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A THERMAL ANALYSIS STUDY OF THE COMBUSTION CHARACTERISTICS OF VICTORIAN BROWN COALS

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Simultaneous TG, DTA techniques have been applied to investigate the combustion characteristics of Victorian brown coal derived from different coal fields and including various lithotypes. TG and DTA profiles of the entire combustion process were obtained to provide a set of parameters which characterize the oxidation potential of these coal samples. These parameters can also be used to predict the combustion performance of pulverized coal in industrial furnaces. The area of the major DTA combustion peak is closely related to the heat released during the combustion process and therefore provides a means of determining the specific energy of the coal. Different lithotypes are also characterized by their corresponding TG and DTA burning profiles.

Thermal analysis techniques have been widely used in the study of coal combustion. It is known that for a range of fuels which have similar TG burning profiles, their performance in an industrial pulverized coal furnace is similar [1]. Thermal analysis data can be applied not only to the characterization of different coals, but also to the evaluation of combustion performance at high temperatures and heating rates. Since only a small sample size is required in the analysis, the burning profile is most useful for evaluating the burning properties of fuel when only small samples are available or when it is impractical to test-fire large quantities of fuel in existing installations [2].

In the present work the combustion performance of some brown coal samples and lithotypes of brown coal is investigated by simultaneous TG and DTA techniques.

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Experimental

Brown coal samples

The samples investigated include three samples of "run-of-mine" brown coal from Morwell, Loy Yang, and Gelliondale coal fields and also two groups of lithotypes from the Morwell and Yallourn coal fields. The samples were air dried and ground to pass through an 80 mesh screen. The analysis data for these samples are shown in Tables 1 and 2.

Thermal analysis procedures

Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) of the coal samples was performed using a Stanton Redcroft STA 780 Thermal Analysis System interfaced with a "CETA" computerised data processing system which allows easy data processing in terms of peak temperatures, areas, onset/offset temperatures or times and TG and DTA derivatives.

The effects of experimental conditions on the TG and DTA curves were initially investigated using samples of Morwell coal, in order to establish optimum sample size, air flow rate and heating rate for the present investigation.

Due to the high reactivity of brown coal with oxygen, sample size must be small. With a large sample size, the heat released during the combustion process causes the temperature of the sample to increase in excess of the programmed temperature increase. However, the accuracy of TG decreases with decreasing sample size. Based on the results obtained, a sample mass of 5 mg was chosen for the present investigation.

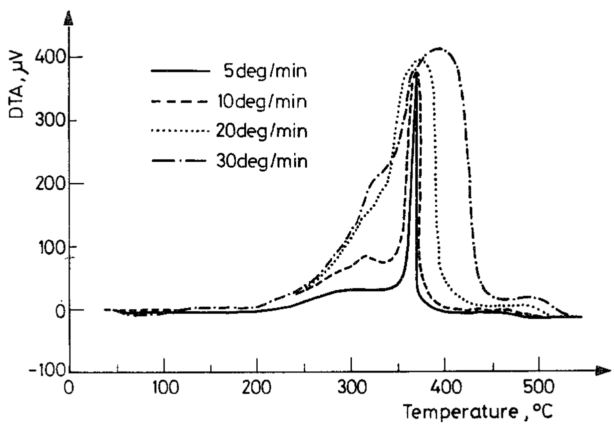

Fig. 1 Effect of heating rate on the combustion of Morwell brown coal

The air flow rate was found to have little effect on the burning profile, except that in static air, due to the lack of oxygen, the burning profile was broad and the intensity was very low. The optimum flow rate was determined to be 30 cm^3/min.

The DTA curves of Morwell coal under different heating rates are shown in Fig. 1. For lower heating rates, the burning profiles of DTA *vs.* T were very sharp. As the heating rate is increased, the main burning peak became broad, and the first peak became a small shoulder. From these preliminary results, 10 deg/min was determined as the optimum heating rate in terms of peak sharpness and reproducibility.

Overall, the experimental conditions used were: sample size, 5 mg; reference, Al_2O_3; heating rate, 10 deg/min; atmosphere, air; flow rate, 30 cm^3/min; crucibles, platinum.

Results and discussion

Oxidation of brown coals from different coal fields

A typical TG and DTG combustion profile of brown coal is shown in Fig. 2. The TG and DTG curves show the relative mass loss during heating in air and the rate of mass loss respectively. The R_m from the DTG curve relates to the maximum combustion rate and T_m is the temperature at which this maximum rate occurs. The mass loss below 150° is largely related to the removal of moisture. Subsequently devolatilization and combustion of volatile matter and char occurs and the sample mass continues to decrease to the complete combustion stage.

Usually, for a higher rank coal, there is an observed mass gain during the low temperature oxidation process which is related to oxygen adsorption on the coal surface [3–6]. However, for all the brown coal samples investigated, no obvious mass gain was observed during the combustion process and this is due to the release of volatile matter, which masked the sorption of oxygen [4].

A typical DTA curve of brown coal is given in Fig. 3. The combustion of brown coal usually corresponds to two or more DTA peaks due to the complicated coal infra-structure. The DTA curve shown in Fig. 3 may be divided into five parts, corresponding to five stages of oxidation [4, 7]. The first stage from T_1 to T_2 is exothermic, which corresponds to the commencement of the thermal decomposition of volatile organic components. The decrease in differential temperature, which follows with an apparent minimum at T_3, is the result of decomposition, polycondensation of pyrolysis products and phase transformations associated with the removal of volatile matter [4, 8]. The third stage from T_3 to T_4 is characterized by a rapid increase of the differential temperature to a maximum

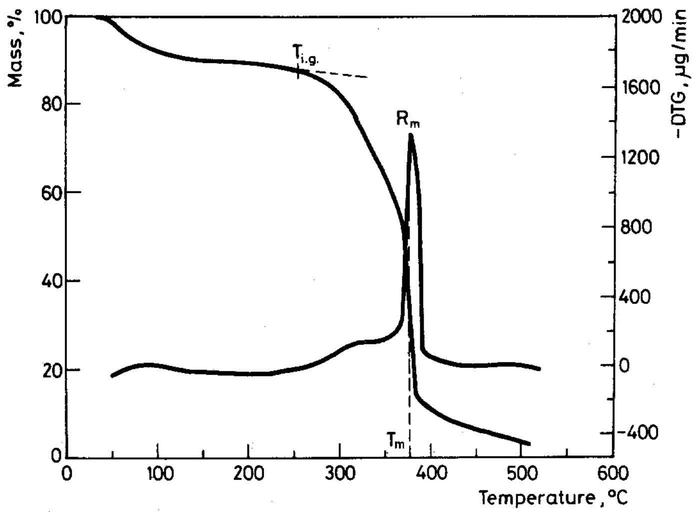

Fig. 2 Typical TG and DTG curves of brown coal combustion

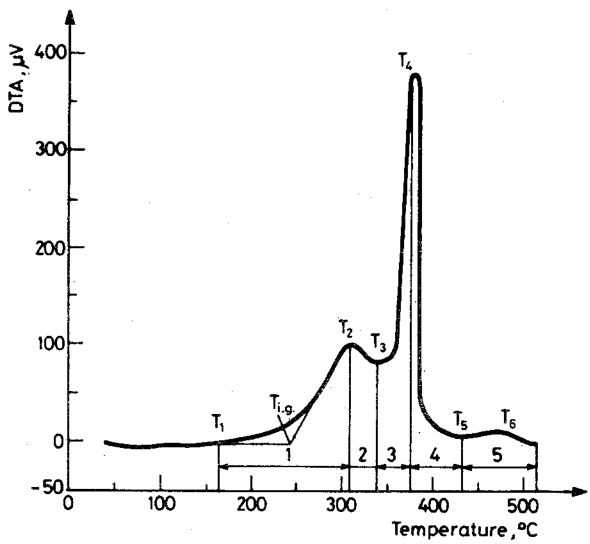

Fig. 3 DTA curve of brown coal combustion

point, resulting from the combuston of the residual char after the volatile matter has been removed. The fourth stage, as represented by a decline of the DTA curve, is due to the decrease of coal mass and an associated decrease of combustion rate. The fifth stage corresponds to a small exothermic peak and it is probably due to the combustion of the amorphous carbon which is formed from aromatization reactions during the heating of the char.

Ignition temperature is an important characteristic of coal combustion, especially for brown coal due to its high intensity of spontaneous combustion. In the present work, the ignition temperature is taken as the extrapolated onset temperature of the first peak of the DTA curve, which also corresponds to the temperature at which the TG curve departs from the base line, as shown in Figs 2 and 3. Since the burning profile of brown coal gives two or more DTA peaks, the ignition of volatile matter and char occurs at different temperatures. This has been commonly referred to as "false ignition" [4], which infers that the coal may ignite at the ignition temperature given by the first DTA peak; however the coal would not necessarily burn out unless the temperature is further increased to effect ignition of the char itself. Ignition temperature, as given in present work, corresponds to the $T_{i.g}$ of the volatile matter.

From Figs 2 and 3, the TG and DTA profiles closely record the behaviour of coal during the entire combustion process, commencing with the release of moisture, volatilization, ignition and finally burn off. The peak value R_m of the DTG curve gives an indication of the intensity of combustion. Mass loss on the TG curve represents the amount of coal burned off. The DTA curve gives a measure of the heat change during the thermal treatment of coal and the area under the DTA curve can be used to estimate the heat released during the combustion process. In general, those coals with low ignition temperature and high mass loss in the lower temperature range can be considered as easy to ignite and burn out.

Figures 4 and 5 show the TG and DTA curves of three brown coal samples obtained from different coal fields. Some characteristics derived from the TG and DTA curves are listed in Table 3. The reproducibility of the characteristic temperatures was determined for all samples to be within 6 deg of duplicate determinations.

The burning profiles of these coal samples are quite different. For Morwell coal, the maximum rate occurred at the lowest temperature. This coal has a much higher rate of mass loss R_m than the other two coals. On the DTA curve of Morwell coal, the first peak relates to the release of volatile matter and is sharper than those of the other two samples. The main burning peak of Morwell coal occurred at the lowest temperature and had the highest intensity, which is consistent with the results obtained from the TG profiles. After the peak temperature had been reached, the curve dropped sharply. The fifth stage was relatively small and combustion of the

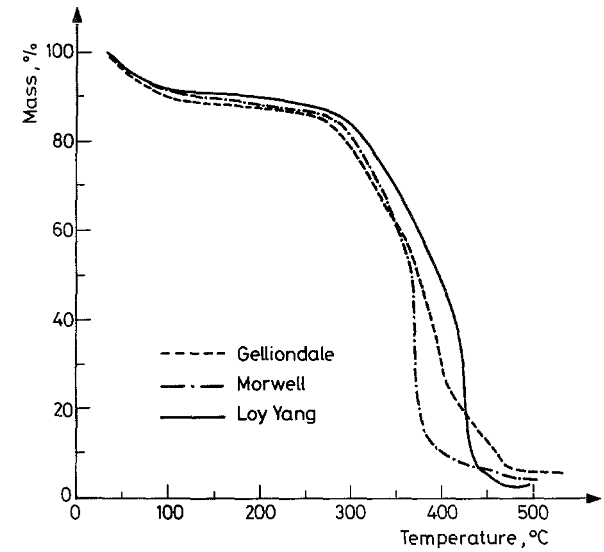

Fig. 4 TG curves of brown coal samples

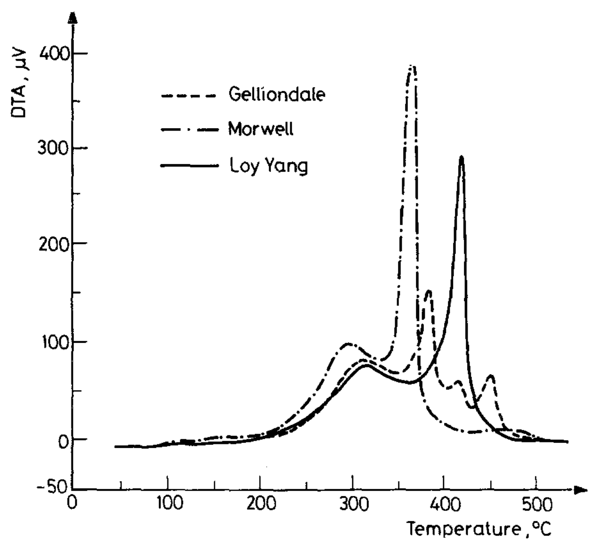

Fig. 5 DTA curves of brown coal samples

coal residue occurrea over to a broad temperature range. All of these properties suggest a high reactivity of Morwell coal with oxygen, consistent with a high intensity of combustion compared to the other two coals.

For Loy Yang coal, the first peak occurred over a wide temperature range with the lowest $T_{i.g}$ and its main burning peak was shifted to a region of higher

Table 1 Analysis of brown coal samples

No. Sample (air dried)	Proximate, %db				Ultimate, %db					$Q_{grossdry}$ (MJ/kg)
	%M	A	VM	FC	C	H	N	S	O	
1 Morwell coal	12.7	3.8	47.7	48.5	69.8	4.8	0.55	0.27	24.6	26.21
2 Gelliondale coal	7.3	5.4	49.0	44.7	66.5	4.7	0.56	0.78	27.5	25.99
3 Loy Yang coal	15.6	1.1	51.7	47.2	68.2	4.9	0.57	0.32	26.0	26.16

Table 2 Analysis of brown coal lithothypes

No. Sample	Proximate, %db				Ultimate, %db				$Q_{grossdry}$ MJ/kg
	%as, M	A	VM	FC	C	H	N	S	
a Morwell pale	56.5	3.7	54.9	41.4	70.1	5.7	0.58	0.69	28.87
b Morwell light	57.8	4.1	50.2	45.7	70.2	5.3	0.66	0.67	28.00
c Morwell med light	57.4	3.4	48.8	47.8	70.4	5.1	0.65	0.57	27.96
d Morwell dark	60.8	3.5	47.0	49.5	69.2	4.8	0.65	0.73	27.64
a′ Yallourn pale	57.2	1.6	60.4	38.0	70.3	6.1	0.52	0.21	28.72
b′ Yallourn med. light	62.6	1.3	51.3	47.4	66.6	4.6	0.56	0.20	25.59
c′ Yallourn med. light/med. dark	65.0	1.5	51.0	47.5	66.5	4.6	0.56	0.17	25.70
d′ Yallourn dark	70.0	1.3	49.2	49.5	66.7	4.6	0.53	0.20	25.76

Table 3 Combustion characteristics of brown coal samples

Sample	TG				DTA peak								
	$T_{i.g}$	T_m C	T_h	R_m μg/min	T_1	T_2	T_3	T_4	T_5 °C	T_6	T_7	T_8	T_9
Morwell	247	366	512	−1494	165	303	338	366	408	481			
Loy Yang	236	422	480	− 991	170	323	365	422	462				
Gelliondale	255	392	492	− 504	160	318	364	392	410	421	441	458	477

temperature. The fifth stage of Loy Yang coal is not clearly defined. Subsequent to the maximum rate temperature, the remaining residue burned out quickly.

The combustion intensity of Gelliondale coal was the lowest of the coals investigated. At the end of fourth stage T_5 (the end of main burning peak), there was still more than 20% of the sample remaining, compared to the 5% and 10% for Loy Yang and Morwell coals respectively. The fifth stage of the DTA profile for Gelliondale coal consisted of two distinct peaks.

From Tables 1 and 3, it is observed that tne volatile matter content of the 3 brown coal samples is similar, but their burning profiles and combustion characteristics such as ignition temperatures $T_{i.g}$, maximum rates R_m and the temperature of maximum rate T_m are significantly different. For higher rank coal, the ignition is mainly controlled by the volatile matter content [10], but for a lower rank coal, the ignition and combustion are largely dependent on the reactivity. Chen and Sun [11] have reported TG and EGA data which indicate that for different coals with similar volatile matter content, the difference in the combustion characteristics are caused by the differences in the composition and content of combustible gases and the initial evolving temperature.

It is known that the area under the DTA curve may be related to the heat change during the process [12]. In this present study, the relationship between specific energy Q_g and DTA peak area A is derived for brown coal samples with $r = 0.95$:

$$Q_g \text{ (MJ/kg)} = 24.76 + 6.68 \times 10^{-5}\ A/W$$

where Q_g is the specific energy (gross dry, MJ/kg) of brown coal, A is the area under DTA peak (μV · sec), and W is the mass of sample (mg). The calculated values and their deviation from corresponding experimental results are listed in Table 4.

Table 4 Specific energy of brown coal samples from DTA peak area

Sample	A/W μV · sec	Q_g, calc. MJ/kg	Q_g, exp. MJ/kg	ΔQ_g, MJ/kg	% error ± %
Morwell	22,011	26.23	26.21	−0.02	0.08
Loy Yang	20,134	26.10	26.16	0.06	0.2
Gelliondale	18,734	26.01	25.99	−0.02	0.08

Oxidation of lithotypes of brown coal

Figures 6 and 7 show the TG and DTA curves of Morwell lithotypes. Some characteristics are listed in Table 5. The burning profiles of Morwell light and Morwell medium light are very similar.

For Morwell pale, the first peak relates to volatilization combined with the main combustion peak forming a single peak which occurs in a lower temperature range. Unlike the other lithotype samples, when ignited, Morwell pale lithotype burns off quickly, that is, there is no "false ignition" phenomena for Morwell pale. The burning profile of Morwell dark shifts towards a higher temperature range and its intensity of oxidation is much lower than those of other lithotypes.

Figures 8 and 9 show TG and DTA curves of lithotypes of Yallourn coal. Yallourn pale has a highest first temperature, corresponding to the release of volatile matter. The main peak of Yallourn med. light/med. dark shifts towards a lower temperature and the fifth stage on the DTA curve is the most pronounced. As

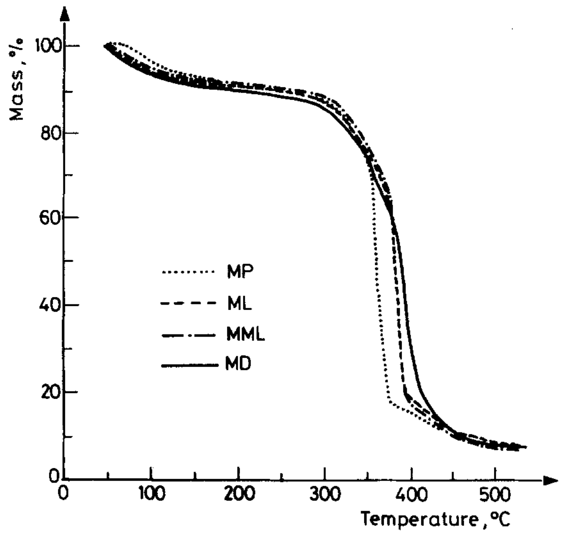

Fig. 6 TG curves of Morwell lithotypes

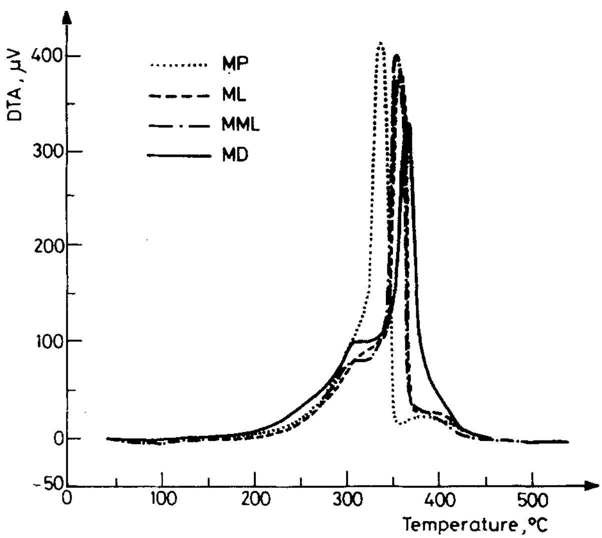

Fig. 7 DTA curves of Morwell lithotypes

Table 5 Oxidation characteristics of different lithotypes

Sample	TG				DTA peak						
	$T_{i.g}$	T_m °C	T_b	R_m μg/min	T_1	T_2	T_3	T_4 °C	T_5	T_6	H/C (atomic)
Morwell coal field											
pale	260	324	480	−1523	153	—	—	333	347	381	0.976
light	254	347	500	−1511	175	315	328	354	378	447	0.906
medium light	254	347	543	−1509	168	313	321	355	381	422	0.869
dark	251	360	454	− 963	150	308	325	364	454	—	0.832
Yallourn coal field											
pale	260	366	510	−2214	181	333	352	372	389	429	1.041
medium light	238	360	470	−1688	145	313	341	366	383	416	0.829
med light/ med. dark	236	352	445	−1538	176	312	331	360	381	404	0.830
dark	253	381	475	− 943	175	330	348	385	450	—	0.828

with the Morwell dark lithotype, the reactivity of Yallourn dark is also less than that of the other lithotypes.

Conclusion

1. Thermal analysis techniques can be successfully applied to the study of coal combustion. The thermal analysis parameter can be used to characterize and compare the reactivity with oxygen of coals from different coal fields and of different lithotypes.

2. Brown coal samples from different coal fields have different combustion reactivity, although these all belong to the same rank. Unlike high rank coals, the combustion of lower rank coals is dependent on both the volatile matter content and the reactivity with oxygen. The high reactivity with oxygen is the probably the result of the high surface area of brown coal.

3. The heat released during coal combustion process is related to the peak area of the corresponding DTA curve. A correlation can be derived between peak area of DTA curve and the specific energy of the brown coal sample.

4. For the different lithotypes investigated in the present study, the dark lithotype is relatively less reactive to oxidation than the other lithotypes, irrespective of the coal field source.

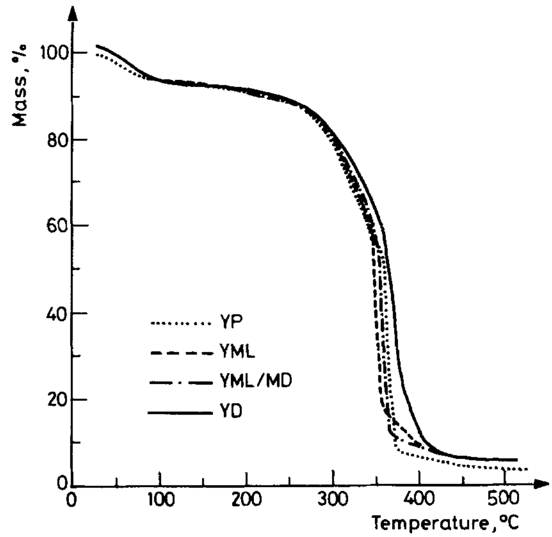

Fig. 8 TG curves of Yallourn lithotypes

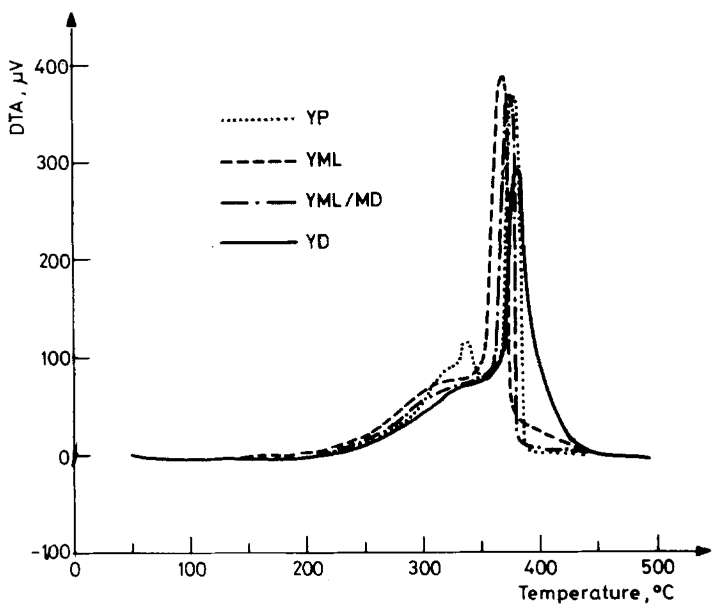

Fig. 9 DTA curves of Yallourn lithotypes

References

1 C. L. Wagoner and A. F. Dazy, Winter Annual Meeting of ASME, Pittsburgh, P.A., USA, 1967, pp. 12–17.
2 C. L. Wagoner and E. C. Winegartner, J. Eng. Power, 4 (1973) 119.
3 D. E. Mainwaring and G. B. Christis, 2nd Coal Research Conference, Wellington, N.Z., 2, 1987, pp. 2–4.
4 M. S. Matyjas Zczyk and R. Przeliorz, Thermochim. Acta, 96 (1985) 169.
6 Z. X. Mao, D. Z. Yan and B. Z. Zhao, Proceedings of 5th Conf. on Engineering Thermophysics, Suzhou, P.R.C., 1986.
6 S. E. Smith, R. C. Neavel, E. J. Hippo and R. N. Miller, Fuel, 60 (1981) 458.
7 T. K. Pong Be Me and I. J. Harris, J. Institute of Energy, 9 (1984) 383.
8 P. A. Morgan, S. D. Roberson and J. F. Unsworth, Fuel, 65 (1986) 1546.
9 J. W. Cumming and J. Mclaughlin, Thermochim. Acta, 57 (1982) 253.
10 J. J. Reuther, International Symposium on Combustion Diagnostics, Akron. Ohio, USA, 1983.
11 J. Chen and X. Sun, J. Eng. Thermophysics, 7 (1986) 172.
12 W. W. Wendlandt, "Thermal Analysis", 3rd Edition, Wiley-Interscience, N.Y., USA, 1986, p. 269.

Zusammenfassung — Verschiedene TG- und DTA-Techniken wurden zur Untersuchung der Verbrennungscharakteristik von Braunkohle aus Viktoria angewendet, die von verschieden Kohlefeldern stammt und verschiedene Hauptstreifenarten besitzt. Die TG- und DTA-Profile des gesamten Verbrennungsvorganges wurden ermittelt, um einen Satz von Parametern zur Charakterisierung des Oxydationspotentiales der Kohleproben zu erhalten. Diese Parameter können auch zur Vorhersage des Verbrennungsverhaltens von Kohlestaub in Industrieöfen benutzt werden. die Fläche unter dem DTA-Hauptverbrennungspeak steht in enger Beziehung zu der während des Verbrennungsvorganges freigesetzten Wärme und bietet somit ein Mittel zur Bestimmung der spezifischen Energie der Kohle. Auch die verschiedenen Hauptstreifenarten werden durch ihre entsprechenden TG- und DTA-Verbrennungsprofile charakterisiert.

Резюме — Для изучения характеристик сгорания викторианского бурого угля различных литотипов и месторождения был использован совмещенный метод ТГ и ДТА. Полученные кривые ТГ и ДТА всего процесса сгорания позволили получить набор параметров, характеризующих окислительный потенциал исследованных образцов угля. Полученные параметры могут быть также использованы для определения характеристик гореня распыленного угля в промышленных печах. Площадь главного ДТА пика горения тесно связана с теплотой, выделяющейся в процессе горения, и поэтому может быть использована для определения удельной энергии угля. Различные литотипы угля также охарактеризованы соответствующими ТГ и ДТА кривыми сгорания.