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Thermochimica Acta 297 (1997) 79–84

thermochimica acta

Aspects of combustion behaviour of coals from some New Zealand lignite-coal regions determined by thermogravimetry

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Received 20 November 1996; received in revised form 8 April 1997; accepted 8 April 1997

Abstract

Thermogravimetric analysis of five Late Cretaceous and Cenozoic New Zealand lignites demonstrate that their combustion behaviour is distinct from that of subbituminous coals and may be characterised by peak temperature (T_6 = 377–416°C), maximum rate of combustion (R_C = 25–31%wt min^{-1}), and temperature of char burnout (T_8 = 421–497°C). These parameters reflect variation in thermal behaviour associated with both the organic and inorganic constituents of the coal. The information obtained is additional to that found by proximate analysis; the latter alone proves insufficient to predict the combustion behaviour of the coals relative to one another. A post-combustion thermal event, T_9, is seen among the lignites as in other low-rank coals combusting below 600°C, which appears to be related to the organic sulphur content of the coal. © 1997 Elsevier Science B.V.

Keywords: Char burnout temperature; Lignites; Maximum combustion rate; New Zealand; Peak temperature; Thermogravimetry

1. Introduction

Lignite-coal regions of New Zealand constitute ca. 75% of the in-ground coal resources of the country. As yet, no critical examination has been made of the validity of using thermogravimetric (TG) and derivative thermogravimetric (DTG) procedures for determining, predicting and rating the combustion behaviour of New Zealand coals of this rank. Both techniques have been used with success to explore the combustion of higher rank coals [1–3] and recent research has demonstrated the usefulness of TG/DTG procedures for evaluating high-volatile, Late Cretaceous and Cenozoic coals of New Zealand [4]. The present account shows the same procedures are applicable for evaluation of coals from the Otago, Southland and Canterbury lignite-coal regions of New Zealand (Fig. 1).

2. Coal samples

New Zealand coals, in general, reveal characteristics distinct from the older Carboniferous and Permian to Mesozoic coals of Europe, North America and Australia. These include a strongly detrital nature, high vitrinite and very low inertinite contents, and

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PII S0040-6031(97)00166-4

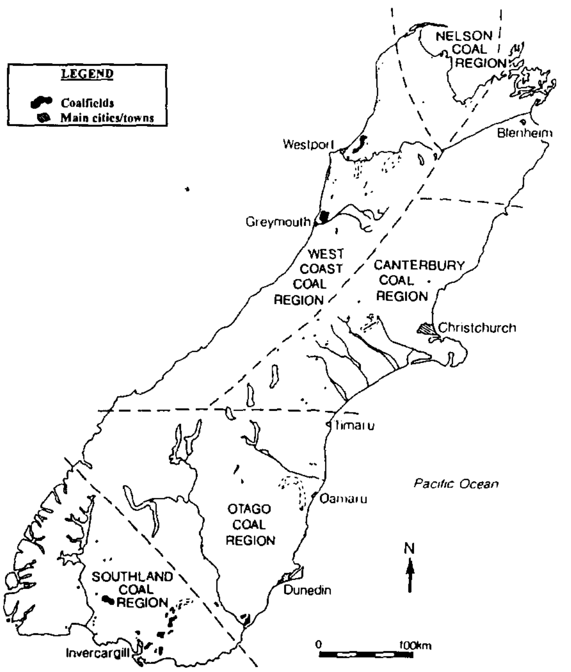

Fig. 1. Map of South Island, New Zealand showing the different coal regions and location of the coalfields within them. (After Barry et al. [5]).

their morphologic appearance [6]. Southland lignites have high proportions of detrital groundmass, with mineral matter spread throughout. Otago and Canterbury Cretaceous lignites have more inertinite than Tertiary lignites, and contain fusinite, absent from the Tertiary lignites. Some are rich in liptinite.

Samples of coal from the Otago, Southland and Canterbury lignite coal regions and their proximate analyses were supplied by the Coal Research Association of New Zealand from its industrial coal database. All samples consist of whole coals and, according to the ASTM rank classification, range from lignite to subbituminous B (Table 1).

3. TG and DTG experimental procedures

Equipment used was a Rheometric Scientific Simultaneous Thermal Analyser, STA 1500, capable of simultaneous determination of DTG, DTA and TG profiles. Details of equipment and procedures used, and repeatability of TG and DTG procedures for New

Table 1
New Zealand sample characteristics

Sample I.D.	Location	Region	T_6 [a] (°C)	R_C [a] (%wt min^{-1}) (daf)	T_8 [a] (°C)	M [b] (% ad)	Ash (% db)	VM [c] (% daf)	ASTM rank
CR54/815	Harliwich	Otago	416	27	497	13.5	7.4	60.9	lig
CR53/830	Idaburn Mine	Otago	394	31	421	13.9	10.8	54.8	lig
CR54/816	New Vale	Southland	393	26	458	17.7	5.8	54.6	lig
CR54/818	Goodwins	Southland	398	25	480	17.6	5.5	54.6	lig
CR54/944	NZ Paper Mill	Southland	377	28	459	14.5	7.1	52.4	lig
CR54/926	Mt. Stomers	Canterbury	449	14	564	12.9	18.6	48.2	subB
CR54/814	Kai Point	Otago	445	13	566	18.5	6.0	48.2	subB

[a] Fig. 2 shows the locations of these characteristic features of burning profiles; R_C, dry ash free (daf), is calculated from the maximum rate of combustion at T_6.
[b] Moisture content.
[c] Volatile matter content.

Zealand coals are given in Benfell et al., [7]. Experimental conditions have been constrained to permit direct comparisons of different samples and to ensure repeatability. Sample mass was 5.00 ± 0.05 mg sieved to < 75 μm size fraction. Purge gas was compressed dry air at 50 ml min^{-1}. Heating rate was 15°C min^{-1} applied from ambient temperature to a maximum of 900°C to allow complete combustion of samples.

Temperatures of several thermal events in the coal combustion process have been defined [2]. The picking of some of these temperatures from a coal's TG and DTG curves can be highly subjective. The peak temperature (T_6), the temperature of char burnout (T_8), and the maximum rate of combustion, R_C, calculated from the peak rate in the DTG trace, have been found to be readily repeatable and to satisfactorily characterise significant events during combustion [4,7]. These parameters reflect the thermal behaviour of the organic fraction during combustion and identify the end of combustion or burnout [4].

4. Results and discussion

Key combustion temperatures and rate data for the analysed coals, along with relevant proximate analyses, are shown in Table 1. Typical profiles are shown in Fig. 2a, b and c.

In Fig. 3, volatile matter contents, dry ash free, are plotted against T_8 values. The Kai Point and Mt. Somers subbituminous B samples almost overlap despite having differing ash values of 6.0 and 18.6% respectively, on a dry basis. They have much higher char burnout temperatures than the other samples, consistent with their higher rank, but these values are also higher than those of other subbituminous coals [4]. Both these coals have similarly high sulphur contents (Table 2), which are predominantly organically bound in the coal [8]. The sulphur may act as an inhibitor to active site formation, thereby retarding combustion.

The Idaburn Mine, New Vale and Goodwins lignite samples have almost the same volatile matter contents, yet their T_8 values lie in the 421–480°C 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 coal. Sentorun and

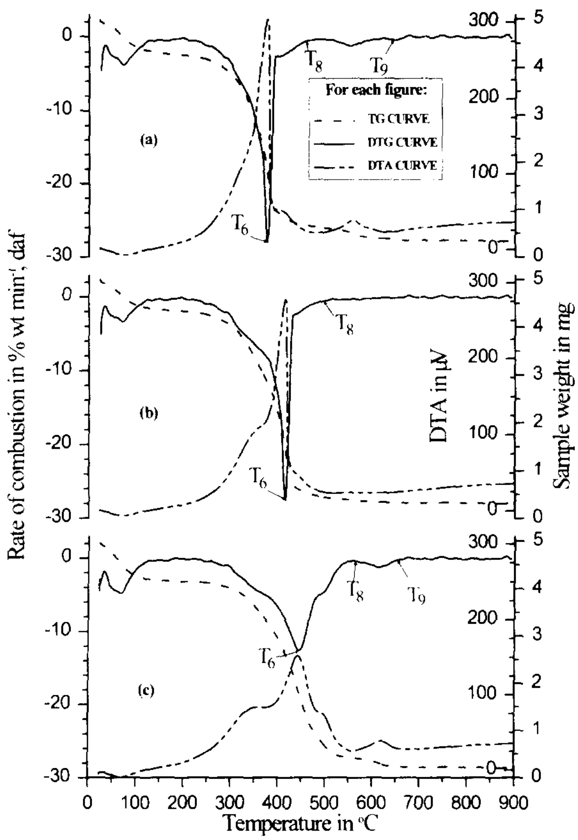

Fig. 2. Typical TG, DTG and DTA curves of (a) – Southland lignite, CR54/944, NZ Paper Mills; (b) – Otago lignite, CR54/815, Harliwich; and (c) – Otago subbituminous B coal, CR54/814, Kai Point.

Table 2
Major inorganic components of the coals determined by whole coal XRF

Sample I.D.	Location	S [a](%)	Fe(%)	Ca(%)
CR54/815	Harliwich	0.58	0.36	1.73
CR53/830	Idaburn Mine	0.49	0.69	1.80
CR54/816	New Vale	0.62	0.95	1.95
CR54/818	Goodwins	0.89	1.22	1.53
CR54/944	NZ Paper Mill	0.82	0.69	2.98
CR54/926	Mt. Stomers	2.88	0.26	1.59
CR54/814	Kai Point	2.44	0.17	1.60

[a] sulphur values supplied by the Coal Research Association of New Zealand.

Küçükbayrak [9] suggest that mineral matter has a significant effect on the combustion behaviour of lignites. Unfortunately, much of their data was for

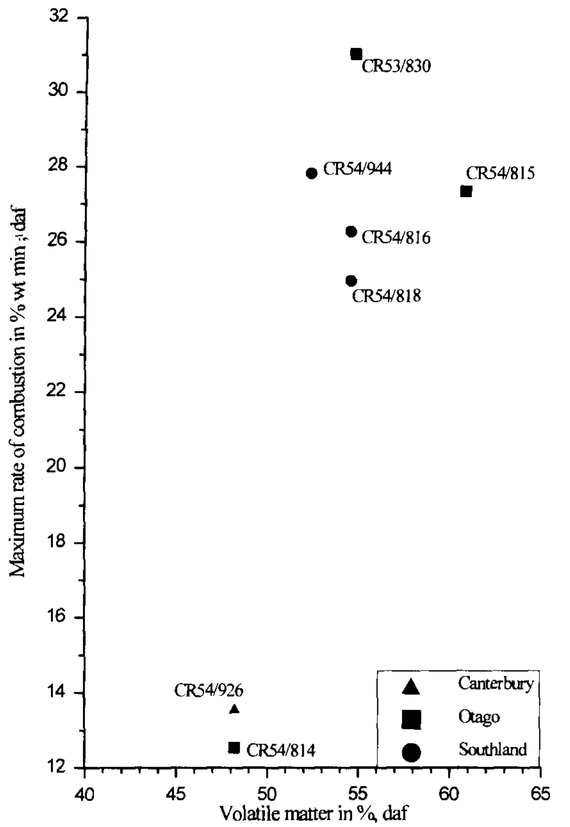

Fig. 3. Variation in temperature of char burnout, T_8, as a function of volatile matter for typical New Zealand lignites.

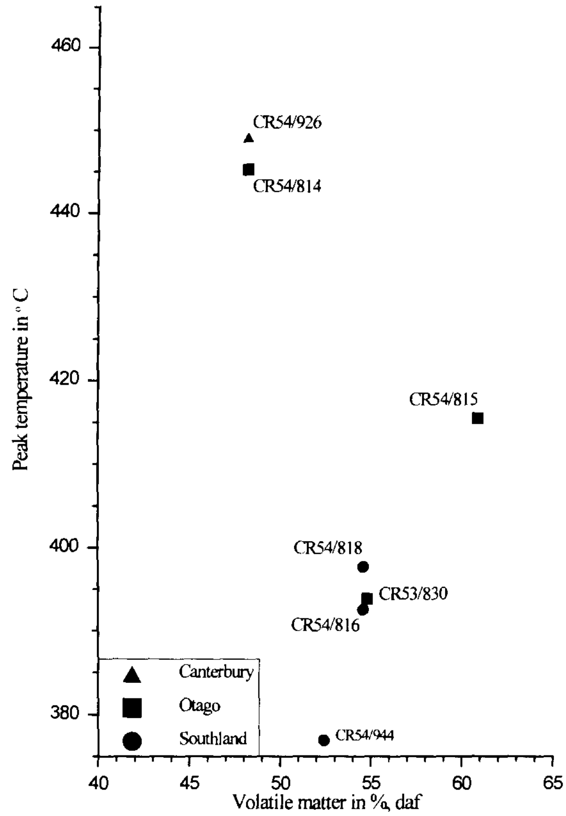

Fig. 4. Variation in peak temperature, T_6, as a function of volatile matter for typical New Zealand lignites.

coals of different ranks, and hence the relationships observed may have been influenced as much by rank as mineral matter. Nevertheless, differences exist in some inorganic constituents of Idaburn Mine, New Vale and Goodwins samples that may be reflected in differences in their burnout temperatures. As for example, the Goodwins sample ($T_8 = 480°C$) has the highest iron content and the Idaburn sample ($T_8 = 421°C$) the lowest (Table 2). The NZ Paper Mill sample has a high calcium content (2.98%) which, according to Sentorun and Küçükbayrak [9], reduces char burnout temperature.

The Harliwich lignite sample has an even higher char burnout temperature, at 497°C, that can be attributed to the high liptinite content of coals from this field [10], consistent with the very high volatile matter obtained for this coal (Jane Newman, personal communication, March 1997).

A plot of volatile matter content against peak temperature, T_6 (Fig. 4), shows a similar distribution of points to that of Fig. 3. However, the separation in the Idaburn Mine, New Vale and Goodwins lignite samples is not seen in this parameter. The temperature for the Harliwich lignite sample is again elevated above the other lignite samples, and the Kai Point and Mt. Somers samples have temperatures reflecting their subbituminous B rank.

The maximum rate of combustion behaviour of the coals is shown in Fig. 5. The Kai Point and Mt. Somers samples have extremely low maximum rates of combustion. In contrast to other New Zealand subbituminous coals [4], the values of these two samples are among the lowest recorded. Again this possibly reflects the high organic-sulphur content of the coal, that would appear to inhibit combustion. The Idaburn Mine, New Vale and Goodwins samples

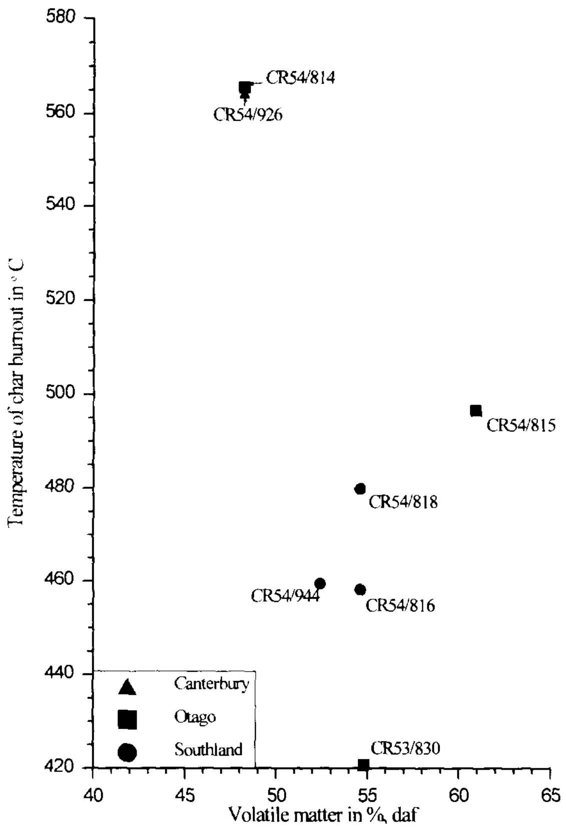

Fig. 5. Variation in maximum rate of combustion, R_C, as a function of volatile matter for typical New Zealand lignites.

show a trend similar to that observed for the char burnout temperature, a fact that suggests the iron content of the coal may also inhibit combustion in these cases.

5. Post-combustion transformation

Most of the present lignites show a distinct plateau on the TG curve following completion of the main combustion phase [4]. This is well developed in five of the samples, NZ Paper Mill, Kai Point, Mt. Somers, New Vale and Goodwins. It is recognized by a change in slope as the TG curve drops to its final level (Fig. 2a, c). This post-combustion event, designated here as T_9, is distinct from the 'delayed burnout' effect reported from some bituminous coals with appreciable swelling properties [11]. The size of this DTG peak is in direct proportion to the sulphur contents of these coals (Table 2). In coals combusting above 600°C, this event is concealed behind the strong exotherm arising from combustion of the coal's fixed carbon.

6. Conclusions

Previous work has demonstrated that thermogravimetric analysis is both versatile and effective in characterising the combustion of a range of coals [2–4]. This study demonstrates that the technique may be used reliably for lignites and to differentiate their thermal behaviour clearly from subbituminous coals. The proximate analysis data alone would not have predicted the combustion behaviour of any of these coals relative to one another. In particular:

1. The low combustion rates of the subbituminous samples (attributable to their high organic-sulphur contents), and their closeness in behaviour despite one having 18.6% ash against the other's 6.0%.
2. The differences in behaviour of Idaburn Mine ($T_8 = 421$°C, $R_C = 31$%wt min^{-1}), New Vale ($T_8 = 456$°C, $R_C = 26$%wt min^{-1}) and Goodwins ($T_8 = 480$°C, $R_C = 25$%wt min^{-1}) samples even though they have similar volatile matter contents, which appears to be more related to their iron contents.
3. The behaviour of the Harliwich sample with T_6 and T_8 values higher than other lignite samples, but with an R_C value in the same range as the other lignites, which can be related to a higher liptinite content.

This information is of obvious importance in ascertaining appropriate industrial end-uses for the coals.

Acknowledgements

The authors gratefully acknowledge Dr R.J. Sims for assistance with the STA 1500 and the Coal Research Association of New Zealand's Programme Development Group for financial support. Equipment was obtained with funding from the University of Auckland Research and Equipment Committees.

References

[1] P.A. Morgan, S.D. Robertson and J.F. Unsworth, Fuel, 65 (1986) 1546.

[2] J.C. Crelling, E.J. Hippo, B.A. Woerner and D.P. West, Fuel, 71 (1992) 151.

[3] S.St.J. Warne, Thermochim. Acta, 272 (1996) 1.

[4] K.E. Benfell, Characterisation of East Australian and New Zealand Coals by Thermogravimetric Analysis, unpublished Masters thesis, University of Auckland, Auckland, New Zealand.

[5] J.M. Barry, S.W. Duff and D.A.B. MacFarlan, Coal Resources of New Zealand, Energy and Resources Division, Ministry of Commerce, New Zealand, Report 16, 1994, pp. 1–73.

[6] P.M. Black, A Reconnaissance Survey of the Petrology of New Zealand Coals, New Zealand Energy Research and Development Committee, University of Auckland, Auckland, New Zealand, Report 51, 1980, pp. 1–49.

[7] K.E. Benfell, B.B. Beamish and K.A. Rodgers, Thermochim. Acta, 286 (1996) 67.

[8] C.F. Budge and F.J. MacKnight, N.Z.J. Sci, 19 (1976) 237.

[9] Ç. Sentorun and S. Küçükbayrak, Thermochim. Acta, 285 (1996) 35.

[10] P.M. Black, Australian Coal Geology, 4 (1982) 131.

[11] J.W. Cumming and J. McLaughlin, Thermochim. Acta, 57 (1982) 253.