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ASSESSMENT OF SPONTANEOUS HEATING OF COAL BY DIFFERENTIAL SCANNING CALORIMETRIC TECHNIQUE – AN OVERVIEW

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ABSTRACT: Differential Scanning Calorimetric (DSC) applications in coal sciences have expanded rapidly. Various researchers observed that some of the methods to determine spontaneous heating are time consuming, tedious and do not give reproducible results. DSC instruments are usually employed under identical experimental conditions to track the reaction type (i.e., endothermic or exothermic), to calculate kinetics and heat flow rates. Application of DSC for determination of spontaneous heating of coal and suitability in this area is described.

INTRODUCTION

The spontaneous heating resulting into mine fire is an inherent problem in coal mining industry, which endangers lives of men in a mine. It also causes serious environmental pollution and economic losses to industry. Therefore, determination of susceptibility potential of coal due to spontaneous heating and their classification are essential to plan the production activities and storage capabilities in a coal mine. Different methods of spontaneous heating susceptibility can be broadly grouped under three headings; examination of chemical constituents of coal, oxygen avidity studies and thermal studies. In chemical composition of coal, attempts have been made to determine the spontaneous heating tendencies of coal based on their constituents obtained from proximate and ultimate analyses. The maceral composition of coals and their susceptibility to spontaneous heating have led to the development of petrological classifications. The oxygen avidity studies include; proxy complex analysis rate study, Russian U-index and other oxidation methods. In thermal studies, different methods are attempted, which include; initial temperature, crossing and ignition point temperature, modified crossing point temperature, puff temperature, Olpinski index, adiabatic calorimetry, thermo-gravimetric (TG) analysis, differential thermal analysis (DTA) and differential scanning calorimetry. Spontaneous combustion of coal is influenced by the nature of the coal, particle size, geological condition and mining environment, all of which govern the thermal processes occurring in the coal. However, generalization of the results on the thermal behaviour of coal has been difficult. In recent years the application of thermal analysis techniques to the study of combustion pyrolysis behaviour and kinetics of coals has gained a wide acceptance among various research workers.

LITERATURE REVIEW

The earliest study on spontaneous combustion was carried out by Mahajan, Tomita and Walker (1976), using DSC technique. They reported differential scanning calorimetry curves for 12 coals of various ranks in a helium atmosphere with a flow rate of 1 ml min^{-1} and temperatures between 100 to 580 °C at a constant heating rate of 10 ^{o}C min^{-1}. The amount of sample used in the study varied between 12 and 20 mg with reference material being alumina. They concluded that the thermal effects of coals, ranging in rank from anthracite to bituminous, were endothermic. Exothermic heats were observed only in the case of sub-bituminous coals or lignite. The net thermal effects were found to be strongly rank dependent. Rai and Tran (1977) conducted a kinetic study on catalyzed and non-catalyzed coal. In their kinetic model, the apparent activation energy was measured to be a rectilinear function, describing the extent of the pyrolysis reaction of the of Hanna coal. The order of reaction was found to be about 0.3 for the pyrolysis step and 0.67 for the hydro-gasification step.

Gold (1980) demonstrated the occurrence of exothermic processes associated with the production of volatile matter in or near the plastic region of the coal samples studied. He observed that the temperature and magnitude of the exothermic peak were strongly affected by the heating rate, sample mass, and particle size. Rosenvold, Bubow and rajeshwar (1982) analysed 21 bituminous coal samples from Ohio by DSC and non-isothermal thermogravimetric. Three regions of endothermic

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activity were distinguished in DSC scans in an inert atmosphere. The first peak (25–150 °C) corresponded to devolatilisation of organic matter, and a partially resolved endotherm occurred at temperatures above 550°C probably correspond to cracking and coking processes subsequent to pyrolysis step.

Rajeshwar (1983) applied differential scanning calorimetry and thermogravimetry to study of coal, oil shale, and oil sands. DSC has been used to characterise 12 U.S. coals of varying rank from anthracite to lignite. Elder and Harris (1984) investigated the thermal characteristics of Kentucky bituminous coals undergoing pyrolysis in an inert atmosphere at three different heating rates and determined the specific heats of the coals. The specific heats of the dry coals lie in the range of 1.21 to 1.47 $Jg^{-1}K^{-1}$. The exothermic heat flow from 300 to 550 °C, where the major weight loss occurred, has been associated with the primary carbonisation process, the development of the plastic state, and the onset of secondary gasification, which is responsible for coke formation. Ismail and Walker (1989) studied oxygen chemisorption on a number of coal chars in oxygen atmosphere at 100 ^{o}C by using DSC and TGA. They studied 16 coal samples having particle size of -100 mesh. The samples were heated in nitrogen atmosphere with a flow rate of 45 ml min^{-1} between ambient to 600 ^{o}C. They correlated heat release and weight of oxygen chemisorbed as a function of reaction time with Elovich plots. They observed that the rate of heat release and weight increase generally decreased with increasing rank of coal. They also observed that the rate of heat release upon oxygen chemisorption generally increased as rates of gasification of chars at higher temperatures in air increased.

Alula, Cagniant and Laver (1990) used thermo-gravimetric and differential scanning calorimetry to characterise low and high-temperature coal tar and petroleum pitches and their fractions, thermal methods to the characterization of pyrolysis coal products. Kok (1997) investigated thermal behaviour of lignite by DSC, TG/DTG, High Pressure Thermo Grvimetric (HPTGA), and combustion cell experiments. He studied one coal sample of particle size of – 60 mesh in air with a flow rate of 50 ml min^{-1}. Different heating rates were applied, i.e. 5, 10, 15, 20 and 25 ^{o}C min^{-1} in a temperature range between 20 to 600 ^{o}C during experimentation. He used different models (Arrhenius, Coats and Redfern, Fassihi and Brigham) to obtain kinetic parameters. The heat flow rate recorded at different temperatures showed that oxidation reaction started around 250 ^{o}C and reached a maximum rate at 410 ^{o}C. Higher heating rates resulted in higher reaction temperatures and heat of reactions. Distinguishing peaks in the DSC curves shifted to higher temperatures with an increase in heating rate.

Garcia, Halla and Fanoor (1999) found that differential scanning calorimetry is a useful technique to investigate early stages of the oxidation of coal. Experiments were carried out on three coal samples of 10 mg each in oxygen atmosphere, at flow rate of 20 ml min^{-1}, heating rate 10 ^{o}C min^{-1}, temperature range ambient to 600 ^{o}C, and particle size of – 100 mesh. They proposed that the onset temperature was a better indicator of propensity of coals to oxidation and this parameter agreed with rank of coals investigated and increased with time of oxidative weathering. Ozbas, Kok and Hieyilmaz (2003) determined combustion behaviour and kinetic analysis of raw and cleaned coal samples of different sized fractions by using DSC. They studied four coal samples of 10 mg each. Experiments were carried out in air atmosphere with a flow rate of 50 ml min^{-1}, at the heating rate of 10 ^{o}C min^{-1} and temperature range between 20 and 600 ^{o}C. DSC curves of three coal samples showed two reaction stages. The first stage of reaction was due to moisture loss (endothermic) and observed in temperature range of ambient to 150 ^{0}C. The second stage was exothermic region due to combustion and observed in the temperature range of 150 to 600 ^{0}C. Kinetic parameters of the samples were determined using Roger and Morris kinetic model. Panigrahi and Sahu (2004) used DSC, DTA, wet oxidation potential, crossing point temperature for determination of susceptibility of 31 Indian coals to spontaneous heating. They used 10 mg coal sample of particle size -72 mesh, , in oxygen atmosphere with a flow rate of 20 ml min^{-1}, the heating rate was at 30 ^{o}C min^{-1}, between ambient to 500 ^{o}C and with alumina as reference material.

Exhaustive correlation studies between susceptibility indices and intrinsic properties were carried out for identifying the appropriate parameter to be used for classifications. The identified parameters were used as inputs to ANN. Adoptive resonance theory of Artificial Neural Network ANN has been applied to classify coal seams into four different categories. Kok (2005) used differential scanning calorimetry and thermogravimetry to obtain information on temperature-controlled combustion characteristics of 17 coals of different origin from Thrace basin of Turkey. Using DSC experiments were performed on 10 mg coals, in air atmosphere with a flow rate of 50 ml min^{-1}, particle size of 60 mesh, ,temperature range between 20 to 600 ^{o}C at a heating rate of 10 ^{o}C min^{-1} by. Kot calculated the kinetic parameters from Arrhenius and Coats–Redfern plots. The study revealed that two temperature regions of evident

The chemical reactivity, elimination of water and primary carbonization were also evident in all of the coal samples It was observed that activation energies of samples were varied from 54 to 92 kJ mol^{-1}. Elbeyli and Piskin (2006) determined thermal characteristics and kinetic parameters of cleaned Tunçbilek lignite by using differential thermal analysis (DTA) and thermogravimetry (TG) DSC thermal analysis system both for combustion and pyrolysis reactions. The experiments were carried out in a 10 mg lignite sample of particle size of - 65 mesh. The tests was carried out in air/nitrogen atmospheres with a flow rate of 100 ml min^{-1}, heating rate 10 ^oC min^{-1} up to 1000 ^oC.

Krzesinska *et al.* (2008) studied three Polish coals of varying rank (82.7, 86.2 and 88.7 wt.% carbon content) and caking ability (weak, moderate and strong) of the Krupinski, Szczygłowice and Zofiowka mines, respectively by TG, DSC and dynamic mechanical analysis (DMA) method. The amount of sample used in their experiment was 7 mg and sample was heated at 10 ^oC min^{-1} up to 520 ^oC in nitrogen atmosphere with a flow rate of 50 ml min^{-1}. The weight loss and heat flow during pyrolysis, and storage/loss elastic modulus measured as a function of increasing temperature were related to the caking ability of coals. Parameters determined with the TG and the DSC methods in the binary and ternary blends were correlated with the proportion of strongly-caking-coal concentration in the blend. The weight loss of coal blends was found to be additive parameter. The DSC thermograms of binary blends were found to be different from those of the ternary blends, which suggested a different course for this blend pyrolysis.

A critical study of the work carried out by different researchers indicates that the different experimental conditions for DSC have been adopted by them for studying the spontaneous heating susceptibility of coal. In order to draw a suitable conclusion from their studies the experimental parameters used by them have been compiled in tabular format and presented in Table 1, which clearly reveals the followings:

- The particle size of coal samples varies from – 60 mesh to - 100 mesh.
- Variation of heating rate was between 5 ^oC min^{-1} to 30 ^oC min^{-1}
- The sample was studied in nitrogen, atmospheric air and oxygen.
- The amount of sample used by them varies from 7 mg to 20 mg.
- The range of flow rate used by them was between 1 ml min^{-1} to 100 ml min^{-1}.
- The reference material was alumina.
- The number of sample analysed by them was one to four except in four cases, i.e. 12, 16, 17 and 31 samples.
- The range of temperature was ambient to 1000 ^oC.

Thus, there is no unanimity on the experimental parameters used by different researchers. If the experimental parameters will be different, the results of two samples analysed by two experimental conditions will not be comparable for indexing the coal with respect to their spontaneous heating. Therefore, the future direction of research should be to finalise the experimental standards for this techniques.

DIFFERENTIAL SCANNING CALORIMETRY

a) Principles

Differential scanning calorimetric is a technique in which the difference in energy in puts into a substance and a reference material is measured as a function of temperature while the substance and reference materials are subjected to a controlled temperature program. In this technique the ordinate value of an output curve at any given temperature is directly proportional to the differential heat flow between a sample and reference material and in which the area under the measured curve is directly proportional to the total differential calorific input. By this technique, coal samples can be studied under experimental conditions that simulate spontaneous heating process of materials.

b) Experimental Set-up

The complete experimental set up comprises the differential scanning calorimeter, sample holder, crucible sealing press (crimper), purge gas supply arrangement, a computer with software and a graphic plotter (Figure 1). In Mettler-Toledo DSC-821e differential scanning calorimeter sensors are single junction thermocouples. Any energy difference in the thermocouples to the sample and the reference is then recorded against the program temperature. Thermal events in the sample thus

appear as deviations from the DSC baseline, in either endothermic or exothermic direction, depending upon whether more or less energy difference to the sample relative to the reference material. In DSC therefore, endothermic responses are usually represented as being negative, i.e. below the baseline, corresponding to an increased transfer of heat to the samples compared to the reference. Purge gas is supplied from a cylinder equipped with suitable regulators. All the operations of the DSC-821e calorimeter are controlled from the personal computer through software STAR^e. The software performs all the controls, calibration, data display, standard calculations, curve comparison and calculations etc.

Figure 1 - Experimental setup of Differential Scanning Calorimetry

c) Sample Preparation

Coal samples were collected from different Indian coalfields covering both fiery and non-fiery coal seams of different ranks. Approximately 5 kg of coal samples was collected by channel and chip sampling method and stored in plastic containers with de-aerated water. Before the experiments, representative samples were prepared from the coals obtained by applying closed circuit crushing and screening. The prepared samples were taken for thermal analysis.

d) Experimental Procedure

DSC apparatus was calibrated via the melting points of indium, zinc, lead metals under the same conditions as for the sample. During the experiments the heat flow as a function of time and temperature were recorded, while the sample was subjected to a computer controlled temperature programme. Sample was placed in the sample pan, covered with a lid and sealed with pressure using a crimper press. The crimped container with the sample was put on the sample furnace while the reference furnace was kept empty. Pinholes were made in the lid. The coal was in a monolayer at the base of the pan to ensure that the entire sample made good thermal contact with the bottom part of the pan and therefore good heat transfer with the sensors of the equipment. If the pinholes were too small oxygen diffused into the pans too slowly and this process determined the rate of oxidation, rather than diffusion into the pore structure of the coal itself. A number of experiments were carried out in the temperature range from ambient (30^0C) to 600^0C with varying atmosphere (Figure 2 to 5). The experiments were repeated under identical conditions to check the reproducibility of the results.

Table 1 - Experimental parameters used by different researchers in DSC studies on spontaneous heating of coal

Sl. No.	Name of the author	Year	Parameters							
			Particle Size (mesh)	Heating Rate ($^oCmin^{-1}$)	Atmosphere	Sample Amount (mg)	Flow Rate (ml min^{-1})	No. of Sample Studied	Reference Material	Temperature Range (^oC)
1.	Mahajan, Tomita and Walker (1976)	1977	-	10	Helium	20, 12	1	12	Alumina	100 to 580
2.	Ismail and Walker (1989)	1989	- 100	10	N_2		45	16		Ambient to 600
3.	Kok (1997)	1997	- 60	5, 10, 15, 20, 25	Air	-	50	1	-	20 to 600
4.	Garcia, Halla and Fanoor (1999)	1999	- 100	10	Oxygen	10	20	3	-	Ambient to 600
5.	Ozbas, Kok and Hieyilmaz (2003)	2003		10	Air	10	50	4	-	20 to 600
6.	Panigrahi and Sahu (2004)	2004	- 72	30	Oxygen	10	20	31	Alumina	Ambient to 500
7.	Kok (2005)	2005	- 60	10	Air	10	50	17	-	20 to 600
8.	Elbeyli and Piskin (2006)	2006	- 60	10	Air Nitrogen	10	100	1	-	Ambient to 1000
9.	Krzesinska *et al.* (2008)	2008	-	10	Nitrogen	7	50	3	-	Ambient to 520

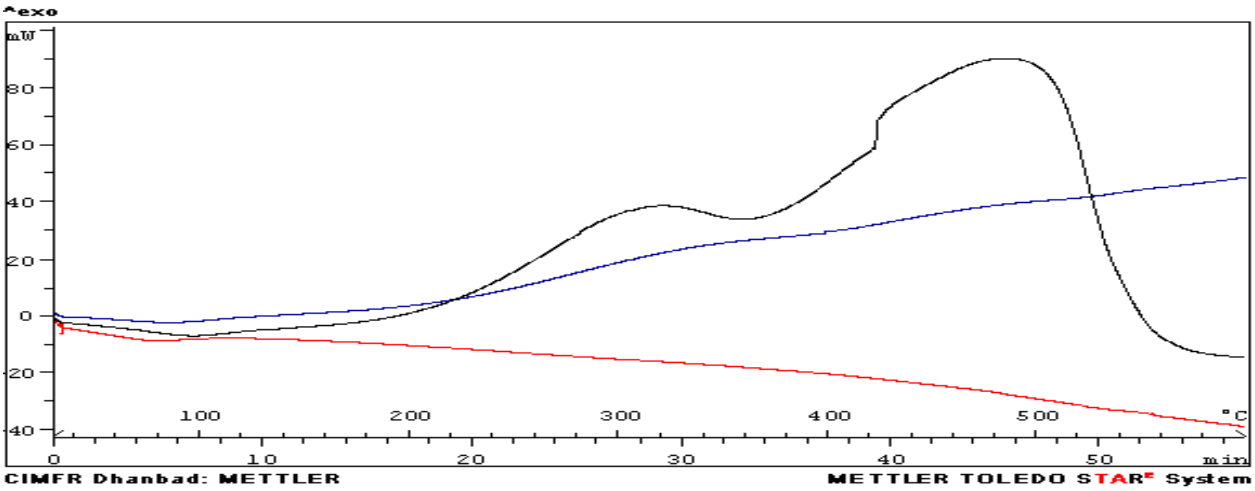

Figure 2 - DSC Thermo-gram of coal sample (Oxygen, Air and Nitrogen Atmosphere)

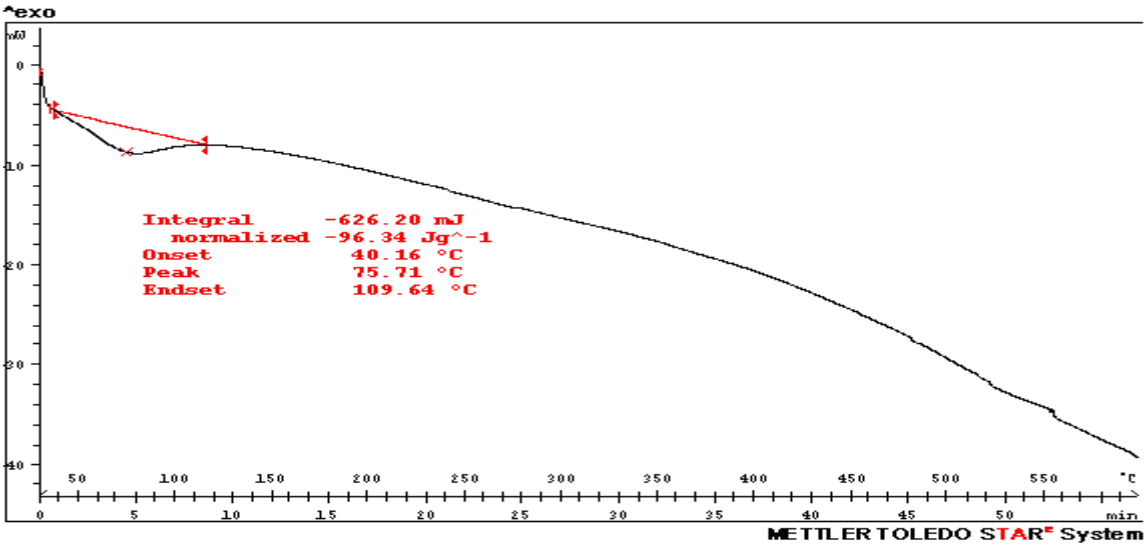

Figure 3 - Different stages of DSC Thermo-gram of coal sample (Nitrogen/Inert atmosphere)

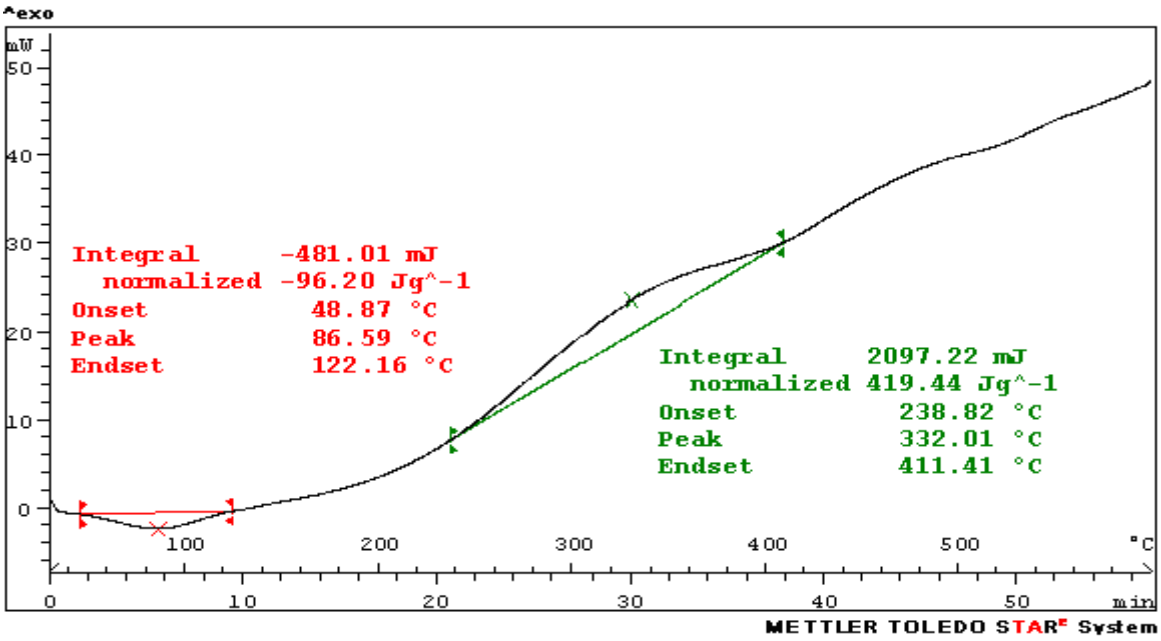

Figure 4 - Different stages of DSC Thermo-gram of coal sample (Air atmosphere)

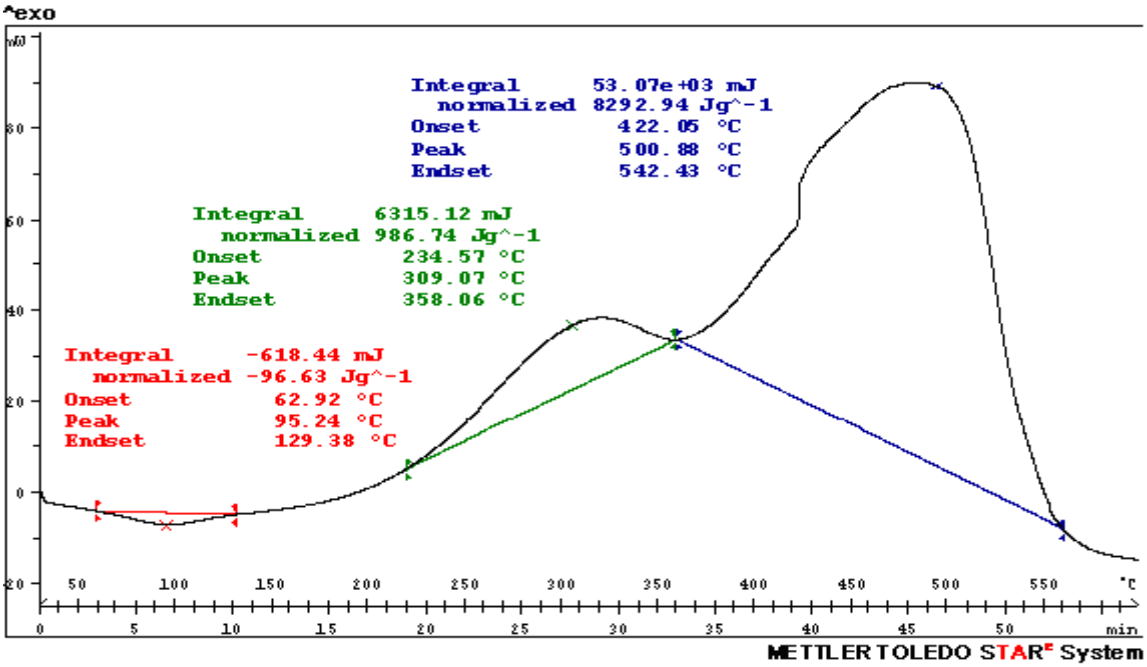

Figure 5 - Different stages of DSC Thermo-gram of coal sample (Oxygen atmosphere)

RESULTS AND DISCUSSION

The combustion process was exceedingly complex and many competing processes contributed to the behaviour of thermal analysis curves. Theoretically, the spontaneous combustion of coal can be initiated whenever oxygen comes in contact with the coal. So, experiments should be carried out in oxygen or air atmosphere because of easy oxidation of coal in air. In case of nitrogen or inert atmosphere, the study showed that oxidation may not take place, thus it was not suitable for the determination of spontaneous heating.

DSC provides both qualitative and quantitative information about material transition during the spontaneous heating process as compared to DTA and TGA study of coal. In the region of first endothermic peak of DSC, the enthalpy oxidation is mainly due to release of moisture. The onset temperature of first exothermic peak in oxygen atmosphere is possibily a measure of the susceptibility of coals towards spontaneous combustion. This has a number of potential advantages. Firstly, the overall weight change at this temperature is negligible, thus avoiding the problems inherent in exotherm integration. The heat evolved during the early stages is crucial to subsequent oxidation by inducing relaxation in the coal structure which enhances the mass transfer of oxygen. For some of these transitions, DSC can provide, not only the temperature at which the transition (reaction) occurs and how much heat is evolved, but can also provide valuable information about the rate (kinetics) of reaction. Furthermore, with the advent of easy-to-use computer based data analysis programs, the ability to obtain such kinetic information has become more practical. Differential scanning calorimetry will be a useful technique to investigate the early stage of oxidation of coal.

CONCLUSION

Differential scanning calorimetry techniques are useful tools to study the combustion, pyrolysis behaviour, kinetics and assessment of spontaneous heating of coal. The critical analysis of the literature survey on the application of DSC technique and summarised data presented in Table 1 clearly reveals the following salient features.

- DSC technique has in general had limited application for studying the susceptibility of coal to spontaneous heating and fire.

- There is no general agreement and unanimity regarding the experimental standards to be adopted for studying the susceptibility of coal to spontaneous heating and fire in above techniques.
- Thermal behaviour of coals depends on experimental conditions such as particle size, sample amount, heating rate, carrier gas and its flow rate.

The DSC study can be used as an indicator to determine the susceptibility of coals to self heating or spontaneous combustion. The acceptability of this method for determining spontaneous heating characteristics of coal mainly depends upon how closely it predicts the spontaneous heating in the field conditions. This will help to scientifically classify the coals with respect to their proneness to spontaneous heating, so that practicing mining engineers, mine planners and mine operators can formulate the ameliorative measures in advance. This will help to save coal from burning, and will contribute to improve production, productivity and safety in mines, as well as reduce atmospheric pollution

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