

THE THERMOGRAVIMETRIC BEHAVIOUR OF COAL

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ABSTRACT

The techniques of thermogravimetry (TG) and derivative thermogravimetry (dTG) have been applied to a range of coal samples using the Stanton–Redcroft type 780 thermal analyser. The work described covers three areas.

(a) A comparison of proximate analysis results obtained using the thermobalance with those established using the British Standard method, for a total of 14 coal samples of widely differing properties.

(b) The establishment of the burning profile test in the authors' laboratory. This is essentially a plot of dTG response against temperature as a 20 mg coal sample is heated in air and gives a measure of the combustibility of the fuel.

(c) The development of the volatile release profile test, similar to the burning profile but in an inert atmosphere. This yields information on the mode of breakdown of the organic substance of the coal as the sample is heated.

BACKGROUND

This paper is essentially an extended version of a presentation made by one of the authors during the Second European Symposium on Thermal Analysis (ESTA-2) at Aberdeen on the 1st–4th September 1981 [1]. The areas covered are (a) proximate analysis of coals by thermogravimetry, (b) the burning profile test for reactivity of coals in air using derivative thermogravimetry, and (c) the volatile release profile test for carbonisation characteristic (in inert atmosphere), also using derivative thermogravimetry. Certain details of the tests and some results which are quoted in this paper do not correspond exactly with those quoted in the Aberdeen paper [1], due to continuing development work and refinements of technique. The work was undertaken as part of a programme by Babcock Power Ltd. to expand their solid fuel testing facilities in response to the current upsurge of interest in coal as a primary energy source.

INTRODUCTION

Proximate analysis

The technique of proximate analysis has been long established in the field of coal technology as a convenient preliminary method of assessing the quality of a coal sample and arriving at a first estimate of its type (lignitic, bituminous, anthracitic). The procedural details of the individual tests which go to make up the proximate analysis vary somewhat among the various standard specifications in common use in the West [2–4], but all involve three basic steps: (a) moisture determination (weight loss on heating at around 100°C in inert atmosphere); (b) volatile matter (weight loss on heating in a closed crucible at a temperature around 900°C, depending on standard, for a specified time); and (c) ash content (weight remaining after combustion of the coal in air at a specified temperature).

These three quantities are expressed as percentages, summed, and the residue to 100% is called the “fixed carbon”. The three measured parameters, i.e. moisture, volatile, and ash are all determined in duplicate on separate aliquots of the analysis sample, making the total analysis very labour intensive and time consuming. It is estimated that a single proximate analysis can involve up to 26 separate weighing operations and while modern automated techniques can reduce weighing time appreciably, it still requires several hours to carry out the ashing procedure to constant weight.

Since all the measurements involve weight changes under specified conditions of temperature, time and atmosphere, it seemed that the technique of thermogravimetry (TG) would be ideally suited to this type of analysis. The first section of this paper deals with an investigation of the application of TG to the proximate analysis of a wide range of coal samples. Results are compared with those obtained by the British Standard (BS) method [2] since we are more familiar with this in the U.K. It must be mentioned that other workers have investigated this area [5–11], but none has used the equipment described in this paper nor, apparently, has any attempted to match the TG operating conditions closely to the BS regime. An exact correspondence with BS requirements is not possible using TG equipment and these limitations will be discussed at a later stage.

Burning profile test

In the design of industrial coal-fired boiler furnaces, it is of importance to have an assessment of the reactivity of the intended fuel. Alternatively, if it is proposed to change the fuel supply for an existing installation, it is advantageous to have a test which allows the burning characteristics of the candidate fuels to be compared with the original in terms of reactivity or burning rate. Early work in this direction was done by the American

Babcock and Wilcox Company [12], who established a test in which the rate of weight loss of a coal sample burning in air was plotted against temperature. This they named the "burning profile" test and the plot obtained typically takes the form of a curve with two or more maxima, corresponding to moisture loss followed by progressive combustion. The temperature at which the maximum combustion rate occurs is taken as a measure of combustibility with lower temperature indicating more easily burned coals.

The apparatus used in this early work was relatively large in comparison with modern TG equipment and employed a 25 mm diameter crucible with a sample weight of 300 mg. This section of the present paper deals mainly with the application of a modern thermobalance to this test and gives examples of the results obtained for a range of ASTM standard coals of differing rank. In a comparative study involving the American Babcock and Wilcox Co. and Exxon Research Laboratories [13], it has been stated that modern TG equipment is not ideally suited to this test because of the small sample weight allowing a too-rapid burnout of the fuel. This is discussed at a later stage. Other investigators who have examined the application of derivative thermogravimetry to solid fuels are Weltner [14,15] in Budapest, and Smith et al., also at Exxon in the U.S.A. [16].

Volatile release profile

This test is very similar to the burning profile test in that a plot is obtained relating rate of weight loss to temperature in an inert atmosphere. The resulting "peaks" arise in this case, not from oxidation, but from loss of volatile material as the various organic constituents of the coal break down. The application to combustion studies is perhaps not immediately obvious, but it is suggested that the test constitutes a more sensitive "fingerprint" for identifying coals than the burning profile and could have a useful application to gasification and carbonisation studies. Because the authors' major interest is in the combustion of coal, less work has been done in this area than in the preceding two. Some curves for various types of coal are presented for comparison purposes. The application of dTG to coal carbonisation has been reported by Mitra et al. in India [17].

EXPERIMENTAL

Apparatus

The apparatus used in this work was the Stanton-Redcroft series 781 simultaneous thermal analyser. This is supplied by the manufacturer with two alternative balance "hangdown" systems, one carrying two matched platinum crucibles for simultaneous TG/dTG/DTA studies and the other

carrying a single larger platinum crucible for TG/dTG studies only. It was this latter system which was used throughout the work reported here. A brief specification of the equipment is given below.

Balance capacity: 5 g max.

Electronic measuring ranges: 0–250 mg, 0–25 mg.

dTG output: 0–100 $\mu\text{g min}^{-1}$ to 0–80 mg min^{-1} in switched ranges.

Furnace: Pt/Rh, 1500°C max.

Temperature programmer: 0.1–9.9 K min^{-1} in 0.1 K min^{-1} steps and 1.0–50 K min^{-1} in 1.0 K min^{-1} steps.

Thermocouples. Pt–Pt/Rh 13% built into crucible holder for sample temperature. Furnace controlled from wall thermocouple.

Atmosphere. Flowing or static gas. Furnace/balance system sealed.

Crucible size. 8 mm high, 12 mm top diam., 10 mm bottom diam.

All coal samples studied were prepared as for the British Standard proximate analysis [2], i.e. less than 210 μm , equilibrated to laboratory conditions of temperature and humidity. Sample sizes for the various tests are described in the relevant sections.

Proximate analysis

As mentioned in the Introduction, the standard proximate analysis of coal involves the direct measurement of moisture, volatile matter, and ash on three separate aliquots drawn from the analysis sample. In the TG method, a very great time saving is achieved by performing all three determinations sequentially on one sample, although, because of instrumental and other constraints, an exact replica of the standard's requirements cannot be achieved. The moisture determination can be duplicated almost exactly by heating the sample to 105°C in nitrogen and holding at this temperature to constant weight, but in the cases of volatile matter and ash some compromises have to be made. For example, in the BS volatile determination, a 1 g sample is weighed into a covered crucible and inserted into a previously heated furnace at 900°C where it is left for exactly 7 min, withdrawn, cooled and reweighed. Thus the heating rate of the sample is non-linear and indeterminate, as is the hold time at 900°C. In the TG method, the sample is heated from 105°C at the conclusion of the moisture determination to 900°C at a rate of 50 K min^{-1} (still in nitrogen), the maximum permissible for the equipment. Thus, the time to attain "volatile" temperature is of the order of 10 min and volatile material is being lost continuously from around 300°C. If the volatile content were taken as the weight loss 7 min after attaining 900°C, a high result might be expected since the sample has experienced temperatures above 300°C for a longer period than in the BS test. In practice, an elapsed time of 7 min from first attaining 900°C was, in fact, found to give the best concurrence with the BS results and this has been used in all the results reported herein.

In the case of the determination of ash content, the BS method requires that a 1–2 g sample contained in an open dish be placed in a cold muffle and heated first to 500°C, held for 30 min, and then to 815°C and held to constant weight. Clearly, this programme could be duplicated exactly in the thermobalance, but would result in little time saving as compared with the standard method. It was therefore decided to burn off the char remaining after the volatile determination and compare the ash figures with the BS values. Before introducing air to the furnace, the temperature was lowered to 815°C so that combustion of the carbon takes place at the temperature specified in the standard.

A refinement which has been found necessary since the authors' previous publication dealing with this work is the application of buoyancy corrections to allow for the small differences in balance reading at the various temperature levels encountered in the test. Thus, at 900°C, the "volatile" temperature, the balance was found to read 0.3 mg low and at 800°C, the ashing temperature, 0.2 mg low, as compared with readings at room temperature (at which the coal sample is originally weighed). Thus for a 50 mg sample, a deduction of 0.6% is made from the apparent volatile reading and an addition of 0.4% is made to the ash value. The correction at the "moisture" temperature, 105°C, is negligible.

In summary, the method used for TG proximate analysis was as follows.

(1) Zero balance with furnace in position, crucible empty and nitrogen flowing at 50 ml min⁻¹.

(2) Lower furnace and weigh 50 ± 0.5 mg coal directly into the crucible.

(3) Raise furnace and set "range" = "weight", i.e. output to recorder is 10.0 mV.

(4) Heat furnace to 105°C at 50 K min⁻¹ and hold until weight drops to a constant value. This gives the moisture content.

(5) Heat furnace to 900°C at 50 K min⁻¹ and measure total weight loss exactly 7 min. after sample temperature first attains 900°C. Subtract moisture loss and buoyancy correction of 0.6% from the total weight loss to give the volatile content.

(6) Drop furnace temperature to 815°C and switch atmosphere to air at the same flow rate.

(7) Record weight left in crucible when carbon has been burnt off and weight reading is steady. Add buoyancy correction of 0.4% to give ash content.

In order to read results to the required level of discrimination, the recorder channel recording the weight signal is used at a sensitivity of 1 mV rather than 10 mV full scale. The instrument employed (Linseis) has an automatic re-set facility so that 100% weight (i.e. 10 mV) is equivalent to 10 traverses of the pen over the full chart width. Thus 1 chart division equals 0.1% change in weight.

TG proximate results are presented for a wide range of coals varying in

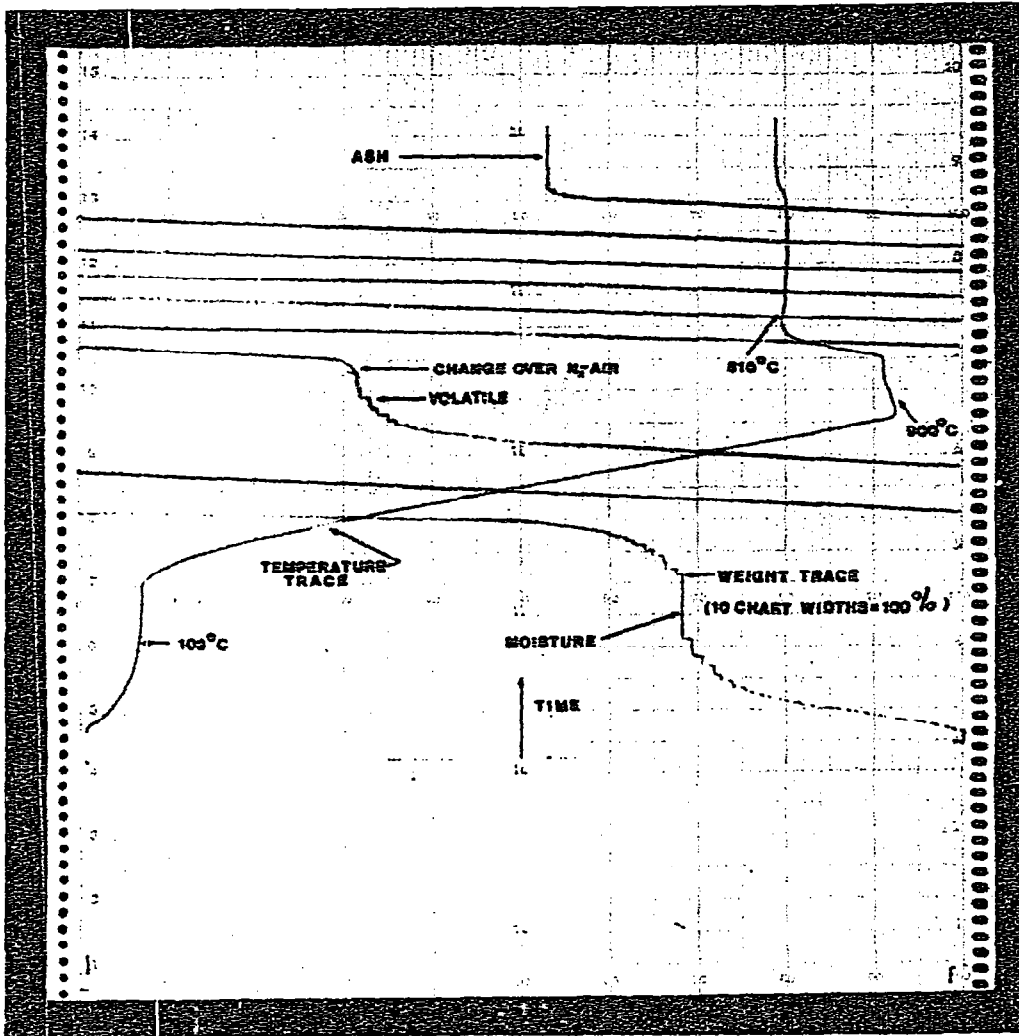


Fig. 1. Typical thermogravimetric proximate analysis trace (bituminous coal).

rank from lignite to anthracite and in ash content from 5.5 to 40% along with the corresponding results obtained using the BS method. Figure 1 is a typical recorder trace obtained for a TG proximate analysis.

Burning profile

As has already been stated, the equipment is used in its derivative thermogravimetric mode for this test. The balance control module of the STA781 has an inbuilt derivative computer which provides a 0–10 mV output proportional to the rate of change of sample weight with time, in a series of switched sensitivity ranges, from 0–100 $\mu\text{g min}^{-1}$ to 0–80 mg min^{-1} . Under the test conditions established for this work, a range of

0–6000 $\mu\text{g min}^{-1}$ was found to give optimum results in terms of a compromise between background noise and reasonable magnitude of response. In the normal mode of operation of this equipment as supplied, the dTG output is displayed against time by the third channel of the strip recorder, along with crucible temperature, weight record, and DTA output, the latter, of course, being unused in this work. This type of presentation is, however, not entirely suitable for the burning profile test, where it is required to relate rates of burning directly to temperature rather than time and a secondary X–Y plotter was added to the system. This was actuated, not directly from the instrument outputs, but from 0–10 V signals re-transmitted from the temperature and dTG channels of the primary Y–T recorder. Thus, a direct burning profile plot was obtained on a sheet of “A3” graph paper without the necessity for manual re-plotting.

The rate of heating used in the burning profile test was 15 K min^{-1} , chosen to correspond with the original American work [12,13] and the air flow was 75 ml min^{-1} . This latter value was the maximum practicable for the apparatus without causing an unacceptable disturbance of the hangdown system and represents a 75% full scale reading on the flowmeter. It is essential in this test to provide a plentiful air supply to ensure that rates of combustion are not controlled by limited oxidant.

In summary, the operating parameters for the burning profile test were

Sample weight	20 \pm 0.5 mg
Air flow	75 ml min^{-1}
Heating rate	15 K min^{-1}
Max. temp.	900°C
dTG range	0–6000 $\mu\text{g min}^{-1}$
Overall dTG sensitivity	1 cm = 120 $\mu\text{g min}^{-1}$

In the following section, burning profiles are presented for a number of selected coals with comments on their use and interpretation.

Volatile release profile

This test is very similar to the burning profile, but utilises oxygen-free nitrogen rather than air as the furnace atmosphere. Since there is no interaction between the atmosphere and the sample, the flow rate is reduced to 50 ml min^{-1} and to ensure an adequate dTG response without increasing the sensitivity and thereby accentuating background “noise”, the heating rate is increased to 23 K min^{-1} . Test conditions are summarised as

Sample weight	40 \pm 0.5 mg
Nitrogen flow	50 ml min^{-1}
Heating rate	23 K min^{-1}

Max. temp.	960°C
dTG range	0–6000 $\mu\text{g min}^{-1}$
Overall dTG sensitivity	1 cm = 120 $\mu\text{g min}^{-1}$

Curves for four selected coals are presented and discussed in the following section.

RESULTS AND DISCUSSION

Proximate analysis

In order to establish the reliability of the TG method before conducting tests on a range of coals, a standard coal sample was obtained from Alpha Resources, Inc., in the U.S.A. The proximate analysis as supplied with the sample had been carried out according to the ASTM procedure [3], which varies from the BS method in the following two main respects. (a) The volatile matter is measured at 950°C as compared with 900°C in the BS method. (b) The ash is measured at 750°C rather than 815°C.

This material was therefore analysed according to the British Standard method and the results are given in Table 1 along with the ASTM results as supplied.

The volatile matter is higher in the American method, presumably due to the higher temperature used, but the ash content is the same by both methods, despite the difference in ashing temperature.

This material was then subjected to six replicate analyses by the TG method and the results are given in Table 2. A note regarding the TG volatile determination is called for at this point, however. In the earlier stages of this work, the volatile loss was measured at an elapsed time of 3 min after the crucible first attained a temperature of 900°C, for the reasons mentioned in the Experimental section, but further experience has shown that a 7 min period gives better correspondence with BS values. This arbitrary choice of elapsed time to give the best correspondence is felt to be quite justified, since

TABLE 1

Comparison of ASTM and BS proximate analyses (dry basis) of standard coal

	ASTM (supplied)	BS
Volatile (%)	37.4	36.1
Fixed carbon (%)	52.5	53.8
Ash (%)	10.1	10.1

TABLE 2

Replicate TG proximate analyses on standard coal (dry basis)

	Volatile (%)	Fixed C (%)	Ash (%)
1	36.2	53.6	10.2
2	35.1	54.8	10.1
3	35.4	54.7	9.9
4	35.0	55.1	9.9
5	35.2	54.9	9.9
6	35.3	54.8	9.9
Mean	35.4	54.7	10.0
BS values	36.1	53.8	10.1

volatile content is not a fundamental property of the fuel and the value depends completely on the temperature, time, and other operating parameters. The BS test remains the ultimate standard for this work and the object was to obtain TG results as close as possible to the standard values.

The results obtained for a series of 14 coals of widely differing characteristics are given in Table 3. All values are on the "dry basis" and both BS and TG results are presented. The final column gives the differences between the two sets of results, a positive value indicating that the TG result was higher than the BS and vice versa.

Before commencing on a critical discussion of these results, it is appropriate to review the reproducibility and repeatability limits permitted in BS1016, Part 3 (i.e. between laboratory and within laboratory, respectively).

The relatively large amount of latitude allowed under the heading Reproducibility for the volatile test in Table 4 should be taken as indicating the difficulty in standardising the operating conditions.

Returning to Table 3, the largest discrepancy in volatile content between the TG and BS methods occurs with sample 6 (1.8%). Only one other sample shows a discrepancy greater than 1% (No. 9), again on the negative side. The remaining twelve samples all gave TG volatile results within 1% of their BS values, which, considering the very large difference between the two techniques, is considered to be fairly satisfactory. It does not quite meet the specified intra-laboratory tolerance of 0.2 or 0.3%, but it would not really be appropriate to apply this to two such diverse methods and it would be more realistic to compare the results with the "reproducibility" column of Table 4, where a tolerance of up to 1% is permitted. The two "rogue" results have been checked carefully and seem to give a consistent discrepancy of the reported magnitude between the volatile contents measured by the two methods. This has, as yet, not been satisfactorily explained, but is perhaps due to differing modes of breakdown of the organic matter of the coal to

TABLE 3

Comparison of BS and TG proximate analysis (dry basis)

Sample	Type	Source	BS results				TG results				BS compared with TG values			
			Volatile (%)	Fixed C (%)	Ash (%)		Volatile (%)	Fixed C (%)	Ash (%)		Volatile (%)	Fixed C (%)	Ash (%)	
1	Lignitic	U.S.A.	41.3	46.1	12.6	41.9	46.3	11.8		+0.6	+0.2	-0.8		
2	Lignitic	U.S.A.	44.4	45.4	10.2	45.0	45.1	9.9		+0.6	-0.3	-0.3		
3	Lignitic	S. Africa	29.8	39.1	31.1	29.4	39.9	30.7		-0.4	+0.8	-0.4		
4	Lignitic	Australia	26.0	34.3	39.7	26.3	33.6	40.1		+0.3	-0.7	+0.4		
5	Bituminous	S. Africa	25.0	53.0	22.0	24.5	53.2	22.3		-0.5	+0.2	+0.3		
6	Bituminous	Scotland	34.2	57.7	8.1	32.4	59.7	7.9		-1.8	+2.0	-0.2		
7	Bituminous	China	19.6	36.8	43.6	19.7	37.2	43.1		+0.1	+0.4	-0.5		
8	Bituminous	S. Africa	27.3	57.9	14.8	26.6	58.9	14.5		-0.7	+1.0	-0.3		
9	Bituminous	England	32.4	49.4	18.2	31.1	50.6	18.3		-1.3	+1.2	+0.1		
10	Bituminous	S. Africa	24.6	59.0	16.4	23.8	59.7	16.5		-0.8	+0.7	+0.1		
11	Bituminous	S. Africa	25.8	58.1	16.1	25.0	58.4	16.6		-0.8	+0.3	+0.5		
12	Anthracitic	Scotland	6.0	88.6	5.4	6.4	88.4	5.2		+0.4	-0.2	-0.2		
13	Anthracitic	Scotland	6.2	83.7	10.1	7.1	83.1	9.8		+0.9	-0.6	-0.3		
14	Anthracitic	Scotland	4.6	87.8	7.6	5.3	87.5	7.2		+0.7	-0.3	-0.4		

TABLE 4
BS tolerances

	Repeatability (% abs.)	Reproducibility (% abs.)
Volatile matter		
< 10%	0.2	0.5
> 10%	0.3	1.0
Ash		
< 10%	0.15	0.30
10–20%	0.20	0.40
> 20%	0.25	0.50

form the gaseous volatile materials. This will be touched on later in the section dealing with the volatile release profile.

Turning now to the results for the ash contents of the fourteen coal samples, it will be seen that the largest discrepancy between the TG and BS results is 0.8% in the case of sample No. 1, with the BS result the higher of the two. Two samples each show a discrepancy of 0.5% (Nos. 7 and 11), but in the opposite sense one from the other, and the remainder all lie within the range 0.4–0.1%.

Table 5 compares these results with the permitted reproducibility limits in BS1016, Part 3 (1973).

Thus eleven TG results are within the BS permitted reproducibility limit and only three outside. Of the latter, sample No. 1 is the worst, with a discrepancy between the BS and TG results of 0.8% as compared with the specified 0.4% limit, while Nos. 11 and 14 are outside their appropriate limits by only 0.1% in each case.

It is perhaps significant that sample No. 1 is a lignite with relatively high alkali metal content. This could lead to an excessive loss of mineral material in the form of alkali salts during the volatile matter determination when the sample is heated to 900°C, i.e. 85°C above the standard ashing temperature.

TABLE 5
TG and BS ash values compared with BS reproducibility limits

Ash range (%)	Permitted deviation (%)	Samples in range	No. within limit	No. outside limit
< 10	0.3	3	2	1
10–20	0.4	7	5	2
> 20	0.5	4	4	0

Burning profile

Before discussing in detail the comparative burning profile curves obtained for various coals, it would be appropriate to devote some attention to the idealised burning profile for a medium-volatile bituminous coal presented in Fig. 2. As already stated, this presents a plot of the rate of loss of weight as the sample burns in air against crucible temperature, while the furnace is heated at 15 K min^{-1} from room temperature.

The peak labelled 1 at just under 100°C is due to loss of inherent moisture, and is not normally included in the burning profile characterisation. The magnitude of this response is, of course, dependent on the inherent moisture content of the sample and is thus, to some extent, indicative of rank. In the temperature range $270\text{--}310^\circ\text{C}$, certain coals in the middle-volatile range exhibit a negative deflection of the burning rate curve, as indicated at point 2. This is caused by a gain in weight due to solid-state oxidation of the organic matter and can amount to as much as 4% of the sample weight. Thereafter, as temperature increases, the weight begins to fall as volatile loss commences and the point where the curve crosses the zero line, labelled 3, is termed the initiation temperature (IT). From this point to point 4, the rate of weight loss rises more or less linearly as the volatile release accelerates with increasing temperature until, at around 450°C , combustion becomes the major mechanism and the slope increases abruptly. Since a large proportion of the volatile material in the coal has been removed by the time point 4 is attained, the inflection temperature is called, for convenience, the "fixed

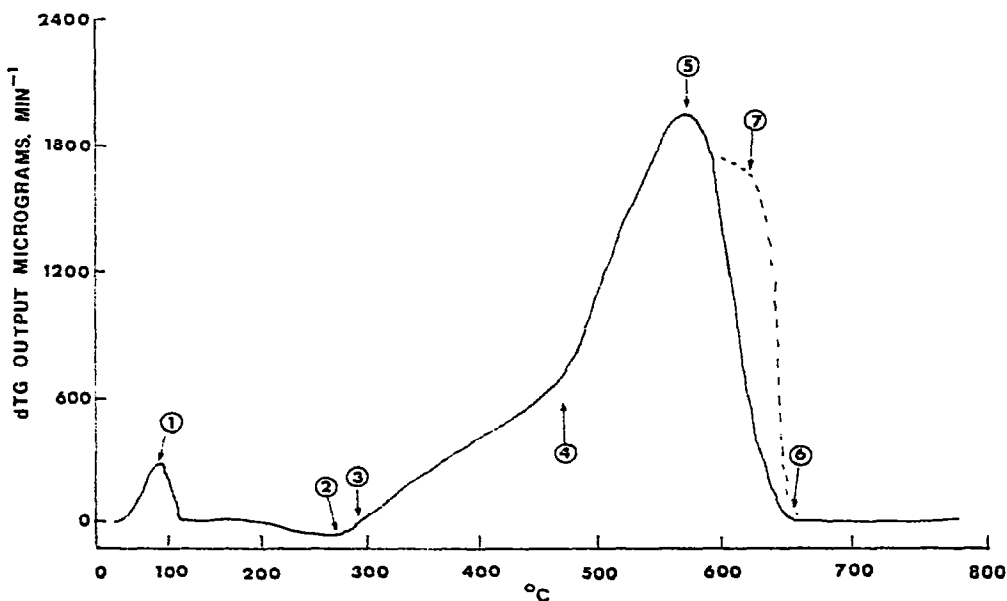


Fig. 2. Idealised burning profile curve.

carbon initiation temperature" (IT_{FC}), although it is appreciated that it does not, in fact, indicate an abrupt change-over from devolatilisation to combustion of fixed carbon.

The main characterising point on the curve is 5, the "peak temperature", where the rate of weight loss is at a maximum. This can range from less than 400 to above 700°C, depending on the rank of the coal, and is the parameter used chiefly in the assessment of combustibility. Beyond the peak temperature, the curve for most coals falls rapidly and smoothly back to the zero line at point 6 and this is called the "burnout temperature" (BT). In a small number of samples, a "shoulder" on the higher-temperature side of the peak temperature has been observed, as indicated at point 7 on the broken line. This has been found invariably associated with coals which possess appreciable swelling properties and is probably due to the samples swelling into an impermeable mass, thus reducing oxygen accessibility and causing a reduction in the combustion rate. This effect is referred to as "delayed burnout". Thus the burning behaviour of a coal sample, as assessed in this test, can be summarised in terms of the four reference points, IT, IT_{FC} , PT, and BT, which can conveniently be stored in a computer file along with the other numerical data on the coal such as proximate analysis, ultimate analysis, ash fusibility temperatures, etc. Figure 3 shows experimental burning profile curves for two bituminous coals superimposed on one chart, where all the points discussed above can be clearly seen. In particular, the delayed burnout effect is very evident in sample 1 and entirely absent in sample 2.

In the case of lignitic coals, the interpretation is complicated by the fact that the burning profile curves frequently display two or more major burning

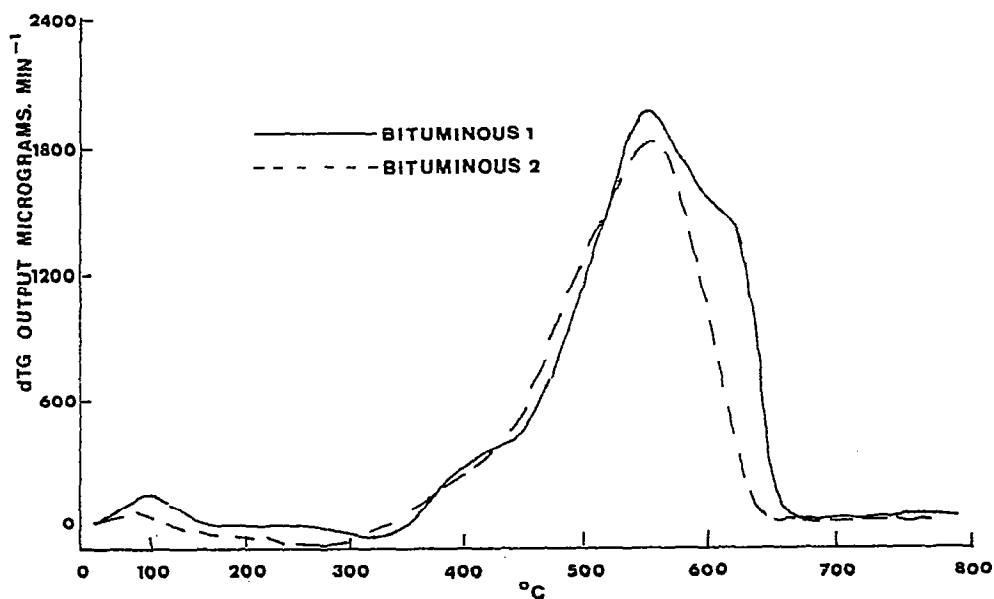


Fig. 3. Burning profile of two bituminous coals.

peaks. This has been termed "false ignition" by Wagoner and Duzy [12], the inference being that such a coal might ignite at a temperature indicated by the first peak, but would not necessarily burn to completion unless the temperatures were further increased.

A burning profile curve for an American lignite prepared in the authors' laboratory is shown in Fig. 4, where this effect is very clearly seen, and there are in this case, three burning peaks at 400, 475 and 500°C. At the other extreme of coal type, Fig. 5 shows a typical burning profile for an anthracite with a dry, mineral matter free volatile content of 5%. It can be clearly seen that the peak temperature is very much higher than any of the previous samples and that its shape is much more symmetrical. There is little indication of the slow initial increase in dW/dt (cf. 3-4 in Fig. 2) associated with devolatilisation, as would, indeed, be expected and, as a result, the main peak is much narrower than that of a bituminous coal of comparable combustible content. The burning profile parameters IT , IT_{FC} , PT and BT for the four coals referred to in Figs. 3-5 are given in Table 6.

Finally in this section, mention must be made of the comparison between burning profile curves produced for the same samples on different equipment. This has been investigated in a collaborative study between the Babcock and Wilcox Co. and Exxon, both in the U.S.A. [13], with the conclusion that the burning profile curve obtained is very dependent on the type of equipment used and such considerations as sample mass, crucible mass, crucible shape, etc. This has been amply confirmed in the course of the present work, where four samples of ASTM standard coals were obtained from the Babcock and Wilcox Co. and subjected to burning profile tests

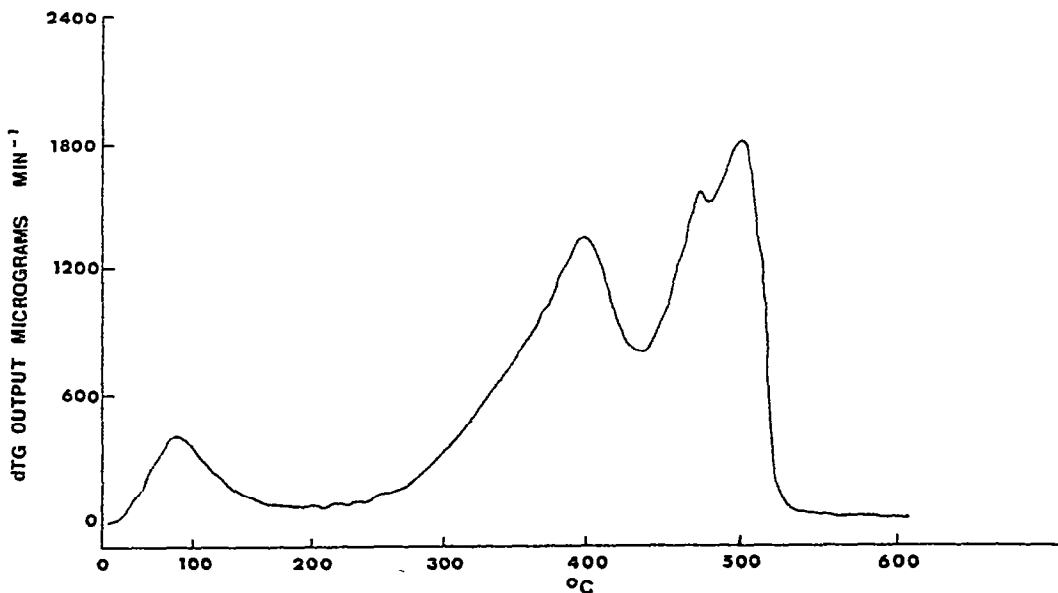


Fig. 4. Burning profile of American lignite.

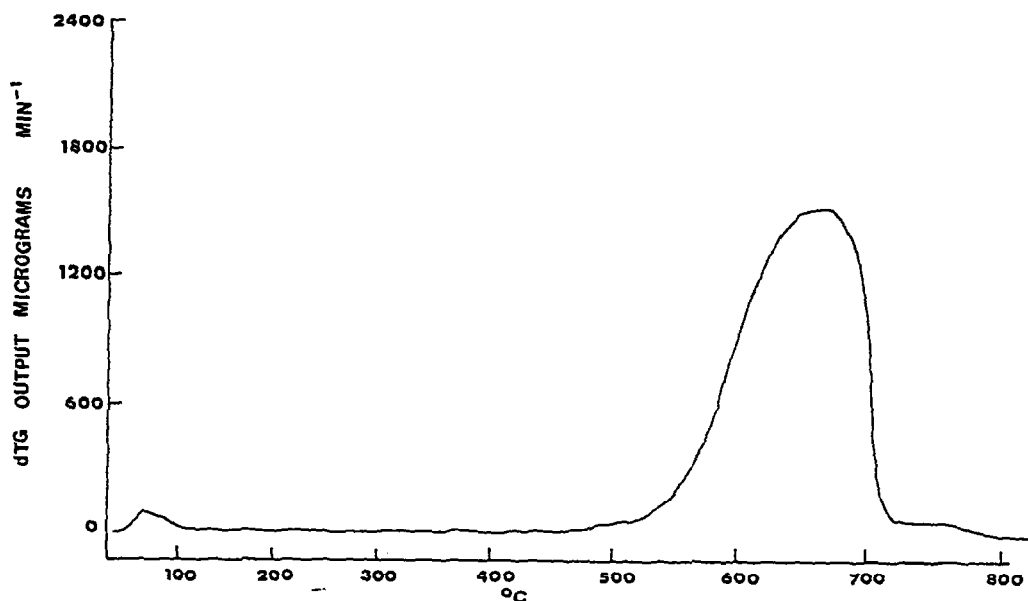


Fig. 5. Burning profile of Scottish anthracite.

using the authors' equipment and test procedure. These coals are used by the Babcock and Wilcox Co. as burning profile standards and the curves provided were very different in superficial appearance from those obtained at Renfrew using the authors' technique. In particular, the Babcock and Wilcox curves tended to exhibit lower peak temperatures than the authors', but much higher burnout temperatures, giving the American curves a much broader appearance. The latter can perhaps be attributed to the much larger sample mass used in the American test (300 mg compared with 20 mg), which could lead to a more delayed combustion, particularly since it would appear that the depth of the sample layer is appreciably greater than in the Renfrew technique. A deeper layer implies slower access of oxygen to those particles which are shielded from the surface by overlying material. The lower peak temperatures obtained by the Americans can be explained by a

TABLE 6

Burning parameters of lignitic, bituminous and anthracitic coals

	Lignite	Bituminous 1	Bituminous 2	Anthracite
IT (°C)	210	350	340	480
IT _{FC} (°C)	435	445	430	
Main PT (°C)	500	555	555	665
BT (°C)	540	665	690	785

TABLE 7

Comparison of Babcock and Wilcox Co. and Babcock Power Ltd. burning profiles for four ASTM standard coals

	IT (°C)		MAIN PT. (°C)		BT (°C)	
	B and W Co.	BP Ltd.	B and W Co.	BP Ltd.	B and W Co.	BP Ltd.
Lignite "A"	170	195	295	385	675	650
Subbituminous "A"	180	190	340	420	695	510
High volatile bituminous "A"	305	300	540	535	820	620
Anthracite	410	450	660	645	990	790

slight difference in experimental technique, in that Babcock and Wilcox plot dTG output against furnace temperature while in the Stanton-Redcroft equipment used by the authors, temperature is measured from the crucible holder. It has been observed during the course of the work that, as the sample burns, the crucible temperature is increased by as much as 30°C due to the exothermic reaction, so that if furnace wall temperature were used as the abscissa, peak temperatures would appear lower by this amount.

In the American procedure, because of the larger sample mass, an even greater increase in crucible temperature might be postulated, easily account-

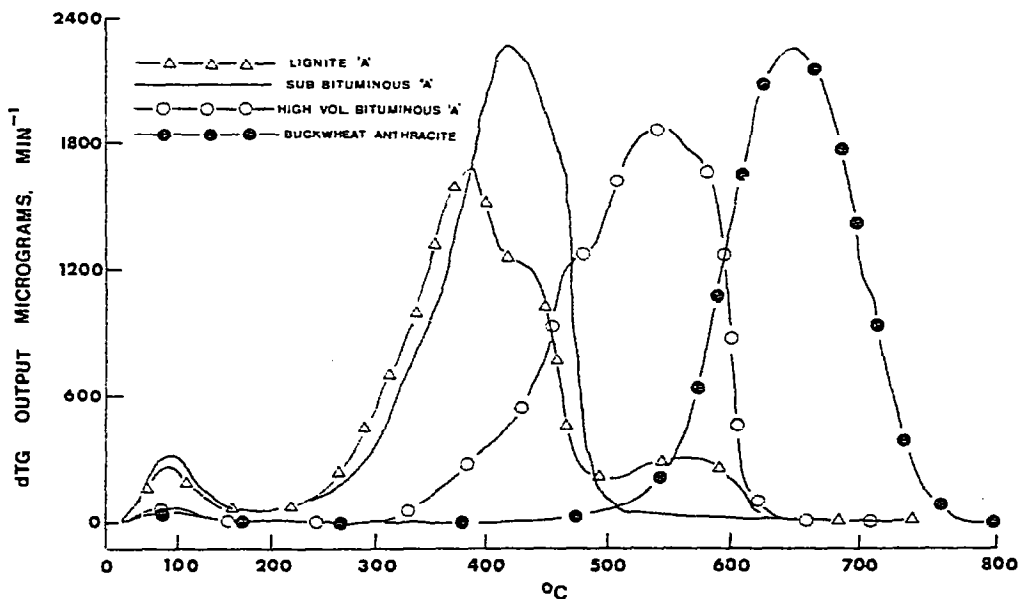


Fig. 6. Burning profiles of four ASTM standard coals.

ing for the apparent discrepancy between the two sets of results.

A resumé of the two sets of burning profiles for the four standard coals in terms of three of the "key" temperatures, IT, PT and BT, is given in Table 7 and the burning profiles as prepared in the authors' laboratory are presented in Fig. 6.

It can be seen from the above that the results from the two experimental regimes are very different, emphasising the empirical nature of the test. Within any one organisation, however, once techniques are established and rigidly adhered to, the burning profile test can provide an invaluable addition to the corpus of data bank material when related to known "standard" fuels of proven industrial performance.

Volatile release profile

This test is probably of greater relevance to carbonisation and coking studies, rather than to combustion, and as such has not been developed in the authors' laboratory in such depth as have the burning profile studies. It is very similar to the burning profile test in that it is essentially a plot of dTG response against crucible temperature as the sample is heated linearly, with the difference that the furnace is flushed with nitrogen rather than air. Thus the derivative weight changes which are recorded represent not combustion, but progressive thermal breakdown of the organic species present in the coal substance and loss of the gaseous products. Because of the slower rates of weight loss and the fact that the total loss in weight is also lower than during combustion, the dTG outputs are proportionally lower than those observed during the burning test. To overcome this, and to avoid increasing the overall electrical sensitivity of the dTG channel with the consequent increase in background "noise", this test is run with a 40 mg sample and a heating rate of 23 K min^{-1} , as stated in the Experimental section. The volatile release profile is much less sensitive to changes in sample mass than the burning profile since there is no reaction between the sample surface and the furnace atmosphere. Volatile loss takes place throughout the bulk of the sample and is not critically dependent on the particle-gas interface. The test is obviously not applicable to anthracitic and other low-volatile coals.

The most significant result to appear in the limited work done is the very different profiles which can be produced from superficially similar coals. For example, in Fig. 7 are presented the volatile release profiles of two bituminous coals containing around 35% volatile matter on the dry, mineral matter free basis, one from Scotland and one from South Africa. While both show a major decomposition peak at about 480°C (as, indeed, do almost all bituminous coals), the subsequent pattern is entirely different. The response of the Scottish sample drops off very rapidly with increasing temperature, indicating that the bulk of the volatile matter is released below 550°C , while

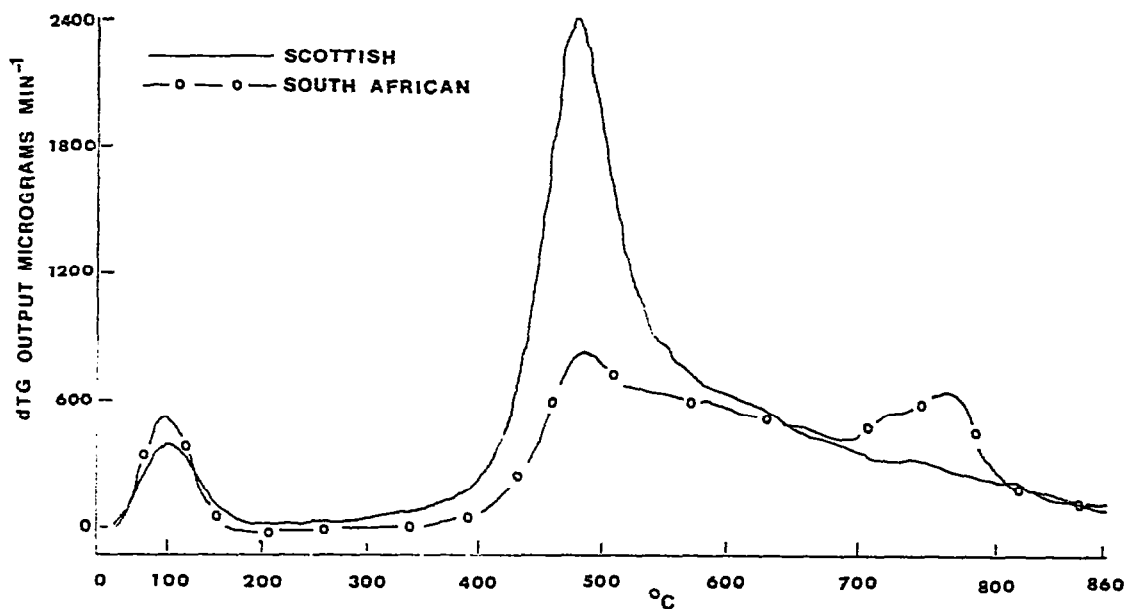


Fig. 7. Volatile release profiles of Scottish and South African bituminous coals.

the South African sample maintains a relatively constant rate of release to 700°C, thereafter accelerating to a second maximum at approximately 760°C. Clearly, this type of information would be of significance in gasification and coking studies and is not readily available from existing standard tests.

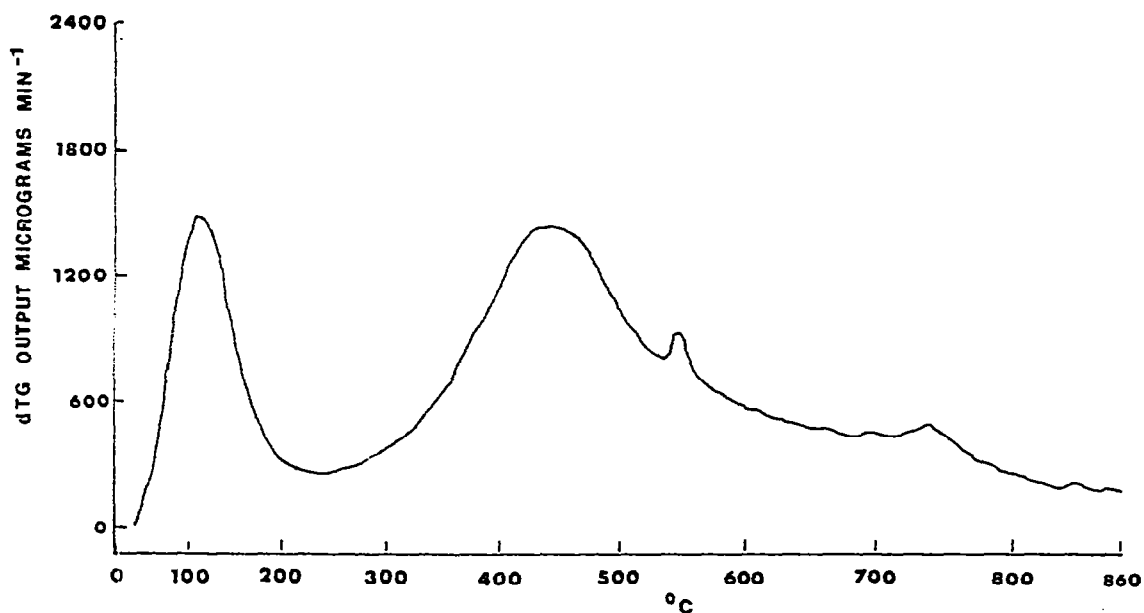


Fig. 8. Volatile release profile of American lignite

Figure 8 shows the volatile release profile for a lignite, where it can be seen that the main devolatilisation response occurs at the slightly lower temperature of 445°C. There is an interesting small, but very sharp, peak at 545°C and a further broader response at 740°C. The former is so well-defined that it is tempting to conjecture that it might represent the pyrolysis of a specific chemical species present in this particular coal.

In general, the volatile release profiles are much more specific to individual coals than the burning profiles, with more fine structure in the form of minor peaks, and as such could act as valuable "fingerprints" for identifying and comparing unknown or disputed samples.

CONCLUSIONS

It has been shown that the techniques of thermogravimetry and derivative thermogravimetry can be usefully applied to the study of coals. The use of thermogravimetry for rapid proximate analysis has been investigated in some depth and the results, while not as yet complying in every case with the reproducibility requirements of BS1016, (1973) Part 3, are very promising and are probably adequate for most work where the highest degree of accuracy is not required.

The burning profile test for solid fuels has been established on a routine and reproducible basis within the authors' organisation and while the curves obtained differ from those of other workers using different equipment, they are highly self-consistent and can yield valuable data on the combustion behaviour of these fuels when backed up by known plant experience.

The volatile release profile test has been established and a limited amount of work done in comparing the behaviour of various coals. It is suggested that this test might find application in the fields of coking and gasification, rather than in combustion and it could be the basis of a system fingerprinting coals.

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