The Contribution of Radical Reactions During Thermal Processing of Low-Quality Coals

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ABSTRACT: It is well known that presence of sulphur in coals leads to technological and environmental problems. The aim of the work is to estimate the participation of sulphur containing compounds in processes of radical formation and recombination during thermal and thermochemical destruction of caking and non-caking coals of different genetic types by reductivity: reduced (RC) and low reduced coals (LRC). For the chemical treatment of coals were used products of coal tar distillation (absorbing oil) and the initiator of radical polymerization - dinitril of an acrilic acid. It was shown the influence of chemical additives and coal type by reductivity on the yield and composition of semi-coking products. Sulphur containing groups promote the breakdown of lateral chains, shortening La and increasing the amount of the paramagnetic centers. It is possible to manage of thermal destruction processes by introduction of radical polymerization additives and not commodity products of coke manufactures.

KEY WORDS: sulphur, coals, semi-coking products, additives, electron spin resonance, DRIFT analysis.

Introduction

Mining of valuable coals suitable for coking has been decreasing in the world. The part of mining of low-caking and noncaking sulphurous coals increases at impressive rates. As it is known, sulphur is the extremely negative component at composing coal blends for coking. Sulphurous compounds negatively influence thermal processing of solid fossil fuels. Their presence leads both to technological and environmental problems and change of coking ability of coals. In this connection there arises the problem of sulphurous coals pyrolysis processes control.

As thermal destruction of fuels is a radical process (Fowler and Bartle 1989, Zhao et al. 2003), it is interesting to estimate participation of coal sulphurous compounds in the processes of radical formation.

In previous papers were described the evidences of free-radical mechanism of coal oxidation and pyrolysis processes (Kucher et al. 1980, Butuzova et al. 1997, Butuzova et al. 1998). Influence of oxygen-containing groups on coal radical reactions has received much attention, but sulphur is also quite significant component. Since, it is very important to study the role of sulphur species during thermochemical treatment of coal for better understanding of the pyrolysis mechanism.

The aim of the work is comparative study of thermal destruction processes of caking and noncaking coals with the different contents of sulphur and revealing an opportunity of control these processes by chemical pre-treatment of solid fuel.

Experimental

In the work the following methods of research were applied: semi-coking process, the proximate and ultimate analysis, the quantitative analysis of semi-coke gas, a method of electron spin resonance (ESR), the X-ray structure analysis of coals and products of their pyrolysis, and also FT-IR spectroscopy.

One of methods of coal quality estimation is «a method of determination of semi-coking products yields» (pyrolysis by Fisher). This method is based on thermal decomposition of fuels at temperature of 520 °C without air access with formation of pyrogenetic water, tar, gas and semi-coke. The yield of semi-coking products is a parameter which reflects the chemical structure and properties of coal organic mass. It is one of classification parameters which are used extensively in the industry for an estimation of technological characteristics of solid fossils fuels with the aim of their more effective use in various conversion processes. The composition of gases which were formed as a result of thermal treatment of solid fuels is the following: carbon dioxide, unsaturated hydrocarbons (ethylene, propylene, butylene), carbon oxide, hydrogen, methane and its homologies and hydrogen sulphide.

The quantitative analysis of semi-coking gas was carried out in apparatus VTI (Vsesouznyj Teplotechnicheskij Institute).

ESR-spectra of coals were recorded on a RE-1306 radiospectrometer. Mn^{2+} powder in a MgO grid was used as an internal standard. The spectra for the samples and the standard were recorded at the room temperature in the air within a 3-cm wavelength range. The line shape was defined by the method of linear anamorphoses. Anisotropy was calculated by the Lebedev method (Lebedev 1962).

Method ESR consists in the resonant absorption of energy of a variable high-frequency magnetic field by paramagnetic substance. This substance should be placed in a constant magnetic field. All free radicals possess paramagnetic properties, but each radical has the characteristic spectrum. This fact allows to determine them.

The electron spin resonance is caused by presence of unpaired electrons (free radicals, ion-radicals or paramagnetic ions) in analyzed substance.

ESR-spectra shows dependence of absorption energy on intensity of a constant magnetic field registers in a differential form in the action. Position of ESR-spectrum lines is determined by the g-factor. It shows how much an orbital movement of free electrons influences their magnetism. It indicates that value of the g-factor depends on a chemical environment of unpaired electron for organic free radicals. Signal intensivety (the area under absorption curve) is proportional to concentration of paramagnetic particles in the researched substance.

Coals are paramagnetic. The information about the ESR signal character can be received from position, intensity, width and the form of a signal. Concentration of unpaired electrons can be determined by a standard sample with known concentration of free radicals.

For studying of coal structure have been carried out X-ray structure researches of samples. X-ray spectra of thermally treated coals were obtained with the apparatus "Kristalloflex Siemens" using filtered cuprum radiation. The interlayer distance (d_{002}), the thickness of carbon package (L_c) and other parameters were calculated with an accuracy of $d_{002} \pm 0.01$ Å and $L_c \pm 1$Å within angles from 5° to 110°.

Coal radiography is based on analogy between diffraction pictures of coal samples and graphite. The analogy specifies presence of some order in directions of graphite structure. Thus it is necessary to take into account the following essential properties: order is partial; spatial (three-dimensional) order is not present; areas with elements of a lattice (crystallites) in the coal structure possess small sizes, and the number of parallel layers is few; strong incoherent scattering which is necessary for taking into account is observed.

IR-spectra of the solid samples were recorded on a FT-IR "Bio-Rad" FTS-7 spectrometer with DRIFT technique. The samples were prepared in the form of 5 % mixture of coal with potassium bromide. Multipoint baseline correction was performed using a standard software package.

For the chemical pre-treatment of coals were used products of coal-tar distillation (absorber oil) and the initiator of radical polymerization – acrylic acid dinitrile (AAD).

Results and discussion

As the basic objects of research were used isometamorphic pairs of caking and noncaking Donetsk coals the same stages of metamorphism of different genetic types by reductivity: reduced (RC) and low-reduced (LRC). The characteristic of researched coals is shown in the Table 1. Samples of RC and LRC coals were selected from the closely-spaced coal seams in the same mine.

Table 2 shows the data received by a method of electron spin resonance. The interpretation of coals ESR-spectra is based on the condition that the signal is caused by free radicals. These radicals are stable as a result of delocalizing free electrons in the polyconjugated system.

Considering the form of absorbing signal of well evacuated samples it is possible to draw the conclusion that the coals contain two various types of paramagnetic centers (PMC). Signals of PMC look like superposition. It is possible that the spectral line turns out overlaying one narrow signal and one wide signal. Consequently, the wide signal was caused by stabilized aromatic free radicals which were formed as a result of splitting in nonaromatic part and a narrow signal was caused by the conjugated aromatic systems (Kucher et al. 1980). We consider that the number of paramagnetic centers (PMC), shape of spectral line depends not only of petrographical structure of coal and also depends of genetic type by reductivity. This idea was promoted by us in this paper.

We tried to estimate the contribution of radical reactions during thermal and thermochemical destruction of coals which differ both on rank and type by reductivity by ESR method.

It has been established, that the number of PMC considerably increased during thermochemical destruction. The specified increase of PMC concentration is observed for the coals of different genetic types by reductivity.

As it is seen from the Table 2, chemical treatment of coal results in change of paramagnetic characteristics, first of all the content of paramagnetic centers. For RC under the oil action ESR line broadening (Ukraine, k_8) or g-factor value decrease (Trudovskaya, k_8) as compared to similar parameters for the LRC. In all the cases the line shape remains a Lorenzian one for semi-cokes which is indicative of strong exchange interaction. The signals observed are asymmetric, with the asymmetry degree depending on the coal rank and type by reductivity.

It should be emphasized that the g-factor for the initial low rank coals approaches that for the radicals of semiquinone type, whereas the g-factor of the semi-cokes signal may be referred to aromatic radicals with the ether-bridge oxygen, and the g-factor for oil-treated or AAD-treated semi-cokes of RC coals approaches that for the unpaired electron (g = 2.0023).

Thus, all the above permits an assumption that paramagnetic centres of semi-cokes are predominantly represented by free valencies in condensed aromatic structures. The additives promote formation of strong intermolecular associates in them.

Coal №	Coal mine, seam, brand	Type	Proximate and ultimate analyses					
			W^a	A^d	V^{daf}	C^{daf}	H^{daf}	S_t^d
1	Cheluskintsev, l_4, D	LRC	0.8	2.4	35.6	79.3	4.94	2.17
2	Trudovskaya, l_4, D	LRC	1.0	1.6	37.3	78.4	4.95	1.05
3	Zasiadko, l_4, J	LRC	1.4	2.6	31.6	87.8	5.16	1.09
4	Gagarina, m_3, J	LRC	1.2	3.7	28.7	87.4	5.06	0.70
1′	Ukraine, k_8, D	RC	1.5	9.9	41.8	77.9	5.30	2.87
2′	Trudovskaya, k_8, D	RC	0.9	4.6	46.2	76.1	5.43	5.85
3′	Zasiadko, k_8, J	RC	0.8	2.7	31.7	87.3	5.23	2.81
4′	Gagarina, m_4, J	RC	0.8	12.2	35.6	83.6	4.88	3.75

■ **Tab. 1.** Characteristics of initial coal.

Coal mine, seam, brand	Type	Type of treatment	N, spin g^{-1} × 10^{-19} (±0.1)	Width of line, (±0.1)	Line Asymmetry, A/B, (±0.01)	Line shape	g-factor (±0.003)
Cheluskintsev, l$_4$, D	LRC	20 °C	0.6	6.2	0.97	L/G	2.003
«-»	LRC	520.°C	3.6	5.6	1.00	L	2.003
«-»	LRC	520 °C, AAD	4.1	5.6	1.00	L	2.003
«-»	LRC	520 °C, oil	4.4	5.6	1.00	L	2.004
Trudovskaya, l$_4$, D	LRC	20 °C	0.6	6.4	0.97	L/G	2.005
«-»	LRC	520 °C	3.5	5.6	1.01	L	2.003
«-»	LRC	520 °C , AAD	3.8	5.6	1.01	L	2.003
«-»	LRC	520 °C, oil	3.9	5.6	1.01	L	2.003
Zasiadko, l$_4$, J	LRC	-	1.0	6.9	0.95	L/G	2.003
Gagarina, m$_3$, J	LRC	-	1.3	6.6	0.96	L/G	2.003
Ukraine, k$_8$, D	RC	20 °C	0.6	5.6	0.84	L/G	2.004
«-»	RC	520 °C	3.3	5.4	1.01	L	2.003
«-»	RC	520 °C, AAD	3.6	5.4	1.01	L	2.003
«-»	RC	520 °C, oil	3.7	5.6	1.01	L	2.003
Trudovskaya, k$_8$, D	RC	520 °C	3.6	5.6	1.00	L	2.005
«-»	RC	AAD	4.2	5.6	1.00	L	2.004
«-»	RC	520 °C, oil	4.1	5.6	1.02	L	2.003
Zasiadko, k$_8$, J	RC	-	1.0	6.0	0.94	L	2.003
Gagarina, m$_4$, J	RC	-	0.8	5.0	0.90	L	2.003

L – Lorents, L/G – Lorents with Gauss broadening

■ **Tab. 2.** The results of the ESR method.

Under these conditions the yield of gas products of pyrolysis is rather low.

In order to check up a hypothesis about different concentration, character and reactionary ability of radicals of different types, the yield and structure of the semi-coking products in the presence and without additives have been investigated because semi-coking is a basic stage of coal destruction. Results of these researches have shown in the Table 3.

It can be seen from the Fig. 1, the yield of semi-coke increases at entering additives in the coal blends. This increase is typical for LRC and RC coals. It testifies to an intensification of polyrecombination reactions at the chemical treatments.

Influence of additives, consequently influence of radical reactions on structure of pyrolysis products is clear from the analysis of semi-coking gas. Figure 2 shows that the content of CH$_4$, H$_2$ and H$_2$S in gas is different for the coals of different types. The action of additives, especially acrylic acid dinitrile, is more expressed on pyrolysis of LRC coals.

Action of additives reduces the concentration of methane and hydrogen, and increases the concentration of hydrogen sulphide. Consequently, chemical pre-treatment initiates radical polymerization reactions, but interferes in dealkylation processes. It is possible to assume, that chemical pre-treatment promotes a dealkylation and aromatization reactions, i.e. aliphatic

Coal field, mine, seam, brand	Type	Chemical treatment	Components of semi-coke gas, ml/g^{daf} H$_2$S	H$_2$	CH$_4$	Yield of semi-coke, % daf
Cheluskintsev, l$_4$, D	LRC	Initial	9.07	12.63	82.28	63.5
«-»	LRC	AAD	10.71	10.11	75.03	70.9
«-»	LRC	Oil	11.21	6.76	40.22	70.0
Trudovskaya, l$_4$, D	LRC	Initial	2.73	20.50	57.85	64.8
«-»	LRC	AAD	2.80	9.60	39.21	64.8
«-»	LRC	Oil	2.87	15.22	57.03	66.3
Borodinskoe, Kansko-Achinsk coalfield	LRC	Initial	1.40	24.96	83.14	53.5
«-»	LRC	AAD	1.69	5.79	53.58	56.6
«-»	LRC	Oil	2.07	13.81	57.05	56.5
Ukraine, k$_8$, D	RC	Initial	9.93	43.85	66.19	62.5
«-»	RC	AAD	12.05	42.99	63.31	66.3
«-»	RC	Oil	13.11	40.02	61.86	64.3
Trudovskaya, k$_8$, D	RC	Initial	29.08	47.18	54.85	62.1
«-»	RC	AAD	32,46	40,12	50,10	63,4
«-»	RC	Oil	32,75	32,13	46,67	64,7
Aleksandriyskoe, Dnepr coalfield	RC	Initial	15,72	38,62	59,28	32,1
«-»	RC	AAD	16,25	33,96	58,54	46,8
«-»	RC	Oil	18,12	28,34	49,39	46,7

■ **Tab. 3.** The data of semi-coking analyses of coals and gases.
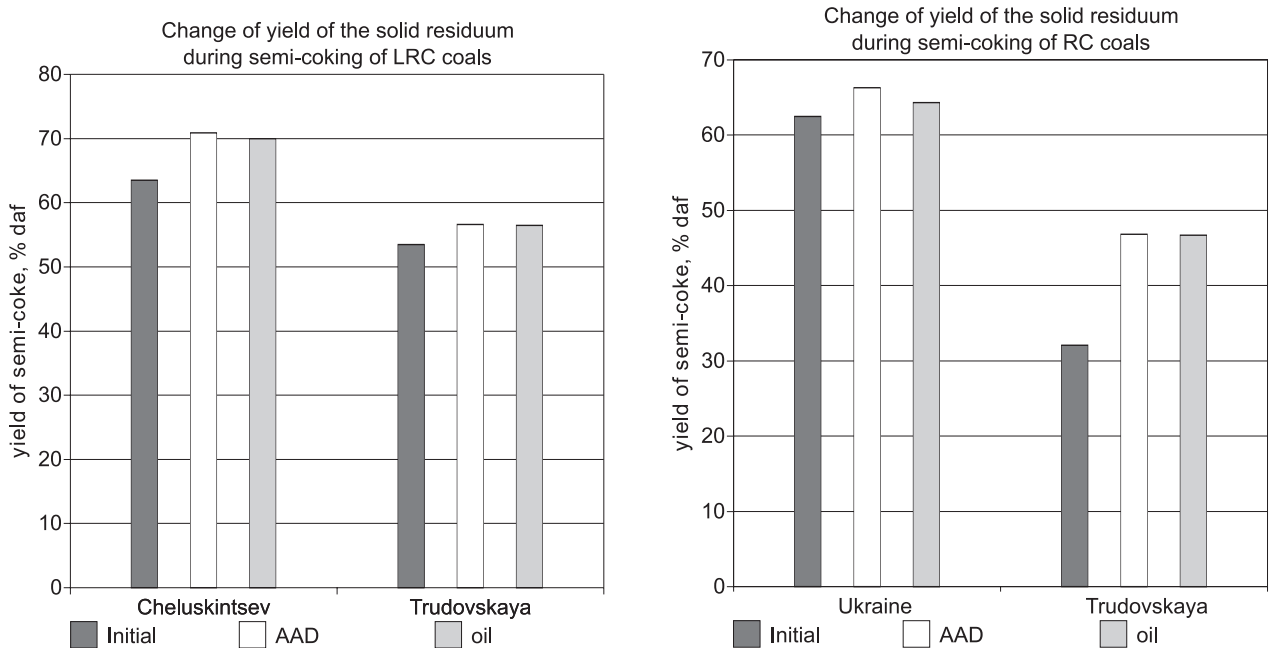
■ **Fig. 1.** Influence of chemical additives on change of yield of the solid residuum for RC and LRC coals.
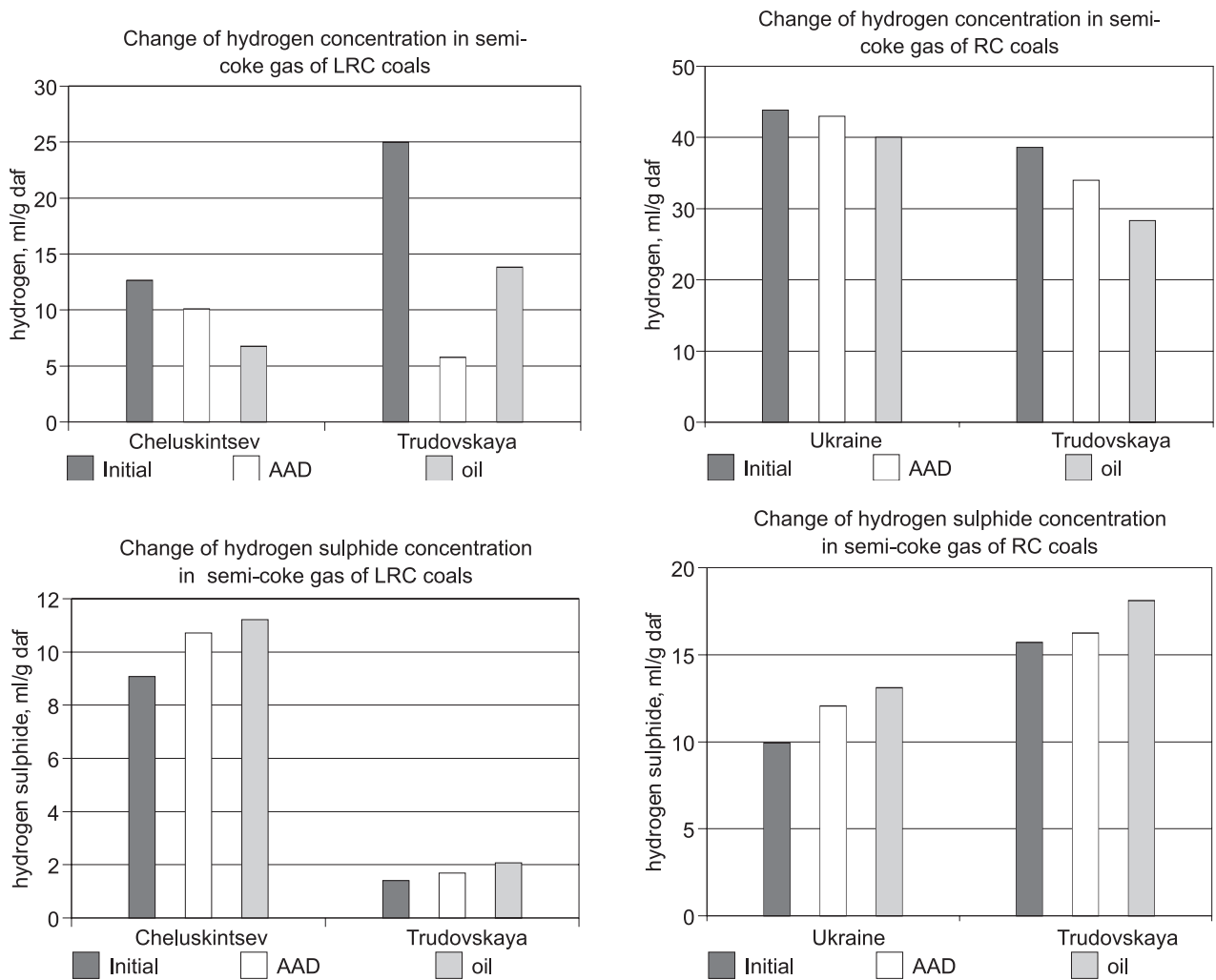
■ **Fig. 2.** Influence of additives on change of the CH_4, H_2, H_2S concentration in semi-coke gas of long-flame coals LRC and RC types.

groups removal from LRC and RC coals. These assumptions prove to be true the data of IR-spectroscopy (Table 4). It compares the relative intensities (areas) of the absorption bands of individual groups in solid samples.

The changes in the character of IR-spectrum of the coals after treatment with oil or AAD are predominantly manifested by a decrease in the relative intensity of the absorption bands of C-O-groups (1280 cm^{-1}), aliphatic hydrogen (2970, 2920, 1440 cm^{-1}) and aromatic hydrogen (700–900 cm^{-1}).

This gives us grounds to assume that chemical additives result in certain changes in polyconjugation system of coal organic mass (COM) due to a change both in the structure of the carbon skeleton and in the system of polar groups participating in conjugation.

Chemical pre-treatment decreases the relative content of –S– groups. It will be coordinated to a high yield of hydrogen sulphide.

Influence of radical formation processes on supermolecular structure of samples studied by the X-ray structure analysis method. Results of X-ray researches are shown in the Table 5. The X-ray structure data showed, that chemical additives used in the given work influenced on the sizes of packages of carbon lattices, namely: for the coals of low-reduced type the appreciable increase of length of a package and relation L_a/L_c is observed. AAD influence on pyrolysis processes of reduced coals is similar. Action of absorbing oil on these coals appears opposite. Probably, sulphur compounds groups promote separation of side chains, shortening L_a and increasing amount of the paramagnetic centers.

Conclusions

The lead large-scale researches of coals of different types by reductivity allow to assume that chemical pre-treatment promotes lacing reactions passing, including recombination reactions. Such conclusion was dictated by increase of semi-coke yield and concentration of the paramagnetic centers. Change of the sizes of a X-ray package testifies for the benefit of the given assumption.

The analyses of semi-coking gas have shown that the concentration of hydrogen sulphide increases under the action of chemical additives, i.e. desulphurization of solid phase and also the concentration of hydrogen and methane decreases occur. Consequently, it is possible to assume, that additives prevent the removal of aliphatic groups, they affected the course of pyrolysis process permitted directed variations in the composition of products and in the semi-coke structure.

The decomposition reactions compete with recombination and condensation leading to char and gases formation. It can be

| Coal field, mine, seam, brand | Type | Chemical treatment | Results of IR-spectroscopy of semi-cokes | | | | |
| | | | $I_x/I_{2,920}$ | | | Relative region $S_x/S_{1,600}$ | |
			1,700 / 2,920	2,970 / 2,920	3,050 / 2,920	$S_{1100–1,000}$	$S_{900–700}$
Cheluskintsev, l$_4$, D	LRC	20 °C	0.76	1.00	0.90	0.12	0.48
«-»	LRC	520 °C	0.94	1.07	1.24	0.26	5.39
«-»	LRC	520 °C, AAD	0.98	1.03	1.23	0.24	3.91
«-»	LRC	520.°C, oil	1.00	1.05	1.28	0.23	3.28
Trudovskaya, l$_4$, D	LRC	20.°C	0.78	1.00	0.92	0.10	0.49
«-»	LRC	520 °C	0.97	1.01	1.07	0.22	4.87
Ukraine, k$_8$, D	RC	20 °C	0.63	1.00	0.80	0.52	0.70
«-»	RC	520 °C	1.11	1.05	1.10	1.29	7.41
«-»	RC	520 °C, AAD	1.09	1.06	1.24	1.24	4.87
«-»	RC	520 °C, oil	1.10	1.06	1.18	1.21	3.57
Trudovskaya, k$_8$, D	RC	520 °C	1.04	1.05	1.08	1.96	6.19

■ **Tab. 4.** The results of IR-spectroscopy.

№	Type	Chemical treatment	T, °C	L_c	L_a	L_a/L_c	d_{002}	h/l	$I_{кр}$	n
1	LRC	–	20	1.27	1.54	1.05	0.356	1.42	0.79	5
		–	520	1.45	2.03	1.40	0.356	2.32	1.59	5
		AAD	520	1.70	2.37	1.39	0.356	2.83	1.48	6
		oil	520	1.63	2.58	1.58	0.356	2.44	1.13	6
2	LRC	–	20	1.16	1.99	1.72	0.356	1.46	0.82	4
		–	520	1.57	2.50	1.59	0.356	3.46	1.77	5
1′	RC	–	20	1.31	1.48	1.25	0.356	0.59	0.69	5
		–	520	1.36	2.65	1.95	0.356	1.43	1.79	5
		AAD	520	1.36	2.73	2.01	0.356	1.67	1.25	5
		oil	520	1.57	2.36	1.50	0.356	1.89	1.23	5
2′	RC	–	20	1.20	1.71	1.43	0.356	0.68	0.42	4
		–	520	1.31	2.92	2.23	0.356	1.97	1.85	5

■ **Tab. 5.** Results of the X-ray analysis of initial coals and products of their pyrolysis.

concluded that radical reactions play the most important role during thermal destruction of coals.

References

BUTUZOVA L., KRZTON A. and KOZLOVA I., 1997. The paramagnetic characteristics of pyrolysis products for coals treated by alkali and acid. Proc. 9th Intern. Conf. of Coal Science. Essen, Germany, Vol. 1, pp. 91-94.

BUTUZOVA L., KRZTON A., SARANCHUK V., KOZLOVA I., DUBER S. and GE Zh., 1998. Structural chemical transformations of modified brown coal during pyrolysis and hydrogenation. Khimiya tverdogo topliva, 4, 36-45 (in Russian).

FOWLER T. and BARTLE K., 1989. Limitation of electron spin resonance spectroscopy in assessing the role of free radicals in the thermal reactions of coal. Energy and Fuels, 3, 515-522.

KUCHER R., KOMPANETS V. and BUTUZOVA L., 1980. Structure of fossil coals and its ability to oxidation. Nauk. dumka, Kiev (in Russian).

LEBEDEV Ja.S., 1962. Analysis of asymmetrical lines in ESR-spectra as a researching method of domestic movements in polymers. Zhurnal Strukturnoj Khimii, 3, 21-27 (in Russian).

ZHAO R., YE S., XIE Y. and CHEN Y., 2003. Study on co-pyrolysis of coking-coal, plastic and dust. Huan Jing Ke Xue, 24(5), 28-33 (in Chinese).