaline aqueous media results in the obtaining of BCA with 70 % yield related to the sum of soluble acids. The oxidation of brown vitrinite (dense) coals results in a rather low yield of BCA, however with increasing the fraction of fusainized components in their composition (for example, in the composition of sooty weathered coals) the yield of the acids considerably increases [7].

One of the oxidation methods those have found no industrial application for the manufacture of organic acids, but actively used in order to study structural features of coals, is ozonization. So, for example, as it was demonstrated in the works [8, 9] devoted to the ozonization of weathered and non-weathered brown coals in chloroform, the composition of water-soluble products is presented mainly by

the multibasic BCA. Basing on these data a conclusion was made that BCA are formed from polysubstituted benzene or low-condensed aromatic structures. The authors of the papers [10, 11] devoted to the ozonization of combustible shale in glacial acetic acid, basing on the analysis of oxidation products composition (*n*-monocarboxylic and *n*-dicarboxylic acids, lactonic acids and methoxy acids) conclude that there is mainly saturated character of their structure, whose parts being connected with multiple carbon-carbon and ester bonds. Properly sapropelic coals (such as balkhashite) are considered by the authors to be naturally occurring saturated compounds of cyclic non-aromatic nature.

The generalization of literature data concerning the ozonization of coals is connected with some difficulties caused both by an experimental technique (different solvents, various ozone concentrations, process duration, the methods used for the separation acids, *etc.*), and the use of fossil fuels with different genesis conditions, petrographic composition and reduction level.

Alongside with valuable power-station coals and coking coals, there are available resources of low-grade low-metamorphized humus brown

and sapromixite coals in the Kuznetsk coal basin. Low prices for this fossil raw material connected with a low energy value of brown coals as well as with a high ash level and an insufficient level of knowledge about the composition and properties of sapromixite coals determine the expediency of searching the methods and technologies for their complex processing to yield more expensive chemical products. In this connection the complex studies concerning the ozonization of these solid fossil fuels (SFF) with close similar chemical maturity stages and different petrographic composition, aimed at obtaining data on the possibility of producing oxygen-containing organic products and, in particular, BCA are considered to be of urgent value.

EXPERIMENTAL

As the subject of inquiry we used Kuznetsk humus brown coals of the Barandat deposit such as non-weathered and naturally oxidized sooty samples representing natural concentrates of the microcomponents of vitrinite (Vt) and inertinite (I) groups, respectively, as well as

TABLE 1

Characteristics of coals and of the ozonization products

Sample, product	Elemental			H/C	O/C	Functional			Mass fraction, % for daf
	composition, % for daf					composition, mg-eq/g			
	C	H	O + N + S			COOH	OH	CO	
Brown sooty coal									
Initial coal	64.4	2.8	32.8	0.52	0.35	4.44	1.52	3.28	–
WS	52.1	2.3	45.7	0.53	0.66	7.32	1.47	5.05	65.8
WIS	60.5	3.2	36.3	0.63	0.45	4.54	1.60	4.79	23.7
Residual coal	64.4	2.6	33.0	0.48	0.36	3.78	2.55	5.32	11.5
Brown coal									
Initial coal	69.4	4.6	26.0	0.79	0.25	1.19	3.83	1.52	–
WS	52.0	3.7	44.3	0.85	0.64	8.06	–	7.31	33.7
WIS	57.4	4.0	38.6	0.83	0.50	5.04	–	4.95	53.2
Residual coal	62.7	3.4	33.9	0.65	0.38	2.64	0.66	4.32	5.4
Sapromixite coal									
Initial coal	82.7	7.2	10.1	1.04	0.07	0.05	0.36	1.24	–
WS	41.9	4.1	54.0	1.17	0.97	8.29	1.03	8.97	15.5
WIS	62.1	5.2	32.7	1.00	0.39	3.28	1.34	4.53	78.5
Residual coal	61.8	5.8	32.4	1.13	0.37	2.47	3.46	4.11	10.7

Note. WS – water-soluble product, WIS – water-insoluble product.

the Barzas sapromixite coal of a lignite maturity stage as a concentrate of liptinite (L). The content of the macerals belonging to Vt, I and L groups in the samples amounted to ~90 %. In order to exclude the influence of mineral impurity, the coal samples chosen were successively treated with the solutions of 10 % hydrochloric acid and 3 % hydrofluoric acid (ash level ranging within 1–7 %) [12]. The samples demineralised were further extracted with chloroform in order to remove bitumenoids. The characteristics of coal samples are presented in Table 1.

The ozonization of samples (0–0.063 mm fraction) was carried out in chloroform medium within a rotating temperature-controlled reactor at 20 °C. The flow rate of the ozone-oxygen mixture amounted to 160 mL/min, the concentration of ozone being at 1–1.5 vol. %. The duration of ozonization (5 h) was determined basing on data concerning the maximal formation rate value for oxygen-containing products in organic matter (OM) and extracted substances. The amount of ozone at the inlet and outlet of the reactor was determined using a volumetric method [13] for periodically sampled gas.

After the process completed, coal was separated from soluble products and washed out with acetone till obtaining colourless solvent coloration. The solvents were distilled out of soluble products to yield the volume about 20 mL, then 100 mL of distilled water was added and the mixture was boiled using a water bath during 5 h for the decomposition of ozonides (intermediate products from ozone interaction of with polyaromatic fragments of OM of coals, transferred into the solution). The mix-

ture of the products was separated using centrifugation to yield water-soluble (WS) and water-insoluble (WIS) substances. Residual coal was subjected to repeated ozonization.

For the characterization of samples the data of elemental analysis, chemical functional analysis, IR spectroscopy, thermogravimetry and chromatography-mass spectrometry were used.

The content of oxygen in the «reactive» form was determined *via* the summation of its amount in the form of phenol, carbonyl and carboxyl groups, that in the “non-reactive” form being determined from the difference. The amount of the carbonyl oxygen-containing groups was determined basing on the reaction with hydroxylamine hydrochloride. The amount of the carboxyl groups was determined via an acetate method, the sum of carboxyl and hydroxyl groups was determined using ion exchange with sodium hydroxide [14].

Diffuse reflection IR spectra were registered using a Tensor-27 spectrometer (Bruker, Germany). The thermogravimetric analysis was performed by STA 409 thermo analyzer (Netzsch, Germany), sample mass being of 10–20 mg, heating up to 600 °C with the heating rate of 10 °C/min in the environment of helium. The chromatography/mass spectrometry analysis was carried out with the help of a 19091S-433 device (Agilent, the USA) within the range of 15–500 a.m.u.; an HP-5MS capillary column (5 % of diphenyl siloxane–95 % of dimethylsiloxane, 30 m × 0.25 mm × 0.25 µm); helium being used as the carrier gas. The products chromatographed were preliminary methylated using diazomethane in diethyl ether [15].

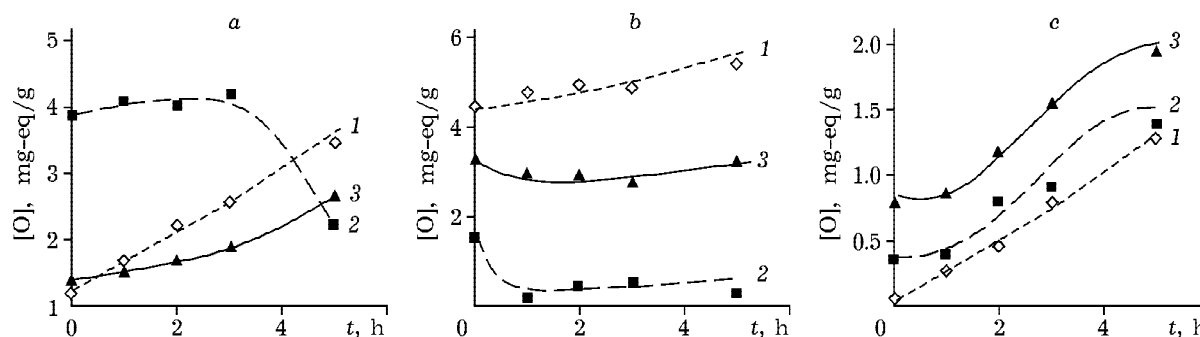


Fig. 1. Accumulation dynamics for oxygen-containing groups under ozonization in chloroform media: brown sooty coal (a), non-weathered coals (b) and Barzas sapromixite coal (c); 1–3 – carboxylic, hydroxyl and carbonyl groups, respectively.

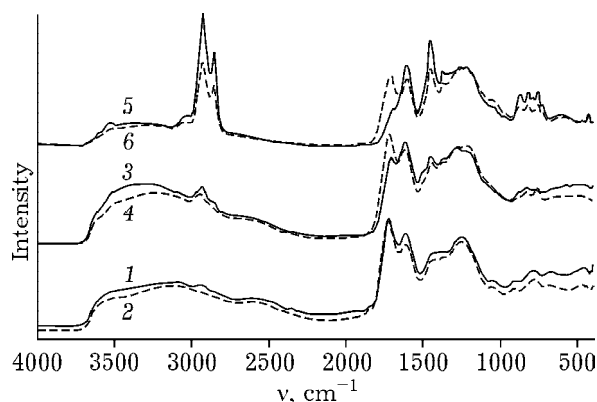


Fig. 2. IR spectra for initial coals (1, 3, 5) and for coals ozonized in chloroform media (2, 4, 6): brown sooty coal (1, 2), non-weathered coal (3, 4) and sapromixite coal (5, 6).

RESULTS AND DISCUSSION

According to the results of functional analysis (Fig. 1) and IR spectroscopy (Fig. 2), the maximal changes in the content of various type oxygen-containing groups due to the ozonization are inherent in the samples of non-weathered brown coal and sapromixite coal. These changes represent an increase in the contribution of carboxyl (1700 cm^{-1}) and carbonyl (1760 cm^{-1}) groups against the background of the decrease in the content of phenolic hydroxyl groups. This fact could be caused by a steric availability of the most ozone-reactive groups and chemical bonds in OM ($\text{C}=\text{C}$ bonds of aromatic cycles, OH groups of phenols and the bonds of aliphatic substituents such as $\text{C}_{\text{Ar}}-\text{C}_{\text{Al}}$) [16]), which is indicated by a decrease in the intensity of the absorption bands at 3040 , 1600 , $780\text{--}870\text{ cm}^{-1}$ (absorption of $\text{C}=\text{C}$ and $\text{C}_{\text{Ar}}-\text{H}$ bonds), 3550 , 1275 cm^{-1} (OH bond absorption) and 2920 , 2850 , 1460 , 1380 cm^{-1} ($\text{C}_{\text{Al}}-\text{H}_x$ absorption). The changes of functional composition for sooty brown coal saturated with oxygen groups under the conditions of hypergenesis (weathering), are less considerable (see Figs. 1, 2) since the accumulation of new O groups, to all appearance, can be compensated by an oxidative destruction of the O groups those are already contained in the OM.

During five cycles of ozonization (25 h) the amount ranging from 87 to 94 % of coal OM was transformed into the soluble state with the highest total yield of products for the Barzas sapromixite coal (see Table 1). Similar results were obtained for the ozonization of vitrinite

fat coal demonstrated a higher reactivity with respect to ozone in comparison with more or less metamorphized humus coals [17]. To all appearance, the features of sapromixite coal genesis have caused the formation of macromolecules with such a structure that is formed in humus coals as an intermediate stage of metamorphism reached (a decrease in the amount of peripheral O groups, cyclization of aliphatic chains, formation of hydroaromatic fragments). This fact caused these genetically different coals to exhibit the same reaction properties with respect to ozone.

In the case of brown coals the maximal yield of target ozonization products is inherent in naturally oxidized sooty sample (see Table 1). To all appearance, in this case the factors of crucial importance are not so much the conditions of ozonization, as the influence of the subsequent acetone extraction of oxygen-containing substances insoluble in chloroform. In this case alongside with the products of ozonization a simultaneous "cleansing" of the surface of coal particles from coal weathering products (the yield of the acetone extract with respect to initial coal amounting to 8 %), which results in a quantitative increase in the yield of extracted substances at each stage of ozonization.

The composition and amount of ozonization products also depend on structural features of coals under investigation. So, the contribution of relatively low-molecular WS products calculated as the ratio of the yield of the fraction under consideration to the total yield of

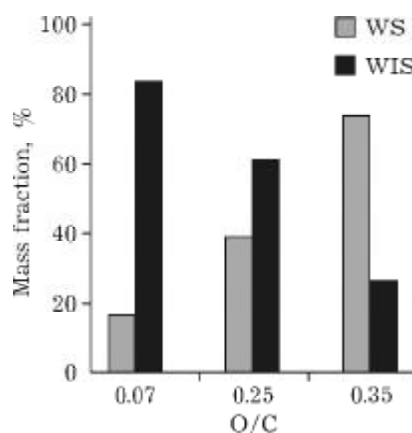


Fig. 3. Fraction of water-soluble (WS) and water-insoluble (WIS) substances among the products of coal ozonization in chloroform medium depending on the atomic O/C ratio.

the extract, increases as the atomic O/C ratio for coals increased, whereas the contribution of WIS substances decreases (Fig. 3). The high yield of WS compounds among the products of brown coal ozonization, to all appearance, could be caused by the release of hydrocarbons and higher acids (the products of vegetative material decomposition and the subsequent coal weathering) from the coal matrix, as well as by the presence in the coal OM of the fragments consisting of low-condensed aromatic rings substituted with linear and (or) branched aliphatic substituents. The latter represent the sources of the formation of relatively low-molecular water-soluble acids in the process of ozolytic destruction. A higher yield of WIS products in the process sapromixite coal ozonization, to all appearance, could be caused by the presence in its structure of larger macromolecular fragments, whose destruction promotes the enrichment of high-molecular WIS fraction.

The results of the ozonization products analysis (see Table 1) demonstrate that the atomic H/C ratio in them corresponds to the H/C value in initial coals that varies depending on the genetic type and the reduction level of the latter. The maximal H/C value is inherent in the products of sapromixite coal ozonization, whereas the minimal one is observed for the products of sooty brown coal ozonization. The ozonization products of brown coals are characterized by close values of the O/C ratio, whereas for the WS products of sapromixite coal this value is much higher, which indicates the prevalence of lower fatty acids in their composition.

The functional composition of WS and WIS products is presented mainly by carboxylic and carbonyl groups (see Table 1). The insignificant amount of hydroxyl groups within products is, to all appearance, connected with a high reactivity of OH groups [16] in the structure of coal OM.

The shape of thermogravimetric curves for the mass loss rate (DTG) indicates the composition of WS substances to be homogeneous (Fig. 4, a). This assumption is confirmed by the occurrence of narrow maxima within the temperature range of 170–180 °C corresponding to the decomposition of compounds (most likely, aliphatic ones) containing thermally unstable carboxylic groups. The shift of the main decay maximum towards a high-temperature region as

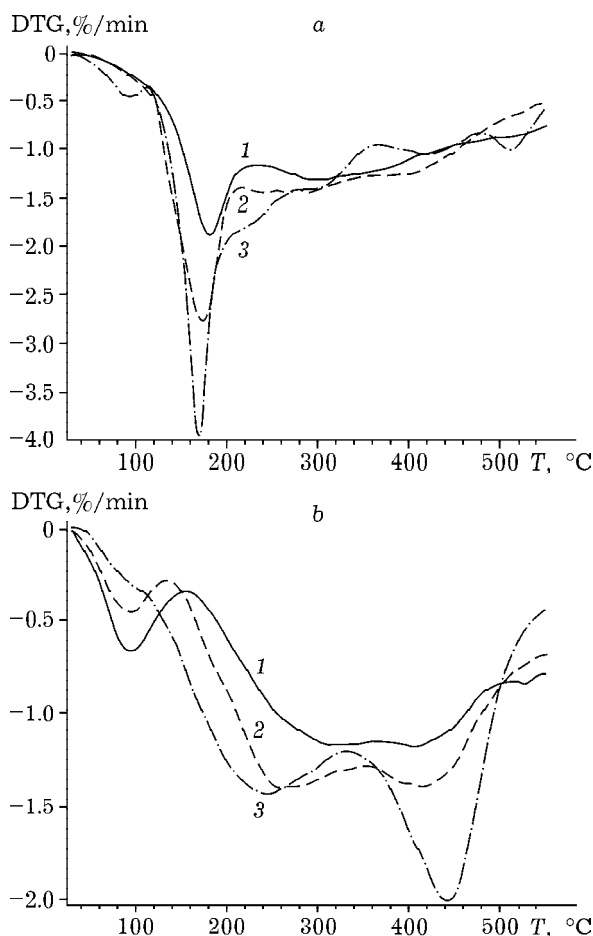


Fig. 4. Temperature dependences of the mass loss rate (DTG) for water-soluble (a) and water-insoluble (b) products of coal ozonization in chloroform medium: 1 - brown sooty coal, 2 - brown non-weathered coal, 3 - Barzas sapromixite coal.

well as the reduction of its intensity for brown coals indicates a relative increase in the contribution of aromatic acids to their composition.

The thermal destruction of WIS products (see Fig. 4, b) proceeds at the least through two stages. The first peak within the temperature range of 170–350 °C, to all appearance, is connected with the destruction of oxygen-containing compounds with various thermal stability values, whereas the second peak (ranging within 380–500 °C) is considered to coincide with the region of intense OM decomposition for corresponding coals. At the same time a lower intensity and elongation of the DTG maxima profiles indicate the complexity and heterogeneity of the composition of the substances those compose the WIS fraction of compounds decaying within close temperature ranges.

TABLE 2

Componental composition of water-soluble products resulted from the ozonization of coals

Type of compound	Relative content of components, % from overall chromatographed:		
	Brown	Brown	Sapromixite
	sooty coal	coal	coal
Methyl esters of fatty acids C ₁₈	7.4	2.7	1.9
Dimethyl esters:			
of fatty acids C ₆ –C ₁₂	6.9	15.1	49.0
of phthalic acid	12.9	5.9	4.9
Methyl esters of steroid acids	3.7	4.0	4.4
Dibutylphthalate	9.7	8.0	6.5
Ethylhexylphthalate	54.4	50.3	33.3
Unsaturated hydrocarbons C ₂₃	5.0	14.0	–

TABLE 3

Componental composition of water-insoluble products resulted from the ozonization of coals

Type of compound	Relative content of components, % from overall chromatographed:		
	Brown	Brown	Sapromixite
	sooty coal	coal	coal
Methyl esters of fatty acids C ₁₆ , C ₁₈	3.6	–	1.5
Dimethyl esters of fatty acids C ₆ –C ₁₂	–	0.8	–
Methyl esters of steroid acids	1.8	9.5	9.6
Dialkylphthalates	43.5	4.1	3.8
Oxyaromatic hydrocarbons	12.3	15.8	4.1
Oxoaromatic hydrocarbons	7.7	6.2	3.0
Hydroxyaromatic hydrocarbons	2.0	–	0.5
Aliphatic hydrocarbons C ₂₀ –C ₃₀	21.2	44.5	63.7
Cycloalkanes	–	0.7	1.7
Aromatic hydrocarbons	1.5	10.9	9.9
Hydroaromatic hydrocarbons	–	3.2	1.5
Unsaturated hydrocarbons	3.0	0.7	–
Nitrogen-containing aromatic hydrocarbons	3.4	3.6	3.7

Using the method of gas chromatography/mass spectrometry, we have identified monocarbonic (C₁₈) and dicarbonic (C₆–C₁₂) fatty acids, steroid (hydrophenantren carbonic) acids, as well as the isomers of phthalic acid among WS products of SFF ozonization (Table 2). The products of brown coal ozonization alongside with oxygen-containing compounds contain a significant enough amount (5–15 %) of long-chained alkenes belonging to carotinoids, the structural fragments composing phytoogenous substances.

As the atomic ratio H/C for coals increased, a relative content of aliphatic acids among the liquid products isolated from the coals, whereas the contribution of aromatic acids decreases. In this case the maximum amount of aromatic dicarbonic acids (80 %) corresponds to sooty brown coal, which is in a good agreement with the concepts about a more aromatized structure of weathered fossil fuels [7].

The composition of relatively high-molecular WIS products is notable for a great variety

(Table 3). The content of acids in these products is insignificant, except for sooty coal products where the fraction of aromatic acids amounts to ~45 %. Among the products of the Barzas sapromixite coal, steroid acids are prevailing species, which adds a considerable support for the hypothesis concerning the presence of cyclohydroaromatic fragments in its structure [18, 19]. Among oxygen-containing compounds, oxo, oxy and hydroxy compounds of aromatic and hydroaromatic nature have been identified, too. A significant contribution to WIS products is presented by long-chained alkanes (C_{20} – C_{30}) whose content neatly increases (from 20 up to 60 %) within the series of sooty brown coal–sapromixite coal.

CONCLUSIONS

It is established that as the result of ozonization in chloroform medium the organic matter of fossil fuels can be transformed with the yield higher than 90 % into the products soluble in polar organic solvents. Taking into account the staged nature of the process and the selective character of ozonization, the composition of low-molecular products resulted from ozonolytic coal destruction could be used for reliably judging the structure of the macromolecular fragments of coal matter authentically.

So, the presence of the proportional amount of dicarboxylic saturated and aromatic acids, as well as steroid acids and long-chain alkanes among the products of sapromixite coal ozonization suggests that the main contribution to the structure of the Barzas sapromixite coal is determined by the fragments with aliphatic and cyclohydroaromatic ring structure.

The most part of the ozonization products of humus brown coal is presented by aromatic dicarboxylic acids whose contribution increases with the increase in the coal weathering level. The absence of multibasic benzenedicarboxylic acids among the products indicates the prevalence

of low-substituted aromatic units with a low condensation level in the structure of the brown coals under investigation.

Owing to such properties as homogeneous composition and high yield (~80 %) of water-soluble compounds under ozonization exhibited by sooty brown coal, the weathered coals from overburden layers could be used as raw material for the obtaining of dibasic benzenedicarboxylic acids.

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