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Application of thermal analysis techniques to assess proneness of coal to spontaneous heating

An overview

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Abstract The paper presents the review of application of three thermal techniques viz; differential thermal analysis (DTA), thermogravimetry (TG) and differential scanning calorimetry (DSC); for studying the susceptibility of coal to spontaneous heating and fire. It also critically analyses the experimental standards adopted by different researchers, while applying these techniques in studying thermal behaviour of coal samples. The paper also presents the future direction of research in this subject area.

Keywords Differential thermal analysis · Thermogravimetry · Differential scanning calorimetry · Spontaneous heating · Coal

Introduction

The spontaneous heating of coal resulting into mine fire is an acute problem in coal mining industry of the world, which endangers not only valuable lives of miners, but also causes serious environmental pollution and economic losses to industry. It is influenced by nature of coal, particle size, geological condition and mining environment, all of which govern the thermal processes occurring in the coal. 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. In order to find out susceptibility of coal to spontaneous heating, the different methods attempted by all researchers of the world can be broadly grouped under three headings such as examination of chemical constituents of coal, oxygen avidity studies and thermal studies. In chemical composition of coal, attempts have been made to determine spontaneous heating tendencies of coal based on their constituents obtained from proximate and ultimate analyses. Geologists also studied the maceral composition of coals and their susceptibility to spontaneous heating and developed petrological classifications. The oxygen avidity studies mainly include peroxy complex analysis, rate study, Russian U-index and other oxidation methods. In thermal studies, researchers have tried different methods, viz. initial temperature, crossing and ignition point temperature, modified crossing point temperature, puff temperature, Olpinski index, adiabatic calorimetry, differential thermal analysis (DTA), thermogravimetry (TG) and differential scanning calorimetry (DSC) for determining the susceptibility of coal towards spontaneous heating.

However, in recent years some of the thermal analysis techniques viz. DTA, TG and DSC; have been increasingly used for assessing the proneness of coal to spontaneous heating. Keeping the importance of this research in view, authors have attempted to critically review the application of these techniques and find out the knowledge gap in this research area, which can be taken up for effectively applying these techniques for assessing the proneness of coal to spontaneous heating. Details of the critical analysis about these three techniques are presented in the subsequent sections of this paper.

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Differential thermal analysis

The DTA technique, a method originally used by Le-Chatelier [1], involves heating a small test specimen, at a constant rate and continuously recording the instantaneous temperature difference (ΔT) between it and an identically heated inert reference material as a function of the temperature (T) prevailing in the inert medium. The resultant curve, a record of temperature difference against temperature with its characteristic heat changes and intensities, depicts the physical or chemical changes of the material at the particular temperature and is a characteristic of the material used.

The DTA technique has been used by a number of researchers for assessing the spontaneous heating susceptibility of coal. Earliest work in this regard has been carried out by Whitehead and Berger [2]. They used this technique in studying the thermal behaviour of coal and coal like materials. They carried out their experiments in air/vacuum with a heating rate between 10 and 20 °C min^{-1}. The temperature ranges for their DTA was between ambient to 550 °C. Glass [3] carried out DTA analysis for coal with particle size of −100 mesh, heating rate from 10 to 20 °C min^{-1} and the range of temperature was ambient to 1,000 °C. He carried out DTA analysis for seven number of coal samples. He suggested that the DTA curves of coking coals might be correlated with the standard German rank classification of coal. Berkowitz [4] studied the characteristics of coals at heating rate of 6 °C min^{-1}, particle size of −65 mesh and the amount of sample taken was 100 mg. He carried out the DTA for six samples in pure nitrogen atmosphere in a flow rate of 2.5 mL min^{-1}. The reference material used in his analysis was dry quartz and the range of temperature was ambient to 500 °C. He observed that the curve of coal samples were substantially a rank dependent over the range of 73–90% of carbon. Banarjee and Chakraborty [5] carried out DTA analysis for six coal samples and the amount of sample taken for each experiment was 600 mg. The medium of experiment was atmospheric air and the reference material was calcined alumina with the experimental temperature was ambient to 400 °C. However, they varied the heating rate at five different steps such as 1, 3, 5, 10 and 15 °C and they took samples at three different size ranges and these were −72, −200 and −10 + 60 mesh. The curve was divided by them into three segments or stages as given in Fig. 1. These were Stages I, II and III. They observed that in Stage I (in the initial stage of heating) endothermic reaction predominated probably due to release of inherent moistures in coal. In the second stage (Stage II), exothermic reaction became significant, but the rate of heat release was not steady all through and it changed with temperature. A steep rise in heat evolution was observed in third stage (Stage III). On the basis of their

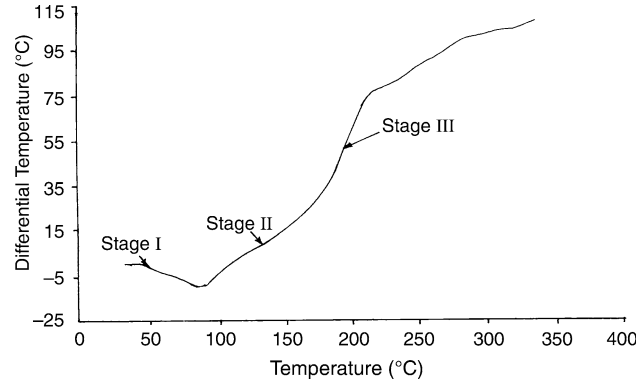

Fig. 1 Different stages of DTA curve of a coal sample

extensive studies, they suggested that the coal samples of −72 mesh at heating rate of 5 °C min^{-1} should be suitable for determining relative susceptibility of coal to spontaneous heating.

Banerjee et al. [6] attempted to classify coals with respect to their susceptibility towards spontaneous heating. They used their experimental data of DTA studies [5] and further carried out three additional types of experiments; i.e., crossing point temperature determination, rate studies of coal oxidation reaction and peroxy complex analysis. They were of the view that none of these four methods could be recommended singly for indexing coals with respect to proneness of their spontaneous heating and suggested that all aforementioned tests might be carried out for correct classification. Gouws and Wade [7] evaluated the spontaneous heating susceptibility of 58 South African coal samples with the help of crossing point temperature and DTA. From the observation on DTA they thought that slopes of Stage II was an indicator of self heating propensity and there was no practical justification for using the transition point between Stage II and Stage III as self heating index. Further Gouws and Wade [8] studied the spontaneous heating propensity of South African coals on the basis of simple indices such as FCC (Feng, Chakraborty and Cochrane) index proposed by Feng et al. [9] and MR index proposed by Mahadevan and Ramlu [10]. They put forward a new index termed as WITS-EHAC index by plotting the reciprocal of crossing pint temperature against the Stage II slope of DTA curves, which indicated the increase in self heating liability with distance from the graph origin. Again Gouws and Wade [11] found this composite index showing good results for South African coals and stated that the laboratory test using DTA could distinguish between thermal behaviour of different coals. They however, cautioned that inferring the self heating from such data might not always be correct. They pointed out that from the knowledge of relative contribution of both the coal type and the environment, it would be possible to quantify the self heating risk in any given mining

situations. Haykiri-Acma et al. [12] applied DTA and TG to study peat, lignite, bituminous coal, anthracite coal and oil shale. Heating rate for the sample as applied by them was 15 °C min^{-1} and the temperature was raised from ambient to 1,000 °C under nitrogen atmosphere. They derived DTG curves of the samples by using TG curves. Gouws and Knoetze [13] used ignition temperature test (crossing point temperature & DTA) and adiabatic calorimetry to determine spontaneous heating tendency of the coal. They observed that self heating propensity was related to dry ash free oxygen content and oxygen to carbon ratio of coal. On the basis of their studies they showed that there was an inverse relationship between spontaneous heating characteristics and explosibility of coal.

Podder et al. [14] used DTA and TG analysis for studying thermal behaviour of Bangladeshi coals. In their study they used the particle size of −100 mesh, heating rate of 10 °C min^{-1} and quantity of sample was 10 mg. The samples were heated in argon atmosphere with a flow rate of 100 mL min^{-1} between 30 and 900 °C. They studied only five numbers of samples and observed the chemical reactivity of coal at two different temperature ranges, i.e., 80–110 °C due to loss of water vapour and similarly two other major reactions at around 420–550 °C due to primary and secondary devolatilisation. Iordanidis et al. [15] carried out DTA and TG experiments for seven lignite samples, which were heated up to 1,000 °C at a constant rate of 10 °C min^{-1} in a 150 mL min^{-1} flow of nitrogen. The burning profiles of the samples were studied considering the results of proximate analysis and calorimetry. The results of this study contributed to a clearer identification of lignite structure and a better understanding of coalification process. Kok [16] investigated the thermal behaviour of four coal samples using DTA and thermogravimetry (TG/DTG) methods. They used the −60 mesh sample size, 10 °C min^{-1} of heating rate and temperature range was between 20 and 900 °C. Experiments were carried out in air atmosphere with a flow rate of 167 mL min^{-1} and amount of sample was 10 mg with alumina as reference material. They observed that when the coal samples were heated in inert atmosphere up to 800 °C, 31.44–43.82 percentage mass loss occurs. They indicated two temperature regions of increased chemically reactivity in the coal samples and finally carried out the kinetic analysis of the samples. Panigrahi and Sahu [17] used DTA, DSC, wet oxidation potential and crossing point temperature for determining the susceptibility of coal to spontaneous heating. They carried out exhaustive correlation studies between susceptibility indices and intrinsic properties for identifying appropriate parameters to be used for classification of Indian coals. The experimental parameters used by them were sample size −72 mesh, heating rate 30 °C min^{-1}, sample amount 600 mg, reference material alpha alumina powder and range of temperature was ambient to 400 °C. They studied the behaviour of 31 coal samples by the aforementioned methods and finally used an adoptive resonance theory of artificial neural network for classifying coal seams into four different categories. Elbeyli and Piskin [18] simultaneously applied DTA and TG for studying the pyrolysis kinetics of Turkish bituminous coals. They used −65 mesh particle size, heating rate of 10 °C min^{-1} with air/nitrogen atmosphere, with a flow rate of 100 mL min^{-1}. They studied only one coal samples of 10 mg in the temperature range between ambient and 1,000 °C. Haykiri-Acma et al. [19] investigated the combustion characteristics of seven coking, semi-coking and non-coking Turkish bituminous coal samples by applying DTA and TG techniques. They used −65 mesh particle size, heating rate of 20 °C min^{-1}, sample amount of 20 mg and the behaviour of samples was studied in the temperature range of ambient to 1,000 °C. The reference material used by them was alumina. Sis [20] examined the relationship between particle size and combustion kinetics and combustion properties of lignite samples by carrying out DTA and TG/DTG techniques. They studied one coal sample and depending upon the size of particles they collected fourteen numbers of size ranges between −8 + 10 and −400 mesh. The heating rate was 10 °C min^{-1} in air atmosphere with a flow rate of 50 mL min^{-1}. The amount of sample was 10 mg and range of temperature during experiments was between ambient and 900 °C. The reference material was alpha alumina. They observed one endothermic peak in the Stage I for all the DTA curves denoting the moisture release from the samples. Two or three exothermic peaks aroused in the Stage II due to stepwise release of volatile matter and the burning of heterogeneous organic matter in the coal samples. The exothermic peak in Stage III was mainly due to the decomposition of mineral matter in the samples.

Ozbas [21] studied 15 numbers of samples and attempted to establish relationship between particle size and pyrolysis characteristics of Elbistan lignite by using DTA and TG/DTG techniques. These experiments were carried out in nitrogen atmosphere up to 900 °C at a heating rate of 10 °C min^{-1} with a flow rate of 50 mL min^{-1}. The amount of samples used in their experiments was 10 mg and the reference material was alpha alumina. They observed three endothermic peaks in DTA curves. Similar to other researchers, he attributed the first peak due to evaporation of moisture. The second and third endotherms aroused in the Stages II & III corresponded to primary and secondary carbonizations (coking) of the lignite.

A critical study of the work carried out by different researchers indicates that the different experimental condition for DTA has been adopted by them for studying the

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

Sl. no.	Name of the author	Year	Parameters							
			Particle size/mesh	Heating rate/°C min^{-1}	Atmosphere	Sample amount/mg	Flow rate/mL min^{-1}	No. of sample studied	Reference material	Temperature range/°C
1.	Whitehead and Breger [2]	1950	–	10 20	Air/Vacuum	–	–	–	–	Ambient to 550
2.	Glass [3]	1955	−100	10 20	–	–	–	7	–	Ambient to 1,000
3.	Berkowitz [4]	1957	−65	6	Nitrogen	100	2.5	6	Dry quartz	Ambient to 500
4.	Banerjee and Chakraborty [5]	1967	−72, −200, −10+60	1, 3, 5, 10, 15	Atmospheric air	600	–	6	Calcined alumina	Ambient to 400
5.	Banerjee et al. [6]	1972	−72	5	Atmospheric air	600	–	6	Calcined alumina	Ambient to 400
6.	Haykiri-Acma et al. [12]	1993	–	15	Nitrogen	–	–	–	–	Ambient to 1,000
7.	Podder et al. [14]	1995	−100	10	Argon	10	100	5	–	30–900
8.	Iordanidis et al. [15]	2001	−16	10	Nitrogen		150	7	Alumina	Ambient to 1,000
9.	Kok [16]	2002	−60	10	Air	10	167	4	Alumina	20–900
10.	Panigrahi and Sahu [17]	2004	−72	30	Atmospheric air	600		31	Alpha alumina	Ambient to 400
11.	Elbeyli and Piskin [18]	2006	−65	10	Air/Nitrogen	10	100	1	–	Ambient to 1,000
12.	Haykiri-Acma et al. [19]	2006	−65	20	Atmosphere	20		7	Alumina	Ambient to 1,000
13.	Sis [20]	2007	−8+10 to −400	10	Air	10	50	1	Alpha alumina	Ambient to 900
14.	Ozbas [21]	2008		10	Nitrogen	10	50	15	Alpha alumina	Ambient to 900

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. A study of Table 1 clearly reveals the followings:

- The particle size of coal samples varies from −8 to −400 mesh.
- Variation of heating rate was between 1 and 30 °C min^{-1}.
- The sample was studied in nitrogen, atmospheric air and vacuum.
- The amount of sample used by them varies from 10 to 600 mg.
- The range of flow rate used by them was between 2.5 and 167 mL min^{-1}.
- The reference material was quartz, calcined alumina, alumina powder and alpha alumina.
- The number of samples analysed by them was varying from 1 to 7 except in two cases. Out of these two cases, 31 samples were analysed in one case and 15 samples in second case.
- The range of temperature was ambient to 1,000 °C.

This clearly reveals that 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 proneness to spontaneous heating.

Thermogravimetry

This technique is based on loss of sample mass at different temperatures as a result of heating. In this technique a given mass of sample is heated via programmed heating process. The mass of the sample and consequently the loss in sample mass at any temperature is recorded. The rates of losses in sample mass are derived and plotted against temperature. These plots are named as TG curves. When this technique is applied under oxidizing conditions, the curve obtained is called the "burning profile" of the sample and one such curve is given in Fig. 2. From burning profile, ignition point, maximum burning rate and temperature of maximum burning rate, end of combustion can be determined. Interpretation of these data only from the TG technique is very difficult. For example, after the end of the moisture release, should the first point of loss in mass be accepted as the ignition point? Coal samples have a considerable amount of volatile matter contents, some of which are easy to desorb from coal surface during heating and they leave coal structure without burning. Furthermore, some of volatile components such as water vapour from clay minerals or carbon dioxide from carbonates releasing at higher temperatures are noncombustible. Losses in mass as a result of the removal of such volatiles may be supposed as burning the sample wrongly.

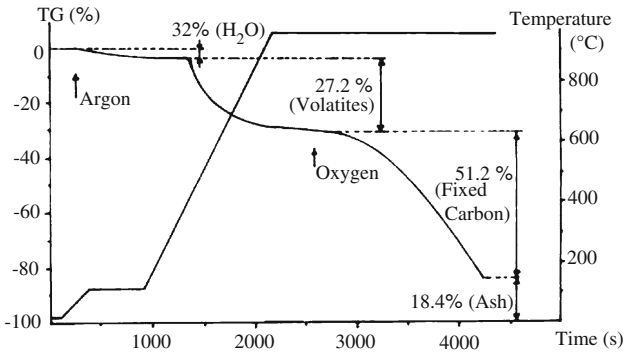

Fig. 2 Different Stages of TG curve of a coal sample

Different researchers have applied TG technique for studying spontaneous heating susceptibility of coal samples. The earliest researchers who contributed in this subject, are Ciuryla and Welmar [22]. They performed thermogravimetric characterization of four different coals at a heating rate of 20 °C min^{-1}, with a flow rate of 1,000 mL min^{-1} in helium atmosphere up to 1,000 °C and their chars to obtain fundamental information on pyrolysis and char reactivity of coals. Mass loss as a function of temperature was systematically determined for each coal heated in helium atmosphere. The results indicate that temperature of the maximum rate of devolatilisation increases with heating rate for all coals. Subsequently, Cumming [23] developed a method for describing the reactivity or combustibility of solid fuels, such as lignite, bituminous coals and petroleum coke, in terms of weighted mean apparent activation energy, derived from simultaneous thermogravimetric analysis (TG/DTG) readings on a 20 mg sample heated at a constant rate 15 °C min^{-1} up to 900 °C in air atmosphere with a flow rate of 75 mL min^{-1}. He studied 22 samples and proposed that mean activation energy method should be the established method that involved recording overall temperatures on the burning profile curve. Smith and Neavel [24] carried out TG experiments of 66 coals in the temperature range between 25 and 1,000 °C using air atmosphere at a heating rate of 15 °C min^{-1}. The amount of sample used in thermogravimetric analysis was 300 mg and they observed that high vitrinite and low inorganic coals played a major role in coal characterization. The rate data were fitted to an Arrhenius equation and plots showed four distinct regions of combustion. Pranda et al. [25] used combustion experiments, i.e., TG/DTA in air atmosphere for one coal of particle size of −72 mesh and the amount of sample taken was 10 mg. The sample was heated during experiments at a

rate of 5 °C min^{-1} for temperature range between 200 and 700 °C. This study showed that the ignition temperature decreased for treated samples, and ignition temperature and kinetics data of the coal sample could be determined from above results. Podder and Majumder [26] investigated the thermal behaviour of five Bangaladesi coals of particle size −100 mesh by using DTA and TG analysis. The experiments were carried out in nitrogen atmosphere with a flow rate of 100 mL min^{-1} and the amount of sample used by them were 10 mg, which was heated at a constant heating rate of 10 °C min^{-1} up to a temperature range from 30 to 700 °C. The TG results indicated that chemical reactivity of the coal samples initially at 80–110 °C was due to loss of water, i.e., about 3–8%. There are two other major reactions at around 300–600 °C region, where the maximum loss of volatile materials of about 20–27% occurs due to primary and secondary devolatilisation.

Alonso et al. [27] studied pyrolysis and combustion behaviour of 10 coals with different ranks and maceral composition by TG. The amount of sample was 13 mg and particle size of samples was −400 mesh. The samples were heated at 25 °C min^{-1} in a temperature range of ambient to 1,000 °C in air atmosphere with a flow rate of 50 mL min^{-1}. Results showed that pyrolysis curves of coals did not match at all with any specific feature of corresponding combustion profiles, and temperature of initiation of both processes were very different in the low-rank end, to become similar only for coal ranks of similar vitrinite reflectance and above. Kok and Keskin [28] applied complex thermal analysis technique (TG/DTG, DTA) in the determination of calorific values of 10 coals from different origins. They used −60 mesh particle size samples, sample amount 10 mg, heating rate 10 °C min^{-1} and the behaviour of samples was studied in temperature range from 20 to 800 °C in nitrogen/air atmosphere with a flow rate of 50 mL min^{-1}. The calorific values, those obtained by thermal analysis, were compared with an adiabatic bomb calorimeter by the standard ASTM method. Thermal behavior of four coal samples was investigated using simultaneous TG/DTG and DTA methods by Kok [16]. The particle size of sample was −60 mesh and amount of sample was 10 mg. Experiments were carried out in air atmosphere with a flow rate of 167 mL min^{-1} and heating rate of 10 °C min^{-1} in a temperature range from 20 to 900 °C. Two temperature regions of increased chemical reactivity were evident in coal samples studied and two different models were applied to determine kinetic analysis of the samples. Avid et al. [29] studied coal samples of Shivee Ovoo deposits in nitrogen/CO_2 atmosphere with different heating rates; i.e., 10, 20, 30, 40 and 50 °C min^{-1} in a temperature range between ambient to 1,000 °C. It has been non-isothermally pyrolysed in a thermogravimetric analyzer to determine the influence of temperature, heating rate and purge gas employed on the thermal degradation of the samples. The coal was also investigated in a fixed bed reactor to determine the influence of temperature and heating rate of the pyrolysis on the yield of products and composition of the gases evolved. The main gases produced were H_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 and also minor concentrations of other gases. Ozbas et al. [30] used TG/DTG to determine the kinetic analysis of four different coals and effect of cleaning process on kinetic parameters of raw and cleaned coal samples from Soma, Tuncbilek and Afsin-Elbistan regions. The amount of sample was 10 mg and particle size was −60 mesh. The samples were heated at 10 °C min^{-1} from 20 to 900 °C in air atmosphere with a flow rate of 50 mL min^{-1}. Kinetic parameters of the samples were determined using Arrhenius and Coats and Redfern kinetic models. Ozbas et al. [31] carried out TG/DTG experiments of four samples of particle size of −60 mesh, amount 10 mg, at four different heating rates, i.e., 5, 10, 15, and 20 °C min^{-1} from 20 to 900 °C in air atmosphere with a flow rate of 50 mL min^{-1} to determine the effect of heating rate on the thermal properties and kinetics of raw and cleaned coal samples from Soma, Tunçbilek, and Afsin-Elbistan regions. Peak and burnout temperatures were measured for all the samples with an increasing heating rate. Kinetic parameters of the samples were determined using an Arrhenius type kinetic model and it was observed that activation energies of all the samples were affected inversely when the heating rate was increased. Peak temperatures of Afsin-Elbistan raw feed increased uniformly as the heating rate was increased. This uniform increase of peak temperature was also observed for Afsin-Elbistan cleaned feed up to a 15 °C min^{-1} heating rate. But the peak temperature of cleaned feed decreased when 20 °C min^{-1} heating rate was applied. The lowest peak temperatures were obtained at 5 °C min^{-1} and 20 °C min^{-1} for raw and cleaned feeds of Afsin-Elbistan, respectively. Burn out temperatures of both samples increased uniformly with an increasing heating rate. The heating rate affected activation energies of Afsin-Elbistan raw and cleaned feeds in a very wide range. The highest activation energies for both samples were calculated at a 20 °C min^{-1} heating rate.

Kizgut et al. [32] characterized a set of seven bituminous coal chars of particle size of −200 mesh by IR spectroscopy, TG and elemental analysis. The amount of samples used in their experiment was 10 mg. The samples were heated at 10 °C min^{-1} from ambient to 700 °C in nitrogen atmosphere with a flow rate of 15 mL min^{-1}. The reactivity of these samples was also studied and correlated with coal parameters of mean vitrinite reflectance, fuel ratio and Hydrogen/Carbon (H/C) ratio. The data suggested that reactivity as determined could be correlated with the

mean vitrinite reflectance, fuel ratio and H/C ratio. Sonibare et al. [33] investigated five coal samples from Nigeria by thermogravimetric (TG) analysis. They performed experiments in following conditions; i.e., particle size of −100 mesh, amount of sample 10–15 mg, heating rate 10 °C min^{-1}, flow rate 50 mL min^{-1}in air/nitrogen atmosphere. Thermal decomposition in air (combustion) and inert (pyrolysis) atmosphere in a temperature range from 25 to 1,000 °C classified the coals as belonging to the low-rank class, within the lignite and sub-bituminous group. The coals were not cokable alone but could serve as suitable blends with coking coal of higher ranks. The apparent activation energies of the combustion and pyrolysis processes ranged from 68.5 to 90.0 kJ mol^{-1} and 34.1 to 57.2 kJ mol^{-1}. Umar et al. [34] studied two Indonesian low rank coals with sample particle size of −200 mesh, heating rate 10 °C min^{-1} from ambient to 800 °C in air atmosphere with a flow rate of 25 mL min^{-1} to know the characteristics of both the raw and upgraded coal by differential thermal and thermo gravimetric analysis. The amount of sample was 500 mg. Mass loss in coal with a temperature below 150 °C related to removal of moisture and mass loss with a temperature above 150 °C was due to the de-volatilization and combustion of volatile matter and char. For upgraded coal, the first peak decreased significantly due to the removal of moisture during upgraded brown coal (UBC) process. The second peak, equivalent to the removal of volatile matter, did not change by the UBC process. Therefore, the third peak increased up to 619 mV that appeared to be the highest. The increase in the third DTA peak, observed for the upgraded coal, was caused by the main heat released in the combustion of upgraded coal. Based on this fact, it seems that the heating value of upgraded coal was higher than that of the raw coal. Gunes et al. [35] heated 12 numbers of Turkish coal samples at a constant heating rate of 20 °C min^{-1} from a temperature range between 140 and 900 °C in nitrogen atmosphere with a flow rate of 250 mL min^{-1}. The kinetic model that described the mass loss of Turkish coals under pyrolysis conditions had been investigated. Non-isothermal thermogravimetric analysis data was compared with the predictions of single first-order and distributed activation energy models. It was observed that the distributed activation energy model appeared to provide a quantitatively satisfactory description of the devolatilization behavior of Turkish coals. Kok [36] used TG/DTG and DSC to obtain information on the temperature-controlled combustion characteristics of 17 coals of different origins from Thrace basin of Turkey. Experiments were performed in air atmosphere with a flow rate of 50 mL min^{-1} from 20 to 600 °C at a heating rate of 10 °C min^{-1}. The amount of sample was 10 mg and particle size was −60 mesh. The DSC/TG curves clearly demonstrate distinct transitional stages in all the coal samples studied. Reaction intervals, peak and burn-out temperatures of the coal samples were also determined. Two different kinetic methods known as, Arrhenius and Coats–Redfern, were used to analyze the kinetic data and the results were discussed. Wachowski and Hofman [37] studied four brown coals from Konin mine and sub-bituminous coal from Sosnica mine, Poland by thermogravimetric (TG-DTG) method. The amount of sample was 10 mg and particle size of sample was −170 mesh. Samples were heated at constant heating rate of 3 °C min^{-1} from a temperature range between 20 and 1,000 °C in helium atmosphere. Analysis of TG-DTG curves had showed that coal samples ammoxidised at the higher temperature show slightly lower thermal stability. It was established the importance of the sequence in processes of carbonisation and ammoxidation. Both the amount of nitrogen introduced on the surface of studied carbonaceous materials and the thermal stability of nitrogen groups were affected. Mianowski et al. [38] carried out four experiments of brick-shaped carbonaceous materials (carbon deposits from coke oven, coke and electrographite) of 500 mg using thermobalance in static air. The sample was heated from ambient to 900 °C at a constant heating rate of 30 °C min^{-1}. Analysis of kinetics of the process was carried out using both classical (Arrhenius law) and newer (three-parametric equation) methods. In classical approach two types of kinetic equations were used in calculations: differential and integral. The results showed that, independently on kinetic variables (α: conversion degree or m: mass of sample) used in differential equations, kinetics of combustion of brick-shaped carbonaceous materials is characterized by only one pair of Arrhenius coefficients: activation energy (E) and pre-exponential constant (A). At the same time the integral equation demonstrated distinction in relation to methods based on differential equations, generating higher activation energies and separate isokinetic effect (IE). Parallel IE showed that kinetic analysis had to encompass activation energy in connection to second coefficient, pre-exponential constant A, depending on assumptions made for kinetic equations. On the other hand three-parametric equations allowed describing kinetic of combustion in alternative way using only one experimental value—initial temperature in the form of point of initial oxidation (PIO)—and also offered new methods of interpretation of the process. Haykiri-Acma et al. [19] used DTA and differential thermogravimetric techniques for studying of seven coking, semi-coking and non-coking bituminous coals from Zonguldak basin, Turky. The amount of sample taken was 40 mg of particle size of −65 mesh and sample was heated up to 1,000 °C at a constant rate of 40 °C min^{-1} in air atmospheres with a flow rate of 40 mL min^{-1}. The thermal data from both techniques showed some differences depending on the

proximate analysis of the samples. Noncombustible components of the volatile matter led to important changes in thermal behaviour. Sis [20] utilized TG/DTG and DTA techniques to examine the relationship between particle size and combustion kinetics and combustion properties of one lignite sample. The sample was heated at constant heating rate of 10 °C min^{-1} from ambient to 900 °C in air atmosphere with a flow rate of 50 mL min^{-1}. The amount of sample was 10 mg and reference material was alpha alumina. DTA curves displayed one endothermic peak in the Stage 1 for all the samples denoted the moisture release from the samples. Two or three exothermic peaks aroused in Stage II were attributed to the stepwise volatile release and the burning of heterogeneous organic matter in coal samples. The exothermic peak in the Stage III resulted from the decomposition of mineral matter in the samples. Sensogut et al. [39] observed that a number of physical features of coal can be determined as the function of temperature by TG. The experimental parameters used by them were sample size −150 mesh, heating rate 10 °C min^{-1}, sample amount 100 mg in nitrogen atmosphere up to temperature range of ambient to 1,600 °C. The thermogravimetric behavior and physicochemical characteristics of 10 Turkish coals have been derived and a statistical relationship was also established between these characteristics. Ozbas [21] determined the relationship between particle size and pyrolysis characteristics of Elbistan lignite by using thermogravimetric (TG/DTG) and DTA techniques of 15 samples. Lignite samples were separated into different size fractions and the amount of sample used in experiments was 10 mg. Experiments were conducted at non-isothermal conditions with a heating rate of 10 °C min^{-1} under nitrogen atmosphere with a flow rate of 50 mL min^{-1} up to 900 °C. The reference material used during experiments was alpha alumina. Pyrolysis regions, maximum pyrolysis rates and characteristic peak temperatures were determined from TG/DTG curves. Thermogravimetric data were analyzed by a reaction rate model assuming first-order kinetics. Apparent activation energy (*E*) and Arrhenius constant (*A*r) of pyrolysis reaction of each particle size fraction were evaluated by applying Arrhenius kinetic model. The apparent activation energies in the essential pyrolysis region were calculated as 27.36 kJ mol^{-1} and 28.81 kJ mol^{-1} for the largest (−2,360 to +2,000 micrometer) and finest (–38 micrometer) particle sizes, respectively.

A critical study of the work carried out by different researchers indicates that different experimental conditions for TG 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 2. A study of Table 2 clearly reveals the followings:

- The particle size of coal samples varied from −8 to −400 mesh.
- Variation of heating rate was between 3 and 50 °C min^{-1}.
- The sample was studied in atmospheric air, nitrogen, helium and carbon dioxide.
- The amount of sample used by them varied from 10 to 500 mg.
- The ranges of flow rate used by them were between 15 and 1,000 mL min^{-1}.
- The reference material was alumina and alpha alumina.
- The range of temperature was from ambient to 1,600 °C.
- The number of samples analysed by them was varying from 1 to 66.

This clearly reveals that there is no unanimity on the experimental parameters used by different researchers while carrying out TG experiments. If the experimental parameters in TG experiments 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 proneness to spontaneous heating.

Differential scanning calorimetry

Differential scanning calorimetry is a technique in which the difference in energy inputs 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 programme. In this technique ordinate value of an output curve at any given temperature is directly proportional to 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. A sample DSC curve is presented in Fig. 3 for reference. By this technique, coal samples can be studied under experimental conditions that simulate spontaneous heating process of materials.

The earliest research was carried out by Mahajan et al. [40] for studying spontaneous heating of coal in DSC technique. They reported differential scanning calorimetric curves for 12 coals of various ranks in a helium atmosphere with a flow rate of 1 mL min^{-1} and temperatures between 100 and 580 °C at a constant heating rate of 10 °C min^{-1}. The amount of sample used in their study was 20 mg and 12 mg and reference material was alumina. They concluded that the thermal effects of coals ranging in rank from anthracite to bituminous coals were endothermic. Exothermic heats were observed only in the case of subbituminous coals or lignite. The net thermal effects were found to be strongly rank dependent. Rosenvold et al. [41]

Table 2 Experimental parameters used by different researchers in TG studies on spontaneous heating of coal

Sl. no.	Name of the author	Year	Parameters							
			Particle size/mesh	Heating rate/°C min^{-1}	Atmosphere	Sample amount/mg	Flow rate/mL min^{-1}	No. of sample studied	Reference material	Temperature range/°C
1.	Ciuryla and Welmar [22]	1979	–	20	Helium	–	1,000	4	–	Ambient to 1,000
2.	Cumming [23]	1980	–	15	Air	20	75	22	–	Ambient to 900
3.	Smith and Neavel [24]	1981	–	15	Air	300	–	66	–	Ambient to 1,000
4.	Pranda et al. [25]	1999	−72	5	–	10	–	1	–	200–700
5.	Podder and Majumder [26]	2001	−100	10	Nitrogen	10	100	5	–	30–900
6.	Alonso et al. [27]	2001	−400	25	Air	13	50	10	–	Ambient to 1,000
7.	Kok and Keskin [28]	2001	−60	10	Nitrogen Air	10	50	10	–	20–800
8.	Kok [16]	2002	−60	10	Air	10	167	4	–	20–900
9.	Avid [29]	2002	–	10, 20, 30, 40, 50	N_2 CO_2	500			–	Ambient to 1,000
10.	Ozbas et al. [30]	2002	−60	10	Air	10	50	4	–	20–900
11.	Ozbas et al. [31]	2003	−60	5, 10, 15, 20	Air	10	50	4		20–900
12.	Kizgut et al. [32]	2003	−200	10	Nitrogen	10	15	7	–	Ambient to 700
13.	Sonibare et al. [33]	2005	−100	10	Air Nitrogen	10, 15	50	5	–	25–1,000
14.	Umar et al. [34]	2005	−200	10	Air	500	25	2	–	Ambient to 800
15.	Gunes et al. [35]	2005		20	Nitrogen		250	12	–	140–900
16.	Kok [36]	2005	−60	10	Air	10	50	17	–	20–600
17.	Wachowski and Hofman [37]	2006	−170	3	Helium	10	–	4	–	20–1,000
18.	Mianowski et al. [38]	2006		30	Air	500	–	4	–	Ambient to 900
19.	Haykiri-Acma et al. [19]	2006	−65	20	Air	20	–	7	Alumina	Ambient to 1,000
20.	Sis [20]	2007	−8+10 to −400	10	Air	10	50	1	Alpha alumina	Ambient to 900
21.	Sensogut et al. [39]	2008	−150	10	Nitrogen	100		10		Ambient to 1,600
22.	Ozbas [21]	2008	–	10	Nitrogen	10	50	15	Alpha alumina	Ambient to 900

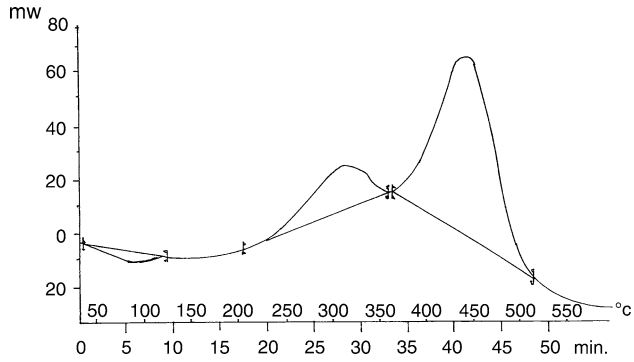

Fig. 3 Different stages of DSC Thermo-gram of a coal sample

analyzed 21 bituminous coal samples from Ohio by DSC and non-isothermal thermogravimetric. Three regions of endothermic 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 at temperatures above 550 °C probably corresponded to cracking and coking processes subsequent to pyrolysis step. Rajeshwar [42] applied differential scanning calorimetry and TG to study coal, oil shale, and oil sands. DSC has been used to characterize 12 U.S. coals of varying ranks from anthracite to lignite. Ismail and Walker [43] studied oxygen chemisorption on a number of coal chars in oxygen atmosphere at 100 °C by using DSC and TG. They studied 16 numbers of 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 °C. They correlated heat release and mass of oxygen chemisorbed as a function of reaction time with Elovich plots. They observed that rate of heat release and mass increase generally decreased with increasing rank of original coal. They also observed that rate of heat release upon oxygen chemisorption also generally increased as rates of gasification of chars at higher temperatures in air increased. Kok [44] investigated thermal behaviour of lignite by DSC, TG/DTG, high-pressure thermo-gravimetric (HPTGA), and combustion cell experiments. He studied one coal sample of particle size of −60 mesh in air atmosphere with a flow rate of 50 mL min^{-1}. Different heating rates were applied; i.e., 5, 10, 15, 20 and 25 °C min^{-1} in a temperature range between 20 and 600 °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 °C and reached a maximum rate at 410 °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 et al. [45] found that differential scanning calorimetry is a useful technique to investigate early stages of the oxidation of coal. Experiments were carried out for three coal samples in oxygen atmosphere with flow rate of 20 mL min^{-1}, heating rate 10 °C min^{-1}, temperature range ambient to 600 °C, particle size of −100 mesh and amount of sample was 10 mg. They proposed that 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 et al. [31] determined combustion behaviour and kinetic analysis of raw and cleaned coal samples of different size fractions by using DSC. They studied four coal samples and amount of sample used in their study was 10 mg. Experiments were carried out in air atmosphere with a flow rate of 50 mL min^{-1}, heating rate of 10 °C min^{-1} and temperature range was between 20 and 600 °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 °C. The second stage was exothermic region due to combustion and was observed in the temperature range of 150 to 600 °C. Kinetic parameters of the samples were determined using Roger and Morris kinetic model.

Panigrahi and Sahu [17] used DSC, DTA, wet oxidation potential, crossing point temperature for determination of susceptibility of 31 Indian coals to spontaneous heating. They used particle size −72 mesh, amount of sample 10 mg, in oxygen atmosphere with a flow rate of 20 mL min^{-1}, heating rate of 30 °C min^{-1}, temperature range between ambient to 500 °C and alumina as reference material in their study. Exhaustive correlation studies between susceptibility indices and intrinsic properties have been carried out for identifying the appropriate parameter to be used for classifications. The identified parameters were used as inputs to artificial neural network (ANN). Adoptive resonance theory of ANN has been applied to classify coal seams into four different categories. Kok [36] used differential scanning calorimetry and TG to obtain information on temperature-controlled combustion characteristics of 17 coals of different origin from Thrace basin of Turkey. Experiments were performed in air atmosphere with a flow rate of 50 mL min^{-1}, particle size of −60 mesh, amount of sample 10 mg, temperature range between 20 and 600 °C at a heating rate of 10 °C min^{-1} by using DSC. He calculated the kinetic parameters from Arrhenius and Coats–Redfern plots. The study revealed that two temperature regions of chemical reactivity, elimination of water and primary carbonization, were evident in all of the coal samples studied. It was observed that activation energies of samples were varied in range of 54–92 kJ mol^{-1}. Elbeyli and Piskin [18] determined thermal characteristics and kinetic parameters of cleaned Tunçbilek lignite by using DTA/TG/DSC thermal analysis system

both for combustion and pyrolysis reactions. The experiments were carried out in one lignite sample of particle size of −65 mesh, sample amount 10 mg in air/nitrogen atmospheres with a flow rate of 100 mL min^{-1}, heating rate 10 up to 1,000 °C min^{-1}. Krzesinska et al. [46] 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) methods. The amount of sample used in their experiment was 7 mg and sample was heated at 10 up to 520 °C min^{-1} in nitrogen atmosphere with a flow rate of 50 mL min^{-1}. The mass 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 mass loss of coal blends was found to be additive parameter. The DSC curves 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 all 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 3. A study of Table 3 clearly reveals the followings:

- The particle size of coal samples varied from −60 to −100 mesh.
- Variation of heating rate was between 5 and 30 °C min^{-1}.
- The sample was studied in nitrogen, atmospheric air and oxygen atmospheres.
- The amount of sample used by them varied from 7 to 20 mg.
- The range of flow rate used by them was between 1 and 100 mL min^{-1}.
- The reference material was alumina.
- The number of sample analysed by them was varied from 1 to 4 except in four cases, i.e., 12, 16, 17 and 31 samples.
- The range of temperature was ambient to 1,000 °C.

This clearly reveals that there is no unanimity on the experimental parameters used by different researchers in DSC experiments. Since the experimental parameters in DSC experiments are different, the results of two samples analysed by two experimental conditions will not be comparable for indexing the coal with respect to their proneness to spontaneous heating.

Table 3 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/°C min^{-1}	Atmosphere	Sample amount/mg	Flow rate/mL min^{-1}	No. of sample studied	Reference material	Temperature range/°C
1.	Mahajan et al. [40]	1977	–	10	Helium	20, 12	1	12	Alumina	100–580
2.	Ismail and Walker [43]	1989	−100	10	N_2		45	16		Ambient to 600
3.	Kok [44]	1997	−60	5, 10, 15, 20, 25	Air	–	50	1	–	20–600
4.	Garcia et al. [45]	1999	−100	10	Oxygen	10	20	3	–	Ambient to 600
5.	Ozbas et al. [31]	2003		10	Air	10	50	4	–	20–600
6.	Panigrahi and Sahu [17]	2004	−72	30	Oxygen	10	20	31	Alumina	Ambient to 500
7.	Kok [36]	2005	−60	10	Air	10	50	17	–	20–600
8.	Elbeyli and Piskin [18]	2006	−60	10	Air Nitrogen	10	100	1	–	Ambient to 1,000
9.	Krzesinska et al. [46]	2009	–	10	Nitrogen	7	50	3	–	Ambient to 520

Conclusions

The critical analysis of the literature survey on the application of DTA, TG and DSC technique and summarised data presented in Tables 1, 2 and 3 clearly reveals the following salient features.

- DTA and TG techniques have been applied extensively for finding out the susceptibility of coal to spontaneous heating.
- DSC technique has been applied by only a few researchers for studying the susceptibility of coal to spontaneous heating and fire.
- Except in one or two cases these three techniques (DTA, TG and DSC) have been applied to less number of samples and generally the number of samples varies from 1 to 10.
- It may also be observed that 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 these three techniques.

Therefore, the future direction of research should be to finalise the experimental standards for these three techniques and applied extensively for large number of coal seams. 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, which will help them to save several million tones of coal burning in mines due to fire all over the world. This will improve production, productivity and safety in mines. In addition, it will reduce the pollution load to the atmosphere.

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