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Mineralogical and Ash Geochemical Studies of Coal-mine Shale and its Hydrocarbon Potential: A Case Study of Shale from Makum Coalfield, Northeast India

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ABSTRACT

The mineralogy and geochemical studies of the coal-mine shale collected from the Tirap opencast coal-mine (Makum coalfield, Northeast India) are reported in this paper. Thermo-chemical conversion (pyrolysis) of coal-mine shale has been studied to see its hydrocarbon potential. A combined approach using X-Ray diffraction (LTA-XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectrophotometer (EDS), X-ray fluorescence spectrometry (XRF), thermogravimetry-derivative and differential thermogravimetric (TG-DTG and DTA) analysis is made to obtain new information on the mineralogical and geochemical studies of a coal-mine shale (CMS) sample. Gas chromatography-mass spectrometry (GC-MS) analysis is performed to evaluate the quality of the liquid fraction (tar) obtained after pyrolysis at 600°C. The shale sample is dominated by quartz, clay minerals (kaolinite and illite), sulphate bearing phase like gypsum with minor proportion of anatase, probably as artifacts of the plasma-ashing process. GC-MS analysis illustrates the presence of highly oxygenated organic components (M.W. around 94-108) and high molecular weight (M.W. 256) cyclic sulphur (e.g. octathiocane with molecular formula S_8) compounds along with the complex N-containing organic sulphur compounds (M.W. around 255-486) in the tar produced.

INTRODUCTION

Coal-mine shale is fissile and fine grained sedimentary rock. It is common in coal bearing sedimentary sequence and is considered to represent an average crustal provenance composition of a coal mining area much better than any other detrital sedimentary rocks (McCulloch and Wasserburg, 1978). The research interest in shale during the last few decades is due to the widespread recognition all over the world that shales are important source rocks for petroleum (oil, gas and solid hydrocarbon) or may be used as natural fuel resources with various mineralogical and textural characteristics (North, 1985). Shales, associated with coal, is available in large quantity in India (more than about 15 billion tons) in different coal mining areas; however, research activities on their field of applications are very limited.

North-East India is endowed with rich deposits of Tertiary coal (Singh et al., 2012; Singh et al., 2013; Saikia et al., 2013; Baruah et al., 2013). Carbonaceous shale is widely distributed on the surface and in sub-surface sedimentary sequences that occur interbedded with the Tertiary coal in Assam and the neighbouring areas of Arunachal Pradesh (Kumar and Mani, 2007). These geological formations outcrop on the surface towards the south of the oil fields in a region called the Belt of Schuppen (Kumar and Mani, 2007; Singh et al., 2012). Studies have indicated that these coals and shale constitute the principal source rocks for the hydrocarbons produced from the region. Organically rich carbonaceous shale rocks are also known as continuous hydrocarbon reservoirs and represent a voluminous, long-term, global source of thermogenic methane and other hydrocarbon gases and oil. However, geochemical and mineralogical research of the coal-mine shale of northeast India has not been carried out much as compared to the coal deposits.

Mineralogy of Coal-mine Shale

The mineralogy of coal-mine shale reflects the initial depositional environment and geochemical characteristics of the parent rock, subsequently modified by diagenetic processes. Depending on the depositional environment and tectonic setting, shale mainly consist of variable quantities of organic matter, mixtures of fine grained quartz and clay minerals and may also contain other minerals like sulphide minerals, carbonate minerals and oxide minerals (O'Brien and Slatt, 1990; Slatt and Rodriguez, 2012; Vine and Tourtelot, 1970; Yaalon, 1962, Arthur and Sageman, 1994; Tourtelot, 1979; Trabucho-Alexandre et al., 2011; Prachiti et al., 2011) and may be formed either in the syngenetic or in the epigenetic stage. Illite, mixed illite layers, smectite, kaolinite and chlorite are the dominant clay mineral present in the shales (Boles and Franks, 1979; Aplin and Macquaker, 2011). Shale and associated minerals when subjected to rising temperatures and pressures, undergo diagenesis. (McDonald and Surdam, 1984; Chermak and Rimstidt, 1990). The nature and modes of the occurrence of the various minerals present in the shale affect the environment during utilisation and therefore, understanding of the mineralogy and ash geochemistry is important.

Pyrolysis of Shale

Pyrolysis of carbonaceous materials leads to thermo-chemical alterations within the substance, which takes place in inert atmosphere, specially N_2 or He, in order to avoid heterogeneous reactions. Pyrolysis of an organic material generates a solid, liquid (tar), and a "non-condensable" gas fraction. The liquid fraction, usually referred to as "tar", contains high molecular weight hydrocarbons larger than C_6 (Campbell, 1978) and has wide industrial application such as the chemical industry, synthetic fibre manufacturing, dyestuff, medication, coating sorbents for treatment of sewage, gas purifying and many others. It may also be used as a liquid fuel and it can be combusted for the production of energy in the form of electricity (Czernik and Bridgwater, 2004). Considering these aspects, the characterization of the molecular structure and composition of the liquid hydrocarbon is important (Jiang et al., 2006).

In the present study, mineralogical and geochemical characteristics

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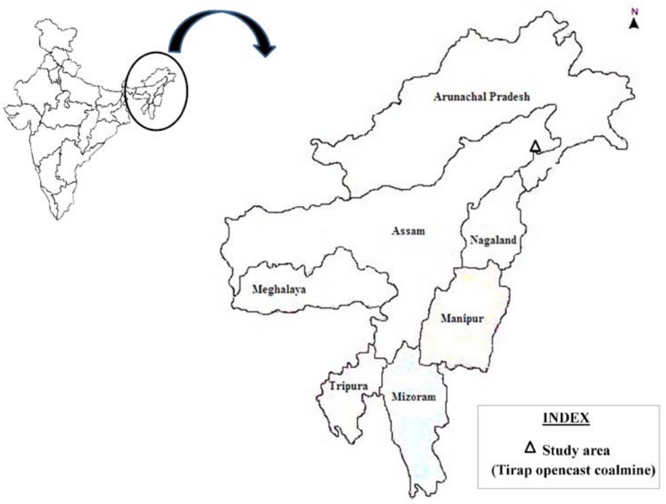

Fig. 1. Location map of Tirap opencast coal-mine (North-East India) (not to scale)

of the coal-mine shale from the Tirap coalmine (North-East India) are investigated. With the help of pyrolysis experiment, an attempt has also been made to assess its hydrocarbon potential.

METHODS AND MATERIALS

Coal-mine shale sample

The Tirap open cast coal-mine is the most active and industrially important coal-mine in the Makum coalfield (NE India). The major workable seams occur in Tikak Parbat and Baragolai formations of the Barail Group. A representative shale sample associated with this coal seam was collected following standard methods (ASTM, 2010).

The lithology of the Makum coalfield consist of massive bedded sandstones with intercalation of shale and carbonaceous shale (Nagaon Formation), interbedded carbonaceous shale, thin sandstones, and thin impersistent coal seams (Boragolai Formation) and the basal part of the sequence is marked by carbonaceous shale, sandy shale and thin sandstones with 18 meter thick coal seams (Tikak Parbat Formation) (Saikia et al., 2015a).

Mineralogical Analysis

The physico-chemical characteristics such as proximate, ultimate (CHN), and sulfur analysis were discussed by Saikia et al. (2016) and is given in Table 1. The mineralogical study was performed through optical microscopy and X-ray powder diffraction (XRD). Low-temperature ashing (LTA) of the coal was performed using an EMITECH K1050X plasma asher prior to XRD analysis. XRD analysis of the low-temperature ashes was performed on a powder diffractometer (D/max-2500/PC XRD) with Ni-filtered Cu-Kα radiation and a scintillation detector. The XRD pattern was recorded over a 2θ interval of 2.6–70°, with a step size of 0.01°. X-ray diffractogram of the LTA samples were subjected to quantitative mineralogical analysis using Siroquant™, commercial interpretation software developed by Taylor (1991) based on the principle of diffractogram profiling (Rietveld, 1969). This technique has also been used for coal-related materials by Ward et al. (1999, 2001), Ruan and Ward (2002), and Dai et al. (2012a,b).

XRF Analysis

The shale sample was ashed at 815 °C and was calcined at 1050 °C, fused with lithium metaborate and cast into discs, following the method of Norrish and Hutton (1969). The discs were analysed by X-ray fluorescence (XRF) spectrometry using a Philips PW 2400 spectrometer and *SuperQ* software, and the results expressed as percentages of the major element oxides in each sample.

SEM-EDS Analysis

A field emission-scanning electron microscope (FE-SEM, FEI Quanta™ 650 FEG), in conjunction with an EDAX energy-dispersive X-ray spectrometer (Genesis Apex 4) was used to study the morphology of the minerals and also to determine the distribution of some elements (Dai et al., 2012a,b). The sample was carbon-coated using a Quorum Q150T ES sputtering coater. Samples were mounted on standard aluminium SEM stubs using sticky electronic-conductive carbon tabs. The working distance of the FE-SEM-EDS was 10 mm, the beam voltage was 20.0 kV, the aperture was 6, and the spot size was 5 micron. The images were captured via a retractable solid state backscatter electron detector.

Differential Thermogravimetric (TGA-DTA) Analysis

The thermal analysis (TGA–DTA) of the shale sample was carried out in a Thermal Analyzer (Model: Netzsch STA 449F3). The temperature calibration was done at a heating rate of 10°C/min by analyzing the DTA/TG signal of the melting peak (Tm) of the pure substances; In (Tm = 431.8 K), Al (Tm = 959.2 K), Au (Tm = 1346.9 K), Sn (Tm = 508.4 K), and Zn (Tm = 700.8 K) using the same crucible (Alumina) and similar conditions. Accordingly a baseline correction was also done in nitrogen and oxygen environments at the same heating rate with an empty crucible. Then, all the TGA–DTA analyses were performed by taking approximately 10 mg of the each sample in the crucible, which was heated to 1200°C at a heating rate of 10°C/min in a nitrogen environment.

FT-IR Spectroscopic Analysis

The FT-IR analysis was performed in a Perkin Elmer system 2000 (Model 640B) apparatus in the range of 400–4000 cm^{-1} using KBr pellets with the same weight as the dried shale samples. The sample (about 6–7 mg) was accurately weighed on a single pan electronic balance (Model: SI-234, Denver instrument) and thoroughly mixed with the spectroscopic grade KBr powder (about 200 mg) in an agate mortar. The FT-IR spectra were processed using the software Spectrum V-3.02 (Version 3.02.01, Perkin Elmer) in an absorbance mode.

Pyrolysis Experiment

Pyrolysis experiment was performed in a low temperature carbonization (Gray-King) apparatus at 600ºC under inert atmosphere (N_2 gas) with heating rate of 30 º/min. 10g coal-mine shale sample was placed into the retort and the free space of the retort was filled with quartz wool and ceramic granules. The retort was inserted into the furnace and heated upto the desired temperatures and kept constant for 1 hour. The retort was cooled, and the coke/char obtained was weighed. The coke/char was dried in oven for about 1 hr at 90°C under static air. The liquid product obtained from pyrolysis was collected from the collection condenser of the pyrolysis apparatus.

Table 1. Physico-chemical characteristics of the shale sample (as received basis; wt %)

Samples	M	A	VM	FC	TS	PS	SS	OS	C	H	N	O
Shale sample	2.41	77.84	17.38	2.37	4.22	0.26	0.57	3.39	9.61	1.00	nd	nd

(M: Moisture; VM: Volatile matter; FC: Fixed carbon; TS: Total sulphur; PS: Pyritic sulphur; SS: Sulphate sulphur; OS: Organic sulphur; C: Carbon; H: Hydrogen; N: Nitrogen; nd: Not determined)

GC-MS Analysis of the Liquid Fraction (tar)

GC/MS analysis was performed in a PerkinElmer AutoSystem XL GC interfaced with a Turbomass Quadrupole mass spectrometer fitted with same DB-5 fused silica capillary column. Injector, transfer line and source temperature was 250 °C; ionization energy 70 eV; helium at 10 psi constant pressure; and mass scan range was 40–500 amu. Characterization was achieved on the basis of retention time, elution order, calculated relative retention index using a homologous series of n-alkanes (C_{10}-C_{32} hydrocarbons, Polyscience Corp. Niles IL), mass spectral library search (NIST/EPA/NIH version 2.1 and Wiley registry of mass spectral data 7th edition).

RESULTS AND DISCUSSION

Mineralogy and Ash Geochemistry

The mineralogy of the low temperature ash (LTA) prepared from the shale is summarized in Table 2. Low-temperature oxygen plasma ashing of the shale sample provides a more definitive assessment of the minerals present, without contamination by mineral artifacts produced in the ashing process (Ward, 2002). According to the LTA-XRD analysis, the common crystalline phases in the shale are predominantly quartz (41.7%), apatite (18.0%), kaolinite (16.4%), illite (14.8%), gypsum (8.9%) with minor amount of anatase (0.3%). The origin of quartz may be of either syngenetic or due to high temperature inputs (Dai et al., 2007). Kaolinite and illite are the dominant clay minerals present in the shale, which may be of detrital or authigenic origin. The gypsum in the shale sample could have been formed through evaporation, and precipitated perhaps from dissolved Ca and SO_4 components in pore water or ground water, or during sample air drying (Ward, 1991). Cd-containing apatite (Fig.2) present in the shale sample represents local remobilization of phosphate formed earlier within the shale and the associated coal seam (Ward and Taylor, 1996). Sometimes such occurrences of apatite may be terrigenous or of volcanic origin (Dai et al., 2013a; Ward, 2002). According to the XRD data, the shale sample does not contain pyrite due to the complete oxidation of the pyrite in oxygen rich atmospheric conditions, either at the mine site or during low-temperature ashing. This suggests that pyrite oxidation is occurring in the strata, and may contribute to the formation of acid rock drainage (ARD) in the region (Evangelou and Zhang, 1995; ICARD, 2000; Rimstidt and Vaughan, 2003). In an another study conducted by Saikia et al. (2015), pyrite oxidation products such as jarosite and melanterite were found to be present in the LTA of coal-mine overburden samples.

Table 2. Mineralogical analysis (wt %) for low temperature coal-mine shale (CMS) ash sample by XRD

Sample	Mineral phases (wt. %)					
CMS	Quartz	Apatite	Kaolinite	Illite	Gypsum	Anatase
	41.7	18.0	16.4	14.8	8.9	0.3

Table 3. Chemical composition of coal-mine shale (CMS) ash (wt. %) by XRF analysis

Ash Composition	CMS Sample
Na_2O%	0.45
MgO%	2.09
Al_2O_3%	20.10
SiO_2%	60.24
P_2O_5%	0.15
SO_3%	0.50
K_2O%	2.45
CaO%	0.72
TiO_2%	1.16
MnO%	0.30
Fe_2O_3%	10.89
LOI	85.76

(LOI: Loss on Ignition)

Based on the XRF analysis, the chemical composition of the high temperature (815°C) ash for the shale sample is given in Table 3. As might be expected from the data summarized in Table 3, the ash of the shale sample is rich in SiO_2 (60.24%), with abundant Al_2O_3 (20.10%). Fe_2O_3 (10.89%) make up most of the remainder, which is formed by pyrite oxidation during ashing, together with minor proportion of MgO (2.09%), K_2O (2.45%) and TiO_2 (1.16%). The shale ash contains small proportions of SO_3, CaO, Na_2O, P_2O_5 and MnO_2. The presence of SO_3 suggests that the CaO may be responsible for retention of sulphur in the ash as $CaSO_4$ (Koukouzas et al., 2009; Saikia et al., 2015a; Van Dyk et al., 2008).

SEM/EDS Analysis of Minerals of the Shale Sample

Figure 3 provides electron microscopic scans conducted for the

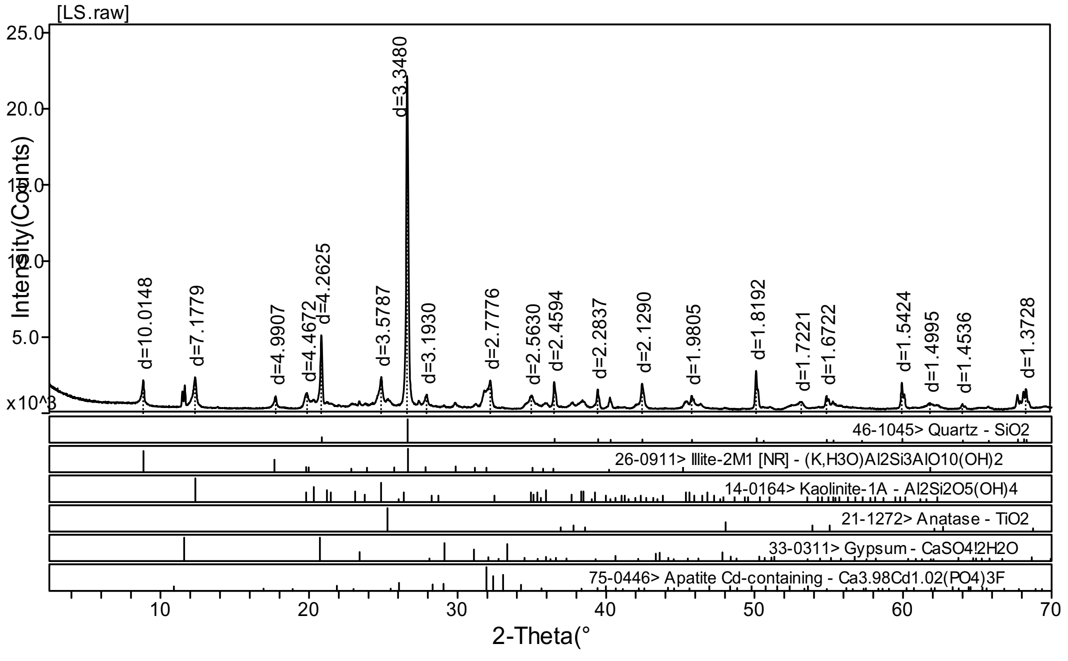

Fig. 2. Quantitative X-ray diffractogram of the CM shale sample

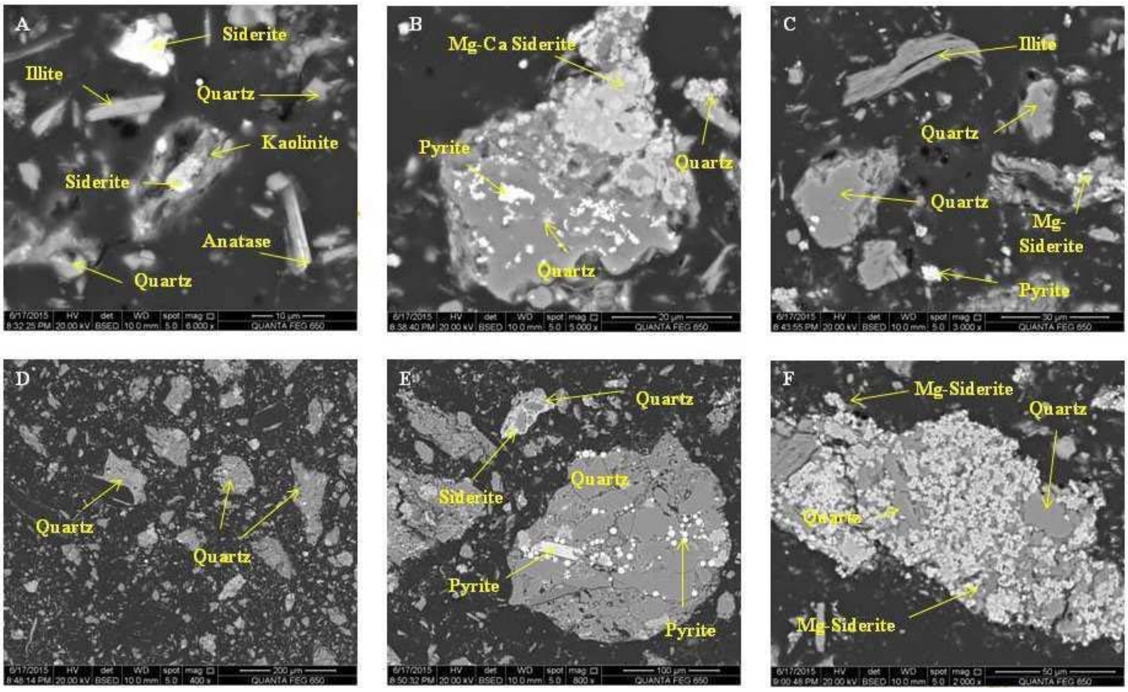

Fig. 3. SEM-EDS micrographs of the CM shale sample

shale sample. In addition to the mineral phases identified by X-ray diffraction, SEM/EDX has identified a number of other components which are present in minor proportions or below the detection limit of XRD. Quartz is the dominant mineral identified by SEM in all the scans of the shale sample and it occurs as terrigenous grains. Minor proportions of disseminated, framboidal and cell-filling pyrite (Figs. 3B, 3C, 3E) and Ca-Mg-bound siderite are also identified by means of SEM within the shale matrix. Such pyrite is of syngenetic origin (Dai et al., 2007). It is also evident that the siderite present in the shale sample is sometimes associated with syngenetic pyrite crystal (Ward, 2002; Kortenski, 1992). Authigenic illite and kaolinite occur as tubular crystals (Fig.3A, 3C) and as dispersive irregular masses (Fig.3B) respectively. Dai et al. (2007) have reported that kaolinite of authigenic origin generally associated with authigenic quartz shows a sheet texture and sometimes occurs as cell-fillings. Anatase is distributed in the mixed-layer minerals within the shale matrix (Fig. 3A). Saikia et al. (2015) also observed the presence of anatase agglomerates and massive rutile agglomerates in some overburden samples from northeast India.

TGA-DTA of the Shale Sample

The thermal curves (TGA-DTA) obtained for the shale sample are shown in Fig. 4. The DTG curve obtained for the shale sample shows the presence of two major changes in the TG pattern at two different temperature regions. Fig. 4 illustrates that the first low temperature region occurs below 150°C where water loss is expected, especially adsorbed and interlayer water from clay minerals present in the shale. The maximum moisture loss is observed at 59.7°C. The second region starts from 400°C to about 680°C, where loss of volatile matter occurs due to primary and secondary volatilization. The maximum loss of volatile matter is observed at 495.8°C during thermal analysis of the shale sample.

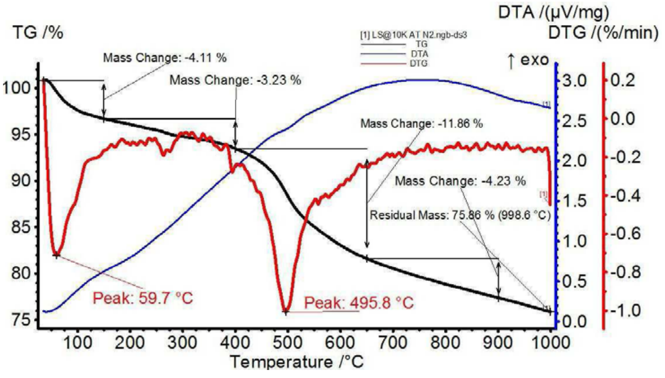

Fig. 4. TGA-DTA pattern of the shale sample

The DTA pattern of the shale sample (Fig. 4) shows only one broad exothermic peak at around 760°C, which may be due to thermal decomposition of minerals like kaolinite, illite, gypsum, siderite etc. present in the shale sample. The XRD data (Fig. 2) also support the presence of these minerals in the shale sample.

FT-IR Analysis of the Coal-mine Shale Sample

Fourier transform infrared (FT-IR) spectroscopy is a powerful characterization technique to get quick information about the rock samples. The FT-IR spectra was carried out in the region 400-4000 cm^{-1} for the shale sample and the respective spectrum is shown in Figure 5. The absorption peak due to stretching vibration of sulphonamide (S-N) occurs in the region 468.2 and 912.6 cm^{-1}. Other absorption peaks due to C-S and S-S, S=O, SO_4^{2-} generally occur in the region 530-700, 700-900 and 1000-1050 cm^{-1} respectively.

The FT-IR spectrum of the shale sample shows absorption bands close to 530, 670 and 690 cm^{-1} and is due to stretching vibration of S-S bonds of sulphides and C-S bonds in primary and secondary thiols (Saikia et al., 2009; Silverstein, 1981). The broad bands appearing in the region 700-900 cm^{-1} and 1000-1050cm^{-1} have been assigned to the symmetrical stretching vibration of S=O (sulphoxide). The presence of S=O bands in the shale sample may also be due to SO_4^{2-} which might have contributed to some extent to the appearance of the band in that region. Most of the peaks in the FT-IR spectra of the shale between 450-1100 cm^{-1} can be assigned to quartz and some clay minerals like kaolinite and illite group (Baruah and Khare, 2007). The distinct peak at 1032.2 cm^{-1} can be attributed to quartz (Silverstein, 1981, Saikia et al., 2007). The FT-IR spectra also show strong intensities of aromatic O-H (phenolic) with sharp peaks in the 3400-3800cm^{-1} range, strong intensities of aliphatic CH_2 stretching vibration

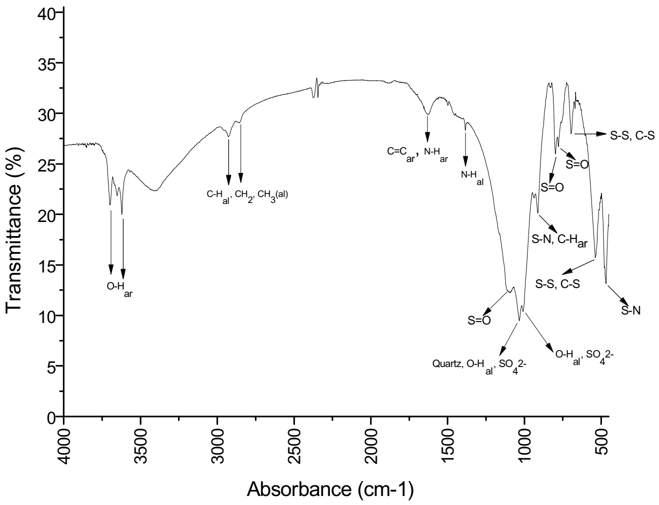

Fig. 5. FTIR spectrum of coal-mine shale (CMS) sample

at 2800-3000 cm^{-1} range, aromatic C=C ring stretching and aromatic N-H bending vibration with broad peaks at 1624.0 cm^{-1} and aliphatic N-H bending vibration at 1384.5 cm^{-1}.

Pyrolysis of Shale Sample

The yield by-products pyrolysis of the shale sample heated at 600°C are summarized in Table 4. The total weight loss after pyrolysis of the shale sample is about 13.83%, which is contributed by both liquid fraction (tar) and gas. The tar contributes 12.21% of the total weight loss, which is appreciably high. The gas fraction (1.62 wt. %) may include compounds such as carbon monoxide, carbon dioxide and methane. However, temperature, pressure, particle size, pyrolysis atmosphere, heating rate, chemical composition of the carbonaceous material are the important variables influencing the nature and yield of the liquid products. According to the TGA-DTA analysis, it is also evident that the maximum weight loss is observed at in the range of 450°C-550°C. The organic matters present in the CMS sample may be responsible for the tar produced during pyrolysis.

Table 4. Product distribution after pyrolysis of CM shale sample

Sample Name	Weight (g)	Coke/char (wt %)	Tar (wt %)	Gas (wt %) (by difference)
CMS	10	86.17	12.21	1.62

GC-MS Analysis of Tar (liquid fraction) Sample

Figure 6 provides the result obtained from GC/MS spectra of the liquid fraction after pyrolysis of the coal-mine shale sample. The result illustrates that the distribution of sulphur containing organic compounds produced from the high-sulphur shale is much more complex. The liquid fraction contains high molecular weight (M.W. 256) cyclic octa-atomic sulphur (octathiocane with molecular formula S_8) compounds along with the complex N-containg organic sulphur compounds (M.W. around 255-486). Since it is found that the liquid fraction is of very poor quality due to the distribution of complex sulphur compounds, it requires costly beneficiation for proper utilization. In addition, Fig. 6 also indicates the presence of phenols (M.W. 94), methylphenols (M.W. 108), and complex organosulphur and organophosphorous compounds (M.W. 174). The presence of oxygen in the form of highly oxygenated organic component especially phenols make the liquid fraction more polar and hydrophilic, which make it difficult to eliminate water from the liquid part (Saikia et al., 2015b). Therefore, the highly oxygenated organic components or oxygenates are required to be separated first and then upgraded in order to reduce the corrosiveness when they are used as a potential liquid fuel (Xu et al., 2011).

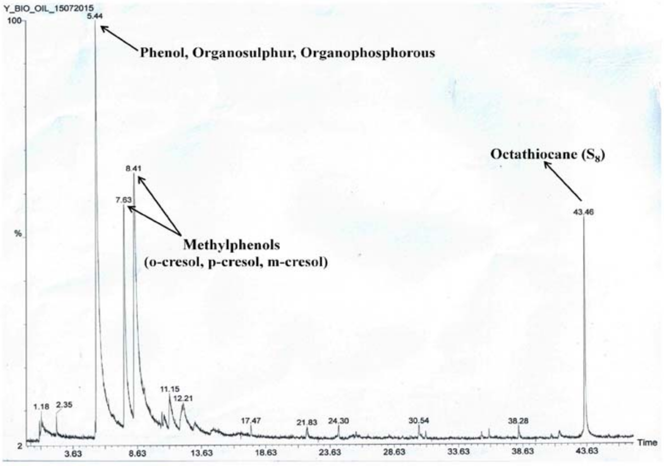

Fig 6. GC-MS results of the liquid fraction after pyrolysis of the shale sample

CONCLUSIONS

The chemical analysis of the Tirap opencast coal-mine shale sample reveals the presence of high sulphate sulphur (>80%) with a high ash content. Mineralogically it is mainly composed of quartz, kaolinite, illite, gypsum, and a minimal proportion of anatase. The absence of pyrite in the LTA of the shale sample reflects the complete oxidation of pyrite during the plasma-ashing process. The GC-MS study proved that the resulting liquids (tar) by pyrolysis are of relatively very poor quality due to the presence of high sulphurous and highly oxygenated complex organic compounds and needs beneficiation and upgradation for utilization. Thus, further studies on different shale samples with different types from different coal mining areas of northeast India region is warranted to arrive at more rational conclusions.

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