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A THERMAL ANALYSIS STUDY OF THE PYROLYSIS OF VICTORIAN BROWN COAL

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The pyrolysis in a nitrogen atmosphere of three run-of-mine samples and a suite of lithotype samples of Victorian brown coal has been investigated using simultaneous TG/DTG/DTA. The TG, DTG curves provide parameters which represent the pyrolysis properties of coal. The pyrolysis profiles can also be used as "fingerprints" of brown coal lithotypes and hence are of value in the context of the broad characterization of coal.

Victorian brown coal is in the low rank category of coals. The moisture content of raw brown coal is high (60 to 70%). This is the major problem in the utilization of Victorian brown coal for it makes long distance transportation uneconomic. The major uses of Victorian brown coal are burning to generate electricity, manufacture of briquettes for industrial and domestic heating, and carbonization of briquettes to produce brown coal char.

Pyrolysis is a fundamental process in the combustion, carbonization and gasification of coal. Volatile matter and the corresponding release profile, including the initial temperature, maximum rate of devolatilization and other factors which affect the release of volatiles, are very important properties which relate to the efficiency of these processes.

Thermal analysis has previously been used in the study of coal pyrolysis [1–11]. Although the sample heating rate is much less than that involved in an industrial furnace ($>6\times10^5$ deg/min), such an analysis can yield considerable information on the pyrolysis properties of coal.

This paper reports the results of pyrolysis of Victorian brown coal as investigated by thermogravimetry and differential thermal analysis.

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Experimental

Brown coal samples

Two sets of coal samples were used in the present study. One set comprises three run-of-mine coal samples obtained from different coal fields (Morwell, Loy Yang and Gelliondale). The other set comprises of 2 suites of brown coal lithotypes obtained from the Morwell and Yallourn coal fields. Tables 1 and 2 show the proximate and ultimate analyses of the three run-of-mine samples and the suite of lithotype samples respectively.

Table 1 Analyses of three samples of Victorian brown coal

Sample	Morwell	Gelliondale	Loy Yang
Proximate analysis			
Moisture (%)[a]	12.7	7.3	15.6
Ash (%d)[a]	3.8	5.4	1.1
M&I (minerals and inorganics) (%db)	2.3	3.0	0.8
VM (volatile matter) (%db)	47.7	49.9	51.7
FC (fixed carbon)	48.5	44.7	47.2
Specific energy			
Q_g (gross dry, MJ/kg)	26.21	25.99	26.16
Ultimate analysis (% dmif)			
Carbon	69.8	66.5	68.2
Hydrogen	4.8	4.7	4.9
Nitrogen	0.55	0.56	0.57
Sulphur	0.27	0.78	0.32
Oxygen (by difference)	24.6	27.5	26.0
H/C atomic ratio	0.83	0.85	0.86
O/C atomic ratio	0.26	0.31	0.29

[a] dry basis.

Table 2 Lithotypes of brown coal

No.	Sample	Proximate %db				Ultimate %db				Q_{gross}, dry 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

All coal samples used for the present study have been air dried and milled to a particle size of minus 72 mesh (212 μm).

Thermal analysis system

Thermal analyses were carried out using Rigaku–Denki, Type 8085 (Thermoflex) TG–DTA Thermal Analysis System under the following conditions: nitrogen atmosphere (flow rate 0.2 dm^3/min); heating rate, 10 deg/min; platinum crucibles; inert reference, Al_2O_3; sample size, 10 mg.

The TG, DTG and DTA curves were recorded simultaneously. The repeatability of the characteristic temperatures is within the range ±2 °C.

Results and discussion

Pyrolysis characteristics of brown coal samples from different coal fields

The corresponding TG and DTG curves for the three samples from the Morwell, Gelliondale and Loy Yang coal fields are shown in Figs 1 and 2 respectively.

Generally, pyrolysis of brown coal can be divided into three stages [5]. Up to 150°, loss of physically absorbed water predominates. Above 150° and below about 310°, a small amount of volatile matter, mainly alkyl aromatics, is evolved. Primary

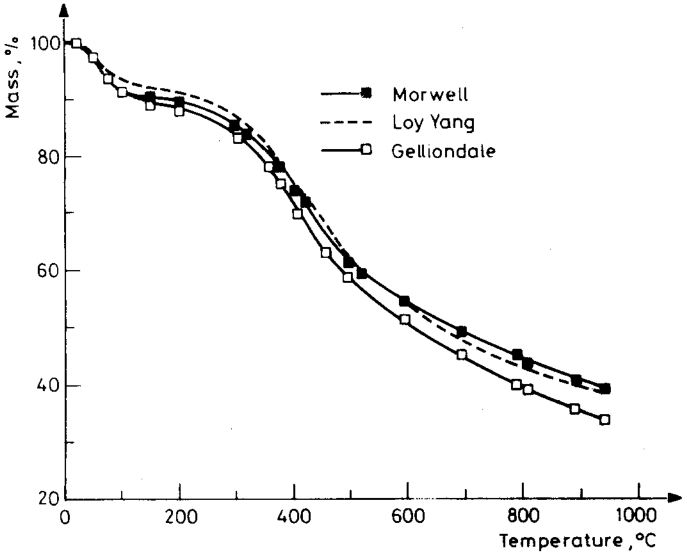

Fig. 1 TG profiles of brown coal samples

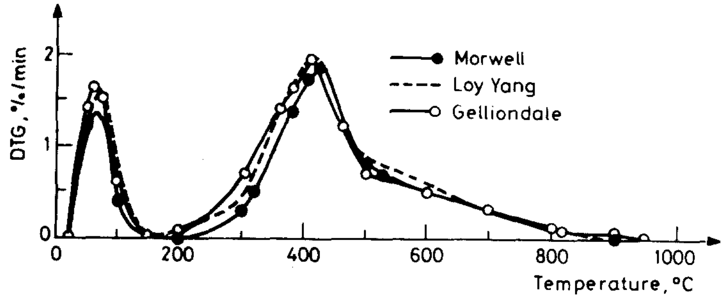

Fig. 2 DTG curves of brown coal samples

carbonization commences between 310 and 500°. The larger proportion of the volatiles is released during this period to form tars and gaseous products. The maximum rate of devolatilization occurs during this period. Subsequently, secondary carbonization occurs above 500°. The sample mass and the rate of devolatilization decreases progressively throughout the pyrolysis process.

The extrapolated onset temperature $T_{e,0}$ of the TG profiles is interpreted as the initial temperature of volatilization and the second peak temperature of the DTG curve corresponds to the temperature T_m at which the maximum rate of volatilization R_m occurs. Mass loss prior to 150° = Moisture %M; mass loss between 150 and 815° = final volatile matter yield %Vf. (At 815°, the rate of mass loss R is equal to about 0.01%/min.) Table 3 summarizes the results of these parameters as derived from TG and DTG profiles for the coal samples investigated.

The Gelliondale sample had the highest volatile matter yield V, and the lowest initial pyrolysis temperature T_i, whereas the Morwell sample had the lowest V_f and the highest T_i values. Thus in general, high F_f values correspond with low T_i values.

From the TG data, a relationship between volatile matter yield and temperature can be derived. For $T > 300$ °C and heating rate $\beta = 10$ deg/min, a possible relationship is:

$$V/V_f = 2.04 - 1.13 \times 10^3/T$$

with correlation coefficient $r = 1.00$.

Table 3 Pyrolysis properties of brown coal samples

Sample	%M (air dry)	V_f, %db	V_f/VM	T_i, °C	T_m, °C	R_m, %/min
Morwell	9.5	52.0	1.09	323	426	1.85
Gelliondale	10.6	56.2	1.13	306	411	1.91
Loy Yang	8.2	53.8	1.04	316	411	1.91

V is the volatile matter yield at absolute temperature T and V_f is the final volatile matter yield. V_f is different from the standard volatile yield VM, due to a difference in experimental conditions. The final volatile yield is affected by variables such as temperature, coal rank, particle size, and may also depend on the heating rate [1]. For the samples investigated, the ratio of V_f to the standard yield of volatile matter VM varies from 1.04 to 1.13. The V/V_f *vs.* $1/T$ plot is shown in Fig. 3.

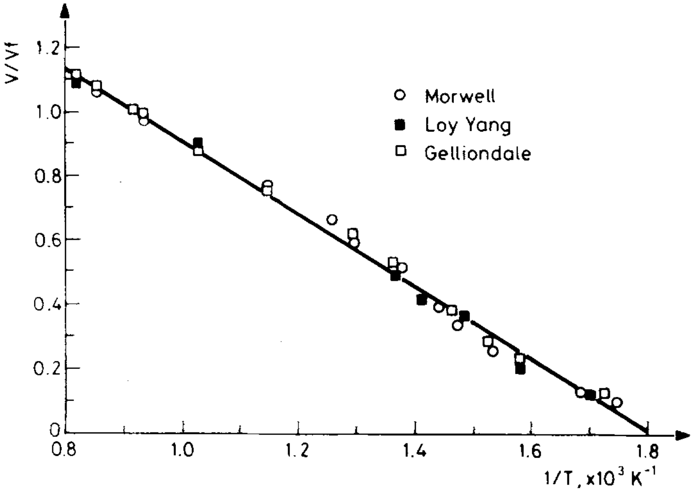

Fig. 3 Relationship between volatile matter yield and temperature

Effect of heating rate on pyrolysis of brown coal

A sample of Morwell Dark coal was investigated using different heating rates from 5 deg/min to 80 deg/min, in order to observe the effect of heating rate. The results are shown in Table 4 and Fig. 4.

From these data, it is apparent that the initial temperature of volatilization increases with increasing heating rate, and hence, the release of volatiles is postponed. This may be explained in terms of the kinetics [3] involved.

Table 4 Pyrolysis properties of Morwell Dark at different heating rates

Heating rate, deg/min	T_i, °C	T_m, °C	R_m, %/min	V_f, %db
5	330	415	1.03	51.0
10	335	440	1.78	48.5
20	352	449	3.54	50.8
40	355	465	8.30	51.5
80	384	484	15.20	50.2

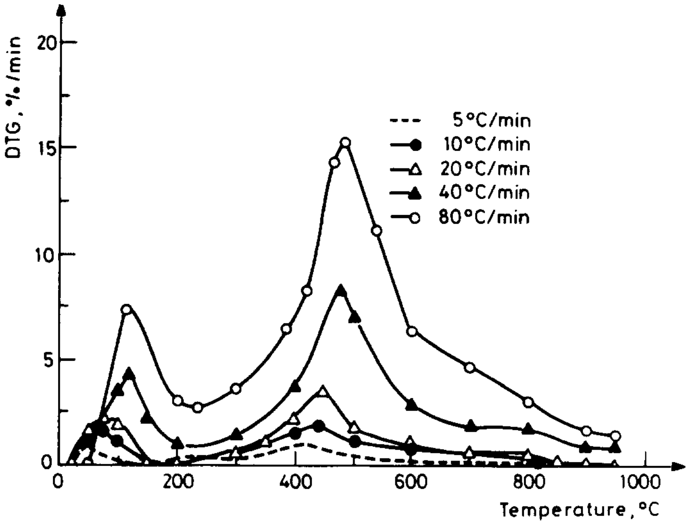

Fig. 4 DTG curves of a Morwell dark lithotype sample at different heating rates

If the total reaction order $n=1$, the rate of pyrolysis can be expressed as

$$v = \mathrm{d}C/\mathrm{d}t = k_0 \cdot e^{-E/RT} \cdot C \tag{1}$$

where C: concentration of volatile; t: time; k_0: frequency factor; E: activation energy; R: gas law constant; T: absolute temperature K.

Equation (1) can be written as:

$$\frac{\mathrm{d}C}{\mathrm{d}T} \cdot \frac{\mathrm{d}T}{\mathrm{d}t} = k_0 \cdot e^{-E/RT} \cdot C \tag{2}$$

$\frac{\mathrm{d}T}{\mathrm{d}t} = \beta$, the heating rate, hence

$$\beta \frac{\mathrm{d}C}{\mathrm{d}T} = k_0 \cdot e^{-E/RT} \cdot C \tag{3}$$

Integration of (3) gives,

$$\beta \ln C/C_0 = \int_{T_0}^{T} k_0 \cdot e^{-E/RT} \cdot \mathrm{d}T \tag{4}$$

Considering C/C_0 does not change with temperature during the initial period,

$$\frac{\mathrm{d}T}{\mathrm{d}\beta} = \frac{k_0}{\ln C/C_0} e^{-E/RT} \tag{5}$$

since $C > C_0$, $k_0 \cdot e^{-E/RT} > 0$,

$$\frac{dT}{d\beta} > 0$$

Thus, as the heating rate β increases the initial temperature of volatilization increases.

From the present thermal analysis data, the initial temperature of volatilization T_i and the maximum mass rate loss temperature T_m increase with heating rate according to following equations:

$$T_i = 298\,\beta^{0.0561}, \qquad r = 0.99$$

$$T_m = 384\,\beta^{0.0533}, \qquad r = 0.99$$

as shown in Fig. 5.

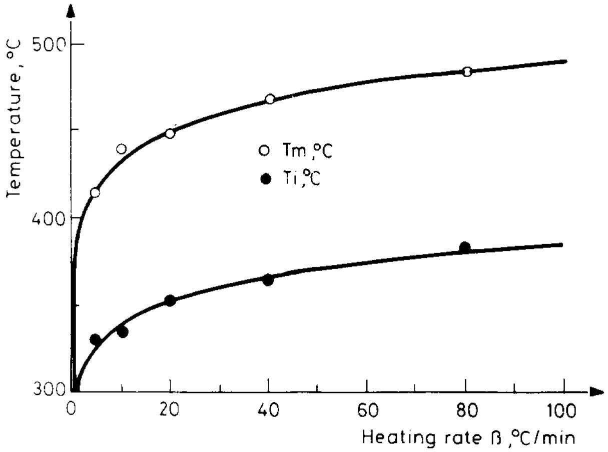

Fig. 5 Increase of T_i and T_m with heating rate β

From Fig. 6, it is apparent that the maximum rate of volatilization increases linearly with increased heating rate according to the equation:

$$R_m = -0.019 + 0.193\,\beta, \qquad r = 1.00$$

The relationship between V/V_f and temperature of Morwell dark coal under different heating rates is presented in Fig. 7. V/V_f at different heating rates changes linearly with $1/T$ (all correlation coefficients $r = 1.00$). The slopes of these lines are in the range 1.12 to 1.25 and the intercepts vary between 2.02 to 2.08.

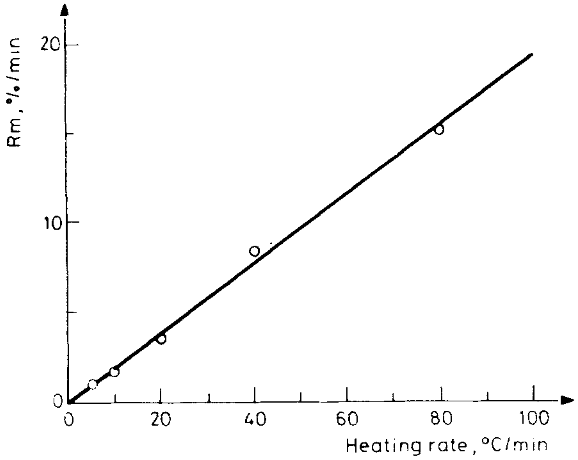

Fig. 6 Relationship between R_m and heating rate β

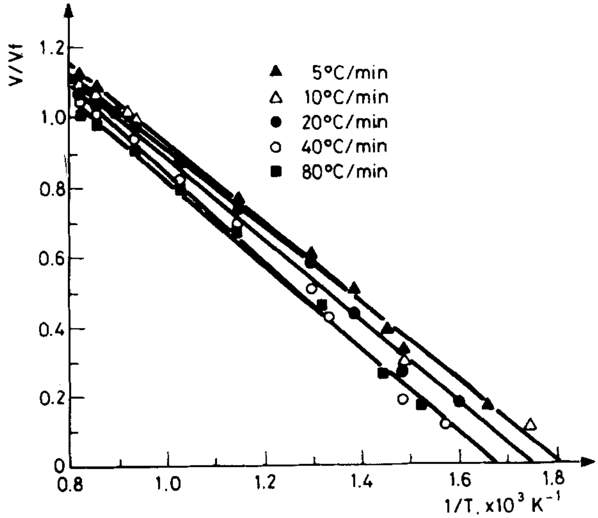

Fig. 7 The relationship between volatile matter yield and temperature of Morwell dark coal at different heating rates

Pyrolysis of different lithotypes of brown coal

Pyrolysis profiles of the 4 lithotypes from the Morwell and Yallourn coal fields are shown in Fig. 8 and Fig. 9 respectively. Some corresponding pyrolysis properties are listed in Table 5.

Among the 4 lithotypes of Morwell coal, Sample a "Morwell Pale" has the highest volatile matter yield and the lowest initial volatilization temperature,

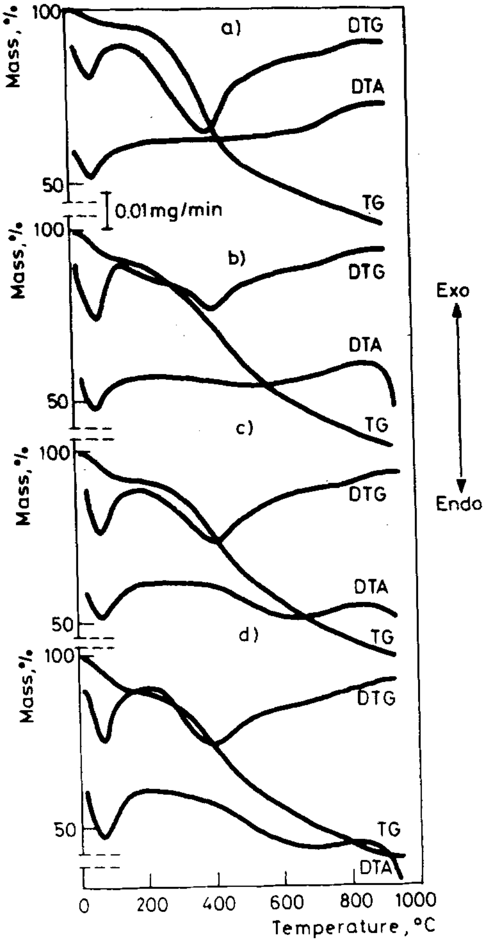

Fig. 8 Pyrolysis profiles of Morwell lithotypes. a) Morwell pale; b) Morwell light; c) Morwell medium light; d) Morwell dark

whereas V_f of Sample d"Morwell Dark" is lowest but the corresponding T_i and T_m are highest. Hence, the more pale the lithotype is, the higher is the corresponding V_f and R_m and the lower is T_i and T_m.

Chemical analysis results, given in Table 1, also indicate a correlation between coal lithotype and chemical properties. The darker the lithotype is, the lower is the H/C ratio. In general, the H/C atomic ratio usually decreases with increasing coal rank and it provides a good indication of the aromaticity of the coal. Figure 10 shows the relationship between H/C and pyrolysis properties of Morwell lithotypes. From

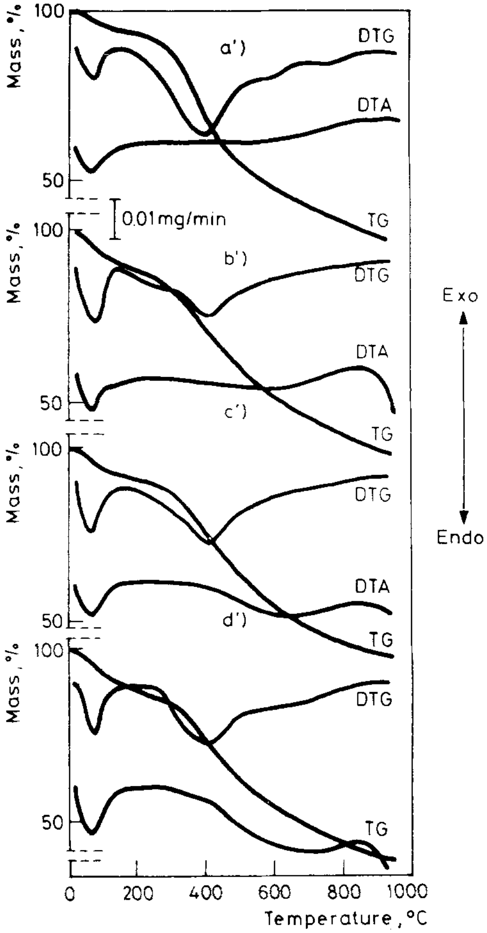

Fig. 9 Pyrolysis profiles of Yallourn lithotypes. a′ Yallourn pale; b′ Yallourn med. light; c′ Yallourn med. light/med. dark; d′ Yallourn dark

Fig. 10, T_i and T_m decrease with increasing H/C ratio, whereas R_m and V_f increase with increasing H/C ratio.

The DTA curves of all lithotypes (Figs 8 and 9) are similar; the endothermic peak below 150° is related to release of moisture. Above 700°, some samples indicate an exothermic drift. However, overall, the associated heat effect is very small and may be neglected. For Sample a, a small exothermic peak at about 110° was observed.

The TG and DTA data for Yallourn lithotypes are similar to those of Morwell lithotypes, except that volatilization commences at a lower temperature. The Yallourn Pale has the lowest T_i and T_m and the highest R_m, whereas the other three lithotypes have similar pyrolysis properties.

Table 5 Pyrolysis data for different lithotypes of brown coal

	Sample	T_i, °C	T_m, °C	R_m, %/min	V_f, %db	H/C (atom.)
a	Morwell pale	320	426	3.15	61.2	0.976
b	Morwell light	330	431	2.51	57.0	0.906
c	Morwell med. light	332	435	2.54	51.0	0.869
d	Morwell dark	335	440	1.78	48.5	0.832
a′	Yallourn pale	300	400	2.95	59.5	1.041
b′	Yallourn med. light	286	408	1.90	56.9	0.829
c′	Yallourn med. light/med. dark	300	410	2.02	53.6	0.830
d′	Yallourn dark	300	414	1.86	53.1	0.828

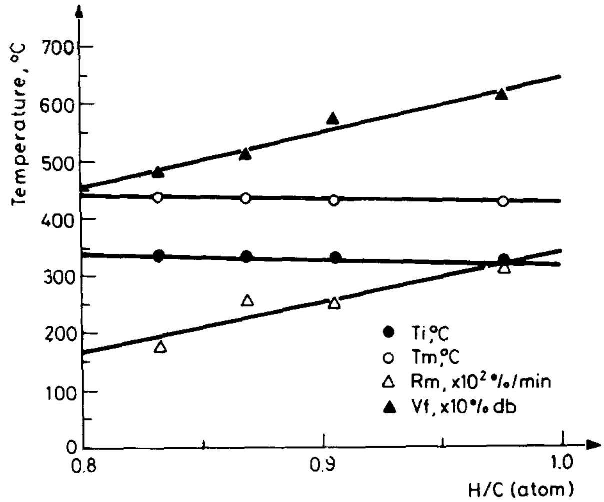

Fig. 10 Relationship between T_i, T_m, R_m, V_f and H/C for Morwell lithotypes

Results given in Figs 8 and 9 and Table 5 indicate that the different lithotypes of brown coal have different pyrolysis profiles. Hence, the pyrolysis profile may be used to characterize different coals, including samples within the same field such as lithotypes.

Conclusions

1. Pyrolysis profiles of brown coal from different coal fields are different and can be used to characterize coal samples.

2. Volatile matter yield varies with experimental conditions. For the brown coal samples investigated, the ratio of V_f/VM ranges from 1.04 to 1.13. For $T > 300°$, a relationship has been derived which correlates volatile yield with temperature. This equation can be used to estimate the volatile matter yield at different temperatures during a pyrolysis or gasification process.

3. For the same coal, volatilization is strongly affected by heating rate and the corresponding temperature T_m increases with increasing heating rate.

4. The pyrolysis properties of different lithotypes vary with H/C ratio. For the lithotype with the higher H/C ratio, the initial temperature T_i and the maximum mass rate loss temperature T_m are lower and the maximum rate of volatilization R_m and the final volatile matter yield V_f are higher.

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Zusammenfassung — Mittels Pyrolyse in Stickstoff wurden unter Anwendung simultaner TG, DTG und DTA drei Förderproben und eine Reihe von Lithotypenproben von Viktoriabraunkohle untersucht. Die TG und DTG Kurven liefern Parameter, die für die Pyrolyseneigenschaften von Kohle charakteristisch sind. Die Pyrolysenprofile können auch als „Fingerabdruck“ von Braunkohlenlithotypen benutzt werden und sind deshalb im Zusammenhang mit einer umfassenden Charakteristik der Kohle von Bedeutung.

Резюме — Совмещенным методом ТГ, ДТГ и ДТА изучен пиролиз трех отмытых образцов и набора литотипных образцов викторианского бурого угля в атмосфере азота. Кривые ТГ и ДТГ дали параметры, характеризующие пиролитические свойства угля. Пиролизные профили могут быть также использованы как «отпечатки пальцев» литотипных образцов бурого угля и могут служить оценкой обширной характеристики угля.