International Research Journal of Multidisciplinary Scope (IRJMS), 2025; 6(3):1399-1407 IRJMS

Original Article | ISSN (O): 2582-631X DOI: 10.47857/irjms.2025.v06i03.05246

Thermal Decomposition Kinetics of Raw and Water Immersed Coal of Raniganj Coalfield Region West Bengal, India

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Abstract

In this work, coal samples were collected from the Kottadih and Kalimati mines of Raniganj Coalfields (RCF). Kottadih is an underground coal mine and Kalimati is an open-cast coal mine, and the samples were divided into two parts. One part of the samples (raw coal) was analyzed by proximate analysis, Thermal Analysis viz Thermo gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) and spectral Analysis i.e. Fourier Transform Infra-Red spectroscopy (FTIR) and the other part of the samples were immersed in water at a ratio of 1:10 for 15, 30, 90 and 180 days. Spectral and kinetic behaviour of water-immersed coal was also studied. In raw coal and water-immersed coal, the dehydration and desorption reaction occur between 40 and 130 °C. The combustion stage is between 260 and 620 °C and finally burn out or decomposition stages start from 620 to 850 °C, the combustion and burnout stages of water immersed coal decreases. The FT-IR analysis of raw coal shows the presence of –OH, –Ar, –CHO, >C=O, >C=C< etc in small amounts and the concentration of these organic functional groups is comparatively higher in water-immersed coal samples. Due to these results, the propensity for spontaneous combustion/fire increases in both water-immersed coal samples of Kottadih and Kalimati mines of RCF.

Keywords: FTIR, Raw Coal, Spontaneous Combustion, TGA/DSC, Water-Immersed Coal.

Introduction

India is the second largest coal production country of the world, prime coal producing region of India is Jharia Coalfield, Raniganj Coalfield (RCF), Singrauli Coalfield etc. Major portion of Indian coal is utilizing in coal-based thermal power stations. These thermal power stations contribute about 70% of electricity production in India. Apart from this, high quality coal produced by Indian coal industries is used by metallurgy industries (1, 2). The importance of Indian coal industry is enormous, but with the time of its production, many problems are approaching, in which mainly environmental pollution, acid mine drainage, coal mine fire and land subsidence are the major ones (3-6). Among all these problems, the problem of coal mine fire is a massive problem, due to which the coal industry is being negatively impacted in two ways, that is, it hindering both coal development and production (7, 8). The principal cause of coal mine fire is spontaneous combustion of coal. Spontaneous combustion of coal is a natural process of oxidation in which coal is oxidized at a slow rate, this is an exothermic reaction by which a small amount of energy is emitted (9-11). This small amount of energy that comes out gradually gets deposited inside the coal mine and this deposited energy increases the rate of chemical reaction that is spontaneous combustion of coal and eventually it takes the form of coal mine fire. This coal mine fire becomes chronic with time and takes the form of smoulder (12, 13). By the study of several research papers related to spontaneous combustion of coal, it is known that the problem of coal mine fire is found more severe form in water-logging coal mines. Water-logging while digging or other mining activities in coal mines is a common occurrence. Due to these the physical and chemical properties of coal alters which accelerates the rate of spontaneous combustion of coal. Whenever water is removed from water-logged coal mine and mining activity is carried out, then the coal dry with the adsorption of water vapour then the temperature of coal surface increases and finally the problem of coal mine fire arises very fast (14). Long term water logging coal may lead to increase

(Received 27th April 2025; Accepted 09th July 2025; Published 30th July 2025)

Long term water logging coal may lead to increase the concentration of –OH, –C=O and other organic functional groups. On the other hand, the moisture content of coal also increases, in this way coal was under the condition of moisture loss with evaporation gradually (15). Due to this moisture loss the coal starts to reveal several degrees of drying contraction and volume contraction and the surface exhibited many cracks, and the crack width, crack length, and humidity in the sample chamber gradually increased. The cause of these changes is the desorption of water molecules from the surface of coal. The increased functional group stuck on the cracks of coal by the process of chemisorption. All these changes occur due to the phenomena of water logging on coal, and this physico-chemical alteration in coal leads to decrease the ignition temperature and makes the susceptible to spontaneous combustion which finally takes the form of coal mine fire (16, 17).

However, in this research, the authors have used proximate analysis, which is a universally accepted method for the physico-chemical study of raw and water-immersed coal samples, taken from underground and opencast coal mines. Also, CPT, TGA and DSC methods have been used for determining the spontaneous combustion characteristics. These methods are known for their accuracy and worldwide acceptance. With the help of FTIR spectroscopy, the organic functional groups present in raw and water-immersed coal have been detected. This helps in confirming which organic functional groups are mainly responsible for spontaneous combustion of coal and which organic functional groups have undergone changes in water-immersed coal. Hence, in this work, an attempt has been made to predict the susceptibility of raw and water-immersed coal in underground and opencast coal mines to spontaneous combustion.

Methodology

Sample Collection and Preparation

Coal samples were collected from two selected coal mines of Raniganj coalfield (Kottadih and Kalimati mines) region West Bengal. The sampling process is done by Indian standard. The collected samples were divided into two parts, first part of the samples was grinding into 212 µ size and placed in air tight container. These samples were analysis by proximate analysis, differential scanning calorimetry (DSC) analysis, thermo gravimetric analysis, crossing point temperature and Fourier-transform infrared spectroscopy (FTIR). The second part of samples were immersed in water in the ratio of 1:10 (Coal: Water) in the lab environment for 180 days. These coal samples were taken out after 15, 30, 90 and 180 days and analysis by the above mention methods. During the process of coal taken out from water, the ratio of coal and water maintained. The details of the samples and their analysis report are given in the following Table 1 and 2.

Table 1: Detailed Analysis Data of Kottadih Colliery, Underground Coal Mines

Colliery Name/ Seam Name	**Sample Code**	IM	VM	Ash	FC	CPT	TGA
Kottadih	KR4/0D	5.99	37.93	15.35	40.73	166.00	276.00
Colliery/ KR4	KR4/15D	8.38	29.89	14.75	46.98	156.00	281.00
	KR4/30D	9.57	38.26	13.43	38.74	144.00	280.00
	KR4/90D	7.29	37.59	20.73	34.39	144.00	280.50
	KR4/180D	5.216	34.16	20.67	39.95	142.00	278.50
	Mean	7.289	35.57	16.99	40.16	150.40	279.20
	Range	5.216-9.57	29.89-38.26	13.43-20.73	34.39-46.98	142-166	276-281

Table 2: Detailed Analysis Data of Kalimati Colliery, Open cast Coal Mines

Colliery Name/ Seam Name	Sample Code	IM	VM	Ash	FC	CPT	TGA
Kalimati	KKM /0D	2.28	25.67	22.10	49.95	185.00	332.00
Colliery/ KM	KKM/15D	5.48	24.88	27.8	41.84	184.00	288.00
	KKM/30D	1.6	22.94	22.98	52.48	179.00	332.00
	KKM /90D	1.69	25.29	20.04	52.98	177.00	332.50
	KKM /180D	1.25	22.01	24.02	52.72	143.00	329.50
	Mean	2.46	24.16	23.39	49.99	173.60	322.80
	Range	1.6-5.48	22.01-25.67	20.04-27.8	41.84-52.98	143-185	288-332

Proximate Analysis

This is universally accepted traditional method of coal analysis for the determination of basic composition of coal, as per Indian standard. This method has done by taking proper care, in this method 1 gram of coal sample having size 212 µ taken in glass crucible and insert into hot air oven at 110°C for an hour the weight difference after heating is the moisture content of coal (18, 19). Another one-gram sample having similar size was taken into a cylindrical silica crucible with lid and heat at 950°C for seven minutes and weight after heating the difference in weight gives the volatile matter content of coal. Finally, 1 gram of coal sample taken in silica crucible and insert into furnace for an hour at 820 ° C after heating the left or residue mass on the silica crucible is ash content of coal (20, 21). The fixed carbon of coal is calculated by using above data and following formula.

% Fixed Carbon = 100 – (% Ash + % VM+ % IM)

The proximate analysis processes have done in CSIR- CIMFR, Barwa road Dhanbad.

Thermal Analysis

Both TGA and DSC analysis is carried out in a single instrument. Thermo gravimetric Analysis (TGA) is based on the variation of mass due to temperature. In this method the coal sample is allow to heat at a range of 30-950°C. The mass of coal decreases with temperature was recorded by the instrument. DSC is also a thermal analysis method in which the sample is first heated by the help of instrumental heat and then by examining the heat emitted or absorbed by the sample, it is ascertained whether the sample reacts exothermically or endothermic ally with oxygen in the presence of air (22, 23). In this work the main purpose to use this instrument is to study the spontaneous behaviour of coal for which we have placed about 10 mg of coal sample in a sample holder and heated the sample at a temperature ranging from 30 to 900°C in the presence of normal air and studied the changes in the thermal behaviour of the sample (24, 25). A number of experiments including repeatability were performed for the two coal samples from the RCF to determine their spontaneous heating behaviour and their results are presented in figure 2 to 5.

Crossing Point Temperature Analysis

The temperature at which the temperature of coal and glycerine bath of Crossing Point Temperature Instrument coincides is called crossing point temperature (CPT). CPT is one of the old methods for determining the susceptibility of coal sample to spontaneous combustion. The spontaneous combustion properties of coal are determined by using CPT methods is based on the rules and circulars of Director General of Mine Safety (DGMS). This method estimates the temperature response of coal sample in a temperature-controlled glycerine bath. This instrument having a controlled heating furnace inside which the coal sample is exposed to temperature rise in presence of oxygen. The susceptibility of coal sample to spontaneous combustion is measured based on the increasing of temperature. In this work air medium has been selected for the application of CPT method. 20 g of coal sample having a particle size of 212 micron is carefully put sample holder, followed by covering the coal sample. The sample holder is placed in a glycerine bath. The temperatures of the glycerine bath and the coal are

carefully recorded using computer-based software tools to determine the CPT of the coal (26).

Fourier Transform Infrared Spectroscopy (FTIR)

Among all the spectroscopy techniques, FTIR spectroscopy is one of the reliable and effective techniques. FTIR spectroscopy mainly detects various functional groups present in an unknown compound by absorbing infrared (IR) light at a specific frequency. The IR spectrum range lies between the visible and microwave of the electromagnetic spectrum. The Infrared (IR) region is divided into three parts, namely, the near IR which is from 12500 to 4000 cm^{-1}, mid IR which is from 4000 to 400 cm^{-1} and far IR which is in the range of 400 to 10 cm^{-1} (27). Apart from this, this spectroscopy has a fingerprint region which is from 650 to 1500 cm^{-1}, which gives the specific identification of the molecule of each compound. For identifying most of the organic compounds, the instrument displays the absorption peak at 4000 to 400 cm^{-1}. Experts identify these peaks and estimate the organic compounds present in them. For this they use previously known reference absorptions like O-H, C-H and N-H stretches in the range of 3000 to 4000 per cm, triple bonds in the range of 2050 to 2500 cm^{-1}, C=O (aromatic ester) or C-N (aromatic amine) in the range of 1126 to 1036 cm^{-1}, C-H (aromatic bonds) in the range of 900-700 cm^{-1}, C=O (aromatic carbonyl) in the range of 1700-650 cm^{-1} etc (28, 29). This instrument has been used to study the functional groups present in raw coal and coal immersed in water.

Results and Discussion

Proximate Analysis

This is universally accepted analytical method for the grading of coal. By this analysis the moisture content (IM), volatile matter content (VM), ash content and fixed carbon content (FC) of coal were determined. IM value of raw KR4 and KKM coal samples were 5.99 % and 2.28% respectively after 15 days of water immersion the value becomes 8.38% and 5.48%. Similarly, the VM content of raw KR4 and KKM coal samples were 37.93% and 25.67% and after water-immersion it reaches to a maximum level of 38%. This value of VM indicates that the coal samples are prone to spontaneous combustion. The experimental data obtained by proximate analysis, TGA/DSC and CPT is shown in Table 1, 2 and Figure 1, 2.

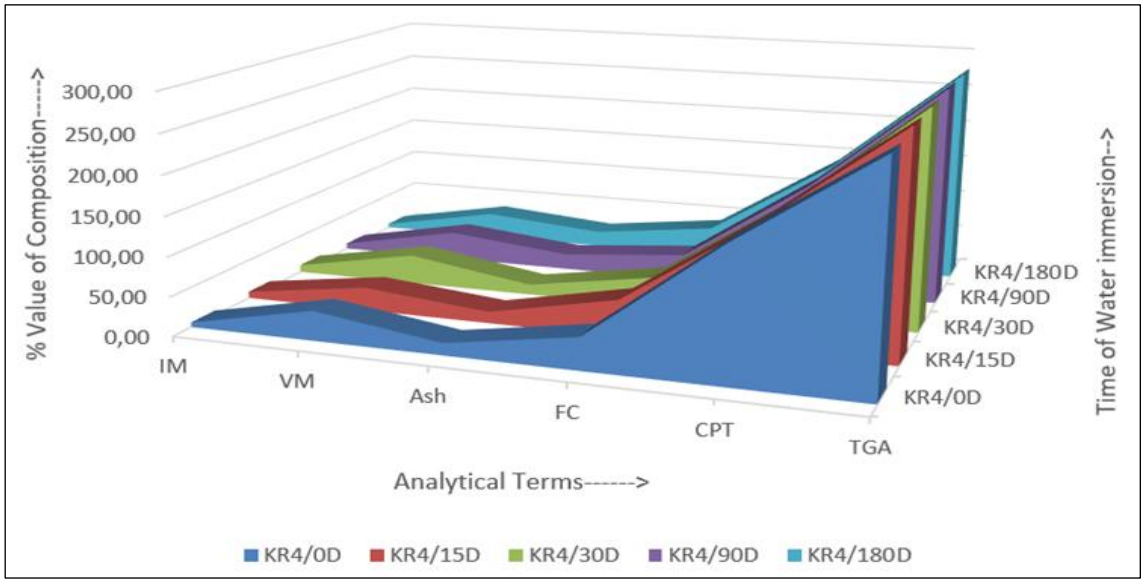

Figure 1: Proximate, TGA, CPT Graph of Kottadih Colliery (Seam KR4) Raw and Water Immersed Coal Samples

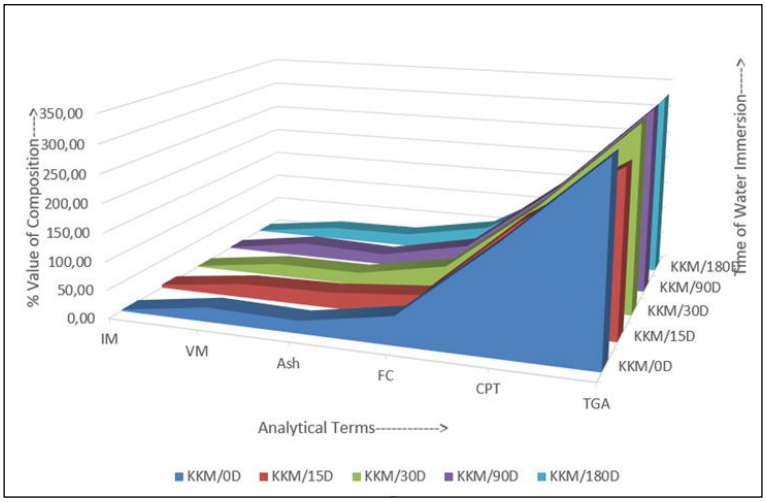

Figure 2: Proximate, TGA, CPT Graph of Kalimati Colliery (KKM Seam) Raw and Water Immersed Coal Samples

Kinetic Parameter Studies

Kinetic parameters like ignition temperature; activation temperature of coal samples was determined by TGA/DSC thermogram. Thermogram of coal samples heat from 30°C to 850°C and measures the change in the weight of the sample with temperature. Raw coal burns 79% whereas 180 days water immersed coal burns only 65.26% on the other hand DSC data shows that the activation energy of coal samples observed as 466°C and 465°C respectively. Similarly, the ignition temperature of raw coal was 221.6°C and 180 days water immersed coal was 218.8°C. The DSC data also shows that the moisture in coal gets removed at a temperature of 110°C and combustion started at 221.6°C in raw coal of KR4 and 255.4°C in raw coal of KKM, which after 180 days of water immersion, becomes 218.8 and 246.2°C respectively. Similarly, combustion of raw coal of KR4 ends at 521.1°C and KKM ends at 619.7°C. After water immersion of 180 days the combustion of KR4 coal sample ends at 517.4°C and KKM coal sample ends at 615.5°C. In both the coal samples the combustion temperature decreases after water immersion. From TGA/DSC data it is clear that the ignition temperature of coal samples decreases due to the action of water. All observed data mentioned in Table 1, 2 and Figure 3 to 6. It is clear from thermogram of TGA/DSC ignition temperature of coal samples decreases after water immersion for 180 days from 221.6°C to 218.8°C, it may be due to physico-chemical changes.

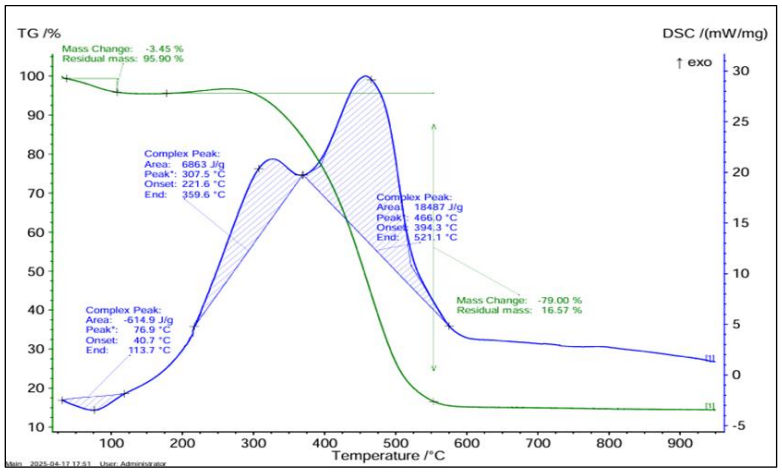

Figure 3: TGA/DSC Thermogram of Raw Coal Sample of Kottadih R4 Coal Mine

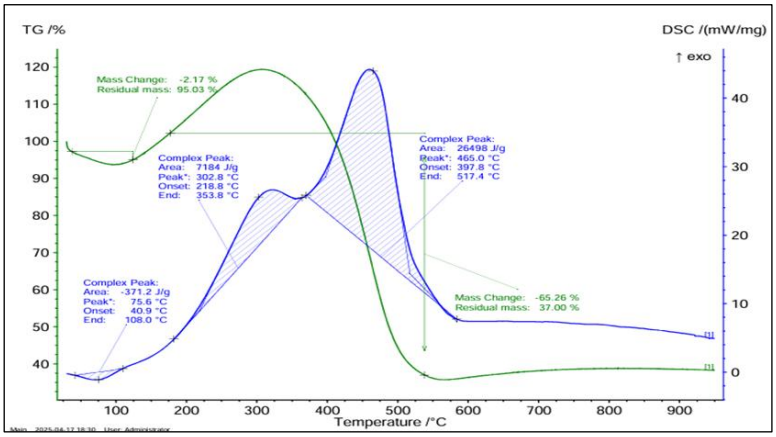

Figure 4: TGA/DSC Thermogram of 180 Days Water-Immersed Coal Sample of Kottadih R4 Coal Mine

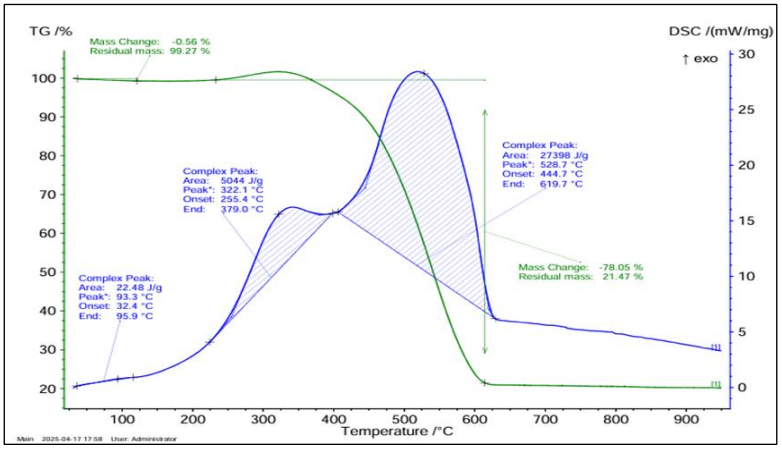

Figure 5: TGA/DSC Thermogram of Raw Coal Sample ff Kalimati Coal Mine

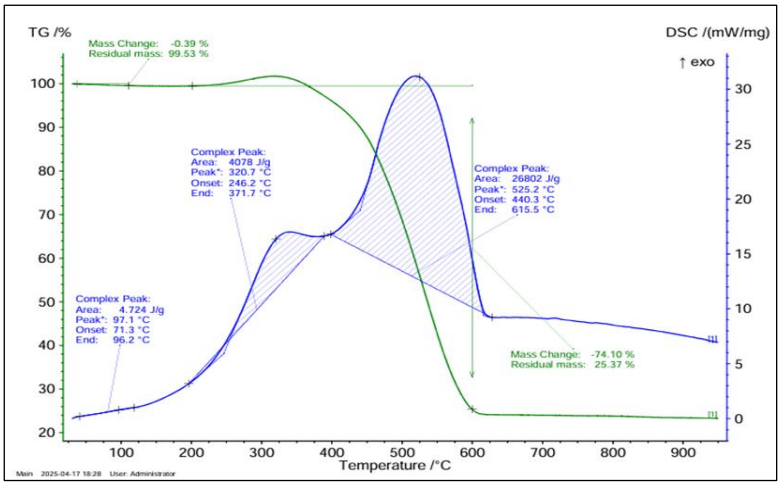

Figure 6: TGA / DSC Thermogram of 180 days water-immersed Coal Sample of Kalimati Coal Mine

Crossing Point Temperature Analysis

The crossing point temperature (CPT) of Kottadih and Kalimati colliery coal samples were determined and this value is used as ignition temperature of coal. The CPT value of raw coal samples of KR4 and KKM samples was 166 and 185°C respectively. After water immersion of 15 days the CPT value of both coal samples and become 156 and 184°C respectively. While after 30 and 90 days of water immersion the CPT value of KR4 was 144°C and after 90 days of water immersion this value reaches to a minimum level of 142 °C. On the other hand, the CPT value of KKM sample after 30, 90 and 180 days of water immersion was 179, 177, and 143 respectively. These decrease value of CPT explain the

propensity of spontaneous combustion of both coal sample, the CPT data shown in Table 1, 2 and Figure 1, 2.

Organic Functional Group Analysis by FTIR Spectrum

The organic functional group present in the coal samples has been detected by FTIR spectrum. All the coal samples have been tested in the Central Instrumentation Facility of BIT Mesra, Ranchi where a small amount of coal sample was taken in the sample holder and then put in the instrument. The observed graph shows that the raw coal samples contain aromatic hydrocarbons (-Ar), aldehyde (-CHO), Ketones (-C=O), Unsaturated hydrocarbon (>C=C<), Hydroxyl group (-OH) etc. in a considerable amount. Whereas the water immersed coal samples having a maximum amount of all these organic functional groups. On the basis of these FTIR data the functional group present in raw and water-immersed coal is classified into three major categories as 900 to 400 cm^{-1} is for aromatic bonds, 1200 to 950 cm^{-1} is for unsaturated hydrocarbons and amines, 1700 to 1300 cm^{-1} for carbonyl compounds and 3600 to 3300 cm^{-1} for hydroxyl compounds. FTIR blended spectra of raw and water-immersed coal were shown in Figures 7 and 8.

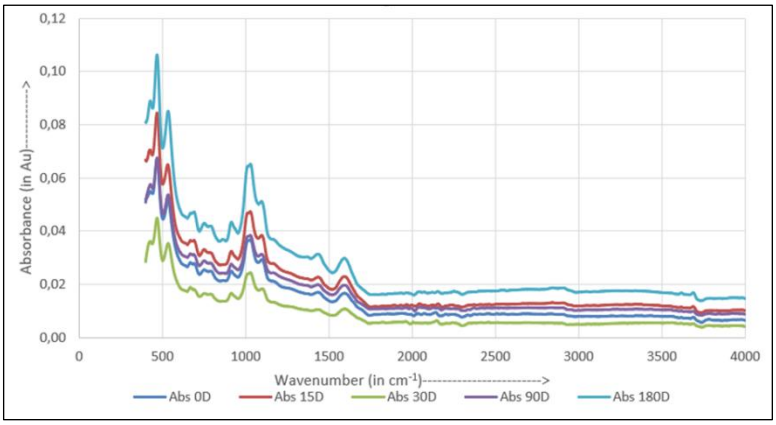

Figure 7: FTIR Graph of Kottadih Colliery (KR4 Seam) Raw and Water Immersed Coal Samples

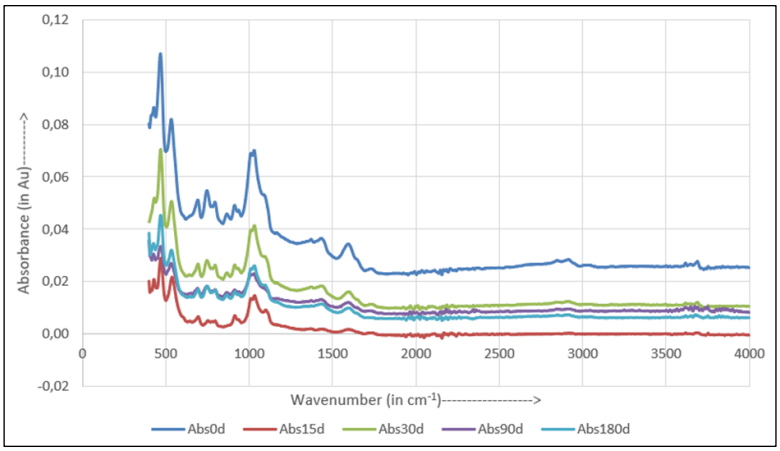

Figure 8: FTIR Graph of Kalimati Colliery (KKM Seam) Raw and Water Immersed Coal Samples

Conclusion

In this research work, raw and water immersed coal of Kottadih (KR4) and Kalimati (KKM) mines of Raniganj Coalfield were analysed by proximate, TGA/DSC, CPT and FTIR techniques. In the result of Proximate Analysis, there is no significant change in the Fixed Carbon (FC) content of the KR4 sample after 180 days of water immersion, whereas the FC content of KKM coal samples increases from 49.95% to 52.75% after 180 days of water immersion. On the other hand, the CPT value of both the samples decreases by 15 to 22 % after water immersion for 180 days. Similarly, a significant decrease has been observed in the ignition temperature of both coal samples obtain from TGA/DSC thermo gram, due to water immersion for 180 days. Also, from the result of FTIR Analysis, the organic functional groups present in the coal, mainly –OH, –Ar, –CHO, >C=O,

>C=C< etc. are found to be present in small quantities, whereas after water immersion of 180 days, the amount of all these organic functional groups increases in both coal samples. Hence, it is clear from all these results that after water immersion, the susceptibility of coal to spontaneous combustion increases, which is confirmed by CPT, TGA, DSC and FTIR Analysis.

Recommendation/ Future work

This research work (immersion of coal in water) may be extended for 2 to 3 years.

Abbreviation

None.

Acknowledgement

I am grateful to the Department of Mine Fire Ventilation CSIR-CIMFR Dhanbad for Proximate and TGA/DSC results and Central Instrumentation Facility (CIF), BIT Mesra, Ranchi for providing the test results of FTIR analysis.

Author Contributions

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication.

Conflict of Interest

The authors declare that there is no conflict of interest between them.

Ethics Approval

This research work following ethical standards, with approval and consent of all participants.

Funding

This research work has not received any funding.

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