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THE ASSESSMENT OF THE COAL-ORGANIC MATTER CONTENTS OF GEOLOGICAL MATERIALS BY DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

The application of DTA to organic-rich materials such as coal and oil shales, using the technique of controlled atmosphere DTA, in conditions of readily available oxygen, provides a method of organic matter content assessment. The method is also applicable to a range of other solid materials where the detection of low contents of organic matter are of potential economic value, such as coal washery reject products and conditioner fines, low-grade hydrocarbon-containing sedimentary fuels, and the residual carbon contents of derived products such as oil shale retort residues and fly ash. The method is capable of detecting organic matter or residual carbon contents down to at least 0.25 to 0.5 weight percent, with detection of low contents being enhanced by determinations in flowing oxygen gas.

INTRODUCTION

The differential thermal analysis (DTA) of coal has been the subject of a considerable number of investigations which have been directed at specific aspects such as rank [1], carbonisation [2] and the identification and content assessment of the mineral components present [3]. For these aspects the strongly exothermic effects of the combustion (oxidation) of the organic matter present was a major consideration. However, exothermic fluctuations due to variations in the availability of oxygen led to the production of non-reproducible but masking peaks on the resultant DTA curves.

The technique of controlled inert atmosphere DTA was therefore applied in order to suppress the masking exothermic burning effects so that other smaller peaks, previously obscured by this peak superposition, could be recorded and evaluated. Furthermore, predictable diagnostic peak movements could be achieved dependent upon the type of flowing purge gas used [4].

It now appears clear that the converse is also of considerable value, e.g., that the encouragement of the vigorous combustion reaction of the organic components present provides a suitable method for the evaluation of its

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content in coal, oil shales and their reject, waste or utilisation end products. Furthermore, it would appear that this method is applicable to other geological materials and their derivatives which contain various amounts of organic materials.

EXPERIMENTAL

The DTA curves figured in this study were obtained using a sub-bituminous coal and equipment and experimental conditions as described previously [3] with a constant heating rate of 15° min^{-1}.

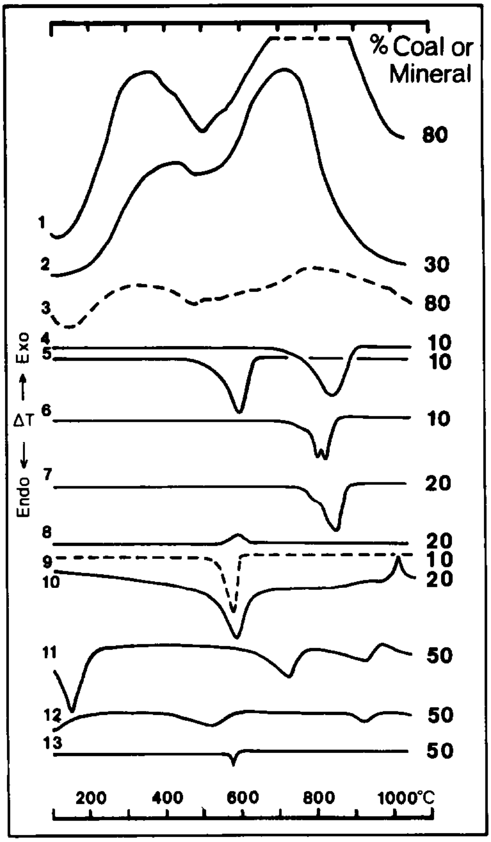

Fig. 1. Individual DTA curves obtained from mixtures of low-ash sub-bituminous coal or minerals commonly found in coal, diluted with calcined Al$_2$O$_3$ as follows: curves (1)–(3) 80, 30 and 80% coal, respectively, (4) 10% calcite, (5) 10% magnesite, (6) 10% dolomite, (7) 20% ankerite, (8), (9) 20 and 10% siderite, respectively, (10) 20% kaolinite, (11) 50% montmorillonite, (12) 50% illite, (13) 50% quartz. (------) Determined in flowing N$_2$, (———) determined in static air.

RESULTS

The combustion of organic matter causes strong exothermic reactions. For coal and oil shale these occur within the broad temperature range 250–900°C on DTA curves determined in air [5,6]. These curves show a large, broad, somewhat poorly delineated exothermic feature which is typically composed of two broad exothermic maxima (Fig. 1, curves 1 and 2). These two wide "humps" represent the combustion/oxidation of the volatile hydrocarbons released during heating followed by the more vigorous burning of the remaining fixed carbon content, a reaction which overlaps and follows at a higher temperature (Fig. 1, curves 1 and 2, and Fig. 2).

The application and value of this method depends on its ability to detect, compare and evaluate various organic matter contents and to do this for the full range of contents down to as low a level as possible.

With this in mind a sub-bituminous rank coal was progressively diluted with inert calcined alumina to produce samples for DTA with coal contents from 40 to 1% by weight (Fig. 2). Coal contents of above 40% gave such vigorous reactions that material was lost from the sample holder and the recorder was mainly off scale. Thus, coal samples would need to be diluted

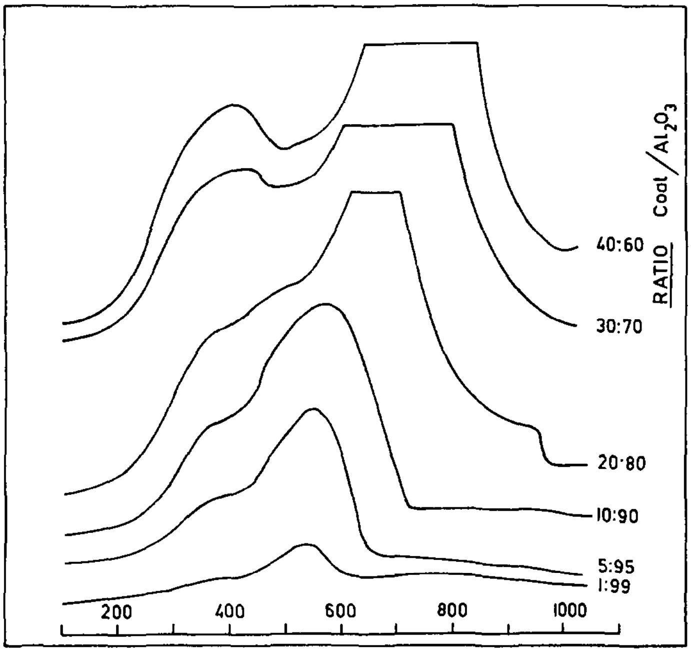

Fig. 2. DTA curves of the same coal as Fig. 1 diluted with various proportions of calcined Al_2O_3, determined in static air. Indicates large exothermic effects due to organic matter content. These diminish in size rapidly with falling coal content and establish detection limits of better than 0.25% for the coal (organic matter) content.

to contents within the range figured in order to obtain assessable, on-scale DTA curves.

The resultant DTA curves, determined in static air with the above equipment and shown in Fig. 2, indicate:

(1) as the coal content falls the exothermic peaks progressively decrease in size and the two-peak configuration gradually tends to coalesce to form a single composite peak;

(2) the detection limits of coal organic matter are in the order of 0.25%.

DISCUSSION

Some variations in peak configurations and temperatures are likely to be dependent upon the type and rank of material under test, and the residual or fixed carbon contents remaining after other processes (e.g., in oil shale retort "spent shale" and power station ash).

The large and rapidly developed exothermic effects figured appear to be very satisfactorily developed under furnace atmosphere conditions of freely available static air. However, where the access of air is restricted, determinations in flowing air may be required, while the detection and assessment of low contents are further assisted by the use of flowing oxygen.

The proposed uses of low-grade solid carbonaceous fuels may well utilise some form of crushing on beneficiation. Here again, assessment sets of DTA curves, due to the combustion of the fuel components at different size or preparation grades, is only a matter of sample preparation.

It is clear that large contents of mineral matter will be present in the materials under discussion. During DTA almost all of the constituent minerals will decompose, mainly with endothermic effects in the temperature range in which the combustion effects take place (Fig. 1). These minerals will be present in the fuel anyway and their decomposition effects will, to some extent, negate the heat produced by burning of the organic content. However, it is the excess exothermic resultant, recorded on the DTA curve, which provides a new method for the evaluation of materials as low-quality heat-source fuels.

Once the initial assessment has been made by this DTA method further quantification by the use of thermogravimetry (TG) would appear attractive as it has already been routinely applied to the proximate analysis of coal [7,8]. However, it must be pointed out that most of the minerals present in significant quantities in the low-quality fuel materials in question decompose in the organic matter combustion temperature range (Fig. 1). Thus, the weight losses associated with these decompositions would need to be taken into account for this complementary or simultaneously applied method [9] to be of value.

CONCLUSIONS

The technique of DTA in an atmosphere of air offers a quick, relatively inexpensive method for the evaluation of the fuel potential of low-quality, high-mineral matter content, solid hydrocarbon-bearing materials.

The resultant large exothermic DTA peaks produced by the combustion of the hydrocarbon/residual carbon contents change markedly in size in response to varying combustible component contents which may be detected down to levels of at least 0.25%.

As low-grade fuels are, or could be, available in large quantities from natural deposits or waste products such as carbonaceous shales, oil shales, coal cleaning/washery refuse products and oil shale retorting spent shale residues, a rapid method of their general assessment as heat sources is needed. Such materials are now becoming economically exploitable due to their availability in large quantities, either as by-products whose production costs have already been met for other purposes and would therefore be available on the spot at no cost, e.g., coal washery refuse or spent shale residues, or are now becoming economically viable due to the very high cost of competing traditional fuel sources.

Conversely, the excellent detection limits of this method make it equally applicable to materials, which contain small amounts of hydrocarbon or carbonaceous matter, such as residual carbon in power station ash, inclusions detrimental to the use of other rock and mineral materials, in fillers and for quality control.

The term "combustion curves" [10] has been used to distinguish such DTA curves from the related DTG method, the curves from which are known as "burning profiles". These terms serve to clearly identify the two methods.

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