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DIFFERENTIAL-THERMAL AND THERMOGRAVIMETRIC ANALYSIS OF SOME GAGATES FROM BULGARIA

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The thermal behaviour of three gagates (Bulgaria) was investigated by DTA and TG. The characteristic endo- and exoeffects and the sequence of the thermal stabilities are established.

The special types of solid fuels include the gagates [1, 2]. These rarely-occurring, shiny black formations are detected included in sedimentary rocks. A major contribution to the geological and petrological investigation of gagates in Bulgaria was made by Minčev [3–7]. This type of solid fuels has not been studied so far by thermal analysis, which has been successfully applied for other types of fuels [8–10].

Experimental

Materials and methods

Three gagate samples from different morphotectonic zones in Bulgaria (the Moesian Platform, the Fore-Balkan folded zone and the Balkan zone) were selected for study. The gagates from the Nikolaevo deposit are identified as separate inclusions in the Aptian sediments of the Moesian Platform, at a depth of about 4 m. The gagates from the Kaleitza deposit, which are Hauterivian in age, are discovered in the central part of the Fore-Balkan folded zone, whereas the Cenomanian deposits of gagates from the Belnovruh deposit are found in situ in the sandstones and silstones of an abandoned coal mine in the Balkan zone. The general characteristics of the initial samples are presented in Table 1. Hygroscopic moisture content (W^a) was established via SMEA standard 751–77, ash content (A^d) via SMEA standard 1461–78, and volatile matter content via Bulgarian State Standard 10239–73. The elemental analyses were performed with an apparatus made by Leco. Microhardness was determined by the method of standard loading, using

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Table 1 Characteristics of the initial samples

Tectonic zone	Moesian platform	Fore-Balkan folded zone	Balkan zone
Deposit	Nikolaevo	Kaleitza	Belnovruh
Geological age	Aptian	Hauterivian	Cenomanian
Moisture, W^a, %	7.9	2.2	3.7
Ash, A^d, %	1.8	6.6	1.8
Volatile matter, V^{daf}, %	55.9	50.3	53.2
Carbon, C^{daf}, %	72.3	77.6	80.1
Hydrogen, H^{daf}, %	5.7	5.8	5.9
Reflectance, R_0, %	0.21	0.40	0.42
Microhardness, mH, 10^7 Pa	27.3	39.5	39.8

a NU–1 microscope (Carl Zeiss, Jena) with an additional "H" device [11]. Reflectance was determined with the same microscope, but with an additional microphotometric CBU–4 device and objective 54^x (Leitz) immersion. Synthetic sapphire with reflectance in immersion $R_0 = 0.60\%$ was used as standard (Bulgarian State Standard 15201–80). The analysed samples had a low ash content (1.8–6.6%), an increased hidrogen content (5.7–5.9%) and a high yield of volatile substances (50.3–55.9%), which is characteristic of this genetic type of coal. These gagates exhibit high microhardness ($27.3\text{–}39.8 \cdot 10^7$ Pa) and low reflectance (0.21–0.42%), which differentiates them from vitrain [3].

The experiments were carried out with an OD–102 apparatus (Hungarian Optical Works, Budapest), at a heating rate of 5 deg min^{-1}, with Al_2O_3 as reference material, a platinum crucible and an uncontrolled air atmosphere.

Results and discussion

The DTA and TG curves obtained are shown in Fig. 1. The endoeffect at about 100°, related to the hygroscopic moisture content, is manifested only in the DTA curve of the sample from the Nikolaevo deposit, which has a higher moisture content (7.9%) than those of the other two samples (Table 1).

In the temperature range 200–500°, the DTA curves display exoeffects which differ in surface area and intensity. Whereas the gagate from the Nikolaevo deposit is characterized by a strong exoeffect with maximum at 240° (Fig. 1a), in the remaining two samples exothermic processes take place in the range 200–350° (Fig. 1,b, c). A second exoeffect, with a large surface area and high intensity appears in the DTA curve of the gagate from Nikolaevo deposit (Fig. 1a). Similar, though

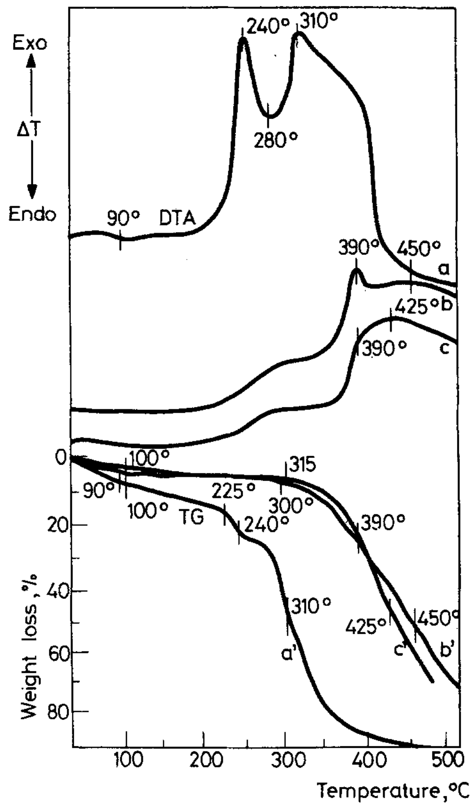

Fig. 1 DTA and TG-curves of gagates: a, b, c – DTA-curves; a', b', c' – TG-curves; a, a' – from Nikolaevo; b, b' – from Kaleitza; c, c' – from Belnovruh

considerably weaker exoeffects with maximum at 390° are recorded for the samples from the Kaleitza and Belnovruh deposits (Fig. 1,b, c). Their intensities and the temperatures at which they are manifested differ for the three deposits investigated. Above 400° the sample from Nikolaevo exhibits no thermal effect (Fig. 1,a). In the interval 425–450° the remaining two samples display slight exoeffects with maxima which are rather hard to determine. Only one endoeffect is observed in the DTA curve of the gagate from the Nikolaevo deposit, which distinguishes this sample from the other two.

The TG curves of the three samples start with a decrease in mass at 90–100°, which is proportional to the analytical moisture content (Fig. 1,a, b, c, Tables 1 and 2).

Comparison of the TG curves reveals that the gagate from the Nikolaevo deposit possesses a considerably lower thermal stability than those of the other two

Table 2 Change of the mass of gagates, %

Type of thermal effect	Peak temperature, °C	Deposit		
		Nikolaevo	Kaleitza	Belnovruh
Exoeffect	90–100	6.2	2.4	4.7
Exoeffect	225–240	12.3	—	—
Endoeffect	280	10.8	—	—
Exoeffect	300	—	—	3.6
Exoeffect	310	21.5	—	—
Exoeffect	315	—	7.1	—
Exoeffect	390	—	17.7	14.5
Exoeffect	425	—	—	22.9
Exoeffect	450	—	22.5	—
—	to 500	41.4	23.7	24.0

samples. This is clearly evident from the strong mass losses at 225°, 240° and 310° for the sample from Nikolaevo, and at 315° and 390° and at 300° and 390° the other samples. The sharp losses in mass at 225–240°, 315° and 300°, respectively are related to the intensive thermal destruction of the gagates (Table 2).

The results of the thermal investigations show that the DTA curves distinguish the gagates from the other types of coal: lower-temperature exoeffects predominate in them. This is probably connected with their poorer thermoresistivity, which was demonstrated in previous investigations [7, 12].

The intensities and the areas of the thermal effects of the gagates are found to decrease in the following sequence: Nikolaevo, Kaleitza and Belnovruh, i.e. from the Moesian Platform to the Balkan zone: temperatures corresponding to their maxima increase, while the losses in mass at the corresponding temperature maximum decrease in the same sequence. The contents of carbon and hydrogen the reflectance and the microhardness increase in the same sequence as well, but the volatile matter content and the oxygen functional group content decrease [7]. The observed changes, probably influenced by different paleothermobaric conditions in the three morphometric zones [13], reveal variations in the macromolecular structure of the gagates; their coalification also changes in the N–S direction, i.e. from the Moesian Platform towards the Balkan zones.

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Zusammenfassung — Das thermochemische Verhalten von drei Gagaten (Bulgarien) wurde mittels DTA und TG untersucht. Die charakteristischen endo- und exothermen Effekte und die Reihenfolge der thermischen Stabilitäten wurden ermittelt.

Резюме — Методом ДТА и ТГ изучено термическое поведение трех образцов гагатов (Болгария). Определены характеристические эндо- и экзотермические эффекты и последовательность их термоустойчивости.