ELSEVIER

Thermochimica Acta 286 (1996) 67–74

thermochimica
acta

Thermogravimetric analytical procedures for characterizing New Zealand and Eastern Australian coals

Kathy E. Benfell[a,*], B. Basil Beamish[a], K.A. Rodgers[b]

[a] *Department of Geology, The University of Auckland, Private Bag 92019 Auckland, New Zealand*
[b] *Research Associate, Australian Museum, Sydney, Australia*

Received 28 September 1995; accepted 27 February 1996

Abstract

Under tightly constrained experimental conditions (particle size < 75 μm, sample mass 5.0 ± 0.5 mg, heating rate 15°C min^{-1}, dry air purge 50 mL min^{-1}, maximum temperature 900°C) a repeatability of < ± 2°C, may be achieved for significant temperatures that characterize the differential thermogravimetric burning profiles of typical medium-volatile, bituminous Australian Gondwanan coals and high-volatile, bituminous New Zealand Cretaceous–Tertiary coals.

Keywords: Bituminous coal; Burning profile; Cretaceous–tertiary coal; DTG; Gondwanan coal; High-volatile coal; Medium-volatile coal; TG

---

1. Introduction

Thermogravimetry offers an alternative to traditional analytical techniques for characterizing coal thermal behaviour. In the late sixties Wagoner and co-workers of the American Babcock and Wilcox Company successfully developed a derivative procedure to determine the burning behaviour of coal, coal chars and petroleum cokes [1,2]. Subsequent evaluations of the method included those of Smith et al. [3], Cumming and McLaughlin [2], Kneller [4], Morgan et al. [5], Warne [6], and Crelling et al. [7]. In a review Carpenter and Skorupska [8] concluded that while thermogravimetric analysis does not simulate pulverized fuel or fluidized bed combus-

---

[*] Corresponding author.

PII: S0040-6031(96)02943-7

tion conditions directly, it is suited to comparative studies, enabling coals to be evaluated on their combustion behaviour.

Most coals analyzed by previous authors range in rank from high-volatile bituminous to semi-anthracite. In contrast, New Zealand Cretaceous–Tertiary coals are largely sub-bituminous to low-volatile bituminous [9], with considerably higher volatile matter content and lower ash than similarly ranked coals analysed worldwide. No similar coals have been examined critically with thermogravimetric procedures to establish the effect such compositions might exercise on the TG profile. The series of experimental runs reported here was undertaken to determine the likely repeatability for the technique on such coals and the experimental constraints necessary to optimize this precision. The principle sample used is a New Zealand Coal Research Association high-volatile bituminous coal from the Buller area, sample 54/804, containing 4.9% moisture (air-dried basis), 39.6% volatile matter (dry ash free), fixed carbon 55.9%, sulphur 0.54% (air-dried basis), and ash 2.5% (dry basis).

A typical Eastern Australian medium-volatile bituminous coal from the Bowen Basin was analysed for comparison. Gondwanan coals contain relatively high inertinite contents and provide a sharp maceral contrast to the younger New Zealand counterparts. The sample contained 1.9% moisture (air dried basis), 20.7% volatile matter (dry ash free), fixed carbon 57.9%, and 21.4% ash (dry basis).

2. Experimental considerations and conditions

Both conventional thermogravimetry (TG), measuring weight change as a function of either time or temperature, and derivative thermogravimetry (DTG), determining rate of weight loss with time as a function of temperature, have been used for coal characterization. Instrument geometry is known to influence results markedly. In so far as TG–DTG is an empirical test, results depend both on coal characteristics as well as experimental conditions, and limit the value of thermogravimetry for quantitative coal analysis [8]. To achieve truly comparative analytical results from different TG equipment, rigorous standardization of instrumental and preparative procedures is required. However, comparative rating of coals by the same apparatus may be satisfactorily achieved where experimental conditions are sufficiently constrained to allow repeatability.

The equipment used in this study was a Rheometric Scientific (formerly Stanton–Redcroft) Simultaneous Thermal Analyzer STA 1500 capable of simultaneous determination of the DTA and TG profiles of samples. A type R (Pt–13% Rh/Pt) flat plate thermocouple system is used for differential and sample temperature measurement. Cylindrical alumina crucibles with 0.5 mm thick walls are placed directly on the thermocouple plates. Accompanying Polymer Laboratories PLus V software (v 5.40) derives DTG data from the recorded TG signal with the resulting plots readily processed and compared, allowing identification of coal profile characteristics and temperatures.

Initial calibration of the sample temperature was made using high-purity indium, tin, lead, zinc and gold. Calibration was checked subsequently using the gold standard. The humidity of the laboratory remained stable and seldom varied beyond the confidence limit of the hygrometer throughout the runs.

In air, a *burning profile* is obtained [2]. In an inert atmosphere e.g. nitrogen, a *volatile release profile* is produced. The burning profile is unique for a given coal; the temperature at which various thermal events occur being affected by coal rank, maceral composition, mineral matter and physical attributes such as porosity and surface area [5,7,9,10]. The following profile temperatures characterize the coal combustion process [7] (Fig. 1):

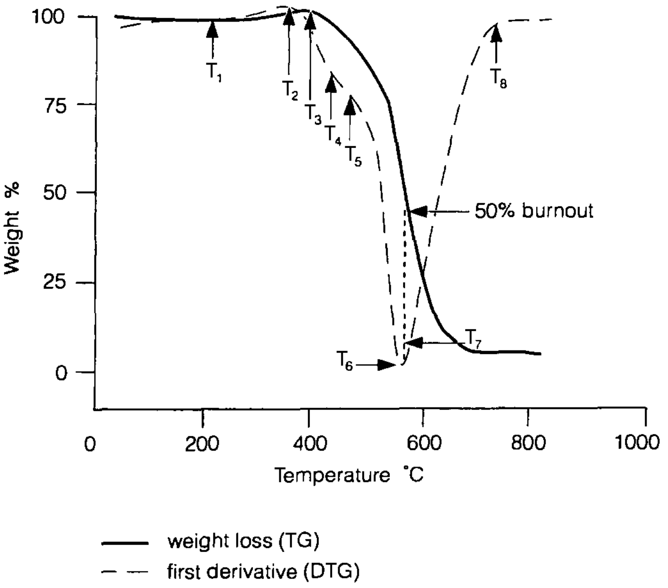
T_1 — initial chemisorption of oxygen (where the DTG curve first inflects);

T_2 — maximum rate of chemisorption (relative maximum of the DTG curve prior to the minimum of T_6);

T_3 — combustion onset;

T_4 — volatile combustion;

T_5 — char combustion;



T_1 temperature of initial chemisorption of oxygen
T_2 temperature of the maximum rate of chemisorption
T_3 temperature of combustion onset
T_4 temperature of volatile combustion
T_5 temperature of char combustion
T_6 temperature of the maximum rate of combustion
T_7 temperature of 50% burnout
T_8 temperature of char burnout

Fig. 1. Typical TG combustion curve for coal (solid line) and corresponding DTG profile (dashed line) showing characteristic temperatures; after Crelling et al. [7].

T_6 — the principal minimum of the DTG curve, defined as the temperature of maximum rate of combustion;

T_7 — 50% burnout, dry ash free [2];

T_8 — char burnout; the point where the derivative of the DTG curve inflects to zero gradient following the T_6 event (i.e.$\partial^2 G/\partial^2 T \rightarrow 0$). This point must concur with similar inflections in both the DTG and TG curves.

Further useful parameters are:

(1) moisture content (the weight loss between the starting temperature and 130°C);
(2) percentage of oxygen chemisorption (weight gain between T_1 and T_3);
(3) maximum rate of combustion (also termed maximum reaction rate, peak rate of weight loss, peak rate, maximum rate of weight loss), R_c, derived from the value of the DTG curve maxima corresponding to T_6.

Experimental factors influencing the thermal profile characteristics include: particle size, sample mass, purge gas and flow rate, heating rate and maximum temperature, equipment geometry. These variables represent a minimum constraint for valid comparisons between different samples and for consistent results from identical samples using the same operator and the same apparatus. Table 1 summarizes experimental parameters used by earlier workers and those in the present study that are similar to those of Morgan et al. [5] and Crelling et al. [7].

Particle size: Temperatures of the maximum rate of combustion (T_6) and the maximum rate of combustion (R_c) were derived for size fractions of <212 μm and <75 μm of a suite of sub-bituminous to anthracite coals. Plots of variation of volatile matter with T_6 and R_c showed that the smaller size fraction had slightly higher R_c; the curves decreasing and then increasing in R_c with increasing volatile matter content (Fig. 2). A particle size of <75 μm was chosen, as recommended by Morgan et al. [5], to better reflect the size range used in pulverized fuel combustion. Kneller [4] noted that sample particles must be of uniform size and consistent packing to mitigate the poor thermal conductivity of coal.

Sample mass: A sample mass of 5.0 ± 0.05 mg was used, as adopted by Morgan et al. [5] and Crelling et al. [7]. Morgan et al. showed that with too large a sample, ignition, a non-repeatable event, may occur. However, small samples must be homogeneous and representative.

Sampling procedure: Samples in this study came as a <212 μm powder in a polythene bag and were mixed thoroughly within the bag to give an even mix. About 1 g was removed and split in two. Half was stored and the remainder ground until it all passed a 75 μm sieve. The 5 mg sample for analysis was then removed and the unused <75 μm portion stored.

Purge gas: The gas used was compressed dry air at a flow rate of 50 mL min^{-1}. Morgan et al. [5] found flow rate had little effect on the burning profile, but Cumming and McLaughlin [2] cautioned that the rate should be such that it not disturb the

Table 1
Analytical parameters for coal thermogravimetric analysis

Ref.	Instrument	Size fraction/ μm	Weight/ mg	Air flow/ (mL min^{-1})	Heating rate/ (°C min^{-1})	Max temp/ °C
Smith et al. [3]	Stone TGA-5B	<149	300	800	15	1100
Cumming and McLaughlin [2]	Stanton–Redcroft STA 781	<210	20 ± 0.5	75	15	900
Ghetti et al. [10]	Mettler TA 2000 C	<297	18	70	15	1000
Morgan et al. [5]	Du Pont 951	<75	5	200	20	Const wt
Crelling et al. [7]	–	<75	4.5–5.0	80	15	Const wt
This study	Rheometric Scientific STA 1500	<75	5.00 ± 0.05	50	15	900

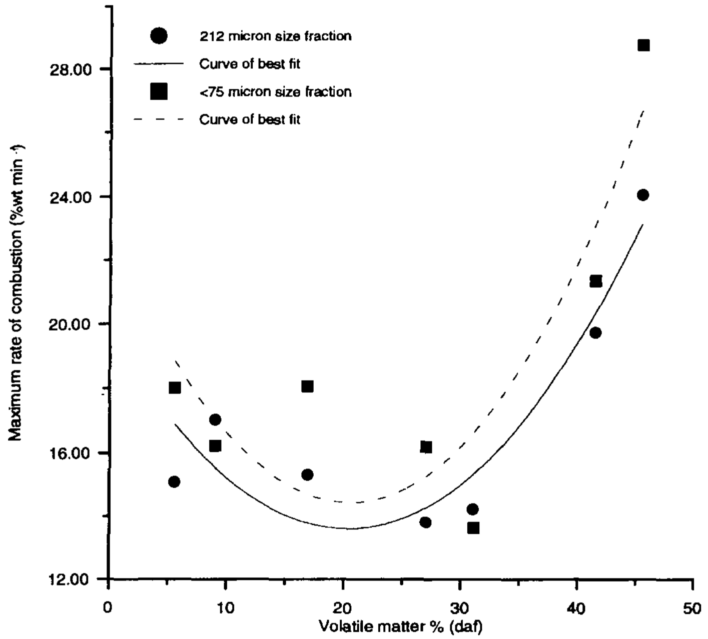


Fig. 2. Variation in the maximum rate of combustion, R_c, with volatile matter content of a suite of New Zealand Cretaceous–Tertiary coals from Huntly and Wairaki, Australian Bowen Basin coals and a USA Pennsylvanian coal, that ranged from sub-bituminous to semianthracite, for size fractions of <212 μm and <75 μm.

hangdown system, but should be sufficient to ensure combustion rates are not affected by limited oxidant.

Heating rate: A rate of 15°C min^{-1} was used, as have most previous workers. Morgan et al. [5] found an increase in heating rate may cause an increase in T_6 for constant sample mass.

Maximum temperature: 900°C proved sufficiently high to allow complete combustion of the New Zealand and Australian sub-bituminous to semi-anthracite samples.

3. Repeatability and precision

Results of ten separate runs for each of the Australian and New Zealand coals are given in Tables 2 and 3. The largest standard deviation of any of the significant temperature points was found for the temperature of the maximum reaction rate, T_6; 1.6°C for the Australian coal for a range of 525–528°C with a mean of 527°C, and 1.9°C for the New Zealand (range 523–528°C, mean 525.9°C). In contrast, the temperature of char burnout, T_8, showed a standard deviation of 0.7°C for the Australian (range

Table 2
Maximum rates of combustion and temperatures of maximum rates of combustion, T_6 and of char burnout, T_8, for repeat DTG combustion runs of East Australian bituminous coal, Collinsville, sample 53/527

Run #	T_6°C	Peak rate/(% wt min^{-1})	T_8°C
764	525.9	15.10	625.2
765	524.6	15.24	624.0
766	524.6	15.35	624.0
767	528.4	15.41	624.0
768	528.4	15.03	625.2
769	527.2	14.78	624.0
770	524.6	14.92	624.0
772	527.2	14.87	625.2
773	525.9	15.00	624.0
774	528.4	15.39	625.2
Mean	526.5	15.11	624.5
σ	1.6	0.2	0.7

Table 3
Maximum rates of combustion and temperatures of maximum rates of combustion T_6, and of char burnout, T_8, for repeat DTG combustion runs of New Zealand bituminous coal, Buller, sample 54/804

Run #	T_6°C	Peak rate/(% wt min^{-1})	T_8°C
748	523.4	13.67	604.8
749	528.4	13.40	606.1
750	525.9	13.72	606.1
751	527.2	13.80	606.1
752	524.6	13.37	604.8
753	523.4	13.37	606.1
754	527.2	13.52	606.1
755	525.9	13.71	606.1
756	524.6	14.03	606.1
757	528.4	13.74	604.8
Mean	525.9	13.63	605.7
σ	1.9	0.2	0.6

624–625°C, mean 624°C) and 0.6°C for the New Zealand (range 650–606°C, mean 605.7°C). The overall repeatability of the temperature measurements, $< \pm 2$°C; a considerable improvement on the results of Morgan et al. [5] whose cited temperatures were within ± 6°C. Crelling et al. [7] considered their values repeatable within ± 4°C. Although this improvement reflects continued developments in instrumentation, it also emphasizes the importance of standardizing and constraining experimental procedures. The systematic error in temperature measurements of the STA 1500, displayed as 0.1°C, is arbitrarily, and conservatively, taken as ± 0.5°C for the entire course of each TGA run.

No appreciable difference was seen between the consistency in thermal behaviour of typical medium-volatile bituminous Australian coal and the high-volatile bituminous New Zealand coal, despite the volatile content of the latter being considerably greater than any previously analysed by thermogravimetry.

As Warne [6] concluded, thermogravimetric analysis provides an efficient and cost-effective way of monitoring a range of thermal events associated with coal combustion and hence of characterizing the coal, but the present study re-emphasizes the need for thermal analytical standards to allow careful and frequent calibration of TG apparatus and interlaboratory correlation.

Acknowledgements

Financial assistance for analytical costs of this project has been provided by the New Zealand Coal Research Association's Programme Development Group. Equipment was obtained with funding from the University of Auckland Research and Equipment Committees. Dr R.J. Sims assisted with the STA 1500. Dr F.L. Sutherland provided useful comments on the draft manuscript.

References

[1] C.L. Wagoner and E.C. Winegartner, J. Eng. Power, 95 (1973) 119.
[2] J.W. Cumming and J. McLaughlin, Thermochim. Acta, 57 (1982) 253–272.
[3] S.E. Smith, R.C. Neavel, E.J. Hippo and R.N. Miller, Fuel, 60 (1981) 458–462.
[4] W.A. Kneller, Thermochim. Acta, 108 (1986) 357–388.
[5] P.A. Morgan, S.D. Robertson and J.F. Unsworth, Fuel, 65 (1986) 1546–1551.
[6] S.St.J. Warne, Trends Anal. Chem., 10 (1991) 195–199.
[7] J.C. Crelling, E.J. Hippo, B.A. Woerner and D.P. West, Fuel, 71 (1992) 151–158.
[8] A.M. Carpenter and N.M. Skorupska, Coal combustion—analysis and testing, IEA Coal Research, London, 1993, 97 pp.
[9] P.R. Gunn, B.B. Beamish and T. DePetris, Proc. 28th Ann. Conf., N.Z. Branch, Aust. Inst. Min. Metal., Taupo, August 1994, 83–99.
[10] P. Ghetti, U.De Robertis, S. D'Antone, M. Villani and E. Chiellini, Fuel, 64 (1985) 950–955.