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## A thermal investigation on coals from Assam (India)

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### ABSTRACT

A thermal characterization of two coal samples from Ledo and Tikak collieries of Makum coalfield, Assam, India using XRD, FT-IR, and TGA was reported in this paper. The coal samples were heated for 20, 40 and 60 min in a 1000-watt heater (temperature  $\sim 250$  °C) in presence of air and characterized by XRD and FT-IR spectroscopy. Both the coals contain amorphous and crystalline phases. The raw coals also contain very small peaks due to quartz, calcite, gypsum, pyrite, and chlorite. The XRD patterns were found to change upon heating. In the coals heated for 20 and 40 min, it was observed that both amorphous and crystalline parts are common in them; crystalline part being the major one in the 40 min heated samples. The XRD patterns of the samples heated for 60 min indicate the presence of major quantities of  $\alpha$ -quartz, hematite, and chlorite in them. They also show some new peaks, which are assigned to be kaolinite, illite, magnetite and very small in comparison to the amorphous portion in raw coals.  $\alpha$ -quartz was found to be most stable crystalline phase of silica in the coals. The crystallinity % (X-ray) of the coals heat-treated for different times was determined and found to be increasing with time of heating. The FT-IR spectra of raw and heat-treated coal samples at 250 °C were also recorded and compared. The spectra were observed to be almost similar and it was observed that few functional groups disappear on heating at 250 °C. The same coal samples were also characterized by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques. On heat treatment in air atmosphere up to 800 °C, 20–27% weight loss occurs due to removal of various volatile materials. DTA results indicate the chemical reactivity of the coal sample initially at 80–110 °C due to loss of water, and two other major reactions at around 420 and 530 °C due to primary and secondary volatilization.

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### 1. Introduction

Coal is a very complex heterogeneous material mainly consists of organic and inorganic matters. It may also be considered as a combustible rock of variable compositions and often called the fuel of industrialization. Thus, coal conversion technologies and virtually all end uses of coal require the application of heat. The structural changes upon heating which accordingly influences all aspects of coal base technology. Coal undergoes variety of physical and chemical changes when heated to a temperature at which thermal decomposition occurs. Thus the

thermal decomposition of coal has been the subject of many investigations [1–4]. All coals release volatile matter when heated. The quantities evolved depend upon coal rank, the heating rate, the ultimate temperature to which the coal is heated, and to the system pressure. The chemical composition of coal has a strong influence on its combustibility and burnability. To a considerable degree, all physical properties of coal and the complex change in their properties on heating are related to its structural features [5,6]. The coal aggregate structure may be loosened by the removal of carboxylic and phenolic groups in coal macromolecule at around 250 °C [7].

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The mixture of species evolved at any given temperature is a function of coal rank, the system pressure and the previous temperature history of the sample. At low temperature i.e. below 200 °C and especially, under reduced pressure, loosely bound H<sub>2</sub>O and CO<sub>2</sub> are evolved early followed by more strongly bound molecules. On the other hand, lignite, which contains many carboxylic functions as part of the structure, will evolve carbon dioxide by thermal decarboxylation. Such changes are usually noted to occur at temperature just above 100 °C. When the temperature of the thermal treatment is increased to the range of 200–370 °C, coals loss variety of lower molecular weight organic species, especially aliphatic compounds, which are believed to be arise from moieties that are “loosely bound” to the more thermally stable part of the coal structure. Some of the lower molecular weight aromatic species may also be obtained. At higher temperature (i.e. 370–700 °C), methane, polycyclic aromatics, phenol and nitrogen compounds are released.

The organic and inorganic matters including sulphur undergo significant changes on heat treatment. These changes depend on many properties including heating conditions. The sulphur transformation on heat treatment is the most important process in gainful utilization of high sulphur coals. Sulphur in coal present both as organic and inorganic forms. Inorganic sulphur exists mainly as pyritic sulphur along with sulphate sulphur. The organic sulphur exists in aromatic and aliphatic forms. The distribution of organic sulphur varies from coal to coal.

Sulphur transformations during heat treatment have been studied and reported [8–10]. Pyrite transforms into sulphide and nascent sulphur at temperature above 350 °C. The active nascent sulphur captures hydrogen from coal to form H<sub>2</sub>S. The nascent sulphur is also captured by organic matrix and mineral matter to form organic sulphur and sulphide minerals (mostly Ca, Na, Fe compounds) respectively in char/coke [11–18]. Maximum sulphur removal takes place in the range of 600–850 °C. It was reported that sulphur evolution rapidly starts from 450 °C onwards. The organic sulphur functionalities present in these high sulphur coals may be in the form of mercaptan/disulphide, thiols, aromatic sulphide and thiophenes [19] which are not easily removed.

The thermogravimetric study of coal is a well-known method for understanding the change in structural features of coal during combustions [20–22]. Coal undergoes appreciable physico-chemical changes when heated in the temperature range of 350–600 °C during which, reacted molecules break along the weakest bonds, forming free radicals which subsequently recombine with other radicals or molecules to form more highly condensed species and volatile compounds. Thus, if the temperature is increased at a constant rate, the primary devolatilization rate passes through maximum. The temperature at which devolatilization is maximum is increased with the rate of heating. The rate of devolatilization decreases with increasing coal rank. This rapid devolatilization essentially complete at 550 °C. Secondary devolatilization of coal, occurring largely in the 600–800 °C ranges, produces H<sub>2</sub> and CH<sub>2</sub> as the major products. Also fractional loss of oxygen is very high in lignites and low-rank coals. Oxygen, on the other hand, is much more tightly bound in higher rank coals, and increasingly higher temperature is required to produce

appreciable devolatilization of the oxygen. Thus devolatilization is a complex process that involves coal decomposition. In the primary volatilization, coals undergo some bond breaking reactions and some light species, which exist as guest molecules are released as a volatile and gaseous product. During the softening stage, materials pass through a mesophase transition. In the secondary volatilization, further bond breaking occurs, leading to evolution of organic matter as tar and gases and thereby condensation reactions (re-solidification) result in the formation of carbon residue.

The mineral matters in coal may be of both inherent and detrital and exist in different forms and quantities [23,24]. The minerals commonly found in coals are silicates, clay minerals, such as kaolinite, illite, quartz, sandstone, pyrites, siderite, ankerites etc. Coals of various sources contain different compositions of mineral matter. The mineral matters in coal have several detrimental effects on coal utilization [25–28]. They undergo major changes during combustion of coal and lead to atmospheric pollution. Mineral matter, however, has some beneficial effects in coal liquefaction [29,30]. Combustion of high sulphur coal forms SO<sub>2</sub>, which in contact with water forms H<sub>2</sub>SO<sub>4</sub>.

A good deposit of high sulphur coals is found in Assam (India). These low-rank coals have different chemical properties in comparison to other Indian coals and found to be suitable in various combustion technologies mostly in generating electricity. The strong caking properties of Assam coals were also observed with caking and swelling index of 17–25 and 4 1/2 respectively. Moreover, the chars from these coals are also found to be suitable in cement industries [31]. Thus, thermal study on these coals is of significant importance to have an insight into the structural changes occurs during heat treatment for designing better technology. The present paper reports a preliminary thermal investigation on two coal samples from Assam (India) by using XRD, FT-IR, TGA and DTA techniques. The XRD and FT-IR techniques were used to study the changes in structural features of coals heated for different times at about 250 °C. TGA and DTA studies were also done in order to observe their types of volatilization processes. In the XRD study, the principle issue adversed in this paper is the observation of the structural features of two coals on mild heating at 250 °C in presence of air for different times. Heating at 250 °C is capable of causing chemical transformation in coals [32]. Aliphatic hydrocarbons, alkylbenzenes and alkyl-naphthalenes were released at 250–350 °C [33–35]. XRD has also been applied in the characterization of mineral phases in the coals for better understanding the structural changes on heating. To see the changes in nature of crystallinity of coals with time of heating by XRD technique is one of the principle concerns.

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## 2. Experimental

### 2.1. Physico-chemical analysis of coals

Freshly mined coal samples were collected from Ledo and Tikak collieries of Makum coalfield (latitudes 27°13'–27°23' N and longitudes 95°35'–96°00' E), Assam (India). The proximate analyses of the coal samples were done by standard methods, (IS: 1350 (Part I-1984)). The elements C, H, and N were analyzed

by an elemental analyzer, Perkin Elmer, model 2400, total sulphur was determined by Eshcka method [36] and the percentage of oxygen was calculated by difference. The forms of sulphur were determined by following standard methods (ASTM D 2492) where, the organic sulphur was calculated by difference. The analyses of the coal samples are given in Table 1. The ash analysis of the coal samples was carried out by standard methods [36,37] and reported in Table 2. The all analyses for the samples were carried out in quadruplicate and mean values have been reported.

## 2.2. Heat treatment and X-ray diffraction analysis

The coal samples were ground to <150  $\mu\text{m}$  (sizes) before use for X-ray diffraction analysis. Five grams of each coal (Ledo and Tikak) samples were isothermally heated in a 1000-watt heater at a temperature of 250  $^{\circ}\text{C}$  for 20, 40 and 60 min (samples Ledo/Tikak-20, Ledo/Tikak-40, Ledo/Tikak-60) in presence of air. X-ray diffraction patterns were obtained using computer controlled X-ray diffractometer Type JDX-11P3A, JEOL, JAPAN, attached with pulse height analyzer and scintillation counter with scintillator NaI (T1) single crystal. The background corrections for intensity measurements were made for XRD patterns (NET DATA) by using software PEAK SEARCH supplied with the XRD unit. Operating parameters were: start angle: 3.00, target: Cu (Fe-filtered), stop angle: 100.0, measuring time: 0.5, step angle: 0.03 and data processing condition: smoothing points, Goniometer radius (R): 240 mm, equatorial angle subtended at the specimen by the detector slit ( $\beta$ ):  $1^{\circ}$ .

## 2.3. Crystallinity % (X-ray) determination

The degree of crystallinity (Kc) was determined from the ratio of the integrated crystalline scattering to the total scattering (both crystalline and amorphous) following the methods given elsewhere, [38].

$$Kc = \frac{\int_0^{\infty} S^2 I_c(S) ds}{\int_0^{\infty} S^2 I(S) ds}$$
, where, Crystallinity Percent =  $Kc \times 100$ ; where  $I(S)$  is the intensity of coherent scattering from coal (both crystalline and amorphous),  $I_c(S)$  is the intensity of coherent scattering from crystalline region and  $S$  is equal to  $2\sin\theta/\lambda$  ( $\lambda$ : 1.5406  $\text{\AA}$ ). In the determination of crystallinity of coal samples from X-ray intensity, the observed intensity data of coal was normalized to electron units and fitted with theoretical independent scattering of carbon atoms in the higher range of  $2\theta$ . Then, the coherent scattering of coals can be obtained by subtracting incoherent scattering of carbon atoms from normalized intensity and the results were divided by coherent scattering of carbon atoms to get reduced intensity of coals. It is to be noted that neither the presence of heteroatom nor mineral matter was taken into account. The effect of these can be neglected in these cases [39].

**Table 2 – Ash compositions of the coals (wt.%)**

Coal	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	SO <sub>3</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Others
Tikak	50.4	25.6	0.11	1.14	0.13	0.50	18.8	3.37
Ledo	63.1	23.6	0.7	1.1	0.5	0.5	9.7	0.8

## 2.4. Thermal and FT-IR analysis

Five grams of each coal sample (<150  $\mu\text{m}$  size) were subjected to the thermogravimetric investigation. The heating was carried out in a thermal analyzer (Model: Perkin Elmer-Pyris-Diamond, TG/DTA) at the rate of 10  $^{\circ}\text{C}$  per min up to 800  $^{\circ}\text{C}$  in presence of air. The FT-IR spectra of the raw coals and heat-treated coals (at 250  $^{\circ}\text{C}$  for 60 min) were recorded by Perkin Elmer system 2000, Model 640B using KBr pellet with spectral resolution of 4  $\text{cm}^{-1}$ . Same weight of coals and KBr were maintained in each time of recording of spectra. The absorbance of the significant O-containing functional groups was determined by using the software associated with the instrument (FT-IR) computer.

## 3. Results and discussions

### 3.1. X-ray diffraction analysis of heat-treated coals

Figs. 1 and 2 show the X-ray diffraction patterns of the Ledo and Tikak coal samples heated for 20 (Ledo/Tikak-20), 40 (Ledo/Tikak-40), 60 (Ledo/Tikak-60) and 0 min (Ledo/Tikak-0) respectively. The XRD patterns of the two coals are found to show almost similar changes on heating for different times. The raw samples (Ledo/Tikak-0) show that the samples are amorphous in nature with very small crystalline matter difficult to quantify.

From the variation of intensity in the patterns of the heat-treated samples, it can be concluded that the volatile organic matter in the coal sample being removed during heating. The major products were CO<sub>2</sub> and H<sub>2</sub>O due to the dehydration and decarboxylation reaction during heat treatment. Some condensation reactions also may take place through the dehydration and decarboxylation. The mass of the coal samples were found decrease on heat treatment and was observed to be 5, 4.60, 4.45 and 3.75 g after 0, 20, 40 and 60 min respectively.

X-ray data were compared with standard powder data available on JCPDS data cards and available literatures [40–46]. The XRD patterns of the samples heated for 20 min show that they contain both amorphous and crystalline part. The crystalline part mainly observed to contain  $\alpha$ -quartz (Q), calcite, hematite, illite, analcime, rutile and a very small quantity of amgentite. The most stable and dominant phase in them are found to be quartz which occurs at  $d=3.32\text{--}3.30 \text{ \AA}$ . The mineral

**Table 1 – Physico-chemical characterizations of the coals (as received basis wt.%)**

Coals	Ash	Moisture	Volatile matter	Fixed carbon	Pyritic sulphur	Sulphate sulphur	Organic sulphur	C	H	N	Total S	O
Tikak	16.9	2.6	34.9	45.6	0.21	0.12	2.58	71.2	7.2	1.0	2.91	0.79
Ledo	10.35	3.07	43.38	43.20	0.58	0.43	2.56	72.6	5.33	0.92	3.57	7.23

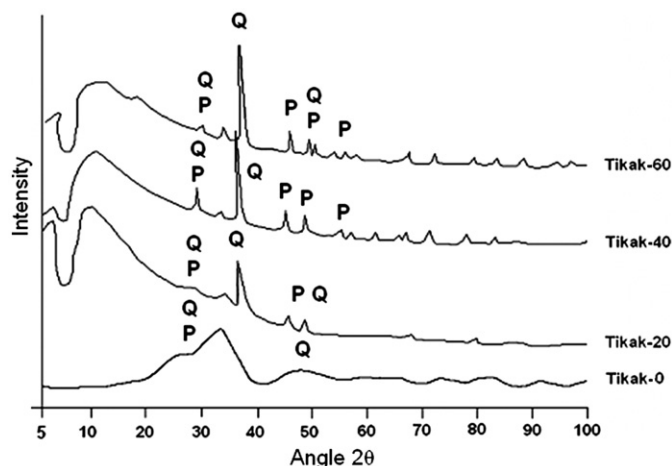


Fig. 1 – XRD of Tikak coal heated for different times (P: pyrite; Q: quartz).

calcite ( $d=3.04, 2.29, 2.11 \text{ \AA}$ ), gypsum ( $d=7.55$  and  $3.06 \text{ \AA}$ ) and pyrite (P) ( $d=3.11, 2.69, 2.43, 1.63, 1.43, 1.25$  and  $1.21 \text{ \AA}$ ) are also found to present in the heated samples for 20 min. The samples also contain marcasite ( $d=2.05, 1.90$  and  $1.68 \text{ \AA}$ ) and chlorite ( $9.353$  and  $2.53 \text{ \AA}$ ). The XRD patterns of the coals show very small changes with increase in time of heating. The XRD patterns of the samples heated for 40 min also show the existence of both crystalline and amorphous materials, the former being the major one. Few new peaks were observed at  $d=7.09, 3.571, 2.516, 1.66, 1.49 \text{ \AA}$  which are due to kaolinite (K) and  $d=7.94, 4.69, 4.50, 1.73 \text{ \AA}$  which have been assigned to chlorite. The crystalline parts in the Ledo/Tikak-40 samples mainly consist of quantities of  $\alpha$ -quartz, hematite, illite, chlorite, kaolinite and noselite. The XRD patterns of the samples heated for 60 min (Ledo/Tikak-60) indicate a small increase in crystalline nature and found to contain quantities of quartz, hematite, and chlorite. The increase in sharpness of the XRD profiles after 40 and 60 min of heating at  $250 \text{ }^\circ\text{C}$  indicates the increase in crystalline phases in the coals by decarboxylation reactions.

The Table 3 shows  $d$ -values of some crystalline phases present along with their assessments in the two coal samples

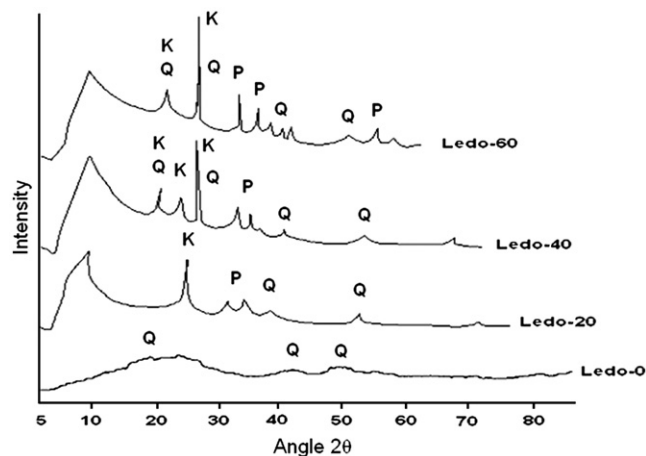


Fig. 2 – XRD patterns of Ledo coal heated for different times (P: pyrite; Q: quartz; K: Kaolinite).

heated for 60 min. The main minerals found to be present are  $\alpha$ -quartz, hematite, magnetite, illite and chlorite. From the change in X-ray diffraction patterns of the two coal samples on heating, it can be concluded that volatile matter in coal samples were released on heating at  $250 \text{ }^\circ\text{C}$ .

### 3.2. Crystallinity % (X-ray) of heat-treated coals

The crystallinity % was found to be 65, 66, 74 and 73% for Ledo coal whereas 62, 63, 72 and 71% for Tikak coal heated for 0, 20, 40 and 60 min respectively. Fig. 3 shows the variation of crystallinity % of the two coals with heating time. The

Table 3 –  $d$ -values and their assignments of heat-treated Tikak and Ledo coals for 60 min

Tikak coal		Ledo coal	
$d \text{ (\AA)}$	Assignments	$d \text{ (\AA)}$	Assignments
7.09	K	7.09	K
4.49	I	7.43	Cl
4.26	Q	4.25	Q
3.69	H	3.35	Q
3.49	Cl	2.70	H
3.35	Q	2.52	H, M
2.70	H	2.46	Q
2.52	H	2.42	Q
2.46	Q	2.36	Q
2.28	Q, H	2.20	Q, H
2.23	Q	2.21	Q
2.21	H	1.84	Q, H
2.13	Q	1.69	Q, H
1.98	Q	1.65	Q, H
1.84	H	1.60	Q, H
1.81	Q	1.54	Q, H
1.69	Q, H	1.48	Q
1.54	Q, H	1.45	Q, H
1.48	Q	1.43	Q
1.45	Q		
1.37	Q, H		
1.31	Q		
0.96	H		

Q:  $\alpha$ -quartz; H: hematite; M: magnetite; I: illite; Cl: chlorite; K: kaolinite.



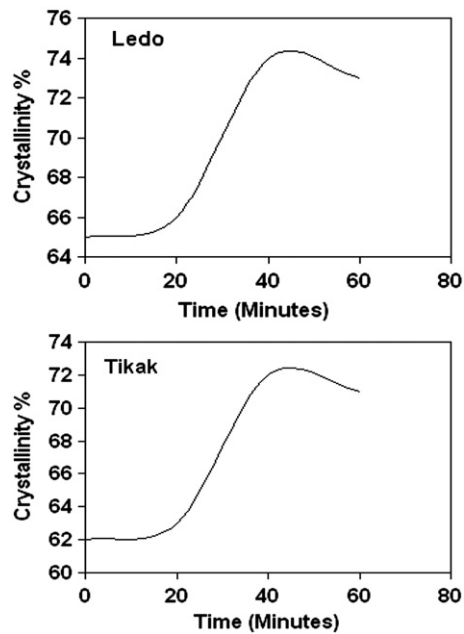


Fig. 3 – Variation in crystallinity % (X-ray) of Ledo and Tikak coal samples with heating time.

crystallinity % was observed to attain a maximum after heating for 40 min for both the coals and come down marginally after 60 min may be due to prominent amount of amorphous silica contents in ash. The carbonaceous materials

in raw coals possibly get oxidized on heating and the mineral phases (crystalline phases) become prominent in comparison to the organic part to produce a little more sharpness X-ray diffractogram. The quartz is found to remain throughout the heating process. This is the most stable form of  $\alpha$ -quartz and stable up to 1470 °C for a considerable period [47]. The presence of the line at 2.52 Å indicates the presence of very small quantity of magnetite in the heated Ledo coal for 60 min.

### 3.3. FT-IR spectral analysis of the coals

Fig. 4 shows the FT-IR patterns of the raw coal samples along with heat-treated coals at 250 °C for 60 min. The bands observed in the raw and heat-treated coals are assessed from the literatures [48–55]. The coal samples exhibit bands at around 2920 and 2865  $\text{cm}^{-1}$  assigned to aliphatic –CH stretching, a sharp band at around 1610  $\text{cm}^{-1}$  due to the C=C aromatic group, and a band at 1445–1428  $\text{cm}^{-1}$  due to C–H deformation. All of these disappear on heating for 60 min at 250 °C in presence of air, indicating disruption of some organic functionality present in the coal samples.

The FT-IR spectra of raw coal samples exhibit a broad band around at 3384–3406  $\text{cm}^{-1}$  due to –OH groups. Some minerals found in coals contain water of crystallization; some clay minerals such as kaolinite, illite etc. also contain structural OH groups. All these substances exhibit bands in this region. The absorbance of the band around 3384–3406  $\text{cm}^{-1}$  decreases in the both coals samples heated at 250 °C. The water of crystallization/interlayer OH in most of the coal minerals was

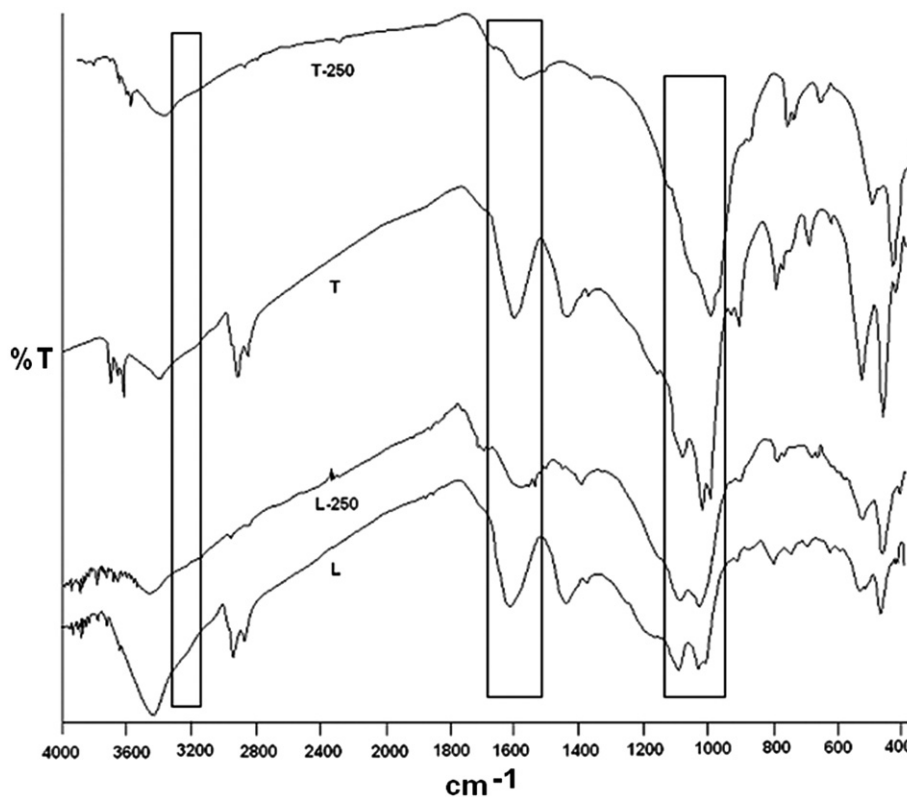


Fig. 4 – FT-IR spectra of heat-treated Ledo (L-250) and Tikak (T-250) coals at 250 °C along with untreated coals showing some significant stretching region of oxygen containing functional groups in rectangles.

**Table 4 – Absorbance of some O-containing functional groups in the raw and heat-treated coals**

Functional groups	Coals	Absorbance
O–H	Ledo	0.71
	Ledo-250	0.68
	Tikak	0.72
	Tikak-250	0.66
C=O	Ledo	0.70
	Ledo-250	0.65
	Tikak	0.71
	Tikak-250	0.66
S=O	Ledo	0.70
	Ledo-250	0.69
	Tikak	0.80
	Tikak-250	0.80

easily lost at this temperature. The coal samples and heated coal samples exhibit a prominent peak at around 1250–1000  $\text{cm}^{-1}$  due to Si–O bending vibration. Bands at around 1032, 1010 and 916  $\text{cm}^{-1}$  indicate the presence of kaolinite. The bands at the 1250–1000  $\text{cm}^{-1}$  region becomes more sharp and the very small peaks at around 1097 and 1030  $\text{cm}^{-1}$  merged to a single peak in the heated coal samples. This merging of peaks at this region is attributed to the orderliness of the silicate structures with temperatures.

All the coal samples exhibit bands in the region of 800–750  $\text{cm}^{-1}$  indicating the presence of quartz [47]. The small bands in the region 694–675  $\text{cm}^{-1}$  and at 471  $\text{cm}^{-1}$  indicate the

Si–O vibration [47]. Thus, FT-IR studies indicate the presence of quartz, aluminosilicates, kaolinite and illite (clay minerals) in the raw and heated coals samples.

The Table 4 demonstrates the absorbance values for O–H, C=O and S=O functional groups present in raw and heat-treated (250 °C) coals. The changes in the absorbance values itself reveal the loss of O–H and C=O functional groups after heating at 250 °C. The absorbance values for S=O functional groups remain same for raw and heat-treated coals even after heating at that temperature which states the inability of breaking the S=O functionality at 250 °C.

### 3.4. Thermal analysis (TGA/DTA) of the coals

The thermal curves (TGA, DTG, and DTA) of the two coal samples are depicted in Figs. 5 and 6. The thermograms are very complex and associated with a number of changes. The TGA curve gives a graphic representation of the relative extents of primary and secondary volatilization reactions.

In the TGA pattern of Ledo coal (Fig. 5) there are two temperature ranges observed: one in the low-temperature region from 80 to 110 °C where water loss is expected and the total moisture content is calculated to be about 3.07 wt.% (Table 1) and the other mainly in the 300–570 °C region, where maximum loss of volatile material about 80 wt.% occurs due to primary and secondary volatilizations. The DTG curve is the derivative expression of TGA curve, which gives the starting and closing temperatures of decompositions and the sharp peak gives the point of decomposition for Ledo coal.

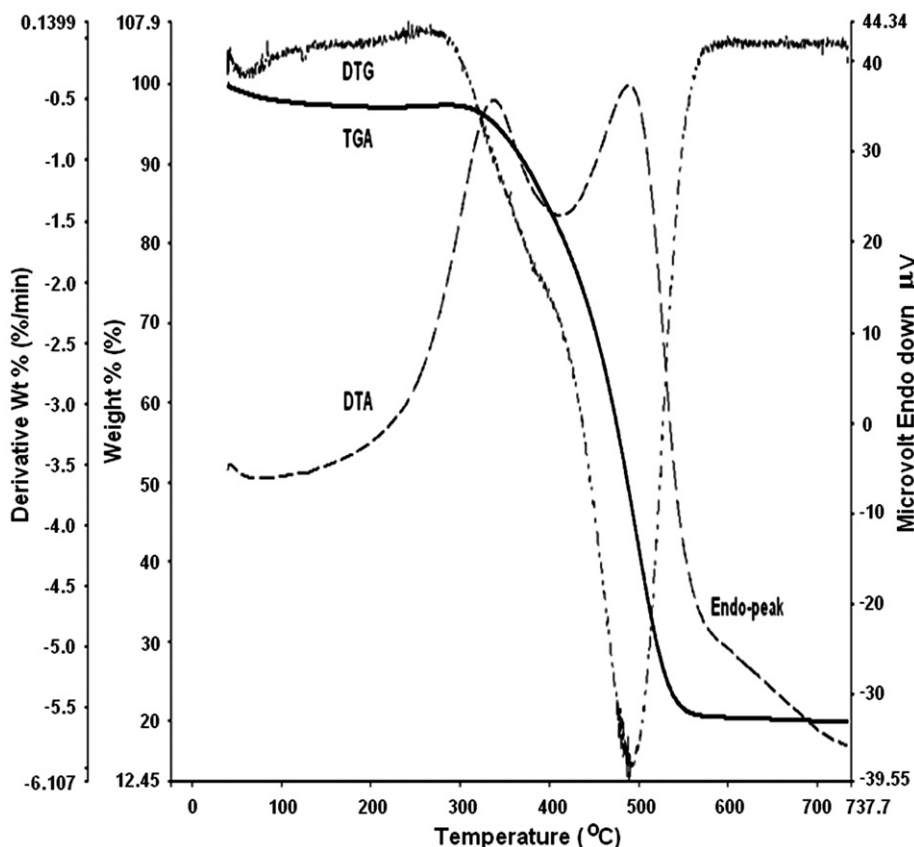


Fig. 5 – TGA and DTA patterns of Ledo coal.

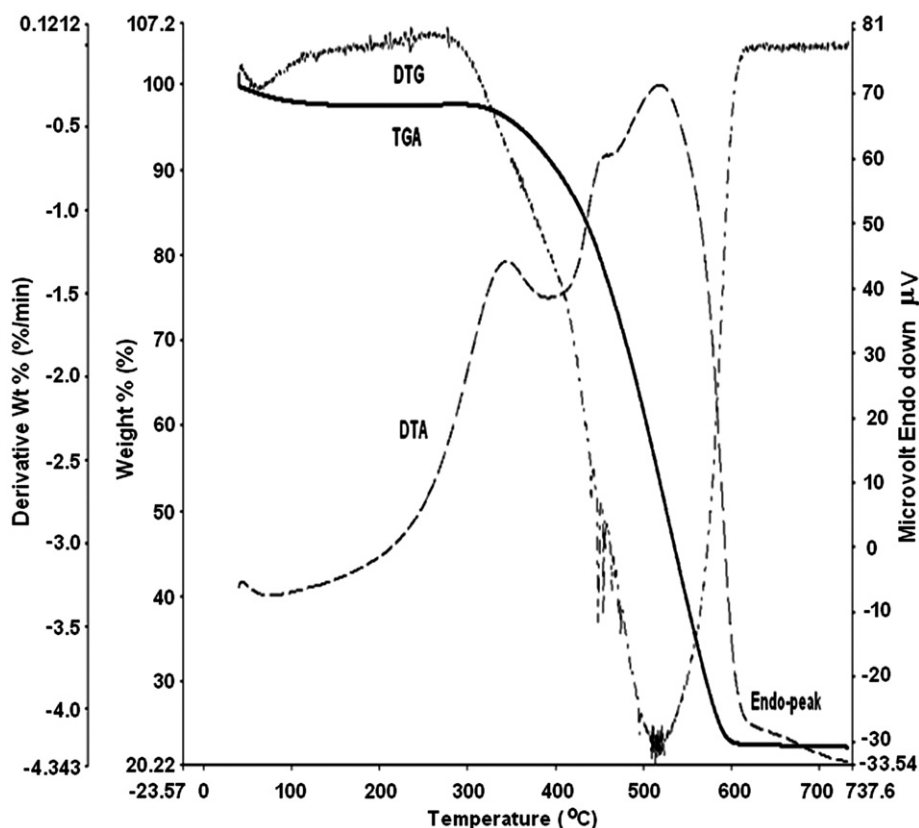


Fig. 6–TGA/DTA patterns of Tikak coal.

The trend in DTA pattern of Ledo coal (Fig. 5) shows mainly two exothermic peaks and one endothermic peak. The exothermic peaks appearing around 350 and 450 °C is related to primary volatilizations [56] during which compound containing C, H and O are released. The aromatic and aliphatic parts of coals are released as CO<sub>2</sub>, CO and CH<sub>4</sub> at this stage. Another very small endo-peak at 590 °C can be interpreted for the secondary volatilizations, during which mainly inorganic compounds containing H is released [56,57]. The uniform formation of coke from Assam coal is also indicated from this weak endothermic peak. Beamish [58] while studying the New Zealand coal also observed such types of two distinct peaks in DTG curve.

In the thermogravimetric analysis, Tikak coal also shows two temperature ranges: one in the low-temperature region from 80 to 100 °C where water loss is expected and the total moisture content is calculated to be about 2.60 wt.% (Table 1) and the other mainly in the 300–600 °C region, where maximum loss of volatile material about 80 wt.% occurs due to volatilization and char oxidation. Fig. 6 shows the TGA and DTA patterns of Tikak coal. The trend pattern also shows mainly two exothermic peaks and one endothermic peak. Two exothermic peaks appearing around 350 and 500 °C, which are related to primary volatilizations during which compound containing C, H and O are released as CO<sub>2</sub>, CO and CH<sub>4</sub>. The very weak third endo-peak at 640 °C is caused by the secondary volatilizations, during which mainly inorganic compounds containing H is released indicating the uniform coke formation.

The TGA/DTA patterns of Ledo and Tikak (Figs. 5 and 6) reveal the same type of decomposition on heating from ambient temperature to 800 °C. The DTA pattern shows mainly two exothermic peaks and one endothermic peak. It was observed from DTA patterns of two coals that the very first release of volatile and gaseous products starts slowly from 200 °C. The various thermal changes and the weight losses observed in TGA/DTA are also associated with the minerals of the coal samples [59] and can be interpreted. Weight loss from gypsum takes place at around 350 °C. The carbonate minerals such as magnesite, siderite, calcite, and dolomite exhibit endotherms at different regions in the range of 545–983 °C. Many clay minerals (viz. kaolinite, illite) exhibit small exotherms around 760 °C. The release of loosely bound volatile matters was also observed in the XRD and FT-IR studies of the heat-treated coals. The thermal changes of the minerals likely to be present in the coal samples may overlap which makes some difficulty in identifying the minerals present in coal by TGA/DTA analysis in air. Macerals found in Assam coals [60] may also be affected differently on heating. The resinite softens and volatilizes almost completely below 200 to 300 °C while vitrinite soften between 330 and 360 °C [61].

#### 4. Conclusions

Assam coal consists of amorphous substances along with very low crystalline matters. The crystalline nature of coal increases upon mild heating to 250 °C. The carbonaceous

materials get oxidized on heating and the crystalline phases become more dominant in coals. Quartz is found to be the dominant phase in raw and heat-treated coals at 250 °C. This component was observed to be present throughout the process of heating and the most stable existing form is the  $\alpha$ -quartz. FT-IR analysis also indicates the presence of  $\alpha$ -quartz. Two temperature ranges are observed in the thermogravimetric study of the two coals: one in the low-temperature region from 80 to 110 °C where dehydration is expected and the other mainly in the 300–570 °C region, where maximum loss of volatile materials occurs due to primary and secondary volatilizations. These findings reveal the usefulness of Assam coals in steel making, metallurgical and hard coke manufacturing industries.

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