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Effect of Oxidative Modifying on the Chemical Composition and Properties of Coal from the Khushuut Deposit (Mongolia)

S. A. SEMENOVA¹, N. I. FEDOROVA¹, D. P. IVANOV², A. N. ZAOSTROVSKY¹ and Z. R. ISMAGILOV^{1,2}

¹*Institute of Coal Chemistry and Material Science, Siberian Branch of the Russian Academy of Sciences, Sovetskiy Pr. 18, Kemerovo 650000 (Russia)*

E-mail: iuxm@yandex.ru

²*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)*

E-mail: bic@catalysis.ru

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Abstract

Results of the comparative analysis of the effect of oxidative modifying performed using ozone, nitrogen (I) oxide and low-temperature oxygen plasma, on the chemical composition of coal from the Khushuut deposit (Mongolia) and its ability to thermal destruction are reported.

Key words: Mongolian coal, ozonation, treatment with nitrogen (I) oxide, oxidation in oxygen plasma

INTRODUCTION

Solid fossil fuels in Mongolia are represented by a wide range of humus coal species: from the least mature brown ones to most metamorphosed lean coal. The Khushuut deposit of lean coal is situated in the western part of Mongolia in Kobdos aimak. The deposit belongs to the Mongolia-Altay basin and is represented by two coal beds 15 and 35 m thick. The explored resources account for about 88 million t. Coal is consumed in small amount by local population for energy needs [1]. Industrial processing of coal to obtain target products is not performed at present. Vast available resources and the high chemical potential of Mongolian coal define the urgency of search for rational ways of integrated use relying on the knowledge of structure, properties of coal, chemical mechanisms of pyro energetic transformations and the methods to govern them.

During the recent decades much attention in studying coal is paid to the search for efficient methods of preliminary activation of the

raw material preceding its thermochemical processing, which allows one to decrease energy consumption or to obtain new, more valuable products with required properties. The goal to enhance the reactivity of coal and to develop efficient technologies of the new generation is to a high extent connected with the development of this direction.

In the present work we describe the results of studies into the effect of various methods of oxidative modification of coal from the Mongolian deposit Khushuut on the changes of its physicochemical properties and reactivity in the process of thermal destruction.

EXPERIMENTAL

As the methods of preliminary action, we used modification methods that are non-traditional for industrial technologies of coal processing: ozonation, treatment with nitrogen (I) oxide and oxidation in the low-temperature oxygen-containing plasma (LTOP). These methods

were attracted [2–4] to modify the surface of polymers, carbon materials and fossil coal for the purpose of rendering hydrophilic properties.

Coal ozonation (weighted portion of 5 g) was carried out in chloroform at 25 °C in thermostated rotating reactor with continuous supply of a mixture of ozone and oxygen (2–2.2 vol. % ozone) for 3 h [5]. The yield of substances soluble in chloroform was <1 %.

The treatment of coal (10 g) with nitrogen (I) oxide of medical grade (99.8 %) was carried out in the reactor made of stainless steel (Parr Instrument) 100 cm³ in volume in benzene medium (1 : 5 ratio). The reactor was blown with helium, and 8.3 g of nitrogen (I) oxide was introduced during mixing. Pressure in the reactor was 16 atm, temperature 230 °C, treatment time 12 h. Treated coal was separated from benzene by filtering and dried to a constant mass in a drying chamber at a temperature of 80 °C [6]. The yield of substances soluble in benzene after treatment was <1 %.

Oxidation in LTOP was carried out in a setup described in [7], in a rotating reactor under the following conditions: frequency 40.68 MHz, capacity 20–70 W, voltage 860–900 W, temperature in the reactor 40–50 °C, oxygen flow 5 mL/min, pressure in the discharge zone of the reactor 3 mmHg, weighted portion of the sample 500 mg. Treatment time (15 min) corresponded to the initial period of oxidation (mass loss not more than 2 %).

The content of oxygen in the active form was determined as a sum of its amount in the form of phenol, carbonyl and carboxyl groups, in the inactive form – as a difference between total oxygen and the content of identified O groups. Oxygenated groups were determined using the following procedures: carbonyl – according to the reaction with hydroxylamine hydrochloride, carboxylic – using the acetate method, a sum of carboxyl and hydroxyl groups – through ion exchange with sodium hydroxide.

The yield of bitumen species (B^d) was determined through extraction of coal with ethanol-benzene mixture (1 : 1) at the boiling temperature of the solvent using Graefe method for 6 h (error 0.2 %).

Technical analysis of coal was carried out using standard procedures. The elemental composition of the organic mass of coal was deter-

mined using a CHNS analyzer ThermoFlash2000; oxygen content was calculated from the difference. The IR spectra were recorded with an Infracalum-FT-801 Fourier Transform spectrometer within the range 400–4000 cm⁻¹. The optical density of the bands was normalized for the band at 1460 cm⁻¹.

High-resolution ¹³C NMR spectra in solid were recorded with a Bruker Avance III 300 WB instrument using a standard procedure of cross polarization with rotation at the magic angle and uncoupling from protons, suppression of rotation satellites (CPTOSS) [8] at the frequency of 75 MHz. Contact time was 2000 μs, accumulation 1024 scans, lag between scans 5 s, the frequency of sample rotation 5 kHz. Integrating the signals in separate spectral ranges we obtained the fraction of the corresponding carbon atoms of their total amount. For this purpose, the regions corresponding to the resonance absorption by the following groups of carbon atoms were allocated in the spectra, ppm [8, 9]: 220–185 – carbon atoms of carbonyl groups (C=O); 185–165 – carbon atoms of carboxylic and ester groups (COO); 165–145 – aromatic carbon atoms bound with oxygen atoms (C_{ar}-OH); 145–110, 110–95 – C- and H-substituted aromatic carbon atoms (C_{ar} + CH_{ar}); 95–60 – carbon atoms of alkyl fragments bound with oxygen atoms (C_{alk}O); 60–50 – carbon atoms of alkyl fragments (C_{alk}); 165–96 – the degree of aromaticity $f_a = (C_{ar}O + C_{ar} + CH_{ar})/100$. An example of the treatment of NMR spectrum is shown in Fig. 1.

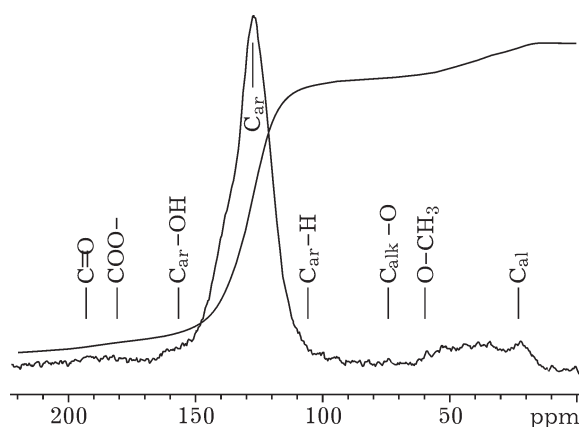


Fig. 1. ¹³C NMR spectrum of coal sample from the Khushuut deposit.

Thermal analysis was carried out using a Netzsch STA 409 thermoanalyzer under the following conditions: sample mass 40 mg; crucible: platinum-iridium; heating to 1000 °C at a rate of 10 °C/min in helium. Mass loss (TG) and the rate of mass loss (DTG) were recorded during analysis. To characterize thermal decomposition, we used the following parameters: T_{\max} – temperature of the maximal decomposition rate; V_{\max} – the maximal rate of mass loss within the range of major decomposition; Δm – mass loss by the sample within temperature ranges.

RESULTS AND DISCUSSION

Coal sample from the Khushuut sample under investigation has the following physicochemical characteristics: analytical humidity $W^a = 1.3\%$, ash content $A^d = 6.2\%$, total sulphur content $S_{\text{total}} = 0.5\%$, vitrinite 42.9%, semivitrinite 15.2%, inertinite 40.7%, the sum of leaning components 51.4%; vitrinite reflection index $R_r = 1.85\%$. This sample is a low-ash, low-sulphur fossil fuel of the IV stage of metamorphism; according to GOST 25543–88, technological grade T (lean fuzinite, 1TF). According to carbon and hydrogen content, H/C ratio, the yield of volatiles (V^{daf}) and substances extractable with ethanol-benzene mixture (B^d), the coal sample under analysis relates to humus coal of reduced type (Table 1).

The functional composition of coal is represented by a small amount of carboxyl, carbonyl and phenol groups (13.3% of total oxygen content). The major part of oxygen (86.7%) is included into macromolecules of coal in the form

of inactive ester and heterocyclic (furan, lactone, and quinoid) groups, which corresponds to the notions on the structure of humus lean coal.

The quantitative analysis of ^{13}C NMR spectra (Table 2) provides evidence that aromatic fragments dominate in the composition of organic matter (OM) of coal: their fraction, characterized by the index of aromaticity degree (f_a), corresponds to approximately 80%. About 11% of them are oxygen-containing aromatic fragments; the fraction of oxygen bound with carbon in aliphatic structures is less than 4%.

According to the results of technical and elemental analysis of coal (see Table 1) the used methods of oxidative action have a modifying nature and do not have any destructive effect on coal OM. For example, the ash content of coal remains almost unchanged, while an increase in the yield of volatiles and substances soluble in ethanol-benzene mixture after treatment with ozone is due to the removal of additionally formed oxygen-containing products.

The oxidative action on the OM of coal promotes qualitative redistribution of oxygen groups in its composition. In particular, after ozonation of coal we observe a substantial increase in the amount of all identified O groups; the amount of inactive groups' decreases, likely due to the involvement of ester links between coal macromolecules into oxidation process (see Tables 1, 2).

First of all, an increase in the concentrations of carboxyl and phenol groups may be promoted by the interaction of ozone molecules with benzene cycles of coal OM with the for-

TABLE 1

Chemical composition of initial and modified coal samples from the Khushuut deposit

Treatment methods	B^d , %	V^{daf} , %	Elemental composition, % daf					Atomic ratio		Functional composition, mg-equiv/g, daf			O content*, % daf
			C	H	N	S	O	H/C	O/C	-COOH	-OH	>C=O	
Without treatment	1.4	14.4	86.8	4.0	1.7	0.5	7.5	0.55	0.06	0.03	0.34	0.39	1.0/6.5
Ozonation	5.4	19.3	84.9	3.8	1.7	0.5	9.6	0.54	0.08	0.56	2.04	0.84	5.7/3.9
N ₂ O	1.5	14.7	87.8	4.3	2.0	0.5	5.9	0.59	0.05	0.05	0.22	1.00	1.3/4.6
LTOP	0.9	13.9	86.2	4.1	1.8	0.5	7.9	0.57	0.07	0.07	0.16	0.46	0.9/7.0

Notes. 1. B^d is the yield of ethanol-benzene extractables, V^{daf} is the yield of volatile substances. 2. LTOP is oxidation in low-temperature oxygen plasma.

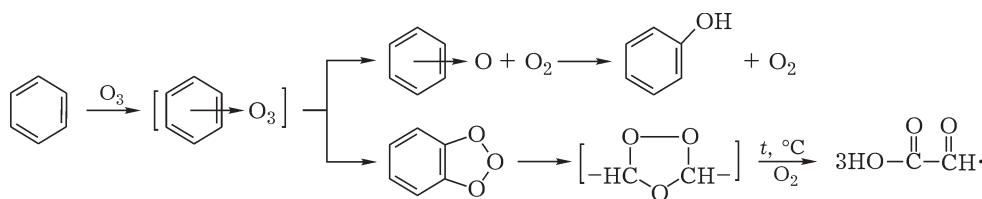
* The first value is the content of active oxygen, the second is the content of inactive oxygen.

TABLE 2

Parameters of the fragment composition of coal samples from ^{13}C NMR spectra

Treatment methods	Distribution of carbon atoms over structural groups, rel. %								f_a
	C=O	COO	C _{ar} O	C _{ar}	CH _{ar}	C _{alk} O	CH ₃ O	C _{alk}	
	Resonance absorption, ppm								
	220-185	185-165	165-145	145-110	110-95	95-60	60-50	50-0	
Without treatment	2.7	2.0	6.4	73.5	2.9	2.4	2.0	8.1	0.83
Ozonation	2.8	3.1	7.1	72.4	2.6	2.8	1.9	7.2	0.82
N ₂ O	2.7	2.2	6.8	77.4	2.4	0.6	1.7	6.2	0.80
LTOP	1.4	1.6	5.9	78.6	2.5	1.5	1.7	6.8	0.87

Note. f_a is the degree of aromaticity, $f_a = (\text{CO}_{\text{ar}} + \text{C}_{\text{ar}} + \text{CH}_{\text{ar}})/100$.



Scheme 1.

mation of π -complex [10]. The final products may be either phenol compounds or saturated (or aromatic in the case of the destruction of polycyclic structures) ozonides decomposing with the formation of aldehyde and carboxylic groups (Scheme 1).

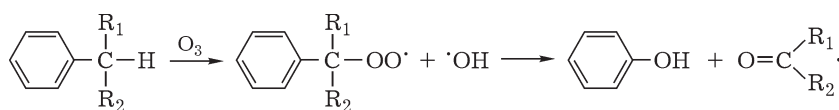
Ozonolysis of alkyl and naphthene aromatic coal structures may lead to burning out of saturated fragments with the formation of the additional amount of phenol and ketone groups [10] (Scheme 2).

A decrease in the fraction of aliphatic carbon is also indicated by the data of ^{13}C NMR spectroscopy (see Table 2).

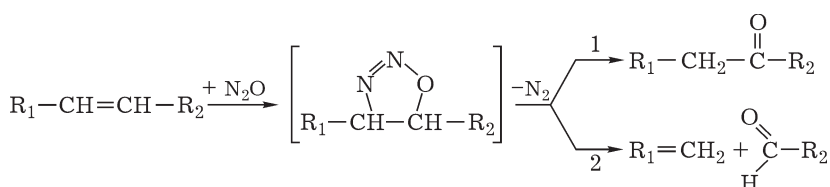
According to the data reported in [3], oxidation with nitrogen (I) oxide is a specific and selective reaction with respect to unsaturated

compounds. It proceeds according to the non-radical mechanism through 1,3-dipolar cycloaddition of N₂O molecule to the C=C bonds of alkenes with the formation of intermediate oxodiazoline intermediate. The intermediate compound decomposes mainly according to the hydrogen shift mechanism with the formation of ketone group at one of carbon atoms at the double bond (route 1). However, decomposition according to so-called diazo mechanism with the rupture of C=C bond and the formation of aldehyde and alkene is also possible (route 2) [3] (Scheme 3).

The selectivity of carbonylation reactions is likely to decrease in application to the organomineral coal substance with irregular structure of the structural fragments. Analysis of



Scheme 2.



Scheme 3.

TABLE 3

Optical densities of absorption bands for coal sample under investigation (normalized for the band at 1460 cm⁻¹)

Treatment methods	Absorption bands, cm ⁻¹											
	3400	3040	2920	1750	1700	1610	1380	1260	1160	1080	870	750
Without treatment	3.17	0.38	0.65	–	0.89	2.21	0.90	0.85	0.65	1.04	0.15	0.37
Ozonation	3.35	0.56	0.98	–	1.00	2.18	0.80	0.96	0.57	0.80	0.13	0.28
N ₂ O	2.88	0.43	0.69	–	0.86	2.00	0.88	0.81	0.56	1.13	0.16	0.29
LTOP	1.32	0.29	1.67	0.42	0.52	1.45	0.90	0.88	0.83	0.75	0.14	0.32

Note. For designations, see Table 1.

the results obtained allows us to assume that under the given experimental conditions, along with ketonization of unsaturated bonds, also thermooxidative destruction of oxygen groups present in OM occurs, in particular phenol and alkyl ester ones (see Tables 1, 2). In addition, it appears that not all nitrogen-containing cycles are subject to destruction with the removal of N₂ because an increase in nitrogen content in the elemental composition of coal is detected. The complicated character of transformations in the OM of coal during its modification in N₂O is also indicated by the data of IR spectroscopy (Table 3). Coal sample treated with N₂O is characterized by a decrease in the optical densities of the absorption bands of OH- and C-O of phenol groups (3400, 1260 cm⁻¹), C-O ester groups (1160 cm⁻¹) and an increase in the optical densities of absorption bands of C-N and N-O bonds (1080 cm⁻¹). The entire set of the data obtained also provide evidence of the possible formation of oxidiazolinic structures in coal matrix.

Under the conditions of low-temperature ($T < 70$ °C) oxygen plasma, the processes of etching the surface of coal particles with accompanying gas formation dominate over the initiation of oxidative transformations [3, 10]. This is indicated by a decrease in the yield of volatile substances and components extractable by neutral solvent from coal after its modification in LTOP. The total content of active O-groups changes only slightly, while the amount of inactive (heterocyclic) ones increases. According to the data shown in Tables 2 and 3, oxidative destruction affects the peripheral phenol (3400 cm⁻¹) and carboxylic (1700 cm⁻¹) groups, which results in the formation of anhydride (the appearance of a band at 1750 cm⁻¹) and ester (1160 cm⁻¹) links; the degree of aromaticity (f_a) increases.

Estimation of the effect of different methods of oxidative modification on the OM of coal was also carried out using thermogravimetric analysis in the oxidative atmosphere (Table 4).

Thermal destruction of initial coal sample is characterized by at least three stages of the

TABLE 4

Results of thermogravimetric analysis of coal samples

Treatment methods	T_{\max} , °C	V_{\max} , %/min	Δm , mass %			
			within temperature range, °C			
			160–350	350–800	800–1000	160–1000
Without treatment	593	0.35	1.25	10.65	2.66	14.56
Ozonation	570	0.36	3.90	11.76	2.05	17.71
N ₂ O	618	0.42	1.79	12.44	3.10	17.33
LTOP	560	0.33	1.41	10.86	2.29	14.56

Note. T_{\max} is temperature of maximal decomposition; V_{\max} is the maximal rate of mass loss within the range of major decomposition; Δm is mass loss within the corresponding temperature range.

decomposition of coal matter. The first stage, within temperature range 25–160 °C, is due mainly to desorption of hygroscopic water and hydrocarbon substances immobilized in pores. Mass loss within this temperature range accounts for 1.5 %, which corresponds to moisture content according to the data of technical analysis (1.3 %). Apparently, the decomposition of fragments containing functional groups O, S and N proceeds within temperature range 160–350 °C. Mass loss by the initial sample within this temperature range is insignificant (1.25 %), which can be connected with the low content of heteroatoms in the OM of highly metamorphosed coal (see Table 1). The period of the major destruction of coal OM is rather extended – from 350 to 800 °C. Within this temperature range, the most significant changes connected with the destruction of C–C bonds, evolution of volatile products and formation of coke residue occur in the OM. The maximum of decomposition rate is observed at 593 °C. The decomposition of OM continues also at higher temperatures (>800 °C), which may be due both to the processes of structuring the carbon residue accompanied by the evolution of low-molecular mass gases (CO, H₂ *etc.*) and to the decomposition of inorganic compounds (silicates and carbonates) incorporated in the mineral part of coal.

After modification of coal, the process of thermal destruction runs in a different manner (see Table 4). For all modified samples, an increase in mass loss (Δm) is observed in the low-temperature range of the process (150–350 °C), which is due to the development of dehydration and decarboxylation of accumulated oxygenated groups (see Table 1). The largest mass loss within this temperature range corresponds to the ozonated sample.

Within the range of major decomposition of coal OM (350–800 °C), the intensity of thermal destruction V_{\max} increases noticeably only for the sample treated with nitrogen (I) oxide; the temperature of maximal decomposition T_{\max} increases by 25 °C in comparison with the initial sample. It is possible that this is promoted by the formation of more thermally stable heterocyclic compounds in OM during the interaction with N₂O; these compounds decompose with the formation of volatile tar products. For other methods of oxidative treatment (in O₃

and LTOP), quite contrary, T_{\max} shifts by 23–33 °C to lower temperature, which is the evidence of the formation of thermally less stable bonds in the OM of coal.

The total mass loss Δm increases (approximately by 3 %) for the samples treated with ozone and nitrogen (I) oxide, in the former case this happens due to intensification of thermal destruction in the low-temperature range of the process (<350 °C), while in the latter case this happens within the range of the major decomposition of coal matter (350–800 °C). Modification in plasma is likely to have surface character because the profile of the DTG curve and the value of final mass loss change insignificantly.

CONCLUSION

Preliminary oxidative treatment of coal from the Khushuut deposit (Mongolia) with ozone, nitrogen (I) oxide and oxygen plasma leads to the redistribution of functional oxygenated groups and changes in the yields of volatile and soluble products (see Table 1).

By means of chemical analysis, IR and ¹³C NMR spectroscopy, it was demonstrated that the most substantial oxidative transformations occur in the OM as a consequence of the treatment of coal with oxygen-ozone mixture. An increase in the total amount of carboxylic, carbonyl and phenol groups (by 4.7 %) is comparable with an increase in the yield of ethanol-benzene extractables (by 4 %) and the yield of volatiles (by 4.9 %).

During the treatment of coal with nitrogen (I) oxide, in addition to the low molecular mass carbonyl-containing products, the formation of nitrogen-containing heterocyclic fragments is possible in the structure of coal matter.

Modification under the conditions of low-temperature oxygen plasma is accompanied by etching of the surface functional groups, which dominates over the initiation of oxidative transformations.

Thermal destruction of oxidized coal samples is accompanied by intensification of gas evolution in the low-temperature region (150–350 °C) and in the region of the major decomposition of coal OM (350–800 °C). In the former case the maximal effect is achieved as a result

of preliminary ozonation of coal, while in the latter case it is achieved through treatment with nitrogen (I) oxide. The action of plasmachemical oxidation does not lead to significant changes in the course of thermal destruction of coal.

The obtained results can be useful for the development of new technological processes of coal processing and improvement of existing ones.

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