



CHARACTERIZATION OF LOW-TEMPERATURE COAL ASH BEHAVIOUR UNDER ATMOSPHERIC PRESSURE

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ABSTRACT

The chemical composition of the virgin coal from Korba coal fields, South central India is determined with the help of Fourier transform Infrared spectroscopy. The process of burning of carbon rich coal is carried out from a temperature of 200°C to 700°C under atmospheric pressure and controlled air in a muffle furnace. The resultant coals are examined with FTIR. The result shows that the residence time of coal ash at high temperature has considerable influence on the composition of coal ash and little effect on the amount of unburned carbon. With increase of temperature the oxygenated groups are released mainly as H₂O and CO, but also as aldehydes, alcohols and acids. The silicate and quartz mineral content remains the same throughout heating.

Keywords: Coal, Minerals, Characterization, FTIR

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Introduction

Fossil energy, particularly derived from coal, has been investigated from many directions. Many environmentalists see coal as inherently dirty. Coal minerals are objectionable due to process as well as environmental problems. Coal minerals may be epigenetic and syngentic. Both constitute the inorganic part of the coal and if its concentration increases above a certain level, it is hazardous to the environment and the furnace. Minerals are needed to certain levels due to the catalytic effects in gasification and liquefaction [1-2]. Efforts are needed to reduce the ash forming inorganic elements and develop clean methods of using coal. Demineralization prior to utilization is an effective way to ensure environmentally friendly combustion of coal as a fuel.

In the present study, FTIR spectra of high volatile bituminous coal from Korba coal field, South central India was analyzed in order to investigate the chemical structure of the semi ranked coals. To study the behaviour of ash from this coal, it is heated at a fixed temperature of 200°C, 400°C, 600°C and 700°C in a muffle furnace with restricted air supply [3-4]. An FTIR spectrum of each sample is recorded within the wave length range of 4000cm⁻¹ to 400cm⁻¹.

Experimental Procedure

Analysis of the sample

Coal sample was handpicked from the mine and was kept in open air for about 6 months at 60% humidity. For analysis, about 100g of the sample was crushed in to a fine powder of about 5µm size. 20g of this sample was taken in different china dish for heating in a muffle furnace for different fixed temperatures 200-700°C. Each sample was heated for about 30 minutes in the furnace for the fixed temperature and allowed to cool slowly in dessicator. 2mg of this 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 13mm diameter die cavity and pressed under high pressure. A portion of each sample was also made into a polished block, according to the standard described by Bustin et al. [5].

The spectra were recorded by using Paragon 500, Perkin-Elmer spectrophotometer in the region 4000-400cm⁻¹. This spectrometer has the resolution of 4cm⁻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 was applied to each transmittance spectra.

Results & Discussion

FTIR Spectral Analysis of the Coal Samples

FTIR spectra of virgin coal sample and heated coal sample are shown in Fig. 1.

Sample 1: Virgin coal

Sample 2: Sample heated to 200°C

Sample 3: Sample heated to 400°C

Sample 4: Sample heated to 600°C

Sample 5: Sample heated to 700°C

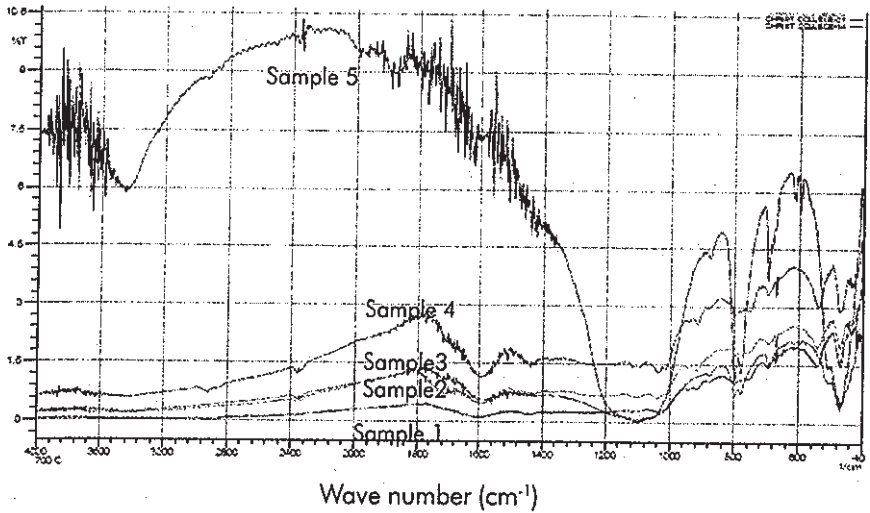


Fig.1. FTIR Spectra of virgin coal and heated coal

Table 1. FT-IR absorption frequencies, relative intensity estimate and their assignments

Wave number cm ⁻¹	Sample					Assignment
	1	2	3	4	5	
470	w	w	w	s	v.s	Clay Minerals / ash
510	v.w	v.w	v.w	m	s	Bands of silicates
535	w	w	w	v.w	s	Si-O-Si
669	w	w	w	w	w	Band of Silicate Minerals/aromatic out of plane C-H deformations
695	m	w	w	w	w	Si-O of SiO ₄
795	w	w	w	s	s	Quartz/C-H bending vibration
935	s	m	m	m	m	OH-out of plane bending
1030	v.s	s	s	v.s	v.s	Si-O stretching/C-O stretching from ether & alcohols
1080-1120	v.s	s	s	v.s	v.s	C-O group
1435	v.s	s	s	s	w	Methylene group
1605	v.s	s	v.s	s	s	Aromatic C=C Stretching
1690	v.s	s	s	m	v.w	Carboxyl Band
2360	-	v.s	s	m	vw	CO/CO ₂ evolution
2850	v.s	v.s	v.s	s	w	Aliphatic CH ₂ -Stretching vibration
2920	v.s	v.s	v.s	s	w	Aliphatic CH ₃ -stretching vibration
3400	v.s	v.s	v.s	s	w	-OH stretching vibration
3670	v.s	v.s	v.s	m	-	OH-in plane degenerated vibration
3700	vw	v.w	vw	m	-	Clay minerals

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

Each absorption band in the spectra was analyzed for the intensity of transmission by Lambert-Beer law [7] and categorized in to 5 spectral regions, very strong(v.s), strong(s), medium(m), weak(w) and very weak(v.w). Bands were assigned according to published articles [1-6]. The assignments of the prominent bands of IR absorption spectra of five samples are given in table 1.

A comparison of the FTIR spectra for the wave number region 400-4000 cm^{-1} for Korba coal field sample and its chars at four different temperatures is presented in figure 1.

It is seen from the figure that the samples have more or less similar broad characteristic absorption bands. All the absorption bands are unresolved indicating that the mineral constituents have either large particle size or contain polymeric units. From the figure and intensity table it is seen that all the samples except sample 5 show weak absorption bands at 3700 cm^{-1} . This is due to clay minerals present in the sample and are in the form of Kaolinite structure [3,7-8].

The unresolved broad band at 3670 cm^{-1} is due to the presence of OH in plane degenerated vibration. The sample shows strong flat band at 3400 cm^{-1} . This band is attributed to the stretching vibration of the hydroxyl group (-OH) due to the water content in the sample. For the samples heated to 200°C, 400°C and 600°C the same peak becomes slightly weaker, because large amount of the functional group (-OH) still remain in the sample. Some water content in the sample seems to be due to the absorption of air moisture by the sample. The 700°C sample presents only a weak peak at the same band because of the remaining -OH and is due to the decrease in oxygen content with increase in temperature. The same result was reported by Andreas G et al. [3, 4].

In the aliphatic stretching region (3000-2800 cm^{-1}) there are distinct peaks at 2850 cm^{-1} and 2920 cm^{-1} , attributed to symmetric and asymmetric -CH₂ stretching respectively. This peak is distinct up to sample 4 which was treated at 600°C. The intensity of this particular band decreases as the temperature of the sample was increased to 700°C as reported by Andreas G et al. [3] on low rank Greek coals. All the samples except the virgin coal (sample 1) show an absorption peak at 2360 cm^{-1} due to the liberation of -CO or CO₂ from the sample as the temperature is increased. The maximum evolution of CO₂ was taken place at a temperature of 200°C and intensity of this peak was reduced to a minimum at 700°C, because of the complete conversion of coal to ash [3, 4, 14].

A great abundance of C=O and C-O-R structure was noted, as revealed by the intensity of peaks in the 1800-1000 cm^{-1} region. This zone of oxygen containing functional groups was characterized by a very intense peak at 1605 cm^{-1} , which was attributed to either C=C or C=O aromatic ring stretching vibrations. The C=C bands, which should be placed between C-O and C=O bands, were not definitely distinguished, since the low rank coals have high oxygen content and these bands almost masked the C=C structures. The same was reported by Thomasson et al. [9]. The intensity of this band decreases with increase of temperature of the sample up to 600°C. The peak was distorted at 700°C, due to the reason that the sample was changed to ash.

At the 1200-1000 cm^{-1} region, a sharp, intense peak were present in all the samples. The C-O groups in the 1080-1120 cm^{-1} and 1030 cm^{-1} region were also very distinct. The 1030 cm^{-1} may also result from silicate minerals (Si-O bonds). As the temperature of the sample increases from 200°C to 600°C, the intensity of this band decreases accordingly as reported by Guo and Bustin [10]. But surprisingly at 700°C, the band shows a sudden increase in its intensity. This is due to the presence of silicate mineral, clay and ash. This is reported by Cetinkaya and Yurum [11]. From this we can infer that the coal sample, while heating, produces ash with more minerals in it.

In addition to the observed bands at 1605 cm^{-1} broad band at 1435 cm^{-1} , 1120 cm^{-1} and a band at 1030 cm^{-1} has been observed in all the samples. These bands observed in this region show that the coal samples constitute complex polymeric materials. The absence of the band at 1500 cm^{-1} was due to benzene rings and its disappearance reveals that the Korba field coals are older than Neyveli lignite and Godavari kani coals [12-13].

The distinct peak at 669 cm^{-1} in the entire sample was attributed to the presence of mineral matter (silicates) than aromatic out of plane bending, because its intensity remains the same in the FTIR spectra throughout the heating. In other words heating can not remove this particular mineral from the coal sample.

It is observed that the penetration depth for the C-H stretching bands near 3000 cm^{-1} is around a quarter of that of the -CH bending vibration near 800 cm^{-1} . The intensity of the bands is directly related to the penetration depth which in turn directly related to wavelength [9].

The bands at 470 cm^{-1} and 510-530 cm^{-1} could be related to the presence of clay, ash and silicate minerals.

The intensity of the mineral bands (in the 400-600 cm^{-1} and 3600-3800 cm^{-1} zone) were more or less remains the same throughout heating except at 700°C in the FTIR spectra of the samples.

Aliphatic bands (3000-2800 cm^{-1}) and oxygenated functional groups (1800-1000 cm^{-1}) show lower intensity with increase in temperature of the sample [3, 4, 14].

Conclusion

FTIR spectroscopy was applied to high volatile bituminous coal from Korba coal from south central India at 4 different final temperatures, in order to investigate their chemical structure. The study reveals a great abundance of C-O and C-O-R structures ($1800\text{-}1000\text{cm}^{-1}$ region), while clay and silicate minerals were identified in the $400\text{-}600\text{cm}^{-1}$ and $3600\text{-}3800\text{cm}^{-1}$ zone. The intensity of the mineral band remains the same in all the samples except sample 5. The aliphatic bands ($3000\text{-}2800\text{cm}^{-1}$) showed a lower intensity with increase of temperature. Major quantity of H_2O is at the wave number of 3400cm^{-1} . A strong peak at 1030cm^{-1} in the entire sample is the evidence of the presence of phenolic and alcoholic C-O bonds as well as C-O-C bonds with aliphatic or aromatic carbons. At 700°C the same peak is showing a sudden change in intensity, may be due to the presence of silicate minerals in the sample. The absorption peak at the wave number 2360cm^{-1} reveals the evolution of -CO and CO_2 from the sample while heating. The evolution of CO_2 is maximum at 200°C and thereafter it decreases with increase of temperature. The absence of the band at 1500cm^{-1} shows that they are older coal. It is observed that the penetration depth for the C-H stretching bands near 3000cm^{-1} is around a quarter of that of the -CH bending vibration near 800cm^{-1} . The intensity of the bands is directly related to the penetration depth which in turn directly related to wavelength.

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