Composition of Products of Gas-Phase Ozonization of Low-Rank Coals of Various Genesis and Petrographic Composition

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Abstract

The effect of gas-phase ozonization on variation of chemical composition of solid combustible minerals of various genetic types and petrographic composition of brown coal maturity and products of their basic hydrolysis has been investigated. It was found that directions of oxonolytic transformations of organic matter as well as the yield and componental composition of products of alkaline extraction of coals are governed by features of their molecular organization. Reactivity of combustible minerals in relation to ozone increases with an increase in the H/C atomic ratio.

Keywords: gas-phase ozonization, low-rank coals, petrographic composition, composition of ozonization products

INTRODUCTION

Oxidizing processing of mineral coal is one of promising directions in the field of its "non-fuel" use [1]. Of special interest are selective ways of the oxidation that make it possible to increase the content of particular functional oxygen-containing groups and to enhance physicochemical properties and reactivity of coal in various processes. To take an example, saturation of organic matter of coals by quinoid groups exerts a favourable action upon the hydrogenation process [2]; coals with a higher than usual content of phenolic hydroxyls find application in production of composites with high-molecular compounds [3]; an increase of carboxylic groups in the composition of low-rank coals makes for an enhanced yield of products that are soluble in alkaline solutions [4].

Ozonization is favourably distinguished among a number of various oxidation methods (by hydrogen peroxide, by nitric acid, by oxygen in a gas phase, and under the alkaline condition under elevated pressure) [4–6]. It is characterized by high speeds and selectivity of the reactions [7] under relatively mild conditions of carrying out the process (ambient temperature, atmospheric pressure) as well as by simplicity of technological implementation and by ecological compatibility.

The direction of oxidizing reactions is governed to a considerable extent by genetic type, metamorphic degree, and petrographic composition of solid combustible minerals (SCM) [4–6]. It has been found that the nature of basic reactions of ozone with organic mass of coals (coal organic matter) varies also depending on the transformation of molecular structure of mineral coals in the metamorphism series [8, 9]. Accordingly, while low-rank vitrinite coals are typified by oxidizing reactions of phenolic hydroxyls and by radical reactions of ozone with alkyl substituents of benzene rings, an increased metamorphic degree of coals makes for the contribution of reactions of electrophilic addition of ozone to π-bonds of condensed aromatic structures.

Comparative estimation of the influence of SCM nature and petrographic composition on reactions of oxonolytic transformation of or-

ganic matter of low-rank coals has not been performed until now. Available in the literature though are communications on an increase of conversion degree (by 1.5 times) and the yield of distillate products (by 3 times) during catalytic hydrogenation after ozonization of brown coal from Kansk-Achinsk basin [10]. Preliminary ozonization of Barzas sapromixite coal also made for an increase of conversion degree in a low-temperature region by 2-4 times during its thermal dissolving in tetralin and for a decrease of the proportion of asphaltenes in liquid products by 2 times [11].

The purpose of the given research is to reveal the features of gas-phase ozonization of combustible minerals of different genetic types and petrographic nature of a brown coal stage of its chemical maturity and to study the composition and the properties of products that were extracted by an alkali.

EXPERIMENTAL

Kuznetsk humic brown coals from Barandat deposit, namely, a not effloresced and a naturally oxidized sooty sample that represent the natural concentrates of microcomponents of vitrinite (Vt) and inertinite (I) groups, respectively, and Barzas sapromixite coal of a brown coal maturity as a concentrate of liptinite (L) have been selected as the subjects of the investigation. The content of groups Vt, I, and L in the samples of macerals comprises ~90 %. To exclude the influence of inorganic (mineral) component on the running process, the select-

ed samples of coals were consecutively treated with 10 % hydrochloric and 3 % fluoric acid solutions (the ash content of 1−7 %) [12]. Demineralised samples were next extracted by chloroform to remove bitumoids. Features of coal samples are given in Table 1.

Ozonization of samples (the fraction of 0−0.063 mm) was conducted at 25 °C in a rotating reactor that provided an intensive stirring of the reaction mixture, with a continuous feed of ozone-oxygen mixture (the volume fraction of ozone was 1−1.5 %). Ozone was obtained in a temperature-controlled laboratory ozonizer from oxygen of qualification "extra pure (os. ch.)". The quantity of ozone at the inlet and the outlet of the reactor were determined from periodically taken samples of gas by a volumetric method [13]. Ozonides, that is, intermediate products of interaction of ozone with polyaromatic fragments of coal organic matter, were destructed in the processed coal by thermal exposition at 100 °C over the course of 2 h.

Initial and ozonized samples were subjected to alkaline extraction by 1 % NaOH over the course of 1 h [12]. Upon acidifying with HCl solution, low molecular mass acids (LMA) (fulvic acids) soluble in acidic medium and extractable from water solution by methyl ethyl ketone were obtained, together with a deposit of amorphous high molecular mass acids (HMA).

Data of elemental, chemical functional analysis, IR spectroscopy, and chromatography mass spectrometry were used for characteristics of samples.

Content of an "active" form of oxygen was determined by summation of its quantity in

TABLE 1

Features of initial coals and of those ozonized over the course of 3 h

Sample	R_0, %	Elemental composition, % per daf			H/C	O/C	Functional composition, meq/g			Oxygen content of groups, % per daf	
		C	H	O + N + S			COOH	OH	CO	active	inactive
Brown	0.4	69.4/68.1	4.6/4.3	26.0/27.4	0.79/0.76	0.25/0.28	1.19/2.01	3.83/3.39	1.52/2.02	11.38/13.72	12.13/11.47
Brown sooty	0.5	64.4/64.6	2.8/2.5	32.8/32.9	0.52/0.46	0.36/0.36	4.44/4.51	1.52/1.91	3.28/3.05	20.58/21.29	9.42/9.14
Sapro-mixite	0.3	82.7/79.3	7.2/6.6	10.1/15.1	1.04/1.01	0.07/0.12	0.05/0.85	0.36/0.53	1.24/1.35	1.79/4.85	6.01/8.15

Notes. 1. The first value for the initial sample, the second for the ozonized sample. 2. R_0 is the index of reflection for vitrinite.

the form of phenolic, carbonyl, and carboxylic groups, and that of an "inactive" form was determined from the difference. Quantity of carbonyl oxygen-containing groups was determined by the reaction with hydroxylamine chloride, quantity of carboxylic groups was determined by the acetate method, and the sum of carboxylic and hydroxyl groups, by ion exchange with sodium hydroxide.

IR spectra of diffuse reflection were registered with a Bruker Optics TENSOR 27 FT-IR spectrometer. Chromatography mass spectrometer analysis was conducted with a 19091S-433 device (Agilent) in the region of 15–500 amu using a HP-5MS capillary column (5 % diphenyl–95 % dimethylsiloxane), 30 m × 0.25 mm × 0.25 μm; the carrier gas was helium. The products for chromatography were previously methylated by diazomethane in ethyl oxide.

RESULTS AND DISCUSSION

Shown in Fig. 1 are curves of changing content of unreacted ozone in a gas mixture at the outlet from a reactor versus the duration of ozonization. Pattern of the received curves is suggestive of at least two stages of the process passing, namely, a fast one (at the initial stage) and a slow one. A decreased speed of the process with an increase in the duration of ozonization is caused presumably by diffusive restraints that appear for ozone molecules by way of blocking the pore "mouths" by products of oxonolytic destruction of coal organic matter (both by low molecular mass volatile matters, and by peripheral O groups) [14] as well as by a decrease in the quantity of frag-
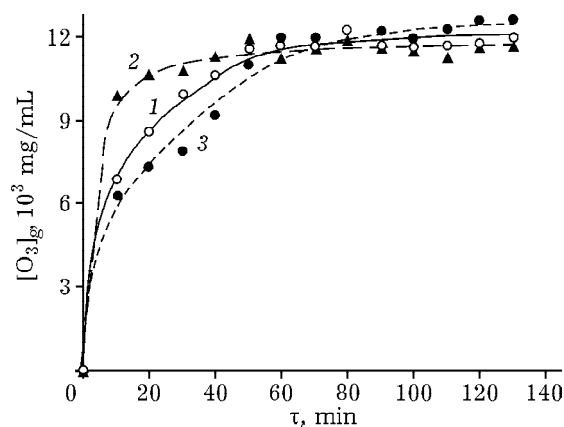

Fig. 1. Experimental curves $[O_3]_g = f(\tau)$ at the reactor outlet for brown coals: 1 – not effloresced, 2 – sooty, 3 – Barzas sapromixite.

ments of coal organic matter that are sterically accessible and reactive with respect to the interaction with ozone. The maximum initial rate of reactions of coal organic matter with ozone is observed on sooty brown coal that contains more aromatic base units by comparison to other coal samples [4], and the minimal rate is observed on Barzas sapromixite coal that has a significant amount of aliphatic fragments in its composition [15].

Maximum changes in the contents of all kinds of functional O groups in coal organic matter are fixed during the first 3 h of ozonization (Fig. 2). Not effloresced brown and sapromixite coals are typified by an increased quantity of carboxylic and carbonyl groups against the background of a decrease of phenolic hydroxyls, which may be related to a high reactivity of the last-mentioned with relation to ozone [7]. Changes in the functional composition of fusainized brown sooty coal that is sated by oxygen groups are insignificant under
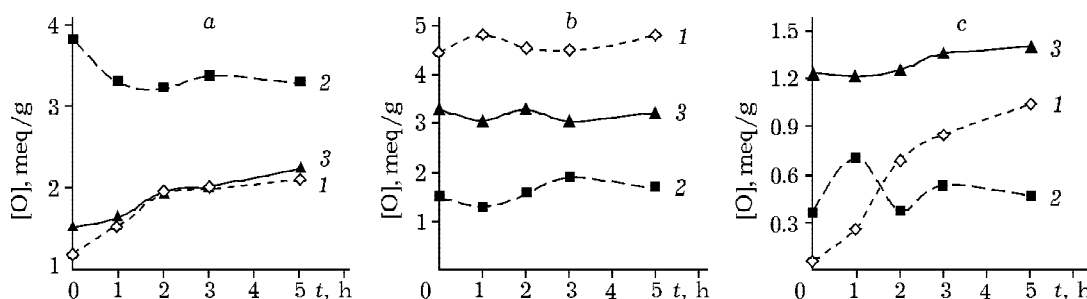

Fig. 2. Accumulation dynamics for functional oxygen-containing groups in the course of gas phase ozonization of brown coals: a – not effloresced, b – sooty, c – Barzas sapromixite; 1–3 – carboxylic, hydroxyl, carbonyl groups, respectively.
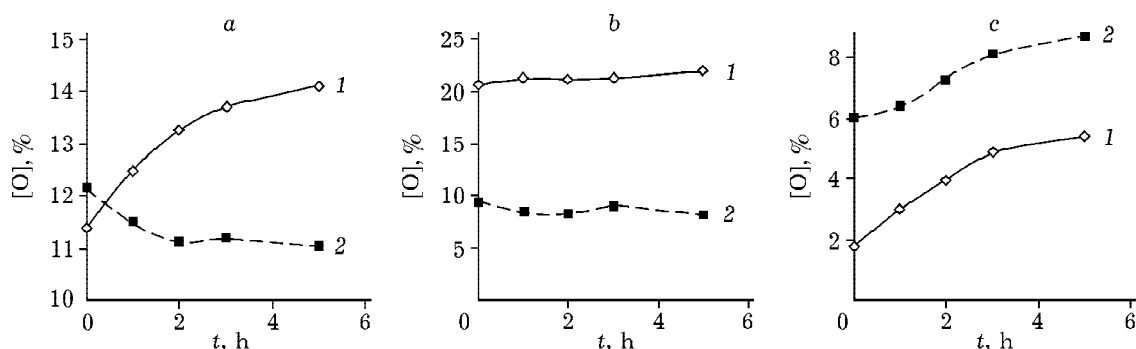
Fig. 3. Variation in the oxygen content of various forms during the gas-phase ozonization of brown coals: *a* − not effloresced, *b* − sooty, *c* − Barzas sapromixite; *1, 2* − "active" and "inactive" forms, respectively.

conditions of hypergenesis (efflorescence), because accumulation of new O groups, apparently, is balanced out by oxidation decomposition of oxygen-containing groups that are already present in the coal organic matter.

Changes in the composition of non-identified forms of oxygen (ethereal, lactone, anhydride, and other groups) are characterized by a decrease in their quantity for not effloresced brown coal, by an increase in their quantity for sapromixite coal, and they slightly show up for sooty brown coal (Fig. 3).

To make a comparative characterization of the variation in fragments of coal organic matter during its ozonization, we used IR spectral parameters in the form of the ratios of the intensities of characteristic absorption bands for aliphatic CH_x (2920 cm^{-1}), aromatic C=C (1600 cm^{-1}), carbonyl C=O (1690 cm^{-1}), and phenolic (3400 cm^{-1}) groups. Structural parameters A_{2920}/A_{1600} and A_{2920}/A_{1690} that reflect the respective proportions of aliphatic fragments in relation to aromatic and oxygen-containing groups in the composition of coal organic mat-

ter objectively rise for initial coals with an increase in their H/C atomic ratio (Fig. 4). These parameters for ozonized coals are subject to unidirectional variation: they slightly decrease for both samples of brown coals and decrease more tangibly for sapromixite coal. Tendencies of a variation in parameter A_{3400}/A_{1690} that defines a ratio of phenolic hydroxyls OH and C=O groups of carboxylic acids are analogous for the ozonized samples to variations in the previous parameters (see Fig. 4) and they are demonstration that to the contribution of carboxylic groups prevails in the coal organic matter of the ozonized samples. The maximum difference in these parameters for Barzas sapromixite coal bears witness to its deeper oxonolytic destruction by comparison to alternative coals, the deeper destruction being caused by an availability of structural fragments in coal organic matter that are sterically more accessible to ozone molecules. It appears that stability of humic brown coals in relation to ozone is associated with a relatively high content of peripheral oxygen-containing groups that either screen
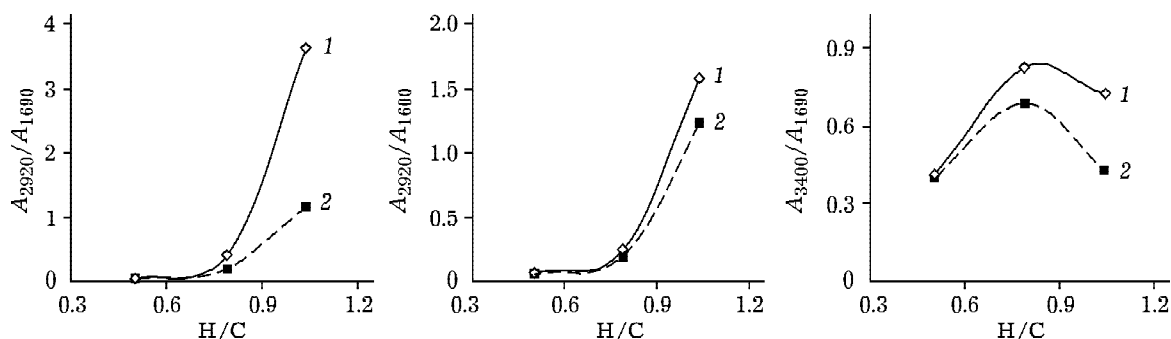

Fig. 4. Variation of IR spectral parameters for initial *(1)* and ozonized *(2)* samples of coals *vs.* the H/C atomic ratio.

TABLE 2

Characteristics of high molecular mass acids (HMA) from initial and ozonized samples of coals

Sample	Elemental composition, % per daf			H/C	O/C	Functional composition, meq/g			Oxygen content of groups, %		Yield, % per daf
	C	H	O + N			COOH	OH	CO	active	inactive	
Brown	63.1/62.4	4.4/4.3	32.5/33.3	0.84/0.83	0.39/0.40	3.57/4.23	1.50/0.56	2.04/2.53	15.45/16.46	17.07/16.84	24/30
Brown sooty	52.5/54.9	2.4/2.1	45.1/43.0	0.56/0.46	0.64/0.59	4.86/5.57	0.76/0.63	3.76/4.49	19.78/22.42	25.27/20.55	94/91
Sapro-mixite*	−/57.8	−/4.7	−/37.5	−/0.97	−/0.49	−/3.87	−/1.6	−/2.69	−/17.00	−/20.51	0/12

Note. The first value is for HMA from the initial sample, the second is for that from the ozonized sample.

*The dash means that data are not available, because no products of basic hydrolysis are being formed from the initial coal.

fragments of coal organic matter, potentially reactive with respect to ozone, or they themselves enter the interaction with ozone (to take an example, phenolic groups). This circumstance is supported by a shift of the absorption bands towards greater wavelengths, which is typically being associated with weakening of hydrogen bonds.

The yield and the composition of products of their basic hydrolysis for ozonized coals also vary (Table 2). Accordingly, HMA yield increases for not effloresced brown and sapromixite coals, and slightly decreases for sooty coal. An increase in the HMA content for the first two samples may be determined by the following oxonolytic transformations:

(i) by partial destruction of the coal organic matter and by the formation of new oxychemicals of a smaller molecular mass that can be separated by alkaline extraction;

(ii) by weakening of carbon-carbon bonds in the coal organic matter owing to their polarization during accumulation of oxygen-containing groups of acidic nature.

It seems likely that ozone action on organic matter of sooty brown coal that has been enriched by peripheral oxygen-containing groups of acidic nature brings about the development of their oxidation decomposition and the formation of intermolecular and interfragmentary cross-links and, consequently, an insignificant decrease of the yield of HMA.

Composition of HMA from brown coal (see Table 2) varies after their ozonization in much the same manner as in the corresponding coals. However, these changes are more significant

for the effloresced sample (see Table 1), which is related apparently to the effect of oxidative-hydrolytic processes that occur under conditions of basic hydrolysis [4].

IR spectra of LMA and HMA of all samples (Fig. 5) contain typical absorption bands intrinsic to OH groups of phenols and carboxylic acids (to those free ($3200-3400$ cm^{-1}) and to those linked by H-bond ($2500-2700$ cm^{-1})); to C=O groups of aromatic, aliphatic acids, of ketones and anhydrides ($1650-1800$ cm^{-1}); to C−O groups of alcohols, phenols, and ethers ($1100-1300$ cm^{-1}). The detailed absorption bands show a greater resolution in spectra of LMA (see Fig. 5) that undergo the greatest transformations as a result of oxonolysis of coals. In so doing, tendencies that are intrinsic to transformations of coal organic matter (a decreased proportion of phenolic hydroxyls (3400 cm^{-1}), aryl (1600,
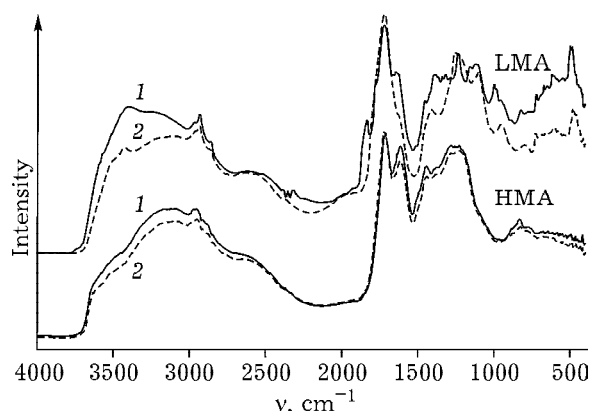

Fig. 5. IR spectra of LMA and HMA from the initial *(1)* and the ozonized *(2)* brown not effloresced coal.

$700-900$ cm^{-1}) groups, and methyl (1380 cm^{-1}) groups) are preserved in IR spectra of products.

Low molecular mass products of basic hydrolysis of coals, soluble in acidic medium (fulvic acids) have been examined by chromatography mass spectrometry method. Mass fraction of di- (C_3-C_5) and tricarboxylic aliphatic acids amounts to ~43 % as a constituent of fulvic acids of the initial, not effloresced brown coal. Aromatic acids are represented by mono- (13 %) and dicarboxylic (30 %) acids. Minor amounts of benzene hydrocarbons (3.5 %), of linear and branched aliphatic (6.1 %) hydrocarbons have been detected together with hydroxy- (2.2 %) and amino-containing (2.0 %) structures that constitute the disintegration products of carbohydrates and amino acids.

After ozonization of brown coal, the proportion of long chain aliphatic and unsaturated hydrocarbons of composition $C_{17}-C_{29}$ in LMA grows considerably (up to 18 and 28 %, respectively). Meanwhile, low molecular mass dicarboxylic acids practically disappear from the composition of LMA, and the proportion of aromatic acids does not change. The availability of saturated hydrocarbons as the constituents of ozonization products of not effloresced brown coals has been reported previously [16] and it was related to their possible release from a coal matrix after a destructive oxidative attack. Unsaturated hydrocarbons that appear depending on the location of a double bond (at the periphery or at the centre of a chain) are possibly caused by the effect of both destructive and secondary polymerisation processes that run as a result of an abstraction of alkyl structural fragments containing COOH groups.

Composition of LMAs that are isolated from effloresced brown coal is represented predominantly by phthalic acid (~75 %) and its derivatives. The remaining part of the products is composed from long chain unsaturated hydrocarbons, the availability of which may be also related to the effect of destructive actions upon coal organic matter of oxidizing efflorescence processes. After ozonization, the componental composition of LMA is practically unaffected, which is in a good agreement with the conclusions that were made previously on the stability of organic matter of sooty coal under its gas-phase modification by ozone.

The low molecular mass acids that are extracted from Barzas sapromixite coal are characterized by the greatest variety of their structural forms and classes of the compounds. Compounds of cyclic (naphtheno-hydroaromatic) nature that are abundant in them are in agreement with an average model of the macromolecule of organic matter of liptinite from Barzas coal [15]. Acids of aliphatic series are represented by mono- (palmitic, C_{16} − 13.9 %) and dicarboxylic (adipinic, C_6 − 14.7 %) acids; aromatic acids are represented by derivatives of phthalic acid (30.9 %). Oxygen-containing cyclic oxo-, oxy-, and hydroxycompounds with saturated, unsaturated, and aromatic structure (21.1 %) are present at less quantities. Nitrogen content of LMA is insignificant (3.8 %), which bears witness to a low activity of nitrogen with respect to destructive actions. This element occurs as a constituent of a complex structured compound, namely, alkyl-substituted pyrrolopyrazine. About 15 % of all substances that can be detected chromatographically belong to unsaturated hydrocarbons with linear (9.7 %) and cyclic (5.7 %) structure. These substances, that is, derivatives of cholestane classed with steroids, have a hydrocarbon skeleton of cyclopentaphenanthrenes. Both reduced and oxidized forms available are demonstration that, besides splitting of C=C bonds and the emergence of phthalic acid in LMA, reactions of ozone may also proceed without destruction of the cycle:
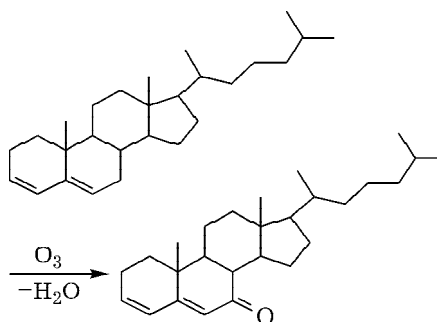
CONCLUSION

Thus it was found that the influence of oxonolytic treatment becomes more intensive with the growing H/C atomic ratio in SCM. Coals with a higher O/C ratio show an enhanced resistance to reactions with ozone in consequence

of shielding the reactive sites of coal organic matter with peripheral O groups.

Features of fragmentary composition of coal macromolecules, namely, the predominance of low-substituted aromatic units in the composition of fusainized sooty coal, the branched alkyl replacement in vitrinite brown coal, and high extent of ring formations within the structural units of liptinite sapromixite coal, could be inferred by the composition of soluble in acidic medium, low molecular mass products of basic hydrolysis that are subject to greatest transformations through oxonolysis of coals.

Relatively smaller changes in composition of multifunctional high molecular substances are obviously determined by basic oxonolytic processes that run in the near-surface layer of coal particles (in a peripheral part of coal organic matter), which is apparently related to diffusive restraints of the gas-phase version of oxidation and to an additional quantity of relatively low molecular mass products that result from the ozonization.

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