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Effect of resinite on the combustion of New Zealand subbituminous coal

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Abstract

Oligocene resin from New Zealand's Rotowaro coalfield displays DTA and DTG traces similar to those of other fossil resins. It modifies the thermal behaviour of low rank coal in raising the peak combustion temperature and lowering its rate of combustion, a behaviour that may be common among liptinite macerals. The effect is not additive and unlike other coal constituents the resinite component does not deteriorate with time. © 1997 Elsevier Science B.V.

Keywords: Thermogravimetric analysis; Resin; Subbituminous; New Zealand

1. Introduction

Resinite is a maceral of the liptinite group. It is common in New Zealand's Waikato subbituminous coals, averaging up to 6% by volume. Macroscopic resin bodies are also common in seams from this region [1], typically ranging in size from small specks to a few centimetres.

Benfell et al. [2] have suggested that liptinite may cause a significant effect on the thermal behaviour of coals of which it is a significant component. In order to evaluate the extent and nature of any modification to combustion that a liptinite maceral may exercise, thermogravimetric analyses were made of an Oligocene resin body from New Zealand's Rotowaro coal-

2. Experimental

Initially a series of tests were made using coal, resin and a 50–50 blend of the two. The same samples were reanalysed 18 months later to assess the effects of sample storage. An additional blend of 5% resin and 95% coal was tested to simulate a maximum in situ coal quality for resinite content.

Both coal and resin samples were prepared for analysis as described by Benfell et al. [3]. Proximate analyses of each sample were made using the procedures described by Beamish [4]. Further fractions of all samples were then analysed by thermogravimetry using the procedures given by Benfell et al. [5] to establish the peak temperature (T_6), the maximum rate of combustion (R_C), and the temperature of char burnout (T_8) [5,6]. These parameters are particularly

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field and of subbituminous coal immediately adjacent to the resin. Results are given below.

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Table 1
Combustion and proximate analytical data for Rotowaro coal, resin and blends

	Run date	Combustion data			Proximate Analysis			
		<i>T</i> ₆ ℃	R _c %wt min ⁻¹ daf	<i>T</i> ₈ °C	Mª %	Ash % db	VM ^a % daf	Fixed carbon %, daf
Rotowaro coal	April 1995	431.0	33.08	476.0	15.0	2.7	47.0	53.0
Rotowaro coal	Nov 1996	427.6	25.45	470.2	12.9	2.7	46.8	53.2
Rotowaro resin	April 1995	534.8	11.03	598.4	1.2	0.0	99.9	0.1
Rotowaro resin	Nov 1996	530.6	11.15	591.9	0.8	0.1	99.9	0.1
Coal : Resin 50 : 50 blend	Nov 1996	441.9	16.65	588.3	—	—	_	
Coal: Resin 50: 50 blend	Nov 1995	430.2	14.77	590.7	6.7	1.3	77.4	22.6
50 : 50 blend (new)	Nov 1996	432.8	15.26	588.1	_			
Coal : Resin 95 : 5 blend	Nov 1996	427.6	24.06	479.2	12.6	2.6	50.9	49.1

^a M = moisture content; VM = volatile matter content.

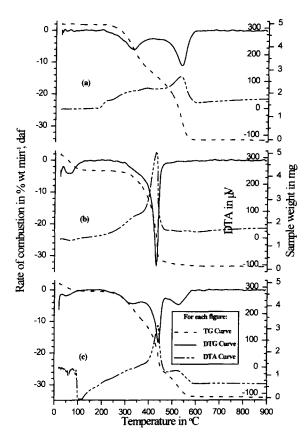


Fig. 1. (a) TG, DTG and DTA curves of Rotowaro resin. (b) TG, DTG and DTA curves of Rotowaro subbituminous coal. (c) TG, DTG and DTA curves of 50:50 Rotowaro coal: resin blend.

suited for the present investigation. Apart from identifying the end of combustion or burnout, they reflect the thermal behaviour of the organic fraction during combustion.

The equipment used was a Rheometric Scientific Simultaneous Thermal Analyser, STA 1500, capable of simultaneous determination of DTG, DTA and TG profiles. Experimental conditions were constrained to permit direct comparisons of different samples and to ensure repeatability. Sample mass was 5.00 ± 0.05 mg sieved to $< 75 \,\mu$ m 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. Results are summarised in Table 1. Combustion profiles are shown in Fig. 1(a-c).

3. Results

The thermal behaviour of the Rotowaro resin shows two distinct broad peaks in its DTG curve at 329.2° C and 534.8° C (Fig. 1(a)). Its DTA record suggests a series of events prior to 450° C. Most are small and illdefined and in this the trace resembles the general thermal behaviour of a series of modern and fossil resins investigated by Broughton [7]. In general, the thermal character of modern resins is determined by their relatively high levels of volatile components whose influence is pronounced at lower temperatures. A number of peaks within the lower portion of their DTA range tend to be of high intensity with some significant events occurring under 100°C. With aging and fossilisation the intensity of thermal events decreases and they become important in the higher temperature portion of the record.

The thermal record of the Oligocene Rotowaro resin most closely matches those of Atlantic Coastal Plain resins [7]. These resins undergo two major thermal events below 600°C, commonly in the range 220– 290°C and about 440–460°C suggesting that a dicarboxylic acid may be a significant component of these resins [cf. [8,9]]. A broad, somewhat hummocky DTA shoulder in the Rotowaro resin record corresponds to the lower temperature of the two prominent events defined in the DTG trace (Fig. 1(a)). This first major event shows a smaller weight loss than the second, which is marked by a large exothermic event in the DTA curve. The pure resin has a high temperature of char burnout, T_8 , and a low maximum rate of combustion (Table 1).

The combustion pattern of the unmodified Rotowaro coal is typical of New Zealand subbituminous coals [3]. The major exothermic event and its corresponding DTG peak are narrow and the maximum rate of combustion is high (Fig. 1(b), Table 1).

The 50-50 blend displays a behaviour that incorporates aspects of both end members (Fig. 1(c)). The

combustion profile has three DTG peaks: the smallest at 333.4°C, a major event at 441.9°C, and a minor, broad but well-defined event at 526.9°C. The first event is akin to that found first in the resin analysis although peaking at a slightly lower temperature. Again no clear record of this event is seen in the DTA trace. The main exothermic event arises from the combustion of coal and is marked by a distinct exotherm in the DTA record that peaks some 10° C higher than when the coal combusts alone. The final event corresponds to the second resin exotherm but again peaking 8°C sooner than occurs for the unblended resin.

The effects of sample storage can be seen in the key DTG parameters presented in Table 1. The proximate analysis data do not show any significant changes that occurred in coal or resin, other than a decrease in the moisture content of the samples. However, T_6 values drop by 3.4°C for coal and 4.2°C for the resin on storage, and T_8 values reduce by about 6°C for both coal and resin. In particular, the maximum rate of combustion of coal is lowered by 23% from its original value, with that of the blend being reduced by 11%. A fresh batch of 50–50 blend, made from the end members, confirmed this result with the standard deviation of these two blend values $(\pm 0.25\% \text{ wt min}^{-1})$ lying within the instrument

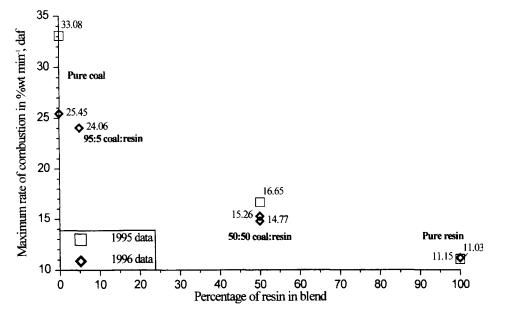


Fig. 2. Combustion rates of Rotowaro coal, resin and blends.

repeatability limits for this type of procedure [5]. The maximum rate of combustion for the resin remained unchanged, consistent with stability of the material.

4. Discussion

The principal modifying effects of resinite on coal combustion are to raise the peak temperature of the coal and to lower its maximum rate of combustion. In these respects, the Rotowaro resinite behaves similarly to sporinite, another liptinite maceral [6].

Benfell et al. [2] noted a New Zealand lignite coal from the Otago region with higher T_6 and T_8 values than those of other coals of similar rank. The thermal behaviour was regarded as a consequence of the high liptinite content of this coal, variously given as 23-27% [10] and 17% [11]. The present result taken along with that of Crelling et al. [6], indicates that where coals have notable liptinite contents, thermogravimetry may be readily used to ascertain the extent and nature of modifications to these coals' combustion behaviour that may constrain their industrial end use. Such information is not provided from standard proximate analyses and rank parameters. The effect is clearly not additive, as can be seen from the maximum rate of combustion for various coal/resin blends (Fig. 2). Also, it is the coal constituents other than the resinite component which are deteriorating with time. The 11% reduction in the 50-50 blend maximum rate of combustion from 16.65% wt min⁻¹ in November 1995 to 14.77% wt min⁻¹ in November 1996 is consistent with the proportion of coal in the blend, as the pure coal showed a 23% reduction in its maximum rate of combustion over the storage interval.

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References

- S.W. Edbrooke, R. Sykes and D.T. Pocknall, Geology of the Waikato Coal Measures, Waikato Coal Region, New Zealand, Institute of Geological and Nuclear Sciences, monograph 6, 1994, 236 pp.
- [2] K.E. Benfell, B.B. Beamish and K.A. Rodgers, Thermochim. Acta, (submitted for publication).
- [3] K.E. Benfell, B.B. Beamish and K.A. Rodgers, Fuel, (submitted for publication).
- [4] B.B. Beamish and N.Z.J. Geol, Geophys., 37 (1994) 387.
- [5] K.E. Benfell, B.B. Beamish and K.A. Rodgers, Thermochim. Acta, 286 (1996) 67.
- [6] J.C. Crelling, E.J. Hippo, B.A. Woerner and D.P. West, Fuel, 71 (1992) 151.
- [7] P.L. Broughton, Can. J. Earth Sci., 11 (1974) 583.
- [8] T. Meisel and L. Erdey, J. Thermal Anal., 1 (1969) 159.
- [9] K. Muraishi, Y. Suzuki and A. Kikuchi, Thermochim. Acta, 239 (1994) 51.
- [10] 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, 49 pp.
- [11] P.M. Black, Australian Coal Geology, 4 (1982) 131.