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A DTG COMBUSTION STUDY ON ANTHRACITIC AND OTHER COAL CHARS *

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ABSTRACT

The DTG burning profile test has been applied to chars prepared from anthracites and other coals of lower rank. Charring temperatures ranged from 600 to 1200 °C and the comparative combustion reactivities of the resulting materials were studied. It was found that increasing the charring temperature gives rise to chars of progressively decreasing reactivity, within the temperature range studied, and that certain anthracitic coals show a pronounced DTG "peak-splitting" effect at charring temperatures of 800 °C and above. The formation of a new higher temperature DTG peak indicates a transformation of the carbonaceous material to a less reactive form, and it is suggested that this is graphite, with supporting evidence from X-ray diffraction studies. Demineralising the coal prior to devolatilising reduces this transformation in some cases, but not in others.

The formation of unreactive graphite during devolatilisation could have important implications in the industrial utilisation of anthracitic and low volatile coals.

INTRODUCTION

In recent years the application of thermogravimetry (TG) and derivative thermogravimetry (DTG) to the study of solid fuels has gained a wide acceptance amongst researchers in the field of energy conversion, Earnest, Fyans, Ghetti and others have described the use of TG for automated proximate analysis [1–6], while other workers have employed simultaneous TG/DTG for studies of combustion reactivity by way of the burning profile test [7–9] and derivations of instrumental or "apparent" activation energies [10,11]. In the latter context, a measure of fuel reactivity is important in the utility boiler industry to allow optimisation of the furnace design; oversizing is uneconomic, while undersizing leads to quenching of char particles and subsequent unburned carbon loss.

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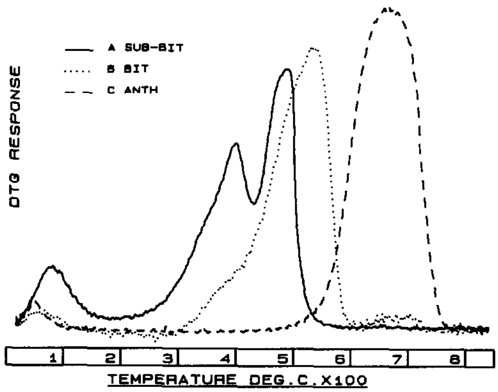

Fig. 1. Burning profiles: various coal ranks.

In the course of investigations into the reactivity of coal chars, the author has applied a modified version of the burning profile test as described by Duzy, Wagoner and Winegartner [8,9] to materials prepared by devolatilising a variety of coals under various conditions. Details of the test procedure can be found elsewhere [4,5], and it is sufficient to note at this point that the burning profile of a fuel is obtained by plotting the DTG response of a small aliquot against the crucible temperature while heating linearly and sweeping the furnace with a stream of air. The higher the "peak temperature", or temperature of the maximum on the DTG curve (PT), the less reactive is the fuel, and vice versa. The PT value is apparatus and conditions dependent, but it is very reproducible under constant experimental conditions, and can be used to assess an unknown coal against a data bank of samples of established plant performance.

To illustrate the use of the test, Fig. 1 shows the superimposed burning profile curves for three coals of differing rank; A, a sub-bituminous coal; B, a bituminous coal; and C, an anthracite. Note that in curve A, the high volatile content and the ease with which the coal decomposes result in the formation of a preliminary peak at around 400 ° C, followed by a fall-back in the DTG response before the major burning peak occurs, with its maximum at 480 ° C. This "double peak" response is often seen in low rank coal samples, and invariably in samples of peat, wood and other minimally transformed vegetable materials. It has been noted by Wagoner and Duzy [8] who refer to it as "false ignition".

Curve B, for the bituminous sample, does not display a double response, but from 300 to 420 ° C there is a gradually increasing DTG response due to the release of volatiles, which in this case are less easily released from the coal matrix, and of course, less plentiful. Beyond this point, a sharp upward inflexion is seen due to true ignition of the partially devolatilised material remaining in the crucible. This low-temperature "shoulder" is typical of

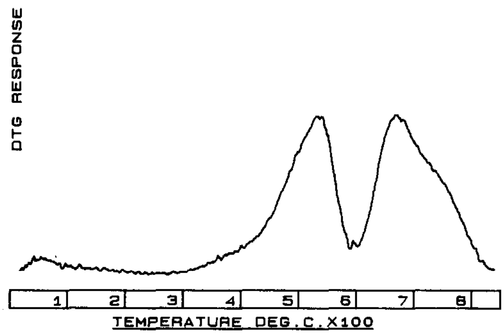

Fig. 2. Burning profile: bituminous/anthracite mixture.

bituminous coals, its size and temperature range depending on the rank and nature of the coal.

The anthracite (curve C) gives an almost symmetrical peak, with no indication of a preliminary volatile response. The temperature of onset (known as initiation temperature, IT) is around 450 °C (cf. 250 for the sub-bituminous and 300 °C for the bituminous samples), while the peak temperature (PT) is at 630 °C (c.f. 485 and 530 °C respectively).

It has been found that when the burning profile test is carried out on a mixture of two fuels of different burning response, e.g. a bituminous coal and an anthracite, two quite distinct peaks are obtained. Figure 2 shows the result of such a test; the two materials burn independently with no indication that the first-burning component ignites the second, giving rise to a premature ignition of the anthracite. This is of significance in the later part of this paper, where this effect will be used to infer the formation of a second, less reactive form of carbon on charring certain anthracitic coals.

EXPERIMENTAL

The apparatus employed in this work was a Stanton–Redcroft series STA-781 simultaneous thermal analyser, used in its TG/DTG (single crucible) configuration. The conditions established for the burning profile test were: heating rate, 15 K min^{-1}, air flow, 70 cm^3 min^{-1}, and sample weight, 20 ± 0.05 mg.

Samples were ground to pass a 212 micron sieve and equilibrated to ambient relative humidity at the time of the test. Data from the three output channels, sample temperature, sample weight and derivative weight, were digitized by a Stanton–Redcroft "DAU" data acquisition unit and processed by a Commodore 8032 microcomputer. During test runs, TG and DTG curves were plotted in real time via the computer and a Hewlett–Packard 7475A digital plotter, and the data were stored on disk files for subsequent retrieval and processing.

TABLE 1

Coals—proximate analyses (as analysed)

Content	Type and source of coal					
	A Sub-bituminous U.S.A.	B Bituminous S. Africa	C Anthracite Scotland	D Anthracite Scotland	E Anthracite Wales	F Low-vol. Wales
Moisture (%)	10.5	3.8	1.9	4.2	1.5	1.6
Volatiles (%)	37.5	24.5	5.6	1.4	9.1	9.7
Fixed carbon (%)	41.5	47.6	87.2	91.4	81.9	62.4
Ash (%)	10.5	24.1	5.3	3.0	7.5	26.3

Char samples were prepared by heating 2 g aliquots of the −212 micron coals, in silica "volatile" crucibles with closely fitting lids, in an electrically heated muffle furnace. Exposure times were normally 15 min, and the charring temperatures ranged from 600 to 1200 °C. Coal samples were drawn from the Babcock Energy Coal Library, held at their Research Centre in Renfrew, Scotland.

Proximate analyses of the coals referred to in this paper are given in Table 1.

RESULTS AND DISCUSSION

Effect of charring temperature

The three fuels whose profiles are given in Fig. 1 were charred at 700 °C for 15 min, and the resulting materials subjected to the test. The peaks obtained were much more symmetrical than those of the parent coals due to the lack of volatile response, and the order of PT values followed that of the original coals in Fig. 1. The PT values for coals A, B and C, and for their 700 °C chars are given in Table 2.

For the sub-bituminous and anthracite samples, there was little difference in peak temperature between the coal and the char, but there was a very significant increase in the case of the bituminous coal. In general, it has been found that for increasing values of charring temperature, there is a systematic upward trend of the PT values of the chars produced, although the effect is not always discernable for 700 °C chars.

Figure 3 shows superimposed burning profiles for a series of chars prepared from a single bituminous coal in 100 K steps from 600 to 1200 °C. For the 600, 700, 800 and 900 °C charring temperatures, there is a very marked upward trend in PT, but beyond 1000 °C the curves are very similar, with PT values all around 635 °C; the upward trend in char PT has ceased.

TABLE 2

PT values for coals and 700 ° C chars

PT	Type of coal		
	A Sub-bituminous	B Bituminous	C Anthracite
Coal (° C)	485 [a]	530	630
Char (° C)	480	573	635

[a] Main burning peak.

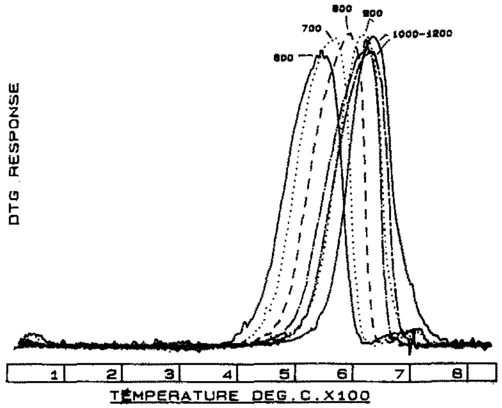

Fig. 3. Bituminous coal chars prepared at 600–1200 ° C.

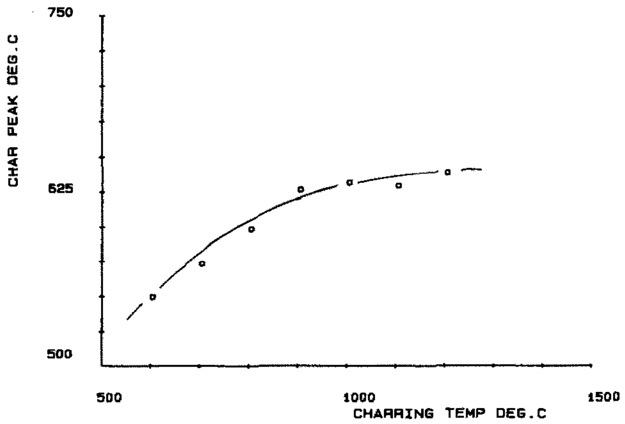

Fig. 4. Char peak temperature vs. charring temperature (bituminous coal).

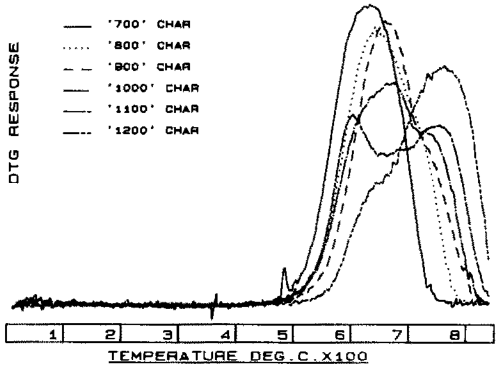

Fig. 5. Anthracite chars prepared at 700–1200 ° C.

This is shown graphically in Fig. 4, where the "levelling-off" effect is clearly seen at around 635 ° C.

The same effect is shown by the anthracite (Fig. 5), charred at 100 K steps from 700 to 1200 ° C, but with a very significant difference. As charring temperature increases, the DTG peak broadens, showing a tendency to split into two components. This effect has been observed in many anthracitic samples, but not in coals of lower rank. Figure 6 presents curves for three further anthracitic coal chars, D, E and F, all prepared at 1100 ° C, which display the same type of peak-splitting effect. All of these samples gave simple symmetrical peaks both for the parent coals and the 700 ° C chars. It is noteworthy that for anthracitic chars, prepared at 800 ° C and above, the up-scale movement of the first peak component ceases, and the overall response is broadened by virtue of the formation of a second component (see Fig. 5). As charring temperature is increased, the upper peak grows at the expense of the lower.

Clearly, a new component is being formed at the higher charring temperatures in the case of anthracitic precursors and the most likely candidate is considered to be graphite. Figure 7 shows the burning profile of a mineral

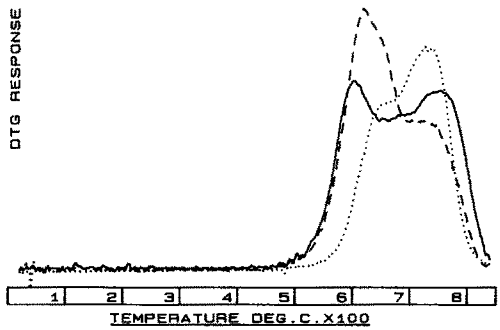

Fig. 6. Anthracite chars prepared at 1100 ° C.

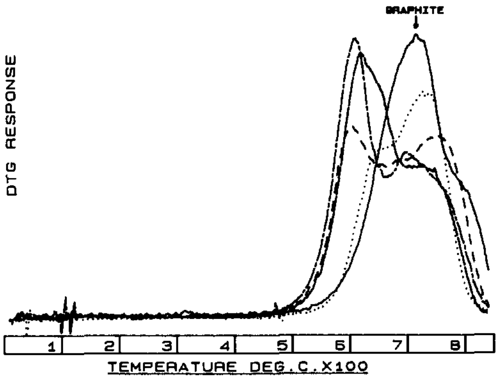

Fig. 7. Graphite + anthracite chars prepared at 1100 ° C.

graphite superimposed on those of the 1100 ° C chars from anthracites C, D, E and F. Graphitization of "amorphous" carbon under the influence of heat is a well-known phenomenon, but it is perhaps surprising to see it occurring at temperatures as low as 800 ° C.

Limited X-ray diffraction studies have indeed shown the presence of a peak corresponding to the 3.35 Å lattice spacing of graphite in both the 700 and 1200 ° C chars prepared from anthracite C. The magnitude of the response was greater for the 1200 than for the 700 sample, in agreement with the DTG results. The X-ray evidence was less conclusive in other samples due to interferences from minerals.

That graphitisation can indeed occur at these relatively low temperatures is confirmed by Oya et al. [12] who attribute it to catalysis by mineral species held within the coal matrix. While this is undoubtedly true, the author has found that some demineralised anthracites still show the DTG peak-splitting effect.

Effect of demineralizing

To study the catalysis effect by minerals on this putative graphitisation, two of the anthracites which showed a marked peak-splitting effect on charring at 1100 ° C (samples C and F) were subjected to a demineralising process before charring. This has been described by Mahajan and Walker [13], and involves a vigorous extraction of the powdered coal with hydrochloric and hydrofluoric acids. The ash contents were measured after this treatment and found to be of the order 0.1%.

These demineralised samples were then charred in the normal way at 1100 ° C and subjected to the burning profile test. Figure 8 shows the curve for the demineralised sample C superimposed on that for the normal 1100 ° C char. It can be seen that there is very little difference between the two curves, either in terms of relative heights of the two peaks or the

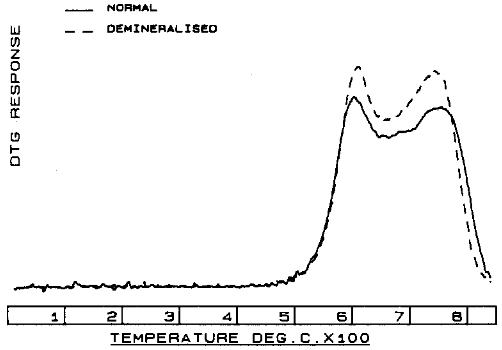

Fig. 8. Anthracite C: normal and demineralised chars.

temperatures of their maxima. The absolute height of the demineralised sample curve is slightly greater than that of the normal curve, as would be expected since there is more combustible material in the former sample. (The area enclosed by a DTG curve represents the total mass loss). Thus the presence of minerals has had a negligible effect in promoting the peak-splitting effect in this case.

Figure 9, on the other hand, presents similar data for sample F. In this instance the normal and demineralised curves are quite different. The normal curve shows the major proportion of the char to be in the new or graphitised condition, while the demineralised curve indicates a much lower degree of conversion. Thus for this sample, catalysis by minerals appears to play an important part in promoting the graphitisation. It would appear from the above that certain anthracitic coals are highly predisposed to graphitisation at these relatively low temperatures, even without the mediation of catalysis by minerals, while for others, the latter effect plays a major role. This can probably be explained by the degree of aromaticity existing in the precursor coal matrix; those with highly ordered aromatic structures will convert more readily than others where there is less ordering.

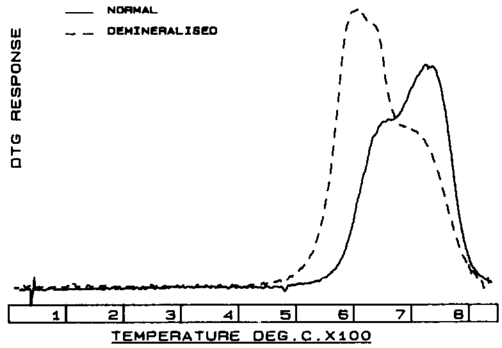

Fig. 9. Anthracite F: normal and demineralised chars.

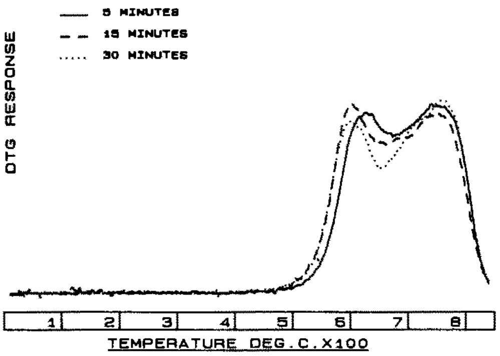

Fig. 10. Anthracite C charred for various times.

Effect of charring time

Having established with reasonable certainty that graphitisation can occur under the conditions described, the next objective was to study its time dependence. If an anthracitic coal were held at a given temperature for a prolonged time, would the char convert to graphite progressively? To this end, two samples were held at a charring temperature of 1100 °C for periods of 5, 15 and 30 min, and Fig. 10 shows the burning profile curves for the three chars thus produced from sample C. Figure 11 similarly shows the curves for the three chars produced from anthracite F.

In Fig. 10, there is very little difference between the curves, while in Fig. 11, there is a noticeable difference between the 5 and 15 min curves, but little between the 15 and 30. It would therefore appear that the major part of the graphitisation takes place over the first 5 min or so and stops thereafter. It might be suggested that the effect occurs during the period of volatile release only, rather than being a progressive conversion of the "amorphous" carbon to graphite.

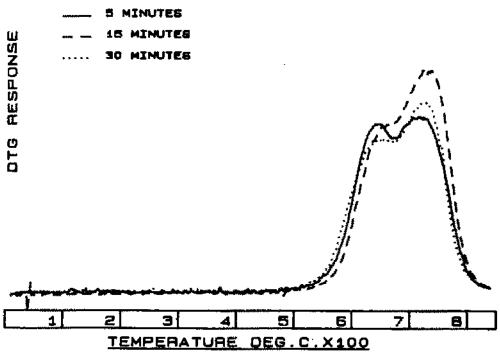

Fig. 11. Anthracite F charred for various times.

CONCLUSIONS

Three main conclusions can be drawn. The first is perhaps self-evident and has been reported by others, but is neatly confirmed by the DTG method. This is that the reactivity of chars prepared at a constant temperature follows the reactivity order of their parent coals.

Secondly, and perhaps this is less expected, increasing the charring temperature for a given coal produces chars of decreasing reactivity, at least up to 1200 °C. The opposite might have been expected since it could be postulated that the higher temperatures would promote a more vigorous volatile release and therefore a more 'open' char structure.

Finally, within the anthracitic range of coals, there is strong evidence of graphitisation in chars prepared at temperatures as low as 800 °C. This is mediated at least in part by the catalytic action of minerals but in some fuels which are highly predisposed to graphite formation (due perhaps to a highly ordered aromatic structure) the transformation can take place in the absence of catalysis. It would appear that the graphitisation process takes place rapidly over the first 5 min or so, and then halts; further exposure time does not increase the degree of conversion. Increasing the charring temperature is necessary to increase the conversion.

What then of the practical implications? Anthracitic coals are used as power station fuels in many parts of the world, and are well-known for giving rise to problems with their combustion. Furnaces must be specially designed to maintain high temperatures and to give long residence times. This is due in part to their low volatile content, but is also attributable to the low reactivity of the chars. If a particular fuel is also one which is predisposed to graphitisation in the manner described, then the char will be particularly unreactive, and special attention will have to be given to the design of any furnace for its utilisation.

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