

ASPECTS OF THERMAL BEHAVIOR OF AMYNTEO LIGNITES, NORTHERN GREECE, DETERMINED BY THERMOGRAVIMETRY

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ABSTRACT

In this study, the burning profiles of seven lignite samples from Amynteo lignite mine, Northern Greece, were obtained using a thermogravimetry technique. The differentiation in the thermal behavior of the samples was investigated using DTG curves. The influence of inorganic constituents (expressed as major oxides content) was evaluated by correlate the major oxides content with burnout time and maximum weight loss rate. Samples from the intermediate lignite beds show a differentiation in their thermal behavior, related to the low sulfur and inorganic constituents content and attributable to their decreased thermal stability. There is a critical value of burnout time when correlate the sum of major oxides with burnout time. The inorganic content has a diverse relationship with burnout time beyond this critical value.

KEY WORDS: Amynteo lignite, DTG, inorganic constituents, burnout time

1. INTRODUCTION

The application of Thermal Analysis techniques to the study of coals and lignites contributes to a better comprehension of their structure, as well as to the improvement in their utilization (Markova et al., 1995; Adanez et al., 1996; Pis et al., 1996; Yong et al., 1996; Houseley and Poole, 1997; Zhang et al., 1997; Wei Xie et al., 2000). Previous works have studied the influence of inorganic constituents in the burning profiles of lignite samples, using either TG/DTG or DTA techniques (Benfell et al., 1997; Kok et al., 1997; Sentorun and Κόηόκbayrak, 1996a, 1996b; Sentorun et al., 1996a, 1996b). Inorganic constituents usually expressed as major oxides content, influence the combustion behavior of coals and thus are important in the design of coal-fired boilers. Since the inorganic components content of the Greek lignites is quite high, it is useful to investigate its influence on the combustion characteristics. Despite of the wide use of thermogravimetry in the investigation of coal and its products, only a few papers deal with the application of thermal analysis techniques to the study of Greek lignites (Valceva et al., 1995; Iordanidis et al., 2001).

For the purposes of the present study, thermogravimetric analysis was performed on seven lignite samples collected from Amynteo lignite deposit, Northern Greece, and attention has been directed to the differentiation in their burning profiles, using the DTG curves, as well as to the effect of inorganic constituents in their thermal behavior.

2. MATERIALS AND METHODS

Seven lignite samples, named as AM1, AM2, AM3, AM4, AM5, AM6 and AM7, were collected from the roof to the floor of the active Amynteo lignite mine. All samples were crushed into coarse fragments, were air-dried in room temperature for approximately 10 days and then ground to a grain size down to 1mm. Proximate analysis, which includes the determination of the moisture, the ash, the volatile matter and the fixed carbon content, was performed on the lignite samples. Moisture, ash and volatile matter content were measured according to the DIN standards (DIN 51718, 1995; DIN 51719, 1978; DIN 51720, 1978). Fixed carbon content was calculated from volatile matter content by difference. Gross calorific value was measured using an IKA C-400 adiabatic Calorimeter. Chemical analysis of major oxides and total sulfur content was performed by XRF method on a whole coal basis. Thermogravimetry was carried out using a NETZSCH STA 409 Simultaneous Thermal Analyzer. One hundred mg of each lignite sample was placed in an aluminum crucible and then put in the analyzer. 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 150cm³/min flow of nitrogen (N₂).

Temperatures of several thermal events in the coal combustion process, derived from DTG curves, and some characteristic calculated values, have been defined. The picking of some of these temperatures from a coal's TG and DTG curves can be highly subjective (Benfell et al., 1997). The following parameters have been found to be readily repeatable and to satisfactorily characterize significant events during combustion:

- The peak temperature at which the rate of weight loss, including the moisture loss, due to combustion of the lignite samples is a maximum. This temperature is called as the "DTG maximum peak temperature" (T_p).
- The rate of weight loss at the DTG maximum peak temperature, which is called "maximum weight loss rate" (R_c).
- The time interval between the beginning of the moisture loss and the end of the combustion process, which is called burnout time (dt).
- The temperature at which the combustion process is completed (T_f).

These parameters reflect the thermal behavior of the organic fraction during combustion and identify the end of combustion or "burnout".

3. RESULTS AND DISCUSSION

Key combustion temperatures and rate data for the analyzed lignites, along with relevant proximate analyses and calorific values, are shown in Table 1. A plot of the rate of weight loss against temperature while burning a sample in air has been referred to as "burning profile". All DTG curves (burning profiles) derived from thermogravimetry of Amynteo lignite samples are shown in Figure 1. The moisture content (Table 1) varies between 12.9 and 41.5%. The ash content varies between 10.8 and 26.1%, while the volatile matter content varies between 60.7 and 66.7%. Gross calorific values range between 3,066 and 4,038 kcal kg^{-1} (on an air-dried basis). Samples AM3 and AM4 show the lowest calorific value (air-dried basis), the highest moisture content (air-dried basis) and the lowest ash content (on a dry basis). The same samples (AM3 and AM4) have the highest calorific values when calculating on a different basis (dry, ash-free basis).

Table 1. Amynteo lignite samples characteristics.

SAMPLE	Moisture	Ash	FC ¹	VM ²	dt ³	Tf ⁴	Tp ⁵	Rc ⁶	Q ⁷	Q ⁷
	(%ad)	(%db)	(%daf)	(%daf)	(min)	(°C)	(°C)	(mg/ /min)	(cal g ⁻¹) (daf)	(cal g ⁻¹) (ad)
AM1	16.0	14.8	37.3	62.7	86	920	120	2.3	5,836	4,038
AM2	16.7	16.1	37.9	62.1	85	920	120	1.8	5,994	4,028
AM3	41.5	11.1	36.3	63.7	73	760	120	5.2	6,468	3,066
AM4	37.8	10.8	39.3	60.7	75	790	120	5.0	6,188	3,181
AM5	14.3	21.2	37.3	62.7	82	870	120	1.7	6,188	3,992
AM6	15.9	16.2	35.3	64.7	76	800	270	2.0	5,526	3,752
AM7	12.9	26.1	33.3	66.7	78	840	120	1.5	5,776	3,524

¹ Fixed Carbon content,

² Volatile Matter content, ³ burnout time, ⁴ Temperature at which the end of combustion is observed, ⁵ Temperature at which the maximum rate of weight loss is observed, ⁶ Maximum rate of weight loss, ⁷ Gross calorific value. ad=air-dried basis, db=dry basis, daf=dry, ash-free basis.

Chemical analyses of major oxides and total sulfur content are shown in Table 2. Samples of the intermediate seams of Amynteo lignite mine (AM3 and AM4) show the lowest concentrations in major oxides. Burnout time lowest values are also shown by samples AM3 and AM4 (73 and 75 minutes respectively). Both these lignites have similarly low ash contents and low total sulfur contents. Sulfur, especially when it is organically bound in the coal, may act as an inhibitor to active site formation, thereby retarding combustion (Benfell et al., 1997). Differences in some other inorganic constituents may be reflected in differences in their burnout temperatures and burnout time. As for example, samples AM3 (dt=73) and AM4 (dt=75) have the lowest iron content (0.95 and 1.10 respectively). This fact suggests that the iron content of the coal may also inhibit combustion, taking into account that a high calcium content reduces burnout temperature (Sentorun and Küçükbayrak 1996a; 1996b).

Table 2. Major inorganic components (wt%) and total sulfur content (wt%) of Amynteo lignite samples, determined by X-Ray Fluorescence on a whole coal basis.

Sample	S	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
AM1	1.6	0.90	0.67	1.80	5.5	1.5	0.062	0.046
AM2	1.4	2.00	1.20	1.20	6.1	1.6	0.055	0.091
AM3	0.8	0.65	0.66	0.95	5.0	1.4	0.049	0.035
AM4	0.8	0.99	0.82	1.10	4.3	1.2	0.048	0.043
AM5	1.1	5.80	3.10	2.00	5.2	1.7	0.067	0.200
AM6	1.1	1.60	1.20	1.90	7.0	1.3	0.055	0.080
AM7	2.0	8.20	3.90	2.40	4.7	1.1	0.075	0.290

DTG curves (Figure 1) generally have the shape of two maxima (peaks), corresponding to water release followed by progressive combustion. Samples AM3 and AM4 show only a very intensive first peak, followed by a rather flattened curve. Maximum rate of weight loss (R_c) is observed at 120°C (first peak) for all samples, corresponding to the moisture loss, except for sample AM6, which shows the maximum rate of weight loss at 270°C. Samples AM3 and AM4 have the highest R_c values (5.2 and 5.0 mg min⁻¹ respectively). The combustion of coal, after the moisture release, involves three stages: the release of volatile matter, the burning of volatile matter in the

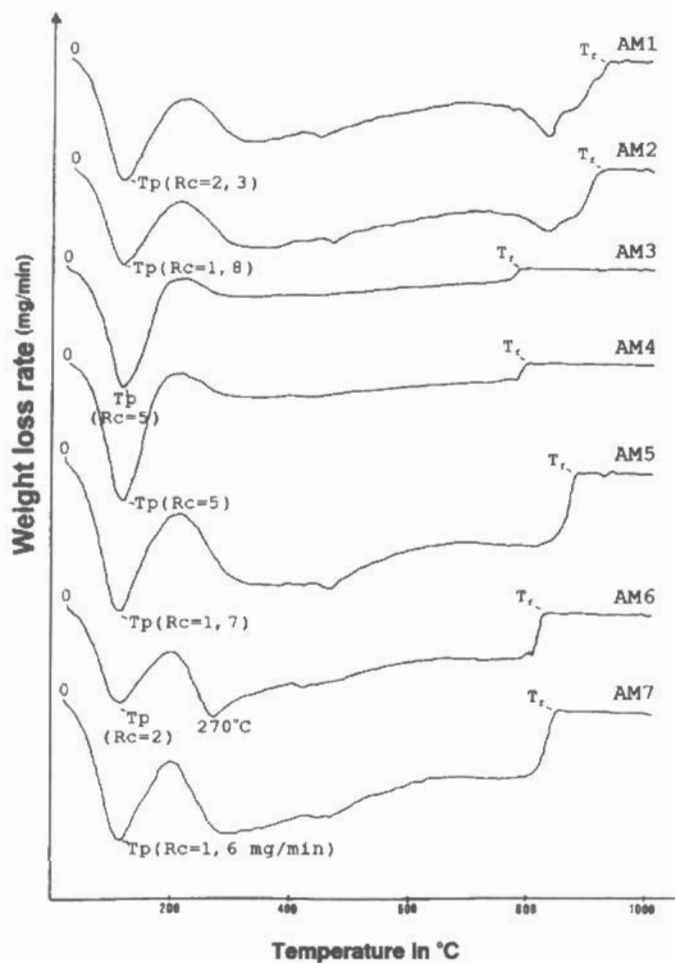


Figure 1. DTG curves (burning rates) of Amynteo lignite samples.

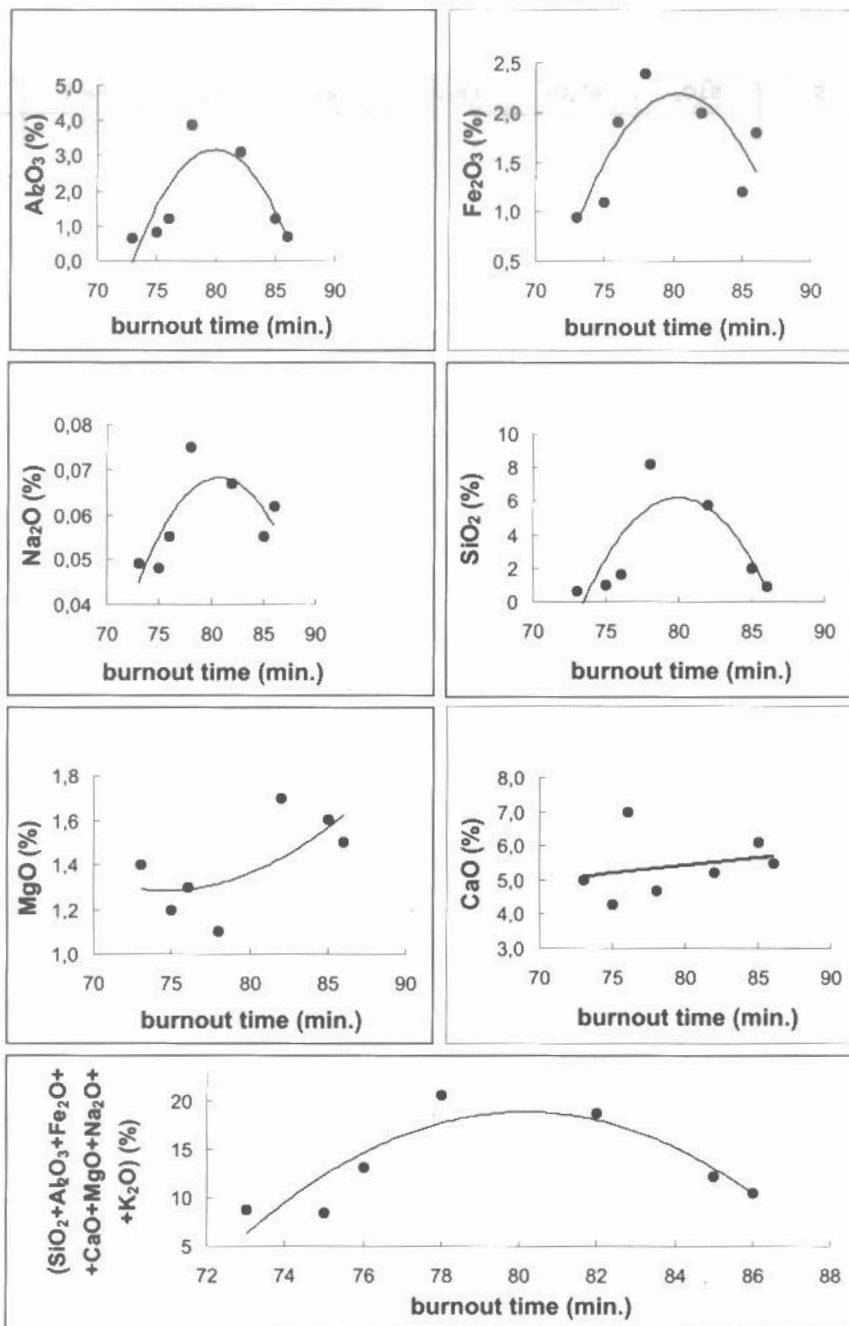


Figure 2. Correlation graphs of the major oxide contents and the sum of the oxides with burnout time.

gas phase, and the burning of the residual char. These processes occur sequentially to some extent; however, overlapping of these three stages depend upon particle size, heating rate and char porosity (Berkowitz, 1985; Sentorun et al., 1996b). A rapid loss of volatile matter occurs within a few seconds; the combustion of the remaining solid residue proceeds within minutes. Hence, the chemical reactivity of the char becomes the most important parameter governing the burnout behavior of the coal. Char oxidation depends on a number of factors including coal structure, diffusion of reactants, particle size, pore diffusion, catalysis by minerals, changes in surface area

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during the reactions, fragmentation of char, temperature and pressure. In this study, attention has been directed to the relationship between burnout time and maximum rate of weight loss with inorganic constituents and calorific value. The Amynteo lignite samples have almost the same volatile matter contents, yet their dt values lie in the 73-86 range. Given the similarity in volatile matter contents, this difference cannot be due to a change in maceral composition. A more likely cause lies in the difference in the inorganic constituents of the lignite. Sentorun and K  okbayrak (1996a, 1996b) suggest that mineral matter has a significant effect on the combustion behavior of lignites. Unfortunately, much of their data was for coals of different ranks, which is not the case in Amynteo lignites. Hence, the relationships observed by the authors may have been influenced as much by rank as mineral matter. The correlation between the major oxides content (Al_2O_3 , Fe_2O_3 , Na_2O , SiO_2 , MgO , CaO , and the sum $SiO_2 + Al_2O_3 + Fe_2O_3 + CaO + MgO + Na_2O + K_2O$) and burnout time is shown in Figure 2. A quadratic model of regression statistics was found to best fit in the above relationships. A critical value of burnout time (which approximately is 80 minutes), is observed (except of MgO and CaO). For burnout time lower than 80 minutes, an increase in the content of inorganic constituents causes an increase in burnout time, while for burnout time higher than 80 minutes, an increase in major oxides content, causes a decrease in burnout time, especially for Al_2O_3 and SiO_2 . The relationship between burnout time and calorific values is shown in Figure 3. A linear regression model was adapted and burnout time was found to be proportional to the calorific value.

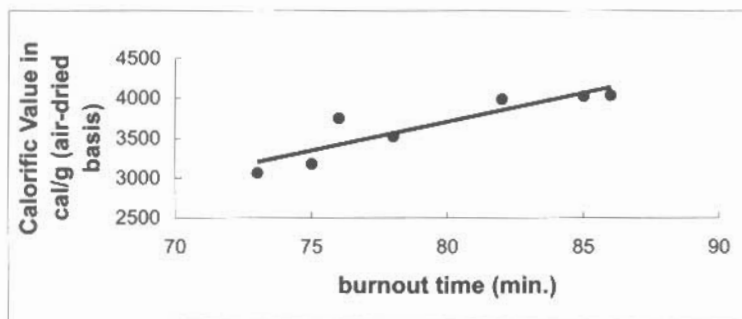


Figure 3. Relationship between burnout time and Calorific Value.

The relationship between maximum weight loss rate and major oxides content ($SiO_2 + Al_2O_3 + Fe_2O_3 + CaO + MgO + Na_2O + K_2O$) is shown in Figure 4. An increase in the amount of inorganic constituents causes a decrease in the maximum weight loss rate. The maximum weight loss rate is also correlated with the calorific values of the lignite samples (Figure 5). Low calorific values are related to high maximum weight loss rates. Finally, the relationship between burnout time and maximum weight loss rate is shown in Figure 6. Samples with high maximum weight loss rates have low values of burnout time (samples AM3 and AM4).

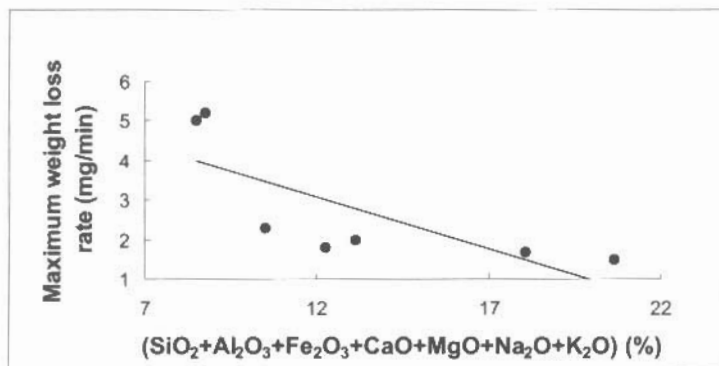


Figure 4. Relationship of the maximum weight loss rate with major oxides.

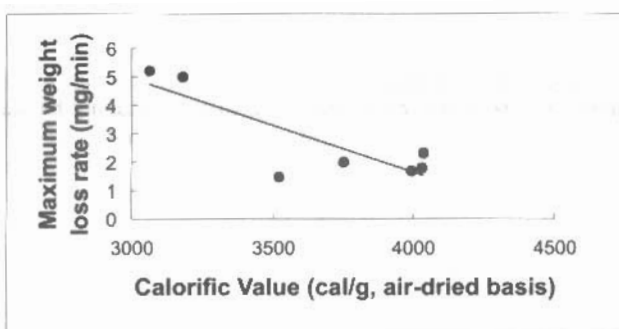


Figure 5. Relationship of the maximum weight loss rate with Calorific Value.

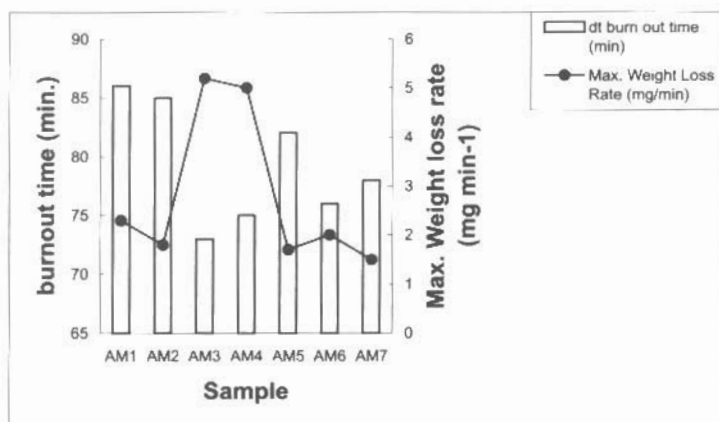


Figure 6. Relationship of the burnout time with the maximum weight loss rate.

4. CONCLUSIONS

In the present study, lignite samples from Amynteo mine were studied using DTG curves. Combined with proximate analysis results and calorific value measurements, the vertical differentiation in the thermal behavior of the lignite samples, as well as the influence of inorganic constituents in the combustion process, is investigated. In particular:

1. Samples of the intermediate lignite seams of Amynteo lignite deposit, i.e. samples AM3 and AM4, show higher maximum weight loss rates (more than 50% of their weight loss occurs until 120°C), shorter burnout times, lower calorific values and lower amount of inorganic components relatively to the other samples. The different thermal behavior appears to be in relation with the low sulfur and low major oxides content. This differentiation was also observed in the DTA-TG curves of the same samples, and is attributable to a decreased thermal stability.
2. Inorganic components of Amynteo lignite deposit can catalytically influence the combustion process. The greater the amount of inorganic components, the lower is the maximum weight loss rate.
3. An increase in the calorific value of the lignite samples causes an increase in burnout time and a decrease in the maximum weight loss rate.
4. There is a critical time interval when correlate burnout time with the major oxides content except of MgO and CaO, which approximately is 80 minutes. Below this time interval, especially for SiO₂ and Al₂O₃, an increase in the content of inorganic constituents causes an increase in burnout time, while above 80 min, the higher the major oxides content the lower the burnout time is.

ACKNOWLEDGEMENTS

The Hellenic Ministry for Development, General Secretariat for Research and Technology, is deeply acknowledged for project funding. The authors are indebted to Dipl.-Ing. Wolfram Möller, Mineral Processing Institute, RWTH-Aachen, Germany, for his assistance in the implementation of Thermal Analysis and to Dr. Peter Winkler, Institute of Nonferrous Process Metallurgy, RWTH-Aachen, Germany, for the conduction of DTG analyses.

REFERENCES

- ADANEZ, J., FIERRO, V., DE DIEGO, J.A., DE DIEGO, L.F. & GARCIA-LABIANO, F. 1996. The effect of the porous structure on sorbent sulfation under coal-fired boiler conditions. *Thermochim. Acta* **277(0)**, 151-164.
- BENFELL, K.E., BEAMISH, B.B. & RODGERS, K.A. 1997. Aspects of combustion behaviour of coals from some New Zealand lignite-coal regions determined by thermogravimetry. *Thermochim. Acta* **297(1-2)**, 79-84.
- BERKOWITZ, N. 1985. *The Chemistry of Coal*, 321pp. Coal Science and Technology 7, (Elsevier, Amsterdam).
- DEUTSCHES INSTITUT F&R NORMUNG e.V. DIN 51718, 1995-09. Testing of solid fuels- Determination of the water content and the moisture of analysis sample.
- DEUTSCHES INSTITUT F&R NORMUNG e.V. DIN 51719, 1978. Testing of solid fuels- Determination of ash content.
- DEUTSCHES INSTITUT F&R NORMUNG e.V. DIN 51720, 1978. Testing of solid fuels- Determination of volatile matter.
- HOUSELEY, K. & POOLE, C. 1997. Enthalpy determinations and adsorption behaviour in the coal pyrite-sodium acrylate co-polymer system: effects of pH. *Thermochim. Acta* **293(1-2)**, 143-151.
- IORDANIDIS, A., GEORGAKOPOULOS, A., MARKOVA, K., FILIPPIDIS, A. & KASSOLI-FOURNARAKI, A. 2001. Application of TG-DTA to the study of Amynteon lignites, northern Greece. *Thermochim. Acta* **371**, 137-141.
- KOK, M.V., OZBAS, E., HIHYILMAZ C. & KARAHAN, O. 1997. Effect of particle size on the thermal and combustion properties of coal. *Thermochim. Acta* **302(1-2)**, 125-130.
- MARKOVA, K.I., SHOPOVA, N.I. & VALCEVA, S. 1995. Investigation of low-temperature autooxidation processes in bituminous coal lithotypes. *Thermochim. Acta* **265(0)**, 111-117.
- PIS, J.J., DE LA PUENTE, G., FUENTE, E., MORAN, A. & RUBIERA, F. 1996. A study of the self-heating of fresh and oxidized coals by differential thermal analysis. *Thermochim. Acta* **279(0)**, 93-101.
- SENTORUN, C. & KÁHÁKBAYRAK, S. 1996a. Effect of mineral matter on the burning profile of lignites. *Thermochim. Acta* **285(1)**, 35-46.
- SENTORUN, C. & KÁHÁKBAYRAK, S. 1996b. The effect of mineral matter on the combustion characteristics of some Turkish lignite samples. *Thermochim. Acta* **287(1)**, 139-147.
- SENTORUN, C., DÁRÁS, B. & KÁHÁKBAYRAK, S. 1996a. Influence of the mineral matter content on the rate of heat release from Turkish lignites. *J. Thermal Analysis* **47**, 821-831.
- SENTORUN, C., HAYKIRI-ACMA, H. & KÁHÁKBAYRAK, S. 1996b. Effect of mineral matter on the combustion curve of chars. *Thermochim. Acta* **277(0)**, 65-73.
- VALCEVA, S., GEORGAKOPOULOS, A. & MARKOVA, K. 1995. The relationship between the petrographic composition and some chemical properties for the Ptolemais basin lignites, Greece. In: Coal Science (Pajares & Tascón, Eds.), Elsevier, Coal Science and Technology, **24**, 259-262.
- WEI XIE, YING XIE, WEI-PING PAN & RIGA, A. 2000. Characterization of the ash deposits from AFBC system using thermal techniques. *Thermochim. Acta* **357-358(0)**, 231-238.
- YONG, C., SHIGEKATSU, M. & WEI-PING, P. 1996. Studying the mechanisms of ignition of coal particles by TG-DTA. *Thermochim. Acta* **275(1)**, 149-158.
- ZHANG, L., TAN, Z., WANG, S. & WU, D. 1997. Combustion calorimetric and thermogravimetric studies of graphite and coals doped with a coal-burning additive. *Thermochim. Acta* **299(0)**, 13-17.

ACKNOWLEDGEMENTS

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REFERENCES

- ADANEZ, J., FIERRO, V., DE DIEGO, J.A., DE DIEGO, L.F. & GARCIA-LABIANO, F. 1996. The effect of the porous structure on sorbent sulfation under coal-fired boiler conditions. *Thermochim. Acta* **277(0)**, 151-164.
- BENFELL, K.E., BEAMISH, B.B. & RODGERS, K.A. 1997. Aspects of combustion behaviour of coals from some New Zealand lignite-coal regions determined by thermogravimetry. *Thermochim. Acta* **297(1-2)**, 79-84.
- BERKOWITZ, N. 1985. *The Chemistry of Coal*, 321pp. Coal Science and Technology 7, (Elsevier, Amsterdam).
- DEUTSCHES INSTITUT F&R NORMUNG e.V. DIN 51718, 1995-09. Testing of solid fuels- Determination of the water content and the moisture of analysis sample.
- DEUTSCHES INSTITUT F&R NORMUNG e.V. DIN 51719, 1978. Testing of solid fuels- Determination of ash content.
- DEUTSCHES INSTITUT F&R NORMUNG e.V. DIN 51720, 1978. Testing of solid fuels- Determination of volatile matter.
- HOUSELEY, K. & POOLE, C. 1997. Enthalpy determinations and adsorption behaviour in the coal pyrite-sodium acrylate co-polymer system: effects of pH. *Thermochim. Acta* **293(1-2)**, 143-151.
- IORDANIDIS, A., GEORGAKOPOULOS, A., MARKOVA, K., FILIPPIDIS, A. & KASSOLI-FOURNARAKI, A. 2001. Application of TG-DTA to the study of Amynteon lignites, northern Greece. *Thermochim. Acta* **371**, 137-141.
- KOK, M.V., OZBAS, E., HIHYILMAZ C. & KARAHAN, O. 1997. Effect of particle size on the thermal and combustion properties of coal. *Thermochim. Acta* **302(1-2)**, 125-130.
- MARKOVA, K.I., SHOPOVA, N.J. & VALCEVA, S. 1995. Investigation of low-temperature autooxidation processes in bituminous coal lithotypes. *Thermochim. Acta* **265(0)**, 111-117.
- PIS, J.J., DE LA PUENTE, G., FUENTE, E., MORAN, A. & RUBIERA, F. 1996. A study of the self-heating of fresh and oxidized coals by differential thermal analysis. *Thermochim. Acta* **279(0)**, 93-101.
- SENTORUN, C. & KÁHÁKBAYRAK, S. 1996a. Effect of mineral matter on the burning profile of lignites. *Thermochim. Acta* **285(1)**, 35-46.
- SENTORUN, C. & KÁHÁKBAYRAK, S. 1996b. The effect of mineral matter on the combustion characteristics of some Turkish lignite samples. *Thermochim. Acta* **287(1)**, 139-147.
- SENTORUN, C., DÁRÁS, B. & KÁHÁKBAYRAK, S. 1996a. Influence of the mineral matter content on the rate of heat release from Turkish lignites. *J. Thermal Analysis* **47**, 821-831.
- SENTORUN, C., HAYKIRI-ACMA, H. & KÁHÁKBAYRAK, S. 1996b. Effect of mineral matter on the combustion curve of chars. *Thermochim. Acta* **277(0)**, 65-73.
- VALCEVA, S., GEORGAKOPOULOS, A. & MARKOVA, K. 1995. The relationship between the petrographic composition and some chemical properties for the Ptolemais basin lignites, Greece. In: Coal Science (Pajares & Tascón, Eds.), Elsevier, Coal Science and Technology, 24, 259-262.
- WEI XIE, YING XIE, WEI-PING PAN & RIGA, A. 2000. Characterization of the ash deposits from AFBC system using thermal techniques. *Thermochim. Acta* **357-358(0)**, 231-238.
- YONG, C., SHIGEKATSU, M. & WEI-PING, P. 1996. Studying the mechanisms of ignition of coal particles by TG-DTA. *Thermochim. Acta* **275(1)**, 149-158.
- ZHANG, L., TAN, Z., WANG, S. & WU, D. 1997. Combustion calorimetric and thermogravimetric studies of graphite and coals doped with a coal-burning additive. *Thermochim. Acta* **299(0)**, 13-17.