Application of TG Technique to Determine Spontaneous Heating Propensity of Coals

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Abstract

The TG method is applied to eleven coal samples of varying rank collected from across the Jharia coalfield, India to determine spontaneous heating susceptibility. Previous literature does not agree as to the TG experimental parameter that characterises the spontaneous heating susceptibility of coal. A series of TG experiments were performed on triplicate samples of each coal to determine the susceptibility of coal to spontaneous heating. Each prepared sample had the following properties: mass-10mg, size distribution -212 μ m, and were subjected to a sample gas flow rate of 40 ml min⁻¹ and a balance gas flow rate of 60 ml min⁻¹ under the following four different heating rates: 1, 5, 15 & 30 °C min⁻¹. The study concludes that the heating rate of 5 °C min⁻¹ should be used to determine the spontaneous heating susceptibility. The experimental data obtained is subjected to chemo-metric tools i.e. principal component analysis (PCA) and hierarchical clustering analysis (HCA) to establish any linkage between the coal characteristics parameters and spontaneous heating susceptibility indices. These analyses reveal that the self-heating (T_{sh}) and ignition temperature (T_{ign}) determined from the TG experiment results may indicate the susceptibility of coal to <u>spontaneous</u> heating, which is corroborated by well-established standard experiments as well as with field observations. **Keywords:** Coal, Thermo-gravimetic Analysis (TG), Spontaneous Heating, Jharia coalfield,

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Highlights:

- Development of an experimental method (i.e. experimental parameters) to determine spontaneous heating of coal.
- There is an increase in the mass of coal samples within the low-temperature zone (200 350 °C) before the ignition point of the coal which may be due to oxygen adsorption at the surface.
- TG experiment results (T_{sh} and T_{ign}) is an indicator to determine the spontaneous heating propensity of coals
- TG experiment results are statistically analyzed to explore the efficacy for its potential wider applicability
- Comparative study of the field observations, TG experiment and standard CPT results with subsequent statistical analysis corroborate the same conclusion

1.0 Introduction

Over the last 140 years, the Indian coalfields have experienced a large number of extensive open and concealed fires[1]. Approximately 70% of these fires are due to spontaneous heating [2]which results in the loss of a key natural resource, which detrimentally impacts the national economy, health, and environment. Literature survey reveals that various researchers have adopted different methods to study the mechanism of spontaneous heating as well as to assess the propensity of coals towards spontaneous heating under laboratory conditions and the related field conditions[3-6]. Amongst these methods, three different thermal analysis techniques i.e. differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) are widely used to study coal characteristics, reactivity potential, compositional characteristics and propensity towards spontaneous heating. In thermal analysis studies, researchers have developed different techniques to determine the susceptibility of coal towards spontaneous heating [4, 5, 7-14]. Researchers standardize the experimental parameters of the DTA and DSC techniques to identify the susceptibility of coal to spontaneous heating. TG techniques have been applied by a few researchers to study the susceptibility of coal to spontaneous heating, but does not agree as to both the choice or change required in the experimental parameters to characterize the susceptibility of the coal to spontaneous heating[8]. TG studies of coal require the specification of the following experimental parameters: the mass of the coal sample, the particle size distribution of the sample, the reaction gas species, the flow rate of the reaction gas and the heating rate applied. There is a need to develop a standard experimental method in the use of TG methods to determine the proneness of coals to spontaneous heating of coal. The process of coal spontaneous combustion could be divided into four stages, including dehydration and desorption Stage, oxidation stage, combustion stage, and burnout stage. The mass-loss rates of coal were independent of heating rates below ignition temperatures but expanded and shifted to higher temperatures above ignition temperatures [15]. The coal quality significantly affected coal's oxidation in lowtemperature oxidation phase and coal samples with smaller sizes were more prone to combustion. At the lowtemperature stage, the coal sample size exerted no effect on coal's oxidation, at medium- and high-temperature stages, smaller coal sample sizes promoted coal's oxidation[16]. The thermal behaviour of weathered and fresh coal was analyzed and characteristic temperatures of fresh coal were higher than those of weathered coal. The total thermal energy generated from the exothermic onset temperature to 200 °C by weathered coal was much less than generated by fresh coal[17]. For the same coal sample, characteristic temperatures increase along with increasing heating rate and decrease along with increasing oxygen concentration. The effects of heating rate and oxygen concentration on the apparent activation energy of coal are not consistent [18]. For a coal sample subjected to TG analysis, following the initial removal of moisture, there is an observed increase in mass of the sample before a sudden inflexion in the mass curve particular in the coal oxidation process. [9-12, 19]. The key functional groups for this typical coal oxidation mass gain were carboxyl (-COOH) and carbonyl (-C=O)[19]. The smaller the mass gain, the lower the ignition temperature and the more susceptible is the coal to spontaneous ignition [20, 21]. The increase in mass observed is believed to be due to the absorption of oxygen and the forming of coal-oxy-complexes over the coal surface in different temperature zone as per the type of coal. The determined increase in mass and temperature zone data may be used to classify coal as either reactive or non-reactive [10].

This study investigates the application of TG techniques to a series of 11 coal samples of varying rank collected from across the Jharia coalfield, India. Initially, six coal samples were investigated over a range of experimental conditions for sample mass, flow rates, particle size, and heating rate to develop suitable experimental parameters for this study. TG experimental results were analyzed to identify an indicator to determine spontaneous combustion of coal. TG results are further statistically explored with results of other standard methods to determine its efficacy and potential for wider applicability.

2.0 Material and Methods

2.1 Sample Collection and Characterisation

Eleven coal sample was collected (using a channel and chip sampling method) from different coal seams within the Jharia coalfield (JCF), India. The selected coal seams were classified as both fiery and non-fiery [11]. The collected samples were subsequently crushed and sieved to less than -212micron and placed in airtight polythene bags to minimize aerial oxidation. Amongst the eleven samples, the first five samples (sample number: 1, 2, 3, 4 and 5) have past field histories of fires & spontaneous heating, and the remaining six coals possessing no history of active heating. Standard proximate, ultimate, petrographic analysis, crossing point temperature (CPT) and modified crossing point temperature (*CPT_{HR}*) analyses were performed on each of the eleven coal samples, a summary of these results are shown in Table 1[22]. The crossing point temperature (Indian method - *CPT_I*) of coal samples were determined as per the Directorate General Mine Safety (DGMS) circular i.e. DGMS Cir.Tech.3/1975. A spontaneous combustion rig (sponcomb rig) comprises of a vertical furnace, sample holder, a number of thermocouples with their attachment were used to determine modified crossing point temperature. The experiments were carried out by heating 100 g of coal samples slowly @1 °C/min in an atmospheric air flow rate of 200mlmin⁻¹ up to 350 °C. The derivative of coal bed temperature will give a trigger point of the reaction known as modified crossing point temperature i.e. *CPT_{HR}* (temperature where dT/dt is equal to 2.0 °C min⁻¹ because the heating rate is double of programmed temperature 1 °C min⁻¹) [22].

2.2 TG Experimental Methods

Subsequently, TG experiments were performed on the prepared coal samples using a PyrisTG1 instrument of M/s Perkin Almer. The low-temperature oxidation of coal depends upon the mass of the sample, the size fraction of the sample, the atmosphere of reaction, the flow rate of purging gas, the heating rate, and temperature range. Initially, six samples were investigated over a range of experimental conditions, namely: (1) three different masses of sample i.e. 10, 20 and 30 mg; (2) three different flow rates of the purge gas i.e. 20, 40 and 80 ml min⁻¹; (3) three different particle size distributions of the sample i.e. -212 + 105, -105 + 75, -75μ m; (4) four different heating rates i.e. 1, 5, 15 and 30 °C min⁻¹. Each experiment is repeated twice to confirm repeatability and the standard error mean for heating rate 30 °C min⁻¹ varies from 0.4 to 5.7. Total of 78 experiments were carried out for this study excluding repeats. An example of the results obtained for coal sample 1 subjected to the experimental parameter matrix changes described above are given in Fig.1 (a), (b), (c), (d) with the details being presented in the appendix (Figs. A1 to A4).

The results of initial experiments for all six fiery coal samples concludes the following observations:

- Mass, particle size of samples and purging gas flow rate plays an important role. The peak temperature is
 proportional to the mass of the sample.
- The peak widths are sharper as the particle size becomes finer and the peak temperature is shifted depending upon the samples.
- The DTG curves exhibit a shift and some of the samples are not fully combusted at low purge gas flow rates. It also depends upon the heating rate.

Taking the above observations into account it was decided to keep the following experimental parameters constant: the mass of the sample 10 mg; flow rate of purging gas (air) 40 cc min⁻¹; particle size of the sample -212 μ m; temperature range 30 to 920 °C; and to only vary the rate of heating for the final TG study of all the samples. Each experiment is repeated three times for repeatability and a total of 132 experiments were carried out for this study.

3.0 Spontaneous heating propensity study

The spontaneous heating propensity of a coal sample determines when the initial reaction takes place, the reaction span, the rate of reaction and physiochemical reactions. A critical study of TG curve reveals there is an increase in mass i.e. maximum mass gain (W_{mwg}) concerning its previous mass within an identified temperature range (Fig. 2). The maximum mass gain (W_{mwg}) of a sample is determined from the differential mass of the sample temperature at which mass increases or by the determination of the initial reaction (T_{ir}) to maximum mass gain temperature (T_{mwg}) at which the initial reaction finishes. First-order derivatives of a TG curve, known as Differential Thermo Gravimetric (DTG) curves of all of the sample were calculated to determine the self-heating temperature (T_{sh}) or minimum dW/dt temperature (T_{sh})= 0.1, dW/dt for ignition temperature (T_{ign}) (Fig. 3). The results of the above experiments for all eleven coal samples are given in Fig. 4a-e.

An analysis of the results obtained from the spontaneous heating study for all coal samples at five different heating rates is presented on Fig. 4. The initial reaction temperature (T_{ir}) for all of the samples across the five different heating rates lies within the temperature range of 100 °C to 300 °C (Fig. 4a). The T_{ir} varies from 105 °C (sample 2: HR-1 °C min⁻¹) to 285 °C (sample 7: HR 30 °C min⁻¹). The observed T_{ir} values are directly proportional to the applied heating rates, across the range of 1 to 30 °C min⁻¹. There is a measured mass gain (W_{mvg}) for all of the samples tested subjected to the four different heating rates within the temperature range of 100 to 400 °C (Fig. 4b) [10, 20]. The W_{mug} is very high at slow heating rates and low at a higher heating rate. The observed mass gain is inversely proportional to the heating rate between the ranges 1 to 30 °C min⁻¹. The W_{mwg} varies from 0.09 % (sample 6: HR-30) to 3.19 % (sample 3: HR-1). The samples 1, 2 and 3 exhibit the lower W_{mvg} values, whereas samples number 5, 6, 9 and 10 have higher values. The maximum mass gain temperature (T_{mwg}) for all of the samples in different heating rates within the temperature range of 288 °C (sample 3: HR-1 °C min-1) to 375 °C (sample 5: HR 30 °C min-1) (Fig. 4 c). The observed T_{mwg} values are directly proportional to the applied heating rates, across the range of 1 to 30 °C min⁻¹. The self-heating temperatures (T_{sh}) for all of the samples across the different applied heating rates lie within the temperature range of 200 °C to 350 °C (Fig. 4d). The T_{sh} varies from a minimum of 249 °C (sample 3: HR-1) to a maximum of 331 °C (sample 5: HR-30). Except of the sample numbers 2, 8, 10, (HR-1 °C min⁻¹) and 9 (HR-30 °C min⁻¹) the measured T_{sh} values are directly proportional to the heating rates between the ranges 1 to 30 °C min⁻¹. The samples 1, 2 and 3

exhibits the lower T_{sh} values, whereas sample number 5, 6, 9 and 10 have relatively higher values. Across all of the applied heating rates, the ignition temperatures values (T_{ign}) for all of the samples lie within the temperature range of 300 °C to 400 °C (Fig. 4 e). The T_{ign} values vary from a minimum of 321 °C (sample 3: HR-5) to 378 °C (sample 5: HR-30). The observed T_{sh} value is high for the heating rate 1°C min⁻¹ as compared to heating rate 5 °C min⁻¹ and directly proportional to the heating rate between the ranges 5 to 30 °C min⁻¹. The samples 1, 2 and 3 exhibits the lower T_{sh} values, whereas sample numbers 5, 6, 9 and 10 have relatively higher values. Above results reveals that the analysis data (T_{ir} , W_{mwg} , T_{sh} , and T_{ign}) from TG and DTG curves for heating rate 5 °C min⁻¹ gives a better indicator to study of spontaneous heating of coal. The same results are subjected to further statistical analysis.

4.0 Data Treatment and Chemo-metric analysis

Statistical treatment of data including correlation analysis and multivariate analysis (i.e. Principal component analysis (PCA) and Hierarchical clustering analysis (HCA)) were carried out using Statistica-7 to determine the relationship between the TG experimental data sets described in the previous section [23, 24]. Correlation studies were performed to identify any potential relationships between the different spontaneous heating susceptibility indices (seven independent variables - CPT_I, CPT_H, T_i, W_{mwg}, T_{mwg}, T_{sh}, and T_{ign}) and the coal characteristic data, independently provided by the proximate, elemental and petrographic analyses conducted on the coal samples (fourteen dependent variables- M, Ad, VMd, FCd, Cd, Hd, Nd, Sd, Od, Vm, Lm, SFm, Fm, and VRm, whose determined values are presented in Table 1.). The values of the correlation coefficients determined (p<0.05 confidence interval) for the above studies are presented in Table 2. The PCA analyses performed considered the relationships between the above fourteen proximate, elemental and petrographic variables with the seven susceptibility indices determined for each coal sample. For these analyses, the principal components (PCs) with Eigen values greater than 2.0 were considered. The eigenvalues of the first three PCs are given in Table 3 and the projections of these variables on the factor plane (1x2) and (1x3) are depicted in Fig. 5. Hierarchical clustering techniques have been applied to classify the coal tested using the Euclidian distance method (average linkage method). The hierarchal clustering (joining tree) was identified using the above mentioned independent variables and dependent variables. The dendograms obtained from HCA analyses for each of the seven spontaneous heating indices are presented in Figs. 6 (a) to (g), respectively.

A study of the data presented in Table 2 reveals that CPT_{HR} , T_{sh} and T_{ign} , possess the highest significance with the ash content (AC) (r=0.87 to -0.94) and the volatile matter (VM) (r=-0.81 to -0.93). A subsequent PCA analysis reveals a cumulative variance for the first three PCs are found to be more than 80.01%, and for the remaining PCs is very small (<10)(Table 3). The eigenvalues of these three PCs, modify the magnitude of the corresponding eigenvectors significantly (Table 3). The projection of the variables on the factor plane 1x2 and factorial plane 1x3 shows that first group i.e. CPT_h , CPT_{HR} , T_{mvg} , T_{sh} , and T_{ign} , M, A_d are opposite and far from the centre to M, VM_d , FC_d , C_d , H_d , O_d , which signifies they are negatively correlated. It was also observed that the above two groups are spatially grouped, which signifies that a significant correlation between them. The number of clusters obtained from the dendograms for these seven cases is 3, which indicates that the identified clusters are natural (Fig. 6). All the samples are forced to one cluster at a linkage distance of approximately 50 except one 80 (Fig. 6). If the number of clusters remains the same (i.e. 3) then the linkage distance could be achieved as a linkage distance of 22, 24, 33, 20, 22, 21 and 22

respectively. Consequently, it may be concluded that in all cases three clusters are chosen for the classification of coals seams. The details of the clusters so identified from the dendograms for coal samples tested are summarised in Table 4. An analysis of this table reveals that CPT_b CPT_{HR} , T_{sh} , and T_{ign} have same sample number in all three clusters. The eleven coal samples studied were divided into three categories as per their susceptibility to self-heating i.e. low (first cluster: coal samples 1, 2, 3 &4), medium (second cluster: coal samples 6, 7, 8, 9 & 10) and high (third cluster: coal samples 5). The samples 1, 2, 3 and 4 have been identified as being more prone to spontaneous heating from the experimental investigation which is further confirmed by the cluster analysis.

5.0 Validation of results with CPT_I and CPT_{HR}

The correlation studies were carried out among selected seven spontaneous heating susceptibility indices and the results summarized in Table 5. It is observed that the crossing point temperatures (CPT_I and CPT_{HR}) have a positive correlation with T_{mwg} , T_{sh} , and T_{ign} . Among these three spontaneous heating susceptibility indices from TG experiments, T_{sh} and T_{ign} possess a stronger correlation with both CPT_I and CPT_{HR} . It is further concluded that the CPT_I and CPT_{HR} values are proportional to T_{sh} where the correlation coefficient between these two parameters is found to be 0.82 and 0.91, respectively (Table 5 and Fig. 7). Similarly, it is concluded that the CPT_I and CPT_{HR} values are proportional to T_{ign} (where the correlation coefficient between these two parameters is found to be 0.76 and 0.93, respectively). Above study recaps that sample number 1, 2, 3 and 4 exhibit actual experimentally measurable characteristics and confirmed the occurrence of the fire at operating or closed mines (Table 1). The combined evidence provided by an examination of all of the experimental results, and the subsequent statistical analyses performed on these data sets and the aforementioned field observations, corroborate the same conclusions. Consequently, it is proposed that the self-heating (T_{sh}), and ignition (T_{ign}) temperatures determined from TG analyses of coal may be used to determine the susceptibility of a coal to spontaneous heating.

6.0 Conclusions

The results obtained from the TG have been used to study coal characteristics for the last several decades. Several studies have been carried out to determine the spontaneous heating of coals. However, the application of this method requires the identification of a set of experimental parameters to determine the spontaneous heating of coal.

An extensive study of six fiery coal samples was conducted in an attempt to identify the appropriate experimental parameters. These parameters included sample fraction size, the mass of sample, flow rate, and heating rate. The result of the above study reveals that the following experimental parameters (sample size $-212 \,\mu$ m, the mass of sample - 10 mg and flow rate -40 ml min^{-1} sample gas and 60 ml min⁻¹ balance gas, heating rate 5 °C min⁻¹) were suitable to assess the spontaneous heating susceptibility of coals.

TG experimental results reveals there is an increase in the mass within the low-temperature zone (200 - 350 °C) before the ignition point of the coal. The increase in mass gain of coal samples may be due to oxygen adsorption at the surface [10, 20]. The maximum mass gain is inversely proportional to the heating rate.

The TG experiments results are further statistically analysed to explore the efficacy for its potential wider applicability. The basic correlation study, PCA and HCA reveal that the constituent of proximate analysis (A, VM and FC) shows

a better correlation with the results of TG experiments and CPT experiments. The TG experiment results (T_{sh} and T_{ign}) may be considered as an indicator for determination of spontaneous heating of coals.

The hierarchical clustering has been applied for classification of coal seams. The coal samples collected from different seams can be categorized into three clusters, viz. highly susceptible, moderately susceptible and poorly susceptible. A comparative study of the field observations, TG experiment results and standard CPT results with subsequent statistical analysis corroborate the same conclusion.

Acknowledgement

Authors are grateful to Commonwealth Scholarship Commission, UK and The University of Nottingham for their financial support (Commonwealth Scholarship and Fellowship Plan –2010, INCS-2010-192). The authors are obliged to Ministry of Human Resources and Development, Government of India and Council of Scientific and Industrial Research (CSIR) for their kind permission to avail the above fellowship. Authors acknowledge thanks to Direct or, CSIR-CIMFR, all staffs of Mine Fire, Ventilation and Miner's Safety Research Group, CSIR-CIMFR for necessary help for the sample collection.

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(b) Different fraction size of sample



(c) Different flow rate for reaction (d) Different heating rate for reaction **Fig. 1** DTG curve for sample 1 in different experimental parameters





Fig. 2 TGA curve and weight changes in TGA curve (Sample 1)



Fig. 3 DTG curve and different characteristics temperatures (Sample 1)



Fig. 4 Results of TGA and DTG Curves (Tir, Wmwg, Tmwg, Tsh & Tign) of all the coal samples subjected to the five different applied heating rates (1, 5, 10, 15, 30 °Cmin⁻¹).



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Fig. A1 Repeatability of sample 3 at heating rate 5 °Cmin⁻¹



Accepted for Publication January 2020: Journal of Thermal Analysis and Calorimetry

https://doi.org/10.1007/s10973-019-09237-x

Fig. A2 DTG curve for different mass of the sample 2, 3, 9, 10 & 11





Effect of Size at Heating rate 5 °C/min (Sample 11)

Size (-212)

Size

400

Temperature/°C (e) Sample 11

micron

micron

700 800 900 1000

(125+75) micron -75 +53

· 009

500

Temperature/ °C

4.5

3.5

0.5

-0.5

100

200

300

%min⁻¹ 2.5) **510** 1.5

(c) Sample 9

800

(d) Sample 10

1000

Fig. A3 DTG curve for different fraction size of the sample 2, 3, 9, 10 & 11



(e) Sample 11

Temperature/°C

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Fig. A4 DTG curve for different flow rate of the sample 2, 3, 9, 10 & 11

Table 1 Proximate, ultimate, petrographic analysis, CPT and CPT_{HR} for coal samples

| <u>Sample</u> <u>No.</u> | <u>Seam and Mine</u> <u>Name</u> | Fire Stat US | <u>M/</u> %wt | <u>A/</u> <u>%wtd</u> b | <u>VM/</u> %wtdb | FC/ %wtdb | <u>C/</u> <u>%wtdb</u> | <u>H/</u> <u>%wt</u> db | <u>//</u> <u>%wt</u> db | <u>S/</u> <u>%wt</u> db | <u>O/</u> %wtdb | <u>СРТт/</u> <u>°С</u> | <u>СРТ_{НВ}/</u> °С | <u>V_m /</u> % | <u>L</u> m [⊥] % | <u>SF_/</u> % | <u>Em/</u> % | <u>VR</u> m |
|-----------------------------|-------------------------------------|--------------------|------------------|-------------------------------|---------------------|--------------|---------------------------|-------------------------------|-------------------------------|-------------------------------|--------------------|---------------------------|--------------------------------|-------------------|------------------------------|------------------|-----------------|-------------|
| 1 | S-14 Chasnala | Yes | <u>1.14</u> | <u>10.43</u> | 27.49 | <u>62.07</u> | <u>69.11</u> | <u>4.41</u> | <u>1.37</u> | 0.25 | 14.42 | <u>145</u> | <u>160</u> | <u>67.2</u> | 2.4 | <u>21.6</u> | 3.6 | <u>0.74</u> |
| <u>2</u> | S–14 Jitpur | <u>Yes</u> | <u>1.18</u> | <u>10.97</u> | 26.30 | <u>62.73</u> | <u>71.02</u> | <u>4.28</u> | <u>1.41</u> | <u>0.24</u> | <u>12.08</u> | <u>142</u> | <u>163</u> | <u>69.2</u> | <u>1.6</u> | <u>18.8</u> | <u>3.6</u> | <u>0.76</u> |
| <u>3</u> | S-13 Chasnala | <u>Yes</u> | <u>1.16</u> | <u>7.87</u> | <u>29.89</u> | <u>62.24</u> | <u>73.57</u> | <u>4.87</u> | <u>1.45</u> | <u>0.28</u> | <u>11.96</u> | <u>136</u> | <u>151</u> | <u>62.4</u> | <u>1.6</u> | <u>10.4</u> | <u>9.2</u> | <u>0.87</u> |
| <u>4</u> | <u>S–16 Jitpur</u> | <u>Yes</u> | <u>1.30</u> | <u>9.46</u> | 27.22 | <u>63.33</u> | <u>71.63</u> | <u>4.45</u> | <u>1.30</u> | <u>0.29</u> | <u>12.87</u> | <u>152</u> | <u>171</u> | <u>72.0</u> | <u>2.8</u> | <u>23.6</u> | <u>6.8</u> | <u>0.97</u> |
| <u>5</u> | S-11 Enna | <u>Yes</u> | <u>0.61</u> | 21.07 | <u>21.27</u> | <u>57.66</u> | <u>64.17</u> | <u>3.96</u> | <u>1.28</u> | 0.00 | <u>9.52</u> | <u>169</u> | <u>207</u> | <u>40.4</u> | <u>0.8</u> | <u>27.2</u> | <u>6.0</u> | <u>1.00</u> |
| <u>6</u> | S-11 Bhalgora | <u>Yes</u> | <u>1.22</u> | <u>16.91</u> | <u>23.48</u> | <u>59.61</u> | <u>69.76</u> | <u>4.20</u> | <u>1.56</u> | <u>0.45</u> | <u>7.12</u> | <u>171</u> | <u>183</u> | 74.4 | <u>3.2</u> | 26.4 | <u>4.0</u> | <u>1.02</u> |
| Z | S-11 Simlabahal | No | <u>1.25</u> | <u>13.57</u> | <u>23.53</u> | <u>62.90</u> | 70.96 | 4.05 | <u>1.50</u> | <u>0.35</u> | <u>9.57</u> | <u>159</u> | <u>177</u> | <u>55.2</u> | <u>1.2</u> | <u>27.2</u> | <u>8.8</u> | <u>1.15</u> |
| <u>8</u> | S–12 Simlabahal | No | <u>1.13</u> | <u>16.93</u> | 21.94 | <u>61.13</u> | <u>66.45</u> | 4.00 | <u>1.37</u> | <u>0.41</u> | <u>10.84</u> | <u>152</u> | <u>177</u> | <u>74.8</u> | <u>5.6</u> | <u>36.0</u> | <u>7.6</u> | <u>1.08</u> |
| <u>9</u> | S-10, Bhalgora | No | <u>0.64</u> | <u>17.30</u> | <u>20.56</u> | <u>62.14</u> | <u>69.41</u> | <u>3.92</u> | <u>1.57</u> | <u>0.29</u> | <u>7.51</u> | <u>165</u> | <u>190</u> | <u>68.4</u> | <u>1.2</u> | <u>46.0</u> | <u>12.8</u> | <u>1.04</u> |
| <u>10</u> | S-10, Simlabahal | No | <u>0.63</u> | <u>16.86</u> | <u>20.86</u> | <u>62.29</u> | <u>69.96</u> | <u>4.12</u> | <u>1.58</u> | <u>0.32</u> | 7.17 | <u>168</u> | <u>180</u> | <u>57.2</u> | <u>1.2</u> | <u>32.0</u> | <u>9.6</u> | <u>1.05</u> |
| <u>11</u> | S-09, Simlabahal | No | <u>0.92</u> | <u>17.04</u> | <u>22.42</u> | <u>60.54</u> | <u>69.30</u> | <u>4.10</u> | <u>1.66</u> | <u>0.41</u> | 7.50 | <u>162</u> | <u>179</u> | <u>64.8</u> | <u>2.0</u> | 25.2 | <u>4.0</u> | <u>1.09</u> |

<u>M- moisture, A -Ash, VM- Volatile matter, FC - Fixed carbon, C- Carbon, H- Hydrogen, N-Nitrogen, S- Sulphur, O- Oxygen, CPT-Crossing point temperature of coal, CPT_{HR} - Modified Crossing point temperature of coal, V_m - Vitrinite, L_m - Liptinite, SE_m - Semi-Fusinite, E_m -Fusinite, VR_m - Vitrinite Reflectance</u>

Table 2 Correlations study between Spontaneous heating susceptibility indices with basic coal

characteristics (significant at p < .05000)

| SI. No. | <u>CPT</u> _I | <u>CPT_{HR}</u> | <u>Tir</u> | <u>W</u> mwg | <u>Tmwg</u> | <u>T</u> sh | <u>Tign</u> |
|------------------------|-------------------------|-------------------------|-------------------|--------------|--------------------|--------------------|--------------------|
| М | -0.57 | -0.66 | <u>0.39</u> | -0.12 | <u>-0.62</u> | <u>-0.72</u> | <u>-0.73</u> |
| <u>A_{db}</u> | 0.86 | <u>0.92</u> | <u>0.09</u> | <u>-0.61</u> | <u>0.75</u> | <u>0.94</u> | <u>0.87</u> |
| <u>VM_{db}</u> | -0.85 | <u>-0.85</u> | <u>-0.16</u> | <u>0.57</u> | <u>-0.83</u> | <u>-0.87</u> | -0.80 |
| FC _{db} | -0.55 | -0.69 | <u>0.07</u> | <u>0.46</u> | <u>-0.31</u> | <u>-0.71</u> | <u>-0.68</u> |
| <u>C_{db}</u> | <u>-0.51</u> | <u>-0.76</u> | -0.04 | <u>0.48</u> | <u>-0.43</u> | <u>-0.76</u> | <u>-0.76</u> |
| <u>H_{db}</u> | <u>-0.75</u> | <u>-0.82</u> | <u>-0.33</u> | <u>0.62</u> | <u>-0.76</u> | <u>-0.79</u> | -0.77 |
| <u>N_{db}</u> | <u>0.39</u> | 0.04 | -0.06 | -0.18 | <u>0.39</u> | 0.21 | 0.02 |
| <u>S_{db}</u> | <u>0.05</u> | <u>-0.31</u> | <u>0.21</u> | <u>-0.46</u> | <u>-0.04</u> | <u>-0.21</u> | <u>-0.47</u> |
| <u>O_{db}</u> | -0.83 | <u>-0.64</u> | -0.08 | <u>0.49</u> | <u>-0.73</u> | <u>-0.70</u> | <u>-0.57</u> |
| <u>V</u> m | <u>-0.30</u> | <u>-0.48</u> | -0.10 | <u>-0.17</u> | <u>-0.48</u> | <u>-0.59</u> | <u>-0.73</u> |
| <u>L</u> | -0.16 | -0.17 | <u>0.10</u> | -0.53 | <u>-0.31</u> | <u>-0.17</u> | -0.36 |
| <u>SF</u> m | <u>0.64</u> | 0.65 | <u>0.19</u> | -0.44 | 0.59 | 0.58 | <u>0.49</u> |
| <u>F_m</u> | <u>0.15</u> | <u>0.17</u> | <u>0.12</u> | <u>0.14</u> | <u>0.31</u> | <u>0.20</u> | <u>0.16</u> |
| <u>VR</u> m | 0.69 | 0.60 | 0.56 | -0.63 | 0.81 | 0.70 | 0.54 |

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 Table 3 Eigenvalues of correlation matrix between Spontaneous heating susceptibility indices

with basic coal characteristics

| SI. No. | Eigenvalue | <u>% Total</u> | <u>Cumulative</u> | Cumulative |
|-----------|-------------------|----------------|-------------------|-------------------|
| 1 | 10.67621 | 50.83909 | <u>10.67621</u> | <u>50.8391</u> |
| 2 | 3.60160 | 17.15045 | <u>14.27780</u> | <u>67.9895</u> |
| <u>3</u> | 2.52588 | 12.02802 | 16.80369 | 80.0176 |
| 4 | <u>1.54092</u> | 7.33771 | <u>18.34461</u> | <u>87.3553</u> |
| <u>5</u> | <u>1.32703</u> | 6.31920 | <u>19.67164</u> | 93.6745 |
| <u>6</u> | 0.55462 | 2.64105 | 20.22626 | <u>96.3155</u> |
| <u>7</u> | <u>0.35072</u> | <u>1.67011</u> | <u>20.57698</u> | <u>97.9856</u> |
| <u>8</u> | 0.23908 | 1.13847 | 20.81606 | <u>99.1241</u> |
| <u>9</u> | 0.09594 | 0.45686 | 20.91200 | <u>99.5810</u> |
| <u>10</u> | 0.08800 | 0.41905 | 21.00000 | 100.0000 |

Table 4 Results of the clustering of the coal sample data sets from the dendograms

| <u>No. of</u> <u>clusters</u> | <u>CPT</u> 1 | <u>CPT_{HR}</u> | <u>Tir</u> | <u>W</u> mwg | <u>T</u> mwg | <u>T</u> _{sh} | <u>Tign</u> |
|----------------------------------|----------------------|---------------------------------|---------------------------------------|-------------------------------------|-------------------------------|---------------------------------|---------------------------------|
| Cluster 1 | <u>1,2,3,4</u> | <u>1,2,3,4</u> | <u>1,2,3,4,6,8,9,10,</u> <u>11</u> | <u>1,2,3,4,6,7,10,1</u> <u>1</u> | <u>1,2,3,4,6,</u> <u>8</u> | <u>1,2,3,4</u> | <u>1,2,3,4</u> |
| Cluster 2 | <u>6,7,8,9,10,11</u> | <u>6,7,8,9,10,1</u> <u>1</u> | <u>5</u> | <u>8,9</u> | <u>5,7,10,11</u> | <u>6,7,8,9,10,1</u> <u>1</u> | <u>6,7,8,9,10,1</u> <u>1</u> |
| Cluster 3 | <u>5</u> | <u>5</u> | <u>Z</u> | <u>5</u> | <u>9</u> | <u>5</u> | <u>5</u> |

Table 5 Correlations study between spontaneous heating susceptibility indices

| | <u>CPT</u> _I | <u>CPT_{HR}</u> | <u>T</u> jr | W _{mwg} | <u>T_{mwg}</u> | <u>T</u> sh | T _{ign} |
|-------------------------|-------------------------|-------------------------|--------------|------------------|------------------------|--------------------|-------------------------|
| <u>CPT</u> 1 | 1.00 | | | | | | |
| <u>CPT_{HR}</u> | <u>0.87</u> | 1.00 | | | | | |
| <u>Tir</u> | 0.24 | <u>0.23</u> | 1.00 | | | | |
| W _{mwg} | <u>-0.56</u> | <u>-0.50</u> | <u>-0.56</u> | 1.00 | | | |
| <u>T_{mwg}</u> | <u>0.77</u> | <u>0.78</u> | 0.31 | -0.35 | 1.00 | | |
| <u>T_{sh}</u> | 0.82 | <u>0.91</u> | 0.21 | -0.50 | <u>0.84</u> | 1.00 | |
| <u>Tign</u> | <u>0.76</u> | <u>0.93</u> | 0.20 | -0.35 | 0.81 | 0.94 | 1.00 |

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Table A1 TGA results

| | | | | | | | | | | | | | | | | cm | | | | | | | |
|-----------|--------------------------|--------------|--------------|--------------|---------------|-------------|--------------|--------------|---------------|--------------|--------------|--------------|-----------------------|-------------|--------------|--------------|----------------------|--------------|--------------|--------------|-----------------------------|--|--|
| Sample | ple <u><i>T</i>ir/°C</u> | | | | <u>Tir/°C</u> | | | | <u>Wmwg/%</u> | | | | <u>Imwg/°C</u> | | | | <u>Tsh/°C</u> | | | | <u>T_{ign}/(°C)</u> | | |
| No. | <u>HR 1</u> | <u>HR 5</u> | <u>HR 15</u> | <u>HR 30</u> | <u>HR 1</u> | <u>HR 5</u> | <u>HR 15</u> | <u>HR 30</u> | <u>HR 1</u> | <u>HR 5</u> | <u>HR 15</u> | <u>HR 30</u> | <u>HR 1</u> | <u>HR 5</u> | <u>HR 15</u> | <u>HR 30</u> | <u>HR 1</u> | <u>HR 5</u> | <u>HR 15</u> | <u>HR 30</u> | | | |
| 1 | <u>104.9</u> | <u>130.6</u> | <u>178.1</u> | <u>195.8</u> | <u>2.85</u> | <u>1.59</u> | <u>0.93</u> | 0.60 | <u>289.0</u> | <u>321.0</u> | <u>342.2</u> | <u>352.8</u> | <u>241</u> | <u>264</u> | <u>302</u> | <u>318</u> | <u>337.4</u> | <u>324.8</u> | <u>349.8</u> | <u>357.3</u> | | | |
| 2 | <u>105.0</u> | <u>125.3</u> | <u>148.3</u> | <u>190.1</u> | <u>2.79</u> | <u>1.49</u> | <u>0.95</u> | <u>0.53</u> | <u>293.1</u> | <u>325.0</u> | <u>345.4</u> | <u>356.6</u> | <u>273</u> | <u>260</u> | <u>299</u> | <u>312</u> | <u>340.3</u> | <u>327.7</u> | <u>352.0</u> | <u>359.4</u> | | | |
| 3 | <u>106.0</u> | <u>122.6</u> | <u>143.7</u> | <u>184.3</u> | <u>3.19</u> | <u>1.73</u> | <u>1.10</u> | <u>0.68</u> | <u>288.1</u> | <u>321.1</u> | <u>340.5</u> | <u>350.3</u> | <u>249</u> | <u>261</u> | <u>295</u> | <u>306</u> | <u>331.7</u> | 321.0 | <u>347.2</u> | <u>354.7</u> | | | |
| 4 | <u>105.5</u> | <u>155.8</u> | <u>175.0</u> | <u>194.9</u> | <u>2.89</u> | <u>1.51</u> | <u>0.95</u> | <u>0.52</u> | <u>293.0</u> | <u>331.0</u> | <u>345.0</u> | <u>360.8</u> | <u>243</u> | <u>263</u> | <u>300</u> | <u>313</u> | <u>340.4</u> | <u>326.6</u> | <u>351.4</u> | <u>357.8</u> | | | |
| 5 | <u>110.7</u> | <u>145.0</u> | <u>190.3</u> | <u>205.0</u> | <u>2.28</u> | <u>1.26</u> | <u>0.86</u> | <u>0.46</u> | <u>310.0</u> | <u>340.6</u> | <u>364.2</u> | <u>374.9</u> | 274 | <u>302</u> | <u>322</u> | <u>331</u> | <u>373.0</u> | <u>359.0</u> | <u>368.5</u> | <u>378.3</u> | | | |
| 6 | <u>132.5</u> | <u>155.9</u> | <u>249.2</u> | <u>275.8</u> | <u>1.99</u> | <u>0.80</u> | <u>0.35</u> | <u>0.09</u> | <u>302.2</u> | <u>328.6</u> | <u>341.1</u> | <u>350.5</u> | <u>267</u> | <u>278</u> | <u>309</u> | <u>322</u> | <u>346.9</u> | <u>332.2</u> | <u>353.6</u> | <u>357.4</u> | | | |
| 7 | <u>153.0</u> | <u>213.7</u> | 236.1 | <u>285.2</u> | <u>2.11</u> | <u>1.08</u> | <u>0.47</u> | <u>0.19</u> | <u>305.0</u> | <u>339.3</u> | <u>355.4</u> | <u>358.1</u> | 275 | <u>281</u> | <u>312</u> | <u>317</u> | <u>355.9</u> | <u>338.9</u> | <u>359.5</u> | <u>363.3</u> | | | |
| 8 | <u>126.1</u> | <u>154.1</u> | <u>235.1</u> | <u>269.5</u> | <u>1.93</u> | <u>0.85</u> | <u>0.42</u> | <u>0.18</u> | <u>298.0</u> | <u>331.0</u> | <u>346.3</u> | <u>356.6</u> | <u>282</u> | <u>281</u> | <u>311</u> | <u>324</u> | <u>352.1</u> | <u>333.2</u> | <u>355.5</u> | <u>356.5</u> | | | |
| 9 | <u>117.1</u> | <u>139.7</u> | <u>142.7</u> | <u>196.8</u> | 2.69 | <u>1.38</u> | <u>0.92</u> | <u>0.52</u> | <u>306.3</u> | <u>338.5</u> | <u>361.0</u> | 372.5 | <u>270</u> | <u>284</u> | <u>325</u> | <u>324</u> | <u>360.5</u> | <u>339.8</u> | <u>365.0</u> | <u>372.6</u> | | | |
| <u>10</u> | <u>127.1</u> | <u>118.9</u> | <u>188.8</u> | <u>201.2</u> | <u>2.61</u> | <u>1.48</u> | <u>0.91</u> | <u>0.53</u> | <u>308.4</u> | <u>339.0</u> | <u>358.9</u> | <u>370.0</u> | <u>284</u> | <u>284</u> | <u>320</u> | <u>330</u> | <u>360.0</u> | <u>339.5</u> | <u>364.9</u> | <u>373.4</u> | | | |
| <u>11</u> | <u>113.9</u> | <u>134.3</u> | <u>171.7</u> | <u>229.2</u> | 2.52 | <u>1.23</u> | <u>0.89</u> | <u>0.40</u> | <u>307.7</u> | 342.8 | <u>357.8</u> | <u>368.3</u> | 276 | <u>287</u> | <u>325</u> | <u>329</u> | <u>353.3</u> | <u>338.7</u> | <u>360.1</u> | <u>369.3</u> | | | |

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