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Investigation of low-temperature autooxidation processes in bituminous coal lithotypes

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Abstract

The kinetics of autooxidation processes in sub-bituminous (vitrain and clarain) and high-bituminous (clarain) coal lithotypes has been calculated by the method of Coats and Redfern. The differences in the E_a values of the thermooxidative processes show structural changes in the investigated lithotypes. Their macerallar compositions and the temperature affect the reactivity of the coal samples during oxidation by atmospheric oxygen.

The results obtained suggest differences between the mechanism of the autooxidation processes occurring both in the homogeneous lithotype vitrain and in the heterogeneous clarain of equal coalification degrees, and between the clarain samples of various coalification degrees.

Keywords: Activation energy; Autooxidation; Clarain; Coal lithotype; Macerals; Vitrain

1. Introduction

Thermal analysis has been successfully used for the elucidation of the kinetics of processes occurring in coal lithotypes [1–5]. For calculation of the kinetic parameters of these processes in bituminous coal, Van Krevelen and Schuyer [1] have proposed a differential method which represents a modification of the method of Freeman and Caroll [3].

Recently, it has been reported that the method of Coats and Redfern can be applied for evaluation of the kinetics of the thermal processes of coal and low-rank coal lithotypes [6,7]. The results allow this method to be used for studying the autooxida-

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tion processes occurring in coals of higher coalification degree, i.e. sub-bituminous and high-bituminous coals.

Although much has been reported on the chemistry of coal and its oxidation, there is very little literature data on the effect of the coal maceral structure on the autooxidation of highly coalified material.

In this paper, an attempt is made to link the kinetics of autooxidation processes in coal lithotypes with their maceral structures.

2. Experimental

For the present investigation, vitrain and clarain samples from the Bobov Dol basin and two clarain samples from the Pirin basin were used. The coals from the Bobov Dol basin have a brilliant brown appearance, with a coalification degree of O_2, and those from the Pirin basin are between brown and black, with a coalification degree of O_3. The sample characteristics are presented in Table 1.

Quantitative maceral analysis was carried out by an MPT 2 Opton microscope, in reflected light with cedar-oil immersion (40 × objective, 12.5 × eye-piece) by recording an average number of 500 points per sample with an Eltinor automatic point-counter [8].

The samples of particle size below 0.25 mm were oxidised for 60 h at 150 and 200°C, under static air atmosphere.

The TG–DTG–DTA studies of both the initial and oxidised lithotype samples were carried out on a derivatograph Q 1500-P (MOM-Hungary). The analysis was performed in static air atmosphere, at a heating rate of 10°C min^{-1} in a platinum crucible; Al_2O_3 was used as the reference substance.

The activation energy of the initial and oxidised samples in the temperature range 50–150°C was calculated by the Coats–Redfern method [6]. The calculations were made according to a suitable computer programme.

Table 1
Characteristics of coal lithotypes

Lithotype	Proximate analysis/wt%			Elemental analysis, (daf)[b]/wt%						
	Moisture	Ash[a]	Volatile matter	C	H	N	S	O	H/C	O/C
Bobov Dol basin										
1. Clarain	5.4	5.3	46.6	74.5	5.0	1.2	2.2	17.4	0.81	0.18
2. Vitrain	5.4	3.3	46.1	74.2	5.5	1.0	1.3	18.0	0.89	0.18
Pirin basin										
3. Middle sample clarain	15.7	10.1	45.5	75.2	5.4	1.7	1.4	16.3	0.86	0.16
4. Clarain	5.1	9.1	49.0	75.0	5.6	1.1	1.3	16.5	0.90	0.17

[a] Ash of dry matter.
[b] daf, dry ash free.

3. Results and discussion

The quantitative maceral analysis (Table 2) shows that the macerals of the huminite group (87–90%) are the main petrographic components in the Bobov Dol coals. The macerals of the vitrinite group (81–87%) are predominant in the Pirin coals. The macerals of the liptinite (L)-exinite (E) groups are poorly represented: 3% in the samples from the Bobov Dol basin and 6–8% in the samples from the Pirin basin.

The resinite in the Bobov Dol samples has impregnated the lignin-cellulose macerals and thus makes quantitative determinations difficult.

The inertinite macerals are present in small amounts (Table 2) and the content of inorganic minerals is also low: 5–8% in Bobov Dol coals and 11% in Pirin coals.

The TG/DTA curves of the investigated lithotypes are shown in Figs. 1 and 2. The values of the activation energy of the thermooxidative processes in the temperature range 50–150°C of both the initial and the oxidized samples are given in Table 3. The differences observed in the E_a values of the samples studied are related to the different mechanisms of the autooxidation processes occurring in them.

Comparing the values of E_a of the initial samples of both lithotypes, vitrain and clarain (Bobov Dol basin), it has been found that the E_a of the initial vitrain is lower than that of clarain (Table 3, Nos. 1 and 2). This observation could be attributed to

Table 2
Quantitative maceral analysis (wt%)

Bobov Dol basin				Pirin basin			
Clarain	Vitrain	Maceral	Group maceral	Group maceral	Maceral	Middle sample clarain	Clarain
1	2					3	4
23	36	Textenite			Telinite	10	16
32	30	Ulminite			Telocollinite	19	8
25	20	Denssinite			Gelocollinite	–	–
5	3	Artinite	Huminite	Vitrinite	Desmocollinite	52	63
–	–	Gelinite	H	V	Corpocollinite	–	–
2	1	Corpohuminite			Vitrodetrinite	–	–
2	2	Sporinite			Sporinite	7	6
1	1	Cutinite	Liptinite	Exinite	Cutinite	–	–
–	–	Resinite	L	E	Resinite	1	–
1	2	Semifusinite			Semifusenite	1	–
1	–	Macrinite	Inertinite				
1	1	Sclerotinite	I				
–	–	Inertodetrinite					
5	3	Pyrite			Pyrite	3	3
3	2	Argillaceous minerals			Argillaceous minerals	8	6

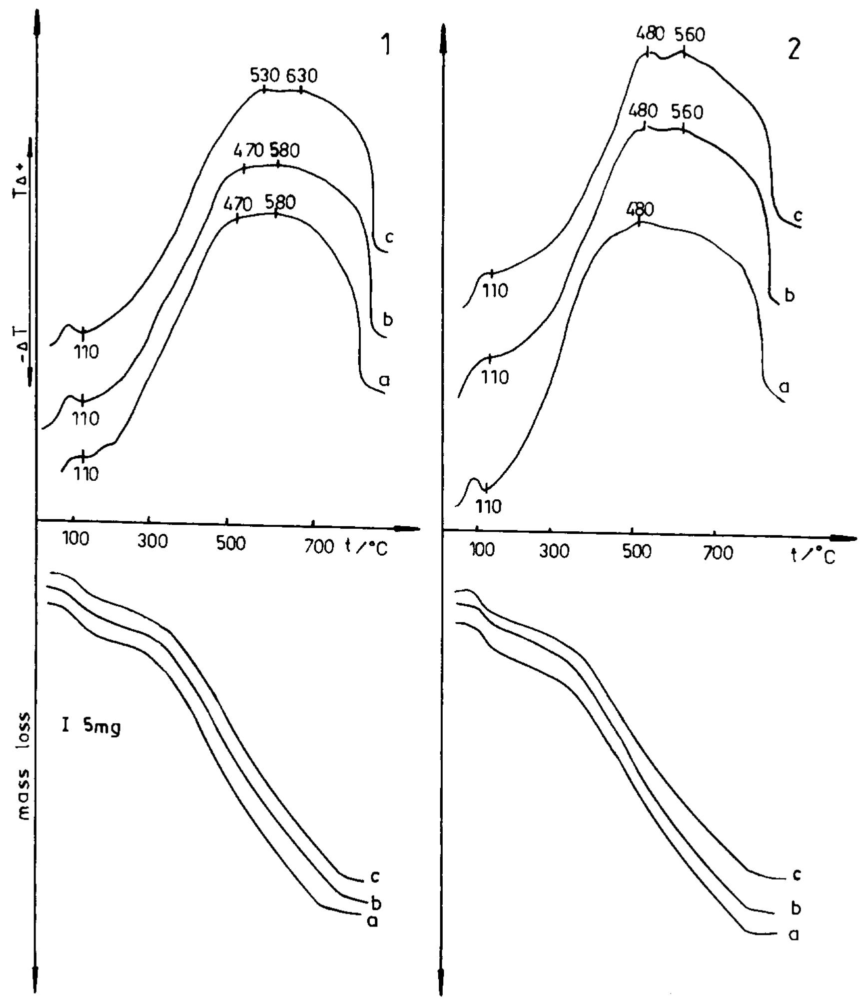

Fig. 1. TG/DTA curves of the clarain (1) and vitrain (2) from the Bobov Dol basin: a, initial sample; b, oxidised sample at 150°C; c, oxidised samples at 200°C.

variation in the petrographic composition of the investigated lithotypes. The higher content of the easily oxidisable texinite [9] in vitrain, 36%, lowers the energetic barrier of the autooxidation process.

Differences have been observed between the values of E_a of the various initial clarain samples from the Pirin basin (Table 3, Nos. 3 and 4). This is probably due to their different contents of telenite and desmokolinite: the higher content of telenite and desmocollinite in clarain sample No. 4 (Table 2) results in an E_a decrease .

The oxidation of the vitrain sample from the Bobov Dol basin at 150 and 200°C leads to an increase in the E_a of the thermooxidative processes compared to those of the

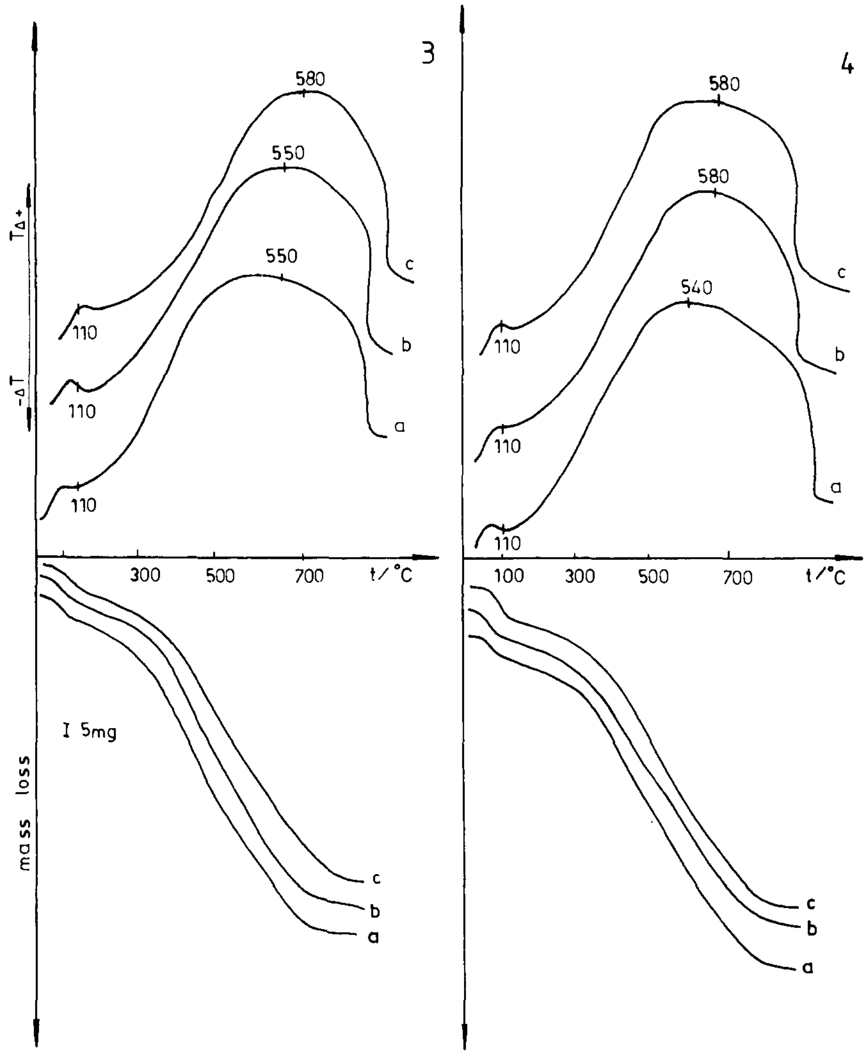

Fig. 2. TG/DTA curves of the middle samples clarain (3) and vitrain (4) from the Pirin basin: a, initial sample; b, oxidised sample at 150°C; c, oxidised samples at 200°C.

initial samples: 2.3 kJ kg^{-1} for the samples oxidised at 150°C, and 11.6 kJ kg^{-1} for those oxidised at 200°C. These results confirm the formation of thermally more stable structures during the oxidation of vitrain. These data confirm the results obtained by Markova and Valčeva for the same coal samples [8].

The values of the activation energy for clarain samples from both basins oxidised at 150°C are essentially higher than those of the initial samples (Table 3, Nos. 1, 3 and 4).

The higher content of the easily oxidisable ulminite in the Bobov Dol clarain enhances its interaction with atmospheric oxygen at 150°C and results in the formation

Table 3
Kinetic parameters of coal lithotypes

Sample	Temperature of oxidation/°C	Time/h	Activation energy[a] E_a/ kJ kg^{-1}	Pre-exponential factor, A	Correlation coefficient
Bobov Dol Basin					
1. Clarain	–	–	66.9	6.25×10^{-3}	−0.9960
	150	60	71.6	2.78×10^{-2}	−0.9949
	200	60	58.0	3.65×10^{-4}	−0.9987
2. Vitrain	–		59.7	5.51×10^{-4}	−0.9898
	150	60	62.0	1.25×10^{-4}	−0.9914
	200	60	71.3	2.79×10^{-2}	−0.9957
Pirin basin					
3. Middle sample clarain	–	–	62.9	2.10×10^{-3}	−0.9820
	150	60	70.3	2.03×10^{-2}	−0.9804
	200	60	64.1	3.77×10^{-3}	−0.9910
4. Clarain	–	–	58.4	4.64×10^{-4}	−0.9932
	150	60	68.2	1.18×10^{-5}	−0.9894
	200	60	46.2	1.90×10^{-2}	−0.9890

[a] Order, n, from 1 to 2.2.

of stable structures. The oxidation of the clarain samples from the Pirin basin shows a similar trend: the E_a of the clarain sample No. 3 increases by 7.4 kJ kg^{-1}, and that of No. 4 by 9.8 kJ kg^{-1}. The high content of desmocollinite and telenite in the clarain samples from the Pirin basin is regarded as being responsible for the formation of structures stable to oxidation.

The values of the activation energy for the clarain sample from the Pirin basin oxidised at 200°C (Tables 3 and 4) decrease. At higher temperature the radical centres are probably activated, resulting in the formation of thermally unstable and easily oxidisable coal structures.

4. Conclusions

The results obtained suggest differences in the mechanisms of the autooxidation processes occurring in the homogeneous lithotype vitrain and in the heterogeneous clarain of equal coalification degrees (Bobov Dol basin), and in the clarain samples of various coalification degrees (Bobov Dol and Pirin basins). Generally, the differences in the E_a values of the thermooxidative processes indicate structural changes in the investigated lithotypes of sub-bituminous (vitrain and clarain) and high-bituminous (clarain) coals during their oxidation by atmospheric oxygen. Their maceral compositions and the temperature affect the reactivity of the coal samples during oxidation.

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