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CHARACTERISATION OF CHARCOALS BY THERMAL METHODS

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ABSTRACT

A number of thermal analysis tests are being developed for the characterisation of charcoals. A TG method has been found to be useful for a rapid compositional analysis whilst DTA and related methods have been used to investigate reactivity towards air.

INTRODUCTION

Charcoal, produced by the partial pyrolysis of wood in an inert atmosphere is a complex material of which the physical and chemical characteristics may vary widely. The properties may vary with the type of wood used, the part of the tree from which the wood is cut, as well as the pyrolysis regime to which the wood is subjected. The aim of the present work is to develop a range of tests for the characterisation of composition and reactivity of charcoals for use in gunpowder.

COMPOSITIONAL ANALYSIS BY THERMOGRAVIMETRY

A rapid method for compositional analysis of a type similar to that used for carbon black in rubbers (1) has been developed, using a thermobalance (Stanton Redcroft TG 761), which determines moisture, volatiles, fixed carbon and ash contents. The method is applicable to powdered samples or solid pieces of charcoal.

The moisture content is determined by heating a 5mg sample under nitrogen flowing at 25 cm^3 min^{-1} to 110°C, and holding isothermally for 5 minutes. The weight record is then expanded to 100% so that the other parameters can be read directly from the chart as percentages of the dry weight. The volatile content is determined by heating at 20°C min^{-1} to 750°C and holding at this temperature for 3 minutes. The weight loss during this stage is due to the evolution of adsorbed volatile matter and further pyrolysis of oxyhydrocarbon functional groups attached to the biopolymer skeleton. A true weight plateau rarely develops at this stage, due partly to the protracted nature of the decomposition,

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and partly to oxidation of the highly reactive carbon remaining by the trace impurities in the purge gas. Although this could be overcome by using purified purge gas and longer isothermal times, the purpose of the test was to provide a rapid assessment of the composition, therefore the volatile content is empirically defined as the weight loss after the 3 minute hold. After cooling to 200°C the purge gas is switched to air, and the sample heated at 50°C min^{-1} to 900°C, when the carbon burns off leaving a weight corresponding to the ash content.

A schematic diagram of a TG curve generated by this procedure is shown in Fig. 1. The sharp weight gain observed on the admission of air is taken to be adsorption of oxygen prior to the initiation of burning.

An illustration of the reproducibility of the method, and the range of charcoal types encountered is given by Table 1.

TABLE 1

Compositional analysis of various alder charcoals

Charcoal	% moisture	Dry weight basis		
		% volatiles	% fixed carbon	% ash
1	4.0 ± 0.1	76.4 ± 0.2	22.1 ± 0.3	1.5 ± 0.3
2	3.3 ± 0.1	56.2 ± 0.1	42.6 ± 0.5	1.3 ± 0.4
3	4.2 ± 0.1	37.6 ± 0.4	60.4 ± 0.6	2.0 ± 0.3
4	4.6 ± 0.0	26.9 ± 0.1	69.1 ± 0.1	4.1 ± 0.1

Due to the small sample size required the TG method has enabled a study of the variation in composition through a single stick of charcoal to be carried out. Dissection of an ovoid-section stick about 5cm in diameter yielded 10 cubes of charcoal each weighing about 5mg which had been taken across the diameter of a thin slice from the stick. The values obtained for the volatiles, fixed carbon and moisture contents are plotted as a function of distance from the edge in Fig. 2 and show the marked variation that can be observed even with such a small stick. The lower volatile content at the centre of the wood can be explained by the fact that the secondary stage of wood pyrolysis (the pyrolysis of released tars) is exothermic (2). In the centre of the wood, a material of low thermal conductivity, the temperature is considerably higher than at the edges, resulting in a greater degree of pyrolysis.

The trend with respect to moisture content is remarkably smooth. As all the samples had been stored under similar conditions of temperature and humidity, this trend is held to reflect the adsorptive capacity of the charcoal, and is clearly related to the degree of pyrolysis.

LOW TEMPERATURE OXIDATION STUDIES

Preliminary DTA work in air had suggested that oxidation of these charcoals began in the region of 100°C, overlapping the endothermic effect due to moisture

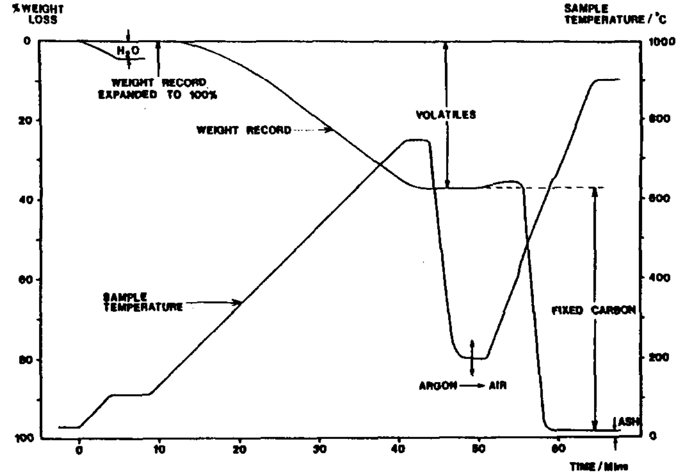

FIG.1 SCHEMATIC DIAGRAM OF THE TG ANALYSIS CURVE FOR A CHARCOAL

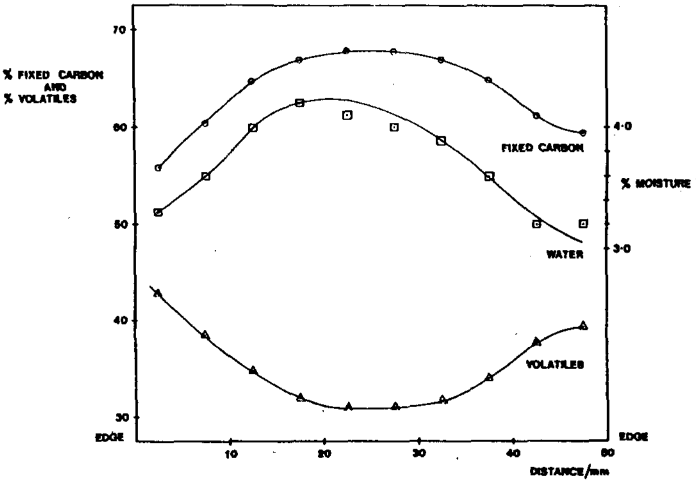

FIG.2 DIAMETRICAL VARIATION OF PROPERTIES THROUGH A CHARCOAL STICK

evolution. A DTA method has been developed to characterise this low temperature reactivity of charcoals. In order to clearly define the oxidation exotherm, the charcoals must first be dried under nitrogen in the instrument (Stanton Redcroft DTA-671B) before cooling, changing the atmosphere to flowing air, and reheating. A thorough study of the effects of experimental variables upon the oxidation was undertaken so that slight variation in the chosen conditions would result in minimal variation in the measured parameters. The conditions finally chosen were a sample weight of 5.0 ± 0.1mg, heating rate of 10°C min^{-1}, air flow rate of 50 cm^3 min^{-1} and DTA sensitivity of 500µV full scale. The sample pan was lightly tapped and drying conditions for the sample were standardised at 5 mins at 120°C in flowing nitrogen. Using these conditions the DTA curve is recorded past the first exotherm which is due largely to oxidation of the released volatiles. A schematic representation of the curve is given in Fig. 3 which shows the measured parameters T_o, T_5, T_{10}, T_{50}, which are the temperatures at which the deviation from the baseline is first detectable and the temperatures of 5, 10 and 50µV deviation from the baseline respectively. The extrapolated onset temperature, T_e and T_p, the peak maximum temperature were also measured. Preliminary work showed that of these T_5 and T_{10} appear to be the most useful in characterising the variation in susceptibility to oxidation at low temperature. Calculations showed that a correction for the temperature dependence of the calibration constant of the DTA unit was unnecessary within the range of values obtained.

The usefulness of this method in detecting subtle changes in the charcoals has been illustrated in a study of the effects of oxidation during air drying of a particular charcoal. Samples of the charcoal were heated in an oven at the stated temperatures for the stated times, and run under the standard conditions on the DTA-671B; the results are given in Table 2.

TABLE 2

The effect of drying a charcoal in air

Oven Temperatures	Drying Period Hours	DTA Characteristics/°C	
		T_5	T_{10}
120	0	135 ± 1	150 ± 1
	1	146 ± 1	162 ± 0.5
	24	164	182
	168	204	215
80	24	138 ± 1	153.5 ± 0.5
	168	145 ± 0	162.5 ± 0.5

Other tests

A number of other tests have been briefly examined for application to charcoal testing. The reactivity of charcoal towards air at high temperatures has been studied using a DTA head originally designed for determination of the

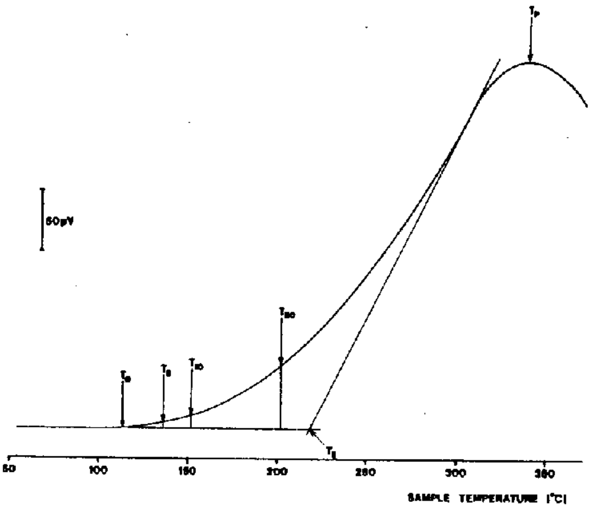

FIG.3 DIAGRAM OF THE DTA CURVE FOR THE OXIDATION OF A CHARCOAL

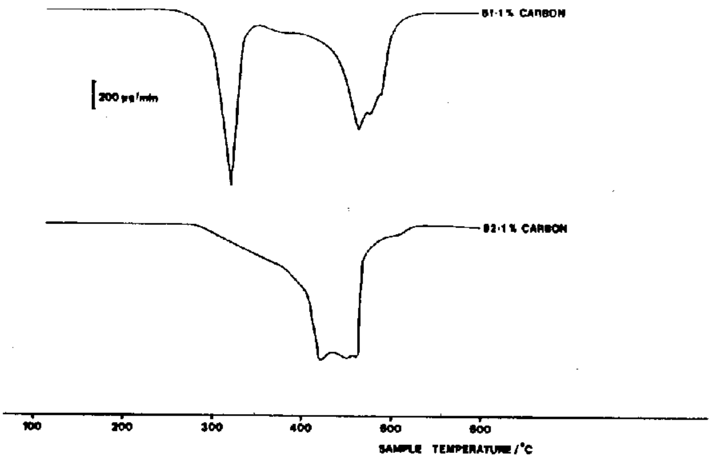

FIG.4 DTG CURVES FOR ALDER CHARCOALS HEATED IN AIR

ignition temperature of coals.

The head consists of two fine gauze pans 15mm in diameter, supported one above the other by mineral insulated chromel-alumel thermocouples. Air at a flow rate of 500 cm^3 min^{-1} is passed over the sample which is contained in the upper pan. The head fits a standard DTA base (Stanton Redcroft DTA 673).

100mg of sieved charcoal samples are heated at 20°C min^{-1}. The ignition temperature of the charcoal is taken from the extrapolated onset of the deviation on the sample temperature trace, caused by combustion of the sample. Results for a range of Alder charcoals are given in Table 3.

TABLE 3

Ignition Temperatures for Alder Charcoals

Carbon Content (%)	Ignition Temperature (°C)
61	245 ± 2
76	218 ± 1
82	212 ± 1
96	447 ± 1

The results show that the ignition temperature decreases with increasing carbon content until at a very high carbon content there is a large increase in the ignition temperature. This tends to indicate that ignition occurs during oxidation of the volatiles until there are insufficient volatiles to cause ignition when the sample ignites at the carbon oxidation stage.

Simultaneous TG-DTG-DTA studies are also being undertaken to characterise the oxidative behaviour of charcoal. Results to date have indicated a marked dependence on experimental parameters particularly packing, but Fig. 4 illustrates that the DTG curves differ markedly for charcoals of differing carbon contents.

DTG curves have also been recorded for the volatile loss under pyrolysis conditions. This technique has been used previously to distinguish between similar coals (3) but although differences are easily detectable between charcoals of different carbon content it may be difficult to differentiate between charcoals with similar carbon contents.

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