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Thermogravimetric analytical procedures for determining reactivities of chars from New Zealand coals

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Abstract

Tightly constrained thermogravimetric experimental procedures (particle size $< 212\,\mu$m, sample mass 15.5 mg, CO_2 reactant gas, near isothermal conditions) allow the reactivity of chars from high volatile New Zealand coals to be determined to a repeatability of $\pm 0.07\ h^{-1}$ at 900°C and $\pm 0.5\ h^{-1}$ at 1100°C. The procedure also provides proximate analyses information and affords a quick (< 90 min) comparison between different coal types as well as indicating likely operating conditions and problems associated with a particular coal or blend. A clear difference is evident between reactivities of differing New Zealand coal ranks. Between 900 and 1100°C, bituminous coals increase thirtyfold in reactivity compared with fourfold for subbituminous, with the latter being three to five times greater in reactivity at higher temperature. © 1997 Elsevier Science B.V.

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1. Introduction

Knowledge of char reactivity is essential if furnace design and fuel efficiency is to be optimized in industrial processes [1,2] as for example, where a coal is used in direct reduction iron making. Char in this paper refers to the devolatilized product of a non-swelling coal. Reactivity is defined as the rate at which coal reacts in an oxidizing atmosphere, subsequent to devolatilization.

Rank of coal exerts a major constraint on char reactivity, with low rank chars being typically more reactive than those prepared from high rank coals [3]. However, coal type [4,5], mineral matter [3,7], char preparation method [3], pore structure [3,6] and reactant gas also exercise varying effects that are little understood.

Although reactivity may be reliably and efficiently determined by thermogravimetry [3,5], no standard testing method has been established. Consequently, while a comparison of qualitative trends arising from coal properties may be made, no meaningful comparison of quantitative results between different researchers or industrial analysts is possible. The following account describes a methodology adopted to determine the reactivity of chars from New Zealand bituminous and subbituminous coals by thermogravimetry following a critical appraisal of existing procedures.

Two groups of sample were used in developing the present methodology. The first consisted of five high volatile bituminous coal types from the Greymouth

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Table 1
Summary descriptions of samples used

Sample	Description
New Zealand Coal Research standard South Island samples	
752-5	Bright lustre, non-banded coal
55/382	Bright lustre, banded coal (< 25% vitrain bands)
55/381	Bright lustre, moderately banded coal (25–30% vitrain bands)
752-8 vit	Pure vitrain band
55/508	Bright lustre, highly banded (> 30% vitrain bands); this Moody Creek sample is of slightly higher rank than other South Island samples
Waikato samples (Huntly and Rotowaro blends)	
NZS 1	Initial BHP New Zealand Steel sample, taken 1 February 1996
NZS 613401	BHP New Zealand Steel stockpile sample used for subsequent detailed analysis

Note: 752-5, 55/382, 55/381, 752-8 vit are iso-rank samples from the same seam.

coalfield. These are distinguished by macroscopic differences in vitrain band percentage and brightness of the attrital layers [8]. Brief descriptions are given in Table 1. The second group were two standard industrial blends of high volatile subbituminous Waikato coals from the Huntly and Rotowaro coalfields obtained from BHP New Zealand Steel Stockpiles. All samples were homogenized to < 212 μm.

2. Experimental considerations and conditions

Laboratory factors affecting measurement of char reactivity include equipment geometry [9] and experimental parameters [1]. The latter include: sample weight; particle size; reactant gas; and temperature at which the reactivity value is calculated. These variables represent a minimum that need to be constrained for valid comparisons to be made between different samples and to ensure consistent results from identical samples by the same operator on the same apparatus. Experimental procedures used in previous studies of char or coal reactivity by thermogravimetry are summarised in Table 2.

2.1. Equipment

The equipment used in this study was Rheometric Scientific (formerly Stanton-Redcroft) Simultaneous Thermal Analyzer 1500. 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. No reference was used during the experiments. Accompanying Polymer Laboratories PLus V software (v 5.40) processed the resulting sample weight versus time record and allowed resulting plots to be compared. The humidity of the laboratory remained stable and seldom varied beyond the confidence limit of the hygrometer throughout the runs.

2.2. Sample weight

The variation in reactivity, due to the initial sample weight, for a typical Waikato coal blend from the Rotowaro and Huntly East coalfields is presented in Table 3. In contrast to the results of Hippo and Walker [10], reactivity can be seen to increase with decreasing bed weight. These authors also calculated the reactivity of a coal sample using different initial char weights and found reactivity to be constant within the experimental error between 2 and 6 mg. Above 6 mg, reactivity decreased continually with increasing bed weight. In the absence of similar behaviour for the Waikato coals this study opted to use a coal sample weight of 15.5 mg, comparable to those used in the more recent literature [6,7]. Following devolatilization, the initial weight was equated to 7.65–7.73 mg char for the high volatile Waikato subbituminous coals and 7.86–9.28 mg char for the bituminous coal types from Greymouth.

Table 2
Parameters used in reactivity studies of coal using thermogravimetry

	Jenkins et al., 1973 [3]	Hippo & Walker 1975 [10]	Crelling et al., 1988 [5]	Johns 1990 [2]	Hurt 1991 [6]	This study
Instrument	Fisher TGA	Fisher TGA	TGA [a]	Du Pont 1090	TGA [a]	Rheometric Scientific STA 1500
Particle size (μm)	< 425	< 425	< 75	na [b]	na [b]	< 212
Sample weight (mg)	5–10 (char)_	2–6 (char)	15 (coal)	na [b]	5–20 (char)	15.5 (coal)
Heating rate (°C min^{-1})	10	10	99	25	na	50
Char preparation temperature	1000	1000	700	930	1200	900
Reactivity measurement temperature (°C)	500	900	500	1050	900	900, 1100
Atmosphere	Air	CO_2	$5\%O_2 + 95\%N_2$	CO_2	CO_2	Air & CO_2
Origin of coal	USA	USA	USA & Australia	na [b]	USA	NZ
Parameters examined	Rank, mineral matter, pore structure, char temperature	Ca, Mg, particle size	Rank, maceral composition	Rank, methodology comparison	Mineral matter - untreated & acid washed coals	Coal type & rank

[a] Make and model not specified.
[b] Information not available.

Table 3
Variation in reactivity due to bed weight for sample NZS1

Initial weight (mg)	Char weight (mg)	Fixed carbon (mg)	Reactivity raw (h^{-1})	Reactivity d.a.f. (h^{-1})
15.51	7.68	7.08	4.85	5.26
9.97	4.84	4.46	6.87	7.45
7.45	3.65	3.33	8.14	8.92
5.00	2.41	2.14	10.13	11.41
2.99	1.55	1.45	12.32	13.17

2.3. Atmosphere and temperature

In the experimental procedure, the coal is heated in nitrogen to form a char. A reactant gas is then introduced into the furnace, and the rate at which carbon loss occurs is recorded by the thermobalance [3,10]. Air, oxygen, steam and carbon dioxide have been used as the reactant gas [11], with air and carbon dioxide being the most common (Table 2). In developing the present methodology, comparative studies were made of reactivity in both dry air at 500 and 900°C and in carbon dioxide at 900 and 1100°C; the last temperature closely reflecting the operating temperature of the BHP New Zealand Steel kilns. Attempts to make measurements at 1300°C in carbon dioxide resulted in an intractable ash becoming fused in the crucible.

3. Method

For coals tested in dry air, 15.5 ± 0.01 mg of each sample was weighed into an alumina crucible and placed within the STA. The STA was flushed with nitrogen for 5 min, and the sample was heated in nitrogen to 110 at 50°C min^{-1}. The sample was held at this temperature for 5 min and then heated to 900°C (at 50°C min^{-1}) where it was held for further 10 min to ensure that all volatiles were driven off and a constant weight attained. The char was then cooled to 500°C and the atmosphere changed to dry air. Weight changes were monitored as a function of time. A second series of runs were made at 900°C with no reduction in temperature before introduction of dry air.

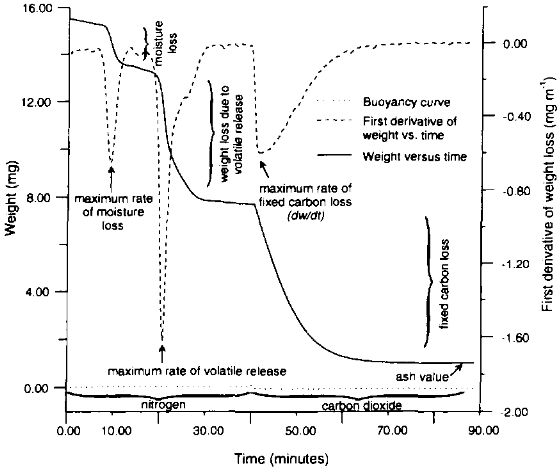

Fig. 1. Characteristics of thermogravimetric reactivity analysis NZS 613401 in carbon dioxide at 900°C.

A similar procedure was used for testing coals in carbon dioxide with the newly-formed char being reacted at either 900°C, or heated to 1100°C before carbon dioxide was introduced.

The temperature plateau at 110°C allows the moisture content of the coal to be calculated as the weight loss at this point [12]. The volatile matter is calculated from the change in weight between the moisture calculation point and that at which the reactant gas is introduced. Ash is determined by re-weighing the crucible after completion of the reaction. This procedure allows both proximate analysis and reactivity data to be obtained from the same test (Fig. 1). A comparison of ash values obtained from all analyses reported here, using carbon dioxide with those conducted with dry air, showed a correlation of $R = 0.98$.

A run was made for all procedures with an empty crucible which was then subtracted from each sample run. This effectively removes the effects of buoyancy in the system that occurs due to changing density of the furnace atmosphere.

The maximum rate of fixed carbon loss along with the maximum rates of moisture and volatile loss may be calculated from the first derivative of the experimentally derived weight trace, corrected for buoyancy fluctuations, as shown in Fig. 1. Reactivity can then be calculated according to $R = -W_0^{-1}(\mathrm{d}w/\mathrm{d}t)$ [3,5,10] where R is the maximum reactivity, W_0 the initial weight of the char on a dry ash-free basis and $\mathrm{d}w/\mathrm{d}t$ the maximum rate of fixed carbon loss. R is expressed in mg h^{-1} mg^{-1} or simply h^{-1}.

4. Reactivity measurements in air and carbon dioxide

Proximate analysis data for the South Island samples used in methodology development, are shown in Table 4. Results of tests carried out in dry air are given in Table 5. Reactivity results for carbon dioxide are shown in Table 6. The Moody Creek sample (55/508) has been separated at the bottom of the tables due to the slightly higher rank and hence lower reactivity.

The reaction between carbon and dry air is exothermic. As air is introduced into the STA the furnace temperature increases. Initial tests showed that the reaction between dry air and the highly reactive Waikato samples at 900°C increased the temperature of furnace as much as 30°C. The less reactive samples from the South Island increased the temperature of furnace to only a few degrees. Reactivity values given in Tables 5 and 6 show the strong influence of tem-

Table 4
Proximate analyses of Greymouth coal type suite

	Moisture content (%)	Volatile matter (%)	Fixed carbon (%)	Ash content (%)	Volatile matter (%) d.a.f	Fixed carbon (%) d.a.f
752-5	6.0	43.3	49.6	1.1	46.6	53.4
55/382	5.9	39.9	52.9	1.2	43.0	57.0
55/381	6.6	36.2	54.0	3.2	40.2	59.8
752-8 vit	7.8	33.8	57.1	1.3	37.2	62.8
55/508	3.2	36.9	57.9	2.0	38.9	61.1

Table 5
Reactivities of Greymouth bituminous coals in dry air at 500 and 900°C

	Air 500°C		Air 900°C	
	Raw value (h^{-1})	Dry ash-free (h^{-1})	Raw value (h^{-1})	Dry ash-free (h^{-1})
752-5	2.05	2.09	10.46	10.68
55/382	1.83	1.86	9.30	9.51
55/381	1.86	1.97	9.15	9.68
752-8 vit	2.22	2.27	9.40	9.61
55/508	0.85	0.87	9.05	9.36

Table 6
Reactivities of Greymouth bituminous coals in carbon dioxide 900 and 1100°C

	CO_2 900°C		CO_2 1100°C	
	Raw value (h^{-1})	Dry ash-free (h^{-1})	Raw value (h^{-1})	Dry ash-free (h^{-1})
752-5	0.22	0.23	7.12	7.27
55/382	0.22	0.22	5.63	5.76
55/381	0.23	0.24	6.10	6.23
752-8 vit	0.21	0.23	6.50	6.88
55/508	0.16	0.17	4.78	4.94

perature on the reaction rate. As the increase in temperature due to the exothermic event is neither controlled nor repeatable, air is unsuitable as a reactant gas for analysing Waikato coal samples under these conditions.

The Bouduard reaction between carbon dioxide and carbon, $C + CO_2 \rightarrow 2CO$, is endothermic. It takes place within the kilns at BHP New Zealand Steel as part of the direct reduction of iron ore to sponge iron. Unlike the reaction in air, the Boudard reaction has only a slight effect on the temperature of furnace. Since it is important to maintain an environment as close to the isothermal as possible during analysis, CO_2 is the more appropriate reactant gas for reactivity measurements of highly reactive coals such as those from Waikato.

5. Repeatability and precision

Ten separate runs were carried out on a typical BHP New Zealand Steel coal sample, NZS 613401, at 900 and 1100°C. Table 7 summarises the maximum rate of fixed carbon loss (dw/dt) and the calculated reactivity value on a raw and dry ash-free basis. Repeatability limits for carbon dioxide for a typical Waikato coal blend, using the method outlined above, are 0.07 h^{-1} for testing at 900°C and 0.5 h^{-1} at 1100°C. By comparison, Crelling et al. [5] achieved repeatability limits of ±0.08 h^{-1} at 500°C in air, with reactivity values ranging from 0.47 to 2.08 h^{-1}, whereas Jenkins et al. [3] reported results that were repeatable within a maximum spread of ±5%.

Initial repeatability runs on sample NZS 613401 were carried out in June and July 1996. A further run on the same sample was carried out five months later in November, to see whether the sample deterioration affects reactivity measurements. Results are shown in Table 8 which also lists the mean values obtained from the initial repeatability testing. Although the moisture content of the samples varied, proximate analysis data on a dry basis and a dry ash-free basis shows no variation. The maximum rate of fixed carbon loss (dw/dt) varies with the re-run sample having a slightly faster maximum loss rate. Final reactivity values show that the sample stored for four months has a slightly faster reactivity.

Table 7
Reactivity measurements for repeat runs of sample NZS 613401 in carbon dioxide at 900 and 1100°C for

900°C				1100°C			
Run	Maximum dw/dt (mg min^{-1})	Reactivity		Run	Maximum (dw/dt) (mg min^{-1})	Reactivity	
		Raw (h^{-1})	d.a.f (h^{-1})			Raw (h^{-1})	d.a.f (h^{-1})
189	−0.567	4.56	5.11	200	−2.53	20.8	23.1
185	−0.572	4.56	5.14	199	−2.57	20.7	22.8
132	−0.580	4.55	5.08	172	−2.58	21.7	24.3
128	−0.558	4.55	5.07	171	−2.64	21.5	23.9
127	−0.557	4.47	4.99	170	−2.61	21.4	23.8
126	−0.561	4.53	5.09	169	−2.61	21.1	23.6
125	−0.557	4.56	5.17	166	−2.63	21.7	24.2
124	−0.564	4.44	5.03	165	−2.66	21.7	24.1
123	−0.555	4.41	4.94	164	−2.61	21.6	24.3
97	−0.548	4.44	5.02	161	−2.62	21.8	24.5
$\bar{x}$	−0.560	4.49	5.05	$\bar{x}$	−2.61	21.4	23.9
σ	0.009	0.06	0.07	σ	0.04	0.4	0.5

Table 8
Proximate analysis and reactivity data for a re-run of sample NZS 613401 made three months after initial repeatability analysis, compared with mean values of earlier tests

	Dry basis			Dry ash-free basis			Reactivity	
	Volatile matter (%)	Fixed carbon (%)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)	dw/dt (mg min^{-1})	Raw (h^{-1})	d.a.f (h^{-1})
$\bar{x}$	43.07	50.66	6.27	45.95	54.05	−0.5619	4.51	5.06
σ	0.63	0.64	0.34	0.65	0.65	0.0092	0.06	0.07
Re-run	43.35	50.96	5.69	45.97	54.03	−0.5930	4.70	5.23

6. Stockpile sample testing

Coal samples collected from the BHP New Zealand Steel stockpiles contain limestone; a necessary component of the steel production process used to control the basicity of the slag. This limestone was removed manually before analysis of the coal but, in addition, samples containing both limestone and coal were also analysed to afford a comparison. These analyses were carried out in carbon dioxide at 900, 1100 and 1300°C. Data are presented in Table 9.

The limestone increases the volatile matter component and the final ash yield of the coal at all the three temperatures. A plot of sample weight versus time, shows the presence of the limestone that affects the DTG profile in the volatile region, reflected by a secondary peak due to the breakdown of calcium carbonate (Fig. 2). The reactivity for the samples

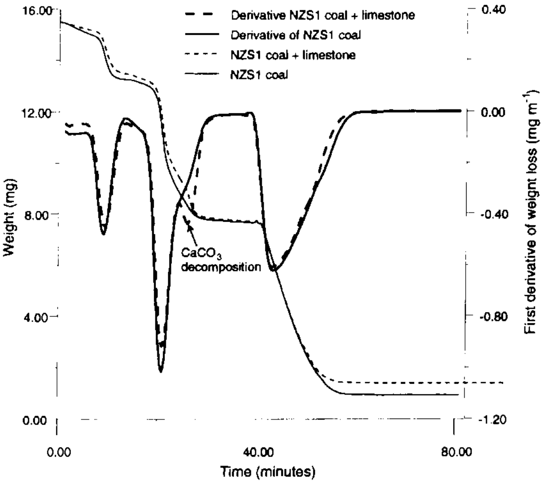

Fig. 2. Comparison of reactivity analyses of BHP New Zealand Steel coal stockpile sample NZS1 with and without limestone.

Table 9
Effect of limestone on the reactivity of sample NZS1 at 900, 1100 and 1300°C

	As received				Dry ash-free basis		Char weight	dw/dt (mg min^{-1})	Reactivity	
	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Volatile (%)	Fixed carbon (%)			Raw (h^{-1})	d.a.f (h^{-1})
900°C										
NZS1	14.55	35.91	45.67	3.87	44.02	55.98	7.68	−0.6210	4.85	5.26
NZS1 + 1st	13.05	37.03	40.69	9.23	47.65	52.35	7.74	−0.6098	4.73	5.80
1100°C										
NZS1	13.63	36.65	46.18	3.55	44.24	55.76	7.71	−2.6446	20.59	22.17
NZS1 + 1st	13.86	36.30	41.08	8.77	46.91	53.09	7.73	−2.6131	20.28	24.61
1300°C										
NZS1	14.53	36.15	45.97	3.35	44.02	55.98	7.66	−3.3432	26.20	28.11
NZS1 + 1st	13.80	36.88	43.77	5.54	45.73	54.27	7.65	−3.2208	25.26	28.46

containing limestone increases from 5.26 to 5.80 h^{-1}, and 22.17 to 24.61 h^{-1} for temperatures of 900 and 1100°C, respectively; both results lying outside the repeatability limits.

7. Discussion and conclusions

Char reactivity measurements by thermogravimetry enable quick comparisons to be made between coals of different rank and type. They also provide indications of possible operating conditions and problems associated with using a particular coal or blend. For example, the increase in reactivity from 900 to 1100°C for the bituminous coal types is of the order of 30 times, whereas the subbituminous coal only increases fourfold for the same temperature shift. Even at the elevated temperature of 1100°C, subbituminous coal proves 3–5 times more reactive tnan bituminous coal. Hence it's attractiveness in a reduction process like that at BHP New Zealand Steel. High rank coals would require higher operating temperatures to achieve good reactivity. Conversely, any drop in operating temperature when using a high rank coal would clog the kiln with unreacted coal.

The high volatile bituminous coal types have quite different reactivities (Tables 5 and 6). The slightly higher rank Moody Creek sample has the lowest reactivity of the Greymouth suite, consistent with decreasing reactivity with increasing rank. Sample 752-5 has the highest reactivity, which is most likely due to a higher liptinite content for this coal type. Samples 55/382, 55/381, and 752-8 vit show an increasing trend of greater reactivity with increasing vitrain percentage.

Reactivity testing at 900°C emphasizes more clearly the differences between coal ranks and enables the subbituminous coals of New Zealand to be analysed in a reasonable time frame (< 90 min) with the added bonus of allowing proximate analytical data to be obtained in the same run.

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