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Application of TG–DTA to the study of Amynteon lignites, northern Greece

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Abstract

In the present study thermogravimetry (TG) and differential thermal analysis (DTA) were carried out for seven lignite samples from Amynteon lignite deposit, northern Greece. The samples were chosen to represent the vertical distribution of the lignite beds in the entire deposit. Samples were heated up to 1000°C at a constant rate of 10°C/min in a 150 cm³/min flow of nitrogen (N₂). The burning profiles of the samples studied, combined with proximate analysis and calorimetry results, contribute to a clearer identification of Amynteon lignites’ structure and a better understanding of the coalification process. DTA and TG curves of all samples studied showed similar patterns. Seven thermal effects were distinguished (three endothermic and four exothermic). A good correlation between the results of proximate and calorimetry analyses and the DTA and TG data is noticed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thermal analysis is the measurement of changes in physical properties of a substance as a function of temperature whilst the substance is subjected to a controlled temperature program [1].

Thermal analysis methods play an important role in the investigation of useful mineral substances. Their application to the study of coal and its products has increased considerably in the last two decades. Ther-

mogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are the methods widely used in the characterisation of coals undergoing combustion.

Most of the published works deal with the effect of physical and chemical properties and the operating conditions in the combustion processes in order to improve the thermal efficiency of coal and its products [2–16]. Few works deal with the characterisation of coal and its products with the help of thermal techniques [17–20].

The aim of the present study is to investigate the vertical differentiation in the thermal behaviour of lignite beds of Amynteon lignite field, northern Greece, using TG and DTA techniques.

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2. Geological setting and samples

Amynteon lignite field is located at northern Greece. It belongs to Florina–Vegoritís–Ptolemais graben, a large basin filled with Neogene–Quaternary sediments, and extends by southeast from former Yugoslavian Republic of Macedonia to Kozani area. The sediments of this basin unconformably overlay both Paleozoic metamorphic rocks and Mesozoic crystalline limestones [21].

The Neogene–Quaternary sediments of the basin are divided into three lithostratigraphic formations. The lower formation (Upper Miocene to Lower Pliocene) consists mainly of conglomerates, marls, sands and clays. The middle formation (Pliocene) contains the lignite beds. The upper formation (Quaternary) consists of terrestrial and fluvio-terrestrial conglomerates, lateral fans and alluvial deposits. The lignite beds alternate with marls, clays and sands. Neotectonic faults have divided Amynteon subbasin and created a great variance in the thickness of the overburden, intermediate and floor rocks as well as in the thickness of lignite seams. The average thickness of the overburden is approximately 260 m and of the lignite beds approximately 20 m.

Samples of lignite strata of the entire stratigraphic column of Amynteon field were collected in situ. The samples were carefully chosen to be representative. Seven lignite samples were totally collected (named as A5, A7, A9, A11, A12, A14 and A15), from the roof to the floor of the active Amynteon lignite mine.

All samples were crushed into coarse fragments and were air-dried in room temperature for approximately 10 days.

3. Experimental

The samples were ground to grain size down to 1 mm. Proximate analysis (which includes the moisture, the ash, the volatile matter and the fixed carbon contents determination) was performed on the lignite samples. Moisture content was measured according to DIN 51718 [22], the ash content according to DIN 51719 [23] and volatile matter according to DIN 51720 [24]. Fixed carbon was calculated from volatile matter by difference. Gross calorific value was measured according to DIN standards, using an IKA C-400 adiabatic calorimeter. Chemical analysis of total sulphur content was also performed by XRF method. The results of proximate analysis, sulphur content and calorific value measurements are shown in Table 1.

One-hundred millilitre of each sample were placed in an aluminium crucible in a NETZSCH STA 409 Simultaneous Thermal Analyser. Al_2O_3 was used as reference material. Samples were heated from ambient temperature up to 1050°C at a constant rate of 10°C/min in a 150 cm³/min flow of nitrogen (N_2). The results of TG are shown in Table 2, while DTA curves are shown in a composite diagram in Fig. 1.

Table 1
Initial characteristics of the samples^a

Sample	Proximate analysis ^b				Calorific values ^b			Total sulphur, S ^a
	W ^c	A ^d	V ^e	C ^e	Q (J/g)	Q (cal/g)	Q ^e (cal/g)	
A5	16.0	14.8	62.7	57.2	16.920	4.038	5.836	1.6
A7	16.7	16.2	62.1	58.3	16.877	4.028	5.994	1.4
A9	16.9	11.1	75.8	37.2	12.846	3.066	6.568	0.8
A11	16.8	10.8	70.9	44.8	13.328	3.181	6.188	0.8
A12	14.3	21.2	62.7	57.4	16.725	3.992	6.188	1.1
A14	15.9	16.2	64.7	54.3	15.722	3.752	5.526	1.1
A15	12.9	26.1	66.6	51.1	14.764	3.524	5.776	2.0

^a All values in weight percent except as noted.

^b W: moisture; A: ash; V: volatile matter; S: sulphur; C: carbon; Q: calorific value.

^c As received.

^d Dry basis.

^e Dry, ash-free basis.

Table 2
Mass loss after TG curves, wt. %

Sample	Thermal effect (°C)							Total
	140 (+)	330–360 (–)	420–490 (+)	550–590 (+)	650–700 (–)	760–840 (+)	800–920 (–)	
A5	14	23	11	15	10	13	6	92
A7	10	24	12	–	22	14	4	86
A9	30	24	10	14	6	8	–	92
A11	36	20	8	13	9	8	–	94
A12	10	22	12	–	22	9	5	80
A14	10	25	13	18	12	4	4	86
A15	10	22	18	–	16	9	3	78

4. Results and discussion

The moisture content of lignite samples range from 12.9 up to 16.9% (air-dried basis), the ash content from 10.8 up to 26.1% (on a dry basis), the volatile matter from 62.1 up to 75.8% (on a dry, ash-free basis) and the calorific values range from 5526 up to 6568 cal/g (on a dry, ash-free basis). Total sulphur has relatively low values, ranging from 0.8 up to 2.0% (Table 1).

Concerning the TG data (Table 2), seven thermal effects are clearly identified for almost all the samples. The correlation between TG data and DTA curves contributed to the interpretation of these thermal effects. Thus, four exothermic (in the temperature ranges 140, 420–490, 550–590 and 760–840°C) and three endothermic (in the temperature ranges 330–360, 650–700 and 800–920°C) were determined.

The DTA curves for all samples studied have similar patterns, where seven thermal effects are distinguished (Fig. 1). The first peak, that is an intensive exothermic effect with temperature maximum at 140°C, corresponds to the decomposition of the humic polymer [25,26] with a mass loss ranging from 10 to 36%. The mass decrease is more significant in the case of samples A9 and A11. It could be assumed that pyrogenic water [27] is the major product that is released in the temperature interval 100–200°C. This thermal effect is followed by an endothermic effect in the temperature range 330–360°C that is probably due to primary gas release. It should be noted that the mass loss corresponding to this thermal effect is the most intensive compared with that registered for the other thermal effects and is nearly the same for all samples.

Belkevich et al. [28], have found a similar significant change of the organic matter in peat and brown coal at this temperature. The exothermal effect registered at 420–490°C is characterised by the smallest surface area. Probably, it may be attributed to processes accompanying the semicoke formation, i.e. pyrolysis products interaction. It is assumed that this exothermic effect might be related to the processes of splitting of the phenol groups, cleavage of C–C bonds and partial transition of the coal matter into plastic state [29]. Simultaneously, the percentage of mass loss during this temperature interval amounts to 8–18%, being the lowest for samples A9 and A11 and the highest for sample A15.

The DTA curves of samples A5, A9, A11 and A14 show a flattened exothermic effect with maximum temperature at 550–590°C and a mass loss within 13–18%. This effect is assumed to be related to high temperature pyrolysis accompanied by polycondensation reactions [30]. The next endothermic effect, with maximum temperature at 650–700°C and a mass loss within 6–22%, is probably due to a secondary high temperature gas release [31]. The clearly manifested exothermal effect at 760–840°C is attributed to high temperature polycondensation processes. It is characterised by a mass loss within 4–14%. The moderately intensive endothermic effect, observed in the temperature range 800–920°C, is accompanied by a minimum mass loss, i.e. –6%, except that of samples A9 and A11.

It should be pointed out that the total mass loss is rather high for the samples under study, i.e. 78–94%, being the highest for samples A11, A9 and A5 and the lowest for sample A15. The results of Table 1 correlate

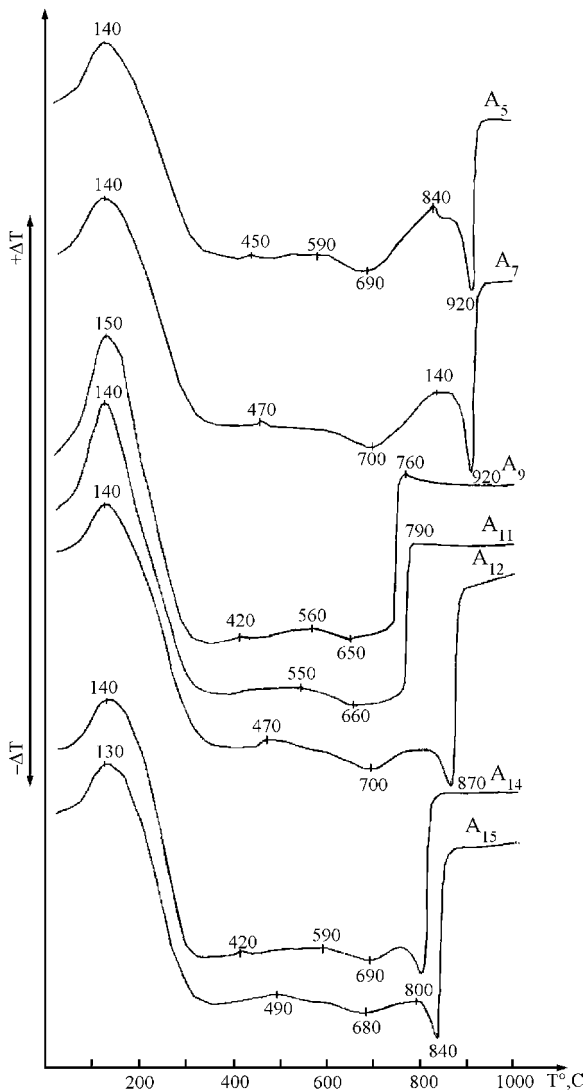


Fig. 1. Composite diagram of DTA curves of Amynteon lignite samples. Temperatures of determined thermal effects are indicated upon the curves.

rather well with DTA and TGA data (Fig. 1; Table 2). They suggest that coal samples A11 and A9 contain structures with decreased thermal stability in their macromolecule. This assumption is also supported by the maximum total mass loss and particularly up to 500°C, the higher analytical moisture amount, the increased volatile matter yield, the lower percentage of carbon per combustible mass and the low calorificity. Hence, it could be concluded that the initial biomass of

these samples has not undergone considerable changes during the coal genesis. In the case of the other samples investigated, the transformations of the coal organic matter have led to the formation of structures with higher thermal stability compared with that of samples A9 and A11.

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References

- [1] M.E. Brown, Introduction to Thermal Analysis Techniques and Applications, Chapman & Hall, London, 1988, p. 211.
- [2] P.A. Morgan, S.D. Robertson, J.F. Unsworth, Fuel 65 (11) (1986) 1546.
- [3] S.A. Jayaweera, J.M. Moss, M.W. Thwaites, Thermochim. Acta 152 (1989) 215.
- [4] K.I. Markova, D. Rustshev, J. Therm. Anal. 37 (1991) 2431.
- [5] K.I. Markova, N. Shopova, J. Therm. Anal. 39 (1993) 771.
- [6] R.M. Morris, J. Anal. Appl. Pyrol. 27 (1993) 97.
- [7] I.A. Mianowski, T. Radko, Fuel 72 (1993) 1537.
- [8] M.R. Stah, N. Ahmed, Fuel Sci. Technol. Int. 12 (1994) 85.
- [9] Y. Chen, S. Mori, W.P. Pan, Thermochim. Acta 275 (1996) 149.
- [10] C. Sentorun, S. Küçükbayrak, Thermochim. Acta 285 (1996) 35.
- [11] C. Sentorun, S. Küçükbayrak, Thermochim. Acta 287 (1996) 139.
- [12] C. Sentorun, H. Haykiri-Acma, S. Küçükbayrak, Thermochim. Acta 277 (1996) 65.
- [13] C. Sentorun, B. Dürüs, S. Küçükbayrak, J. Therm. Anal. 47 (1996) 821.
- [14] M.V. Kok, E. Okandan, J. Therm. Anal. 46 (1996) 1657.
- [15] M.V. Kok, E. Ozbas, C. Hiçyılmaz, O. Karaçan, Thermochim. Acta 302 (1997) 125.
- [16] W. Gabzdyl, A.K. Varma, J. Therm. Anal. 39 (1993) 31.
- [17] H. Haykiri, S. Küçükbayrak, G. Okten, Fuel Sci. Technol. Int. 11 (1993) 1611.
- [18] S. Valceva, A. Georgakopoulos, K. Markova, in: Proceedings of the Eighth International Conference on Coal Science, 1995, p. 259.
- [19] K.E. Benfell, B.B. Beamish, K.A. Rodgers, Thermochim. Acta 297 (1997) 79.

- [20] M.V. Kok, *J. Therm. Anal.* 49 (1997) 617.
- [21] S.B. Pavlides, D. M Mountrakis, *J. Struct. Geol.* 9 (4) (1987) 385.
- [22] Deutsche Norm, Testing of solid fuels — determination of the water content and the moisture of analysis sample, DIN 51718, 1995.
- [23] Deutsche Norm, Testing of solid fuels — determination of ash content, DIN 51719, 1978.
- [24] Deutsche Norm, Testing of solid fuels — determination of volatile matter, DIN 51720, 1978.
- [25] G. Šiškov, K. Markova, Petrology and geochemistry of bulgarian lignites: DTA and TGA analyses of homogeneous lithotypes, *Ann. De l' Univ. de Sofia, Fac. de Geol. et Geogr. Geol.* 1 (1980) 237.
- [26] L.F. Butuzova, L.N. Issaeva, Derivatographic studies of brown coal, in: *Coal Structure and Properties*, Naukova Dumka, Kiev, 1986, p. 146.
- [27] D. Rustshev, *Chemistry of solid fuel*, L. Khimiya (1976) 254.
- [28] N.I. Belkevich, A.E. Thompson, K.A. Gaiduk, *Chem. Solid Fuel* 6 (1986) 18.
- [29] L. Butuzova, R. Kucher, Study of vitrinite and fusinite microcomponents of Donetsk coal by derivatographic methods, *Chem. Solid Fuel* 2 (1979) 46.
- [30] V.I. Kasatochkin, N.K. Larina, *Coal Structure and Properties*, Nedra, Moscow, 1975, p. 159.
- [31] V. Saranchuk, L. Butuzova, V. Minkova, *Thermochemical Destruction of Brown Coals*, Naukova Dumka, Kiev, 1993, p. 222.