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DIFFERENTIAL THERMAL ANALYSIS OF LOW-RANK COALS

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Abstract

Differential thermal analysis (DTA) of low-rank coals of high lignite to subbituminous rank from coal mines of Pakistan is reported. The studies carried out in dynamic oxygen atmosphere indicate that the exothermic reactions occur between 300 and 650°C and that the samples undergo stepwise oxidation of the organic matter rather than a continuous process as indicated by the pattern of shoulders from 250 to 350°C accompanying the main peak around 450°C. The effect of heating rate, particle size and volatile content was also studied in relation to oxidation. The results show that the increase in heating rate from 10 to 80 deg·min^{-1} results in a marked shift in all the events in the DTA curve towards higher temperatures. As for the effect of particle size, the DTA records of 100–75, 150–100, 250–150 μm and greater than 250 μm fractions show that the magnitude and position of shoulder peaks are more sensitive to changes in particle sizes compared to the main peak. The curves recorded to study the effect of changing volatile content of samples between 30–40% indicate a complex pattern of shoulders accompanying the main peak. In general, the number of shoulder peaks increases with increasing volatile content of samples but their positions do not follow any trend. The DTA curves recorded in nitrogen contain ill-defined exothermic effects over the 300–750°C temperature range. These curves consist of an endothermic peak around 150°C, two exothermic shoulders in the temperature region 300–400°C and a large broad exothermic whip between 500 and 700°C. The heating rates have similar effects as in oxygen while the particle size do not influence the results.

It has been concluded that the organic matter in the coals studied here is extremely heterogeneous with different burning characteristics; as a result it is very difficult to quantify energy changes associated with poorly resolved exothermic events along the DTA curve. The effects also dominate in N_2 atmosphere thus making identification of mineral matter difficult. The overall pattern of DTA events in oxygen can be correlated with the heating rate, particle size and volatile content of samples.

Keywords: low rank coals

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Introduction

Thermoanalytical techniques such as TG, DTG, DTA, DSC, EGA and TMA cover a wide range of applications in research, development and economic assessment of fossil fuels. Thus for DTA/DSC alone a list of 26 areas of application has recently been published [1]. The main studies of coal using DTA include characterization, high pressure application to coal hydrogenation, catalytic effects due to inorganic substances, mineralogy, and quantitative aspects such as determination of heats of reaction, coal organic and mineral matter assessment [2–8]. However, most of these studies have been directed to high rank coals with less attention given to peat, lignites and subbituminous coals. Current interest in utilization of lower rank coals for electricity generation has attached greater importance to their detailed investigations, such as rank, nature and composition of organic and mineral matter and magnitude of exothermic and endothermic reactions involved. DTA is an appropriate technique as its record of energy charges resulting from heating, can be interpreted to get the required information. In the present investigations on coals of high lignite to subbituminous rank [9] derived from the Lakhra coal field of Pakistan, the use of DTA is aimed at studying the effects of heating rate, particle size and of the atmosphere surrounding the sample. In addition to this, the dependence of peak configuration, initiation temperature of burning and maximum temperature of the main peak on the volatile content of samples is also studied.

Experimental

The coal samples used in this study were obtained from different sites of Lakhra Coal mines, the largest coal field of Pakistan. Typically 4 kg samples of coal were collected while mining. It was immediately packed in air tight polyethylene bags. 1 kg aliquot of this sample was homogenized, and sieved to get particles of the required size ranges. Before sieving, the powdered samples were analysed for moisture, volatile matter and fixed carbon using a LECO-MAC 400 proximate analyser. The samples contained moisture in the range 6–20%, whereas on dry basis the percentages of volatile matter, fixed carbon and ash ranged as 32–42, 24–36 and 25–35% respectively. The percentage of sulphur determined using a LECO-SC-132 sulphur analyser ranged between 6 to 10%. The DTA experiments were carried out on a Perkin-Elmer TGS-2 instrument system, equipped with DTA 1700 and data processor 3600. The upper limit of the temperature of the furnace of this instrument is 900°C, therefore all DTA runs were carried out from 30 to 900°C. Generally 10 mg sample of coal was loaded in the aluminum sample pan with Al_2O_3 as reference. The sample was held at 50°C for five minutes in flowing nitrogen to drive off adsorbed moisture. The furnace was again cooled to 30°C and weights corrected. Care was taken to avoid abrupt burning of samples. High purity oxygen and nitrogen gases were allowed to flow at 100 ml/min around the sample to provide the required atmosphere.

Results and discussion

The representative DTA curves in oxygen and nitrogen atmospheres are shown in Fig. 1 and Fig. 5 respectively. The curves in oxygen are characterised by two temperature regions. The first one is 80–180°C where the broad endothermic trough results from loss of moisture. It was necessary to expel adsorbed moisture by maintaining the sample in the cell at 50°C for five minutes, which otherwise caused increased deviation from the base line at the start of experiments. The second region is 250–650°C where exothermic effects due to combustion are recorded. Similar exothermic effects in this region have been reported using DTA/DSC for lignites and subbituminous coals of Australia, Japan and USA [10–12], where curves having one to three configuration resulted. According to Dugan *et al.* [13] these peaks are caused by internal burning/oxi-

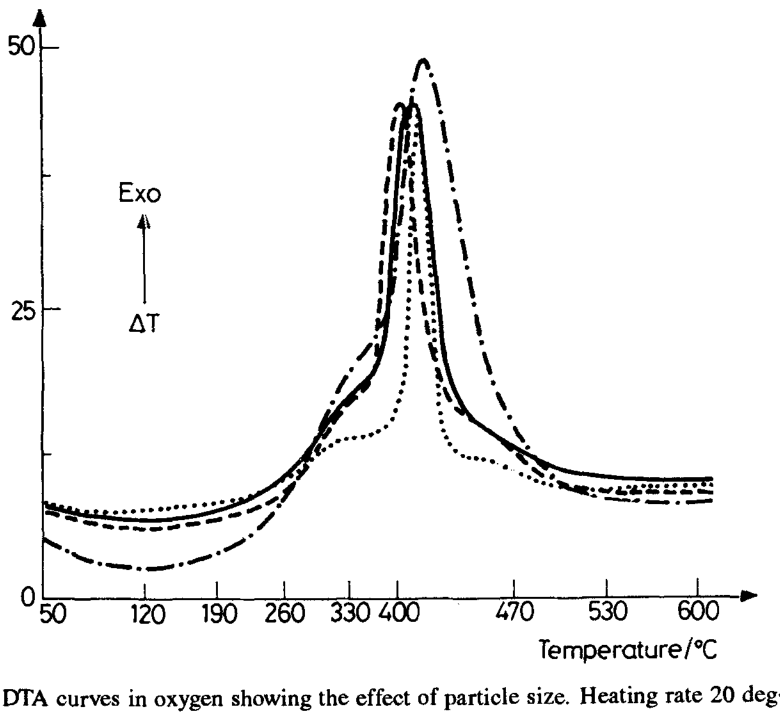

Fig. 1 DTA curves in oxygen showing the effect of particle size. Heating rate 20 deg·min^{-1}. ····· 100–75 μm, – – – 150–100 μm, –·–·–150–250 μm, —— >250 μm. Sample weight 10 mg

dation of coals and they can be used as indicative of spontaneous combustion. Weltner [14] attributed these peaks to interaction of O_2 with non-aromatic and aromatic constituents of low and medium rank coals. The part of curve between 200–300°C has also been interpreted [4] as indicative of spontaneous oxidation on the basis of the manner in which heat flows in the region.

The coals studied in this work are of high lignite to subbituminous rank and their combustion is interesting. The initiation temperature, maximum temperature and burnout temperature are dependent on the content of volatile matter, particle size, heating rate and atmosphere whether static air of dynamic oxygen are used. The initial reaction gives rise to one to three shoulders and more in the samples with high volatile content followed by a main peak and a shoulder at the end of reaction. These shoulders are present in all the samples with particle sizes below 150 μm. Thus the DTA curves reflect the composition of organic and inorganic matter and indicate the slow burning of organic constituents which continues even after the burning of fixed carbon and is recorded as the end shoulder. When samples were heated at rates of 10, 20, 40, 60 and 80 deg·min^{-1}, both the initial and the end shoulders were lost above 30 deg·min^{-1}, the main peak shifted to higher temperatures (Fig. 2) with a relative increase in broadness. Generally, heating rates equal to or below 20 deg·min^{-1}, samples of particle size below 100 μm and volatile content be-

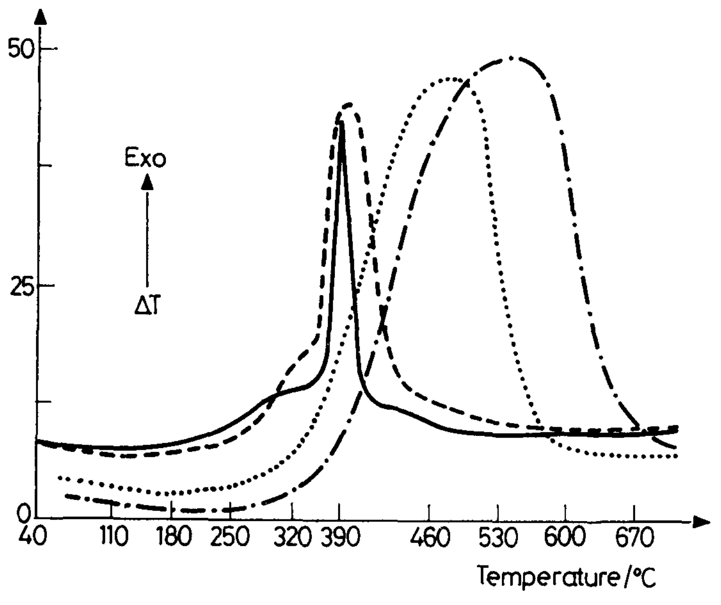

Fig. 2 DTA curves of samples in oxygen showing the effect of heating rate. —10 deg·min^{-1} - - - 20 deg·min^{-1}, ••••• 60 deg·min^{-1}, –•–•–80 deg·min^{-1}. Sample weight 10 mg

tween 33–34% gave satisfactory results. The main peak obtained thereby was sharp with shoulders of approximately equal size on both of its ends.

In order to study the effect of particle size, the DTA curves were recorded for samples with volatile content between 33–34% at heating rates of 20 deg·min^{-1}. The representative curves of the samples having particle size in the range 100–75, 150–100, 250–150 and above 250 μm are also shown in Fig. 1. It can be seen that the decrease in particle size results in well defined shoulders and increased sharpness of the main peak. There is also a progressive decrease of 10–15°C in the initiation temperature. Surprisingly larger particles i.e. above 150 μm do not exhibit the end shoulder and particles below 63 μm (not shown in Fig. 1) show a single sharp exothermic peak with the maximum temperature lowered by 50°C as compared to larger particles. The effect of the particle size on the ignition shows that with increasing surface area the adsorption of oxygen is enhanced and organic matter burns more efficiently, and as a result, endothermic peaks due to mineral matter is completely masked. Limited interaction of oxygen with larger particles, i.e. above 150 μm, on the other hand, enhances the decomposition of mineral matter such as siderite which is known [15] to decompose around 600°C and endothermic effects become operative, causing suppression in the ongoing process of oxidation.

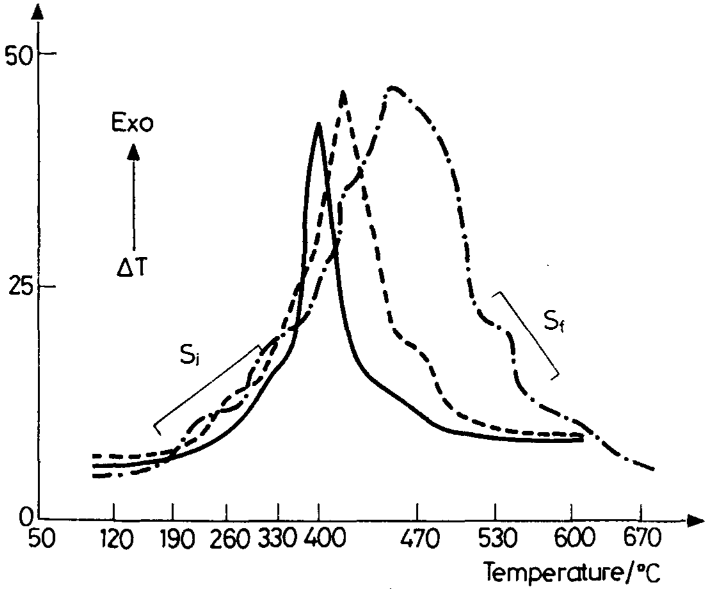

Fig. 3 DTA curves showing the effect of the volatile content of samples on the peak configuration. Volatile content: — 33%, - - - 36%, -•-•- 39%. Si and Sf refer to shoulder peaks prior to and after the main peak, respectively. Sample weight: 6 mg; particle size: 150–100 μm

Effect of volatile matter content

The effects on peaks due to differences in volatile content of samples were also studied. Twelve samples of coal with volatile content between 30–40% were selected, ground, and sieved to get particle sizes below 100 μm. A 6 mg sample was subjected to DTA measurements at heating rates of 20 deg·min^{-1}. Some of the curves are shown in Fig. 3. The results show that samples with low volatile content i.e. 30–34% do not produce the end shoulders and that the pattern of initial shoulders is not well defined. A small endothermic peak appears at the position of the end shoulders in some of the samples which is probably caused by some decomposition reaction. Its magnitude decrease to 33% after which it disappears. From 35 to 37% two-shoulder configuration is displayed and above this three shoulders of varying sizes appear prior to the main peak, and the end shoulder is retained. At the highest levels of volatile content i.e. 40% the reactions become vigorous, the height and width of peaks increase but their shape becomes highly asymmetrical. These characteristics are indicative of the heterogeneous nature of the organic matter and its stepwise combustion rather than a continuous process.

In view of these characteristics, the initiation temperature, and maximum temperature of oxidation were correlated with the volatile content of samples. The results are shown in Fig. 4. It may be noted that the initiation temperature

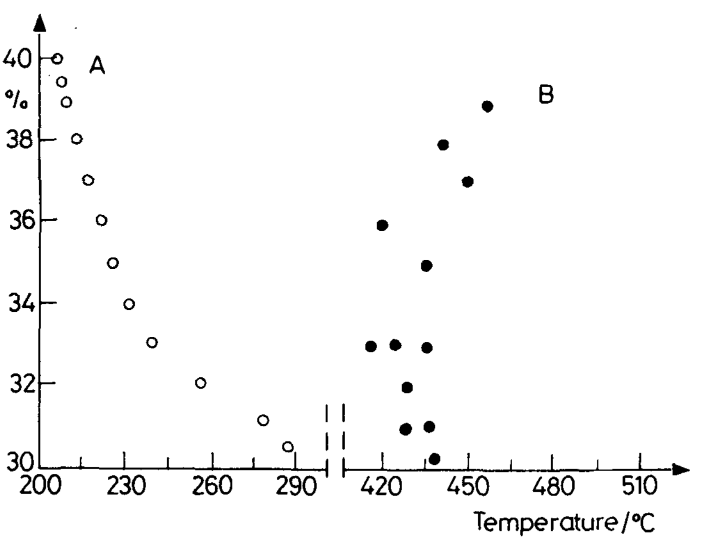

Fig. 4 Relationship showing the variation of initiation temperature (A) and maximum temperature (B) with the volatile content of samples

values for higher volatile content do not differ remarkably but there is a marked shift towards higher temperatures as the volatile content of samples decreases. The maximum temperature values of oxidation on the other hand do not show any correlation except for samples with high volatile content, where there is a slight shift to higher temperatures.

DTA in nitrogen

In nitrogen the DTA curves are not very informative, as their ill-defined exothermic features spread over the 300–750°C temperature range. The curves recorded in this work consist of an initial endothermic peak around 150°C followed by two exothermic bends between 300–400°C for samples having volatile content between 37 and 39% only and a broad exothermic bend between 500–700°C. Except the initial endothermic peak which is due to loss of moisture, the rest of the curve is devoid of any peak indicative of endothermic activity. In fact, in inert atmosphere the region 500–750°C can be expected to display peaks caused by the decomposition of minerals such as siderite, magnesite, pyrite etc., but probably in younger coals the combustion is a major problem. Although it is much more suppressed yet it is able to mask endothermic reactions caused by comparatively smaller amounts of minerals. To overcome the effects due to organic matter the samples were also diluted with 20, 40, 60

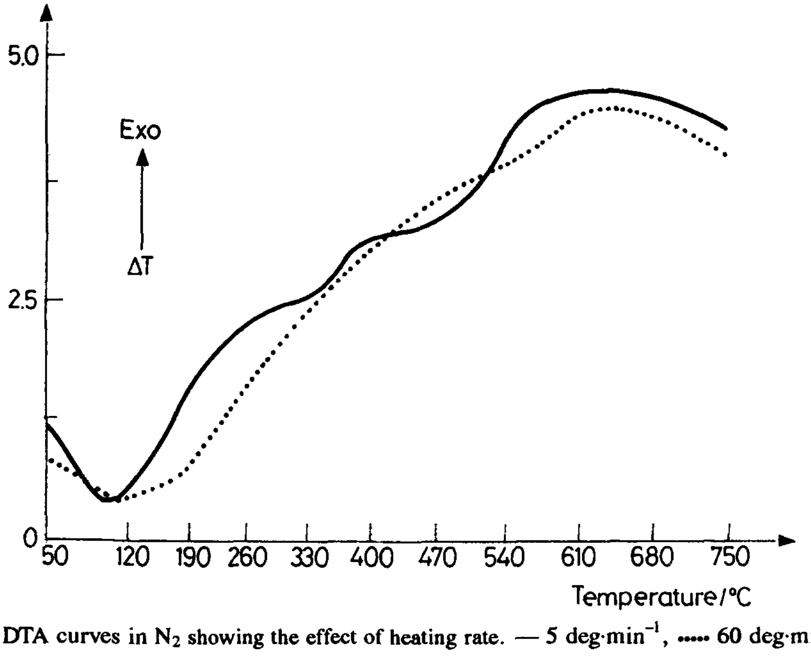

Fig. 5 DTA curves in N_2 showing the effect of heating rate. — 5 deg·min^{-1}, ... 60 deg·min^{-1}. Particle size 250–100 μm. Sample weight 10 mg

and 80% Al_2O_3 but it did not have any effect on the features of the curves. Similar behaviour for low rank coals has been reported by Mahajan *et al.* [16] and others [17], who used DSC technique in their studies. When heating rates were increased from 5 deg·min^{-1} to 60 deg·min^{-1}, the two shoulders merged into a single one at 40 deg·min^{-1} and at heating rates above this it was completely lost. There is also a shift to higher temperatures in the maximum temperature of the broad exothermic peak. The particle size was found to have no significant effect on the characteristics of the curve.

In general the shape of the curves (Fig. 5), deviation from base line and broadness of the exothermic peak are all indicative of complex reactions which these coals undergo in inert atmosphere.

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Zusammenfassung — Es wird eine DTA-Analyse von niederinkohlten Kohlearten des Inkohlungsgrades Hochlignit bis Subbitumen aus Kohlenminen in Pakistan beschrieben. Die in dynamischer Sauerstoffatmosphäre durchgeführten Untersuchungen zeigten, daß zwischen 300 und 650°C eine exotherme Reaktion abläuft und daß die Proben eher einer stufenweisen Oxidation der organischen Bestandteile unterliegen als einem kontinuierlichem Prozeß, wie es durch den Verlauf der Schultern von 250 bis 350°C am Hauptpeak um 450°C angedeutet wird. Bezüglich der Oxidation wurde auch der Einfluß von Aufheizgeschwindigkeit, Partikelgröße und Gehalt an flüchtigen Stoffen untersucht. Die Resultate zeigen, daß eine Erhöhung der Aufheizgeschwindigkeit von 10 auf 80 deg·min^{-1} eine merkliche Verschiebung aller DTA-Ereignisse in

Richtung höhere Temperaturen verursacht. Für den Einfluß der Partikelgröße zeigen die DTA-Aufnahmen für die Fraktionen 100–75, 150–100, 250–150 m und größer als 250 m, daß Höhe und Lage der Schulterpeaks mehr durch die Partikelgröße beeinflußt werden, als der Hauptpeak. Die registrierten Kurven zur Untersuchung des Effektes unterschiedlichen Gehaltes an flüchtigen Substanzen zwischen 30 und 40% zeigen einen komplexen Schulternverlauf am Hauptpeak. Allgemein nimmt die Anzahl der Schulterpeaks mit zunehmenden Gehalt der Probe an flüchtigen Substanzen zu, aber ihrer Lage ist keine Regel abzuerkennen. Die in Stickstoff aufgenommenen DTA-Kurven enthalten schlecht definierte exotherme Effekte im Temperaturbereich 300–750°C. Diese Kurven bestehen aus einem endothermen Peak bei 150°C, zwei exothermen Schultern in der Temperaturregion 300–400°C und einem großen breiten exothermen Signal zwischen 500 und 700°C. Die Aufheizgeschwindigkeiten besitzen ähnliche Einflüsse wie in Sauerstoff, während die Partikelgröße die Ergebnisse nicht beeinflußt.

Es wurde geschlußfolgert, daß der organische Gehalt der hier untersuchten Proben äußerst heterogen ist mit verschiedenen Verbrennungscharakteristiken; im Endergebnis ist es sehr schwer, die zu schwach aufgelösten exothermen Ereignissen in der DTA-Kurve gehörenden Energieänderungen zu quantifizieren. Die Effekte dominieren auch in Stickstoffatmosphäre, was eine Identifikation der Mineralsubstanz schwierig macht. Der Gesamtverlauf der DTA-Ereignisse in Sauerstoff kann mit der Aufheizgeschwindigkeit, der Partikelgröße und dem Gehalt der Proben an flüchtigen Substanzen korreliert werden.