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DTA AND TGA OF COALS AND BITUMINOUS ROCKS

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ABSTRACT

DTA and TGA have been applied to study different genetic types of coals: humic, saprohumic (cannel), sapropellitic (boghead) coals and bituminous rocks. The effect of the petrographic and chemical composition of their organic matter on the character of the DTA- and TG- curves has been demonstrated.

INTRODUCTION

The success of thermography in recent years in the solution of geochemical and petrochemical problems/1,2/made it possible for us to use DTA and TGA to study different genetic types of coal and bituminous rocks.

MATERIAL AND METHODS

The experiments were carried out on selected samples of the basic genetic types of coal: humic, saprohumic (cannel), sapropellitic (boghead) coals and bituminous rocks, represented in the coal basins in Bulgaria: Pirin, Borov Dol and Nikolaevo. The coal-bearing and bituminous sediments of the Pirin basin are of Middle-Upper Oligocene age, whereas those of the Borov Dol and Nikolaevo basins are of Upper Eocene age. The characteristic chemical and petrographic parameters of the samples are given in Table 1.

The experiments were organized on a predetermined programme and were carried out using a derivatograph produced by the firm MOM (Budapest). Samples with particle size below 0,25 mm were placed in platinum crucibles. The heating rate was 10 $^{\circ}$C/min until 900 $^{\circ}$C. The inert substance was Al_2O_3.

RESULTS AND DISCUSSION

The thermograms obtained are shown on Fig.1. At the beginning of the DTA-curves of humic coals, as well as of cannel and boghead coals, there is a clearly manifested endothermal effect (100°-

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120°C), which is due to the hygroscopic moisture released. The amount of this moisture, determined by chemical methods, is correlated with the intensity of this effect and with the respective decrease in the mass (Figs.1,2, Table 1). The greater intensity of this thermal effect in humic coals is related to the increased content of humovitrinite, respectively of the functional oxygen groups which are the carriers of the hydrophilic properties.

xothermal effect (330°-340°C) dominates in the thermograms of humic coals, resulting from the decomposition of the humic polymer. With the advancing degree of coalification, its area decreases in the following order: Nikolaevo, Pirin, Borov Dol. The mass of the Nikolaevo and Borov Dol samples decreases by 8%, that of the Pirin sample-by 7 %. For the cannel and boghead coals such a thermal effect is registered at 320°C. In the case of boghead coals the area and the change of their mass (6,5%) are greater compared with the cannel coals (4,5 %), which is probably related to the increased percentage of liptinite-exinite (alginite), respectively to the content of oil components/3/.

Table 1

Characteristics of the initial samples

Type of the sample	W^a %	A^d %	Petrographic composition, %				Functional oxygen groups, mgeqv/1g			
			H	L	I	M	-OH	=CO	-COOH	total
Humic coals	6,5	3,9	82	16	1	1	1,5	0,6	0,4	2,5
Cannel coals	2,3	21,8	26	49	1	24	0,3	0,3	0,1	0,7
Bitum. rocks	1,2	68,8	3	9	-	88	0,2	0,4	0,2	0,8
Humic coals	7,3	10,6	85	4	1	10	1,3	0,5	0,4	2,2
Boghead coals	3,1	45,1	8	75	2	17	0,3	0,3	0,1	0,7
Bitum. rocks	1,7	71,0	5	20	-	75	0,2	0,4	0,2	0,8
Humic coals	0,3	23,8	74	12	1	13	1,8	1,0	0,5	3,3
Bitum. rocks	2,7	83,2	3	14	-	83	0,3	1,6	0,3	2,2

A second less intensive exothermal effect (430°-460°C) is registered for the humic coals, whose maximum temperature increases with the increased coalification (Fig.1). At this temperature the decrease in the mass is considerable (Fig.2). This effect is assumed to be related to the processes of splitting of the phenolic hydroxyl groups, breaking of the -C-C- bonds and partial transition of the coal matter into plastic state. Three exothermal effects - at 320°, 450° and 540°C- appear for boghead coals, while for cannel coals there is only one-at 320°C. In the above thermal effects both boghead and cannel coals lose a large part of their mass, the losses being considerably greater for boghead coals. These differ-

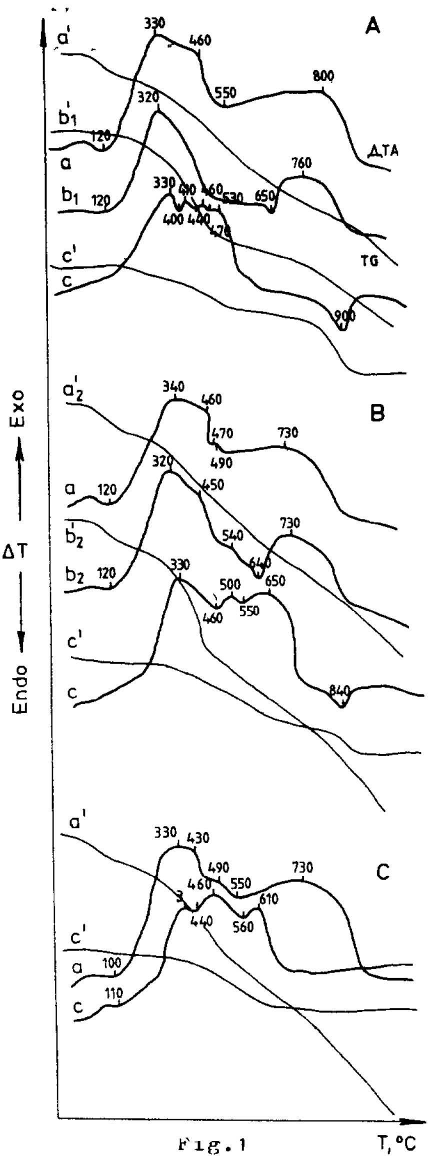

Fig.1

DTA- and TG-curves of coals and bituminous rocks from Pirin(A), Borov Dol (B) and Nikolaevo(C) a-humic coals;b_1-saprohumic(cannel) coals,b_2-sapropellitic (boghead) coals,c-bituminous rocks;

ences are probably due both to their different lipid composition and to the presence of lignine components in cannel coals/3/.

The DTA-curves of humic coals reflect intensive endothermal effect (550°C) related to secondary gas release and transition of the coal matter into plastic state. The weak intensity of this thermal effect demonstrates their poor clinkering capacity. In cannel and boghead coals such an endothermal effect is manifested at 640°-650°C (Fig.1).

For humic coals the high-temperature exothermal effect in the 700°-800°C interval is connected with the formation of semi-coke. A similar exothermal effect is also found for boghead and cannel coals. All three types of coal lose a large part of their mass at these high temperatures.

The DTA- and TG-curves of the bituminous rocks differ essentially from those of humic,boghead and cannel coals(Fig.1). In the 330°-650°C interval there is a series of exo- and endothermal effects, evidently related to the thermooxidative destruction taking place in three stages. at 330, 410°-510° and 530°-610°C.The first maximum corresponds to the processes of low-temperature oxidation, while the second and third maxima are determined by the glowing of the bituminous rocks,im-

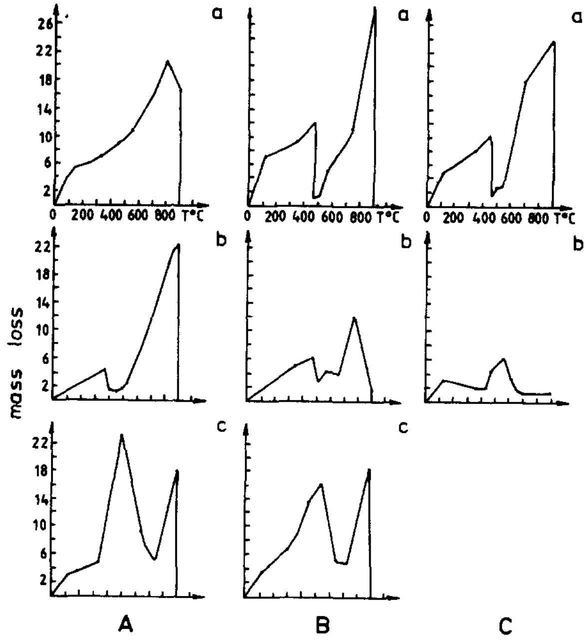

Fig.2
Change of the mass of coals and bituminous rocks from Pirin(A),Borov Dol (B) and Nikolaevo(C) deposits
a-humic coals;b-bituminous rocks; c_1-cannel coals;c_2-boghead coals;

poverished in organic matter/4/. Their mass losses are the highest at 330°C (Fig.2). Above 540°C there appear endothermal effects, related to processes of release of the constitutional water from the clayey minerals which are well represented in these rocks. An endothermal effect (420°C) is registered for the Pirin bituminous rocks, related to the high pyrite content (14 %).

The observed differences for the various genetic types of coal could be explained by the different petrographic and chemical composition, predetermined by the type of the original vegetation. While for the humic coals there is predominance of aromatic and branching aliphatic structures produced by higher vegetation, sapropellitic deposits are dominated by aliphatic structures related to cycloparaffin chains and hydroaromatic rings,which result from the predominant participation of lower algal vegetation in their formation.

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