



## PETROLOGICAL STUDIES OF LOW TEMPERATURE OXIDATION OF LIGNITES

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**Abstract.** The low temperature oxidation processes which has taken place in lignites and their lithotypes (xylain, humovitrain, semifusain, fusain and liptain) from the East Maritza basin have been studied. The changes occurring in the coals/lithotypes composition and structure during their oxidation have been followed by examining reflectance, microhardness, proximate, ultimate, functional, and increment analyses. The main kinetic parameters such as duration of the induction period, maximum and stationary rates and the apparent activation energies were evaluated. The complex investigation provides a detailed information for the behaviour of low rank coals and their lithotypes towards the action of atmospheric oxygen. Thus some suggestions concerning the mechanisms of their oxidation reactions can be made. The individual way of the genesis of each one of the lithotypes and the resulting physicochemical structure predetermine the basic mechanism of these reactions. However, it has been found that in spite of the similar genesis the lithotypes differ in the mechanism of their oxidation. For xylain the oxidation takes place mainly via aryl radicals yielding tertiary peroxide and carbonyl groups. The oxidation of humovitrain is characterised by the dominant participation of aroxyl radicals resulting in accumulation of primary hydroperoxide and phenol groups. The oxidation of semifusain leads mainly to the formation of molecular products. The oxidation of fusain is found to be essentially different from that of other lithotypes. It is characterised by the formation of carbonyl groups attached to biphenyl aromatic structures. The peculiar petrographic composition and structure of liptain account for the occurrence of oxidation processes accompanied by destruction reactions at relatively lower temperatures. It has been established that the intensity of the oxidation processes varies from one lithotype to another. Xylain and humovitrain oxidise most intensively. The intensity drops off from the first towards the second member of the corresponding genetic series, i.e. from xylain to humovitrain and from semifusain to fusain.

**Key words:** lignites, lithotypes, oxidation, East Maritza Iztok basin.

### INTRODUCTION

There has been considerable interest in evaluating the effect of autooxidation processes during coal processing, transportation and storage (Van Krevelen, 1961; Kucher *et al.*, 1978, 1980; Volborth, 1979; Saranchuk, 1982; Saranchuk *et al.*, 1994; Markova, Rustshev, 1991, 1994; Wagner, 1995). The research in this field could contribute to the solution of a wide range of problems related to purely geological and petrological goals and also for evaluating coals as raw material for industrial purposes. On the other hand, these processes are closely connected with coal selfignition thus being of great ecological interest. However, the different opinions on the character and mechanisms of autooxidation processes occurring in low rank

coals, the limited range of study from petrological standpoint as well as the lack of similar concepts and studies on the separate lithotypes of lignite coals impose the performance of a complex and expanded in petrological aspect investigation. Thus, following the structural changes in lignite coals and their lithotypes, it is possible to supplement and clarify some obscure steps in the mechanisms of the autooxidation processes in lignite coals and propose an appropriate mechanism pathways for these processes in low rank coal lithotypes.

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## EXPERIMENTAL PROCEDURE

The petrological investigations were carried out on low rank coals from the biggest Bulgarian coal basin — Maritza East, and its homogeneous lithotypes: xylain, humovitrain, semifusain, fusain, and liptain before and after oxidation. The coal lithotypes are members of the separate genetic series as follows: I series — wood-xylain-humovitrain, II series — wood-semifusain-fusain, and III series — wood-liptain. The petrological characteristics of the initial samples are given in **Table 1** and their maceral composition in **Table 2**.

and a 15<sup>x</sup> eye-piece. Ten determinations of plastic deformations were made for each polished section every 15 sec., with a diamond pyramid, with an apex angle of 136° and a load of 50 g.

The proximate analysis includes the determination of the content of analytical moisture ( $W^a$ , %), ash ( $A^d$ , %) and the volatile matter ( $V^{daf}$ , %), and has been carried out by standard methods. The carbon and hydrogen content was evaluated by "LECO-CHN-4000" apparatus, the total sulphur content by "LECO-CS-32" apparatus, and that of nitrogen by the Kjeldahl,

Table 1

Characteristics of initial samples

Lignite coals	Proximate analysis			Ultimate analysis							Reflectance $R_o$ [%]	Microhardness mH [kg/mm <sup>2</sup> ]
	$W^a$ [%]	$A^d$ [%]	$V^{daf}$ [%]	$C^{daf}$ [%]	$H^{daf}$ [%]	$N^{daf}$ [%]	$S_o$ [%]	$O^{daf}$ [%]	H/C	O/C		
Mean sample	14.8	19.2	58.1	61.5	5.6	1.6	6.7	24.6	1.09	0.29	0.15±0.03	—
Xylain	7.2	2.6	61.1	68.7	6.8	0.7	4.7	19.1	1.19	0.21	0.13±0.02	20.9
Humovitrain	10.0	5.9	56.4	66.9	5.2	1.2	3.2	23.5	0.93	0.26	0.14±0.03	25.2
Semifusain	9.4	9.2	35.1	71.1	4.3	0.8	3.3	20.5	0.73	0.22	1.80±0.04	34.5
Fusain	8.8	4.4	17.0	87.2	3.1	0.8	1.9	7.0	0.43	0.06	2.50±0.6	77.9
Liptain	4.0	2.4	70.9	70.8	7.0	0.8	3.7	17.7	1.19	0.19	0.14±0.03	—

For the purposes of modelling the autooxidation processes, the coals were oxidised at 150°C for 45 h in static air atmosphere (Markova, 1976). The initial and oxidised samples were subjected to petrographic, proximate, ultimate, functional, and IR spectral analyses.

The petrographic studies, respectively the quantitative maceral analysis, reflectance ( $R_o$ , %) and microhardness (mH, kg/mm<sup>2</sup>) of the initial and oxidised samples were determined by standard procedures. The quantitative maceral analysis was carried out using a MPT "Opton" microscope, in reflected light with cedar-oil immersion on anschliff-briquettes (40<sup>x</sup> objective, 12.5<sup>x</sup> eye-piece) by recording an average number of 500 points per sample with an "Eltinor" automatic point-counter. Reflectance was determined with the above mentioned microscope-photometer, supplied with a RGA 1F photomultiplier and an Antiflex-Epi 40/0.65 objective and TF-5 optical glass as a standard ( $R_o = 0.58$  %). The experiments were carried out according to Bulgarian Standard (BS 15201-80) in a polarised monochromatic light ( $\lambda = 546$  nm) and a 4  $\mu$ m stop. Microhardness was determined with PMT-3 microphotometer with 32.5<sup>x</sup> objective

method. The oxygen content was established by the difference to 100% after determination of organic sulphur.

The oxygen-containing functional groups were determined as follows: the hydroxyl (phenol) ones — by barium hydroxide, the carbonyl ones — by hydroxyl-aminehydrochloride, and the carboxyl ones — by calcium acetate (Blom *et al.*, 1957; Kucher *et al.*, 1980).

The quantitative IR spectral analysis was carried out on a spectrophotometer IR-75 Carl Zeiss Yena after the method of Oelert (1965, 1967). On the basis of the quantitative increment analysis of the demineralized by KBr technique initial samples the content (%) of  $H_{ar}$ ,  $C_{ar}$ ,  $H_{CH_3}$ ,  $C_{CH_3}$ ,  $H_{CH_2}$ ,  $C_{CH_2}$ ,  $H_{OH}$  and  $C_{OH}$  and the aromaticity ( $f_a$ ) were determined.

In addition to the analyses pointed above, the coal samples were oxidised by molecular oxygen in a manometric apparatus (Ivanov, Karshalykov, 1974; Ruschtev *et al.*, 1978; Markova *et al.*, 1995). The maximum ( $W_{max}$ ) and stationary ( $W_{stat}$ ) rates of oxidation, the duration of the induction period ( $\tau_{ind}$ , min.) and the apparent activation energies ( $E_A$ , kJ/kg) have been determined.

## RESULTS AND DISCUSSION

The microscopic data presented in **Table 2** reveal that xylain is composed of two maceral groups — huminite and liptinite and humovitrain consists mainly of textinite (49%). The content of gelinite in atrinite is negligible. The liptinite

maceral group is presented by resinite (45%). The percent of clay minerals and pyrite is minimum 1%.

Humovitrain is characterised by a higher content of gelinite (52%) and smaller amounts of textinite, densinite and

Table 2

Quantitative maceral composition of coal lithotypes

			Lithotype				
			Xylain	Humovitrain	Semifusain	Fusain	Liptain
Per total matter	Huminite	textinite	48	11	—	—	22
		ulminite	—	7	—	—	—
		atrinite	4	—	—	—	—
		densinite	—	9	—	—	1
		gelinite	2	50	—	—	6
		corpohuminite	—	—	—	—	—
	Liptinite	sporinite	—	—	—	—	—
		cutinite	—	—	—	—	—
		resinite	44	19	—	—	70
	Inertinite	semifusinite	—	—	52	3	—
		fusinite	—	—	35	90	—
		inertodetrinite	—	—	12	—	—
		sclerotinite	—	—	—	—	—
	Mineral matter	clay minerals	1	2	1	6	1
pyrite		1	2	—	1	—	
Per organic matter	Huminite	textinite	49	12	—	—	22
		ulminite	—	7	—	—	—
		atrinite	4	—	—	—	—
		densinite	—	9	—	—	1
		gelinite	2	52	—	—	6
		corpohumanite	—	—	—	—	—
	Liptinite	sporinite	—	—	—	—	—
		cutinite	—	—	—	—	—
		resinite	45	20	—	—	71
	Inertinite	semifusinite	—	—	53	3	—
fusinite		—	—	35	97	—	
inertodetrinite		—	—	12	—	—	
sclerotinite		—	—	—	—	—	

ulminite. The liptinite macerals are presented only by the presence of resinite (20%). The content of mineral matter is twofold higher than that of xylain, and that of pyrite and clay minerals is equal 2%.

Semifusain is composed mainly of the maceral semifusinite (53%), followed by fusinite (35%), and lastly — inertinite (12%).

It is seen that the fusinite content in fusain reaches 97% while that of semifusinite amounts only to 3%. The clay minerals are 6%, and pyrite is 1%.

Liptain contains basically resinite and textinite, the first maceral being in much higher amount (71%) than the second one which is 22%. Small amounts of huminite macerals, i.e. gelinite (6%) and densinite (1%) have been also found. Clay minerals are nearly absent in liptain.

The autooxidation processes results in increase in the reflectance values which tendency is more pronounced for the first members of the two genetic series — xylain and semi-

fusain, and the representative of the third genetic series — liptain (Fig. 1). After oxidation, the microhardness of xylain, humovitrain and semifusain increases, and that of fusain decreases. As a result of the lithotype autooxidation, the content of absorption water for xylain, semifusain and fusain is reduced, but for humovitrain, liptain and the average coal sample is increased. For all samples studied, the ash content and the volatile matter yield increase. The only exception is the average coal sample which is characterised by a decrease of the latter parameter.

For all lithotypes as well as for the average coal sample, the content of carbon and hydrogen drops, that of nitrogen and organic sulphur remains unchanged, and the oxygen percentage is increased. These alterations are relatively more substantial in case of xylain, semifusain and liptain as compared with those registered for fusain (Table 3, 4).

The autooxidation processes also lead to change in the content of the oxygen-containing functional groups in these

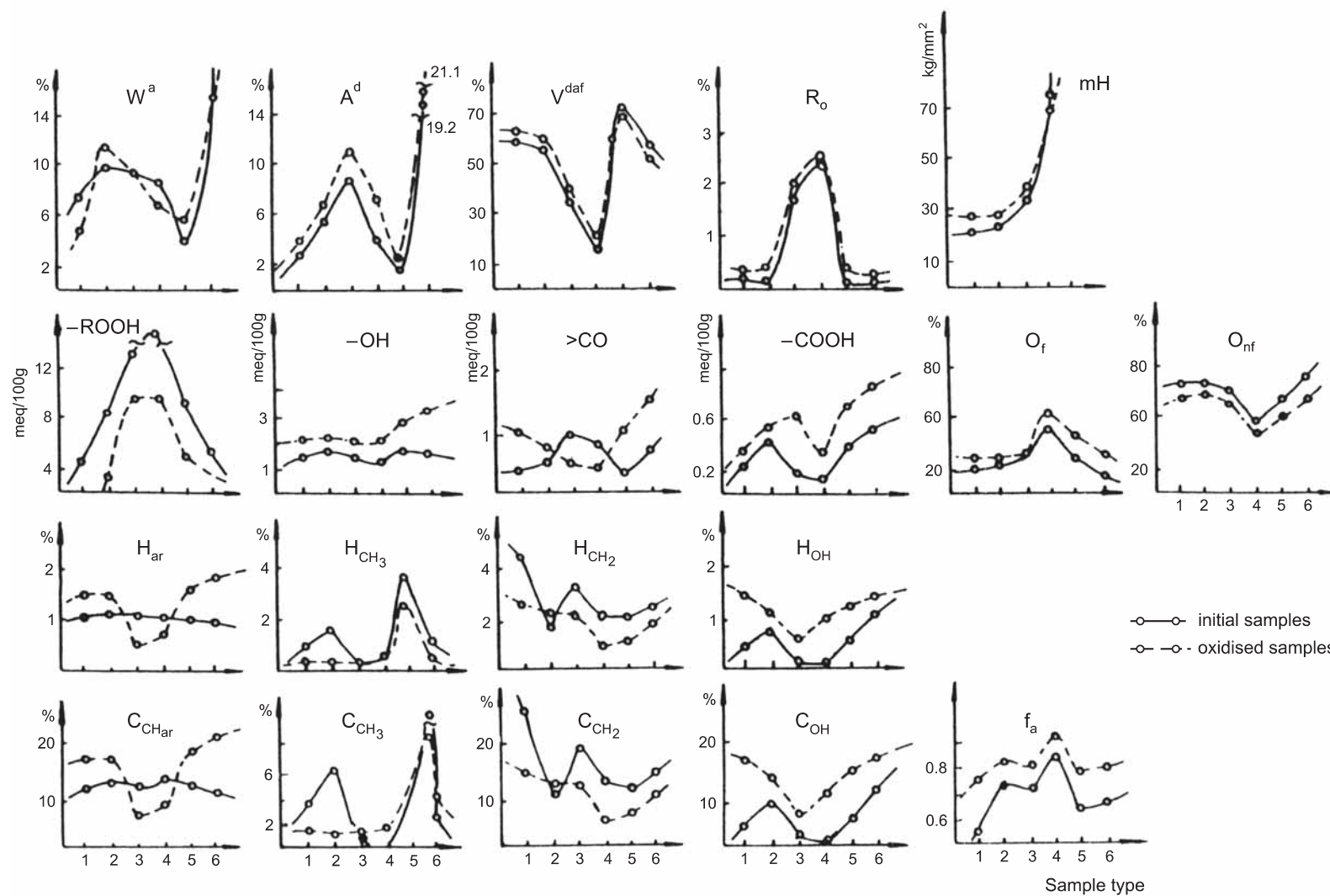


Fig. 1. Main parameters of lignite coals and their lithotypes

Sample type: 1 — xylain, 2 — humovitrain, 3 — semifusain, 4 — fusain, 5 — liptain, 6 — lignite coal

Table 3

Change of the elemental composition of East Maritza coal and lithotypes

Sample	T [°C]	C <sup>daf</sup> [%]	H <sup>daf</sup> [%]	N <sup>daf</sup> [%]	S <sub>o</sub> [%]	O <sup>daf</sup> [%]	H/C	O/C
Mean sample	initial	61.5	5.6	1.6	6.7	24.6	1.09	0.29
	150	61.4	5.4	1.6	6.4	25.2	1.06	0.31
Xylain	initial	68.7	6.8	0.7	4.7	19.1	1.19	0.21
	150	66.8	5.7	0.7	4.7	22.1	1.02	0.25
Humovitrain	initial	66.9	5.2	1.2	3.2	23.5	0.93	0.26
	150	65.7	4.8	1.2	3.2	25.1	0.87	0.29
Semifusain	initial	71.1	4.3	0.8	3.3	20.5	0.73	0.22
	150	69.8	3.5	0.8	3.3	22.6	0.60	0.24
Fusain	initial	87.2	3.1	0.8	1.9	7.0	0.40	0.06
	150	86.8	2.9	0.8	1.9	7.6	0.40	0.07
Liptain	initial	70.8	7.0	0.8	3.7	17.7	1.19	0.19
	150	69.7	6.1	0.8	3.7	19.7	1.05	0.21

Table 4

Activation energy of lignites and their lithotypes

Mean lignite coal sample	E <sub>a</sub> [kJ/kg]
Xylain	—
Humovitrain	60.04
Semifusain	52.76
Fusain	77.71
Liptain	134.82

coals which has been observed earlier during our investigations (Roushev *et al.*, 1975; Markova, 1976; Markova *et al.*, 1984; Markova, 1989). For all samples the oxidation results in rise of the content of acid groups (—OH and —COOH) (Fig. 1). The increase in the amount of the hydroxyl (phenol) groups is more intensive for the mean coal sample, liptain and xylain. Simultaneously, the content of carboxylic groups is the highest for the mean coal sample, liptain and semifusain. The alterations in the >CO percentage are quite various. The amount of >CO increases significantly for the members of the first and third genetic series as well as for the mean coal sample but for the members of the second genetic series it is reduced (Fig. 1). The changes for the mean coal sample, xylain and liptain are more substantial than for the other samples.

For all oxidised samples, the percentage of functional oxygen (O<sub>F</sub>) rises, and that of nonfunctional oxygen (O<sub>NF</sub>) decreases (Fig. 1). The ratio O<sub>F</sub>/O<sub>NF</sub> is increased, too. It should be noted that greater part of the total oxygen content in fusain is in the form of functional oxygen both before and after oxidation. A similar trend is observed for the oxidised liptain sample.

Another important correlation to be considered is that between reflectance and the oxygen-containing functional groups for the initial and the oxidised coal samples (Fig. 2). The increase of the reflectance is accompanied by a decrease of the

acid groups, i.e. —OH (phenol) and —COOH ones. This tendency is preserved for the oxidised samples. For the carbonyl groups such a correlation is not observed, it has even an inverse character. Similar conclusion can be drawn also for the percentage of the functional oxygen. With the increase of the reflectance, the percentage of the functional oxygen is raised and that of the nonfunctional oxygen is reduced (Fig. 2) both for the initial and oxidised samples. However, the drop of O<sub>NF</sub> content for fusain is more intensive and reaches values much smaller than those of the functional oxygen (Fig. 2).

The autooxidation process carried out at 150°C leads to rise of the content of aromatic hydrogen and carbon for the members of the first and third genetic series, i.e. xylain and humovitrain and liptain, and the mean coal sample, too (Fig. 1). The same parameters decrease their values for the members of the second genetic series, i.e. semifusain and fusain. The alterations registered for the mean coal sample and liptain are higher than those for xylain and humovitrain. The hydrogen and carbon content in the methyl groups rises (Fig. 1), these changes being more intensive for humovitrain, and partially for liptain. The content of hydrogen and carbon in the methylene groups is reduced in all samples, except for humovitrain which parameter increases negligibly. Particularly higher are these changes in case of xylain. It has been found that the content of H<sub>OH</sub> and C<sub>OH</sub> for the mean coal sample and all lithotypes rises (Fig. 1). The comparison between the various lithotypes reveals that these changes are more intensive for xylain, fusain and liptain, more moderate for humovitrain and the mean coal sample. The autooxidation also leads to rise in the aromaticity (f<sub>a</sub>), which is more intensive for xylain, liptain, and the mean coal sample.

The main kinetic parameters for the oxidation of lignite coal and their lithotypes are presented in Figure 2. With increasing temperature, the maximum rate of oxidation for xylain has a maximum at 110°C. The variations in the stationary rate follow the same trend. The induction period is the shortest at 120°C and at lower temperature the oxidation is retarded. For humovitrain, the value of the maximum rate is the highest at

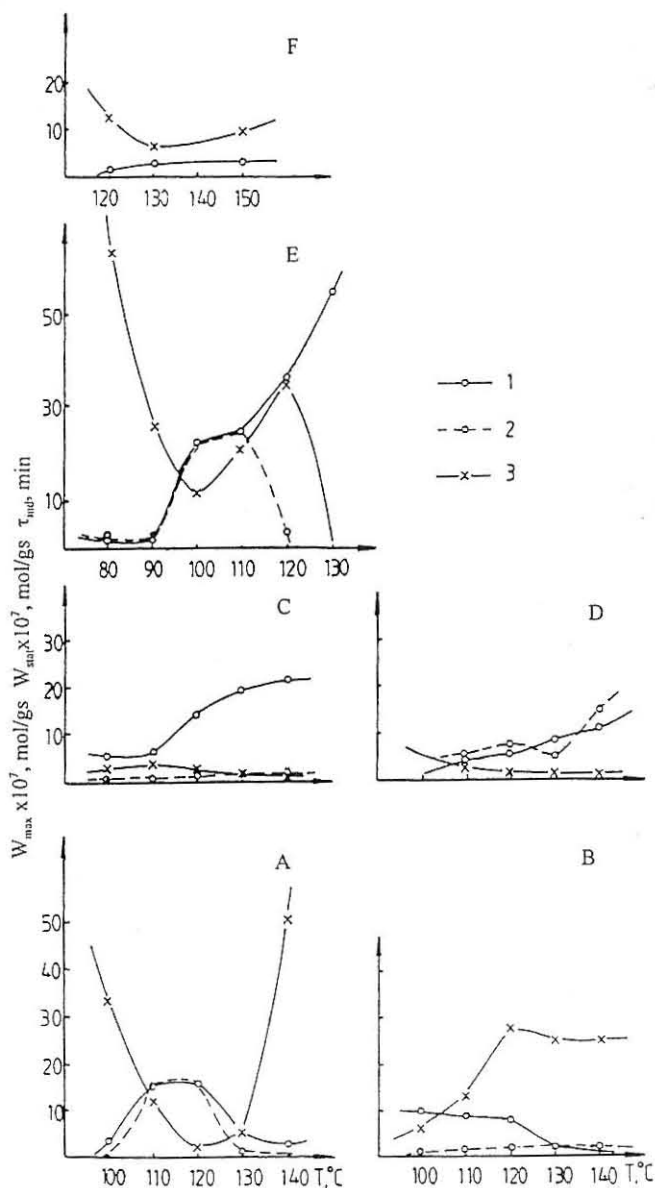


Fig. 2. Temperature dependence of the kinetic parameters of lignite coals and their lithotypes

A — xylain; B — humovitrain; C — semifusain; D — fusain; E — liptain; F — lignite coal; 1 — maximum rate  $W$ , [(mol/g s) × 10], 2 — stationary rate,  $W$ , [(mol/g s) × 10], 3 — induction period,  $\tau$ , [min]

100°C. Contrary to it, at this temperature the stationary rate attains its minimum value. The induction period for humovitrain oxidation is the shortest at 100°C.

The temperature increase in case of semifusain autooxidation leads to rise of the maximum and stationary rates, and decrease of the induction period. The increase of the maximum rate of oxidation is more significant than that found for the stationary rate.

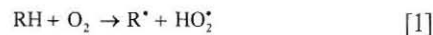
Up to 100°C fusain does not undergo oxidation. Only after 110°C its maximum rate increases gradually. The stationary rate begins to rise after 140°C. Simultaneously, the induction period decreases gradually.

Liptain autooxidation is characterised by an increase both of maximum and stationary rate with temperature, particularly above 90°C. The latter oxidation has the longest induction period.

With the autooxidation of the mean lignite coal sample, the rise in the maximum rate is more intensive below 130°C than at higher temperatures. The duration of the induction period decreases with temperature rise and at 130°C it has a minimum value.

The kinetic parameters and the apparent activation energy of the autooxidation process reveal that xylain is more susceptible to oxidation than humovitrain. It should be also noted the intensive oxidation of semifusain. The higher activation energy for fusain suggests that this lithotype is more stable against oxidation and confirms the proceeding of the oxidation reaction in the kinetic region. The value of the activation energy for liptain suggests a high activation barrier for the initiation step of the overall process. The low activation energy, found for lignite coal similar to that of peat (Roushev *et al.*, 1978), demonstrates the similar character of the mechanisms of these autooxidation process and the participation of similar easily oxidizable and dominating structures.

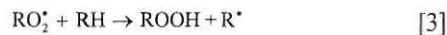
The overall results from the study of the autooxidation processes of lignite coals and their lithotypes at 150°C allow us to assume a probable mechanism for these processes from the standpoint of the chain-radical theory of liquid phase oxidation of hydrocarbons (Semenov, 1934; Emanuel', Knorre, 1962; Denisov *et al.*, 1975). The observed generation of paramagnetic particles (Markova *et al.*, 1993) during the oxidation of these lithotypes supports the proceeding of the following reaction:



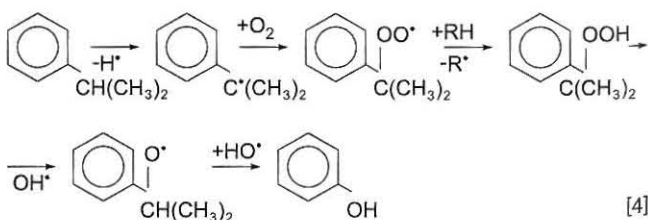
The generation of free radicals in coal induces their oxidation and formation of peroxide radicals:



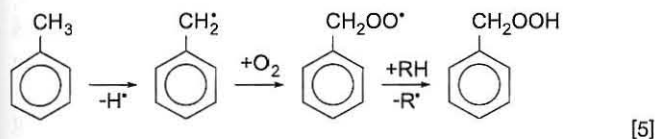
The latter react further with other radicals or groups leading to the formation of peroxides and regeneration of alkyl radicals —  $R^*$ , which propagate the chain:



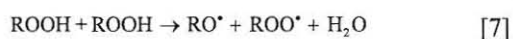
The kinetics of peroxides change during coal autooxidation at 150°C reveals the probable formation of two types of peroxides. The first one — hydroperoxides, decompose readily at this oxidation temperature, and the second type which are thermally more stable, includes polymer or endocyclic type peroxides (Windaus, Brauker 1928; Kucher *et al.*, 1980). Probably the oxidation of xylain yields tertiary hydroperoxides that is also confirmed by the reduced percentage of  $-CH_3$  and  $-CH_2$  groups (Fig. 1):



The decrease of the  $-\text{CH}_3$  amount and the rise of  $-\text{CH}_2$ , the analytical moisture and  $-\text{OH}$  groups registered for humovitrain suggests the formation of primary hydroperoxides:

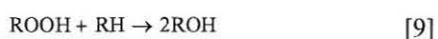


The decomposition of the thermally (at this temperature) unstable hydroperoxides could be accomplished via monomolecular or bimolecular reaction pathway:

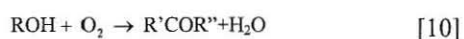


The proceeding of the above processes is also confirmed by the termination of the kinetic chain through deactivation of the free radical in the system —  $\text{R}^\bullet$ ,  $\text{RO}^\bullet$ ,  $\text{RO}_2^\bullet$ ,  $^\bullet\text{OH}$  at the addition of an inhibitor — phenol and aniline (Rustchev, Jetscheva-Markova, 1969; Roushev *et al.*, 1975; Markova, 1976).

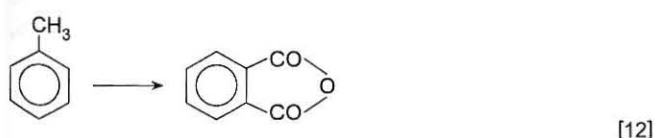
The results from the IR and functional analysis together with the data obtained in our earlier investigations (Roushev *et al.*, 1975; Markova, 1976, 1989; Markova, Petrova, 1984; Saranchuk *et al.*, 1994) indicate that peroxides play the role of intermediates in the process of further molecular products formation:



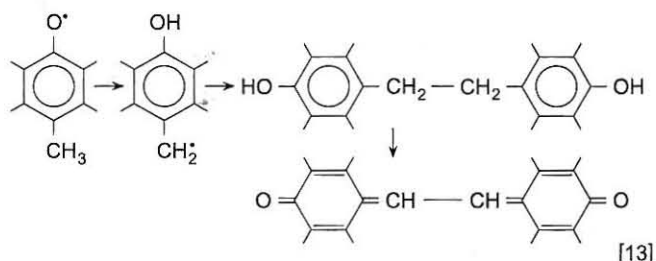
Simultaneously, the phenol and carbonyl groups, present in the coal macromolecule, are further oxidized as shown below:



The data from the ultimate analysis (Fig. 1) combined with the kinetics of the oxygen-containing functional groups alterations as well as some of the ESR results, i.e. the PMC concentration and the ESR signal linewidth (Markova *et al.*, 1993), point out that reactions [8] and [10] are dominating for xylain and lead to higher concentrations of  $>\text{CO}$  groups. Simultaneously, the amount of  $-\text{OH}$  increases, too. For humovitrain in addition to the two reactions typical for xylain, proceeding to a lesser extent, the reactions yielding acids [11] take place with a higher rate. The change of the content of oxygen-containing groups suggests that the humovitrain autooxidation concerns mainly the phenol groups which are further converted into carboxyl ones. The reduced content of  $-\text{CH}_3$  groups for this lithotype suggests the formation of oxygen-containing cyclic structures of phthalate type:



The increase in the PMC during humovitrain oxidation (Markova *et al.*, 1993), the higher amount of  $-\text{OH}$ ,  $>\text{CO}$  and  $-\text{CH}_2$  functional groups in its macromolecules, as well as the reduced  $-\text{CH}_3$  amount and the increased aromaticity confirm the proceeding of rearrangement processes of aroxyl radicals into benzyl one. The latter undergo dimerization and oxidation giving quinones:



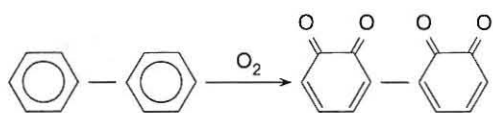
Thus, it may be concluded that the first product of the microbial-oxidative destruction of the lignin-cellulose tissues, i.e. xylain, composed mainly of textinite (Table 2) with preserved lignite matrix partially filled with resinite (Šiškov, 1988), is oxidised predominantly to  $>\text{CO}$  containing products. The increased content of  $-\text{OH}$  groups may be related to the formation of tertiary hydroperoxides which precursors are the tertiary carbon atoms of textinite.

The rearrangement of the aroxyl radicals into benzyl ones followed by dimerization and oxidation to quinones after reaction [13] is also relatively intensive. The xylain oxidation leads to the formation of relatively unstable structures which is also confirmed by the lower value of the activation energy.

The final product of the microbial-oxidative destruction of the lignin-cellulose tissues, i.e. humovitrain, is oxidised less intensively than xylain. Its autooxidation is characterised by the formation of primary hydroperoxides, hydroxyl (phenol) and carboxylic groups. The rearrangement of the aroxyl radicals into benzyl ones with their consecutive dimerization and oxidation is also registered. The autooxidation process, similarly to that of xylain, occurs with a high intensity which is probably related to destructive reactions resulting in water liberation (Kasatochkin, Larina, 1975).

The first member of the second genetic series, semifusain — fusain, resulting from the thermooxidative processes, consists of partially preserved lignin-cellulose tissues and resinite and a higher content of oxygen-containing functional groups. At  $150^\circ\text{C}$ , its carbonyl groups are predominantly oxidized to carboxyl ones via reaction [11]. These oxidation steps are accompanied by the occurrence of destructive reactions which comprise a part of the non-functional oxygen. This assumption is supported by the reduced percentage of aromatic hydrogen and carbon, and the  $-\text{CH}_3$  groups formation (Fig. 1) (Hofmann, 1963; Saranchuk *et al.*, 1994).

The end member of this genetic series — fusain, differs by its mechanism of oxidation from the other lithotypes. Its peculiar biphenyl structure (Markova *et al.*, 1993; Markova, Budinova, 1996) and the higher content of carbonyl groups in the oxidized samples (Fig. 1) point that the oxidation takes place through the following reaction:



[14]

The higher amount of  $-OH$  groups could be attributed to the rearrangement of semiquinones to parabenzoquinones. In contrast to the other lithotypes, fusain oxidizes much more slowly as evidenced by the higher value of the activation energy of oxidation.

Liptain which is formed under direct oxygen assess and is composed of fossil plant fragments highly impregnated by resinous components (Šiškov, 1988) is oxidized much more readily than other lithotypes. This fact has been also observed in previous kinetic studies of Markova and Ivanov (1992). Liptain which consists of lignin-cellulose tissues of textinite structure, impregnated with terpene resinite (Šiškov, 1974, 1976), begins to oxidize at relatively low temperatures (Markova, Ivanov, 1992; Markova *et al.*, 1995). This observation could be explained by the more active participation of acid structures, i.e.  $-COOH$  and quinone  $>CO$  type (Markova *et al.*, 1984) in the oxidation process. The kinetics of  $-OH$  and  $>CO$  groups variations with the simultaneous decrease in  $-CH_3$  groups and the higher aromaticity suggest the formation of benzyl radicals, their further dimerization and oxidation to quinones. The value of the activation energy, determined from the dependence — temperature — induction period, shows that the rate of initiation is characterised by a higher activation barrier. Thus, it can be assumed that upon liptain

oxidation oxygen attacks the energetically high chemical bonds on its surface.

The mechanism of the autooxidation processes occurring in the mean coal sample, similar to that in the lithotypes, has a chain-radical character (Markova, 1976, 1989). It is known that the oxidation of the aryl type radicals, present in them, yields peroxides and phenols, while those of aroxyl type lead to the formation of a number of oxygen-containing compounds such as peroxides, phenols, aldehydes, ketones, lactones, quinones and acids (Kuhl, Smolinska, 1965; Forrester *et al.*, 1968; Vasileva *et al.*, 1974). The increased accumulation of phenol and carbonyl groups most probably is due to the presence of a higher concentration of aroxyl radicals. On the other hand, the high content of terminal nonaromatic structural elements in the low rank coal macromolecule results in accumulation of carboxylic groups. The change in  $-OH$ , the reduced percentage of  $-CH_3$  and  $-CH_2$  groups (Fig. 1) points to the formation of tertiary hydroperoxides via reaction [4]. The high concentration of aroxyl radicals in the macromolecule of these coals, the decrease in the  $-CH_3$  and  $-CH_2$  content, and the rise of the aromaticity (Fig. 1) is indicative of the rearrangement of the aroxyl radicals in benzyl which are further dimerized and are converted into quinones according to reaction [13].

The results obtained from the complex study of the autooxidation processes in lignite coals and their lithotypes show that they take place via radical-chain mechanism. However, it has been found that in spite of the similar genesis the members of the separate genetic series differ in their oxidation mechanism. The latter depend on the individual way of development of each lithotype and the generated physico-chemical structures.

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