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THERMAL ANALYSIS OF AUSTRALIAN COALS— A SHORT REVIEW

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It is evident that thermal analysis studies of Australian coals are of primary significance in the rationalisation of the various physical and chemical processes inherent in energy generation from these fossil fuels. To data, considerable such data has been accumulated correlating combustion efficiency with the coal primary structure, surface phenomena, included metal ions, volatile matter release profiles, particle size and corresponding char properties. The kinetics of these complex processes are now also modelled.

This short Review is designed to provide an overview of current thermal analysis investigations of Australian coals, particularly Australian brown coal. Specific reference is made to our present, as yet unpublished work and this is discussed in conjunction with similar and related published studies.

Excellent Reviews of thermal analysis data for coal, other solid fuels and oil shales have recently been published by Warne and Dubrawski [1] and Rustschev [2] and these together provide a most comprehensive coverage of the field.

Coal is Australia's major fossil fuel resource which is used primiarily for the production of electrical energy. Hence coal research in Australia is largely focused on coal combustion and significant thermal analysis studies of this process are therefore in progress. Australian coal combustion research has been reviewed by Smith [3].

The majority of current thermal analysis studies in Australian coals relate specifically to Victorian Brown Coal which is the primary energy source for the State of Victoria. This major coal deposit is estimated at 120,000 million tonnes and the coal seams range in thickness from 6–140 metres, located at a depth ranging from 10–30 metres. Thus the coal is easily and economically mined by the "open-

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cut" method and the present annual production is about 30 million tonnes—the bulk of which is used for "on-location" electricity generation.

Brown coal is a young, soft, low rank coal containing 50–70% water, which is considerably higher than for the higher rank coals: sub-bituminous coal, 25–30%; bituminous coal 5–10% and anthracite 2–5%. As coal rank increases, the carbon content of the coal increases, aromaticity increases and the proportion of volatile matter decreases. For brown coal (dry basis), volatile matter amounts to 45–55% compared to bituminous coal, 20–40% and anthracite 5–7%. Brown coal also has a low specific energy (heat energy per g), 25–30 $kJ \cdot g^{-1}$ compared to bituminous coal, 30–35 and anthracite, 35–38 $kJ \cdot g^{-1}$ respectively.

The principal characteristics for efficient combustion of coal are high volatility, low ash content and low abbrasiveness. In these respects, Victorian brown coal is an excellent energy source but has the major disadvantage of having the highest overall moisture content of any brown coal source worldwide (Fig. 1) and hence a relatively low calorific value. However, in terms of economic energy production, these disadvantages are somewhat overcome by the relatively low mining and transportation costs involved.

The chemical structure of brown coal is complex but may be represented schematically as shown in Fig. 2. Significant intrinsic structural features include: a

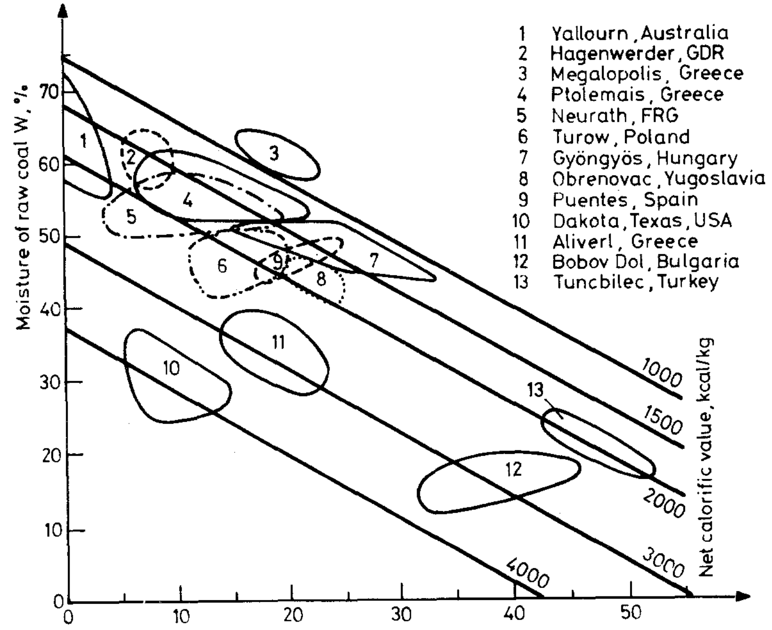

Fig. 1 Relative moisture and ash contents and calorific value of Victorian Brown coal

high proportion of carboxylic and phenolic groups, the presence of inter and intramolecular hydrogen bonding and the inclusion of metal ions within the overall structure. These features collectively define the essential chemical properties of the coal.

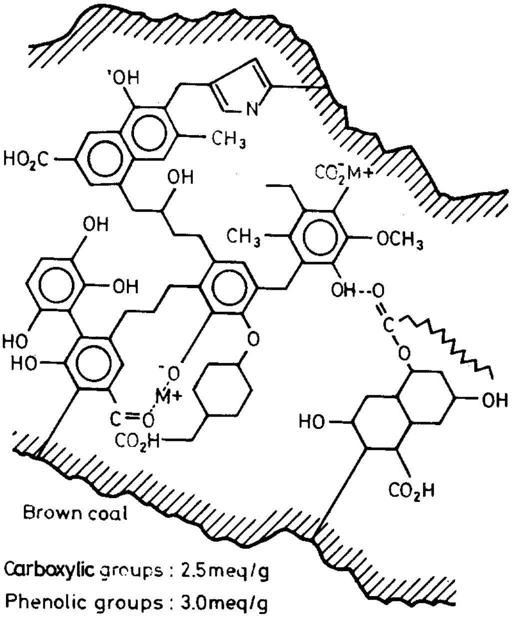

Fig. 2 Schematic structure of Brown coal

The composition of coal may be given in terms of its "proximate analysis" which quantitatively defines water, volatile matter and ash contents and indirectly, the fixed carbon content. Proximate analysis data does not provide information on coal structure, but such data, in combination with specific energy data, may be directly correlated with the behaviour of coal in many industrial processes, in particular, those involved with energy production. It is well-known that proximate analysis data can be determined by thermogravimetry and Hill et al. [4] have applied TG to determine the proximate analysis of the five main lithotypes of Victorian Brown Coal and these data, which exemplify the relatively high volatiles content and relatively low ash content of this coal variety are reproduced in Table 1.

Mainwaring and Christie [5] have investigated by DTA the mechanisms of heat evolution of low rank coals and the ultimate spontaneous combustion thereof. The rate of energy release by the oxidation of the coal surface was determined. Brown coals produce oxidation exotherms in the low temperature region up to 400° whereas higher rank coals undergo combustion at higher temperatures as shown in

Table 1 Summary of proximate analysis data for Victorian Brown Coal

Lithotype	Mean mass loss (untreated sample) ($\bar{X}$ & σ)				Mean mass loss (Dry sample) ($\bar{X}$ & σ) %		
	Moisture	Volatiles (-moisture)	Carbon	Ash	Volatiles	Carbon	Ash
Pale	52.2 ±0.9	27.1 ±0.5	19.2 ±0.1	1.4 ±0.5	56.7 ±0.3	40.0 ±1.0	2.9 ±1.1
Light	58.9 ±0.8	21.3 ±0.7	19.5 ±0.6	0.3 ±0.5	51.8 ±1.3	47.4 ±1.1	0.7 ±1.1
Medium Light	60.5 ±0.7	19.6 ±0.5	19.0 ±0.3	0.9 ±0.1	49.7 ±0.3	48.0 ±0.4	2.2 ±0.3
Medium Dark	61.1 ±0.6	18.7 ±0.2	19.1 ±0.2	1.1 ±0.3	48.0 ±0.5	49.1 ±0.4	2.8 ±0.8
Dark	61.9 ±0.4	17.3 ±0.4	19.5 ±0.3	1.3 ±0.5	45.4 ±0.7	51.1 ±0.7	3.5 ±1.3

Fig. 3. It was further shown that the coal surface functional groups and included metal ions exert a significant influence on the low temperature oxidation of the coal since if samples are pre-heated in an inert atmosphere or acid washed, the temperature of spontaneous combustion increases. These two effects are shown in Figs 4 and 5 respectively.

Ma et al. [6] have investigated the pyrolysis of Victorian Brown Coal by simultaneous TG/DTG/DTA and have found that the TG profiles of coal samples obtained from different fields are significantly different (Fig. 6) and hence these can

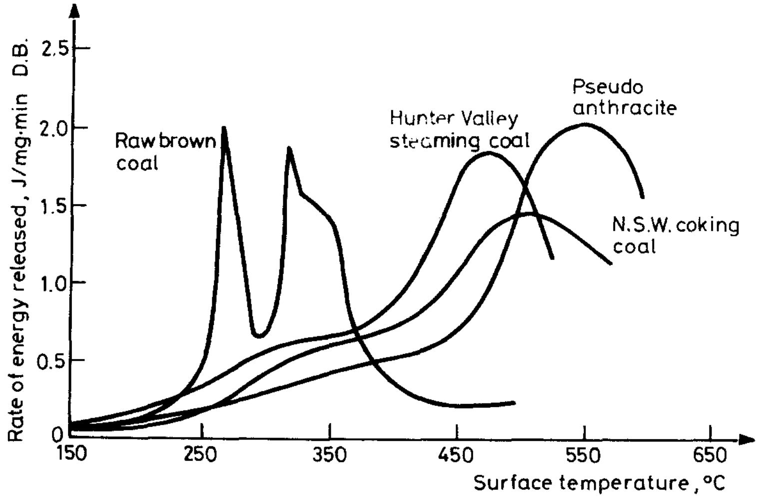

Fig. 3 Reactivity exotherms of a range of Australian coals

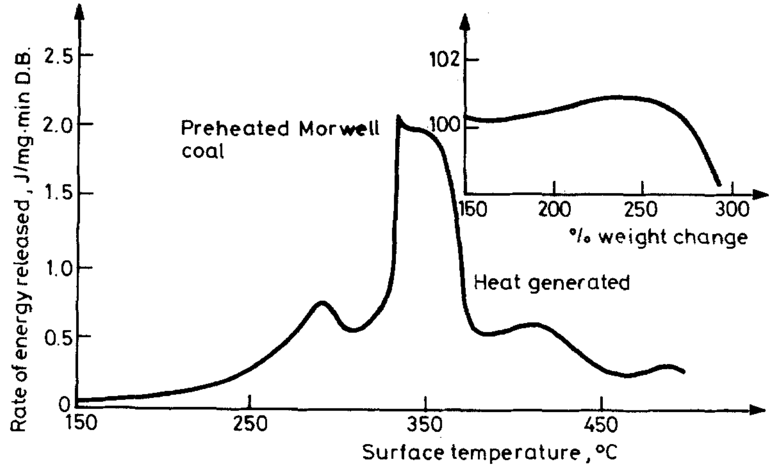

Fig. 4 Reactivity exotherm and low temperature weight change of preheated Morwell coal

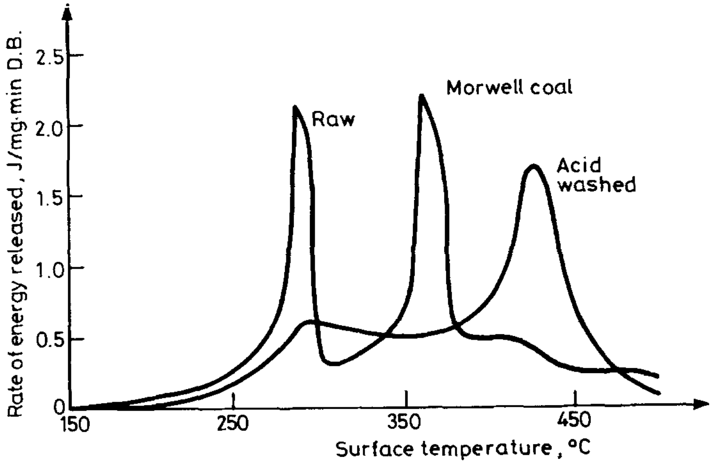

Fig. 5 Reactivity exotherms of raw and acid washed Morwell coal

be used as "fingerprints" in the general characterisation of coal. At temperatures $>300°$ the volatile matter released is temperature dependent (Fig. 7) and heating rate dependent (Fig. 8). Also, the efficiency of pyrolysis is dependent on the H/C ratio. As this ratio increases, the temperature corresponding to initial pyrolysis T_i and the temperature corresponding to maximum pyrolysis rate T_m decrease whereas the maximum rate of pyrolysis R_m and final volatile matter yield V_f increase (Fig. 9).

Ma et al. [7] have studied the combustion characteristics of Victorian Brown Coal by TG/DTA and have shown that combustion reactivity is dependent on coal source and lithotype (Figs 10, 11 respectively). Further, a linear relationship is derived between coal specific energy Q_g (MJ/kg), DTA peak area (μV sec) and sample mass W (mg):

$$Q_g = 24.76 + 6.68 \times 10^{-5}\, A/W$$

Some relevant results are reproduced in Table 2.

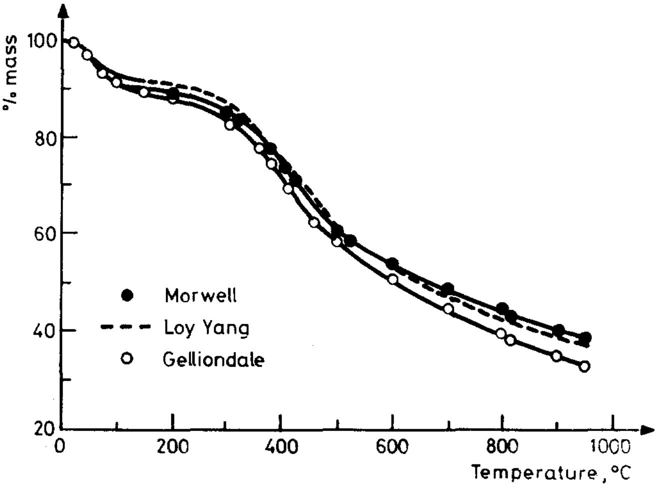

Fig. 6 TG profiles of brown coal samples

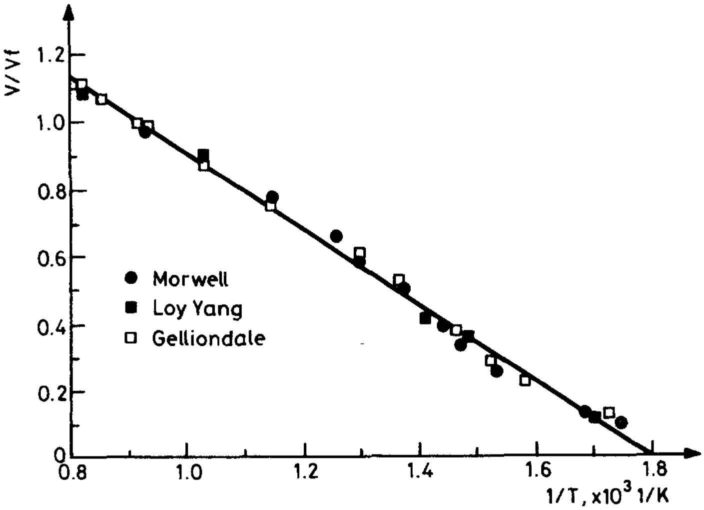

Fig. 7 Relationship between volatile matter yield and temperature

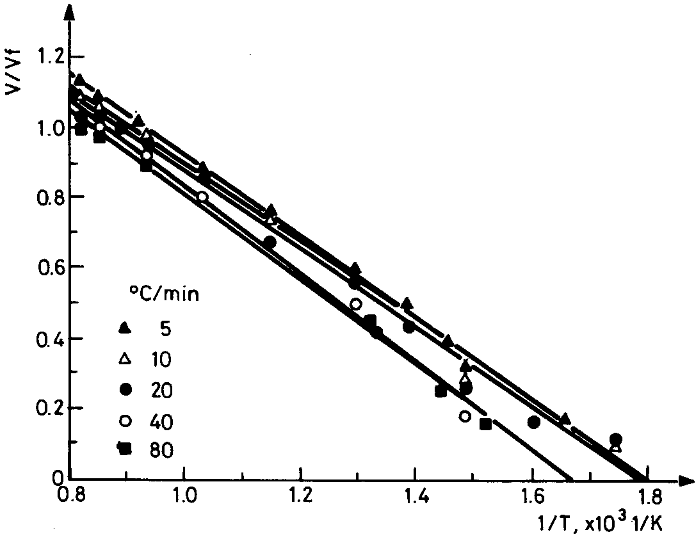

Fig. 8 The relationship between volatile matter yield and temperature of Morwell dark coal at different heating rate

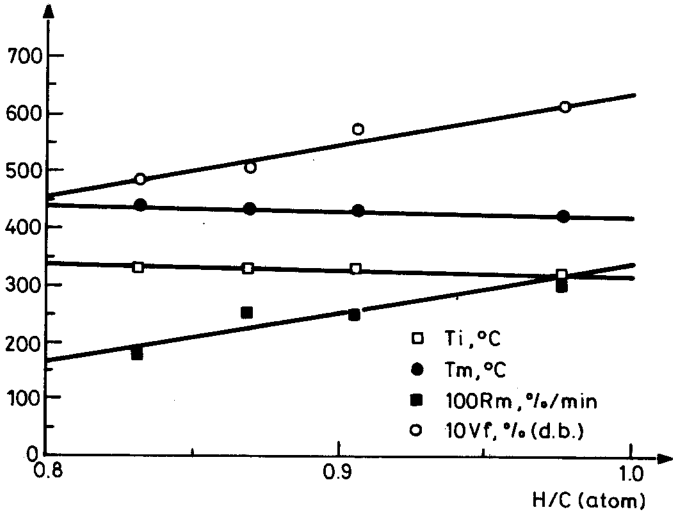

Fig. 9 Relationship between T_i, T_m, R_m, V_f, and H/C for Morwell lithotypes

Table 2 Specific energy of brown coal samples from DTA peak area

Sample	A/W, μV·sec	Q_g, calc., MJ/kg	Q_g, expt.[a], MJ/kg
Morwell	22011	26.23	26.21
Loy Yang	22134	26.10	26.16
Gelliondale	22011	26.01	25.99

[a] From combustion bomb experiments.

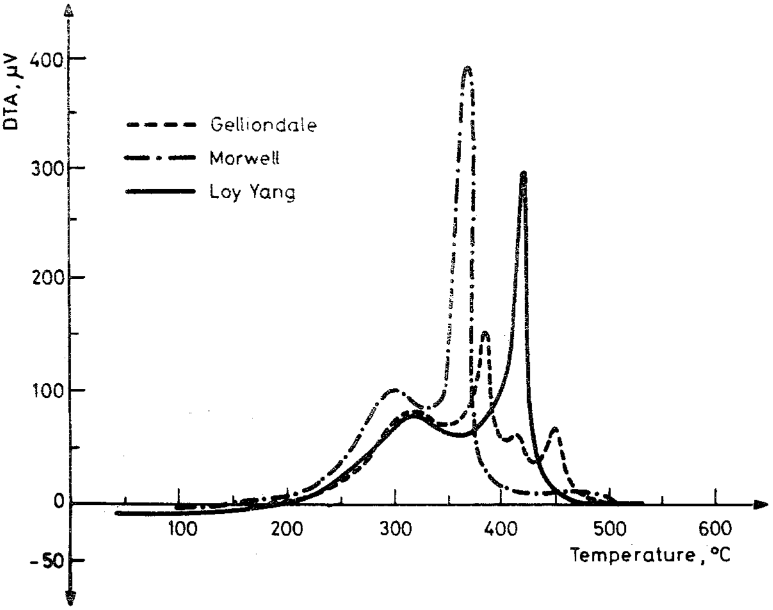

Fig. 10 DTA curves of brown coal samples

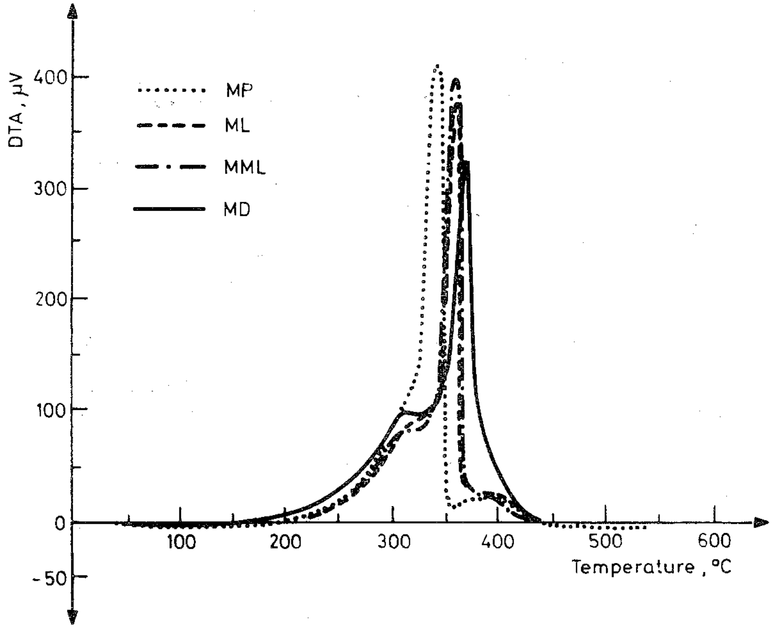

Fig. 11 DTA curves of Morwell lithotypes

Pong Be Me and Harris [8] have reported a detailed DTA study of the catalytic effect of the impregnation of Victorian Brown Coal with various metallic ions on the oxidation process. It appears that Cu^{2+} ion has the most significant catalytic effect (Fig. 12).

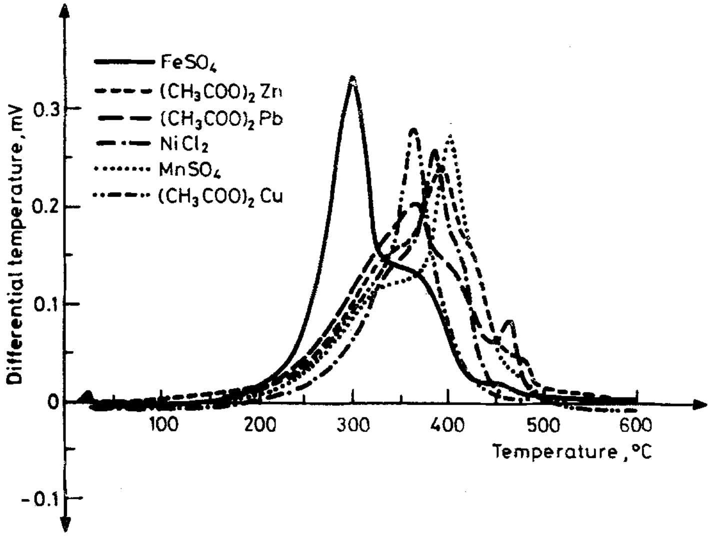

Fig. 12 DTA of brown coal impregnated with various compounds

Similarly, Rogers [9] has employed DTA to investigate the catalytic effect of metal ions on the hydrogenation of N. Z. lignites. It appears that Pb^{2+} and Ni^{2+} produce the most significant catalytic effect (Fig. 13) and these may be suitable catalysts for the hydroliquefation of low-rank coals generally.

King and Attwood [10] have assessed two equations for the calculation of the specific energy Q_g (MJ/kg) of coals based on ultimate analysis data:

$$Q_g = 0.3517[C]+1.1625[H]+0.0628[N]+0.1047[S]-0.110[O] \quad \text{(Boie)}$$

$$Q_g = 0.3383[C]+1.4428[H]+0.09421[N]+0.1804[O] \quad \text{(Dulong)}$$

and have shown, via extensive examples, that neither of these are applicable to brown coal.

Ma and Hill [11] have derived relationships between Q_g (MJ/kg) and proximate and ultimate analysis data for Victorian Brown Coal:

$$Q_g = 443.9/M-0.176A+0.075VM+20.33$$

(M = moisture content (% d.b.): A = ash content (% d.b.)
VM = volatile matter content (% dmif))

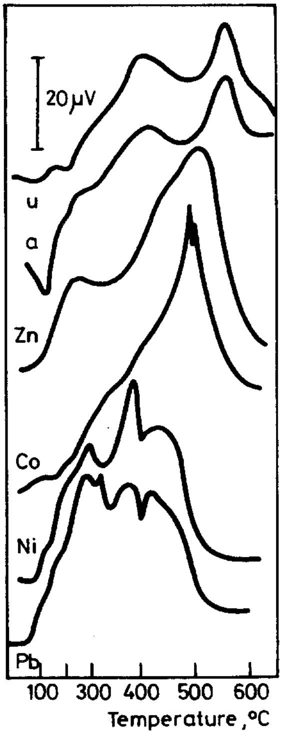

Fig. 13 DTA in hydrogen at 8.0 NPa of Mataura lignite: *u*, untreated, 6.0 mg; *a*, acid-washed, 5.5 mg; and ion exchanged with Zn, 5.1 mg; Co, 5.3 mg; Ni, 5.2 mg; Pb, 5.8 mg

$$Q_g = 0.160[\mathrm{C}] + 0.992[\mathrm{H}] - 0.208[\mathrm{O}] + 16.055$$

Via extensive examples, it was shown that the equation based on ultimate analysis data provides the closest correspondence between calculated specific energy and that measured directly by bomb calorimetry.

Extensive further thermal analysis studies relate to the kinetics of combustion of Australian coals and the related chars. Sanders and Jones [12] have studied the gasification kinetics of Victorian Brown Coal in several atmospheres and at various

Table 3 Kinetic parameters and relative reactivity for reaction of WP25 in air at increasing pressures

Pressure (O_2), kPa	Activation energy (E), kJ·mol^{-1}	Frequency factor, (k_0C^n), s^{-1}	Relative reactivity
21	50	12	1
126	61	158	3.3
441	60	158	3.8
1281	50	32	4.5

pressures using the classical non-isothermal TG technique. A typical family of mass-loss curves for a brown coal sample heated in air at various pressures is shown in Fig. 14 and corresponding kinetic data are given in Table 3. Reactivity increases with increasing pressure which indicates a progressive increase in active surface area available for oxidation. An interesting additional feature is exhibited by a corresponding group of chars—the reactivity of which increases with pyrolysis temperature up to 680° and thereafter decreases (Table 4). This phenomenon

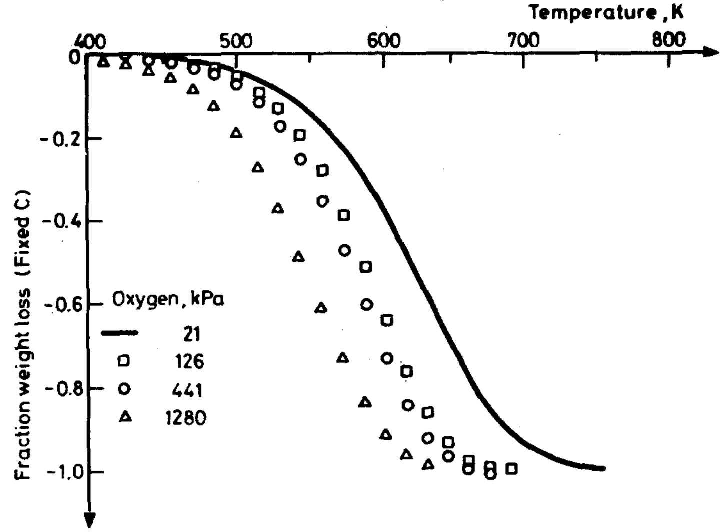

Fig. 14 Non-isothermal reaction of WP25 in air at increasing pressures

Table 4 Relative reactivity of WP25 and its chars in air at 400 °C

Sample	Relative reactivity
WP25	1
WP602#	13
WP685	3
WP745	5
WP800*	0.1
WP910*	0.2

* Data obtained from isothermal experiments.

\# Maximum temperature of char preparation: 600 °C (WP602); 670 °C (WP685); 740 °C (WP745); 800 °C (WP800); 910 °C (WP910).

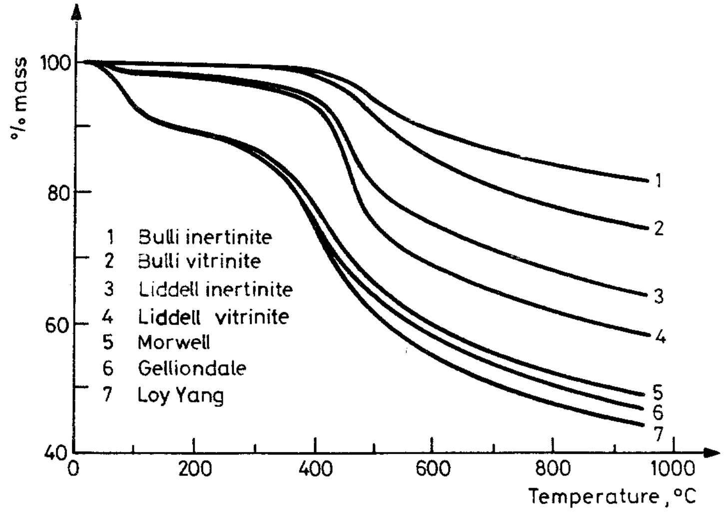

Fig. 15 TG curves for the pyrolysis of coal samples

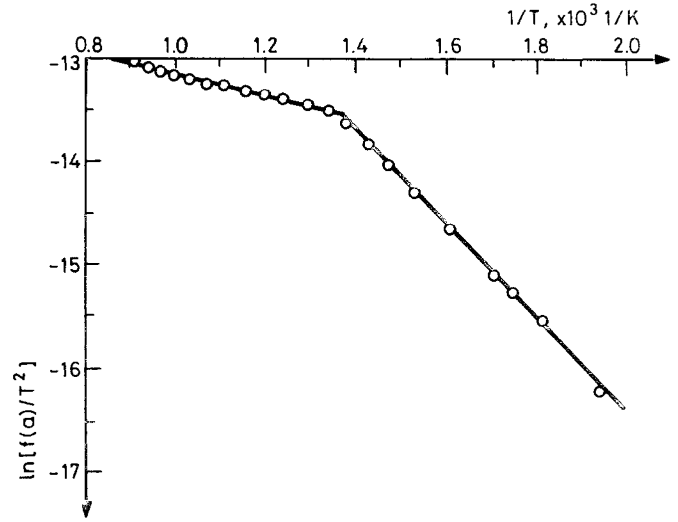

Fig. 16 Arrhenius plot/Morwell coal pyrolysis

attributed to pore structure formation below 680° which subsequently collapses at higher temperatures.

Ma et al. [13] have investigated the pyrolysis kinetics of several Australian coals including brown coal. Typical TG curves for these coals pyrolysed in nitrogen are shown in Fig. 15. For brown coal, the corresponding Arrhenius plot (Fig. 16)

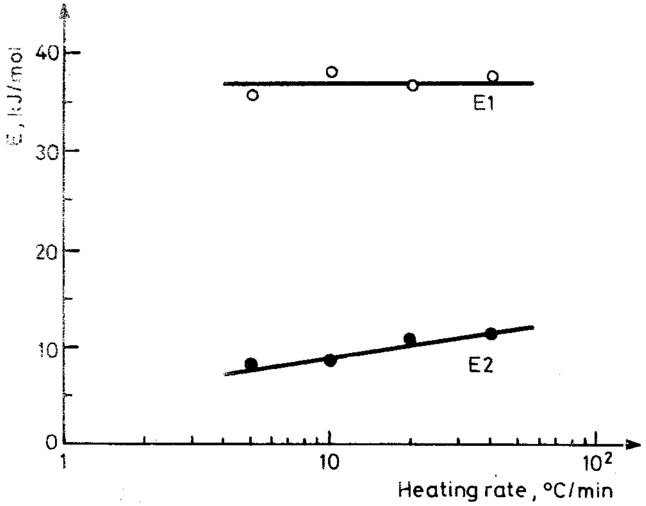

Fig. 17 Effect of heating rate on the activation energy for the pyrolysis of Morwell coal

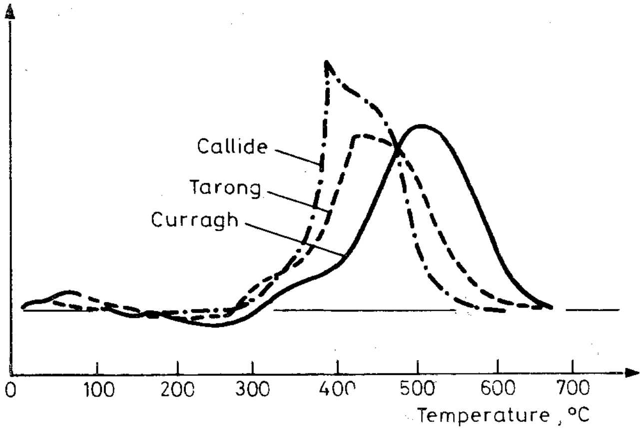

Fig. 18 DTG burning profiles for coals

clearly indicates a two stage pyrolysis process and both stages consistent with first order kinetics. The corresponding activation energies are in the ranges 36–39 and 7–9 kJ·mol^{-1} respectively. These E values suggest that the primary pyrolysis is associated with chemical decomposition whereas the secondary pyrolysis is dominated by mass and heat transfer processes. Such correlation are further verified by the measured effect of heating rate on the two activation energies (Fig. 17). The bituminous coals investigated have higher E values for both pyrolysis stages and are less easily pyrolysed than the brown coals.

Table 5 Combustion kinetic parameters for Queensland coals

Coal	E, kJ·mol^{-1}·K^{-1}	B, kgm^{-2} s^{-1} atm^{-1}
Tarong	71.8	18
Curragh	73.6	10
Callide	89.9	750

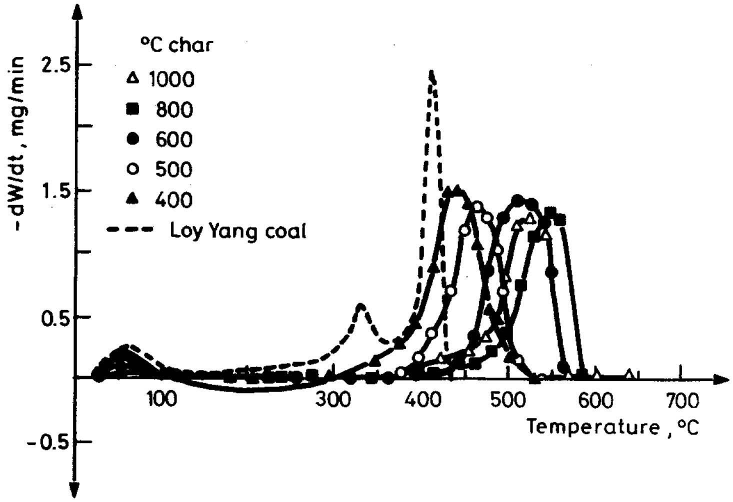

Fig. 19 DTG curves of the combustion of brown coal chars

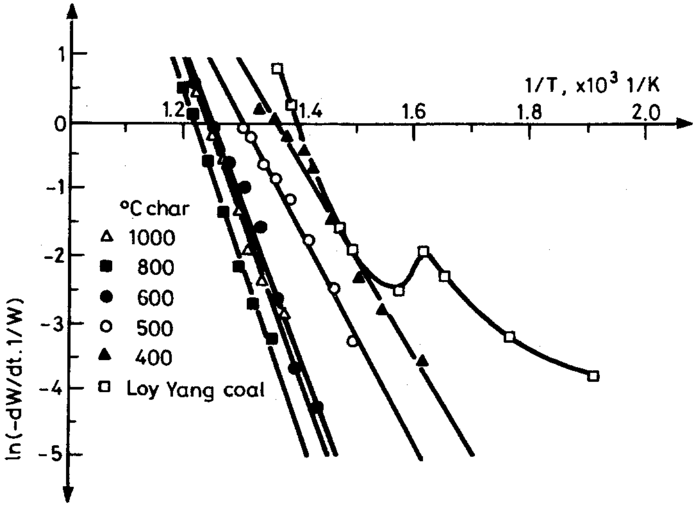

Fig. 20 Arrhenius plots of the combustion of brown coal chars

Stanmore and O'Sullivan [14] have applied TG to derive the char combustion kinetics of three Australian (Queensland) coals from their corresponding burning profiles. The burning profiles for Callide, Tarong and Curragh coals are shown in Fig. 18 and the corresponding kinetic parameters are given in Table 5 as related to mean particle sized of 50, 42 and 54 μm respectively for these 3 coals. Particle size appears to have a dramatic effect on combustion rate.

Ma et al. [15] have applied simultaneous TG–DTG/DTA techniques to derive kinetic parameters for the oxidation of a brown coal sample and a series of corresponding chars. The DTG burning profile of Loy Yang coal and a series of corresponding chars obtained at various temperatures are shown in Fig. 19. This family of profiles shows that all chars are less reactive than the parent coal and this phenomenon is confirmed by the corresponding Arrhenius Plots shown in Fig. 20 which simultaneously indicate that char combustion is consistent with first order kinetics.

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Zusammenfassung — Für die Rationalisierung der physikalischen und chemischen Prozesse bei der Energiegewinnung aus australischer Kohle sind thermoanalytische Untersuchungen dieser fossilen Rohstoffe von erstrangiger Bedeutung. Es wurde eine bedeutende Menge von Angaben gesammelt, die eine Beziehung zwischen dem Verbrennungsgrad und der Primärstruktur der Kohle, Oberflächenerscheinungen, enthaltenen Metallionen, des Emissionsprofiles flüchtiger Verbindungen, der Partikelgröße und der entsprechenden Halbkokseigenschaften herstellen. Die Kinetik dieser komplexen Vorgänge wurde nun auch modelliert.

Резюме — Очевидным является тот факт, что термические аналитические исследования австралийских углей имеют первостепенное значение в рационализации различных физических и химических процессов, протекающих при получении энергии из этих ископаемых топлив. До настоящего времени собраны значительные данные, коррелирующие эффективность сгорания с первичной структурой угля, его поверхностными явлениями, с включенными в него ионами металлов, профилями выделяющегося летучего продукта, размером частиц и соответствующими свойствами угля. Смоделирована также кинетика этих сложных процессов.