MJS, Vol. 7, No. 1, January - June 2008, pp. 41-50
ISSN 0975-3311
https://doi.org/10.12725/mjs.12.4

CHARACTERIZATION OF COAL SAMPLES FROM GODAVARI KANI DEPOSITS USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

Manoj B., Chandrasekharan K.A.** & Kunjomana A.G.****

ABSTRACT

Coal is one of the most abundant organic fuels available in India. Understanding the properties of minerals and ash in coal will be helpful in providing a better knowledge of the factors that control their performance in furnaces. The conventional tool for the analysis of mineral content is X-ray diffraction (XRD) method. The capability of XRD for quantitative analysis is restricted to the minerals with good crystal structures. For the amorphous and low crystalline minerals, XRD can not provide accurate quantitative information. At the same time, even for minerals with a good crystal structure, XRD measurement is a time consuming technique. However, studies on minerals have suggested that FTIR spectroscopy is a superior alternative with respect to speed, accuracy and lower cost. FTIR technique has been used widely in the

---

* *Corresponding author, Lecturer, PG Dept. of Physics, Christ College, Bangalore - 560 029, E-mail: manoj.b@christcollege.edu.*

** *Dean of Science, Christ College, Bangalore - 560 029.*

*** *Professor, PG Dept. of Physics, Christ College, Bangalore - 560 029.*

study of coal, minerals, fly ash and rock. Fourier transform infrared (FTIR) spectra of sub bituminous coal samples, collected from a borehole located at Godavari kani deposit, Andhra Pradesh were recorded between 400 and 4000cm^{-1}. A comparative study of mineral content in coke sample imported from china is also performed using FTIR spectroscopy.

1. Introduction

Due to its origin, coal is a chemically and physically extremely complex and heterogeneous material, consisting of organic and inorganic constituents. The acceptance of coal for particular processes in industry depends critically on both components. The organic structure of coal can be regarded as consisting of heterogeneous aromatic structure, with aromaticity increasing from low rank (lignite) to high rank (anthracite) coals [1]. The organic part of coal also contains sulphur, oxygen, and nitrogen in functional groups. Fourier transform infrared (FTIR) spectroscopy is a widely used analytical technique for determining the different functional groups in coal structure. This method, being able to reveal carbohydrogenated structure (aromatic and aliphatic) and hetero atomic functions (mainly oxygenated) as well as the presence of minerals, is currently one of the most powerful techniques for coal characterization and thus is of paramount importance in the various utilization procedures of coal. The use of low rank coals in industrial combustion may affect the performance of furnace by forming slag at the bottom of furnace, which in turn affect efficiency, and lead to costly maintenance. Further the effluent gas coming out of furnace may increase pollution in the atmosphere. Characterization and various demineralization techniques of coal have been done by various groups [2-6].

In the present work, FTIR spectra of sub bituminous coal sample collected from Godavari coal field, Andhra Pradesh, South India, were used to investigate the chemical structure of these semi ranked coals. The results were compared with that of the industrial coke imported from China. The study is restricted to the absorption bands within the range 4000 cm^{-1} to 400 cm^{-1} mainly because almost all minerals show absorption in this region.

2. Experimental Procedure

2. 1 Analysis of sample

Three samples – Coal-1, Coal-2 and Coal-3 were handpicked from Singerini Coal mines of Godavari Coal deposit at a depth of about 10m, 30m, 60m from the mine 8 incline. All these samples were kept open in air for 3 months at 60% humidity.

For analysis, about 20g of the sample is crushed in to fine powder of about 5 μm size. 2mg of the powdered sample was then mixed with KBr in the ratio 1:200 and ground for about 10 minutes. The grinding time and the sample to KBr ratio 1:200 were kept constant for all the samples under study to ensure uniformity. The mixture was then placed in a 13 mm diameter die cavity and pressed under high pressure. A portion of each sample was also made in to a polished block, according to the standard technique described by Bustin et al. [7].

The spectra were recorded by using Paragon 500, Perkin – Elmer spectrophotometer in the region 4000 - 400 cm^{-1}. This spectrometer has the resolution of 4 cm^{-1}. A standard polystyrene film was used for calibration purposes. To obtain consistent records the FT-IR spectra were recorded in 16 scan mode. Kramers-Kronig transformation [8] was applied to each transmittance spectra.

3. Result & Discussion

3.1 FTIR Spectral Analysis of Godavari Kani Coal Samples

FTIR spectra of coal samples collected from Godavari coal field by random sampling are shown in Fig. 1.

Coal - 1 : Sample collected from 10m depth
Coal - 2 : Sample collected from 30m depth
Coal - 3 : Sample collected from 60m depth

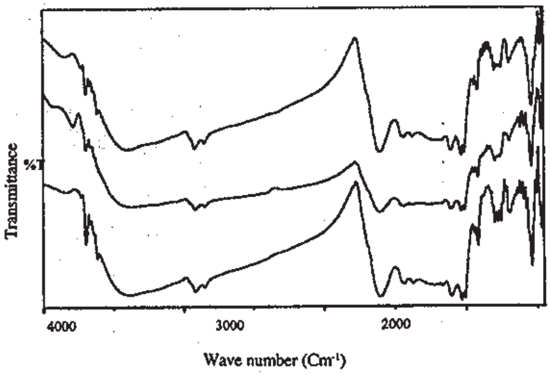

Fig. 1 : FTIR spectra of samples from Godavari Kani, Singerini coal mines

Each absorption band in the spectra was analyzed for the intensity of transmission by Lambert-Beer law [9] and was categorized in to 5 spectral regions, very strong (v.s), strong (s), medium (m), weak (w) and very weak (vw). Bands were assigned according to published articles [2-5, 10]. The assignments of the prominent bands of IR absorption spectra of the three samples are given in table 1.

Table 1. FTIR absorption frequencies, relative intensity estimate and their assignments

Frequency (cm^{-1})		Intensity		Assignments
	Coal-1	Coal-2	Coal-3	
3700	m	m	m	Absorption bands of Kaolinite
3670	m	-	m	OH-in plane degenerated vibration
3620	s	-	s	Inner O-H group of absorbed water
3440	vs	vs	vs	OH-stretching (absorbed water)
2920	vs	vs	vs	Aliphatic CH_3
2850	vs	vs	vs	Aliphatic CH_2
1695	vw	vw	vw	Carbonyl stretching
1605	vs	vs	vs	Aromatic C=C stretching
1500	w	w	w	Phenyl propane structure
1435	vs	vs	vs	Methylene groups
1375	vs	vs	vs	Methyl group
1165	vs	vs	vs	C-O stretching of phenols
1105	vs	vs	vs	Si-O stretching
1030	vs	vs	vs	Si-O stretching
1010	vs	vs	vs	Si-O stretching
935	m	s	m	OH out of plane bending
915	m	s	m	-CH out of plane bending
795	w	m	w	Quartz
775	w	w	w	Quartz
756	w	-	w	-CH out of plane bending
695	m	m	m	Si-O of SiO_4
630	vw	-	-	Si-O of SiO_4
615	vw	w	-	Al-OH
595	vw	w	-	Form of Fe-O
575	w	-	vw	Form of Fe-O
540	s	s	m	Si-O-Al^{IV}
495	w	w	w	Si-O-Al^{IV}
470	w	w	w	Si-O-Si

vw = very weak; w = weak; m = medium, s = strong; vs = very strong

From Table 1 it is seen that all the samples show weak absorption bands at 3700 cm^{-1}. This is due to clay minerals present in the sample and is in the form of Kaolinite structure. The same result is reported by Venkatachalapathy et al. [11] on Neyveli lignite samples.

It is seen from Fig. 1 that the samples have more or less similar broad characteristic absorption bands. All the absorption bands are unresolved indicating that the material constituents have either large particle size or contain polymeric units. There is a broad and strong band observed in all the samples at 3440 cm^{-1} which can be attributed to hydroxyl stretching vibrations. This is well reflected from the observations of Osawa and Shih [12], Subkowiak et al. [13] and Chomnanti et al. [4] in the case of coal, oil shale and lignite samples. The absence of the band at 3030 cm^{-1} which is characteristic of –CH groups in the entire coal sample shows that they probably contain phenyl propane structures. It is also indicative of the fact that the aromatic condensation has not set in, a clear indication of early stage of formation of wood peat to coal stage. All these samples show remarkable similarity with wood peat spectrum. This is reported by Venkatachalapathy et al. [11] in the case of Neyveli lignite. Sharp intense bands observed at 2920 and 2850 cm^{-1} in all the samples can be attributed to the presence of valency oscillations of CH_3 and CH_2 aliphatic groups. Of these 2850 cm^{-1} band can be attributed to methoxy groups present in the samples. Chomnanti et al. [4] observed similar sharp bands at 2920 and 2850 cm^{-1} in the case of tertiary lignite. The sharpness of the bands in the studied samples indicates that the probable age of the coal as belonging to tertiary formations. Fujii et al. [5] calculated the specific extinction coefficients (K) of the absorption bands at 3030, 2920 and 1605 cm^{-1} of twelve Japanese coal samples from lignite to anthracite. These bands arise due to aromatic-CH, aliphatic-CH_3 and C=C aromatic groups respectively. The intensity of the bands directly gives the percentage of carbon content in the sample. The intensity increases gradually as coal rank increased up to 86.2% carbon and then decreases with further increase of the coal rank. In very low rank coals the intensity of 2920 cm^{-1} is found to be very small due to the fact that the proportion of the aliphatic -CH_3 hydrogen is substituted by hydroxyl groups.

Weak broad band at 1695 cm^{-1} and strong prominent band at 1605 cm^{-1} observed in all the samples can be attributed to carboxyl and C=C stretching respectively. Starsinic et al. [14] assigned the band at 1695 cm^{-1} to carboxyl groups, possibly Ketones. Supaluknari et al. [15] observed the bands at 1695 and 1605 cm^{-1} in the case of brown coals and oxygen rich sub bituminous coals, while in higher rank coals with a low oxygen content the absorption at 1695 cm^{-1} appears as a shoulder on the 1605 cm^{-1} band. The strong band near 1695 cm^{-1} is attributed predominantly to carboxylic acid and a relatively weak band at 1670 cm^{-1} is assigned to ketonic structures. They also observed that the total absorbance of all the carboxyl bands for the brown coal sample is greater than those for the higher rank coal samples. The Brown coal with higher oxygen content (O/C = 0.26) contain less amount of carboxyl group (both as acids and esters) and has lower intensity for 1695 cm^{-1} band than brown coal with low oxygen content.

It is clear that the samples having higher oxygen content have low intensity absorption band at 1695 cm^{-1} while the samples having low oxygen content show well resolved and intense band at 1695 cm^{-1}. The presence of weak absorption band in the spectra shows that coal samples are rich in oxygen content. Such a result is in conformity with the observations of Supaluknari et al. [15] in the case of oxygen rich Australian Brown coal.

A very pronounced absorption band at 1605 cm^{-1} is present in all the coal samples, due to C=C aromatic stretching. Brown [2] observed prominent band at 1605 cm^{-1} in the case of coal samples and suggested that this band can arise due to aromatic ether linkages. Motterra and Low [10] found the band at 1605 cm^{-1} in the case of wood charcoal and assigned it to aromatic C=C vibrations. Low and Glass [5] made elaborate discussion of 1605 cm^{-1} band of coal. They assigned the band in case of in low rank coals and chars which have been formed at relatively low temperature, to aromatic ring stretch of small, discrete aromatic entities. They also suggested that the oxygen containing structure may or may not be involved in the formation of 1605 cm^{-1} band.

On the basis of above observations the band observed at 1605 cm^{-1} can be attributed to aromatic ring stretch of small, discrete aromatic groups present in Godavari samples. In addition to the above absorption band observed at 1605 cm^{-1}, broad bands at 1435, 1375, 1165, 1105 cm^{-1} and shoulder band at 1030 cm^{-1} has been observed in all the samples. Unresolved plateau like bands observed in this region shows that the coal samples constitute complex polymeric materials.

Chomnanti et al. [4] observed similar type of bands in the case of lignite sample. They assigned the band at 1435 cm^{-1} to methylene and methyl deformation vibrations, 1370 cm^{-1} to methyl deformation vibrations and a plateau of absorption around 1100 to 1300 cm^{-1} to C-O vibrations. Buravas et al. [3] studied the infrared spectra of tertiary lignite and woody peat. They observed the bands at 1500, 1435, 1410, 1375 cm^{-1} and to a lesser extent around 1200 cm^{-1}, where lignite shows a plateau of more or less unresolved absorption bands. Pleistocene lignite and woody peat showed absorption bands at 1500, 1435 and 1410 cm^{-1}. Pleistocene-Miocene (66-74%C) lignite showed a peak at 1500 cm^{-1} and broad absorption throughout 1450-1410 cm^{-1}. In the case of coal sample, marked absorption was observed on only at 1500 cm^{-1}. The band at 1500 cm^{-1} is due to benzene rings and this disappears in older lignite & coal [11]. This is probably due to the increasing substitution of the aromatic rings. From these observations they concluded that the absorption band at 1500 cm^{-1} can be associated with the presence of phenyl propane type structures and it can be used in the dating of solid fuels. They assigned the band at 1450-1410 cm^{-1} to deformation vibrations of methylene groups and the band at 1375 cm^{-1} to the methyl groups.

Kister et al. [16] found weak broad residual absorption band between 1200 to 1300 cm^{-1} in the case of low rank Gardanne coal and assigned the band to C-O bonds, as in phenols or ethers. Zelei et al. [17] studied the infrared spectra of Mesburg, GDR brown coals and assigned, the bands at 1435 cm^{-1} to deformation vibrations of CH_3 group, 1375 cm^{-1} band to out of plane bending mode of CH_2 group and deformation vibrations of CH_3 group, 1375 cm^{-1} band to out of plane bending mode of CH_2 group and deformation vibrations of CH_3 group, 1270 cm^{-1} band to antisymmetric (C-O-C) stretching in aliphatic esters, 1165 cm^{-1} band to C-O stretching modes and 1105 to 1010 cm^{-1} band to Si-O-Si bands in silicate minerals. Cannon et al. [18] found the IR bands in the case of Rawhide sub bituminous coal and Texas lignite sample at 1165 cm^{-1} and assigned the band to C-O stretching of phenolic hydroxyl groups. Olson et al. [19] found the band at 1030 cm^{-1} in the Beulah lignite sample and this band was assigned to the clay absorption.

From the above observations the weak broad bands observed at 1435 and 1375 cm^{-1} can be assigned to stretching modes of methylene and methyl groups present in the samples. The broad band observed at 1165 cm^{-1}, 1105 cm^{-1} and 1030 cm^{-1} can be attributed to C-O stretching of phenolic hydroxyl groups and trace amount of silicate minerals associated with the lignite samples respectively. The plateau like unresolved strong absorption region at 1165 cm^{-1} indicates the presence of C-O stretching of phenolic hydroxyl groups and the complex nature of the polymeric material present in the samples.

A close scrutiny of the IR spectra reveals that the coal and woody peat shows a distinct though weak absorption band at 1500 cm^{-1} [3,11]. This band indicates the presence of benzene rings in phenyl propane type structures and also indicates that these samples belong to Pleistocene-Miocene age. The present samples show a weak peak at 1500 cm^{-1} and can be safely assigned to Pleistocene-Miocene period on the lines suggested by Venkatachalapathy [11] and Buravas et al. [3].

Sobkowiak et al. [1] reported that sub bituminous coal samples have large absoptivities for different aliphatic –CH bonds, the highest being most likely for –CH bonds in long chain methylene structure. They also reported that the absoptivities for aromatic –CH bonds is very small.

In the present study, sample shows very strong absorption at 2920 cm^{-1} and 2850 cm^{-1} which is assigned for aliphatic $-CH_3$ and $-CH_2$ groups respectively and weak absorption bands in the region 915 cm^{-1} & 756 cm^{-1} is due to aromatic $-CH$ out of plane structure [1]. From this information we can conclude that the sample is moderately ranked sub bituminous coal.

Maria et al. [21] assigned the band at 3440cm^{-1} for -OH stretching (absorbed water) and 400 cm^{-1}-600$cm^{-1}$for silicate and clay minerals for low rank coals.

From the above information it is inferred that the Godavari kani coal samples constitute high moisture content and more of clay minerals with low carbon content. This indicates that they are low rank sub bituminous coal. Using this coal for industrial purpose requires cleaning. The formation of this coal has taken place during Pleistocene-Miocene period.

FTIR Analysis of Coke

The coke sample in the present analysis is an imported Chinese coal for the use of a thermal power plant in Karnataka. The sample was exposed to a temperature of 30°C and 60% humidity for about 3 months. FTIR of this sample also recorded as per the procedure mentioned above. The wave number vs transmittance IR spectrum is shown in Fig.2

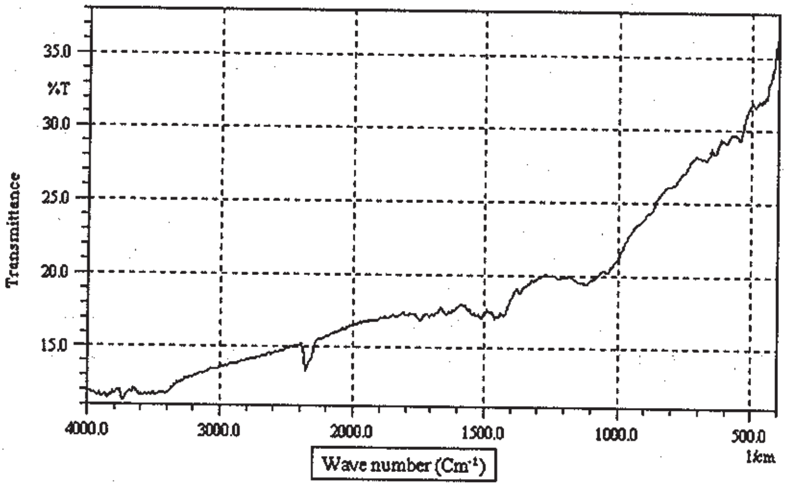

Fig. 2 : FTIR of Coke sample

The spectrum is analyzed by Lambert-Beer law [9] for intensity comparison as mentioned above. Bands are assigned according to published article [2-10, 20].

Table. 2: FTIR absorption frequencies, relative intensity estimate and assignments of coke sample.

Frequency (cm^{-1})	Intensity	Assignments
3390	w	OH stretching of absorbed water
2921	w	Aliphatic CH_3
1435	w	$CaCO_3$
1110	m	carboxyl stretching
1030	s	Si-O stretching
874	w	Si-O Al
797	w	Aromatic- CH out of plane bending
536	w	Fe-O Stretching
472	w	Fe-S Stretching

w = weak; m = medium, s = strong

From Fig. 2 it is observed that the pyrolysis has changed the structure of coal. When heating coal, the structural collapse of the minerals have taken place and the water molecules are removed. At 150°C the absorbed water molecules gets evaporated out, which is well reflected from the absence of 3400 cm^{-1} band. At 450°C the inner hydroxyl water molecules are removed which can be observed from the reduction of intensity of 3700 cm^{-1} band. At 650°C the clay structure gets destructed which reflects that triplet band at 1100 cm^{-1} is reduced to singlet. The above features indicate that, during pyrolysis, when the coal samples were heated to above 800°C for making coking coals, mineral structure is destructed and inter layer water is removed. It is well reflected from the IR spectrum of the coke sample. The well absorption bands at 1430 cm^{-1} along with 875 cm^{-1}arises due to residual clay minerals along with carbonate minerals found in the coking coal sample [20].

Conclusion

FTIR analysis of Godavari kani coal shows the presence of aliphatic CH_2, CH_3 structures along with aromatic C=C stretching. High moisture and clay minerals content with low carbon content reveals that they are low rank sub bituminous coals. Coal samples show high amount of clay content which necessitates cleaning for industrial applications. The absence of the band at 3030 cm^{-1} which is characteristic of aromatic -CH bond in the entire coal sample shows that they contain phenyl propane structures. It is also indicative of the fact that the aromatic condensation has not set in, a clear indication of early stage of formation of wood peat to coal stage. The presence of weak band at 1500 cm^{-1} show that the aromatization of sample is not completed after formation and preferably assigned to Pleistocene-Miocene period. The absence of minerals, clay and water in coke sample indicates that, it can be used as a better fuel in furnace than coal for better calorific value and less environmental pollution.

References

1. Sobkowiak M, Painter P C. Fuel, 71, 1105 (1992).
2. Brown J.K, J. Chem. Soc. 747, (1950).
3. Buravas S, Gaines A F, Hasadsri T, Prasertwitayakh A and Mrs Sucharitakul, Fuel 49, 180 (1970).
4. Chomnanti S, Deemak P, Gaines A F, Kasomson K, Keowkamnerd K, Lorvidhya V, Pomilying C, Mrs. Sucharitakul N, Witsuksomba V V and Wiroyamon W, Fuel 49, 180 (1970).
5. Fujii S, Osawa Y and Sugimura H, Fuel 49, 68 (1970)
6. Low M J D and Glass A S, Spectrosc. Lett. 22 (4), 417 (1989).
7. Bustin R M, Cameron A, 'Coal Petrology, Its Principles, Methods and Applications', Geological Association of Canada, Short Course Notes, 2nd Edn,(1985).
8. Hawrane J P, Neelakantan P, Young, R.P. Spectrochim.Acta, Part A, 32, 85 (1976).
9. Solomon P R, Carangelo R M and Zubkova Fuel, 67, 949, (1988).
10. Morterra C and Low M J D, Spectrosc. Lett. 15 (9), 689 (1982).
11. Venkatachalapathy R and Ramaswamy K, Asian Chemistry Letters, 3, 160-166 (1999).
12. Osawa Y and Shih J W, Fuel 50, 53 (1971).
13. Sobkowiak M, Reisser E, Given P and Painter P, Fuel 63, 1245 (1984).
14. Starsinic M, Michael Y, Otake, Yoshinobu,. Walker P L. Jr Painter and Paul C, Fuel 63,1002 (1984).
15. Supaluknari S, Larkins F P, Redlich R and Jackson W R, Fuel process. Technol. 18,147 (1988).
16. Jacky Kister, Michel Guiliano, Gilberr mille, and Henri Dar Fuel, 67, 1076 (1998).
17. Landais P, and Rochdi A, Zelei. Energy Fuels, 4, 290 (1990).
18. Traverse A, Kolvoord R W, and Cannon. Science, 159, 302 (1968).
19. Olson Energy & Fuels 21, 341 (1988).
20. Das T K Fuel, 80, 489 (2001).
21. Maria Mastalerz, Max Bustin, R.74, 14,536 (1995).