

Liquid-Phase Ozonation of Highly Metamorphized Coal

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(Received May 23, 2005; in revised form July 6, 2005)

Abstract

Dynamics of the accumulation of oxygenated groups during coal ozonation in chloroform is investigated. It is shown that the oxygen content of the organic matter of coal is determined by the availability of reaction centres for ozone molecules. High-molecular water-insoluble acids prevail among coal ozonation products.

INTRODUCTION

Ozonation of solid fossil fuel and the products of its processing: shale oil [1, 2], brown coal [3, 4], coal carbonization tar [5, 6], humic acids [7] – in different solvents is widely used to investigate the structure of the products. Up to 90 % and more of the organic mass may be successfully transformed into soluble products at rather low temperatures.

The kinetic regularities of the yield of products formed in the oxidation of shale oil kerosene depending on the amount of absorbed ozone were established [1]. Due to ozonation of the polyfunctional and humic acids, the high-molecular compounds comprising their basis are transformed into the low-molecular form [7]. Assumptions were made concerning the mechanisms of ozonation of neutral oxygen-containing fractions and pyrobitumen of coal-tar pitch; on this basis, it was proposed to use the possibilities of the method to obtain dicarboxylic fatty and aromatic acids.

Previously we investigated [8, 9] the effect of gas-phase ozonation on changes in the organic mass of coal (OMC) at different stages of metamorphism. It was shown that the treatment of coal with ozone promotes an increase in the yield of the compounds extractable with a mixture of alcohol and benzene and with py-

ridine. The fraction of low-molecular *n*-alkanes in the hydrocarbon part of extracts increases, while the fractions of di- and tricyclic condensed arenes and the degree of substitution in the aromatic rings decrease [10]. It was established that the contribution from the reactions of electrophilic addition of ozone to π -bonds of aromatic rings increases with an increase in the degree of coal metamorphism; this results in the accumulation of carboxylic and phenol groups. Because of this, highly metamorphized coal can be considered as a raw material to obtain benzenehydroxycarboxylic and polybasic acids by means of treatment with ozone.

In the gas phase, ozonation of organic compounds proceeds an order of magnitude slower than in solution [11], while the limiting factor of coal oxidation is the diffusion of oxidant molecule to the reaction surface [12], the access to which is hindered by the formed reaction products. Taking this fact into account, we may assume that ozonation in chloroform would be more efficient in comparison with the gas phase (the ozone molar concentration in it is 2.12 times higher than that in the gas phase above the solution [11]). Indeed, a comparative analysis of the dynamics of accumulation of oxygen-containing groups in OMC under ozonation in the gas phase and in chloroform (Fig. 1) demonstrated the advantages of the liquid-

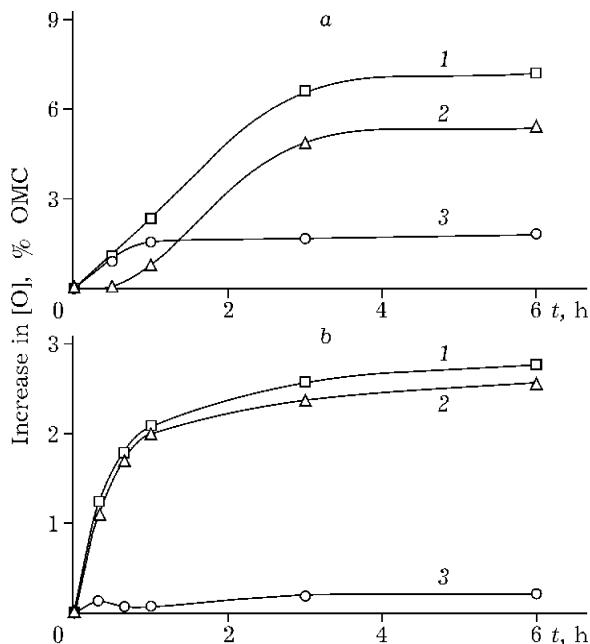


Fig. 1. Changes in the total content (1), in inactive (2) and active (3) oxygen-containing groups in the OMC under ozonation in chloroform (a) and in the gas phase (b).

phase version of process performance. Total increase in the oxygen content as a result of ozonation (6 h) in chloroform is about 2.5 times higher than in the case when the process is carried out in the gas phase. It should also be noted that in the case of liquid-phase ozonation much larger amount of oxygen is accumulated in the active form in the organic matter of carbon.

The goal of the work was to reveal the features of the process and to investigate the composition and properties of the extracts of water-soluble products of ozonation of highly metamorphized coal in chloroform.

EXPERIMENTAL

The subject of investigation was vitrinite concentrate of grade T coal from the Kuznetsk basin (vitrinite content 95–97%). Isolation was performed by layering the coal on the basis of density under the static conditions in a mixture of CCl_4 and C_6H_6 . The characteristics of the sample are, %: ash value A^d 2.0, humidity W^a 1.3, vitrinite reflection index R_0 2.56. Elemental composition, mass %: C 90.5, H 4.3, (N + S) 2.2, O 3.0.

Ozonation was carried out at 25 °C in a thermostated rotating reactor providing

intensive mixing of the reaction mixture, with continuous admission of the ozone-oxygen mixture (with the ozone content of 1.5 vol. %). Chloroform (100 ml) was used as a solvent. A weighed portion of coal (the fraction 0–0.063 mm) was 5 g. After a definite time interval (1, 3, 6 and 12 h) the process was interrupted, coal was separated from chloroform and soluble products by filtering, then washed with acetone till the colourless state of the solvent was achieved. Ozonides, intermediates of the reaction of ozone with the polyaromatic fragments of OMC, in the residual coal were destroyed by thermal exposure at 120 °C for 3 h. The solvents were distilled from soluble products till the residual volume of about 20 ml was obtained, then 100 ml of distilled water was added, and the mixture was boiled in a water bath for 5 h to decompose the ozonides that passed into the solution.

A mixture of products was separated by centrifuging into water-soluble (WS) and water-insoluble (WI) products. The former ones were sequentially subjected to exhaustive extraction with diethyl ether (ES) and *n*-butyl alcohol (BS). After distillation of the solvents and drying, the yield of ozonation products was determined.

To characterize the samples, we used IR spectroscopy, thermogravimetry, elemental and functional analysis. The IR spectra were recorded with a Fourier transform System-2000 spectrometer of Perkin Elmer Co. Thermal analysis was performed with STA 409 thermoanalyzer of Netzsch Co., sample mass was 10–20 mg, heating up to 500 °C at a rate of 10 °C/min in helium. Elemental analysis in microsamples was carried out according to the procedure described in [13]. The content of oxygen in the active form was determined on the basis of the sum of its amount in phenol, carbonyl and carboxylic groups, while its amount in the inactive form was determined on the basis of the difference. The number of carbonyl oxygen-containing groups was determined with the help of the reaction of hydroxylamine hydrochloride, carboxylic groups were determined with the acetate method, the sum of carboxylic and hydroxyl oxygen-containing groups was determined by means of ion exchange with sodium hydroxide.

RESULTS AND DISCUSSION

A maximal increase in the content of all the kinds of oxygenated groups in the organic matter of coal is observed during the first 3 h of ozonation. As the process duration increases from 6 to 12 h, the amount of active and inactive groups remains approximately equal (Fig. 2). A maximum at the curve of accumulation of phenol groups is observed at 3 h. The maximal amount of carboxylic and carbonyl groups is accumulated in the OMC after 5 and 12 h of ozonation, respectively. Taking into account the obtained dependencies of accumulation of oxygen-containing groups, we may distinguish the following directions of OMC transformation under ozonation:

1. The interaction of ozone with polycyclic OMC fragments which are present in increased concentrations in highly metamorphized coal. An increase in the content of carboxylic groups can be due to the destruction of the benzene ring through the stage of ozonide formation, phenol groups may appear in the reactions of ozone with condensed aromatic structures of OMC without the destruction of cycles, while carbonyl groups are formed in the oxidation of

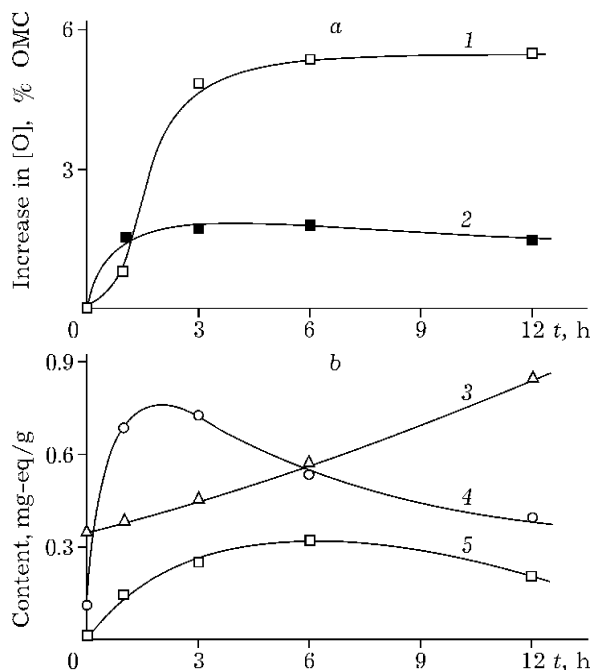
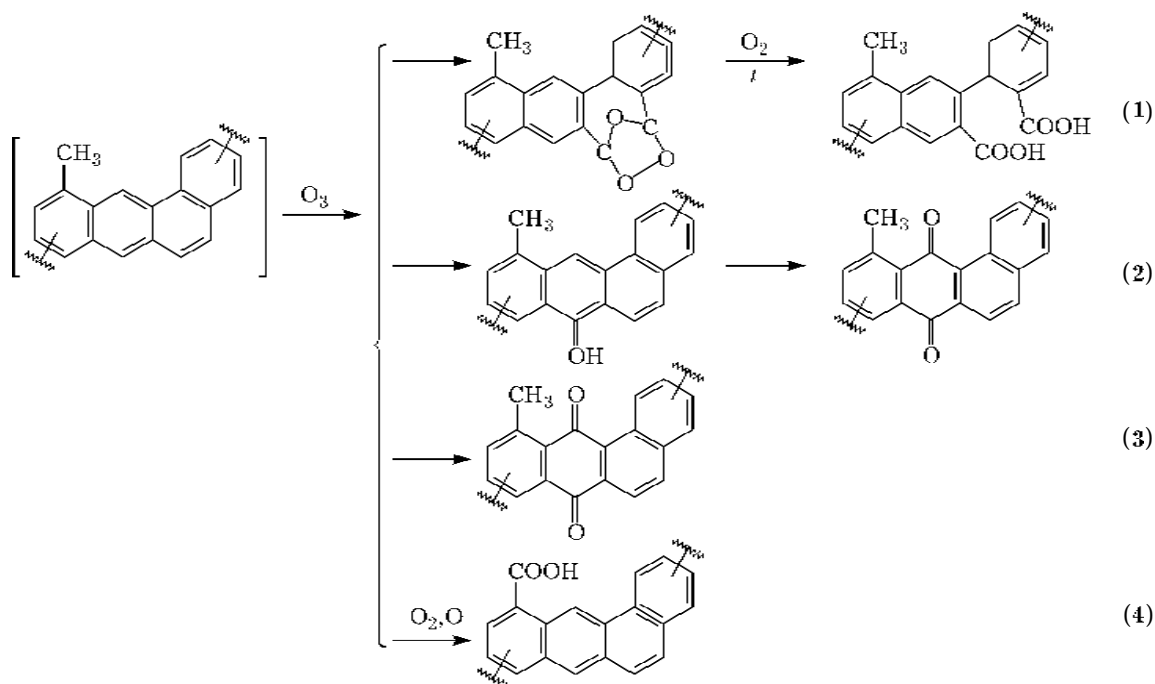


Fig. 2. Increase in oxygen content in the inactive (1) and active (2) forms (a) and changes in the amount of carbonyl (3), phenol (4), carboxylic (5) groups in the OMC during ozonation (b).

anthracene fragments to anthraquinone ones (Scheme (1)).

2. Radical oxidation of the aliphatic fragments of the OMC by atomic and molecular



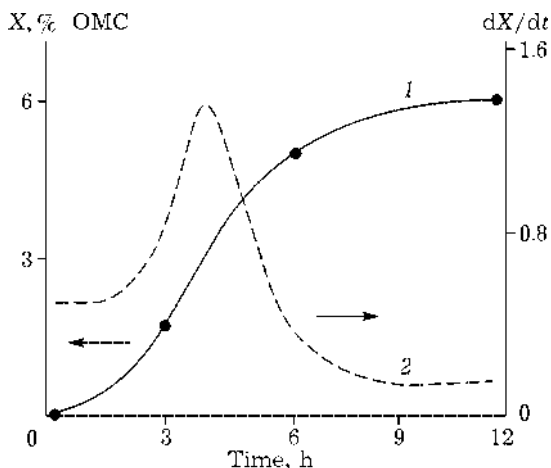


Fig. 3. Total amount (X) of extractable substances (1) and the rate (dX/dt) of their formation (2) depending on ozonation time.

oxygen, resulting in an increase in the number of carboxylic groups. However, these reactions are secondary as a consequence of relatively low content of aliphatic fragments in highly metamorphized coal, as well as due to the high rate constants of the interaction of ozone ($k = 10^2 - 10^3 \text{ l}/(\text{mol s})$) with polynuclear aromatic compounds [14].

The results of extraction of WS compounds isolated from the ozone-treated coal as shown in Fig. 3. The appearance of the curve of the rate of formation of extractable provides evidence of the heterogeneous character of ozonation, that is, ozone affects only the external surface of coal particles, and the process itself is limited by the availability of the reaction surface for ozone molecules. The maximal rate of formation of soluble compounds is observed for the process duration equal to 4 h. As ozonation time increases, the rate of the process decreases; after 8 h it remains almost constant (see Fig. 3). Since long-term ozonation causes the secondary oxidative destruction of the functional groups formed on the surface of a coal particle, the yield of soluble products does not increase. To avoid these phenomena, it may be recommended to use a stepwise ozonation with periodic removal of soluble reaction products by extraction with a polar solvent.

The maximal fraction of WI products in the extract, and correspondingly the minimal fraction of WS and BS compounds correspond to ozonation for 6 h (Fig. 4). The fraction of ES

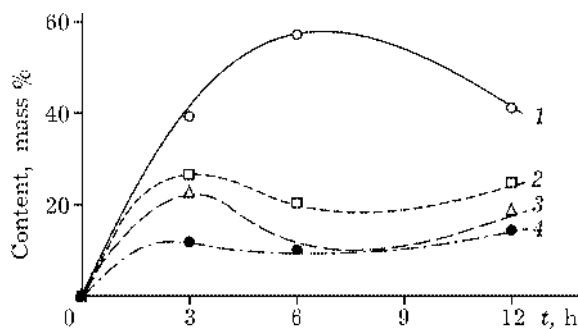


Fig. 4. Fraction of WI (1), BS (2), WS (3) and ES (4) compounds in the extract depending on ozonation time.

compounds changes only slightly during the whole process. Subsequent decrease in the fraction of WI compounds in the extract is an evidence of the start of destruction of high-molecular polyfunctional products to form the compounds with smaller molecular mass (soluble in water, ether and butanol).

According to the data of elemental and functional analyses, the oxygen-richer products are those remaining in the aqueous solution after extraction with ether and with the alcohol (Table 1). These products may include low-molecular aliphatic carboxylic acids: oxalic, acetic, formic, *etc.* Water-insoluble compounds are characterized by the minimal amount of hydrogen and the minimal H/C ratio, which may be the evidence of predominance of carboxylic acids of the aromatic series. The amount of carboxylic groups in all the soluble products is 2.5–3.5 times larger than the amount of phenol groups (see Table 1).

The most intensive absorption bands in the IR spectra of all the fractions under investigation (Fig. 5) are those related to oxygen-containing groups: for example, the bands in the region of $3100 - 3500 \text{ cm}^{-1}$ relate to the vibrations of OH groups in phenol compounds and in carboxylic acids participating in the formation of hydrogen bonds; the bands within the range $2500 - 2700 \text{ cm}^{-1}$ correspond to the stretching vibrations of OH groups bound with stronger intramolecular bonds. The absorption bands within the range $1610 - 1780 \text{ cm}^{-1}$ correspond to -C=O groups of aromatic, aliphatic acids, esters and lactones. Within the range $1100 - 1300 \text{ cm}^{-1}$, a broad band with a maximum at 1260 cm^{-1} corresponds to the in-plane

TABLE 1

Composition of the products of coal ozonation (ozonation time: 6 h)

Products	Elemental composition, % per OMC			H/C	O/C	Functional composition, mg-eq/g		Yield, % OMC*
	C	H	O			COOH	OH	
Water-insoluble	62.9	3.0	34.1	0.57	0.41	4.47	1.70	2.9
Ether-soluble	65.7	5.5	28.8	1.00	0.33	4.48	1.80	0.5
Butanol-soluble	63.6	5.6	30.8	1.06	0.36	4.94	1.28	0.9
Water-soluble	44.4	3.4	52.2	0.92	0.88	7.34	2.13	0.4
Residual coal	84.6	4.0	9.2	0.57	0.08	0.33	0.53	98.5

*Calculation was carried out per the initial (before ozonation) organic mass of carbon.

deformation vibrations of OH groups and the stretching vibrations of C–O groups of alcohols and phenols.

Relatively low intensity of absorption bands of CH-aromatic groups at 3040 cm^{-1} , in combination with rather clearly exhibited absorption of C=C bonds at 1600 cm^{-1} , as well as the appearance of the absorption curve in the region $810\text{--}750\text{ cm}^{-1}$ in the spectra of BS and WI fractions point to the high degree of substitution of aromatic rings in benzenecarboxylic acids. The presence of aliphatic compounds in characteristic of BS and ES fractions, as evidenced by the high intensity of the absorption bands of CH_2 groups at 2920 and 1440 cm^{-1} .

Since thermal decomposition of organic compounds are to a large extent determined by the content and forms of oxygen present in them, the results of thermogravimetric analysis may give reasons to consider the features of the composition of ozonation products. The appearance of temperature dependencies of mass loss curves provides evidence of the differences in

the stability of oxygenated groups incorporated into the extracted products (Fig. 6). Water-soluble products, represented by the largest number of carboxylic groups (see Table 1), decompose within the low-temperature region with a maximum at $165\text{ }^\circ\text{C}$ [15]. The decomposition of ES compounds proceeds in several stages with the maxima at 165 , 200 and $295\text{ }^\circ\text{C}$. Such a character of the DTG curve points to the presence of the compounds of more diverse composition in the ether extract than in the BS fraction. For WI and BS products, the mass loss curves of low intensity stretched over the whole temperature range are characteristic, as well as the absence of clearly exhibited extreme points, which is the evidence of the high-molecular polyfunctional character of the fragments with close regions of thermal decomposition.

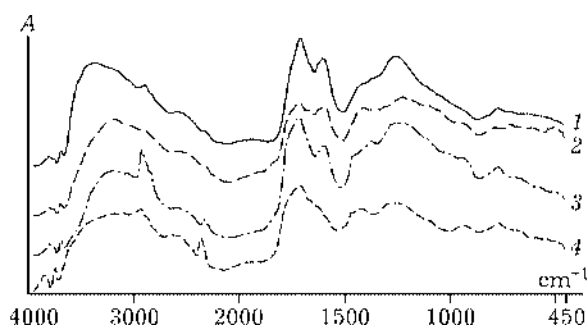


Fig. 5. IR spectra of WI (1), ES (2), BS (3) and WS (4) products of coal ozonation.

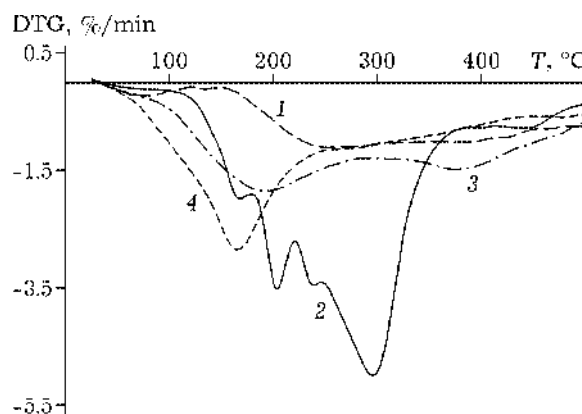


Fig. 6. Mass loss rate for WI (1), ES (2), BS (3) and WS (4) products of coal ozonation.

CONCLUSIONS

The features of ozonation of highly metamorphized coal in chloroform and the properties of individual fractions extracted from the soluble products were revealed as a result of the investigation. It was shown that high-molecular water-insoluble compounds are prevailing in the composition of coal ozonation products.

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